Experiments and Modeling of the Autoignition of Methyl-Cyclohexane at High Pressure

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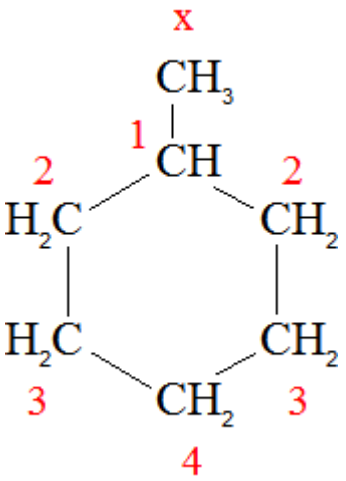
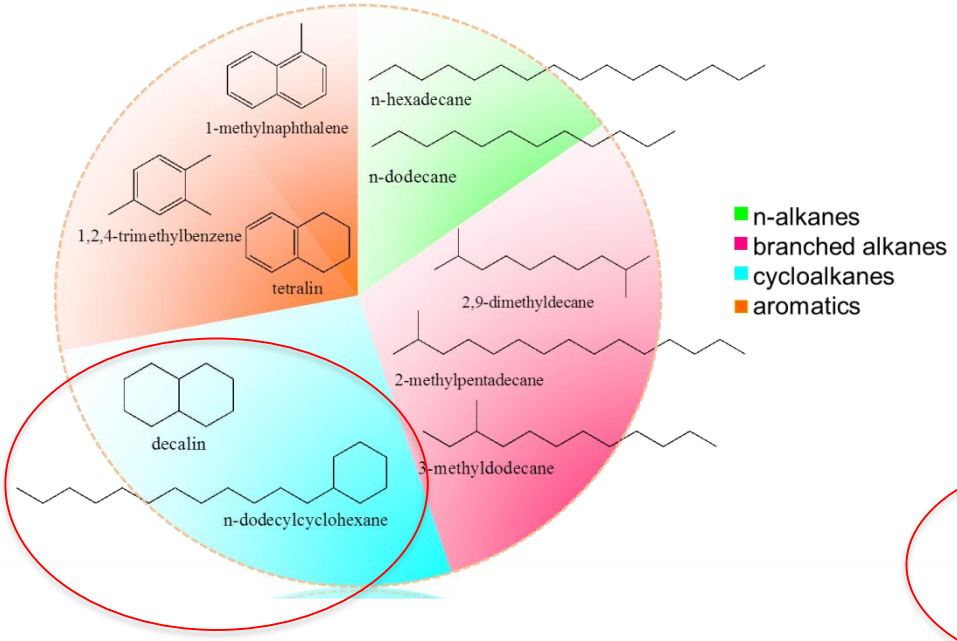
Introduction

- Cycloalkanes and alkyl-cycloalkanes are well known as components of many transportation fuels
- Methyl-cyclohexane (MCH) has been suggested as a candidate to model the cycloalkane and alkyl-cycloalkane content of real fuels
- Low Temperature Combustion (LTC) is important to the operation of advanced engine concepts
- Therefore, detailed kinetic models may be required to predict combustion phasing, heat release rates, and especially engine-out emissions

