Experiments and Modeling of the Autoignition of Methyl Pentanoate at Low to Intermediate Temperatures and Elevated Pressures in a Rapid Compression Machine

Ms. Ref. No.: JFUE-D-17-02705

We would like to thank the reviewers for their thoughtful comments. Below are detailed responses to each of the reviewers' comments. In the attached marked revision, deleted text is marked in red and added text is marked in blue.

Reviewer #1:

Reviewer: The authors study ignition of methyl pentanoate, a small methyl ester, in the current study. The data from the current study is helpful in establishing the reaction rates which can be systematically used for developing the kinetic models for large esters and hence very valuable for developing kinetic models of biodiesel. The study also shows the poor performance of the literature models in estimating the ignition delays underscoring the need for such novel experimental datasets and hence would recommend this work for publication. However, I think the manuscript needs to be revised before it can be published. Below are the specific comments which I think need to addressed before it can be published.

Our Response: Thank you for your comments. Detailed responses to each comment are below.

Reviewer: Please improving the quality of figures. For eg: First stage and total ignition delay Symbols in Figs 5a & 5b are very hard to differentiate. Figure 1 could also be improved.

Our Response: We have increased the mark size on Fig. 5 to better distinguish the overall ignition delay and the first-stage ignition delay. On Fig. 1, we made several changes to improve the clarity, including swapping the colors of reactive and non-reactive pressure traces, changing the non-reactive pressure to a dashed line style, and making the black lines thinner.

Reviewer: Regarding the statement "The NTC region of MV is mapped out to provide additional information on the fidelity of using MV as a biodiesel surrogate." I am not convinced that MV could be a biodiesel surrogate, in my opinion it helps in understanding the chemistry of large esters.

Our Response: We agree with the reviewer that it is possible that MV will not be a good surrogate for biodiesel. Nonetheless, to our knowledge, there has been no study to suggest that it is not a good surrogate, probably because very few studies of MV have been conducted, so there is not enough information to judge. However, we think that judging the suitability (or lack thereof) for MV as a surrogate of biodiesel is outside the scope of this work, so we are simply noting that this study provides part of the necessary experimental information so that others may judge for themselves. We also agree with the reviewer that the scope of this work is actually wider than we had noted previously, so we have added a note that this study provides further information on the autoignition chemistry of large methyl esters near line 41:

"The NTC region of MV is mapped out to provide additional information on the fidelity of using MV as a biodiesel surrogate and on the autoignition chemistry of large methyl esters."

Reviewer: Specify the units of coefficients B, C and, temperature T in equation (1)

Our Response: The coefficients are in kPa and K. This has been added to the text near line 112 and in the caption of Table 2.

"... where A, B, and C are substance-specific coefficients, given in units of K and kPa."

Reviewer: The authors report an ignition delay of 100 ms at 640 K f=2, MV/air mixture at 15 bar. So at 30 bar I would expect an ignition delay which is for sure will be more than 10 ms. So I am surprised by the statement "For the phi = 2:0 condition, only PC = 15 bar is considered because we could not achieve

TC values low enough that the ignition during the compression stroke can be prevented'. Can the authors comment on this.

Our Response: The reason for this is because of physical limitations of the experimental apparatus and the fuel. In particular, achieving sufficiently low temperatures on our apparatus requires increasing the reaction chamber volume at the end of compression, which in turn requires substantially higher initial pressures to reach the EOC pressure of 30 bar. The initial pressure in the RCM reaction chamber is limited by the pressure in the mixing tank, and the total pressure in the mixing tank is limited by the vapor pressure of MV at the preheat temperature. The combination of these factors meant that we could not prepare a mixture with sufficiently high tank pressure to enable repeated experiments with the EOC volume required to reach temperatures where the ignition delay would be measurable. However, we feel that this explanation would only confuse the manuscript, so we omit it.

