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Predicting the Combustion Behaviour of Tailorable Advanced Biofuel Blends Using Automatically Generated Mechanisms

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Abstract

Emerging processes such as biomass alcoholysis have the potential to provide tailorable, advanced biofuels to replace conventional fossil fuels. To model the combustion characteristics of the resultant complex blends, automatic mechanism generation (AMG) techniques are applied to produce detailed ethyl (ethyl levulinate, diethyl ether, ethanol) and butyl (n-butyl levulinate, di-n-butyl ether, n-butanol) kinetic mechanisms. The predictive capabilities of these mechanisms are evaluated, showing a high degree of accuracy when compared to ignition delay time (IDT) and speciation measurements, at thermodynamic conditions of relevance to engine technologies.

Introduction

Global energy demand is predicted to grow significantly, due largely to a rise in global population and the increasing demands of developing regions for transportation and goods haulage [1]. These sectors are heavily reliant on crude oil, raising environmental concerns which must be addressed rapidly. In Europe, the Renewable Energy Directive II (RED II) requires that member states meet legally binding renewable energy targets, including a minimum of 14% renewables for all road and rail transport by 2030 [2]. Furthermore, this directive limits the contribution of unsustainable first-generation biofuels to this target, while encouraging the use of advanced biofuels with periodic requirements. Emerging technologies, such as the alcoholysis of biomass, have the potential to provide economically viable, tailorable, advanced biofuel blends [3].

The alcoholysis of biomass produces three primary products: an alkyl levulinate, a dialkyl ether, and an alcohol. The ratios of these components can be tailored by altering process parameters, allowing for the production of bespoke fuel blends to meet specific combustion requirements [4]. Ethyl and butyl alcoholysis processes are currently the most feasible for advanced biofuel production, as biogenic sources for ethanol and butanol are functional and well understood [5,6]. Tailoring fuels requires a comprehensive understanding of the combustion behaviour for each independent component and their blends.

Howard et al. [4] investigated the ignition behaviour of various blends of ethyl levulinate (EL), ethanol, and diethyl ether (DEE), using an ignition quality tester (IQT) and rapid compression machine (RCM). The work described blending regimes for Derived Cetane Number (DCN) and Research Octane Number (RON), and identified a blending ratio for a RON 95, MON 88.3, "ethanolic gasoline" (EG). Upon comparison to a FACE-F gasoline of almost identical octane ratings, they found that their EG produced similar reactivity at a compressed pressure (P_c) of 20 bar, including the presence negative temperature coefficient (NTC) behaviour. However, this behaviour

was muted for the EG blend, providing a shallower profile. This was attributed to the increased role of HO_2 related chain termination, but uncertainty in the DCN determination and the resultant DCN to RON relation are also potential sources of significant error [4,7].

Galletti et al. [8] reported on the performance and emissions impacts of blending diesel with ternary mixtures of n-butyl levulinate (nBL), n-butanol, and di-n-butyl ether (DBE). Biofuel fractions of up to 20% were shown to produce reductions in CO and particulate emissions, with no significant changes to engine power or fuel efficiency [8]. Despite these promising results, ignition studies of butyl levulinate and butyl blends are entirely absent from the literature, while studies of ethyl levulinate and ethyl blends are scarce. Characterising the blending space for ethyl and butyl systems experimentally would be extremely costly. However, computer modelling provides an opportunity to predict combustion behaviour relatively cheaply and quickly. Such modelling requires a robust, detailed chemical kinetic mechanism. The large, detailed mechanisms typical of advanced biofuels may contain hundreds of species and thousands of reactions. Creating such mechanisms by hand is often tedious, prone to human error, and requires extensive expert knowledge of reaction pathways. AMG methods limit the likelihood of human error by automating tedious processes and embedding expert understanding [9].

This study uses AMG to produce detailed kinetic mechanisms for ethyl and butyl blends. The predictive capabilities of these mechanisms are evaluated against literature data for IDTs and speciation measurements, and the autoignition behaviour for select ethyl and butyl blends are predicted.

Methodology

Mechanism Generation

Reaction mechanisms for each component are produced using Reaction Mechanism Generator (RMG) [10]. Individual mechanisms are then combined to produce full blend mechanisms for ethyl and butyl cases. RMG is one of the most frequently utilised AMG packages, commonly applied in the construction of

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detailed kinetic models, as well as the estimation of thermochemical properties [11,12]. Full details of RMG are given in the literature [10], though the general methodology is briefly summarised here. To initialise mechanism generation, RMG must first be provided with reactor conditions, species concentrations, termination criteria, and model tolerances. Initial species are then reacted together in the model core using a predefined set of reaction templates to form a model edge of product species. The rates for these reactions are estimated using a built-in database of literature sourced rate rules and training data. It is therefore imperative that this underlying database contains accurate training data. All possible elementary reactions are considered, while a rate-based algorithm determines whether to include each edge species (and the associated reactions) in the model core [13]. Thermodynamic data for each species is predicted by group additivity. The core expansion process is then repeated with the new enlarged core, until the predefined termination criteria are met. Kinetic and thermodynamic data may also be provided in the form of seed mechanisms and thermodynamic libraries.

