Ethanollic Gasoline, a Lignocellulosic Advanced Biofuel

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Complete List of Authors:	Howard, Mícheál; University of Limerick, Department of Chemical Sciences; Trinity College Dublin, School of Physics Issayev, Gani; King Abdullah University of Science and Technology, Clean Combustion Research Center Naser, Nimal; King Abdullah University of Science and Technology, Clean Combustion Research Center Sarathy, Subram ; King Abdullah University of Science and Technology, Clean Combustion Research Center Farooq, Aamir; King Abdullah University of Science and Technology, Mechanical Engineering Dooley, Stephen; Trinity College Dublin, School of Physics; University of Limerick, Department of Chemical Sciences
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Journal of Sustainable Energy and Fuels
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Dr Stephen Dooley

Assistant Professor of Energy Science
School of Physics
Trinity College Dublin, the University of Dublin
stephen.dooley@tcd.ie
+353 1896 2030

Regarding: Paper submission to RSC
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Dear Prof. James Durrant:

I am pleased to submit an original research article entitled "Ethanollic Gasoline, a Lignocellulosic Advanced Biofuel" by Mícheál Séamus Howard, Gani Issayev, Nimal Naser, S. Mani Sarathy, Aamir Farooq and Stephen Dooley for consideration for publication in the *Journal of Sustainable Energy and Fuels*. The paper formulates an apparent drop-in gasoline that is synthesizable from feedstocks that are entirely biologically derived, more than this, our analysis indicates that this fuel may be technically superior in important aspect to conventional gasoline.

We previously established the ignition behavior of the biomass derived biofuel component, ethyl levulinate (Ghosh et al., 2018). In other previous work we have also identified synthetic conditions for ethyl levulinate production, where we additionally identify ethanol and diethyl ether as co-products of the synthesis. In this manuscript, we build on these studies showing that by blending the three biofuel components; ethyl levulinate, diethyl ether and ethanol, it is possible to produce a dynamic range of fuels of varying ignition quality, including mixtures of equivalent ignition quality to that of market diesel and market gasoline.

The paper accounts a detailed fundamental comparison of the ignition of one such "Ethanollic Gasoline" to that of a real petroleum derived conventional gasoline. Surprisingly, we show that despite being equivalent according to the conventional fuel ignition descriptors, the biofuel shows a significantly superior anti-knock ignition behavior to the petroleum derived gasoline, showing a considerably reduced range of reactivity.

We believe that the findings accounted in the manuscript are very important for the transition away from petroleum and so we would like to share them with the world by publication in the *Journal of Sustainable Energy and Fuels*. As the paper presents both practical findings and fundamental analysis it should excite and interest your readers as to the potential for innovative uses of biofuels when formulated as mixtures. This work also questions the paradigm of using conventional fuel quality metrics for emerging biofuels, the discussion of which will certainly impact the future development of sustainable biofuels.

This work has not been published wholly or partly before and is not under consideration for publication elsewhere. We have no conflicts of interest to disclose.

Thank you for your consideration,
I look forward to building a sustained presence in your journal,

Kindest Regards,

Stephen Dooley

Sustainable Energy and Fuels

ARTICLE

Ethanollic Gasoline, a Lignocellulosic Advanced Biofuel

Mícheál Séamus Howard^{a,b}, Gani Issayev^c, Nimal Naser^c, S. Mani Sarathy^c, Aamir Farooq^c, Stephen Dooley^{*a,b}

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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 show 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 HO₂ radical. 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.

Introduction

Growing concern about the consequences of societies 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 "first 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.

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

^a Department of Chemical Sciences, University of Limerick, Ireland.

^b School of Physics, Trinity College Dublin, Ireland.

^c King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Centre, Physical Sciences and Engineering Division, Thuwal, Saudi Arabia.

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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, Flannelly 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 $< 5^{\circ}\text{C}$ (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 (29, 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 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 suppress 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:

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

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 $\Phi = 0.5$, at 600 – 900 K. Exemplar experimental pressure histories can be seen in Figure 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, OH, HO_2 , O and $\dot{C}H_3$, 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 Figure S2):

1. The hydrogen abstraction reactions are assigned to describe abstraction by the same set of species from each fuel component, i.e., H, OH, CH₃, CH₃O, CH₃OO, HO₂, O, O₂ and C₂H₅ were considered by Ghosh et al. (33), but C₂H₅OO, CH₃C(O)OO, 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.
2. The formation enthalpy of the diethyl ether peroxy alkylhydroperoxide radicals were previously arbitrarily reduced in the Sakai model by 10 kJ/mol 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 RO₂ and alkylhydroperoxide radical species to describe the important equilibrium of elimination pathways, the recommended rate constant and equilibrium constant 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:

$$DCN = \sum_i DCN_i (a_i x_i + b_i (x_i)^2 + c_i (x_i)^3) \quad \#(2)$$

where 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.

Table 1 DCNs and parameters for Eq. (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

The experimental data is summarized in Figure 1, and tabulated as Supplementary Information (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). Equation (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:

$$\text{RON} = 116.609 - 0.784(\text{DCN}) - (0.00662(\text{DCN}^2)) - (3.401 \times 10^{-4}(\text{DCN}^3)) \quad \#(3)$$

Figure 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 ~17 – 27% 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.

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

^aFrom Equation 2. ^bEstimated using DCN-RON relationship summarized by Equation 3 (49). ^cMeasured in this work. ^dMeasured by Naser et al. (28). ^eMeasured by Sarathy et al. (25).

Figure 2, shows the ignition delay data of the EL/DEE/EtOH Gasoline measured in a rapid compression machine, also tabulated as Supplementary Information (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

Figure 2 RCM ignition delay times for the EL/DEE/EtOH Gasoline and FACE-F [15]. Symbols correspond to measurements. Lines correspond to model simulations. FACE-F data are taken from [15].

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, outline 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 potential important complicating implications.

Singh et al. have shown that for gasoline surrogate mixtures (toluene/iso-octane/n-heptane/1,2,4-trimethylbenzene), 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 Figure 2. For the EL/DEE/EtOH Gasoline, this is the first time such a multicomponent 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 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 Figure 3, S3, and 5.

The mode of consumption of all three fuel components of the EL/DEE/EtOH Gasoline is similar. Hydrogen abstraction by $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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

Figure 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, $\Phi=1$. For ethyl levulinate “Isomerization” refers to conversion to the EL1/3/4/6/7J radicals. 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

decompose to two $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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 promoting 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 ("C4H9Ob"), 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 -hydroxyethyl) undergoing the concerted elimination to form HO₂ and acetaldehyde, a pathway important in alcohol combustion

Figure 4 Normalized small radical rate of production for the EL/DEE/EtOH Gasoline and FACE-F [15] after 65% of the computed ignition delay time at 750 K and 1200 K, 25 bar, and $\Phi=1$.

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 Figure 3).

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 undergoes elimination to olefin and HO_2 , and 75% isomerizes 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 the 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 olefin 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 – 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 Figure 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

Figure 5 Sensitivity analysis to ΔT for the EL/DEE/EtOH Gasoline and FACE-F [15] 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.

radicals, thus maintaining or enhancing the population of the reactivity driving $\dot{\text{O}}\text{H}$ 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, $\dot{\text{O}}\text{H}$ 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 $\text{C}_2\text{H}_5\text{O}$) 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 $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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 ~ 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 olefin 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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Ethanollic Gasoline, a Lignocellulosic Advanced Biofuel

Mícheál Howard^{1,2}, Gani Issayev³, Nimal Naser³, S. Mani Sarathy³, Aamir Farooq³, Stephen Dooley^{1,2}

¹Department of Chemical Sciences, University of Limerick, Ireland

² School of Physics, Trinity College Dublin, Ireland

*³ King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Centre,
Physical Sciences and Engineering Division, Thuwal, Saudi Arabia*