Reviewer: *The comparison of ignition delays of MV from current work and that of Hadj-Ali et al .[9] would be helpful.*

Our Response: The ignition delays of MV measured in the work of Hadj-Ali et al. [9] were conducted at several pressures and roughly a single EOC temperature (near 815 K). However, none of the pressures considered in that study match the pressures considered in our study, so we feel that including the data on one of our existing plots would be very confusing. Moreover, the influence of facility-specific effects make a direct comparison of ignition delays from different RCMs somewhat challenging, particularly without an accurate chemical kinetic model to capture the facility effects. Therefore, we have not added a figure with this comparison.

Reviewer: *On discussion related to Dievart model in figure 5, it is surprising that phi=0.25 and phi=0.5 simulations show NTC but phi=1 and phi=2 simulations do not. The trend is counter intuitive as the cool flame chemistry and NTC response are expected to increase with increase in equivalence ratio. This needs to be clarified. My guess is that the location of the NTC is not captured accurately by model. NTC region predicted by model is shifted to high temperatures where ignition is observed in RCM simulations. Showing Adiabatic constant volume simulations to understand the location of NTC at different equivalence ratios.*

Our Response: We agree with the reviewer that the location of the NTC region with respect to inverse temperature is not well captured by the model. It does seem as though the NTC has been shifted to higher temperatures with respect to the data, in addition to the model being too reactive. This is supported by the newly added Fig. 6, which compares adiabatic, constant volume simulations with the RCM simulations from Fig. 5. It is apparent from this figure that the predicted ignition delays in the $P_C = 15$ bar, $\phi = 2.0$ and the $P_C = 30$ bar, $\phi = 1.0$ simulations fall on the low temperature side of the NTC, while the $P_C = 15$ bar, $\phi = 0.25$ and 0.50 simulated ignition delays are on the high-temperature side of the NTC, but approaching the NTC range such that they start to assume the characteristic curvature as the temperature decreases. In addition to the figure, we have added some text near line 290 to clarify this point.

Reviewer: *Figure 5 caption could also be revised.*

Our Response: We have modified the text of the caption of Fig. 5 to read:

"Comparison of experimental and simulated ignition delays computed using the procedure described in Section 3.1. a) 15 bar, b) 30 bar."

Reviewer: *From Figure 5a for phi=2, 15 bar and fig. 5b phi=1, 30 bar the Dievart et al. model consistently under predicts the ignition delays which contradicts the statement "While the model of Dievart et al. [15] over-predicts the first-stage ignition delay, it also over-predicts the first-stage pressure rise, thereby leading to rapid overall ignition." This needs to be revised.*

Our Response: This statement has been removed from the manuscript.

Reviewer: On discussion related to RMG model from Figure 5, the authors state " model over-predicts the low-temperature ignition delays and does not predict.." define low temperature ignition delays." The ignition delays from RMG model and experiments cross over around 720 K so the statement that low temp. ignition delays are overpredicted is not completely accurate.

Our Response: In this context, we are defining low temperature ignition delays as those to the right of the experimental NTC region on the Arrhenius plot. We have added the following text near line 308:

> "... the RMG model tends to over-predict the low-temperature ignition delays (i.e., those to the right of the experimental NTC region on the Arrhenius plot)..."

Reviewer: Regarding the heat of formation shown in Table 3, it is interesting that the heat of formation of radical 3 and 4 estimated by RMG are different. I would request the authors check their numbers.

Our Response: We have checked the values for the estimates in the mechanism, and they are identical to the values in Table 3 and further identical to the values available from the RMG website at `http://rmg.mit.edu`. As such, no changes have been made to the manuscript in response to this comment.

Reviewer: The authors use the branching ratios of fuel decomposition to fuel radicals to state the importance of fuel chemistry in the current work. The relative consumption shown in Table 4 demonstrates that the branching ratios do not exhibit strong sensitive to thermochemistry which is supported by the fact that RMG and RMG switched show nearly identical branching ratios. I am not convinced that the importance of the thermochemistry is elucidated by the current discussion related to Table 4 and the discussion in my opinion does not provide any kinetic insights. May be the discussion could be removed.