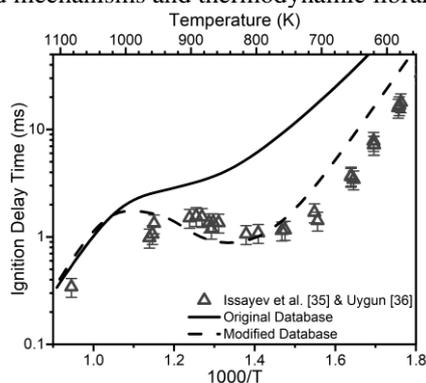


Figure 1. The impact of database modifications on the prediction of IDTs for DEE. Stoichiometric, $P_c=20$ bar.

The ethyl and butyl mechanisms are seeded with literature sourced sub-mechanisms for DEE [14], ethanol [15], DBE [16], and n-butanol [17]. Sub-mechanisms for EL and nBL are produced based on literature sourced rates for appropriate esters, ketones, ethers, and alkanes [18–31]. A C0-C4 core seed is provided using the widely validated AramcoMech 2.0 [32]. To minimise parameter error in the estimation of reaction rates, modifications were made to RMGs open-source database. This is necessary for the accurate prediction of many oxygenated compounds, as training data for the associated functional groups is not comprehensive. Database modifications such as these can have significant impacts on the predictive capabilities of RMG mechanisms, as shown in figure 1.

After generation is complete, each mechanism is subject to a suite of post-processing techniques. This includes local [OH] and brute force $\Delta H_{f,298K}$ sensitivity analysis, rate of production analysis, and the identification of collision rate violators. Sensitive reactions and species identified for further investigation are updated with high quality rate parameters and thermodynamic data from the literature. Rate of

production analysis is applied in combination with knowledge of low temperature combustion to locate and investigate atypical behaviour, such as missing reaction pathways or unusual reaction products. Finally, the identification of collision rate violators is used to locate non-physical reaction rates. These are usually introduced by seed mechanisms as parameters are extrapolated outside of the validated regime. It is unfortunately common for literature mechanisms to contain several such violators [33], which must be removed and replaced with higher quality literature data or RMG generated values.

Using this process, an ethyl blend mechanism has been produced containing 533 species and 10742 reactions, and a butyl blend mechanism generated containing 906 species and 21388 reactions.

Model Simulations

IDT simulations are performed using the closed homogeneous gas-phase reactor module available in CHEMKIN-PRO [34]. Variable volume simulations are performed by applying case dependant volume histories to account for RCM facility effects.

Speciation predictions are compared against literature data for jet stirred reactors (JSRs). Simulations for JSR data are completed by applying the perfectly stirred reactor module of CHEMKIN-PRO, using an iso-thermal, constant pressure approach.

Mechanism Performance

Diethyl Ether

Predicted IDTs for DEE are displayed in figure 2, compared against the experimental RCM and shock-tube (ST) data of Issayev et al. [35] and Uygun [36]. This figure clearly shows an excellent representation of the experimental results by the RMG mechanism, throughout the temperature regime and NTC region, at both compressed pressures. Interestingly, these IDT simulations out-perform the mechanism of Tran et al. [14], which served as the source for the DEE seed. This includes the prediction of a convoluted second stage of NTC behaviour, evident as a shoulder to the NTC region. Such behaviour is indicative of the multistage ignition behaviour of DEE [35].

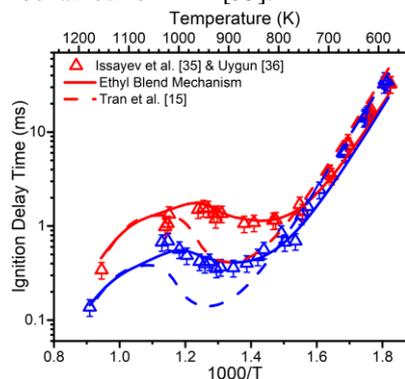


Figure 2. Stoichiometric DEE IDTs [35]. Symbols represent experimental data; lines show model predictions for $P_c=20$ bar (red) and 40 bar (blue).

