

Supplemental Material for

Methylcyclohexane pyrolysis and oxidation in a jet-stirred reactor

Tony Bissoonauth ^a, Zhandong Wang ^{a*}, Samah Y. Mohamed ^a, Jui-yang Wang ^a, Bingjie Chen ^a, Anne Rodriguez ^b, Ophélie Frottier ^b, Xiaoyuan Zhang ^c, Yan Zhang ^c, Chuangchuang Cao ^c, Jiuzhong Yang ^c, Olivier Herbinet ^b, Frédérique Battin-Leclerc ^b, S. Mani Sarathy ^a

^a King Abdullah University of Science and Technology (KAUST), Clean Combustion Research Center (CCRC), Thuwal 23955-6900, Saudi Arabia

^b Laboratoire Réactions et Génie des Procédés, CNRS, Université de Lorraine, ENSIC, 1, rue Grandville, BP 20451, 54001 Nancy Cedex, France

^c National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, Anhui 230029, P. R. China

* Corresponding author: E-mail: zhandong.wang@kaust.edu.sa (Z. Wang)

Section 1 Additional information for model development of MCH

Figure S1. (a) Upon addition of O₂ to MCHR2 and the formation of MCH2OO, the production of six isomers can ensue, resulting in a large number of pathways. The species in red are from 1,5-hydrogen migration (six-membered). (b) Rate constants for the isomerization pathways of MCH2OO. 1,5-hydrogen migration (six-membered) pathways in solid lines show significantly larger rate constants over the temperature range 500-1100 K. Rate constants taken from Xing et al. [1].

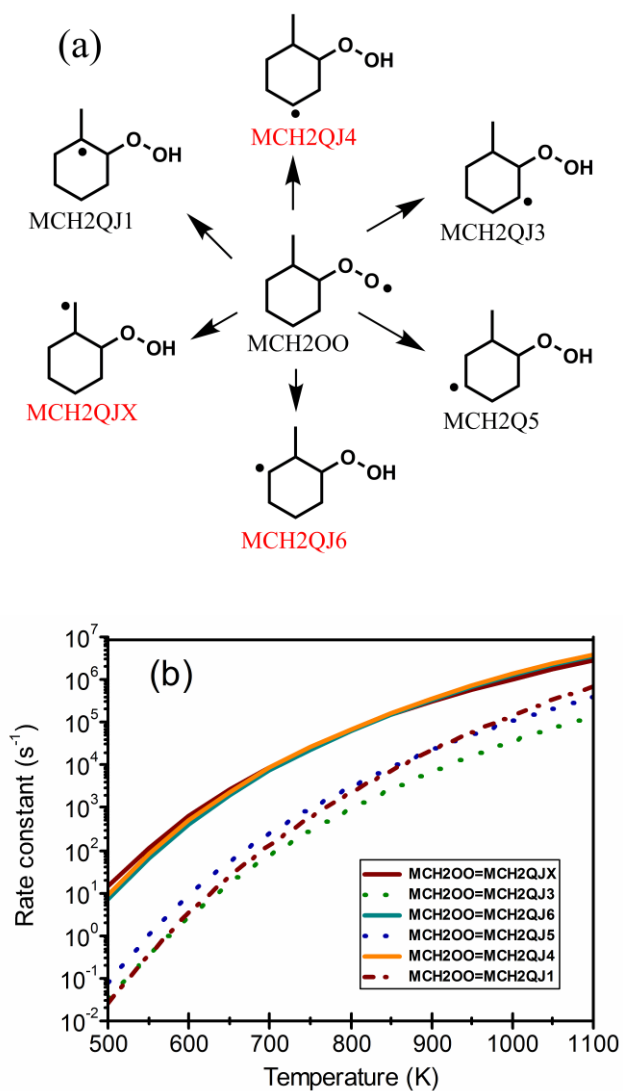


Figure S2. Comparison of simulated IDT by two versions of Weber et al. mechanism [2]; original mechanism, including all isomerization pathways of ROO (solid lines); and the removal of non-six membered pathways of ROO (dashed lines).