Our Response: We have clarified the discussion of this point. In particular, we have emphasized that the results show that both the thermochemistry and reaction pathways are important, and cannot easily be disentangled from each other, requiring a thorough, detailed investigation of the methyl valerate reaction system which we consider outside the scope of the present work. In addition, we have noted that improper prediction of the thermochemistry of species may affect the RMG model in particular, due to the rate-based algorithm used in RMG, which may miss important reactions if the thermochemistry is not accurate. We have modified the text beginning near line 394, but do not copy the modification here for space.

Reviewer: Alternatively, it would be interesting to compare the thermochemistry of the low temperature chemistry related reactions (RO2 chemistry) from models and ab-initio works like those Hayes and Burgess and also try adopting the reaction rates from ab-initio calculations and see to if the mechanism performance improves.

Our Response: We feel that the poor performance of both mechanisms indicates that a thorough and detailed study of the entire methyl valerate system is warranted, and small modifications, such as the replacement of only a few rates related to low-temperature chemistry, will not be sufficient to significantly improve the performance of the model. In addition, we feel that such ad-hoc replacement of rates without detailed study, even if it should improve the performance, could not be shown to be anything more than fortuitous without further study, which is outside the scope of the present work. Finally, in a separate work, Diévart et al. (Combustion and Flame, 159 (5) 1793–1805, 2012) note that "preliminary tests with up-to-date kinetic parameters [including the work of Hayes and Burgess] for the generic low temperature scheme have shown an enhancement of the fuel reactivity at the end of the NTC region." Since the model already over-predicts the reactivity of the RCM data, particularly at the end of the NTC region, further enhancement is not likely to improve agreement.

Therefore, we have not included these modifications in the manuscript; we have, however, added a note to the end of the discussion that references the work of Hayes and Burgess [14] to indicate that some of the necessary detailed work has been started.

Reviewer #2:

Reviewer: *The measurement of Methyl Valerate at these temperature and pressure conditions constitutes important work and the manuscript of well laid out and has potential to be widely circulated. The arguments in the article are sound and the figures are clear.*

Our Response: Thank you for your comments. A detailed response is below.

Reviewer: *I would like to ask the authors to check one item definitively before the article is published. I am concerned that at these higher pressures and equivalence ratios close to 1, there would be ignition which occurs during the compression stroke. This would not be noticed if some of the fuel condenses during the charging process and thereby you are dealing with lean mixtures than those cited in the paper. The authors are encouraged to make sure this is not the case by possibly sampling the charge after filling through a GC or by a quantitative absorption method as that used routinely by Stanford.*

Our Response: With regards to ignition during the compression stroke, we have compared each reactive pressure trace to its corresponding non-reactive trace and found they are in good agreement until the end of compression, indicating that there is no heat release during the compression stroke. With regards to the filling process, we have thoroughly checked the temperatures throughout the apparatus and found them to be quite consistent, including the mixing tanks, the piping connections, and the reaction chamber itself. Moreover, we have conducted several studies in the past utilizing GC to determine mole fractions of components. All of these studies determined that the vaporization procedure used on this apparatus is sufficient to produce a homogeneous mixture of fuel and oxidizer, even for fuels with relatively low vapor pressures. We have added references to these prior studies in the present manuscript near line 105:

> "Previous work has shown this procedure to completely vaporize the fuel and prevent fuel cracking during the heating process [25, 26, 27]."

Reviewer: *In the future, a possible direct charging method might be encouraged instead of a mix vessel.*

Our Response: As we do not think it is appropriate to digress to specific discussion of various mixture preparation methods in this response or in the manuscript, we simply note in passing that each method has its own advantages and disadvantages, and each method should be used where its advantages provide the most benefit. We feel that such discussion in the manuscript would be beyond the scope of the current work, and we have not made any changes in response to this comment.

Reviewer: *It would also be good to include some of the pressure profiles so that others in the community can check.*

Our Response: Pressure profiles are available in the data files that will be posted on the Combustion Diagnostics Laboratory website and on FigShare, with URLs given in the manuscript. We have endeavored to provide the community with all of the information necessary to reproduce these experiments, including the pressure traces and versions of software packages used in the processing. Moreover, we include several pressure traces with discussion in Section 4.2 of the manuscript. As such, no changes have been made to the manuscript in response to this comment.