Mole fractions for the oxidation of DEE in a JSR can be seen in figure 3, wherein experimental data is

reproduced from the JSR-GC measurements of Tran et al. [14]. The model continues to provide a very good representation of the experimental data, producing vastly more accurate predictions than the DEE mechanism of Sakai et al. [25] and the EG mechanism of Howard et al. [4]. While the Tran et al. [14] mechanism fails to predict NTC IDTs (figure 2), it does produce the most accurate prediction of low-pressure DEE consumption (particularly for the double NTC behaviour), highlighting a small degree of performance loss in this regard for the RMG mechanism.

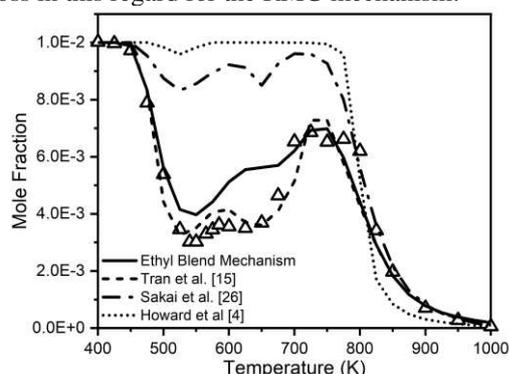


Figure 3. Concentration of DEE in a JSR with varying temperature. Stoichiometric, 106.7 kPa, 2 s residence time, 1/6/93 mol% DEE/O₂/He. Symbols show the measurements of Tran et al. [14], lines show the predictions of various models.

Diethyl Ether/Ethanol Blend

Upon blending with ethanol in a 50/50 by mole mixture, reactivity decreases significantly throughout the investigated regime and the NTC intensity is suppressed. This behaviour can be observed in the RCM data of Issayev et al. [35], and is replicated accurately by the RMG generated ethyl blend mechanism, as shown in figure 4. For the ethyl blends, ethanol and DEE are the least and most reactive components, respectively. Therefore, for the purposes of fuel tailoring, it is important that the mechanism accurately predicts the impacts of their blending on the overall fuel reactivity.

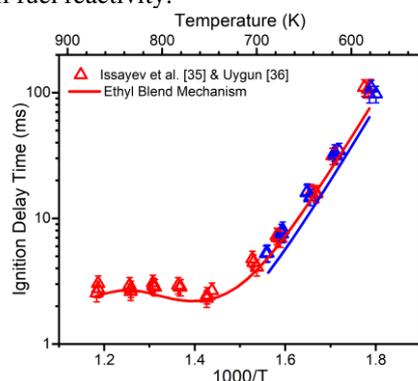


Figure 4. IDTs for a 50/50 by mole DEE/ethanol blend [35]. Symbols represent experimental data; lines show model predictions for $P_c=20$ bar (red) and 40 bar (blue).

Ethyl Levulinate

The availability of fundamental combustion data for EL is limited, and low temperature IDT measurements do not currently exist. This is likely due to the

molecule's low vapour pressure (0.17 mbar at 298 K), which makes gas-phase experiments incredibly difficult. However, Ghosh et al. [37] utilised a heavily diluted EL (0.5% by mole) mixture to measure ST IDTs, for stoichiometric and lean ($\phi=0.5$) mixtures. The experimental results of Ghosh et al. [37] and the predictions of the RMG mechanism can be seen in figure 5. Predictions are again extremely accurate. However, these IDT measurements all occur at high temperatures (>1100 K) and therefore do not reveal much information about the low temperature behaviour of interest for conventional engine technologies.

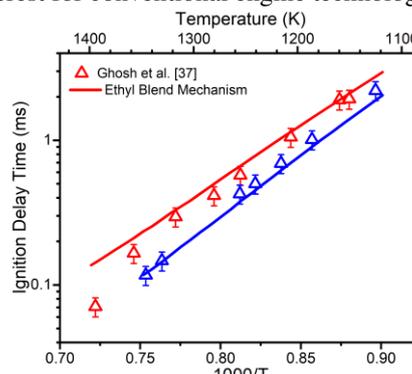


Figure 5. IDTs for a highly diluted (0.5% mol), stoichiometric, EL mixture at 10 bar [37]. Symbols represent experimental data; lines show model predictions for $\phi=1.0$ (red) and 0.5 (blue).

Some information about the low temperature oxidation of EL can be determined from the JSR mole fraction data shown in figure 6. Mole fraction measurements here are reproduced from the work of Wang [38]. At these conditions, EL displays no notable NTC behaviour. This is predicted by the mechanism, as are the mole fractions for C₂H₄, which serve as a convenient marker for assessing the unimolecular decomposition of EL into levulinic acid. The accuracy of predictions for this speciation data provides a degree of confidence in the reproduction of EL's low temperature behaviour.

