

Dear reviewers,

Sincerest thanks for your consideration and response on our manuscript. We have proposed a modifications in the paper in response to the extensive and insightful comments. We have presented a point-wise response to the comments raised by each reviewer below.

**1. Reviewer #1**

**The study presents an investigation on binary mixture of methyl butanoate and methyl crotonate. The work involves experimental investigation in an RCM, kinetic modeling, and a discussion of most relevant pathways for the single components and the binary blend. Overall, the paper is well written and well structured. Furthermore, the topic fits to the goals of the upcoming symposium and would be therefore suitable for publication. Despite these positive aspects there are also some shortcomings that lower the overall rating of the paper as detailed below:**

The authors thank the reviewer for highlighting the worth and relevance of the proposed work. The shortcomings indicated by the reviewer are adequately addressed by the following responses.

- 1. Despite good performance of the model at high temperatures (ST - IDTS), flames, and speciation data, it shows discrepancies in the medium temperature regime (RCM - IDTs) for the blend but also for the single components that are often outside the experimental uncertainties. However, only the discrepancies for the blend at lean conditions are mentioned and a discussion on the potential root causes or the attempt to optimize the model in this regard is missing/not described.**

→ We will add a discussion on the sensitive reactions responsible for intermediate temperature reactivity of neat MB and MB2D and its blend. Also, We will ensure the complete description of discrepancies.

Sensitivity analysis indicates that the same set of reactions are influential across different lean, rich, and stoichiometric conditions for blend (see Figure 2 (a-c)). Reducing the rates of the sensitive reactions with positive sensitivity coefficients leads to a decrease in reactivity, resulting in improved prediction of ignition delay at stoichiometric and rich conditions but worsening the prediction accuracy at lean conditions.

- 2. Is it reasonable that experiments show such a weak dependency on pressure for lean conditions? The two measurements at  $\phi = 1.5$  at the lower temperature end fall out of the trend. What are potential reasons for this strange behavior?**

→ Ignition delay data for rich and stoichiometric conditions were obtained in the temperature range of 856 K to 932 K. Conversely, ignition delay data for lean conditions at a pressure of 30 bar were obtained in the temperature range of 835 K to 858 K. Experiments indicate that the pressure dependence becomes weaker toward the lower temperature regime. We have confidence in the reported data, since three experimental trials were conducted for each point. Therefore, we consider the experimental data to be reasonable; however, the model is unable reproduce the exact ignition delays.

In Fig. 1 (c), it is observed that the model exhibits higher reactivity at rich conditions compared to what is observed in the experiments, particularly at the low-temperature end, therefore two measurements appears to be out of trend. As mentioned above, we believe that the experimental data is valid and the model needs to be improved at these conditions.

- 3. Validation against single fuel experiments are essential to evaluate the model performance but are only shown in the supplemental material. At least the RCM experiments from previous studies are directly linked to the current work and should be shown in the main text together with a comparison to previous models for the single components. Standard**