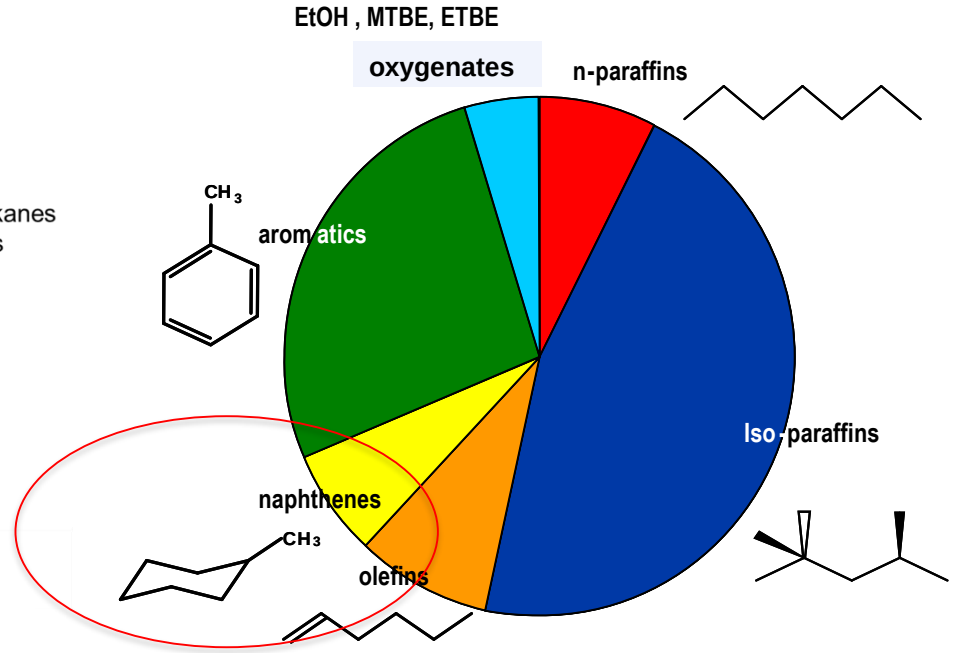


Cyclohexanes are prevalent in transportation fuels

Chemical classes in diesel



Chemical classes in gasoline



Slide courtesy Dr. Bill Pitz, LLNL, from paper 1B12

Introduction

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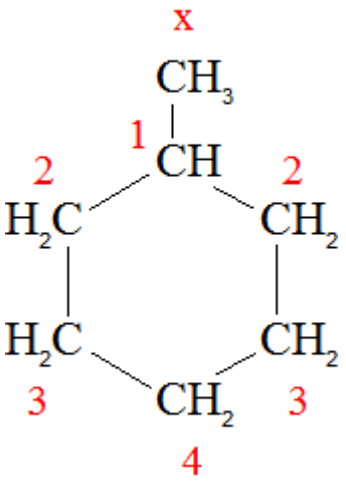
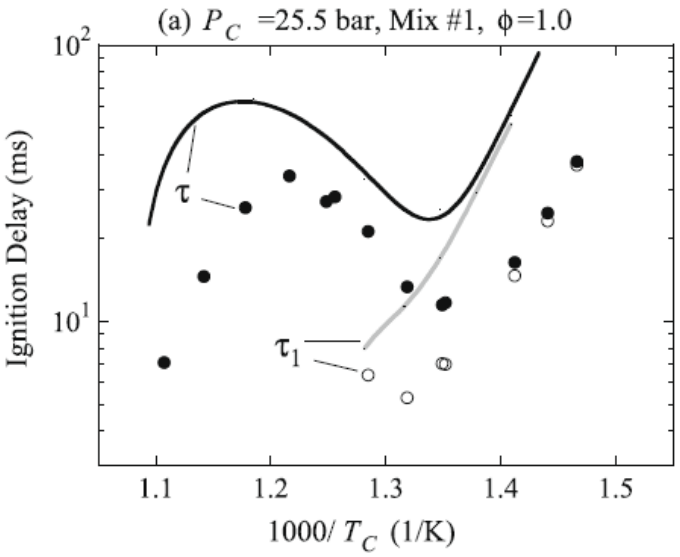
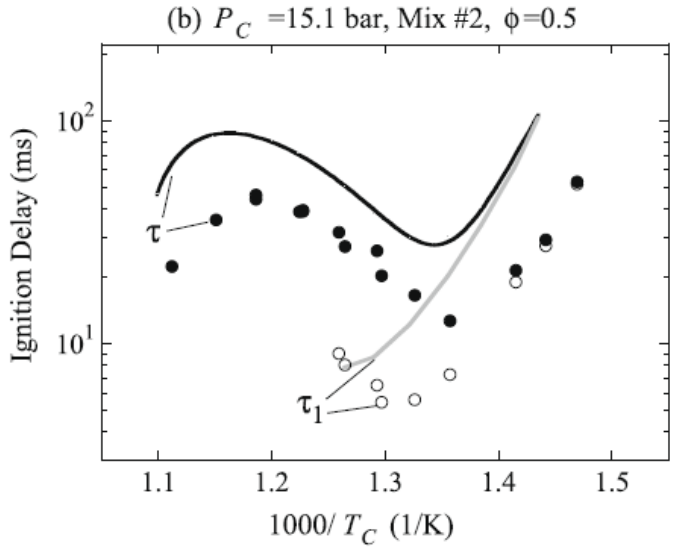


Motivation

- Previous work* comparing MCH ignition delays to a model from 2007† showed significant over-prediction of both first stage and overall ignition delay
- Our objective is to update and extend the model to better predict existing and new experimental conditions

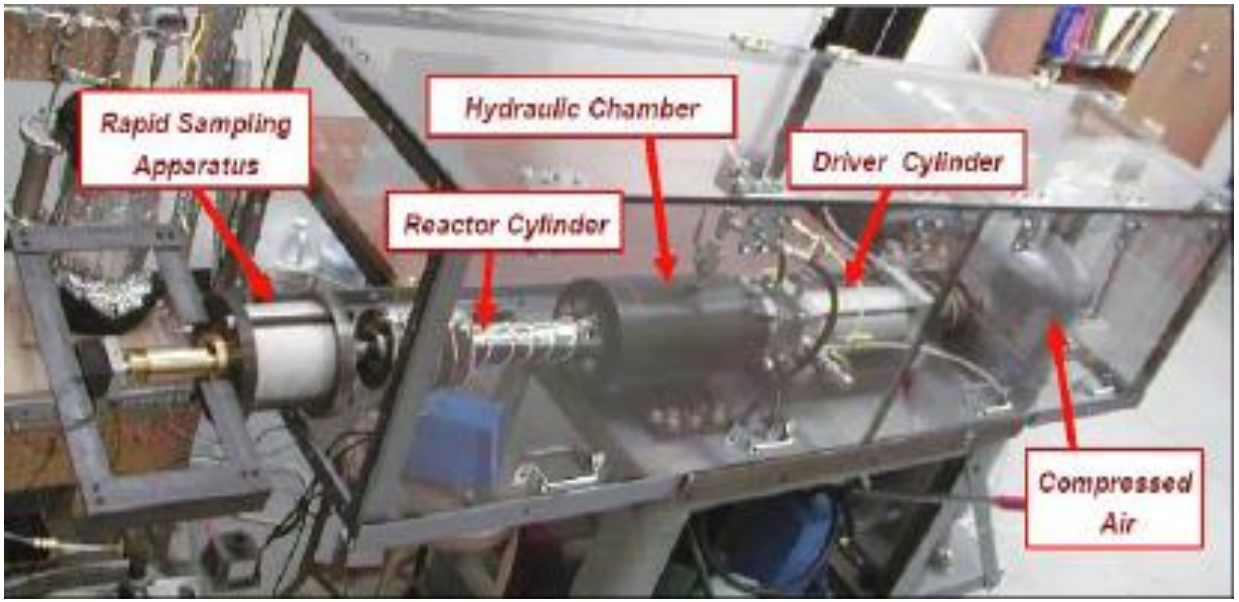




*Mittal & Sung, *Combustion and Flame*, 2009, **156**, 1852-1855
†Pitz et al., *Proc. Combust. Inst.*, 2007, **31**, 267–275

