On the Chemical Kinetics of an Unsaturated C7 Ester: Methyl 3 Hexenoate Ignition and Speciation Studies

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Motivation

Growing support for renewable fuels that also potentially reduce harmful combustion emissions and yield higher efficiencies

Methyl and ethyl esters are primary components of biodiesel compounds

For example, biodiesel composition for rapeseed methyl ester (RME) and soy methyl ester (SME) [1]:

Ester		C=C	% of RME	% SME
methyl palmitate	saturated, $C_{17}H_{34}O_2$	0	4.3	6-10
methyl stearate	saturated, $C_{19}H_{38}O_2$	0	1.3	2-5
methyl oleate	unsaturated, $C_{19}H_{36}O_2$	1	59.9	20-30
methyl linoleate	unsaturated, $C_{19}H_{34}O_2$	2	21.1	50-60
methyl linolenate	unsaturated, $C_{19}H_{32}O_2$	3	13.2	5-11

In general, large esters are difficult to study, consequently published data are scarce.

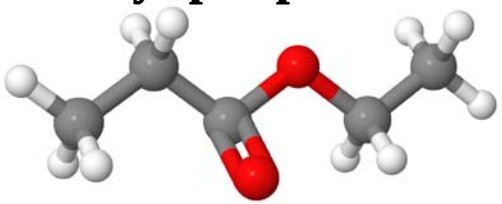
However, there are some studies; including (C_7) methyl hexanoate [2,3], (C_8) methyl heptanoate [4], (C_{11}) methyl decanoate [5], (C_{17}) methyl palmitate [6], and (C_{19}) methyl oleate [7]

[1] C. K. Westbrook, C. V. Naik, O. Herbinet, W. J. Pitz, M. Mehl, S. M. Sarathy, H. J. Curran, *Combust. Flame* 158 (2011) 742-755.
[2] K. HadjAli, M. Crochet, G. Vanhove, M. Ribaucour, R. Minetti, *Proc. Combust. Inst.* 32 (2009) 239-246.
[3] G. Dayma, S. Gaïl, P. Dagaut, *Energy & Fuels* 22 (2008) 1469-1479.
[4] G. Dayma, C. Togbé, P. Dagaut, *Energy & Fuels* 23 (2009) 4254-4268.
[5] P. A. Glaude, O. Herbinet, S. Bax, J. Biet, V. Warth, F. Battin-Leclerc, *Combust. Flame* 157 (2010) 2035-2050.
[6] M. H. Hakka, P. A. Glaude, O. Herbinet, F. Battin-Leclerc, *Combust. Flame* 156 (2009) 2129-2144.
[7] S. Bax, M. H. Hakka, P. A. Glaude, O. Herbinet, F. Battin-Leclerc, *Combust. Flame*, 157 (2010) 1220–1229.

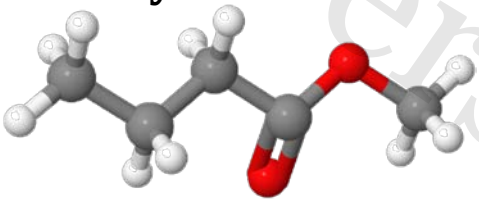
Background

Recent experimental and computational work has focused on C_5 and smaller esters (saturated C_5) methyl butanoate [2,8-17] and (unsaturated C_5) methyl crotonate [10,11,12]

