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Analysis of Detailed Kinetic Models for the Oxidation of Butene Isomers

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Highlights

- Comprehensive kinetic study for Butene isomers
- Comparison of Burning Velocity and Ignition Delay Time modeling with experimental data
- Evaluation of kinetic models for light alkenes at several compositions and temperatures
- Chemical reaction relevance determination.

1. Introduction

Butenes are common components in practical fuels, the heaviest gaseous alkenes at room temperature and the first alkenes with proper isomeric structures, whose chemical effects can be isolated and studied easier than for other substances, due to the close mass diffusivity coefficients of the isomers. Furthermore, butenes are key compounds for detailed kinetic analyses as well as for the comparison of partial or total oxidation of isomeric substances.

The aim of this work is to validate and evaluate detailed kinetic mechanisms for the oxidation of 1-Butene, 2-Butene and iso-Butene by comparing Laminar Burning Velocity (LBV) and Ignition Delay Time (IDT). More specifically, models developed by Lawrence Livermore National Laboratory Mechanism (LLNL) [1], NUI Galway Saudi Aramco Mechanism 2.0 (SAM) [2] and University of Southern California JetSurf 1.0 Mechanism (USC) [3] have been tested and validated with respect to experimental data retrieved from literature. The goodness of fitting among the studied models has been evaluated through different statistical parameters and tools, such as the Quadratic Sum (QS) of the difference between the model values and experimental data; the coefficient of determination R^2; Fractional Bias (FB), Normalized Mean Square Error (NMSE). Finally, a sensitivity analysis for the involved reactions has been performed [4].

2. Methods

The analysis and validation of the kinetic mechanisms have been performed by calculating the LBV and IDT of the three Butene isomers in air by means of the Cantera software, by varying the equivalence ratio (φ) and initial temperature. In this work, the model results have been accepted if: the absolute value of FB is smaller than 0.3, and the random scatter of data, evaluated through NMSE, resulted to be smaller than 0.5 [5, 6]

The reactions were sorted by relevance in LBV determination, by considering the absolute value of the Normalized Sensitivity Coefficients (NSC) obtained by sensitivity analysis [4].

3. Results and Discussion

Obtained results indicate that SAM and LLNL are suitable models in reproducing the LBV values. More specifically, LLNL shows the best fit for 1-Butene and iso-Butene, whereas SAM is the best fit for 2-Butene. In addition, the model SAM predicts relatively well IDT in all the studied operating conditions and fuels compositions, except for 1-Butene where USC and LLNL show a higher fitting quality. An overall evaluation on fitting quality for LBV is reported in Figure 1, showing LLNL model as the best fitting model for LBV being the closest to the origin axis.

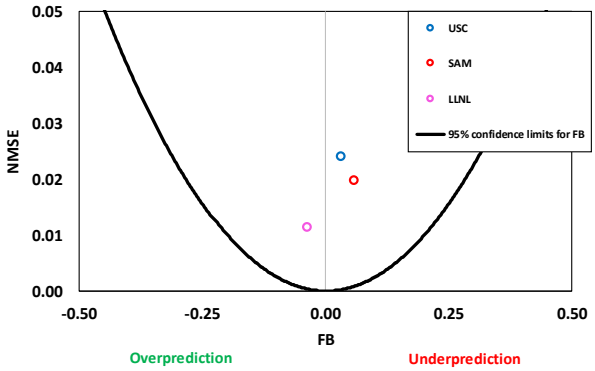

Fig ure 1. Unified model fitting quality for all the Butene isomers as well as all initial the conditions (T, P, φ) analyzed in this work.

IDT fitting quality evaluation is reported in Table 1, in terms of QS, suggesting SAM as the best fitting model for IDT estimations.

Table 1. Average QS values for IDT fitting quality evaluation for Butene isomers

Fuel	USC	SAM	LLNL
1-Butene	$1.11 \cdot 10^{-1}$	2.95	$1.14 \cdot 10^{-1}$
2-Butene	$5.03 \cdot 10^{-2}$	$5.97 \cdot 10^{-4}$	$3.19 \cdot 10^{-2}$
iso-Butene	$1.12 \cdot 10^{+4}$	$2.75 \cdot 10^{-2}$	$1.46 \cdot 10^{+2}$
Overall	$3.72 \cdot 10^{+3}$	$9.92 \cdot 10^{-1}$	$4.86 \cdot 10^{+1}$

The sensitivity analysis has shown that the formation of the radical C_4H_7 represents the main difference among studied model affecting the overall value of LBV.

4. Conclusions

All the studied models are suitable for LBV and IDT prediction for the considered range of temperature, pressure and composition, respecting all the stated acceptance criteria, moreover, used statistical approach indicate LLNL and SAM as the best fitting model for LBV and IDT estimations, respectively.
In our opinion, additional data not affected by extrapolation technique are required to achieve a greater understanding of butene isomers oxidation kinetics, especially for 1-Butene air mixtures. For this reason, methodologies obtaining LBV values by interpolation, such as Heat Flux Burner, are suggested.

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Keywords
Kinetic model, Butenes, Laminar Burning Velocity (LBV), Ignition Delay Time (IDT).