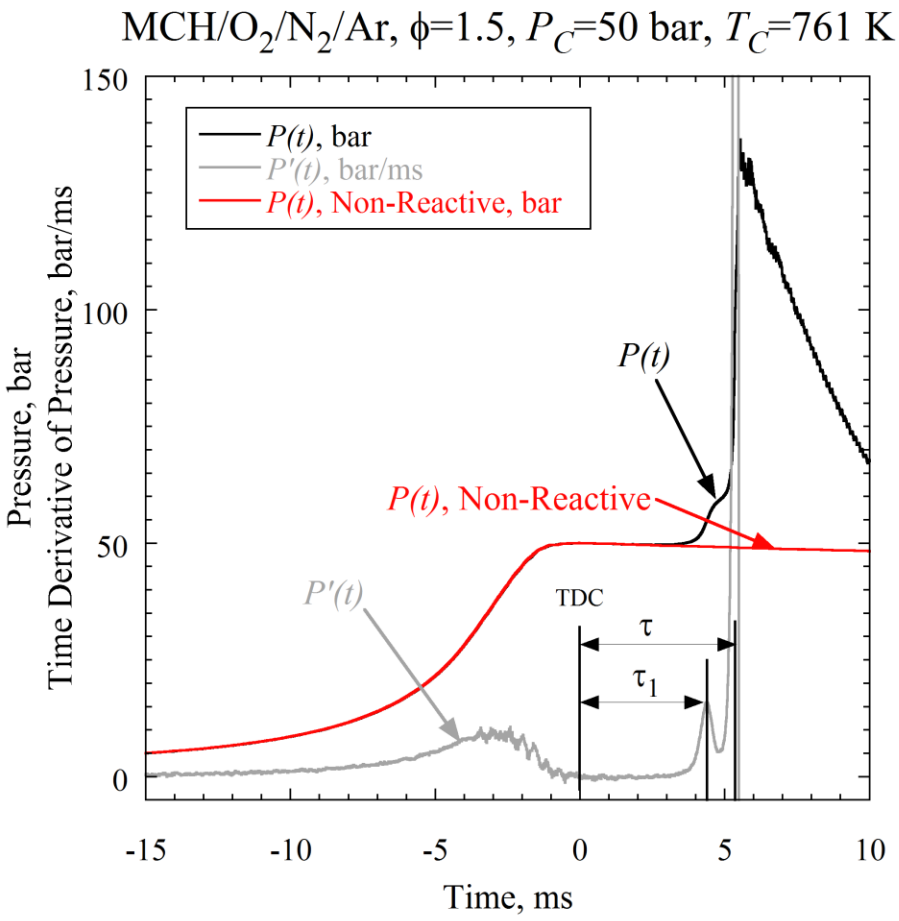
Experimental Methods

- Experiments to measure the ignition delay of methyl-cyclohexane (MCH) are performed in a heated Rapid Compression Machine (RCM)
- Homogeneous gas-phase mixtures of fuel and oxidizer are compressed and the piston is held in place at Top Dead Center (TDC), creating a constant volume reactor
- The compression ratio of the RCM, and the initial pressure and initial temperature of the mixture are varied to vary the pressure and temperature at TDC
- The pressure and temperature at TDC are referred to by subscript "C" – i.e. P_C & T_C respectively



Experimental Methods

- The end of compression (when the piston reaches TDC) is defined as the maximum of the pressure prior to the ignition
- The ignition delays are the times from the end of compression to the local maxima of the time derivative of the pressure
- During the ignition delay, the reactants are losing energy by heat transfer to the relatively colder reactor walls
- Because we have a constant volume, closed reactor, the heat loss produces pressure drop
- We characterize this pressure drop by replacing oxygen with nitrogen in the mixture to eliminate the explosion but retain a similar heat loss profile to the reactive experiments
- T_C is taken as the temperature at TDC of a non-reactive simulation



Experimental Conditions

- Experiments are conducted for three mixtures, whose diluent compositions contain varying amounts of N_2 and Ar to maintain a similar specific heat ratio for all of the mixtures