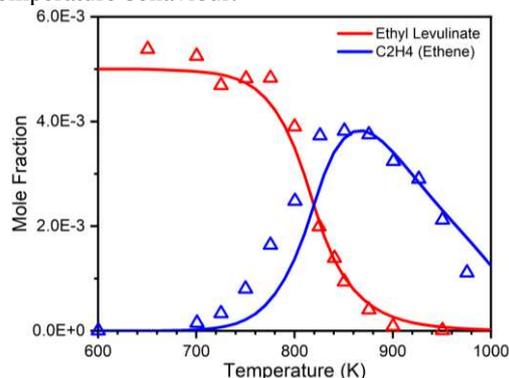


Figure 6. EL conversion and C₂H₄ production as a function of temperature. Stoichiometric, 0.5% mol EL, 1 bar, 2s residence time. Symbols represent the data of Wang [38], lines show model predictions.

Ethanol Gasoline (EL/DEE/Ethanol blend)

Fundamental measurements of ethyl blend combustion are only available from a single literature source, wherein Howard et al. [7] determined IDTs for

a blend of 35/27/38 mol% EL/DEE/ethanol (EG). These results are reproduced in figure 7, alongside the associated predictions of the mechanism produced in this study. IDTs in both the low and high temperature regimes are well predicted by the model, for $P_c=20$ and 40 bar. Importantly, the model also provides a good representation of the NTC intensity exhibited by the RCM data. This highlights the capabilities of the AMG generated mechanism and the generation methodology applied in this study, for predicting the combustion behaviour of potential advanced biofuels.

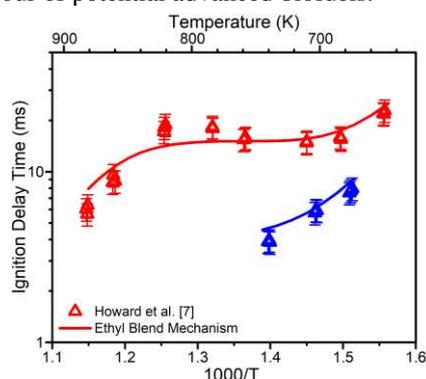


Figure 7. IDTs for EG at stoichiometric conditions. Symbols represent experimental data [7], lines show model predictions for $P_c=20$ bar (red) and 40 bar (blue).
Di-n-Butyl Ether

DBE IDTs, measured by Hakimov et al. [39] and predicted using the RMG generated butyl mechanism, are presented in figure 8. Unfortunately, measured IDTs in the intermediate temperature region (700-900 K) do not appear in the literature for DBE, so it is not possible to determine the capabilities of the mechanism for predicting NTC behaviour in this case. However, predictions of shock tube (ST) provide a good representation of observed data for both pressures (20, 40 bar) and equivalence ratios ($\phi=1, 0.5$).

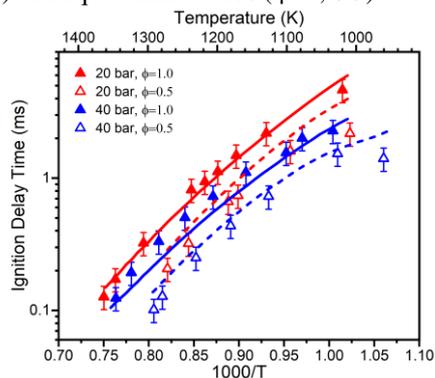


Figure 8. DBE IDTs for pressures of 20 and 40 bar, at $\phi=1.0$ and 0.5. Symbols represent experimental data [39], lines show model predictions.

n-Butanol

The RCM IDTs of n-butanol, for stoichiometric, lean ($\phi=0.5$), and rich ($\phi=2.0$) equivalence ratios are reproduced from the work of Weber et al. [40] and shown in figure 9. The combined butyl mechanism provides reasonable predictions for these measurements at all the investigated equivalence ratios, but clearly performs the best for the stoichiometric

mixture. There is some under-prediction of reactivity at the high and low temperatures for the lean and rich conditions, respectively. This may be indicative of inaccurate rate parameters, possibly for oxygen sensitive reactions such as oxygen addition and competing pathways, but more investigation is required.