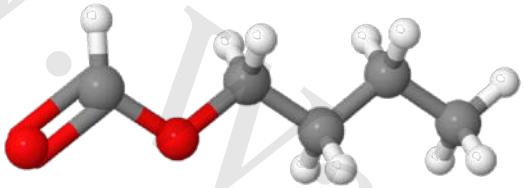
ethyl propanoate



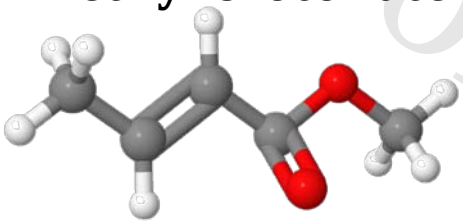
methyl butanoate



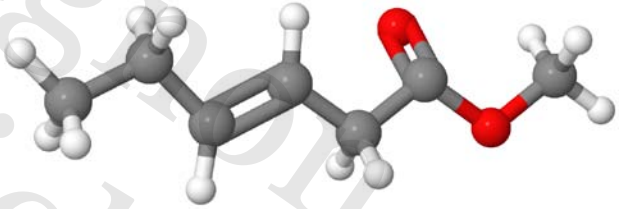
butyl methanoate



methyl crotonate

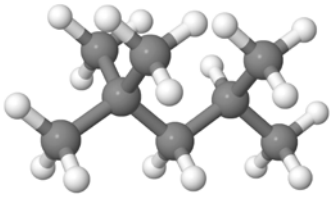


methyl 3 hexenoate



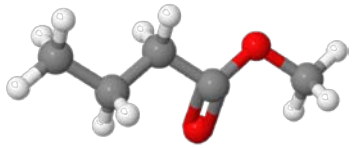
[8] S. M. Walton, M. S. Wooldridge, C. K. Westbrook, *Proc. Combust. Inst.* 32 (2009) 255-262.
[9] S. Gaïl, M. J. Thomson, S. M. Sarathy, S. A. Syed, P. Dagaut, P. Diévart, A. J. Marchese, F. L. Dryer, *Proc. Combust. Inst.* 31 (2007) 305-311.
[10] S. Gaïl, S. M. Sarathy, M. J. Thomson, P. Diévart, P. Dagaut, *Combust. Flame* 155 (2008) 635-650.
[11] S. M. Sarathy, S. Gaïl, S. A. Syed, M. J. Thomson, P. Dagaut, *Proc. Combust. Inst.* 31 (2007) 1015-1022.
[12] W. K. Metcalfe, S. Dooley, H. J. Curran, J. M. Simmie, A. M. El-Nahas, M. V. Navarro, *J. Phys. Chem. A* 111 (2007) 4001-4014.
[13] A. Farooq, D. F. Davidson, R. K. Hanson, L. K. Huynh, A. Violi, *Proc. Combust. Inst.* 32 (2009) 247-253.
[14] S. Dooley, H. J. Curran, J. M. Simmie, *Combust. Flame* 153 (2008) 2-32.
[15] M. H. Hakka, H. Bennadji, J. Biet, M. Yahyaoui, B. Sirjean, V. Warth, L. Coniglio, O. Herbinet, P. A. Glaude, F. Billaud, F. Battin-Leclerc, *Int. J. Chem. Kin.* 42 (2010) 226-252.
[16] B. Akih-Kumgeh, J. M. Bergthorson, *Energy Fuels* 24 (2010) 2439-2448.
[17] S. M. Walton, D. M. Karwat, P. D. Teini, A. Gorny, M. S. Wooldridge, "Speciation Studies of Methyl Butanoate Ignition," accepted to *Fuel*, January 2011, in press.

Previous UM RCF Studies and Program Objectives



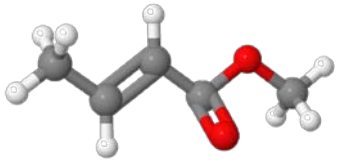
Iso-octane [18]

- RCF, Φ = 0.2-1.98, inert:O_2 = 1.38-5.89, P = 8.7-16.6 atm, T = 903-1020K
- $\tau_{ign} = 2.8 \times 10^{-3} \times P^{-1.25} \times \Phi^{-0.79} \times \chi(O_2)^{-1.14} \times \exp(27300/R_{[cal/mol/K]}T)$



Methyl butanoate [8]

- RCF, Φ = 0.3-0.4, inert:O_2 = 3.76, P = 4.7-19.6 atm, T = 935-1117K
- $\tau_{ign} = 3.2 \times 10^{-3} \times P^{-1.21} \times \Phi^{-0.77} \times \chi(O_2)^{-1.62} \times \exp(30300/R_{[cal/mol/K]}T)$



Methyl crotonate [19]

- RCF, Φ = 0.3, inert:O_2 = 3.76, P = 10.5 atm, T = 951-1066K
- $\tau_{ign} = 5.6 \times 10^{-7} \times \exp(33200/R_{[cal/mol/K]}T)$

Goals

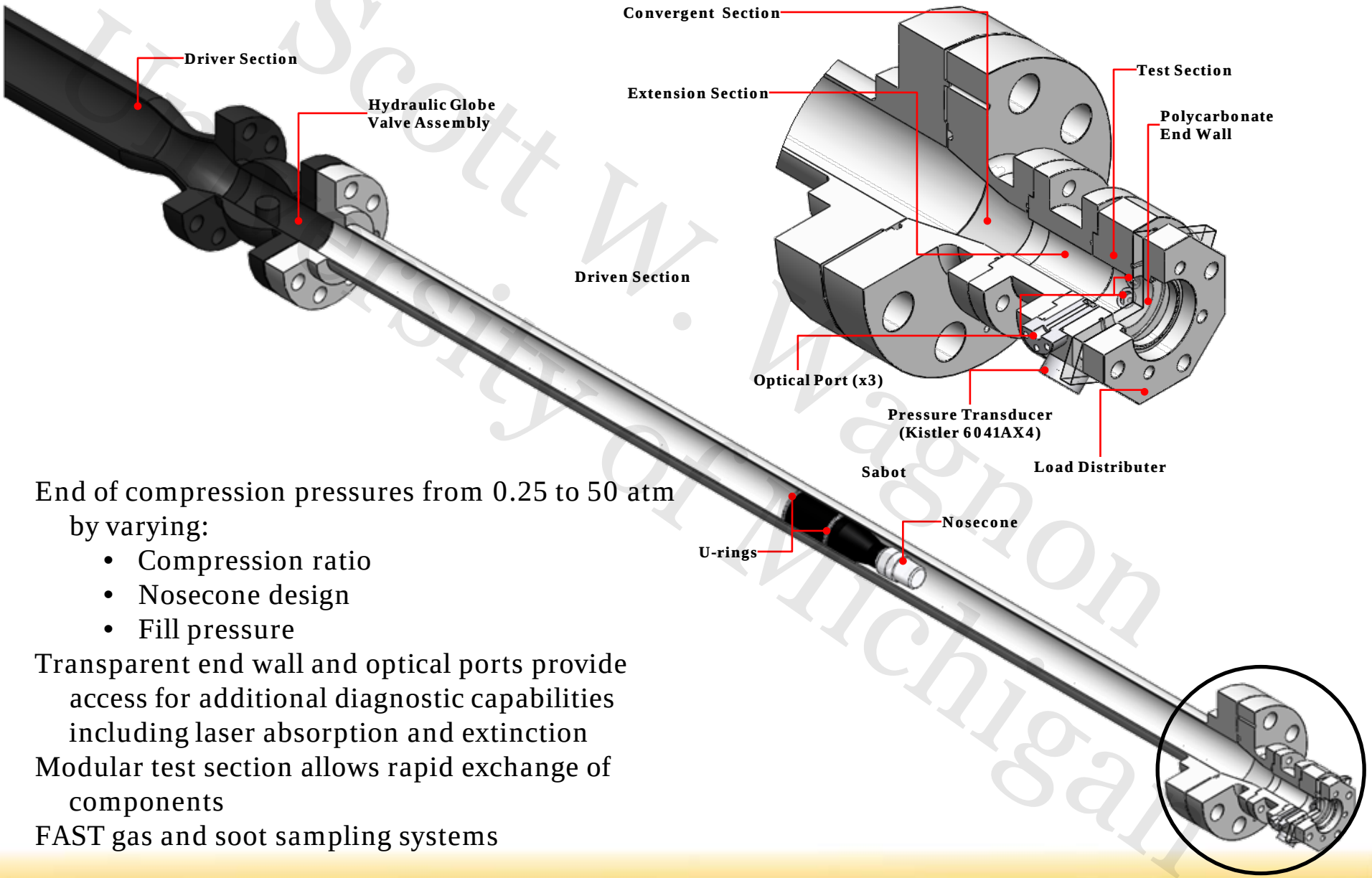
- Better understanding of combustion chemistry through ignition and speciation studies
- Provide new data enabling biodiesel use in advanced engine strategies