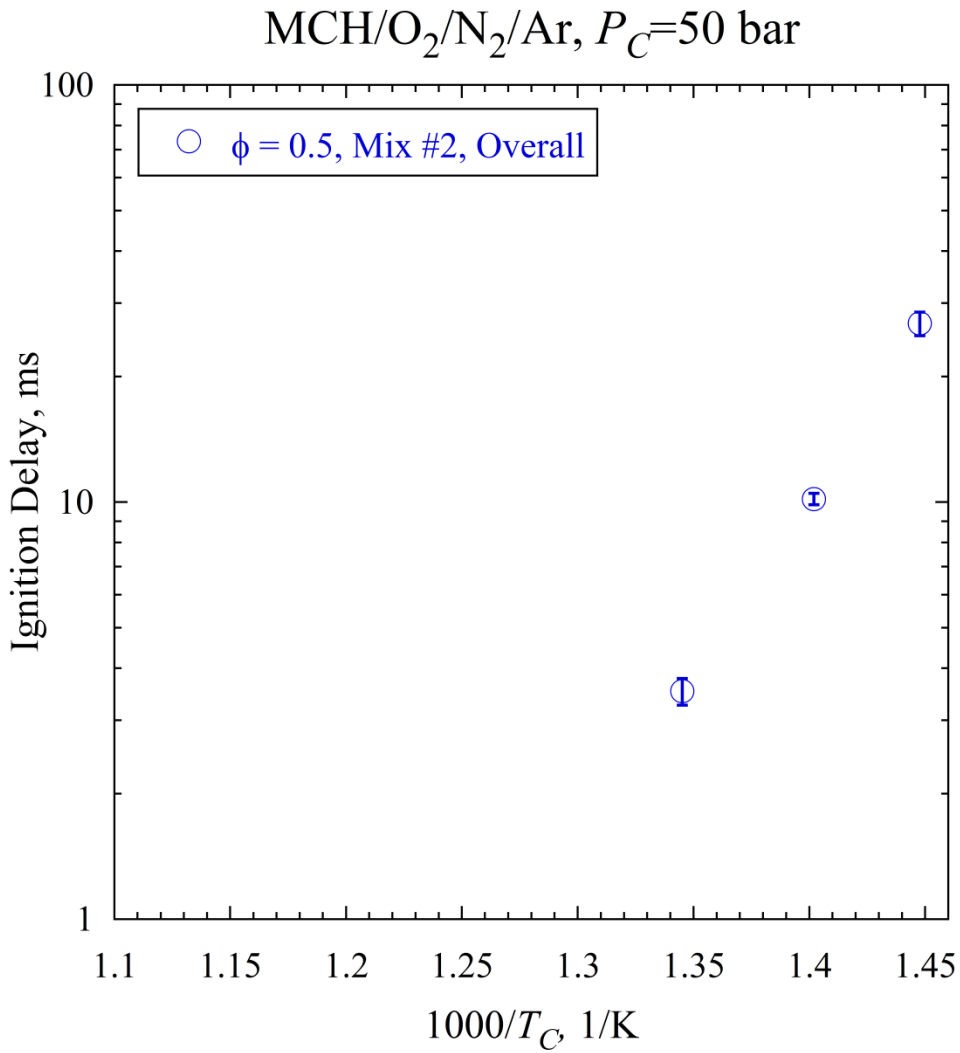
Mix #	ϕ	MCH	O_2	N_2	Ar
1	1.0	1	10.5	12.25	71.75
2	0.5	1	21.0	0.00	73.50
3	1.5	1	7.0	16.35	71.15

- The equivalence ratio is adjusted by varying the initial oxygen mole fraction at constant fuel mole fraction
- MCH ignition delays were previously measured in our RCM at $P_C = 15.1$ and 25.5 bar*
- New experimental ignition delays are measured in this work at $P_C = 50$ bar
- The temperature range for the three pressure conditions is similar from $690 - 910$ K