Reviewer #3:

Reviewer: *The authors perform a shock tube study measuring ignition delay times of methyl pentanoate, and compare with a kinetic model taken from the literature and one they generated using a Reaction Mechanism Generator, showing that neither model can predict the ignition data satisfactorily; they investigate and discuss possible reasons, but (very reasonably) leave solving this discrepancy as an open challenge to the combustion modeling community.*

Our Response: Thank you for your comments. Detailed responses to each comment are presented below.

__Reviewer:__ I would suggest using the preferred IUPAC name "Methyl pentanoate" in the title (and mentioning the common name "Methyl valerate" in the abstract and a keyword).

Our Response: We have modified the title to read "Experiments and Modeling of the Autoignition of Methyl Pentanoate at Low to Intermediate Temperatures and Elevated Pressures in a Rapid Compression Machine", as the reviewer suggests. Methyl valerate and methyl pentanoate are already keywords. We have opted to retain methyl valerate as the primary name used for the compound throughout the text because of the convenient MV acronym (MP is ambiguous, because it could mean methyl propanoate as well).

__Reviewer:__ Regarding: > "available on the web at https://combdiaglab.engr.uconn.edu/database/rcm-database and on figshare at https://doi.org/10.6084/m9.figshare.5213341. In addition, ChemKED-format [33] files are available in the main ChemKED database repository at https://github.com/pr-omethe-us/ChemKED-database."
None of the links work or contain the relevant data. Presumably the authors embargoed it and plan to post it upon acceptance of the manuscript.
But I am pleased to see this sharing of data, as well as the extensive supplementary materials aiding in reproducible science. Bravo.

Our Response: This is indeed the case, and the relevant files will be posted after acceptance. We have double checked that the URLs are correct, just in case. Thank you for your kind words.

__Reviewer:__ Regarding: > "At 15 bar, the experimental ignition delays are under-predicted by the Diévart et al. [15] model for the three equivalence ratios shown. For the <phi> = 0.25 and 0.5 conditions, the model appears to be predicting an NTC region of the ignition delays as the temperature decreases"
Figure 5 does not show, to my eye, any NTC behaviour in the simulations, as asserted in this sentence. Perhaps if the simulations were plotted at a wider range of temperatures (they're simulations, so no experimental reason not to?) this may show up, but at present I feel the figure does not support this statement. For <phi>=0.5 simulations are not even plotted over the whole range of the experimental data, let alone extrapolated to lower temperatures where NTC may be predicted.

Our Response: We interpret the increasing curvature of the model response for the $P_C = 15$ bar, $\phi = 0.25$ and 0.5 conditions as the beginning of an NTC region. The RCM simulations are not extrapolated because they use the volume profile associated with a single experiment. However, the simulations are plotted over the whole range of the $\phi = 0.5$ experiments; the large discrepancy between the simulations and experiments causes the illusion that the whole range is not covered.

In addition, we have added a new Fig. 6 that compares adiabatic, constant volume simulations with the model of Diévart et al. [15] with the RCM simulations presented in Fig. 5. The adiabatic, constant volume simulations can be extrapolated over a wide range of temperatures. From Fig. 6, it can be seen that the curvature in the RCM simulations at $P_C = 15$ bar, $\phi = 0.25$ and 0.5 is related to the NTC region of the ignition delay, while the lack of curvature in the $P_C = 15$ bar, $\phi = 2.0$ and the $P_C = 30$ bar, $\phi = 1.0$ simulations is because those lie on the low-temperature side of the predicted NTC.

__Reviewer:__ I have other questions about possible causes of the discrepancies, but answering them is beyond the reasonable scope of this paper, and the fact that I have them is a good sign regarding the potential impact of this paper. I think people will find it interesting.

Our Response: Thank you again for your comments. We are also interested in the resolution of these questions, but we agree that they are out of scope for this work.