Approach

- Utilize the University of Michigan Rapid Compression Facility (UM RCF) to conduct ignition and speciation studies
- Compare fuel combustion metrics of ignition delay times, activation energies, intermediate species and reaction pathways

[18] S. M. Walton, X. He, B. T. Zigler, M. S. Wooldridge, A. Atreya, *Combust. Flame* 150 (2007) 246-262.
[19] S.M. Walton, Ph.D. Dissertation, 2008, "Experimental Investigation of the Auto-Ignition Characteristics of Oxygenated Reference Fuel Compounds," University of Michigan.

UM RCF – Experimental Approach
Ignition Studies



End of compression pressures from 0.25 to 50 atm by varying:

- Compression ratio
- Nosecone design
- Fill pressure

Transparent end wall and optical ports provide access for additional diagnostic capabilities including laser absorption and extinction

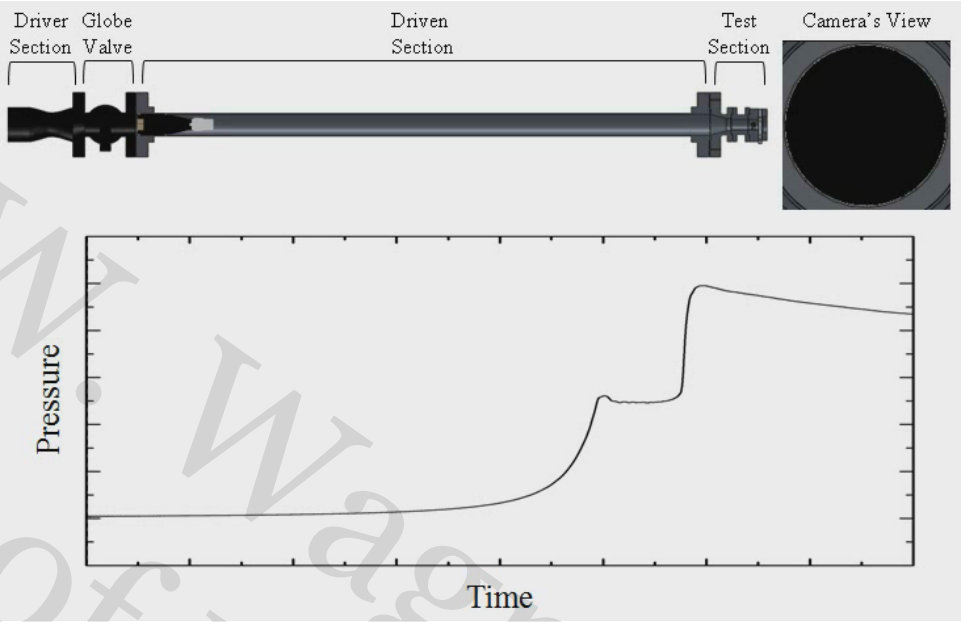
Modular test section allows rapid exchange of components

FAST gas and soot sampling systems

Defining Test Conditions in the UM RCF

$$P_{eff} = \frac{1}{t_{\frac{dP}{dt}max} - t_{P_{max}}} \int_{t_{P_{max}}}^{t_{\frac{dP}{dt}max}} P\,dt$$

$$\int_{T_o}^{T_{eff}} \frac{\gamma}{\gamma - 1}\, d\ln T = \ln\left(\frac{P_{eff}}{P_0}\right)$$