Supplementary Information

Reaction	A (cm ³ mol ⁻¹ s ⁻¹)	n	Ea (cal mol ⁻¹)	k @ 800 K (cm ³ mol ⁻¹ s ⁻¹)	Reference
R+O2=RO2					
EL1J+O2=EL1OO	7.54x10 ⁺¹²	0	0	7.54x10 ⁺¹²	Analogy to IC3H7+O2<=>C3H7O2 [1]
EL3J+O2=EL3OO	7.54x10 ⁺¹²	0	0	7.54x10 ⁺¹²	Analogy to IC3H7+O2<=>C3H7O2 [1]
EL4J+O2=EL4OO	7.54x10 ⁺¹²	0	0	7.54x10 ⁺¹²	Analogy to IC3H7+O2<=>C3H7O2 [1]
EL6J+O2=EL6OO	7.54x10 ⁺¹²	0	0	7.54x10 ⁺¹²	Analogy to IC3H7+O2<=>C3H7O2 [1]
EL7J+O2=EL7OO	7.54x10 ⁺¹²	0	0	7.54x10 ⁺¹²	Analogy to IC3H7+O2<=>C3H7O2 [1]
RO2=Olefin+HO2					
EL3OO=EL34D+HO2	8.08x10 ⁺¹²	0	32821	8.74x10 ⁺⁰³	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [2]
Reverse	5.05x10 ⁺¹⁰	0	10416	7.21x10 ⁺⁰⁷	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [3]
EL4OO=EL34D+HO2	8.08x10 ⁺¹²	0	32822	8.73x10 ⁺⁰³	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [2]
Reverse	5.05x10 ⁺¹⁰	0	10416	7.21x10 ⁺⁰⁷	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [3]
EL6OO=EL67D+HO2	1.06x10 ⁺¹³	0	33040	1.00x10 ⁺⁰⁴	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a primary carbon. [2]
Reverse	6.22x10 ⁺¹⁰	0	8987	2.18x10 ⁺⁰⁸	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a primary carbon. [3]
EL7OO=EL67D+HO2	6.47x10 ⁺¹²	0	31792	1.34x10 ⁺⁰⁴	Recommended rate involving a peroxy group on a primary carbon and a H atom on a secondary carbon. [2]
Reverse	6.45x10 ⁺¹⁰	0	13000	1.81x10 ⁺⁰⁷	Recommended rate involving a peroxy group on a primary carbon and a H atom on a secondary carbon. [3]
RO2=QOOH					
EL1OO=EL1OOH3J	2.50x10 ⁺¹⁰	0	20450	6.48x10 ⁺⁰⁴	Analogy to C7H15O2-1<=>C7H14OOH1-3 [1]
EL3OO=EL3OOH1J	3.75x10 ⁺¹⁰	0	24000	1.04x10 ⁺⁰⁴	Analogy to C7H15O2-3<=>C7H14OOH3-1 [1]
EL3OO=EL3OOH4J	2.00x10 ⁺¹¹	0	26450	1.19x10 ⁺⁰⁴	Analogy to C7H15O2-3<=>C7H14OOH3-4 [1]
EL4OO=EL4OOH3J	4.00x10 ⁺¹¹	0	26450	2.38x10 ⁺⁰⁴	Analogy to C7H15O2-4<=>C7H14OOH4-3 [1]
EL6OO=EL6OOH7J	3.00x10 ⁺¹¹	0	29000	3.59x10 ⁺⁰³	Analogy to C7H15O2-2<=>C7H14OOH2-1 [1]
EL7OO=EL7OOH6J	2.00x10 ⁺¹¹	0	26450	1.19x10 ⁺⁰⁴	Analogy to C7H15O2-1<=>C7H14OOH1-2 [1]
QOOH=Olefin+HO2					
EL3OOH4J=EL34D+HO2	1.94x10 ⁺¹³	0	18156	2.13x10 ⁺⁰⁸	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [4]

Reverse	1.92x10 ⁺¹²	0	10743	2.23x10 ⁺⁰⁹	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [3]
EL4OOH3J=EL34D+HO2	1.94x10 ⁺¹³	0	18157	2.13x10 ⁺⁰⁸	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [4]
Reverse	1.92x10 ⁺¹²	0	10743	2.23x10 ⁺⁰⁹	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a secondary carbon. [3]
EL6OOH7J=EL67D+HO2	1.67x10 ⁺¹³	0	16686	4.61x10 ⁺⁰⁸	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a primary carbon. [4]
Reverse	1.83x10 ⁺¹²	0	13100	4.84x10 ⁺⁰⁸	Recommended rate involving a peroxy group on a secondary carbon and a H atom on a primary carbon. [3]
EL7OOH6J=EL67D+HO2	3.66x10 ⁺¹³	0	19055	2.28x10 ⁺⁰⁸	Recommended rate involving a peroxy group on a primary carbon and a H atom on a secondary carbon. [4]
Reverse	3.18x10 ⁺¹²	0	13380	7.03x10 ⁺⁰⁸	Recommended rate involving a peroxy group on a primary carbon and a H atom on a secondary carbon. [3]
QOOH+O2=O2QOOH					
EL1OOH3J+O2=>EL1OOH3OO	4.52x10 ⁺¹²	0	0	4.52x10 ⁺¹²	Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1]
EL3OOH1J+O2=>EL3OOH1OO	4.52x10 ⁺¹²	0	0	4.52x10 ⁺¹²	Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1]
EL3OOH4J+O2=>EL3OOH4OO	4.52x10 ⁺¹²	0	0	4.52x10 ⁺¹²	Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1]
EL4OOH3J+O2=>EL4OOH3OO	4.52x10 ⁺¹²	0	0	4.52x10 ⁺¹²	Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1]
EL6OOH7J+O2=>EL6OOH7OO	4.52x10 ⁺¹²	0	0	4.52x10 ⁺¹²	Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1]
EL7OOH6J+O2=>EL7OOH6OO	4.52x10 ⁺¹²	0	0	4.52x10 ⁺¹²	Analogy to C3H6OOH2-1+O2<=>C3H6OOH2-1O2 [1]
O2QOOH=Ketohydroperoxide+OH					
EL1OOH3OO=EL1O3OOH+OH	2.50x10 ⁺¹⁰	0	21000	4.58x10 ⁺⁰⁴	Analogy to C7H14OOH1-3O2<=>NC7KET13+OH [1]
EL3OOH1OO=EL3O1OOH+OH	1.25x10 ⁺¹⁰	0	17450	2.14x10 ⁺⁰⁵	Analogy to C7H14OOH3-1O2<=>NC7KET31+OH [1]
EL3OOH4OO=EL3O4OOH+OH	1.00x10 ⁺¹¹	0	23450	3.93x10 ⁺⁰⁴	Analogy to C7H14OOH3-4O2<=>NC7KET34+OH [1]
EL4OOH3OO=EL4O3OOH+OH	1.00x10 ⁺¹¹	0	23450	3.93x10 ⁺⁰⁴	Analogy to C7H14OOH4-3O2<=>NC7KET43+OH [1]
EL6OOH7OO=EL6O7OOH+OH	1.00x10 ⁺¹¹	0	23450	3.93x10 ⁺⁰⁴	Analogy to C7H14OOH2-1O2<=>NC7KET21+OH [1]
EL7OOH6OO=EL7O6OOH+OH	2.00x10 ⁺¹¹	0	26000	1.58x10 ⁺⁰⁴	Analogy to C7H14OOH1-2O2<=>NC7KET12+OH [1]
Ketohydroperoxide Decomposition					
EL1O3OOH=OCCHO+C2H5OCOCH2CHO+OH	1.00x10 ⁺¹⁶	0	39000	2.22x10 ⁺⁰⁵	Analogy to NC7KET13<=>NC4H9CHO+CH2CHO+OH [1]
EL3O1OOH=CH2O+C2H5OCOCH2COCOJ+OH	1.00x10 ⁺¹⁶	0	39000	2.22x10 ⁺⁰⁵	Analogy to NC7KET31<=>CH2O+NC4H9COCH2+OH [1]
EL3O4OOH=CH3COCOJ+C2H5OCOCHO+OH	1.00x10 ⁺¹⁶	0	39000	2.22x10 ⁺⁰⁵	Analogy to NC7KET34<=>NC3H7CHO+C2H5CO+OH [1]
EL4O3OOH=CH3COCHO+C2H5OCOCOJ+OH	1.00x10 ⁺¹⁶	0	39000	2.22x10 ⁺⁰⁵	Analogy to NC7KET43<=>C2H5CHO+NC3H7CO+OH [1]
EL6O7OOH=CH3COC2H4COOCOJ+CH2O+OH	1.00x10 ⁺¹⁶	0	39000	2.22x10 ⁺⁰⁵	Analogy to NC7KET21<=>CH2O+NC5H11CO+OH [1]
EL7O6OOH=CH3COC2H4COOCHO+HCO+OH	1.00x10 ⁺¹⁶	0	39000	2.22x10 ⁺⁰⁵	Analogy to NC7KET12<=>NC5H11CHO+HCO+OH [1]
QOOH=Cyclic Ether+OH					