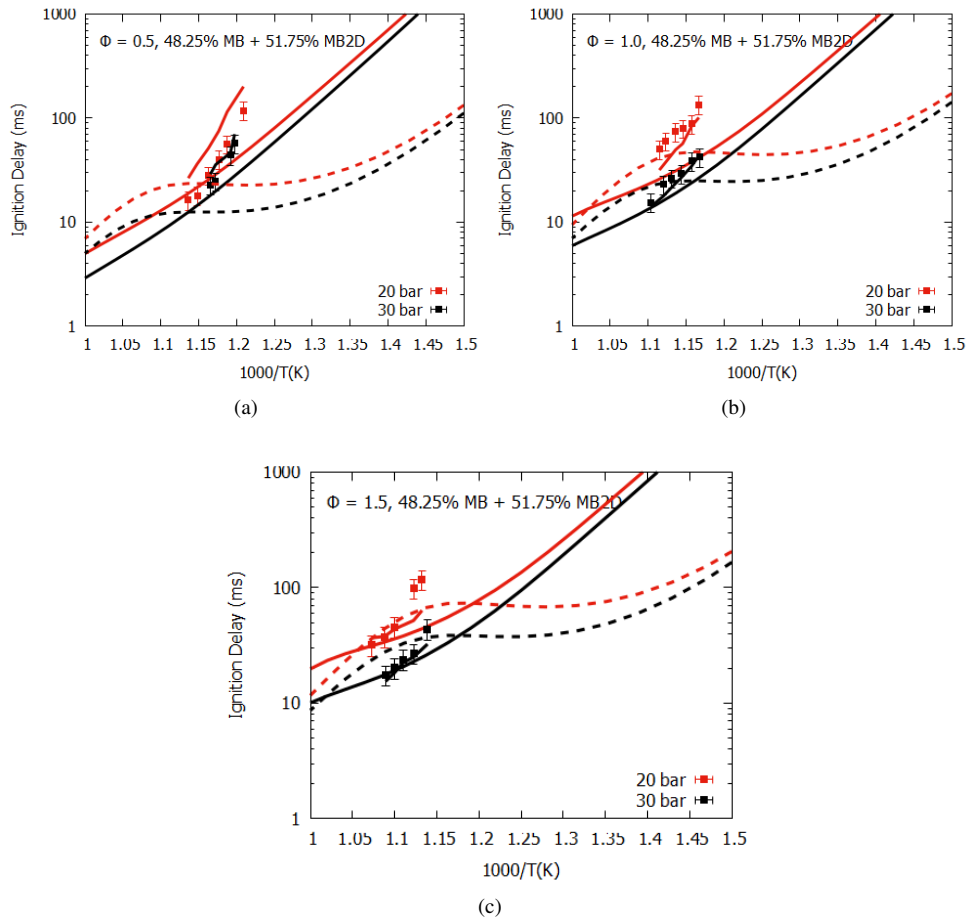


Fig. 1: Ignition delay times of MB/MB2D/O<sub>2</sub>/N<sub>2</sub>/Ar mixtures in a RCM at (a)  $\phi = 0.5$ , (b)  $\phi = 1.0$ , and (c)  $\phi = 1.5$ , for pressures of 20 and 30 bar. Symbols corresponds to experimental data points and comparison of RCM simulation (short solid lines) and adiabatic simulation results using the present model (long solid lines) and model prior to revision (dashed lines).

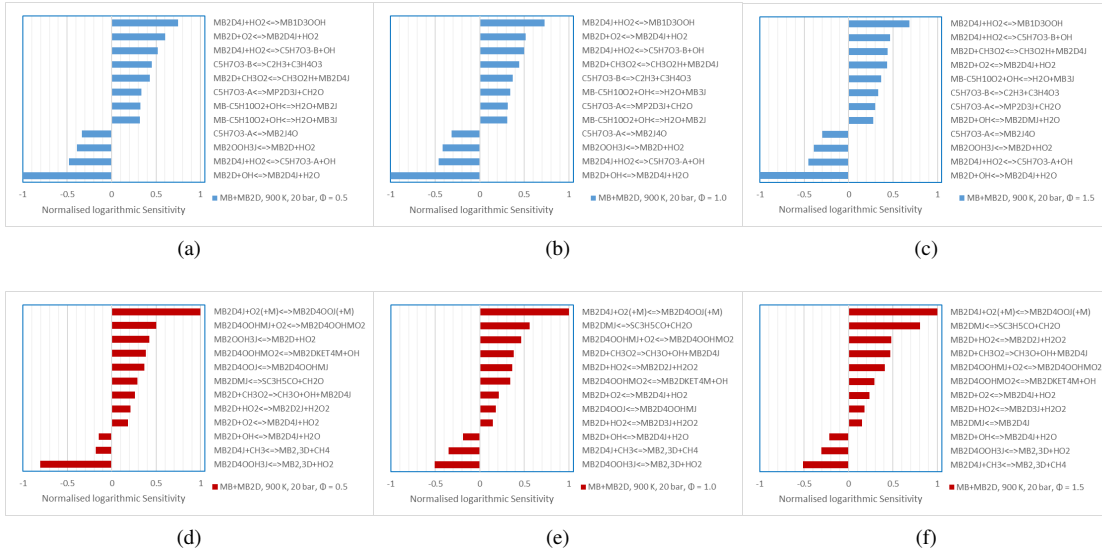


Fig. 2: Sensitivity analysis of MB/MB2D/O<sub>2</sub>/N<sub>2</sub>/Ar for hydroxyl radicals, calculated at the onset of sudden rise in hydroxyl radicals concentration using (a-c) present model (blue) and (d-f) model prior to revision (red).

figures like Fig. 1 do not provide any significant input and could be easily transferred into the SM.

→ We agree that this is important information that will add value to the manuscript. In fact, We calculated the predictions of intermediate temperature ignition delays using the current model and several literature models, as shown in Figures 3, 4, and 5 for both blend and single fuels. Our present model shows better agreement with experimental data across the different conditions when compared to the literature models. These comparative figures, along with supporting discussions, will be incorporated into the manuscript.

4. The number of new experiments is limited. As the blend effect is in the focus of the current work, an experimental variation of the blend composition would be essential.

→ We agree that extra data will be valuable. However, it's important to note that MB and MB2D have already been well-constrained by valuable data obtained from the blend investigated in this study. The set of reactions has all been assigned with accurate rate constants, as mentioned in section 3. Considering this dataset, the developed model can be treated with confidence to predict other blending ratios. The analysis presented in section 5.2 hinges on the confidence on the proposed model's consistency, considering the comprehensive reaction pathways, accurate and appropriate rate assignments and extensive validation against all available data sets.

5. Section 5.3 just details the explanation for the blend effect provided in section 5.2. Thus, both sections could be joined.

→ It is true that both the sections talks about intermediate temperature relevant reaction pathways. Since both refer to different figure, we made two separate sections for better readability.

Section 5.2 and 5.3 are arranged in the following way:

Section 5.2:

- (1) Paragraph 1: Introduction
- (2) Paragraph 2: Discussion on the NTC behaviour of neat MB and MB2D, referring to simulation results in the Fig. 6 in the manuscript.

