Development of Kinetic Models for Biodiesel Combustion

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Combustion Energy Frontier Research Center

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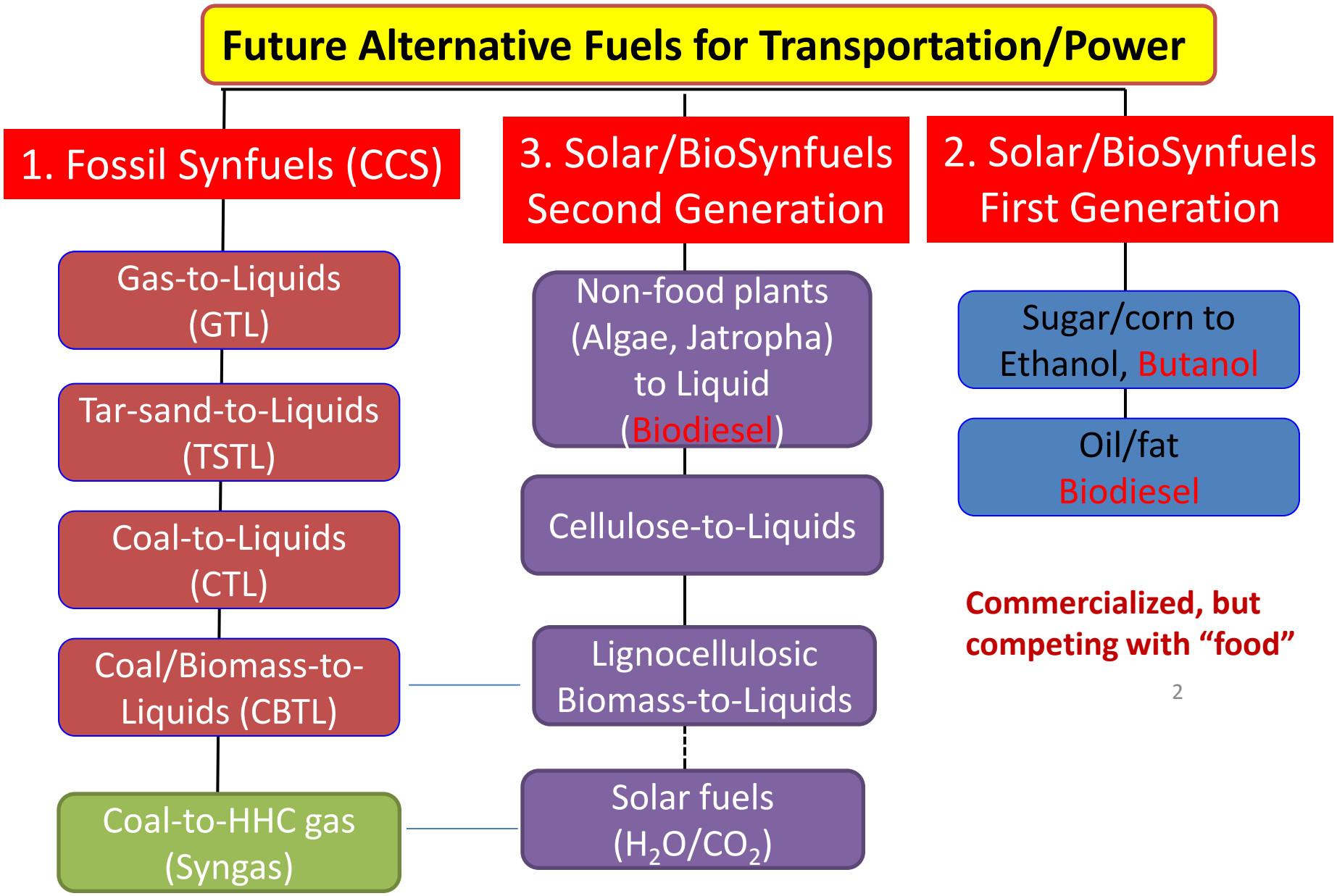
Future Alternative Fuels for Transportation/Power



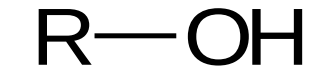
Commercialized, but competing with "food"

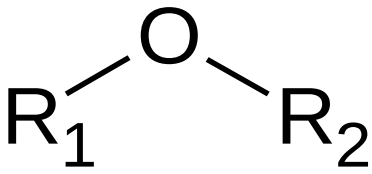
Engine design, efficiency, emissions?