EL10OH3J=EL13CY+OH	7.50x10 ⁺¹⁰	0	15250	5.12x10 ⁺⁰⁶	Analogy to C7H14OOH1-3<=>C7H14O1-3+OH [1]
EL3OOH1J=EL13CY+OH	7.50x10 ⁺¹⁰	0	15250	5.12x10 ⁺⁰⁶	Analogy to C7H14OOH3-1<=>C7H14O1-3+OH [1]
EL3OOH4J=EL34CY+OH	6.00x10 ⁺¹¹	0	22000	5.86x10 ⁺⁰⁵	Analogy to C7H14OOH3-4<=>C7H14O3-4+OH [1]
EL4OOH3J=EL34CY+OH	6.00x10 ⁺¹¹	0	22000	5.86x10 ⁺⁰⁵	Analogy to C7H14OOH4-3<=>C7H14O3-4+OH [1]
EL6OOH7J=EL67CY+OH	6.00x10 ⁺¹¹	0	22000	5.86x10 ⁺⁰⁵	Analogy to C7H14OOH2-1<=>C7H14O1-2+OH [1]
EL7OOH6J=EL67CY+OH	6.00x10 ⁺¹¹	0	22000	5.86x10 ⁺⁰⁵	Analogy to C7H14OOH1-2<=>C7H14O1-2+OH [1]
Cyclic Ether Decomposition					
EL13CY+OH=C2H5OCOCH2CHO+HCCO+H2O	2.50x10 ⁺¹²	0	0	2.50x10 ⁺¹²	Analogy to C7H14O1-2+OH<=>PC4H9+C2H3CHO+H2O [1]
EL34CY+OH=C2H5OCOCH2CHO+HCCO+H2O	2.50x10 ⁺¹²	0	0	2.50x10 ⁺¹²	Analogy to C7H14O1-2+OH<=>PC4H9+C2H3CHO+H2O [1]
EL67CY+OH=C5H7O3-OJ+CH2CO+H2O	2.50x10 ⁺¹²	0	0	2.50x10 ⁺¹²	Analogy to C7H14O1-2+OH<=>PC4H9+C2H3CHO+H2O [1]
EL13CY+HO2=C2H5OCOCH2CHO+HCCO+H2O2	5.00x10 ⁺¹²	0	17700	7.31x10 ⁺⁰⁷	Analogy to C7H14O1-2+HO2<=>PC4H9+C2H3CHO+H2O2 [1]
EL34CY+HO2=C2H5OCOCH2CHO+HCCO+H2O2	5.00x10 ⁺¹²	0	17700	7.31x10 ⁺⁰⁷	Analogy to C7H14O1-2+HO2<=>PC4H9+C2H3CHO+H2O3 [1]
EL67CY+HO2=C5H7O3-OJ+CH2CO+H2O2	5.00x10 ⁺¹²	0	17700	7.31x10 ⁺⁰⁷	Analogy to C7H14O1-2+HO2<=>PC4H9+C2H3CHO+H2O4 [1]
EL13CY+CH3=C2H5OCOCH2CHO+HCCO+CH4	2.00x10 ⁺¹¹	0	10000	3.71x10 ⁺⁰⁸	Analogy to C4H8O1-2+CH3<=>CH2O+C3H5-A+CH4 [1]
EL34CY+CH3=C2H5OCOCH2CHO+HCCO+CH4	2.00x10 ⁺¹¹	0	10000	3.71x10 ⁺⁰⁸	Analogy to C4H8O1-2+CH3<=>CH2O+C3H5-A+CH5 [1]
EL67CY+CH3=C5H7O3-OJ+CH2CO+CH4	2.00x10 ⁺¹¹	0	10000	3.71x10 ⁺⁰⁸	Analogy to C4H8O1-2+CH3<=>CH2O+C3H5-A+CH6 [1]
Hydrogen Abstraction from Olefin					
EL34D+H=EL34D4J+H2	6.02x10 ⁺⁰⁵	2.4	2583	1.10x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+H=EL67D6J+H2	6.02x10 ⁺⁰⁵	2.4	2583	1.10x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+OH=EL34D4J+H2O	2.93x10 ⁺⁰⁴	2.53	-1659	1.85x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+OH=EL67D6J+H2O	2.93x10 ⁺⁰⁴	2.53	-1659	1.85x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+CH3=EL34D4J+CH4	9.04x10 ⁻⁰¹	3.46	4598	5.56x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+CH3=EL67D6J+CH4	9.04x10 ⁻⁰¹	3.46	4598	5.56x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+CH3O=EL34D4J+CH3OH	1.90x10 ⁺¹⁰	0	2800	3.26x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+CH3O=EL67D6J+CH3OH	1.90x10 ⁺¹⁰	0	2800	3.26x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+CH3O2=EL34D4J+CH3O2H	1.37x10 ⁺⁰²	3.12	13190	3.89x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+CH3O2=EL67D6J+CH3O2H	1.37x10 ⁺⁰²	3.12	13190	3.89x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+HO2=EL34D4J+H2O2	4.33x10 ⁺⁰²	3.01	12090	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+HO2=EL67D6J+H2O2	4.33x10 ⁺⁰²	3.01	12090	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+O=EL34D4J+OH	1.97x10 ⁺⁰⁵	2.40	1150	8.98x10 ⁺¹¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+O=EL67D6J+OH	1.97x10 ⁺⁰⁵	2.40	1150	8.98x10 ⁺¹¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+O2=EL34D4J+HO2	1.00x10 ⁺¹³	0	48200	6.80x10 ⁻⁰¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+O2=EL67D6J+HO2	1.00x10 ⁺¹³	0	48200	6.80x10 ⁻⁰¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+C2H5=EL34D4J+C2H6	1.00x10 ⁺¹¹	0	7900	6.95x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+C2H5=EL67D6J+C2H6	1.00x10 ⁺¹¹	0	7900	6.95x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+C2H5O=EL34D4J+C2H5OH	5.63x10 ⁺¹⁰	0	3650	5.66x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon