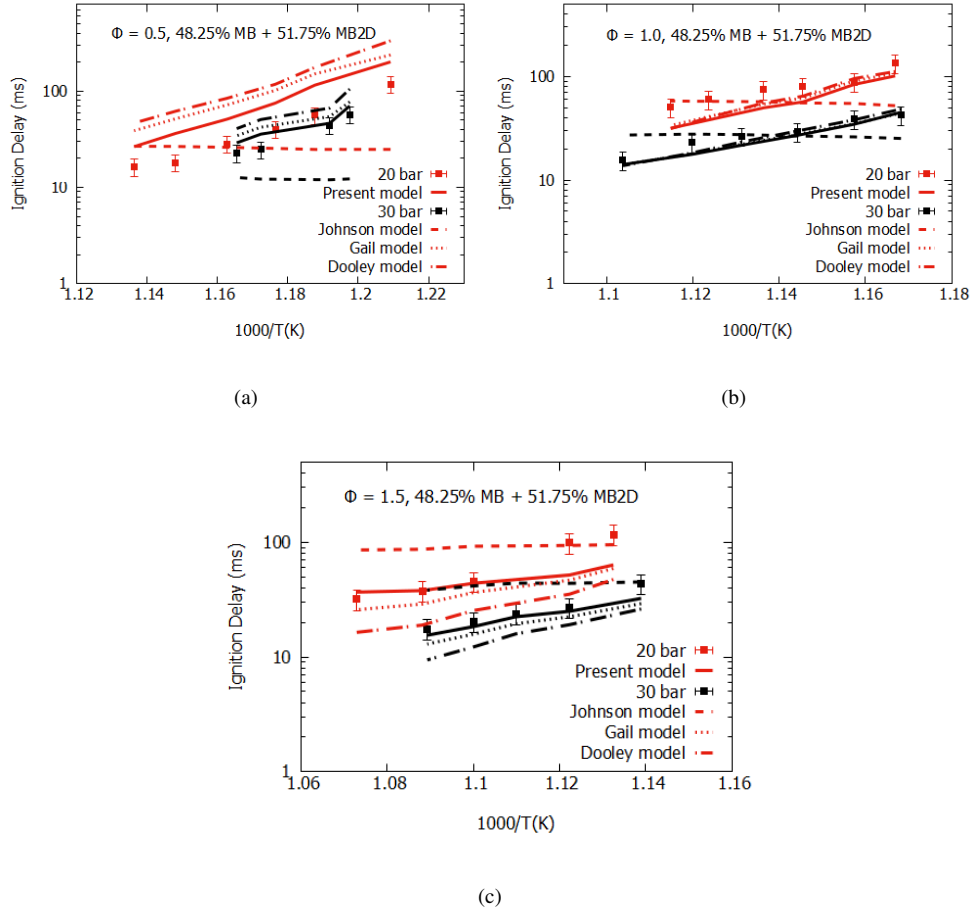


Fig. 3: Ignition delay times of MB/MB2D/O<sub>2</sub>/N<sub>2</sub>/Ar mixtures in a RCM at (a)  $\phi = 0.5$ , (b)  $\phi = 1.0$ , and (c)  $\phi = 1.5$ , for pressures of 20 and 30 bar. Symbols correspond to experimental data points and comparison of simulation results using the present model (solid lines), Johnson model (- - lines) [1], Gail model (... lines) [2] and Dooley model (-. lines) [3].

- (3) Paragraph 3: Discussion on the change in reactivity with composition of MB and MB2D, referring to the simulation results in the Fig. 6.

#### Section 5.3:

- (1) Paragraph 1: Discussion on the consumption pathways of MB and subsequent formation MB2D as a byproduct, referring to reaction pathways in the Fig. 7.
  - (2) Paragraph 2: Discussion on the distinct reaction pathways in MB2D as compared to MB and subsequent connection between chemistry of two, referring to reaction pathways in the Fig. 7.
  - (3) Paragraph 3: Summary
6. **In contrast to the text in the manuscript, experimental data and effective volume profiles are not provided in the SM. Also, the kinetic model is missing as SM. Thus, a detailed review of the model was not possible so far.**

→ We apologize for the lack of supplementary material. We will ensure that the following items are included in the supplementary material:

