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

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Introduction

- The EU Renewable Energy Directive II requires a minimum of 3.5% advanced biofuels for all road and rail transport by 2030 [1].
- Biomass alcoholysis has the potential to produce economically viable, tailorable, advanced biofuels.
- This utilises lignocellulosic biomass to produce three primary products: an alklyl levulinate, a dialkyl ether, and an alcohol.
- Ethanolysis and butanolysis are currently the most feasible.
- There are gaps in knowledge due to the rapid development of such biofuels and the complex nature of low temperature combustion.
- Computer modelling provides opportunities to predict combustion behaviour cheaply and quickly.
- Automatic mechanism generation (AMG) tools can automate the tedious production of detailed mechanisms, utilising expert knowledge of complex reaction pathways, reducing human error.
- This study applies AMG to produce detailed kinetic mechanisms for ethyl and butyl blends and evaluates their predictive capabilities against literature data.
- The autoignition behaviour for selected blends are also predicted.

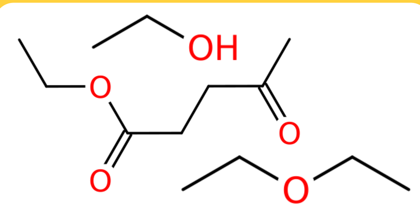

Figure 1. Molecular structures for ethanolysis products. From top to bottom: ethanol, ethyl levulinate (EL), diethyl ether.(DEE)

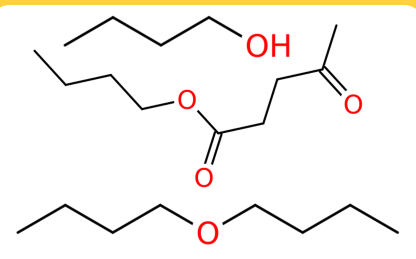

Figure 2. Molecular structures for butanolysis products. From top to bottom: n-butanol, n-butyl levulinate (nBL), dibutyl ether (DBE)

Mechanism Generation

- Mechanisms are produced for each component using Reaction Mechanism Generator (RMG) [2].
- Individual mechanisms are combined to produce ethyl and butyl blend mechanisms.
- Mechanisms are seeded with literature sourced sub-mechanisms for ethanol [3], diethyl ether [4], dibutyl ether [5], and n-butanol [6].
- Sub-mechanisms for ethyl and butyl levulinate are produced based on literature sourced rates for appropriate esters, ketones, ethers, and alkanes.
- A C0-C4 core is provided using AramcoMech 2.0 [7].
- For the functional groups of interest, the training data available in the RMG database is not comprehensive.
- Therefore, extensive modifications to RMGs open-source database are necessary.
- After generation, each mechanism is subject to: local [OH] and brute force $\Delta H_{f,298K}$ sensitivity analysis, rate of production analysis, and the identification of collision rate violators.
- 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.

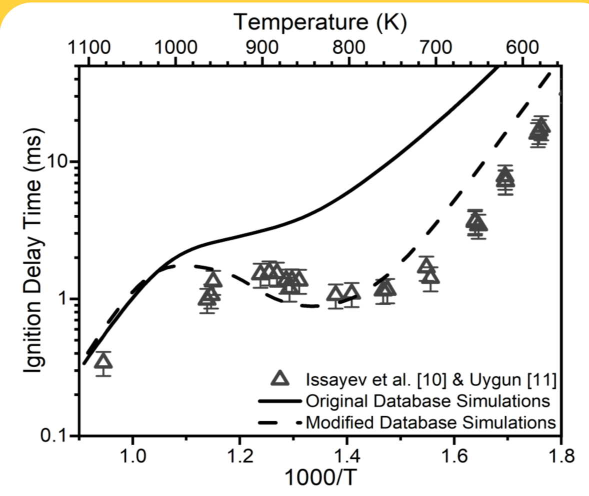

Figure 3. The impact of database modifications on the prediction of ignition delay times (IDTs) for DEE.