EL67D+C2H5O=EL67D6J+C2H5OH	5.63x10 ⁺¹⁰	0	3650	5.66x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+C2H3=EL34D4J+C2H4	2.50x10 ⁺¹¹	0	15450	1.50x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+C2H3=EL67D6J+C2H4	2.50x10 ⁺¹¹	0	15450	1.50x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+C2H5O2=EL34D4J+C2H5O2H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+C2H5O2=EL67D6J+C2H5O2H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+CH3CO3=EL34D4J+CH3CO3H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+CH3CO3=EL67D6J+CH3CO3H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+O2CHO=EL34D4J+HO2CHO	2.80x10 ⁺¹²	0	16010	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+O2CHO=EL67D6J+HO2CHO	2.80x10 ⁺¹²	0	16010	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+C4H9OaOO=EL34D4J+C4H9OaOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+C4H9OaOO=EL67D6J+C4H9OaOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL34D+C4H9ObOO=EL34D4J+C4H9ObOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
EL67D+C4H9ObOO=EL67D6J+C4H9ObOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
Olefin Radical Decomposition by Beta-bond Scission					
EL34D4J=>CH3COCHCCO+C2H5O	2.64x10 ⁺¹⁴	0	53796	5.30x10 ⁻⁰¹	Analogy to reverse of CH3COCH2CHCO + C2H5O = EL4J [5]
CH3COCHCCO=>CH3CO+CO+C2H	7.71x10 ⁺¹²	0	26385	4.78x10 ⁺⁰⁵	Analogy to reverse of CH3CO+C2H3COOH = C5H7O3-2J [5]
EL67D6J=>CH3COCH2CH2COJ+CO+CH2	1.13x10 ⁺²¹	-1.73	40550	8.95x10 ⁺⁰⁴	Analogy to reverse of CH3CHO + CH3COCH2CH2COJ = EL6J [5]
Hydrogen Abstraction from Minor Species					
C2H5OCOCH2CHO+H=C2H5OCOCH2COJ+H2	6.02x10 ⁺⁰⁵	2.4	2583	1.10x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+H=C2H5OCOCOJ+H2	6.02x10 ⁺⁰⁵	2.4	2583	1.10x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+H=CH3COCOJ+H2	6.02x10 ⁺⁰⁵	2.4	2583	1.10x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+H=CH3COC2H4COOCOJ+H2	6.02x10 ⁺⁰⁵	2.4	2583	1.10x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+OH=C2H5OCOCH2COJ+H2O	2.93x10 ⁺⁰⁴	2.53	-1659	1.85x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+OH=C2H5OCOCOJ+H2O	2.93x10 ⁺⁰⁴	2.53	-1659	1.85x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+OH=CH3COCOJ+H2O	2.93x10 ⁺⁰⁴	2.53	-1659	1.85x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+OH=CH3COC2H4COOCOJ+H2O	2.93x10 ⁺⁰⁴	2.53	-1659	1.85x10 ⁺¹²	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+CH3=C2H5OCOCH2COJ+CH4	9.04x10 ⁻⁰¹	3.46	4598	5.56x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+CH3=C2H5OCOCOJ+CH4	9.04x10 ⁻⁰¹	3.46	4598	5.56x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+CH3=CH3COCOJ+CH4	9.04x10 ⁻⁰¹	3.46	4598	5.56x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+CH3=CH3COC2H4COOCOJ+CH4	9.04x10 ⁻⁰¹	3.46	4598	5.56x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+CH3O=C2H5OCOCH2COJ+CH3OH	1.90x10 ⁺¹⁰	0	2800	3.26x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+CH3O=C2H5OCOCOJ+CH3OH	1.90x10 ⁺¹⁰	0	2800	3.26x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+CH3O=CH3COCOJ+CH3OH	1.90x10 ⁺¹⁰	0	2800	3.26x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+CH3O=CH3COC2H4COOCOJ+CH3OH	1.90x10 ⁺¹⁰	0	2800	3.26x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+CH3O2=C2H5OCOCH2COJ+CH3O2H	1.37x10 ⁺⁰²	3.12	13190	3.89x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+CH3O2=C2H5OCOCOJ+CH3O2H	1.37x10 ⁺⁰²	3.12	13190	3.89x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon

CH3COCHO+CH3O2=CH3COCOJ+CH3O2H	1.37x10 ⁺⁰²	3.12	13190	3.89x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+CH3O2=CH3COC2H4COOCOJ+CH3O2H	1.37x10 ⁺⁰²	3.12	13190	3.89x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+HO2=C2H5OCOCH2COJ+H2O2	4.33x10 ⁺⁰²	3.01	12090	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+HO2=C2H5OCOCOJ+H2O2	4.33x10 ⁺⁰²	3.01	12090	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+HO2=CH3COCOJ+H2O2	4.33x10 ⁺⁰²	3.01	12090	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+HO2=CH3COC2H4COOCOJ+H2O2	4.33x10 ⁺⁰²	3.01	12090	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+O=C2H5OCOCH2COJ+OH	1.97x10 ⁺⁰⁵	2.40	1150	8.98x10 ⁺¹¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+O=C2H5OCOCOJ+OH	1.97x10 ⁺⁰⁵	2.40	1150	8.98x10 ⁺¹¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+O=CH3COCOJ+OH	1.97x10 ⁺⁰⁵	2.40	1150	8.98x10 ⁺¹¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+O=CH3COC2H4COOCOJ+OH	1.97x10 ⁺⁰⁵	2.40	1150	8.98x10 ⁺¹¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+O2=C2H5OCOCH2COJ+HO2	1.00x10 ⁺¹³	0	48200	6.80x10 ⁻⁰¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+O2=C2H5OCOCOJ+HO2	1.00x10 ⁺¹³	0	48200	6.80x10 ⁻⁰¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+O2=CH3COCOJ+HO2	1.00x10 ⁺¹³	0	48200	6.80x10 ⁻⁰¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+O2=CH3COC2H4COOCOJ+HO2	1.00x10 ⁺¹³	0	48200	6.80x10 ⁻⁰¹	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+C2H5=C2H5OCOCH2COJ+C2H6	1.00x10 ⁺¹¹	0	7900	6.95x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+C2H5=C2H5OCOCOJ+C2H6	1.00x10 ⁺¹¹	0	7900	6.95x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+C2H5=CH3COCOJ+C2H6	1.00x10 ⁺¹¹	0	7900	6.95x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+C2H5=CH3COC2H4COOCOJ+C2H6	1.00x10 ⁺¹¹	0	7900	6.95x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+C2H5O=C2H5OCOCH2COJ+C2H5OH	5.63x10 ⁺¹⁰	0	3650	5.66x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+C2H5O=C2H5OCOCOJ+C2H5OH	5.63x10 ⁺¹⁰	0	3650	5.66x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+C2H5O=CH3COCOJ+C2H5OH	5.63x10 ⁺¹⁰	0	3650	5.66x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+C2H5O=CH3COC2H4COOCOJ+C2H5OH	5.63x10 ⁺¹⁰	0	3650	5.66x10 ⁺⁰⁹	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+C2H5O=C2H5OCOCH2COJ+C2H5OH	2.50x10 ⁺¹¹	0	15450	1.50x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+C2H5O=C2H5OCOCOJ+C2H5OH	2.50x10 ⁺¹¹	0	15450	1.50x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+C2H5O=CH3COCOJ+C2H5OH	2.50x10 ⁺¹¹	0	15450	1.50x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+C2H5O=CH3COC2H4COOCOJ+C2H5OH	2.50x10 ⁺¹¹	0	15450	1.50x10 ⁺⁰⁷	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+C2H5O2=C2H5OCOCH2COJ+C2H5O2H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+C2H5O2=C2H5OCOCOJ+C2H5O2H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+C2H5O2=CH3COCOJ+C2H5O2H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+C2H5O2=CH3COC2H4COOCOJ+C2H5O2H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+CH3CO3=C2H5OCOCH2COJ+CH3CO3H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+CH3CO3=C2H5OCOCOJ+CH3CO3H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COCHO+CH3CO3=CH3COCOJ+CH3CO3H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH3COC2H4COOCHO+CH3CO3=CH3COC2H4COOCOJ+CH3CO3H	2.80x10 ⁺¹²	0	16000	1.19x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCH2CHO+O2CHO=C2H5OCOCH2COJ+HO2CHO	2.80x10 ⁺¹²	0	16010	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C2H5OCOCHO+O2CHO=C2H5OCOCOJ+HO2CHO	2.80x10 ⁺¹²	0	16010	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon