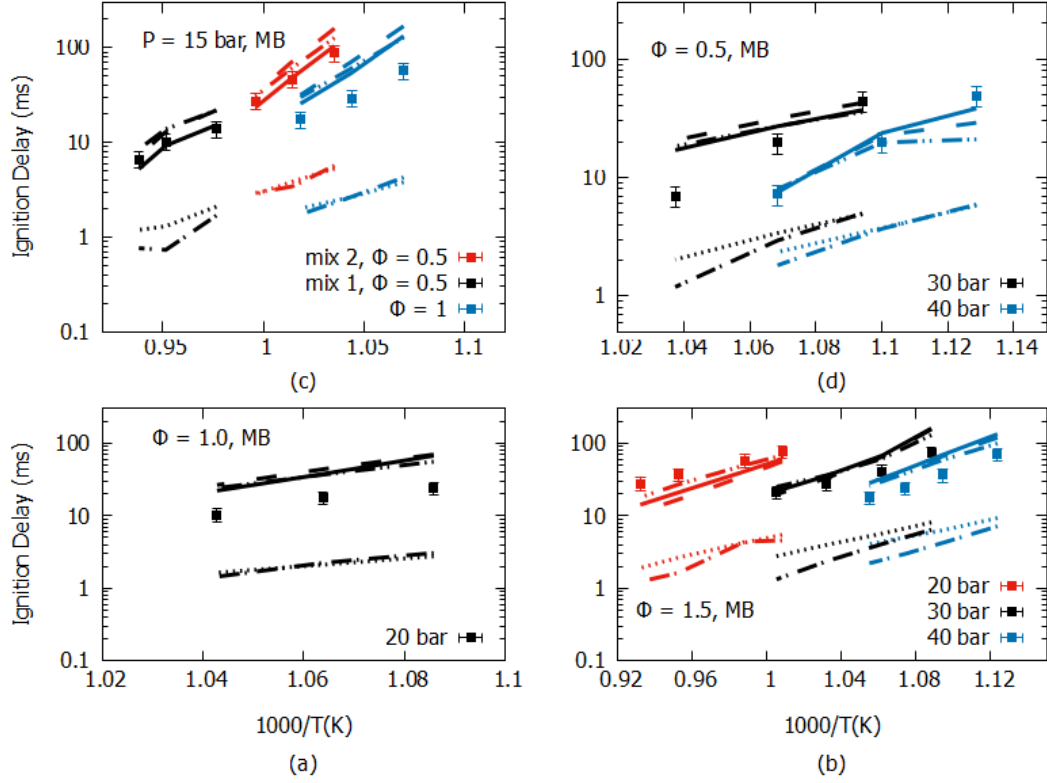


Fig. 4: Ignition delay times of MB/O<sub>2</sub>/Ar/N<sub>2</sub> mixtures in a RCM at (a)  $\phi = 1.0$ , (b)  $\phi = 1.5$ , (c-d)  $\phi = 0.5$  with varying pressures (15-40 bar). Symbols correspond to experiment (uncertainty of 20%) from Lele et al. [4] and simulation results using the present model (solid lines), Lele model (- - lines) [4], Gail model (... lines) [2], Dooley model (-. lines) [3], and Johnson model (.-.- lines) [1].

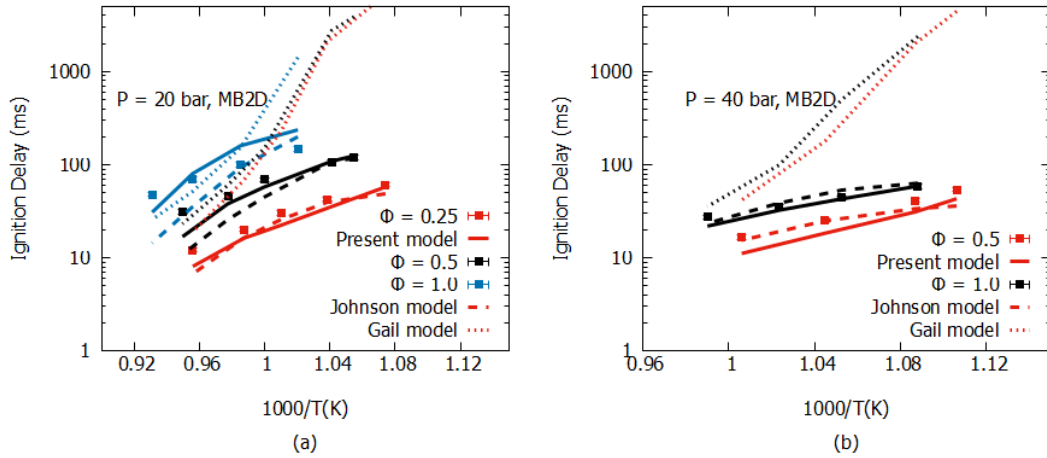


Fig. 5: Ignition delay times of MB2D/O<sub>2</sub>/Ar/N<sub>2</sub> mixtures in a RCM at pressures of (a)  $P = 20$  bar and (b)  $P = 40$  bar for different equivalence ratios (0.25, 0.5, and 1.0). Symbols correspond to experiment from Vallabhuni et al. [5] and simulation results using the present model (solid lines), Johnson model (- - lines) [1], and Gail model (... lines) [2].

- (a) Figures and tables supporting the discussion presented in the article.
- (b) Experimental data and effective volume profiles.

(c) Kinetic model files

7. Minor comments:

- **Fig. 1 is not properly integrated in the manuscript**
- **Font sizes within the figures is very small and should be increased**
- **In Table 1 the naming of methyl crotonate is MC, whereas in the text MB2D. This should be consistent.**
- **Although the effective volume approach is common practice for simulating RCM experiments, a proper reference for this method should be provided.**
- **Is there any reason for the uneven ratio between MB and MB2D?**

→ - Figure 1 will be moved to supplementary document.

- We will increase the font size of the content within figures.

- Yes, we will maintain consistent nomenclature in the manuscript.

- Present work used effective volume approach to account the heat loss as suggested by Mittal et al. [6]

- We used equal volumes of MB and MB2D, each being  $0.003785 \text{ m}^3$ . However, due to the different densities and molar masses of MB and MB2D, this led to uneven mole fractions of MB and MB2D. We will mention this information in the revised manuscript in section 2.