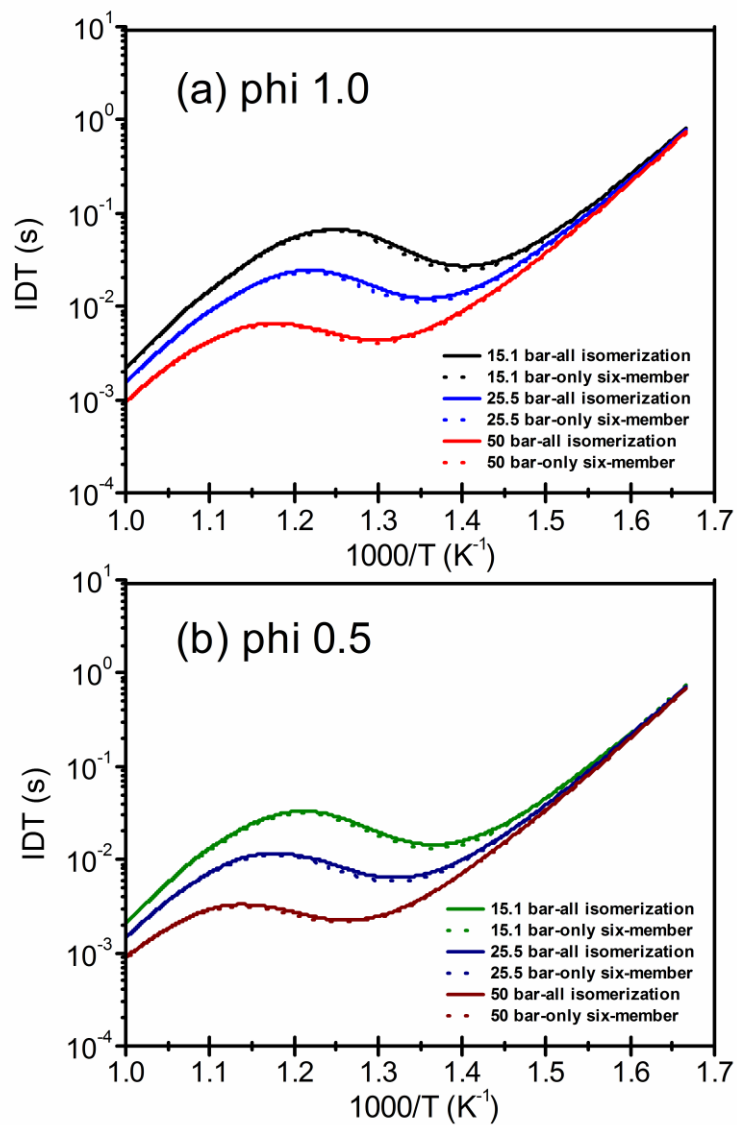
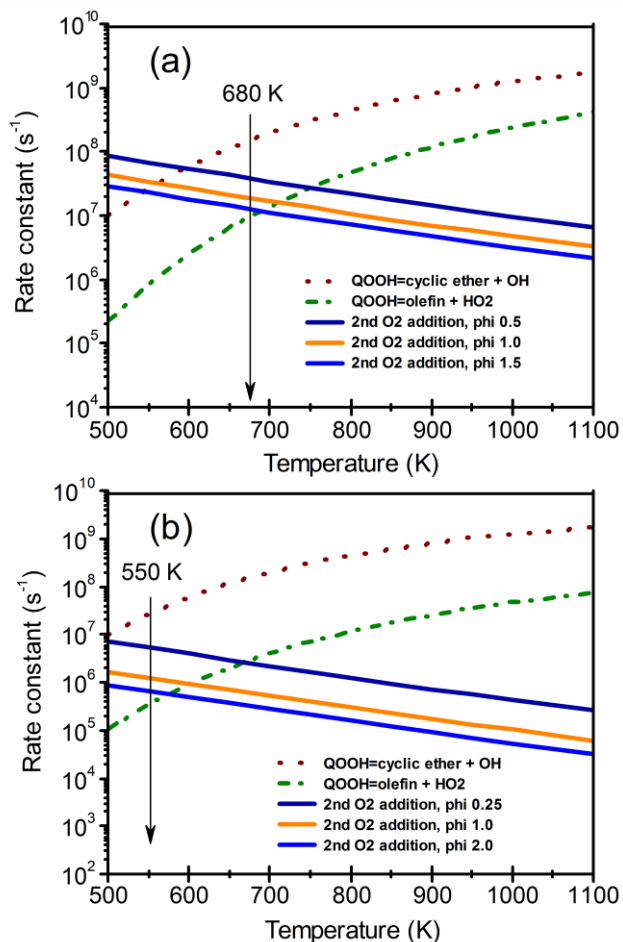