CH ₃ COCHO+O ₂ CHO=CH ₃ COCOJ+HO ₂ CHO	2.80x10 ⁺¹²	0	16010	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH ₃ COC ₂ H ₄ COOCHO+O ₂ CHO=CH ₃ COC ₂ H ₄ COOCOJ+HO ₂ CHO	2.80x10 ⁺¹²	0	16010	1.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C ₂ H ₅ OCOCH ₂ CHO+C ₄ H ₉ OaOO=C ₂ H ₅ OCOCH ₂ COJ+C ₄ H ₉ OaOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C ₂ H ₅ OCOCHO+C ₄ H ₉ OaOO=C ₂ H ₅ OCOCOJ+C ₄ H ₉ OaOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH ₃ COCHO+C ₄ H ₉ OaOO=CH ₃ COCOJ+C ₄ H ₉ OaOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH ₃ COC ₂ H ₄ COOCHO+C ₄ H ₉ OaOO=CH ₃ COC ₂ H ₄ COOCOJ+C ₄ H ₉ OaOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C ₂ H ₅ OCOCH ₂ CHO+C ₄ H ₉ ObOO=C ₂ H ₅ OCOCH ₂ COJ+C ₄ H ₉ ObOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
C ₂ H ₅ OCOCHO+C ₄ H ₉ ObOO=C ₂ H ₅ OCOCOJ+C ₄ H ₉ ObOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH ₃ COCHO+C ₄ H ₉ ObOO=CH ₃ COCOJ+C ₄ H ₉ ObOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
CH ₃ COC ₂ H ₄ COOCHO+C ₄ H ₉ ObOO=CH ₃ COC ₂ H ₄ COOCOJ+C ₄ H ₉ ObOOH	1.81x10 ⁻⁰¹	3.98	9058	2.18x10 ⁺⁰⁸	Assumed to be equal to hydrogen abstraction from tertiary carbon
Decomposition of Minor Species Beta-bond Scission					
C ₂ H ₅ OCOCH ₂ COJ=EFF+CO+CH ₂	8.83x10 ⁺¹⁴	-0.67	35550	1.95x10 ⁺⁰⁴	Analogy to reverse of C ₂ H ₃ COCH ₃ + EFF = EL3J [5]
C ₂ H ₅ OCOCH ₂ COCOJ=EE2J+CO+CO	2.63x10 ⁺¹⁰	0.84	26100	5.35x10 ⁺⁰⁵	Analogy to reverse of CH ₂ CO + EE2J = ELCOJ [5]
CH ₃ COCOJ=CH ₃ +CO+CO	1.00x10 ⁺¹⁴	0	31000	3.40x10 ⁺⁰⁵	Analogy to reverse of CH ₃ + COCHCH ₂ CO ₂ CH ₂ CH ₃ = EL3J [5]
C ₂ H ₅ OCOCOJ=C ₂ H ₅ O+CO+CO	6.82x10 ⁺¹⁶	-1.34	26930	3.86x10 ⁺⁰⁵	Analogy to reverse of CH ₃ COCH ₂ CHCO + C ₂ H ₅ O = EL4J [5]
CH ₃ COC ₂ H ₄ COOCOJ=CH ₃ COCH ₂ CH ₂ COJ+CO ₂	1.13x10 ⁺²¹	-1.73	40550	8.95x10 ⁺⁰⁴	Analogy to reverse of CH ₃ CHO + CH ₃ COCH ₂ CH ₂ COJ = EL6J [5]

Table S1. Reaction pathways, estimated rate constants and sources for the reactions of the low temperature ethyl levulinate sub model. Rate coefficients are in the form $k = AT^n \exp(-E_a/RT)$.

Mixture #	X _{Ethanol}	X _{Diethyl Ether}	X _{Ethyl Levulinate}	IDT (ms)	Standard Deviation (ms)	Measured DCN	Standard Deviation
1	0	0.75	0.25	2.73	0.04	77.31	1.78
2	0	0.5	0.5	4.28	0.04	48.07	0.41
3	0	0.37	0.63	6.42	0.1	33.42	0.63
4	0	0.25	0.75	12.18	0.32	21.25	0.35
5	0	0.1	0.9	47.84	3.75	10.3	0.36
6	0.1	0.2	0.7	15.89	1.6	18.18	1.2
7	0.1	0.5	0.4	3.01	0.07	67.83	1.65
8	0.1	0.4	0.5	4.46	0.08	46.36	0.78
9	0.1	0.7	0.2	2.91	0.05	70.88	1.55
10	0.25	0.65	0.1	3.17	0.07	63.83	1.65
11	0.25	0.5	0.25	4.38	0.05	47.1	0.53
12	0.25	0.25	0.5	11.81	0.74	21.69	0.8
13	0.25	0.1	0.65	71.39	6.86	8.71	0.32
14	0.25	0	0.75	139.72	5.77	6.83	0.09
15	0.4	0.5	0.1	4.49	0.08	46.01	0.73
16	0.5	0.4	0.1	6.48	0.1	32.8	0.56
17	0.5	0.25	0.25	17.47	0.59	17.13	0.32
18	0.5	0.1	0.4	98.29	9.89	7.72	0.34
19	0.5	0	0.5	136.53	10.46	6.89	0.17
20	0.75	0.2	0.05	63.65	4.15	9.11	0.26
21	0.75	0.1	0.15	101.04	7.9	7.63	0.21
22	0.75	0	0.25	133.99	5.31	6.92	0.09

Table S2. Mixture mole fractions, ignition delay times and ignition quality tester measured derived cetane numbers.

Initial Pressure (bar)	Initial Temperature (K)	Compressed Pressure (bar)	Compressed Temperature (K)	Ignition Delay Time (ms)
Reaction Mixture (Mole Fractions)				
Ethyl Levulinate/Diethyl Ether/Ethanol/O ₂ /N ₂ = 0.0124/0.0095/0.0134/0.2026/0.7621				
$\Phi = 1.0$				
0.64	338	20.13	765	426.8
0.63	338	20.2	765	391.4
0.63	338	20.19	765	404.2
0.63	353	19.99	793	107.5
0.63	353	20.06	793	105.1
0.63	353	19.88	792	109.7
0.63	368	19.54	817	40.7
0.63	368	19.61	817	40.7
0.63	368	19.51	817	40.4
0.63	383	19.36	844	17.6
0.63	383	19.64	846	17.1
0.63	383	19.36	844	17.7
0.63	398	19.28	870	8.2
0.63	398	19.32	871	8.1
0.63	398	19.22	870	8.1
0.63	413	19.15	897	4.0
0.63	413	19.12	897	3.9
0.63	413	19.18	897	3.9
1.22	323	39.99	741	185.6
1.22	323	40.10	741	179.6
1.22	323	40.03	741	178.9
1.22	338	39.64	769	70.4
1.22	338	39.64	768	69.9
1.22	338	39.52	768	70.3
1.22	353	39.35	796	29.6
1.22	353	39.31	796	27.2
1.22	353	39.31	796	29.1
1.22	368	38.65	821	13.3
1.23	368	39.11	823	13.0
1.23	368	39.12	823	13.1
1.23	383	38.50	848	5.8
1.23	383	38.66	849	5.7
1.23	383	38.79	849	5.8
1.23	398	38.70	876	2.4
1.23	398	38.44	875	2.0
1.23	398	38.58	876	2.3

Reaction Mixture (Mole Fractions)				
Ethyl Levulinate/Diethyl Ether/Ethanol/O ₂ /N ₂ = 0.0063/0.0049/0.0068/0.7758/0.2062				
$\Phi = 0.5$				
0.61	353	19.28	842	151.1
0.61	353	19.21	841	165.8
0.61	353	19.19	841	156
0.61	368	18.88	868	45.8
0.62	368	19.27	870	39.7
0.62	368	19.11	868	43.1
0.62	383	19.43	901	15.6
0.62	383	19.53	902	15.7
0.62	383	19.45	900	15.6
0.62	398	19.33	929	6.8
0.62	398	19.32	930	6.7
0.62	398	19.03	927	6.4
0.62	413	19.12	958	3.2
0.62	413	19.11	958	3
0.62	413	19.13	958	3.2
1.18	323	39.81	790	254.2
1.18	323	39.74	790	249.3
1.18	323	39.77	790	247.2
1.18	338	39.45	820	74.0
1.18	338	39.33	820	74.5
1.18	338	39.35	820	74.5
1.18	353	38.35	846	28.4
1.19	353	38.60	846	27.6
1.20	353	39.65	850	27.8
1.19	368	39.28	880	11.9
1.19	368	39.31	880	11.7
1.19	368	39.22	879	11.8
1.20	383	38.32	905	4.7
1.21	383	38.90	907	4.7
1.21	383	39.34	908	5.1

Table S3. Rapid compression machine initial and compressed conditions, and ignition delay times.

Figure S1. Exemplar rapid compression machine experimental pressure histories for the EL/DEE/EtOH Gasoline at compressed conditions of 20 bar, 793 K and $\Phi = 1.0$.

Figure S2. Comparison of modifications made to the kinetic model developed in this work. Adjustment 1 refers to the standardization of all the H-abstraction rate constants, and Adjustment 2 refers to the increasing of the formation enthalpy of the peroxy alkylhydroperoxide radicals (OOQOOH) in the diethyl ether sub model by 10 kJ/mol. Adjustment 3 refers to the addition of the EL low temperature combustion pathways.