Mechanism Performance

Diethyl Ether

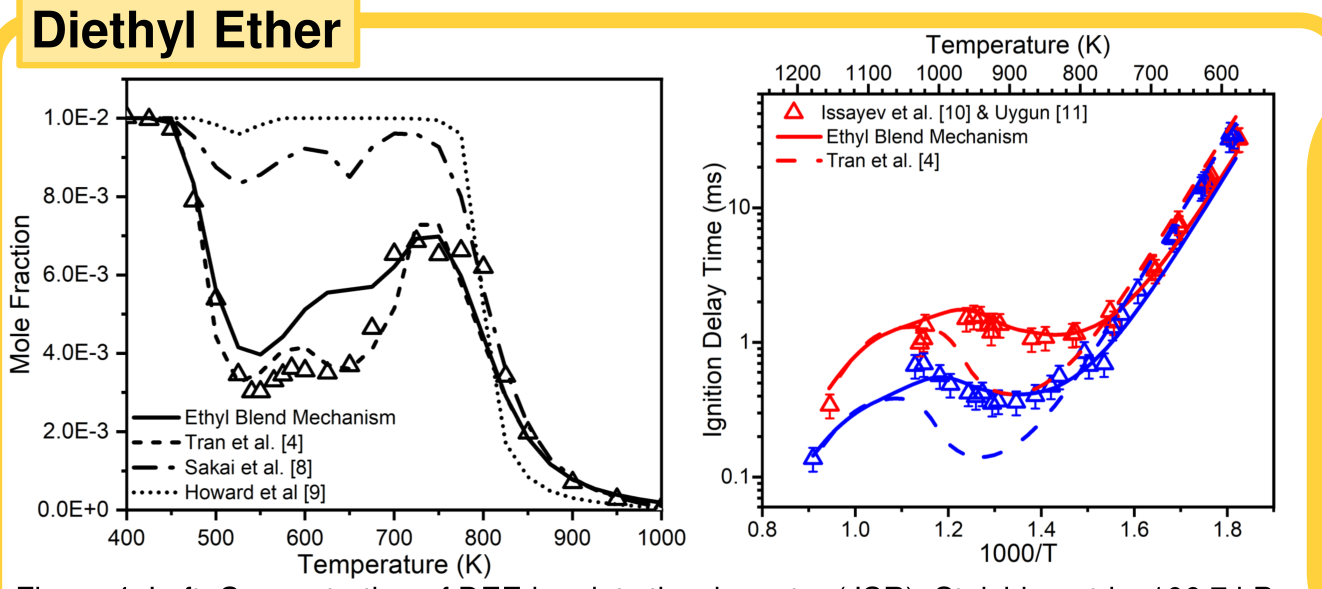

Figure 4. Left: Concentration of DEE in a jet stirred reactor (JSR). Stoichiometric, 106.7 kPa, 2 s residence time, 1/6/93 mol% DEE/O2/He. Right: Stoichiometric IDTs for P_c=20 bar (red) and 40 bar (blue). Both: Symbols represent experimental data; lines show model predictions.

- Excellent representation of DEE IDT data throughout the regime.
- IDT simulations out-perform the seed mechanism [4], particularly in the negative temperature coefficient (NTC) region.
- Good prediction of DEE JSR data when compared to other literature mechanisms.
- Small performance loss for the prediction of JSR data.

Dibutyl Ether

- Measured IDTs in the intermediate temperature region (700-900 K) do not appear in the literature.
- Therefore, it is not possible to determine the accuracy of NTC predictions.
- Predictions of shock tube IDTs provide a good representation for both pressures and equivalence ratios.