Figure S3. (a) Rate constant comparison for the pathways of β -QOOH intermediate species, $\phi = 0.5, 1$ and 1.5 with an $O_2\% = 21.7, 10.7, 7$, respectively at a pressure of 15.1 bar. Simulations match the conditions used in Mittal and Sung's experiments [3]. The arrow indicates the lowest temperature for the RCM experiment. (b) Rate constant comparison for the pathways of β -QOOH intermediate species, $\phi = 0.25, 1$ and 2 with an $O_2\% = 24, 6, 3$ respectively at a pressure of 1.07 bar. Simulations match the conditions used for the JSR experiments conducted in this study. The arrow indicates the temperature when the JSR oxidation reaction happens.



Section 2 Additional information for low-temperature oxidation of MCH

Figure S4. Mass spectrum from MCH oxidation at 570 K and photon energy of 10.5 eV. The peaks labeled with molecular formula are the major products observed from experiment. The mass peak labeled red is multiplied by 30.

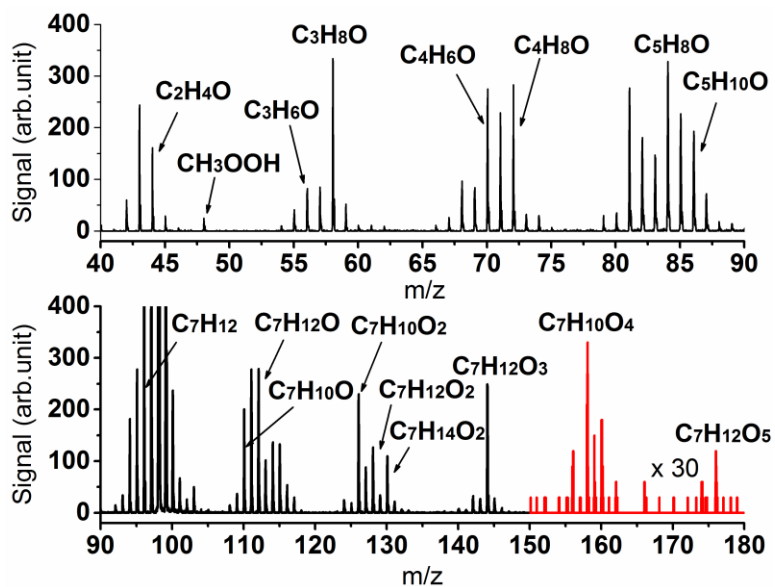


Figure S5. Temperature sensitivity analysis of MCH ignition delay time at 25.5 bar and equivalence ratios of 1.0 and 0.5. The initial temperature is 830 K. The reaction with absolute sensitivity coefficient large than 0.05 is presented. The reactions of the second O₂ addition to QOOH are italic and highlighted in red.