Figure S3. Reacting flux analysis at 65% of the ignition delay time for combustion simulation in a closed constant volume homogenous reactor, for FACE-F, at 750 K, 25 bar, and $\Phi=1$. Oxidation reactions are highlighted in blue and elimination reactions in red.

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Ethanollic Gasoline, a Lignocellulosic Advanced Biofuel

Mícheál Séamus Howard^{a,b}, Gani Issayev^c, Nimal Naser^c, S. Mani Sarathy^c, Aamir Farooq^c, Stephen Dooley^{*a,b}

^aDepartment of Chemical Sciences, University of Limerick, Ireland.

^bSchool of Physics, Trinity College Dublin, Ireland.

^cKing Abdullah University of Science and Technology (KAUST), Clean Combustion Research Centre, Physical Sciences and Engineering Division, Thuwal, Saudi Arabia.

Response to Referees

Referee: 1

Comments to the Author

This article contains some fascinating new science on the autoignition chemistry of mixtures, a challenging and currently important topic. Therefore, my recommendation is to publish after what I hope is minor revision, although some issues I bring up may require a bit more.

The idea of using mixed bio-derived components to produce a fuel with better properties than can be obtained with any of the individual components is of great interest in the fuels and combustion community today. The authors have done a nice job in identifying a potential process that produces an interesting mixture of three oxygenates, with the blend composition somewhat tunable. I think that the EL/DEE/EtOH system is an outstanding model system for examination of mixture autoignition chemistry – a topic that is also of great interest to the community because of synergistic and antagonistic interactions that are not understood in a very detailed way. However, there are some significant issues with actually commercializing this material as a spark-ignition engine fuel that the authors gloss over in their introductory material, which I think gives readers a false impression of the actual commercial potential of this fuel (which, in my opinion, is near zero – but then again, I could be wrong). Also, while for the most part the discussion of the autoignition mechanism and kinetics is really good, there are a few points of confusion that should be addressed. I offer specific comments on the various sections of the paper below.

We thank the reviewer for their careful examination of the manuscript and for their positive appraisal.

Introduction

1. Page 1, first paragraph, right hand column (RHC): “Given the diverse range of combustion qualities of these three components, mixtures of alkyl levulinate, alcohol and ether may be very compatible with existing fuel infrastructures.” This makes no sense to me. Infrastructure compatibility is more about materials compatibility and fire safety, not about “combustion qualities” which, within the context of this paper, means autoignition delay.

By the term 'existing fuel infrastructures' we refer to the method by which liquid fuels are currently combusted, i.e. in spark ignition or compression ignition engines and of course the combustion properties which the reviewer alludes to, the autoignition delay. However, to avoid confusion the statement has been altered to the following:

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.

2. Page 2, second paragraph, left hand column (LHC): The authors correctly note the the cetane number and solubility issues of blending ethanol into diesel fuel. However, there are other issues that are also notable and relevant to this work. While low cetane number and poor solubility can be dealt with using additives and co-solvents, the fact that blending ethanol (even with co-solvents) lowers the flashpoint to a very dangerous 20C is the real limiting factor in blending ethanol into diesel (https://www.afdc.energy.gov/pdfs/barriers_ediesel.pdf).

Discussed with Issue 3.

3. Page 2, third paragraph, LHC: While DEE does have an excellent cetane number, it will also dramatically lower the flashpoint of the diesel fuel into the dangerous range, and thus has no practical potential as a diesel blend component or a co-solvent for ethanol.

We thank the reviewer for highlighting this issue. As pure components both EtOH and DEE have low flashpoints, and when blended with diesel, they can significantly reduce the flashpoint of diesel below current regulatory requirements (1, 2). The reviewer alludes to this property as being a limiting factor for the commercialization of this biofuel technology. While we agree that the low flashpoint of these pure components needs to be recognized, we do not propose to use these two components as standalone diesel fuel components.

The current paper focuses on the development of a technology platform for the use of the ethanolic fuel mixture formulated as gasoline not diesel, here the vapour pressure arguments are different as gasoline is already quite volatile, with a flash point entirely different to that of diesel. Furthermore, the likely proposition is that the ethanolic fuel components be blended with petro fuels, and not used as "pure" biofuels.

Also, the reviewer's analysis omits the third and most important ethanolic fuel component, ethyl levulinate, which is derived from the cellulosic biomass. In relation to usable flashpoints, EL has a very helpfully high flashpoint of 90°C (3), thus significantly mitigating the limiting effect of the low flash point of the other two components, for potential use with diesels.

The text has been modified to include a discussion on fuel physical properties, and the likely use of the advanced biofuels as blend components with petrofuels. We stress to the

reviewer and in the text, that in Europe, member states are required to have at least 6.7% of the transportation fuel mix derived from non-food biomass – "advanced biofuel" [RED II]. Basic and fundamental research is required to make this happen.

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 (4). 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) (5) and 2008/68/EC (diesel) (6), 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 (7), and cetane number (8). 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 (3). 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. (9) 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 (10); this is further supported by the combustion kinetic model developed by Ghosh et al. (9).

Obviously, ethanol (EtOH) is well-established as an octane booster in gasolines (11). 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% (12). 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 (1).

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) (13) and is long known as an ignition enhancer to improve the reactivity of several other fuels, such as biodiesel (14). 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 (15). Alike ethanol, diethyl ether also has a very low flashpoint; thus its use as a standalone fuel additive is limited (2).

4. Page 2, fourth paragraph, LHC: “The blending of ethanol and diethyl ether to formulate fuels of particular combustion properties has been extensively studied (10, 13). The inclusion of alkyl levulinates in this biofuel mix is therefore of obvious technical and commercial potential.” The technical and commercial potential is certainly not obvious to me. The justification for studying these three things together seems to be that they can be produced together as a mixture from biomass. And as pure components they have substantially different autoignition chemistry, making a study of the autoignition of a mixture fundamentally interesting.

While this work presents a fundamental comprehension of the autoignition of three biofuel components, there are many technical and commercial advantages to studying this mixture of biofuels. Firstly, as the reviewer mentioned, these three components can be produced together in controlled fractions through the acid hydrolysis of waste biomass in ethanol. Using these three components as a mixture would remove the need for separation and isolation processes in the synthesis stage. This is a huge technical advantage over other advanced biofuel technologies. Secondly, as the reviewer noted, ethanol and diethyl ether both have significant limitations as standalone biofuel additives in terms of ignition behaviour and also flashpoint. Using these components as part of a mixture with ethyl levulinate, which has a significantly high flashpoint would allow for the blending of these biofuel components in higher fractions with conventional fuels while still maintaining regulatory requirements. Examination of upcoming regulatory requirements highlights that this biofuel mixture is of significant technological and commercial potential and worthy of study. Currently, EU regulations mandate that all road transportation fuels must be comprised of a minimum of 6% biofuels, this increases to 10% by 2020. Currently, 1st generation biofuels, derived from for-food feedstocks are used to attempt to meet this obligation. However, over the coming decade, the Revised Renewable Energy Directive (RED II) will require all road transportation fuels sold in the EU to limit the 1st generation fraction to ~4%. RED II requires the balance to be replaced by a minimum 6% of advanced biofuels. Advanced biofuels are derived from feedstocks that are not in direct competition with food feedstocks. Thus, this work presents a possible pathway to utilize the current ethanol production infrastructure and upgrade the first-generation ethanol to an advanced biofuel through the acid hydrolysis with waste lignocellulose.

To provide some regulatory context to the commercial advantages of this biofuel system the following has been added to the introduction:

Growing concern about the consequences of societies 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 (16-18). 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 (19). 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 "first generation" (from food) biofuels limited to only 4% (20). 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.

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 (19). 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 (21). 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, Flannelly 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 (22).

The statement in question by the reviewer was also elaborated upon to further highlight the technical and commercial advantage of such a biofuel system

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.