Test Section Characteristics

~~V~~ ≈ 200 cm^3

~~V~~: A_S ≈ 0.8-1.1

T_{Axis} ≈ ± 5% of $T_{Isen.}$

65% of ~~V~~ at ± 10% of T_{Axis}

Thermal boundary layer ≤ 5 mm after 30 ms

Long test times, >90% of P_{max} after 30 ms

~~Transport effects?~~
~~Gas motion?~~
~~Temperature gradients?~~

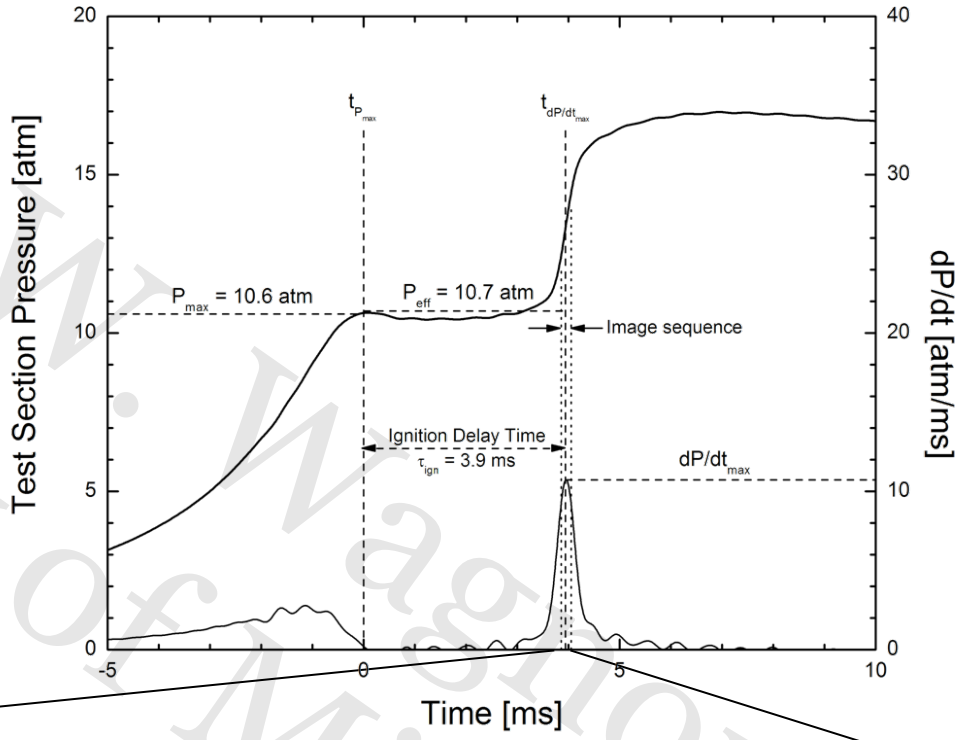
Minimized by uniformity, allowing isolation of chemical kinetics.

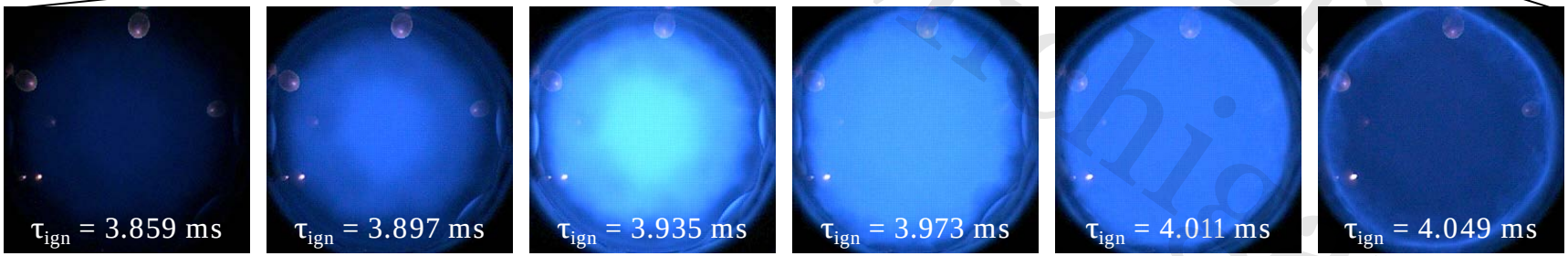
[20] M. T. Donovan, X. He, B. T. Zigler, T. R. Palmer, M. S. Wooldridge, A. Atreya, *Combust. Flame* 137 (2004) 351-365.