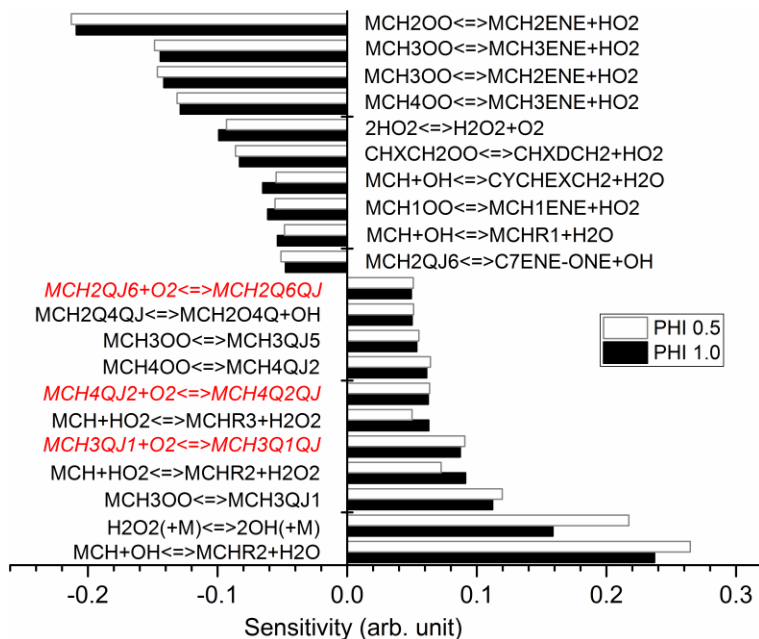


Table S1. Structure of the eight C₇H₁₂O intermediates measured in JSR-2






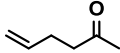

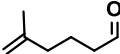
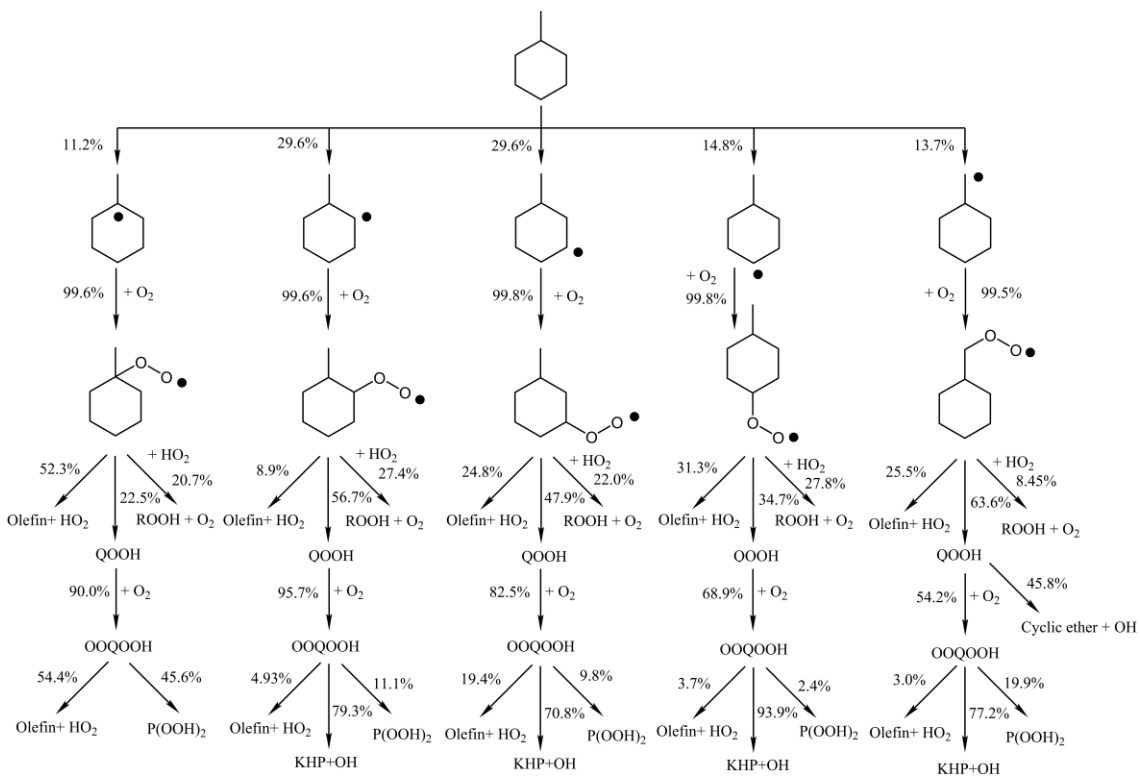
Name	structure	Name	structure
cyclohexanecarboxaldehyde		1-methyl,7-oxabicyclo[2.2.1]heptane	
2-methyl-cyclohexanone		1-methyl,7-oxabicyclo[4.1.0]heptane	
3-methyl-cyclohexanone		6-heptenone	
1-oxaspiro[2,5]octane		5-methyl,5-hexenal	