5. Page 2, fourth paragraph, LHC: I think it is also important to note some things about the properties of EL. It boils at 206C, which is well above the allowable T90 level for conventional gasoline. Also, it has been demonstrated that EL is not that soluble in diesel boiling range hydrocarbons, separating out as an insoluble liquid phase upon cooling. While the freezing point of EL is less than -60C, in blends of 10 volume percent in a diesel having a cloud point of -25C, the blend cloud point was found to be 4C (Energy Fuels 2011, 25, 5422–5428). While it may be more soluble in gasoline, this needs to be proven. Of course, in this paper it appears that the EL/DEE/EtOH blend is proposed as a stand-alone fuel, not blended in hydrocarbon, however these properties are worth mentioning. Finally, because DEE makes up 27% of the RON-95 mixture, the vapor pressure (i.e. RVP or modern equivalent DVPE) might be expected to be very high as DEE is extremely volatile. Similarly, because of the high boiling point of EL, and the mixture contains 35% EL, one wonders if the distillation T90 of the mixture is within the normal gasoline range.

The issues raised by the reviewer are all legitimate concerns for the use of ethyl levulinate as a standalone biofuel additive and are important to recognize. To inform the reader of these concerns the following has been added to the introduction.

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 (3). An appropriate co-solvent would be required in order to improve the solubility of ethyl levulinate in diesel fuels.

Again, these issues can be mitigated to a certain degree by blending ethyl levulinate with the other proposed biofuel components. For example, as previously mentioned diethyl ether is well established as an excellent co-solvent used to improve the solubility of other additives in diesel.

It is important to note that, this initial work sets out to characterize the autoignition behaviour of the ternary biofuel mixture. The results of which provides justification for the further examination of the fuel properties that the reviewer suggests, for this biofuel mixture as a potentially viable biofuel.

Experimental and Numerical Methods

6. My only comment on this section is that the measurement of DCN using the IQT is a standardized method that is very well described in the ASTM test method and in the literature. The detailed description given here seems unnecessary to me. Suggest shortening pretty dramatically.

We thank the reviewer for their suggestion and have amended the section to the following for brevity:

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 (23), the ignition delay time obtained with an IQT is a combination of overlapping physical and chemical processes (24, 25) 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 (26, 27).

Results and Discussion

7. Page 5, second paragraph, RHC: EL is referred to as the “value-added” component, because it is derived from a waste stream. Are you considering it value-added because it will be low cost? Or because it will have a lower life-cycle greenhouse gas emissions footprint? Or both?

Ethyl levulinate is considered the value-added component as it is derived from lignocellulosic waste material. It is therefore an advanced biofuel component which can be added in

unconstrained amounts according to upcoming regulations. For this reason, in addition to the (assumed) lower greenhouse gas footprint relative to petroleum it is a value added component.

8. Page 5, second paragraph, RHC: “The RON could not be measured due to limitations in the fuel handling system while working with a diethyl ether blend.” Given that MON could be measured in the same apparatus (but under different experimental conditions), and that 95 RON is right in “sweet spot” for accurate RON measurements with conventional fuels, I think the authors need to provide much more detail on what the problem was.

To elaborate on the issue raised by the reviewer, the RON could not be measured for the EL/DEE/EtOH Gasoline due to a flow rate limitation in the fuel intake system of the specific device used. The following was included in the paper to explain the issue:

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 (28) and ASTM D2700-18 (29). 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.

9. Page 6, first paragraph, RHC: Discussion of Figure 2. The authors refer to “truncated Arrhenius reactivity” for the EL/DEE/EtOH mixture. I was unsure what this really meant, and suggest being more descriptive. For example, something like, ignition delay times for the EL/DEE/EtOH mixture were above 500 ms for $T < 740\text{K} - 760\text{K}$, while measurable ignition delays were obtained down to 645K for FACE F.

We accept the reviewer’s comments on the need to be more descriptive. As such, as per the reviewer’s recommendations the section has been amended to the following:

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 $\sim 750\text{ K}$. This is strikingly different to that observed for FACE-F, where measurable ignition delays were obtained at temperatures as low as 645 K.

10. Discussion of Figure 2 in general. Clearly the autoignition delay curves are dramatically different for the EL/DEE/EtOH mixture relative to FACE F. FACE F exhibits pronounced NTC behavior that is indicative of a fuel with a relatively low octane sensitivity i.e. like the PRF; while the bioderived mixture behaves like a fuel with a high octane sensitivity i.e. like toluene or neat ethanol. Thus, it seems strange to expect these fuels to have the same RON and MON. However, based on measurements they have the nearly the same MON. On page 7 the authors cite reference 46 and note that this paper finds a good correlation between RON and ignition delay at 750K and 25 bar (in an IQT). Recognizing that the data in Figure 2 are from an RCM, not an IQT, and that data at 25 bar are not reported, we can nevertheless look at the 20 bar curves and wonder “if these two fuels have the same RON then perhaps they will have the same ignition delay at 750K?”. However, at 20 bar (or 40 bar, for that

matter) this is not the case and the EL/DEE/EtOH mixture has more than 10x longer ignition delay at 750K. Ignition delays at $\phi=1$ do not become the same till T is over 830K. To me, this strongly suggests that the RON of this material is well above 95 – this would mean a significantly higher octane sensitivity for the bioderived blend – consistent with the lack of NTC behaviour.

The reviewer raises an interesting point on the topic of RON and MON and their relationship to the observed gas phase reaction kinetics. As a result, we have included the following discussion to deal with the issue in the paper:

Table 1 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

^aFrom Equation 2. ^bEstimated using DCN-RON relationship summarized by Equation 3 (30).

^cMeasured in this work. ^dMeasured by Naser et al. (25). ^eMeasured by Sarathy et al. (31).

Using RON and MON as Reactivity Indicators for Oxygenated Biofuels.

As summarized in Table 1, 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, outline by Haas et al. (30) and Naser et al. (25), 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 potential important complicating implications.

Singh et al. have shown that for gasoline surrogate mixtures (toluene/iso-octane/n-heptane/1-hexene/1,2,4-trimethylbenzene), there is a relationship between octane sensitivity and the occurrence of NTC autoignition behaviour (32). 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 (26, 27, 33-37) 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 (28). 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 (26, 38). Furthermore, ignition in the IQT occurs in locally rich equivalence ratio regions, as discussed below (39, 40), 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 (33).

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 (38). 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 (34). 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 (35, 41). 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.

11. The discussion of Figures 3 -5 is outstanding and the best part of the paper. This analysis will be cited by others who are examining mixture autoignition chemistry. One minor error in Figure 3, the DEE mechanism, species “C4H9ObOO” is shown in the stick molecule drawing as ROOH, when I think it should be ROO.

We thank the reviewer for their careful examination of the manuscript. This error has been amended in Figure 3.

12. Page 7, third paragraph, LHC: The authors note that for FACE F H-abstraction is almost all by OH, while for the bioderived blend H-abstraction is by both OH and HO₂. Everyone seems to agree that HO₂ is much less reactive than OH and that H-abstraction by HO₂ will be much slower. Is the reason that so much of the H-abstraction for the bioderived mixture simply because HO₂ is produced as a major product of the autoignition reactions of this material? Perhaps it should be noted here something like “as we show below, HO₂ is the dominant radical produced from EL and EtOH oxidation and so is present in higher concentrations for the EL/DEE/EtOH blend”.

The reviewer is correct in their analysis, a larger proportion of H-abstraction in the EL/DEE/EtOH Gasoline fuel is by HO₂ radicals in comparison to FACE-F as a result of the larger population of HO₂ radicals in the radical pool. H-abstraction by HO₂ results in the formation of H₂O₂, a chain terminating processes which consumes a reactive radical until the temperature of the system reaches a sufficient temperature for the H₂O₂ to decompose. This is a further contributing factor of the reduced reactivity of the EL/DEE/EtOH Gasoline.

The following has been added to the manuscript to make this analysis more apparent to the reader:

As will be show below, HO₂ 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 HO₂ radicals is very different to the competing process of hydrogen abstraction by OH radicals. Hydrogen abstraction by HO₂ leads to the formation of H₂O₂ which, as summarized by Westbrook (42), is accumulated until the system reaches a sufficient temperature for the H₂O₂ to decompose to two OH radicals. Thus, this process consumes a reactive radical to form H₂O₂ 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.