Typical M3H Ignition Data

Frame rate = 26,000 fps
Exposure = 38 µs

P_{eff} = 10.7 atm
T_{eff} = 1040 K
Φ = 0.3
Inert:O_2 = 3.76
τ_{ign} = 3.9 ms

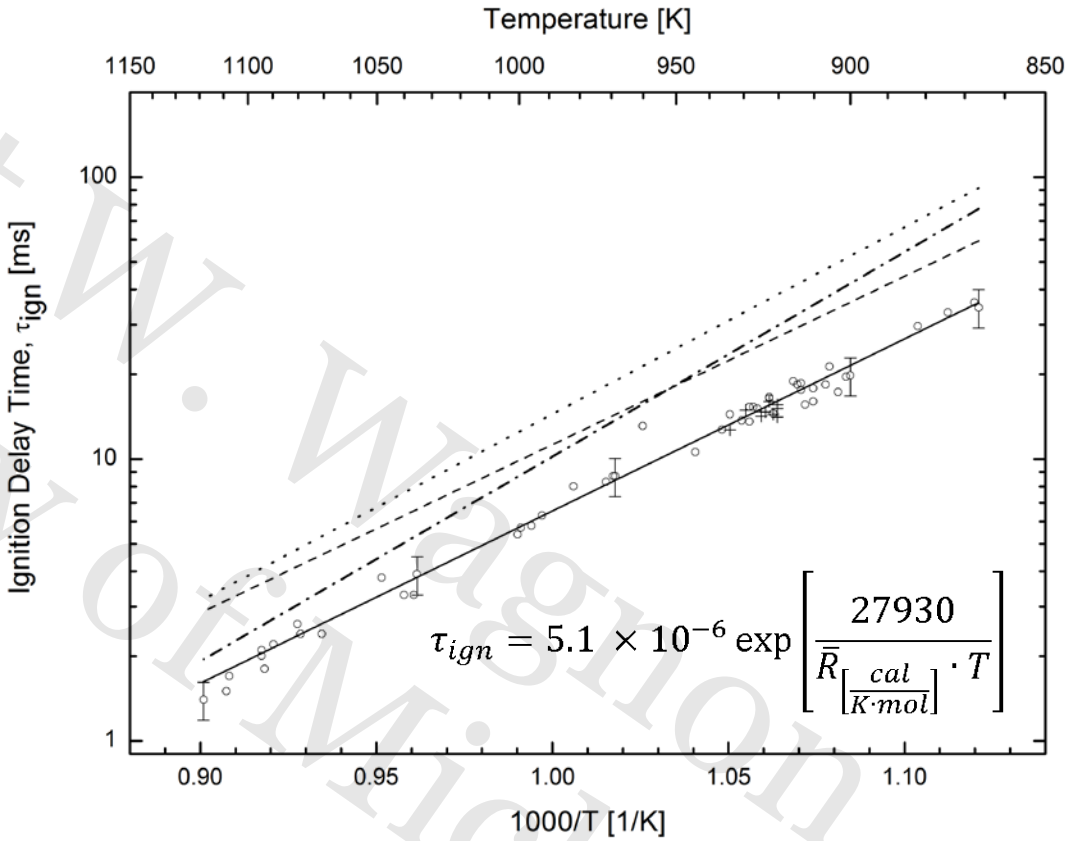




Summary of M3H Ignition Data

○ M3H ignition
\+ M3H ignition and gas sampling
—— Best fit linear regression
····· Iso-octane [18]
- - - - - Methyl butanoate [8]
-·-·- Methyl crotonate [19]

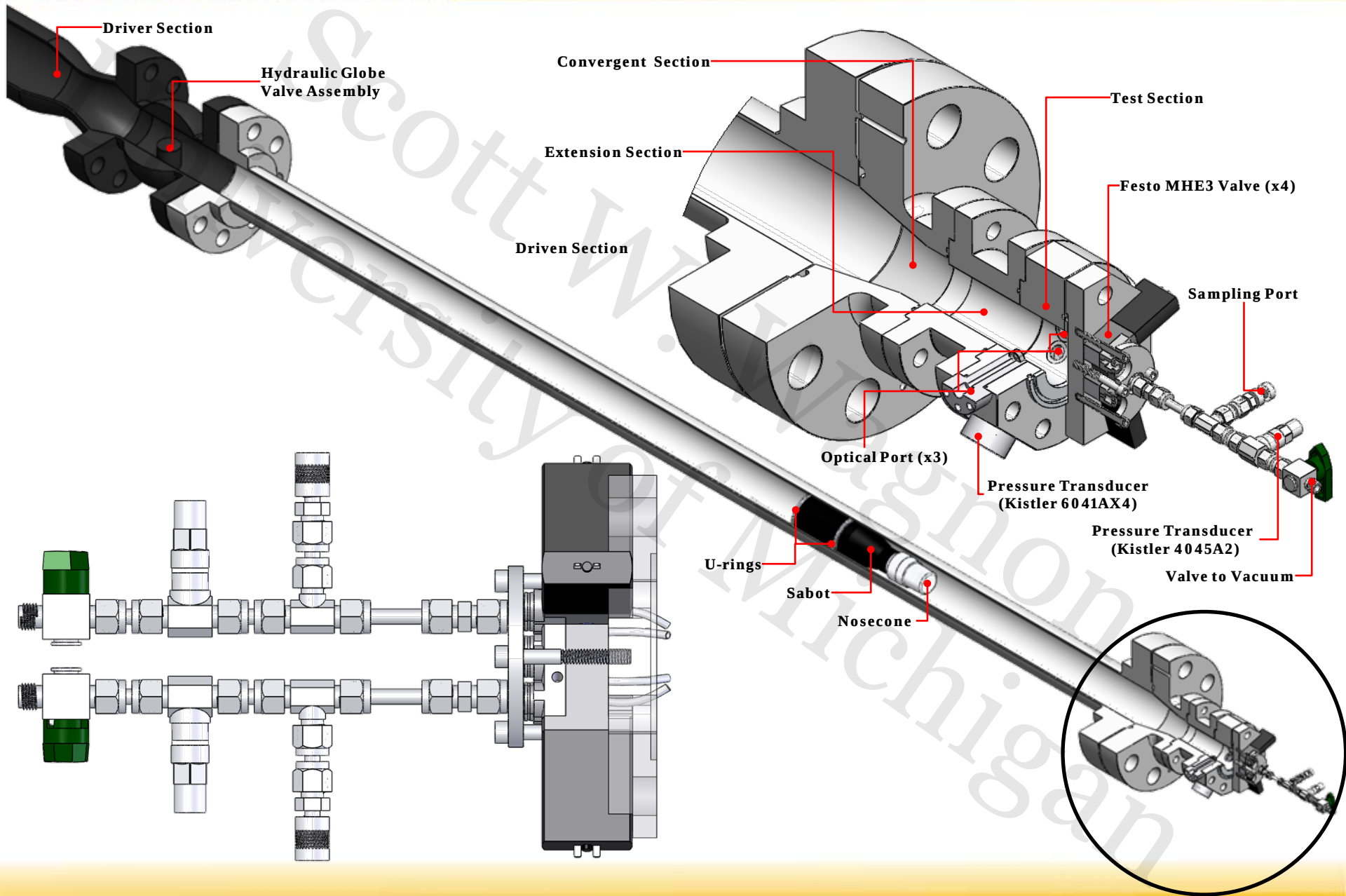
P = 9.5-11.6 atm
T = 892-1102 K
Φ = 0.3
$\chi(O_2)$ = 20.9%
Inert:O_2 = 3.76
τ_{ign} = 1.4-35.9 ms