Figure S6. Reaction pathway analysis of MCH JSR oxidation in Nancy JSR-2. The equivalence ratio is 1.0 and temperature is 600 K.



Section 3 Pyrolysis and high-temperature oxidation of MCH

Fuel decomposition and oxidation at high temperatures affect the energy efficiency and engine stability since the major heat release in combustion occurs at high temperatures. Figure S7 presents the reactants (MCH and O₂), major products (e.g., CO, CO₂, H₂, CH₄, C₂H₄, C₃H₆, 1,3-butadiene, acetaldehyde, propanal, methylcyclohexenes, and cyclic ethers) measured from MCH pyrolysis in JSR-1 at KAUST and oxidation with equivalence ratios of 0.25, 1.0, and 2.0 in JSR-2 at Nancy. The mole fraction of MCH and the pyrolysis intermediates (except for 1,3-butadiene) are multiplied by a factor of 5.7 for clarity in the figure. The pyrolysis of MCH starts at 950 K, which is 150 K higher than MCH oxidation. According to previous studies [4] and the kinetic analysis in this work, MCH is mainly consumed by the H-atom abstraction from OH radical and H atom, which leads to different MCH radical isomers. The unimolecular reactions of these radicals via C-C β-scission and subsequent ring opening form alkenyl radicals, which further undergo dissociation to form alkenes and dienes, such as C₂H₄, C₃H₆, and 1,3-butadiene (Fig. S7g-i). Another important reaction pathway for MCH radical isomers is the O₂ addition to the radical site to form ROO radical. At this temperature range, the concerted elimination of ROO to methylcyclohexenes (Fig. S7l-m) is more favorable than its isomerization to cyclic ethers (Fig. S7n-p). In general, the model prediction for MCH pyrolysis and high-temperature oxidation is satisfactory. Discrepancy of a factor of 2-3 between experiment and simulation for C₇H₁₂ and C₇H₁₂O exists. In the case for propanal, the discrepancy is even larger.

Figure S7. Mole fractions of MCH pyrolysis and oxidation ($\phi = 0.25, 1.0, 2.0$). Symbols are GC data while lines are model predictions. The mole fractions in MCH pyrolysis are multiplied by a factor of 5.7, except for 1,3-butadiene. The experimental and simulated profiles of C_7H_{12} in Fig. S7m are summed mole fraction of the molecule shown in the figure. The experimental profiles of $C_7H_{12}O$ in Fig. S7n and Fig. S7p are summed mole fraction of the molecule shown in the figures, while that for simulation is the summation of all the isomers with similar structures.