## 2. Reviewer #3

This work developed the kinetic model of methyl butanoate/methyl crotonate by incorporating new reaction pathways and latest theoretical reaction rates. The newly modified model was validated by comparing to experimental results in literatures. Ignition delay times of mixtures of methyl butanoate and methyl crotonate were measured using a Rapid Compression Machine (RCM) and the results fitted well with the improved model. The simulated results of ignition delay times for different blends of MB and MB2D is interesting, however, it is a pity that the experimental support is insufficient. In addition, the paper needs to be checked carefully.

We thank the reviewer for the feedback. We have addressed the concerns in the following.

1. **First, as the title claimed, this work is an 'Experimental and kinetic modeling study'. However, the experimental results in this work were only used to validate the reliability of the improved model. As for 'Interactions in the binary mixture of methyl butanoate and methyl crotonate', no more experimental evidence was presented. To illustrate this interaction, can you provide experimental results for ignition delay times of different blends of MB and MB2D?**

→ We agree with perspective put forth by reviewer 3. To comprehensively understand the impact of the interaction between MB and MB2D, it is necessary to assess how reactivity changes with the proportion of MB and MB2D in the mixture. We acknowledge that conducting experiments for different blends including neat fuels at same conditions would undoubtedly provide additional insights. Nonetheless, in light of the proposed model's consistency, comprehensive treatment of reaction pathways, accurate and appropriate rate assignments and extensive validation against all available data sets, the developed model can be treated with confidence to predict other blending ratios. Reconsidering the focus of our current work, we have revised the title of the paper to "Exploring intermediate temperature reactivity: Experimental and kinetic modeling insights into 50/50% blend of methyl butanoate and methyl crotonate".

The highlights of the our research work are:

- (1) An improved kinetic model for methyl butanoate and methyl crotonate.
- (2) Several recent rate constant from theoretical studies and new reaction pathways have been incorporated within this model.
- (3) Comprehensive validation of present model with respect to the experimental studies for methyl butanoate and methyl crotonate has been carried out.
- (4) Experimental ignition delay data for mixture of methyl butanoate and methyl crotonate for intermediate temperatures.
- (5) Insights into important pathways that influence intermediate temperature reactivity for the blend of MB and MB2D have been provided.

We believe this is valuable and worthy to the combustion community.

2. **Second, why do you want to study the mixtures of methyl butanoate and methyl crotonate instead of individually study these two substances in the low to intermediate temperature regime? It seems that the improved model can be obtained even if without experiment data of the mixtures. The motivation to study the mixtures of MB and MB2D is not forceful. Is there more literature or theory on how studying mixtures can contribute to a deeper understanding of reaction mechanisms, and not just because no one has studied them?**

→ The importance of MB and MB2D as molecules relevant to biodiesel surrogates has long been recognized. In the past, researchers have selected a surrogate mixture comprising MB to represent the ester group, n-heptane for the paraffinic content, and MB2D for both the ester

and unsaturation content, considering the molecular structure of biodiesel methyl esters [7, 8]. Due to the extensive availability of experimental data and theoretical studies for MB and MB2D compared to those produced for larger biodiesel surrogates, it is feasible to develop high-fidelity and relatively short biodiesel surrogate mechanisms.

In order to construct reaction mechanism for biodiesel surrogate mixture consisting MB, MB2D, and n-alkane, it is important to ensure that kinetic model is able to validate mixture of MB and MB2D. Actually, conducting experiments for the mixture of these three components would be more relevant in this context. Nonetheless, since MB2D is a byproduct in the oxidation of methyl butanoate at intermediate temperatures, the chemistry of MB and MB2D is more interconnected than with the chemistry of n-alkane. Consequently, experimental data for the blend of MB and MB2D provide additional constraints to the kinetic model, thereby demanding necessary refinement in the kinetics.

In the past, Johnson et al. [1] developed a comprehensive and well-validated kinetic model for methyl crotonate, building upon the methyl butanoate model from Lele et al. [4]. Despite the extensive validation of the Johnson model for experiments involving MB and MB2D, we observed that it is unable to accurately reproduce the reactivity trend observed in experiments for the blend of MB and MB2D (refer to Fig. 3). This discrepancy prompted us to revisit the relevant the chemistry of MB2D and MB in order to better predict the trend of reactivity. This work also gave us a learning that even though a model is validated for individual components, it does not ensure its effectiveness for a blend, particularly when the chemistry of the two components is interconnected.

Similarly, in the past, well validated mechanisms by Burke et al. [9] and AramcoMech3.0 [10] for propane and propene fell inadequate in predicting the low-temperature ignition delay observed in experiments for blends of propane and propene [11]. Henceforth, the respective researchers proceeded to update the chemistry of propane and propene within the NUIGMech1.0 mechanism. Additionally, researchers have also delved into studying mixtures of components relevant to fuel surrogates in the past to understand the combustion behavior of mixture and kinetic model improvement [12, 13].