13. Page 7, third paragraph, LHC: The authors refer to the “synergistic behaviour” of EL, which I think refers to the consumption of OH and generation of the effectively chain terminating HO₂ – in the sense that OH is mainly generated by DEE and rather than this OH causing ignition of the other components EL scopes it up and terminates the reaction. A very brief additional explanation of what is meant by synergistic behaviour would help the reader who may not be an expert in autoignition kinetics.

The synergistic behaviour actually refers to the interaction between ethyl levulinate and diethyl ether. As a standalone fuel ethyl levulinate is consumed by molecular elimination to levulinic acid and ethylene. However, in this mixture diethyl ether produces a large population of reactive radicals, thereby promoting the dominance of the H-abstraction consumption of ethyl levulinate over the molecular elimination pathways.

As per the reviewer’s suggestion, this has been elaborated in the manuscript to the following, in order to assist the readers comprehension:

For ethyl levulinate, this synergistic blend behaviour, consumption by hydrogen abstraction, is very significant. As a pure component fuel (43)), 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 promoting 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.

Referee: 2**Comments to the Author**

in this work, Derived Cetane Numbers are measured for a wide variety of blend fractions of Ethyl levulinate, diethyl ether and ethanol, using Ignition Quality Tester measurements. EL/DEE/EtOH mixtures of ignition quality equivalent to market diesel and gasoline were identified. One mixture of Research Octane Number (RON) 95 is selected for detailed analysis in comparison to a FACE gasoline as a representative of petroleum-derived gasoline, with a similar RON of 94.4. the ignition delay times of these 2 fuels were measured using RCM and compared with each other. detailed chemical kinetic analyses were performed to understand the similarities and differences between these mixtures. the manuscript is generally well written and the presented data are very interesting and will certainly be useful to the research community. i therefore recommend the acceptance of the current work after the authors address my comments below.

We thank the reviewer for their careful examination of the manuscript and for their positive appraisal.

1. the manuscript contains few typos and mistakes. i recommend a thorough revision of the language prior to the acceptance of the work.

We thank the reviewer for their careful examination of the manuscript. The manuscript has been prudently reviewed for spelling and grammatical errors.

2. the major concern i have about this work is the fact that the authors claim that the two fuels have similar RON and MON and yet they have fairly different ignition delay times at the studied conditions. i know that the authors measured MON and could not measure the RON due to facility limitations but after inspecting the results i believe that RON measurement for the gasoline-like blend is necessary to this study. the studied blend has orders of magnitude longer ignition delay times when compared to FACE F and i believe this will somehow be reflected on RON measurements at some point. else, reasonable explanation need to be provided before this manuscript can be accepted.

Further to our comments to Reviewer #1, it is an experimental fact that both fuels have the same MON. It is another experimental fact that both fuels have very different gas phase ignition delays. On the basis of the similarity in MONs and the similarity in IQT measured ignition delay, we argue that one can reasonably expect the RONs to be relatively similar. However, this is speculation on both sides. The point of the analysis is that one should not expect the gas phase ignition delay to be equivalent merely because any octane number is equivalent if one is dealing with fuel components that are substantially different to the calibration reference points of the octane scales: n-heptane and iso-octane. This will be the case for any oxygenated fuel component that is typical of advanced biofuels.

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Sustainable Energy and Fuels

ARTICLE

Ethanollic Gasoline, a Lignocellulosic Advanced Biofuel

Mícheál Séamus Howard^{a,b}, Gani Issayev^c, Nimal Naser^c, S. Mani Sarathy^c, Aamir Farooq^c, Stephen Dooley^{*a,b}

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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 show 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 HO₂ radical. 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.

Introduction

Growing concern about the consequences of societies 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 "first 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.

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

^a Department of Chemical Sciences, University of Limerick, Ireland.

^b School of Physics, Trinity College Dublin, Ireland.

^c King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Centre, Physical Sciences and Engineering Division, Thuwal, Saudi Arabia.

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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, Flannelly 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 $< 5^{\circ}\text{C}$ (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 (29, 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 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 suppress 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:

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

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 $\Phi = 0.5$, at 600 – 900 K. Exemplar experimental pressure histories can be seen in Figure 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, OH, HO_2 , O and $\dot{C}H_3$, 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 Figure S2):

1. The hydrogen abstraction reactions are assigned to describe abstraction by the same set of species from each fuel component, i.e., H, OH, CH₃, CH₃O, CH₃OO, HO₂, O, O₂ and C₂H₅ were considered by Ghosh et al. (33), but C₂H₅OO, CH₃C(O)OO, 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.
2. The formation enthalpy of the diethyl ether peroxy alkylhydroperoxide radicals were previously arbitrarily reduced in the Sakai model by 10 kJ/mol 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 RO₂ and alkylhydroperoxide radical species to describe the important equilibrium of elimination pathways, the recommended rate constant and equilibrium constant 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:

$$DCN = \sum_i DCN_i (a_i x_i + b_i (x_i)^2 + c_i (x_i)^3) \quad \#(2)$$

where 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.

Table 1 DCNs and parameters for Eq. (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

The experimental data is summarized in Figure 1, and tabulated as Supplementary Information (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). Equation (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:

$$RON = 116.609 - 0.784(DCN) - (0.00662(DCN^2)) - (3.401 \times 10^{-4}(DCN^3)) \quad \#(3)$$

Figure 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 ~17 – 27% 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.

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

^aFrom Equation 2. ^bEstimated using DCN-RON relationship summarized by Equation 3 (49). ^cMeasured in this work. ^dMeasured by Naser et al. (28). ^eMeasured by Sarathy et al. (25).

Figure 2, shows the ignition delay data of the EL/DEE/EtOH Gasoline measured in a rapid compression machine, also tabulated as Supplementary Information (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

Figure 2 RCM ignition delay times for the EL/DEE/EtOH Gasoline and FACE-F [15]. Symbols correspond to measurements. Lines correspond to model simulations. FACE-F data are taken from [15].

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, outline 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 potential important complicating implications.

Singh et al. have shown that for gasoline surrogate mixtures (toluene/iso-octane/n-heptane/1,2,4-trimethylbenzene), 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 Figure 2. For the EL/DEE/EtOH Gasoline, this is the first time such a multicomponent 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 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 Figure 3, S3, and 5.

The mode of consumption of all three fuel components of the EL/DEE/EtOH Gasoline is similar. Hydrogen abstraction by $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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

Figure 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, $\Phi=1$. For ethyl levulinate "Isomerization" refers to conversion to the EL1/3/4/6/7J radicals. 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 OH population, red indicates chain termination pathways

decompose to two $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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 promoting 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 ("C4H9Ob"), 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 -hydroxyethyl) undergoing the concerted elimination to form HO_2 and acetaldehyde, a pathway important in alcohol combustion

Figure 4 Normalized small radical rate of production for the EL/DEE/EtOH Gasoline and FACE-F [15] after 65% of the computed ignition delay time at 750 K and 1200 K, 25 bar, and $\Phi=1$.

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 Figure 3).

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 undergoes elimination to olefin and HO_2 , and 75% isomerizes 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 the 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 olefin 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 – 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 Figure 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

Figure 5 Sensitivity analysis to ΔT for the EL/DEE/EtOH Gasoline and FACE-F [15] 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.

radicals, thus maintaining or enhancing the population of the reactivity driving $\dot{\text{O}}\text{H}$ 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, $\dot{\text{O}}\text{H}$ 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 $\text{C}_2\text{H}_5\text{O}$) 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 $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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 $\dot{\text{O}}\text{H}$ 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 ~ 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 olefin 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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82x40mm (300 x 300 DPI)

69x28mm (300 x 300 DPI)

165x161mm (300 x 300 DPI)

Ethanollic Gasoline, a Lignocellulosic Advanced Biofuel

Mícheál Séamus Howard^{a,b}, Gani Issayev^c, Nimal Naser^c, S. Mani Sarathy^c, Aamir Farooq^c, Stephen Dooley^{*a,b}

^aDepartment of Chemical Sciences, University of Limerick, Ireland.

^bSchool of Physics, Trinity College Dublin, Ireland.

^cKing Abdullah University of Science and Technology (KAUST), Clean Combustion Research Centre, Physical Sciences and Engineering Division, Thuwal, Saudi Arabia.

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