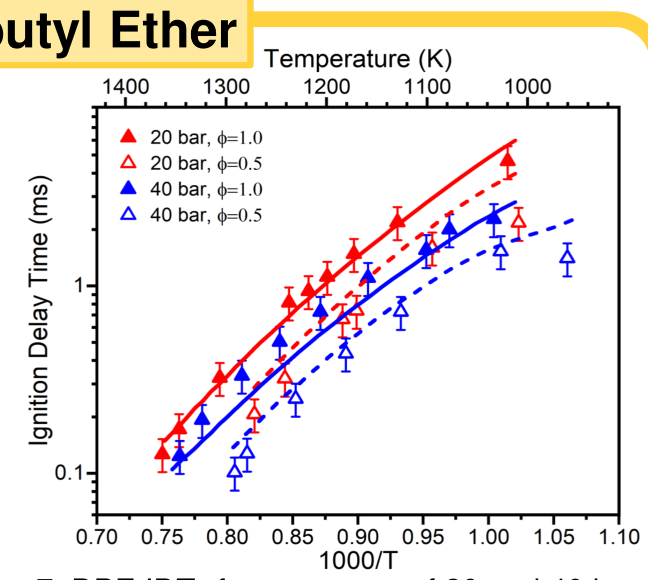

Figure 7. DBE IDTs for pressures of 20 and 40 bar, at φ=1.0 and 0.5. Symbols represent experimental data [14], lines show model predictions.

DEE/Ethanol Blend

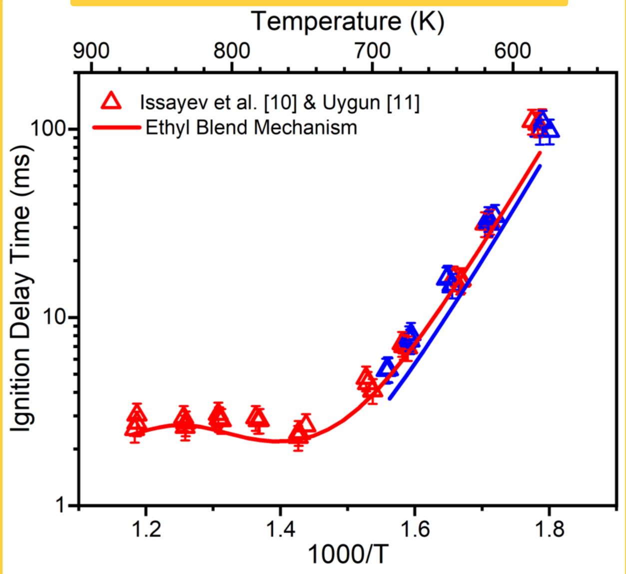

Figure 5. Stoichiometric IDTs for a 50/50 by mole DEE/ethanol blend. Symbols represent experimental data; lines show model predictions for P_c=20 bar (red) and 40 bar (blue).

- Upon blending DEE with ethanol, NTC intensity is suppressed.
- This behaviour is captured by the RMG generated model.
- Accurately replicating blending behaviour such as this is important for fuel tailoring.

Ethyl and Butyl Blends

- Fundamental measurements are available for a single RON 95 ethyl blend termed 'ethanolic gasoline': 35/27/38 mol% EL/DEE/ethanol [9].
- Ethanolic gasoline IDTs are well predicted by the ethyl blend model.
- Importantly, the model also provides a reasonable representation for the NTC intensity exhibited by RCM data.
- This highlights the capabilities of the AMG generated mechanism and the generation methodology applied in this study.