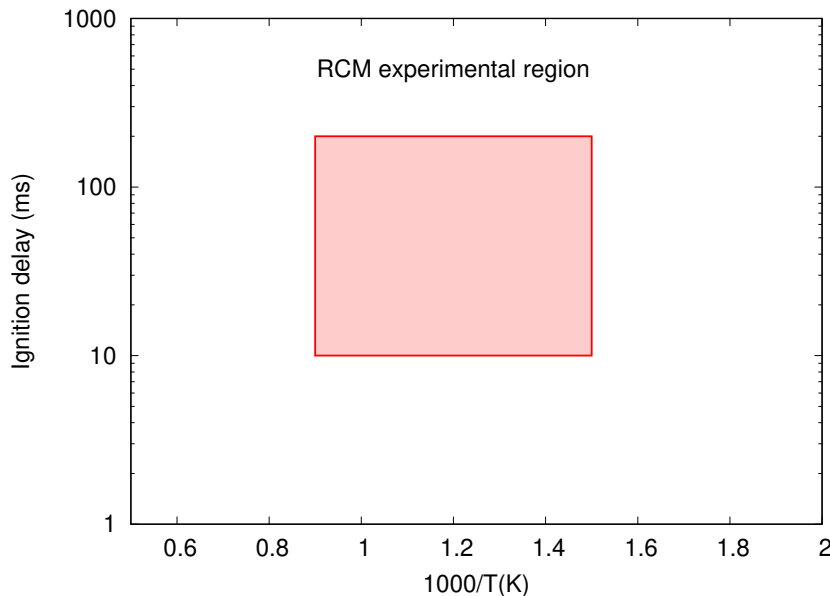


Fig. 6: Experimental working region of RCM setup.



3. **Finally, the author added thermal decomposition pathways of MB (pathways 6-10 in Fig. 2) and claimed that thermal decomposition pathways primarily influence reactivity at high temperatures ( $> 1400$  K). However, the results in Fig. S1-S7 show that simulation results by present model and pre-revised model have nearly no distinction. As you focused on the low to intermediate temperature regime in this work, how does this change help the improvement of the model?**

→ As mentioned in the manuscript section 4, "Overall, there have been no significant changes in the reactivity and species predictions for MB due to the revisions made in the present model (see section S1, Figs. S1–S7), compared to the model prior to the revision." Additional thermal decomposition pathways have been included for the completeness of the kinetic model, which did not change the high-temperature reactivity. The current model has undergone revisions for both high and low-temperature chemistry of MB and MB2D.

We agree with your point that section 3.1 on unimolecular decomposition do not affect the results at low temperatures. Therefore, we have decided to move section 3.1 to the supplementary materials.

4. **Corrections:**

- **Figure 1 is very bad, please do not use the screenshot. The horizontal headings are even obscured.**
- **Fig. S12, there is a mistake in 'Ignition delay times of MB/O<sub>2</sub>/Ar/N<sub>2</sub> mixtures'. It should be MB2D.**
- **Fig. S8, I suggest the authors use a more distinct color.**
- **In several places in the text, writing in English requires editing. Please check the singular and plural in the article, as well as capital and lower-case letter.**
- **In page 3 the first line of Section 2, the abbreviations of RCM have appeared in the previous.**
- **In page 5 the third paragraph, MB2D4J appears for the first time without associated abbreviated comment.**
- **Check the format of the references carefully. In the title of Ref. 8, 22, 23, 25, 26 and 28, there was an error in the capitalization of the formula. It need sa dot after the abbreviation (i.e., change 'Combust Flame' to 'Combust. Flame'). Journal names do not use standard abbreviations for Ref. 14-18 and 20.**

→ We are thankful for bringing these errors to our attention. We will meticulously address the mistakes in the manuscript.

5. **In RCM experiments, why do you use 50-50% mixture composition of argon and nitrogen as bath gas?**

→ We observed a significant decrease in reactivity with an increase in nitrogen content. Figure 6 shows the experimental working region of the RCM setup at PTB, Germany. To obtain ignition delays within the operational range of the RCM setup, we serially determined the mixture of Nitrogen and Argon, which increased the reactivity of the mixture. The 50/50 mixture of Ar and N<sub>2</sub> gave us the desired level of higher reactivity to enable measurement at intermediate temperatures.

6. **Fig. S2 and Fig. S9, how about the simulated results using pre-revised model?**

→ We expect the pre-revised model to predict similar laminar flame speeds for MB and higher speeds for MB2D compared to those produced by the improved model. We will include these comparison figures in the supporting documents.

### 3. Reviewer #4

The paper presents an updated kinetic mechanism for methyl butanoate and methyl crotonate as well as new experimental data of their mixtures. The mechanism development is well documented and a satisfactory validation of the individual submechanisms based on literature data is provided as supplemental material. Unfortunately, the new data don't include the low temperature region even though several model comparisons later presented in the paper focus on this specific range of operating conditions. Since the emphasis is on the ignition behavior, the authors should consider a more complete validation of the autoignition behavior.

We are grateful for the high ranking given to our paper, which highlights the significance of the proposed study and serves as a motivating factor for our research efforts. We have addressed all the queries in the following.

1. **Hadjali (Proceedings of the Combustion Institute, Volume 32, Issue 1, 2009, Pages 239-246) measured ignition delay times of methyl butanoate in the low temperature region but these data have not been considered by the authors. Also, other data by Walton et al (Proceedings of the Combustion Institute, Volume 32, Issue 1, 2009, Pages 255-262), Kumar and Sung (Combustion and Flame Volume 171, September 2016 Pages 1-14) were not included in the validation.**

→ Thank you for recommending the experimental data regarding the intermediate temperature ignition delays of MB. Figure 7 shows glimpse of validations of current and literature models. This data has revealed us with new insights into the predictive capabilities of our model. Our proposed model demonstrates overall better predictions for experimental ignition delays when compared to existing literature models under various conditions.