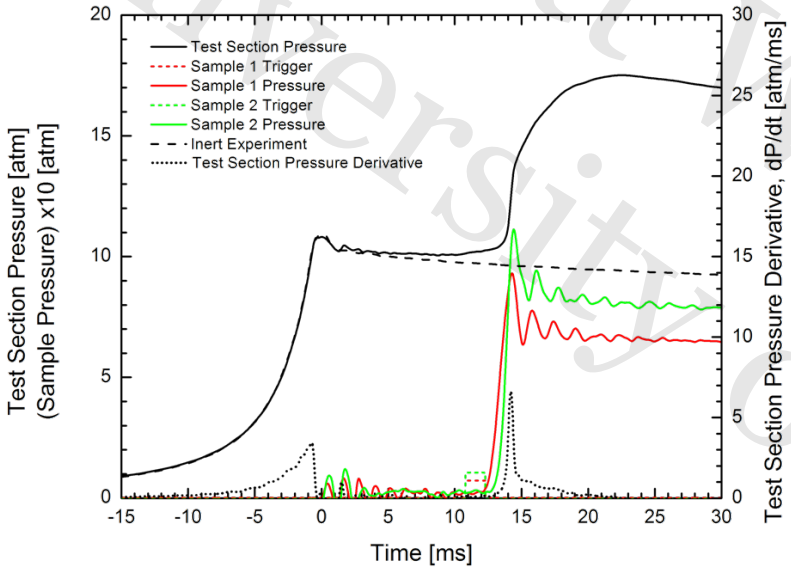
[18] S. M. Walton, X. He, B. T. Zigler, M. S. Wooldridge, A. Atreya, *Combust. Flame* 150 (2007) 246-262.
[8] S. M. Walton, M. S. Wooldridge, C. K. Westbrook, *Proc. Combust. Inst.* 32 (2009) 255-262.
[19] S.M. Walton, Ph.D. Dissertation, 2008, "Experimental Investigation of the Auto-Ignition Characteristics of Oxygenated Reference Fuel Compounds," University of Michigan.