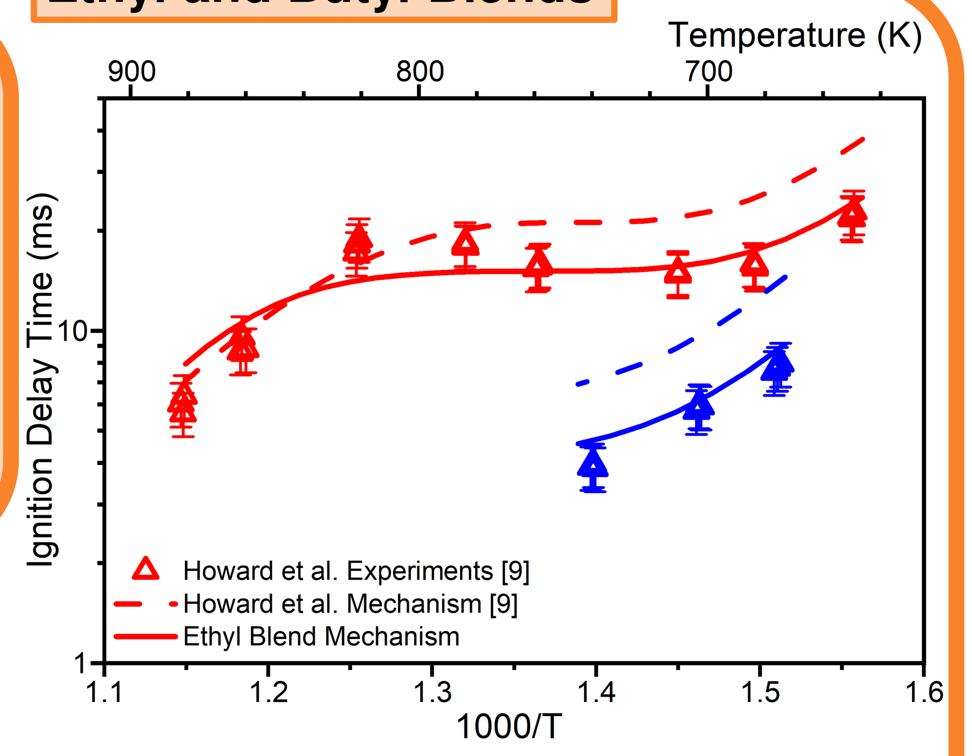

Figure 10. IDTs for 'ethanolic gasoline' at stoichiometric conditions. Symbols represent experimental RCM data, lines show model predictions for P_c=20 bar (red) and 40 bar (blue).

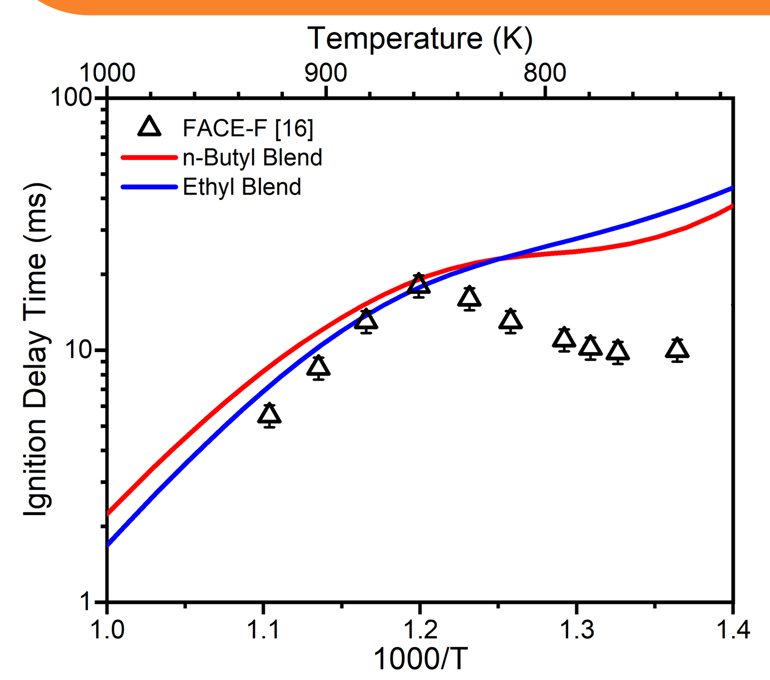

Figure 11. Predicted homogeneous gas-phase IDTs for RON 95 ethyl and butyl blends, and FACE-F gasoline IDTs. P_c=20 bar, stoichiometric.