*Mittal & Sung, *Combustion and Flame*, 2009, **156**, 1852-1855

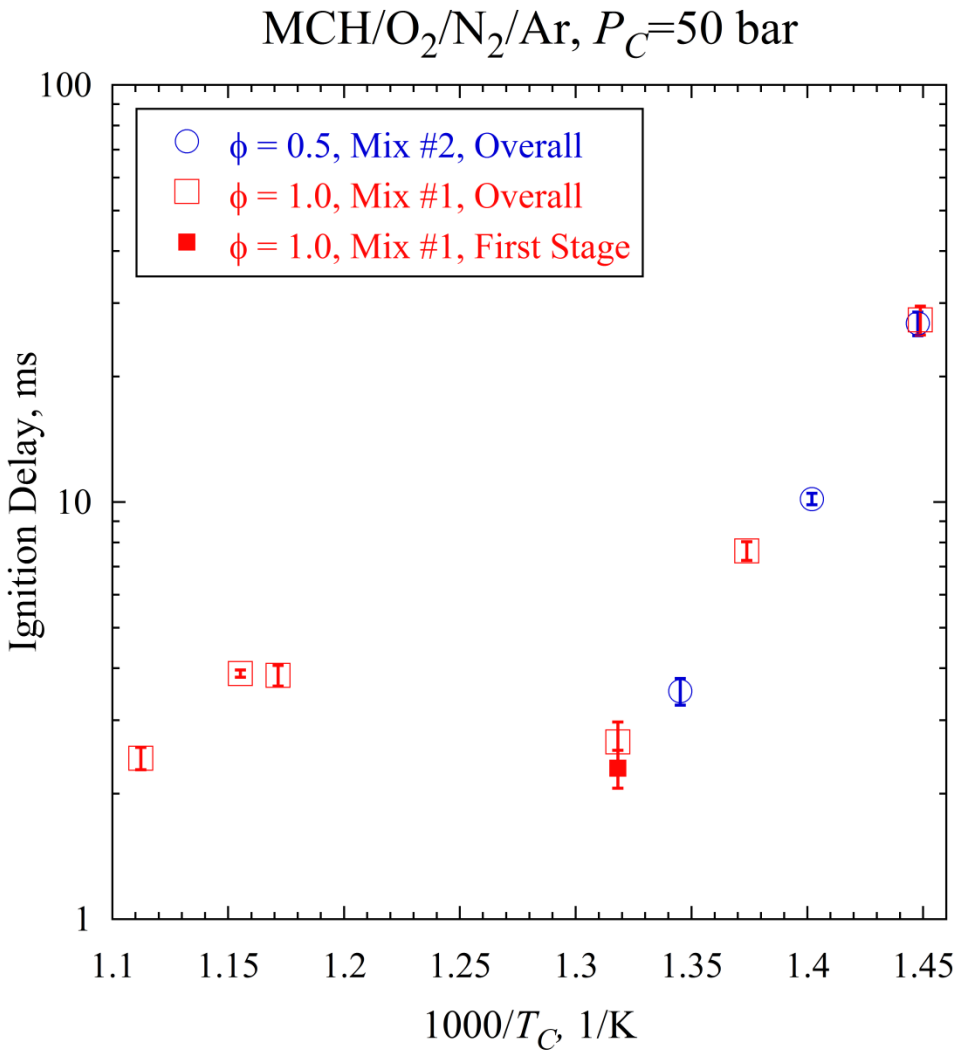
Experimental Results

- Ignition delays in the NTC region for Mix #2 ($\phi = 0.5$) are not reported because substantial reactivity occurred during the compression stroke for $T_C > 740$ K
- Mix #2 does not have two-stage ignition in the temperature range investigated here



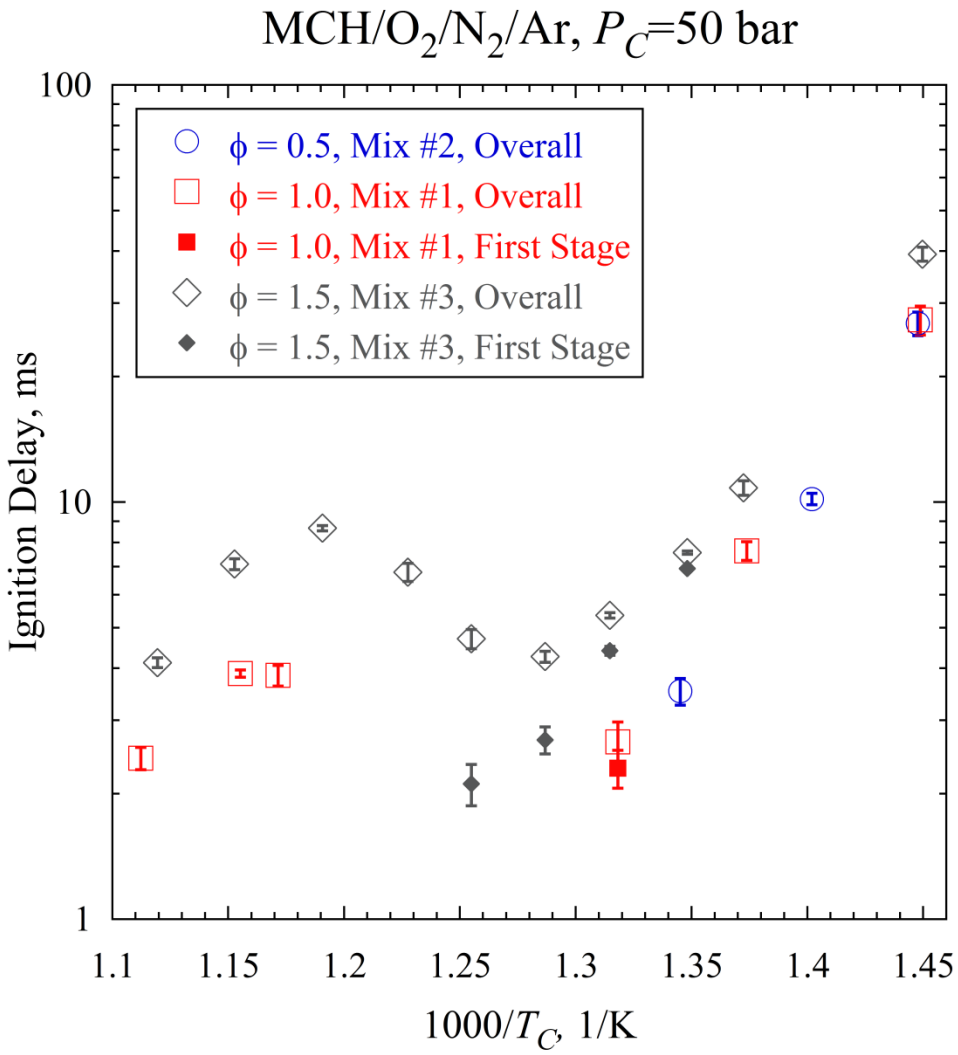
Experimental Results

- Reactivity during the compression stroke prevents reporting complete resolution of the NTC region for Mix #1 ($\phi = 1.0$)
- Two-stage ignition is reported for one experimental condition for Mix #1

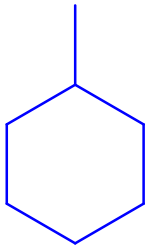


Experimental Results

- Mix #2 is the most reactive because it has the highest initial O_2 concentration
- The NTC region for Mix #3 ($\phi = 1.5$) approximately extends from 775 K to 840 K
- Two stage ignition was measured for Mix #3 for temperatures from 740 K to 800 K