We will include all the comprehensive validation plots and supporting discussions.

2. **The authors mention that methyl butanoate and crotonate are biodiesel surrogates. This is a misrepresentation, as both fuels chain length are too short to sustain the same low temperature reactivity exhibited by FAME. It would be more correct to identify them as model molecules relevant to biodiesel, as they present the same moieties. It should be stressed though, that the boundary effects imposed by the close vicinity of the ester group and methyl tail still influences the reactivity of the CH<sub>2</sub> and vinyl carbons within the chain.**

→ We agree with your point. Biodiesel methyl esters inherently feature lengthy saturated carbon chains spanning C16-C18, relying solely on a small ester is inadequate in capturing the comprehensive behavior of biodiesel molecules such as low temperature combustion which is resultant of long carbon chain existing in the biodiesel molecules. Consequently, researchers selected long methyl esters such as long-chain alkanes like n-heptane [16], n-decane [17], n-dodecane [18], and n-hexadecane [19], as surrogate component to include the paraffinic content present in actual biodiesel molecules. Overall, biodiesel surrogate mixture contain (a) methyl ester (b) long chain alkane (c) unsaturated molecule in order to represent the long chain unsaturated esters. Therefore, mixture of MB, MB2D, and long chain alkane is used to formulate biodiesel surrogate.

Indeed, carbon sites near to ester groups are more susceptible to nucleophilic reactions. This makes the abstraction of hydrogen atoms from nearby carbon sites relatively harder. We will correct the discussion in the introduction section.

3. **Why 48.25% MB and 51.75% MB2D? Are these molar or mass fractions (minor difference but it's not specified...)?**

→ 48.25% MB and 51.75% MB2D indicates composition ratio of molar fractions. We used equal volumes of MB and MB2D, each being 0.003785 m<sup>3</sup>. However, due to the different densities and molar masses of MB and MB2D, this led to uneven mole fractions of MB and MB2D. We will mention this information in the revised manuscript in section 2.

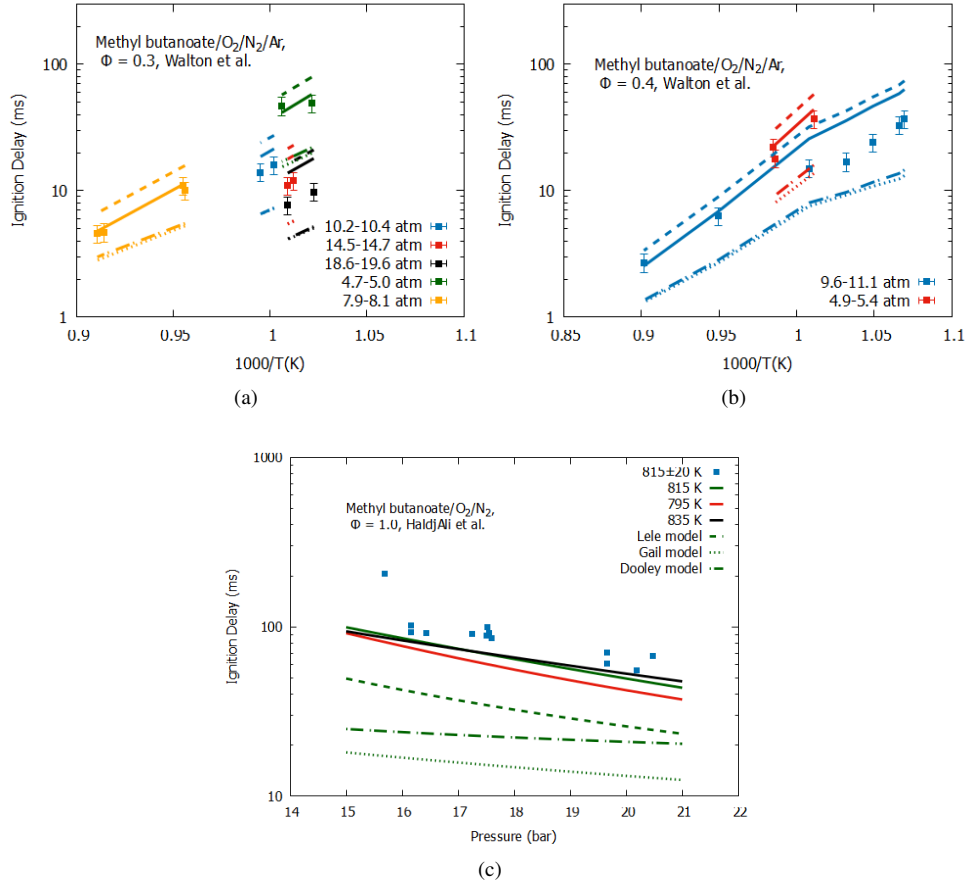


Fig. 7: Ignition delay times of MB/O<sub>2</sub>/N<sub>2</sub>/Ar mixtures [14] in a RCM at (a)  $\phi = 0.3$  and (b)  $\phi = 0.4$ . Plot (c) Ignition delay times of MB/air mixtures in a RCM at stoichiometric condition [15]. Symbols corresponds to experimental data points and comparison of simulation results using the present model (solid lines), Lele model (- - lines) [4], Gail model (... lines) [2] and Dooley model (-.- lines) [3].