- RON 95 ethyl and butyl blends are formulated using a linear by mole blending rule and predicted by the respective models.
- These are compared against RCM measurements for a common RON 95 gasoline (FACE-F) [16].
- IDT cross-over for the two biofuel blends is present due to the larger NTC intensity of butyl components.
- Difference in low temperature IDTs compared to FACE-F is likely due to the use of an inappropriate linear blending law.
- More accurate blending rules are required for advanced biofuels.

n-Butanol

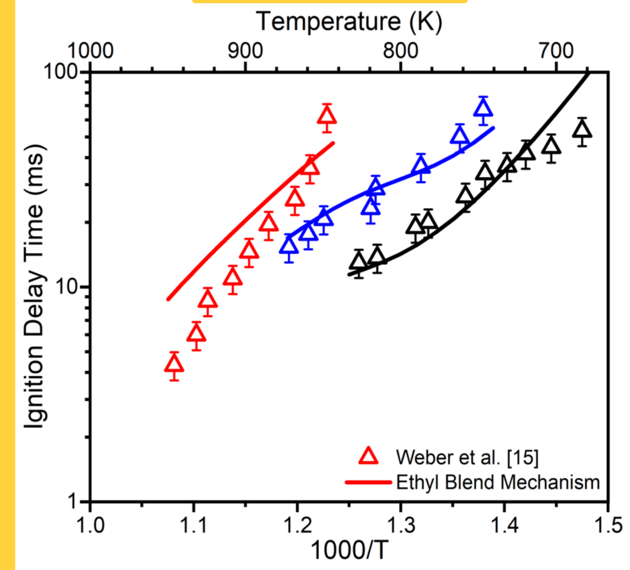

Figure 8. IDTs for n-butanol at P_c=15 bar. Symbols represent experimental data, lines show model predictions for φ=0.5 (red), 1.0 (blue), and 2.0 (black).

- Reasonable predictions for all the investigated equivalence ratios.
- Under-prediction of reactivity in lean and rich mixtures may be indicative of inaccurate rate parameters for oxygen sensitive reactions, such as oxygen addition and competing pathways.