Updates to MCH mechanism



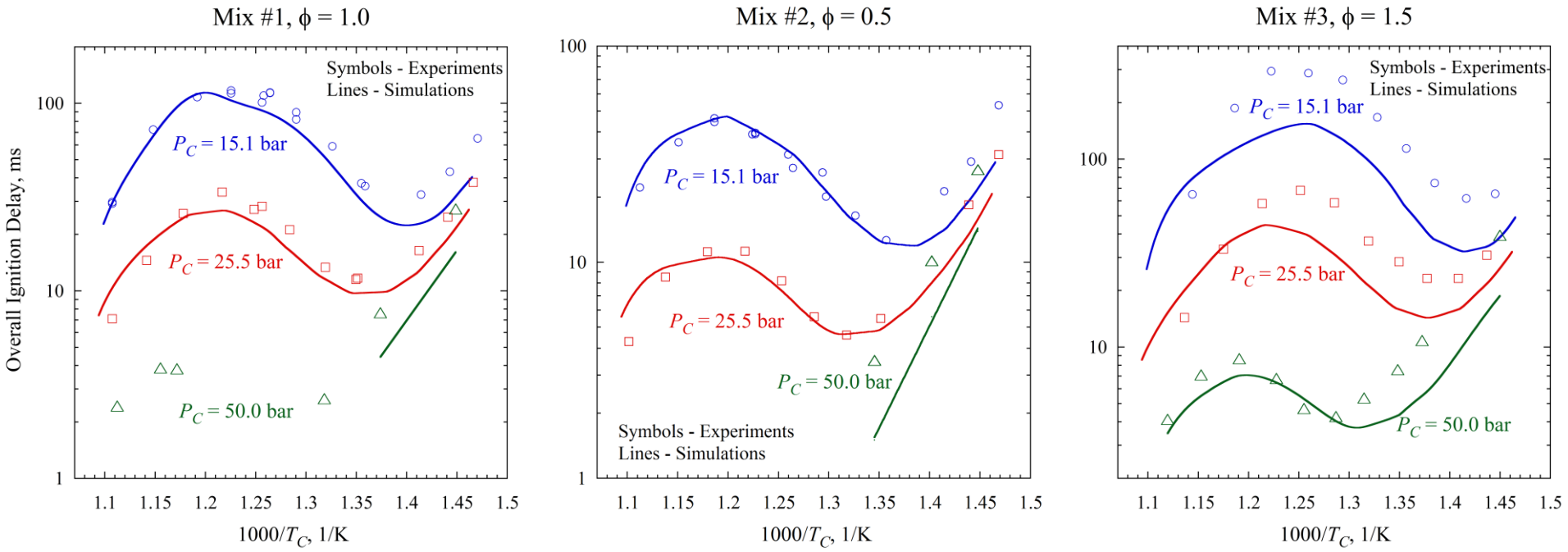
- New C1-C4 base chemistry from NUIG
- New aromatics base chemistry from NUIG-LLNL
  - Based on work by Metcalfe et al. and Mehl et al.
- Cyclohexane submodel is more recent LLNL version*
- Unsaturated ring intermediate products resolved with much more fidelity (previously lumped)
- MCH abstraction reactions:
  - MCH + OH rates from ANL experiments†
  - Others using latest LLNL reaction rate rules
- RO_2 isomerization rate constants
  - from Fernandes et al‡ for cases involving cyclohexane ring
  - new ab initio rate constant computed for case involving methyl group (*this work*)

*Silke et al., *J. Phys. Chem. A.*, 2007, **111**, 3761-3775

†Sivaramakrishnan and Michael, *Combust. Flame*, 2009, **156**, 1126-1134

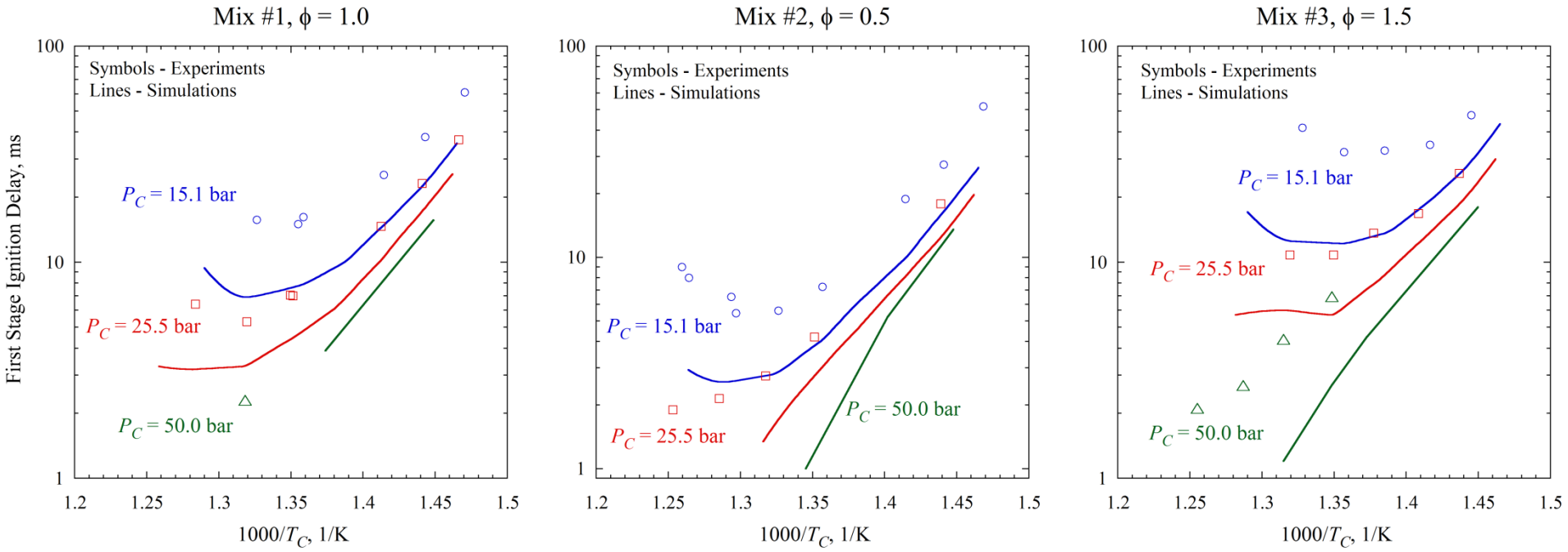
‡ Fernandes et al., *Phys. Chem. Chem. Phys.* 2009, **11**, 1320–1327