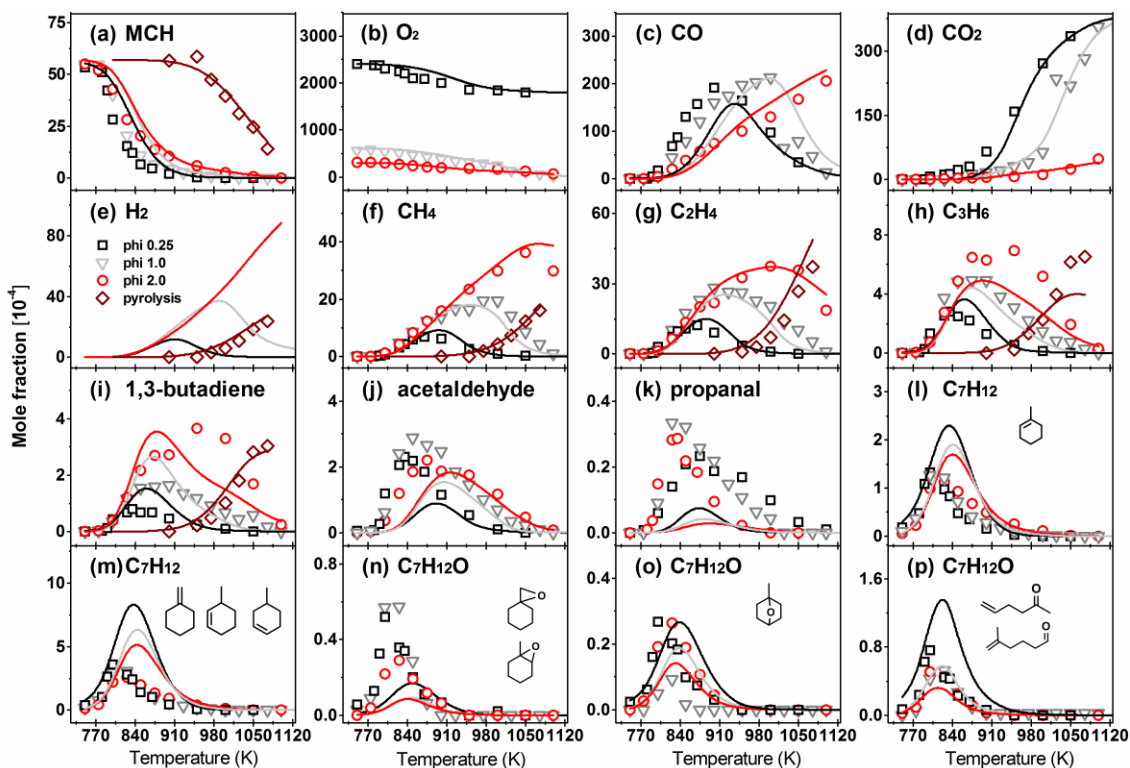


Figure S8. C6 and C7 species in MCH pyrolysis at 30, 150 and 760 Torr in flow reactor. The symbols are experiment measurement by Wang et al. [4] while lines are simulation in this work.