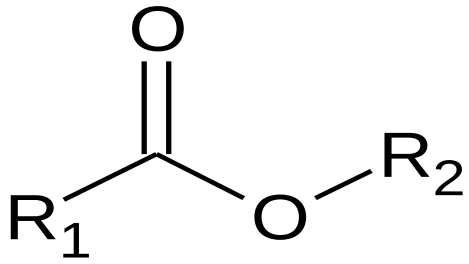
Impact of molecule structure on combustion and emissions

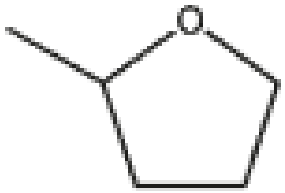
- **Alcohols (e.g. ethanol, butanol, …)**
- **Ethers (e.g. dimethyl ether)**
- **Biodiesels (: Esterse.g. butanoate)**
- **Furanic biofuels**
- **Aromatics**

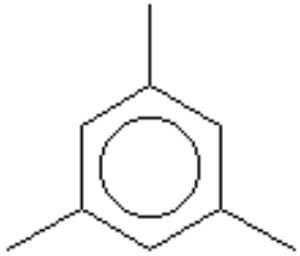
…











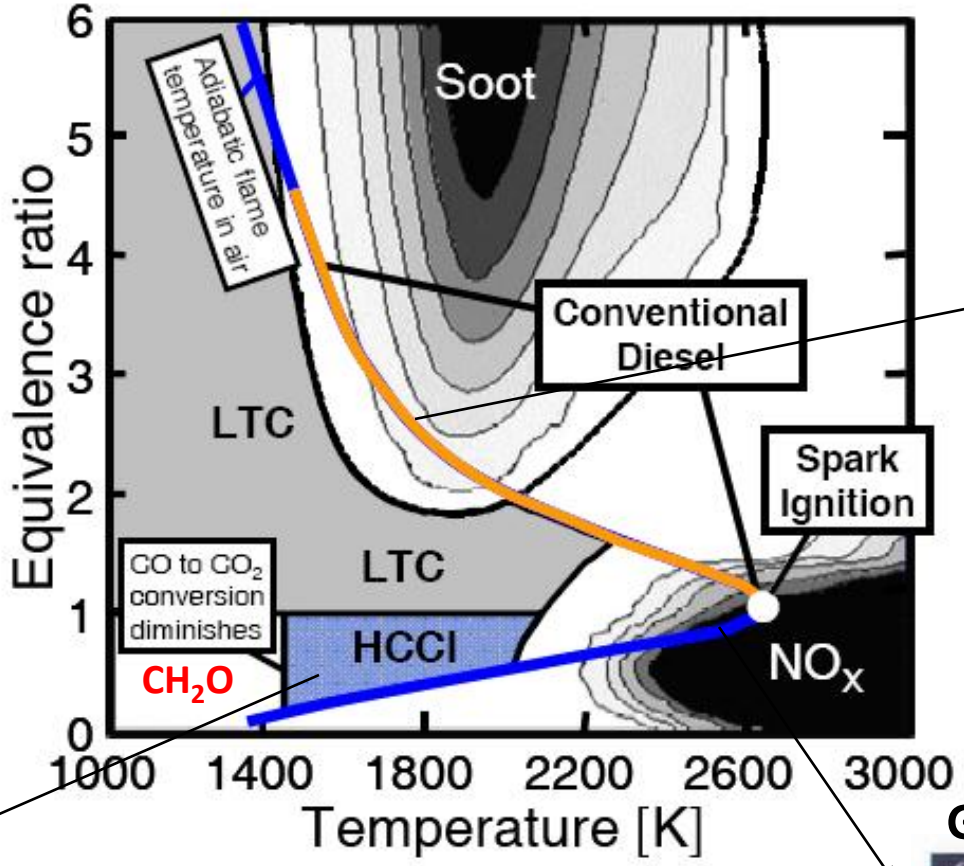
CH_2O emissions
CO emission
NOx emissions
…

Address the fuel design and energy efficiency as a whole?!