Comparison with Modeling – Overall Ignition Delays



- The model has improved significantly since 2007!
- Experimental ignition delays in the high temperature region are predicted well
- Low temperature ignition delays are generally under-predicted, especially for the $\phi = 1.5$ case

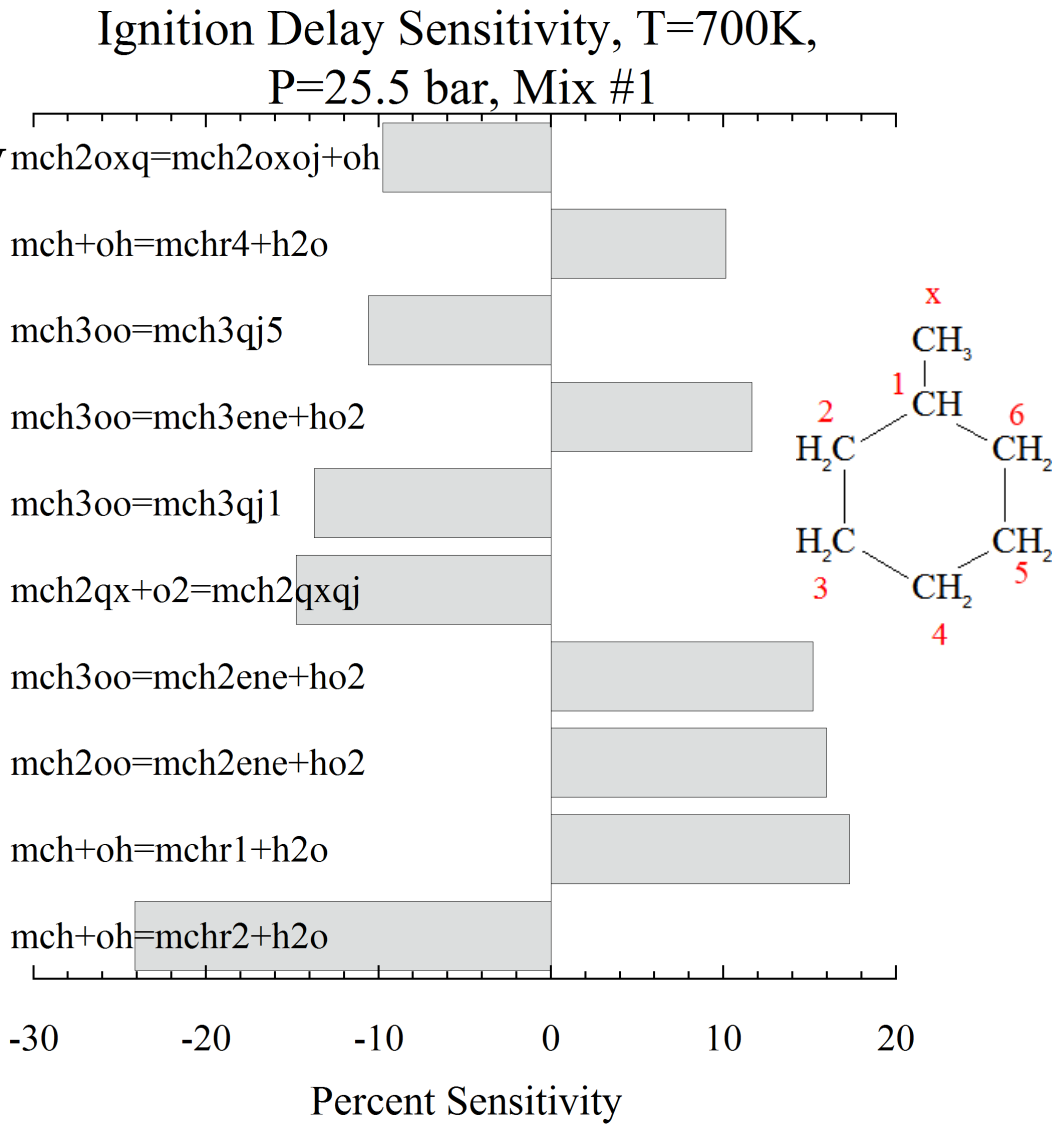
Comparison with Modeling – 1st Stage Ignition Delay