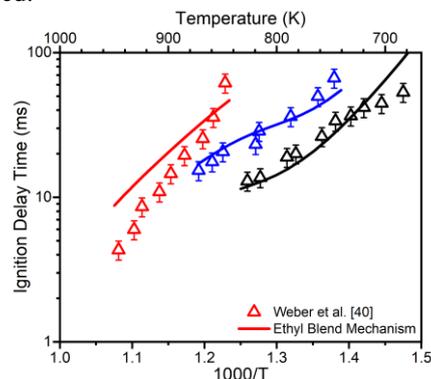


Figure 9. IDTs for n-butanol at $P_c=15$ bar. Symbols represent experimental data [40], lines show model predictions for $\phi=0.5$ (red), 1.0 (blue), and 2.0 (black).
n-Butyl Levulinate

It is not possible to evaluate predictions of nBL against fundamental combustion data, as none exists in the literature. Like EL, this is due to the difficulty in performing gas-phase experiments with such a low vapour pressure molecule. The predicted IDTs for nBL are shown in figure 10, compared to the predicted IDTs of ethyl levulinate at the same conditions. By comparing the two and applying knowledge of other oxygenated molecules, it can be seen that nBL behaves as expected in comparison to EL; nBL IDTs are much shorter at low temperatures and higher at high temperatures, due to a cross-over in reactivity. This cross-over is due to the presence of NTC-like behaviour, owing to the longer carbon chain present in nBL. However, until experimental data becomes available these predictions are speculative.

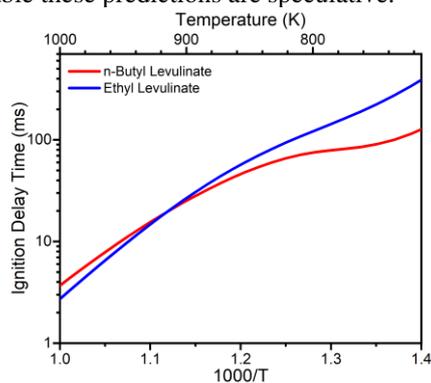


Figure 10. Predicted IDTs for EL and nBL. $P_c=20$ bar and stoichiometric conditions.

Butanolic Blend

RON 95 blends (determined by a linear by mole blending rule) for ethyl and butyl mixtures are predicted and the IDTs are presented in figure 11, for stoichiometric conditions at $P_c=20$ bar. Both IDT profiles are extremely similar, as expected for fuels of the same octane rating. Many of the characteristic

differences between EL and nBL are also present in the comparison of these blends, including cross-over behaviour and the presence of greater NTC-like behaviour for the butyl blend. Experimental data for a RON 95 FACE-F gasoline are reproduced in this figure from the work of Sarathy et al. [41]. It is clear that, while high temperature IDTs are similar between the FACE-F and biofuel blends, low temperature and NTC reactivity are not alike. This is indicative of the use of an inappropriate linear blending law and highlights the need for more accurate blending rules.

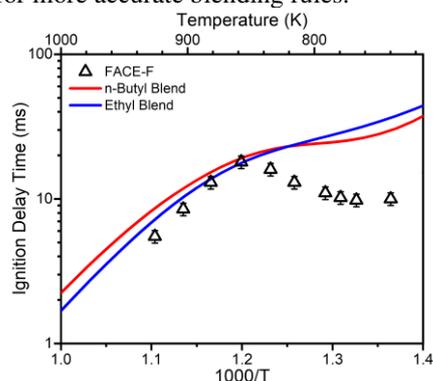


Figure 11. Predicted IDTs for RON 95 ethyl and butyl blends, and FACE-F gasoline IDTs reproduced from Sarathy et al. [41]. $P_c=20$ bar, stoichiometric.

Conclusions

AMG tools are effective at producing accurate models for complex fuels, when applied appropriately. The method employed in this study, which utilises database modification based on low uncertainty, high quality, literature data and various post-processing steps, has been shown to produce highly accurate predictions for a range of species and target parameters. The automatically generated mechanisms produced in this study may also be extrapolated outside the regime of their seed mechanisms, though some relative performance loss is observed in exchange for this increased versatility (as shown by figure 3).

Predictions for ethyl and butyl blends show that these advanced biofuel blends are capable of replicating the ignition behaviour typical in modern gasolines [7], including the NTC region. Butyl blends appear to be marginally more relevant for use in conventional spark-ignition engines, due to the more significant NTC-like behaviour of nBL in comparison to EL. This pseudo-NTC decreases reactivity at the high temperature end of the regime, increasing the knock resistance of the fuel.

Future work should focus on the collection of fundamental ignition data for both EL and nBL and their blends with other fuel components, in regions of relevance to engine technologies. This will assist validating the mechanisms and reveal insights into the underlying chemistry of alkyl levulinate oxidation.

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