Ethyl Levulinate

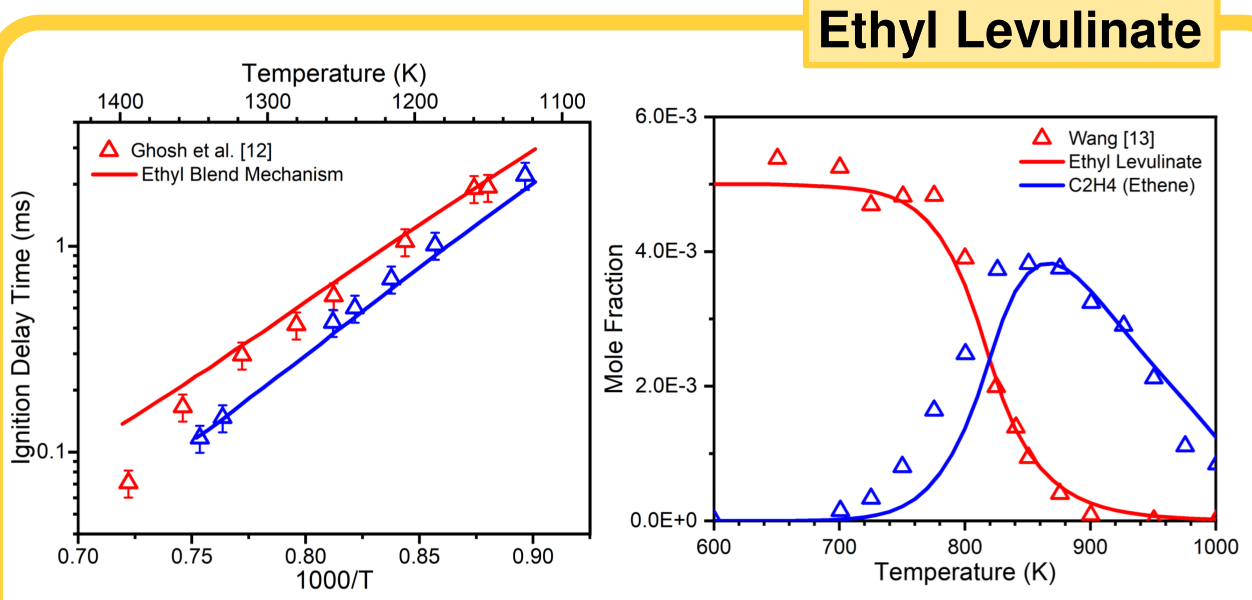

Figure 6. Left: EL IDTs at P_c=10 bar, φ=1.0 (red) and 0.5 (blue). Right: EL conversion and C_2H_4 production as a function of temperature. Stoichiometric, 1 bar, 2s residence time. Both: 0.5% mol EL. Symbols represent experimental data; lines show model predictions.

- No low temperature IDT measurements for EL due to experimental difficulties.
- Low vapour pressure (0.17 mbar at 298 K).
- For the available high temperature (1100 K) data, model predictions are accurate.
- From JSR data and modelling: EL displays no notable NTC.
- The accuracy of the JSR predictions gives confidence in the reproduction of low temperature behaviour.

n-Butyl Levulinate

- Not possible to evaluate predictions for nBL, as no fundamental data exists.
- Like EL, this is due to the difficulty of performing gas-phase experiments.
- However, when compared to EL, predicted nBL IDTs behave as expected.
- nBL IDTs are much shorter at low temperatures and higher at high temperatures.
- Cross-over is due to the presence of NTC-like region for nBL.

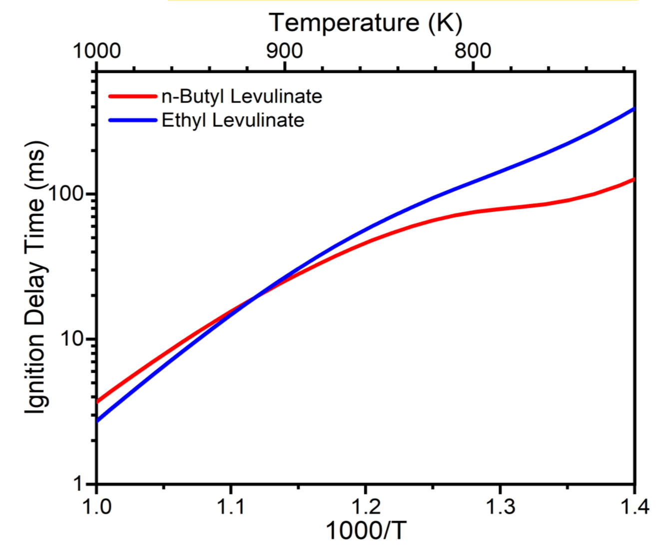

Figure 9. Homogeneous gas phase IDT predictions for EL and nBL. P_c=20 bar and stoichiometric conditions.

Conclusions

- AMG tools are effective at producing accurate models for complex fuels. However, expanding the underlying database of such tools based on low uncertainty, high quality, literature data is necessary for representing advanced oxygenated fuels.
- Mechanisms generated in this study replicate experimental data excellently and may also be extrapolated beyond the regime of their seed mechanisms, though some relative performance may be lost in exchange for this versatility.
- Ethyl and butyl blends are both capable of replicating the ignition behaviour of modern gasolines, including the NTC region.
- Butyl blends are marginally more relevant for spark-ignition applications due to the larger degree of NTC intensity, increasing knock resistance at high temperatures relative to ethyl blends.
- More experimental data is required at engine relevant conditions for a comprehensive evaluation, particularly for EL, nBL, and their blends with other fuel components.

Acknowledgements

This research is funded by the EPSRC grant EP/T033088/1 and was conducted as part of the SusLABB (Tailored Production and Utilisation of Sustainable Low Cost Lignocellulosic Advanced Biofuel Blends as Diesel and Petrol Substitutes) project. Acknowledgements are extended to Dr Andrew Ross, Dr Hu Li, Dr Valerie Dupont, Dr Stephen Dooley, and all other members of the SusLABB project for their valuable inputs. Thanks also to the RMG group at MIT for providing an array of open source tools and learning materials.

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