## References

- [1] P. N. Johnson, M. L. Lavadera, A. A. Konnov, K. Narayanaswamy, Oxidation kinetics of methyl crotonate: A comprehensive modeling and experimental study, *Combust Flame* 229 (2021) 111409.
- [2] S. Gail, S. Sarathy, M. Thomson, P. Diévert, P. Dagaut, Experimental and chemical kinetic modeling study of small methyl esters oxidation: Methyl (e)-2-butenate and methyl butanoate, *Combust Flame* 155 (4) (2008) 635–650.
- [3] S. Dooley, H. J. Curran, J. M. Simmie, Autoignition measurements and a validated kinetic model for the biodiesel surrogate, methyl butanoate, *Combust Flame* 153 (1-2) (2008) 2–32.
- [4] A. D. Lele, S. K. Vallabhuni, K. Moshhammer, R. X. Fernandes, A. Krishnasamy, K. Narayanaswamy, Experimental and chemical kinetic modeling investigation of methyl butanoate as a component of biodiesel surrogate, *Combust Flame* 197 (2018) 49–64.
- [5] S. Vallabhuni, P. Johnson, B. Shu, K. Narayanaswamy, R. Fernandes, Experimental and kinetic modeling studies on the auto-ignition of methyl crotonate at high pressures and intermediate temperatures, *Proc. Combust. Inst.* 38 (1) (2021) 223–231.
- [6] G. Mittal, M. P. Raju, C.-J. Sung, Computational fluid dynamics modeling of hydrogen ignition in a rapid compression machine, *Combustion and Flame* 155 (3) (2008) 417–428.
- [7] H. K. Ng, S. Gan, J.-H. Ng, K. M. Pang, Development and validation of a reduced combined biodiesel–diesel reaction mechanism, *Fuel* 104 (2013) 620–634.
- [8] H. M. Ismail, H. K. Ng, S. Gan, T. Lucchini, A. Onorati, Development of a reduced biodiesel combustion kinetics mechanism for cfd modelling of a light-duty diesel engine, *Fuel* 106 (2013) 388–400.
- [9] S. M. Burke, U. Burke, R. Mc Donagh, O. Mathieu, I. Osorio, C. Keesee, A. Morones, E. L. Petersen, W. Wang, T. A. DeVerter, et al., An experimental and modeling study of propene oxidation. part 2: Ignition delay time and flame speed measurements, *Combustion and Flame* 162 (2) (2015) 296–314.

- [10] C.-W. Zhou, Y. Li, U. Burke, C. Banyon, K. P. Somers, S. Ding, S. Khan, J. W. Hargis, T. Sikes, O. Mathieu, et al., An experimental and chemical kinetic modeling study of 1, 3-butadiene combustion: Ignition delay time and laminar flame speed measurements, *Combustion and Flame* 197 (2018) 423–438.
- [11] A. Ramalingam, S. Panigrahy, Y. Fenard, H. Curran, K. A. Heufer, A chemical kinetic perspective on the low-temperature oxidation of propane/propene mixtures through experiments and kinetic analyses, *Combustion and Flame* 223 (2021) 361–375.
- [12] M. Mehl, W. J. Pitz, C. K. Westbrook, H. J. Curran, Kinetic modeling of gasoline surrogate components and mixtures under engine conditions, *Proceedings of the Combustion Institute* 33 (1) (2011) 193–200.
- [13] G. Kukkadapu, C.-J. Sung, Autoignition study of binary blends of n-dodecane/1-methylnaphthalene and iso-cetane/1-methylnaphthalene, *Combustion and Flame* 189 (2018) 367–377.
- [14] S. Walton, M. Wooldridge, C. Westbrook, An experimental investigation of structural effects on the auto-ignition properties of two c5 esters, *Proceedings of the combustion institute* 32 (1) (2009) 255–262.
- [15] K. HadjAli, M. Crochet, G. Vanhove, M. Ribaucour, R. Minetti, A study of the low temperature autoignition of methyl esters, *Proceedings of the Combustion Institute* 32 (1) (2009) 239–246.
- [16] O. Herbinet, W. J. Pitz, C. K. Westbrook, Detailed chemical kinetic oxidation mechanism for a biodiesel surrogate, *Combust Flame* 154 (3) (2008) 507–528.
- [17] Y. Chang, M. Jia, Y. Li, Y. Zhang, M. Xie, H. Wang, R. D. Reitz, Development of a skeletal oxidation mechanism for biodiesel surrogate, *Proceedings of the Combustion Institute* 35 (3) (2015) 3037–3044.
- [18] J. Yu, Y. Ju, X. Gou, Surrogate fuel formulation for oxygenated and hydrocarbon fuels by using the molecular structures and functional groups, *Fuel* 166 (2016) 211–218.
- [19] P. Dagaut, S. Gai, M. Sahasrabudhe, et al., Rapeseed oil methyl ester oxidation over extended ranges of pressure, temperature, and equivalence ratio: Experimental and modeling kinetic study, *Proc. Combust. Inst.* 31 (2) (2007) 2955–2961.