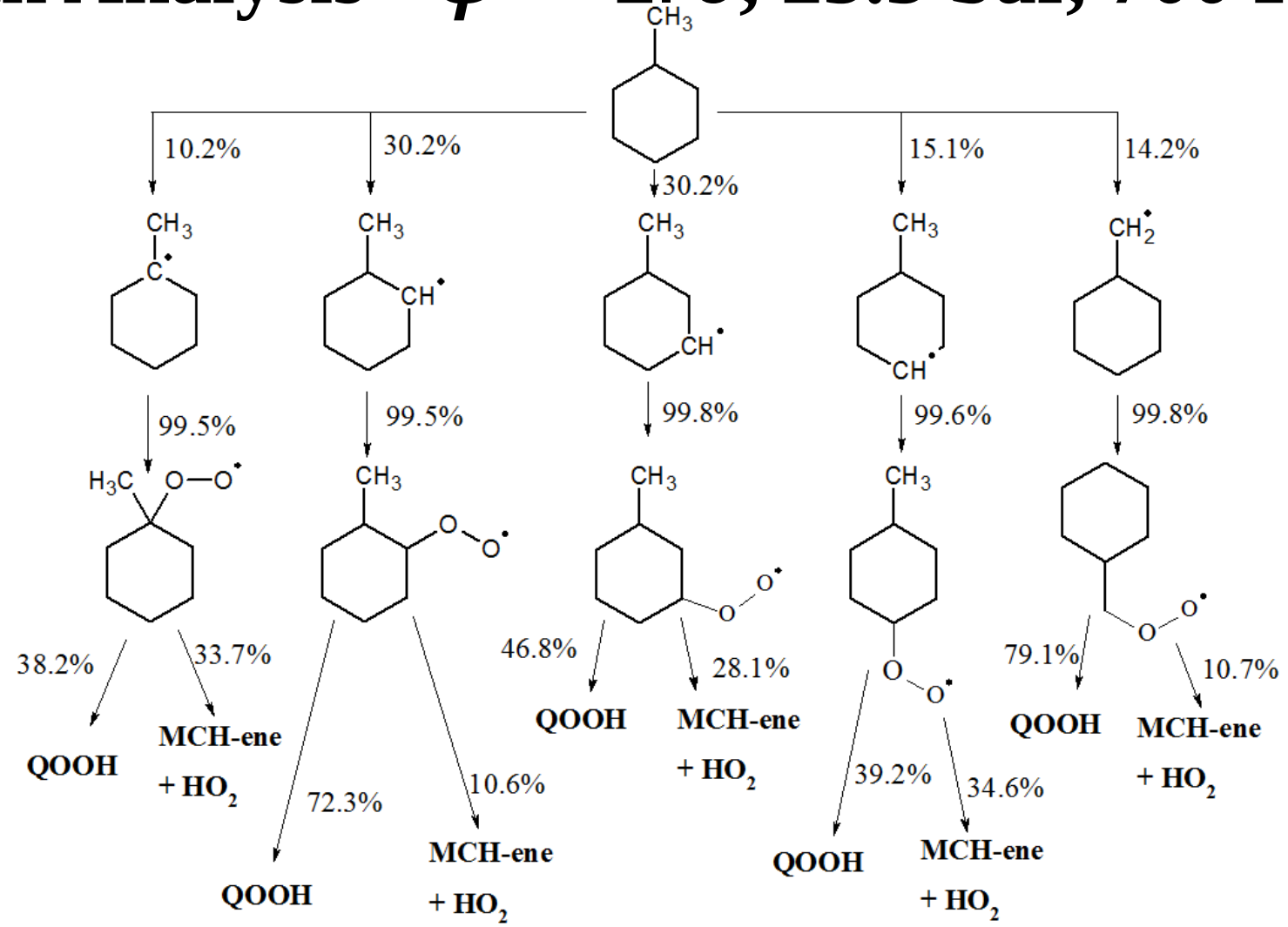
- First stage ignition delays are under-predicted for all equivalence ratios and pressures, but are within factor of 2 of the experimental data
- First stage ignition is also predicted for conditions where it was not found experimentally at 50 bar and all three equivalence ratios

Sensitivity Analysis

- Sensitivity analysis of the overall ignition delay shows that the important reactions are the initial H-abstractions from the fuel, the direct reaction of peroxyl radicals to form HO_2 and methylcyclohexene, and isomerizations of the peroxyl radicals
- Similar analysis for first stage ignition shows that the same reactions are important



Path Analysis - $\phi = 1.0$, 25.5 bar, 700 K



- Path analysis shows the model exhibits the expected decomposition pathways, including formation of methylcyclohexenes, QOOH and ROOH species

Conclusions

- New experimental data has been collected for MCH in a heated RCM at conditions of $P_C = 50$ bar, $\phi = 0.5, 1.0, 1.5$, and $T_C = 690 - 910$K
- The 2007 model for MCH combustion by Pitz et al. has been updated with improved rate rules and new reaction classes
- The new model is able to predict overall ignition delays to within a factor of 2 for most conditions
- First stage ignition delays are under-predicted for all conditions, but are nevertheless within a factor of 2 of the experiments
- First stage ignition is predicted for conditions at high pressure that do not have first stage ignition experimentally

Thank you!

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MCH CONV Simulations