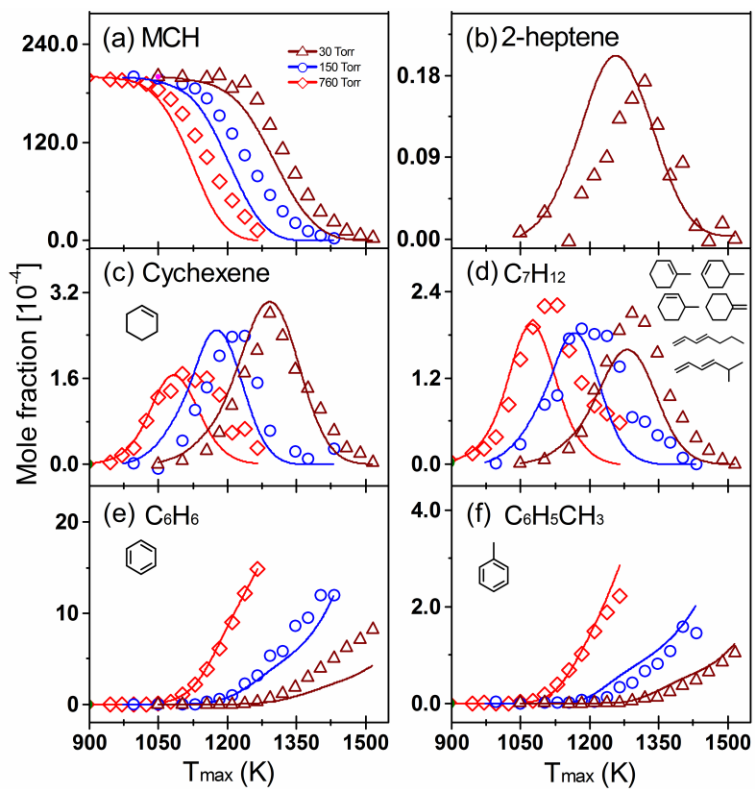
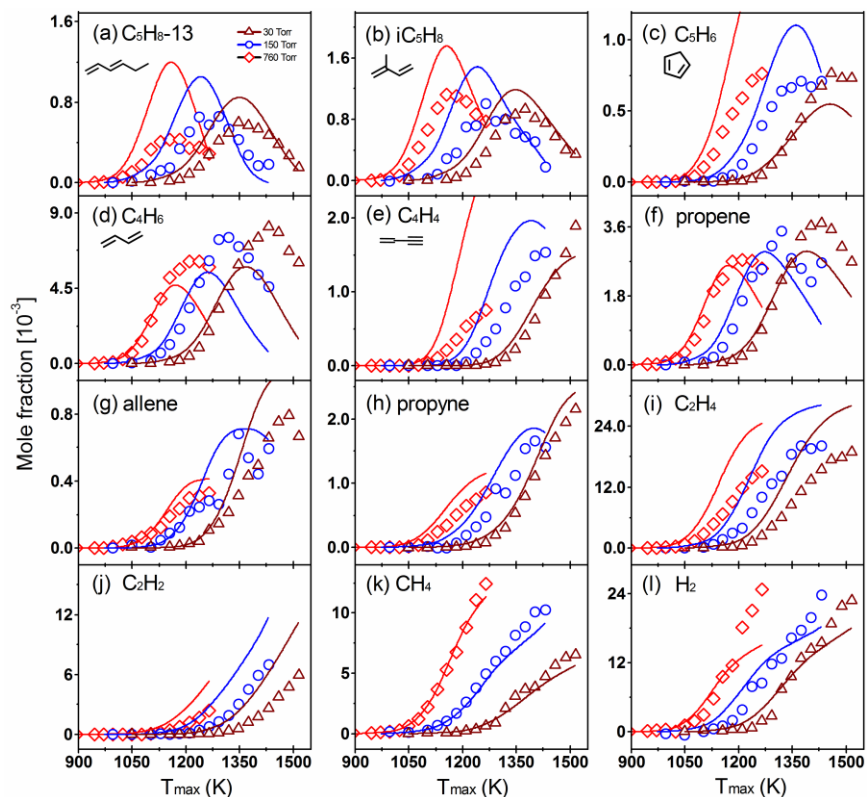


Figure S9. C1 to C5 species in MCH pyrolysis at 30, 150 and 760 Torr in flow reactor. The symbols are experiment measurement by Wang et al. [4] while lines are simulation in this work.



Reference

- [1] L. Xing, L. Zhang, F. Zhang, J. Jiang, *Combust. Flame* 182 (2017) 216-224.
- [2] B.W. Weber, W.J. Pitz, M. Mehl, E.J. Silke, A.C. Davis, C.-J. Sung, *Combust. Flame* 161 (2014) 1972-1983.
- [3] G. Mittal, C.-J. Sung, *Combust. Flame* 156 (2009) 1852-1855.
- [4] Z. Wang, L. Ye, W. Yuan, L. Zhang, Y. Wang, Z. Cheng, F. Zhang, F. Qi, *Combust. Flame* 161 (2014) 84-100.