combustion LABORATORY

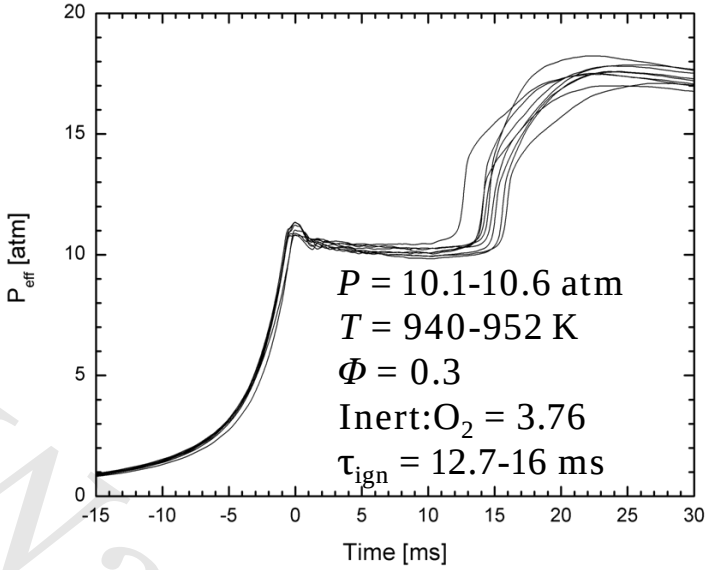
UM RCF – Speciation Studies

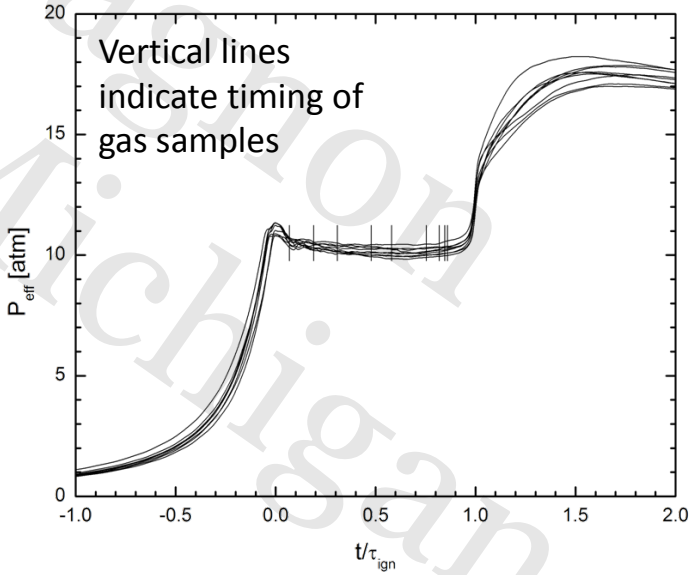


Typical M3H Sampling Data



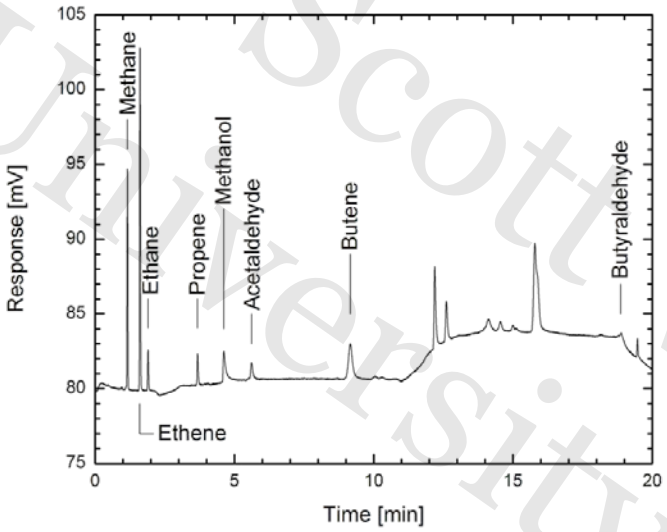
P_{eff} = 10.3 atm
T_{eff} = 944 K
Φ = 0.3
Inert:O_2 = 3.76
τ_{ign} = 14.2 ms



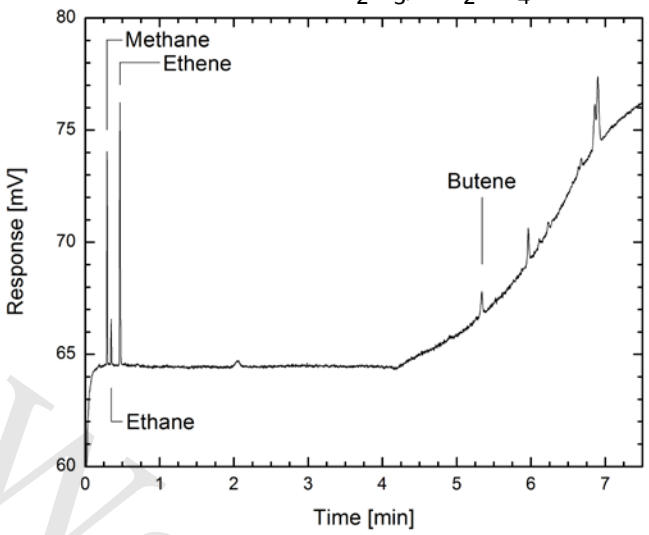


Results of Gas Chromatography

Varian CP-PoraBOND Q



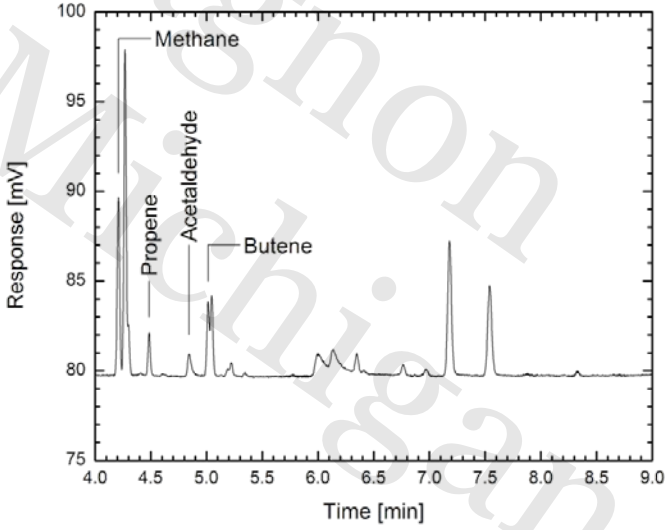
Varian CP-AL_2O_3/Na_2SO_4



<u>Species detected, but not quantified:</u>
propene, butyraldehyde

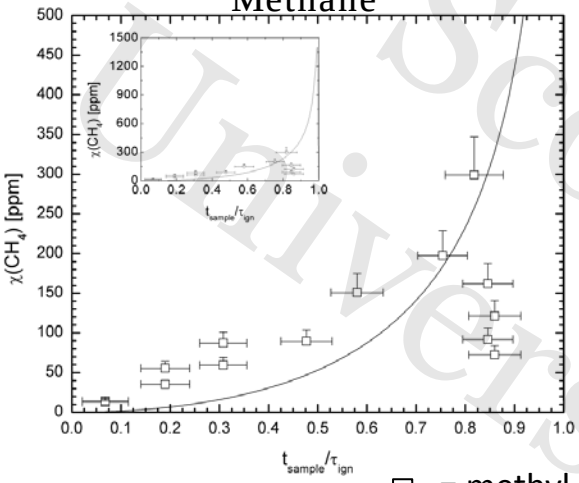
<u>Species below detectable limits:</u>
carbon monoxide, acetylene, ethanol, 3-buten-1-ol

Restek RTX-1

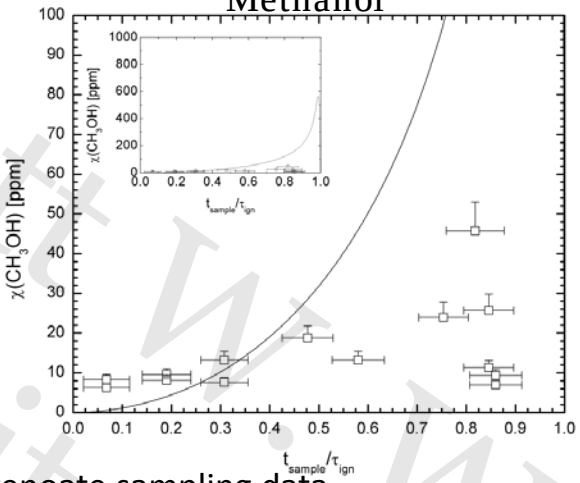


Time Histories of Stable Intermediate Species Present During M3H Ignition (experimental data) and MH Ignition (modeling results)

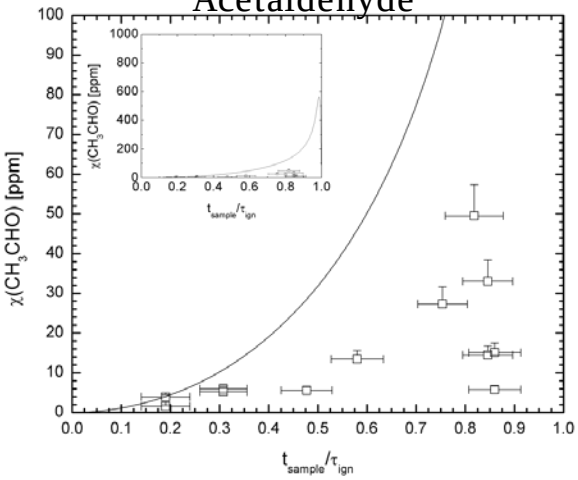
Methane



Methanol



Acetaldehyde

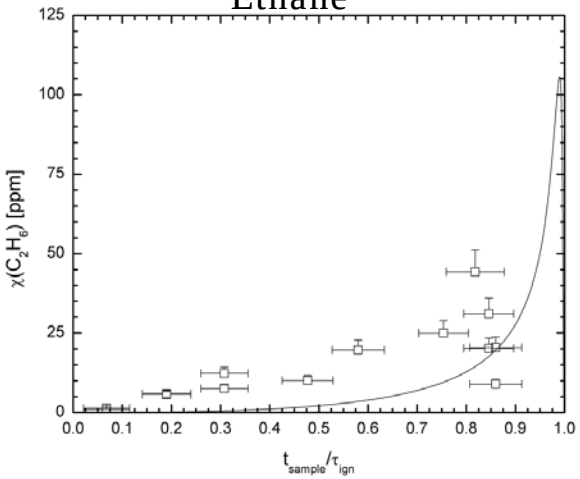


□ = methyl 3 hexenoate sampling data

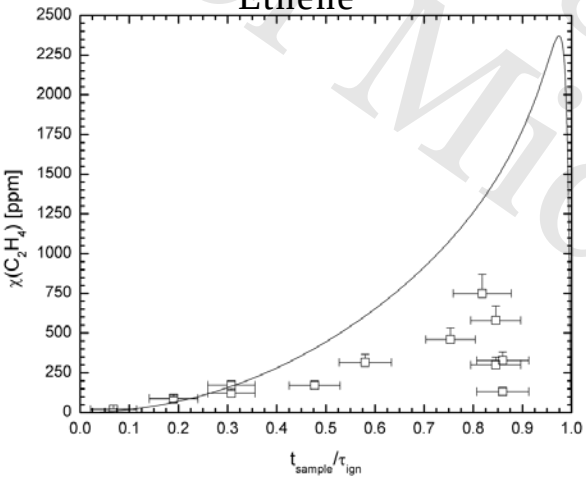
— = methyl hexanoate mechanism [3] Chemkin simulation:
Adiabatic, 0-D, constant volume @ 945 K, 10.5 atm

Fuel = 0.68 %
O_2 = 20.80 %
N_2 = 75.68 %
CO_2 = 2.84 %

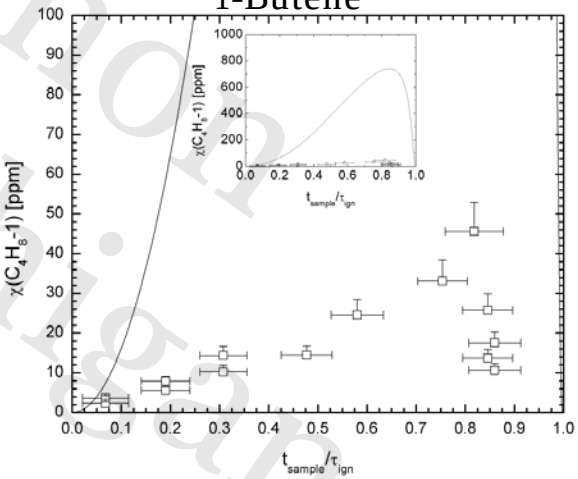
Ethane



Ethene



1-Butene



[3] G. Dayma, S. Gaïl, P. Dagaut, *Energy & Fuels* 22 (2008) 1469-1479.

Conclusions and Current Work

Summary and Conclusions

- First ignition and speciation data for methyl 3 hexenoate
- Ignition delay time and species measurements exhibit low scatter
- M3h exhibits faster reactivity compared to longer alkane, smaller saturated and unsaturated esters
- NTC behavior was not observed in m3h for conditions studied, although not unexpected
- Large quantities (>200 ppm) of ethene are formed quickly (t/τ_{ign} <30%) during m3h ignition; whereas 1-butene remains below 100 ppm throughout the ignition delay period; contrary to the reaction pathways predicted for the saturated counterpart to m3h, methyl hexanoate
- These data are important to create an accurate understanding of combustion chemistry of even larger unsaturated esters

Current work

- Further identification and calibration of intermediate species
- The ignition and speciation data guide our development of a m3h reaction mechanism

Acknowledgements

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