Increase of Thermochemical Energy Conversion Efficiency Future Transportation Engines (e.g. HCCI)

Challenges in combustion:

- **Low temperature**
- **High pressure**
- **High turbulence**
- **Biofuels**
- **Ignition control**
- **Emissions**

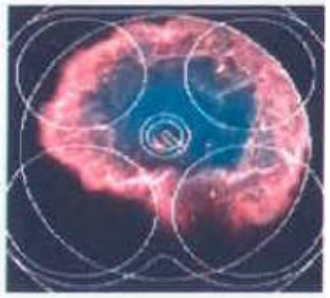


Diesel ICE

Efficiency: 38%

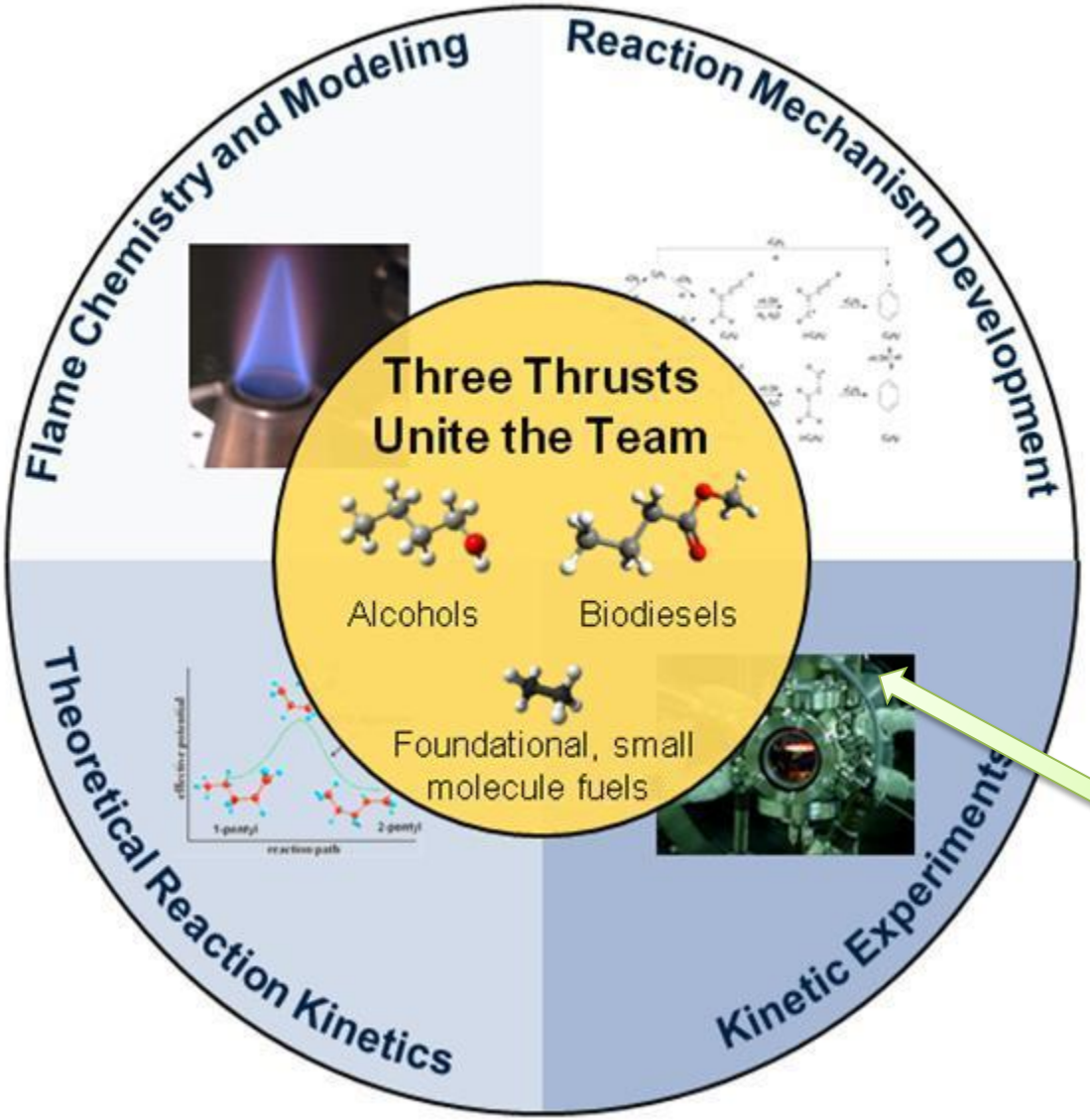
(Homogeneous Charged ICEs: HCCI)
Efficiency: 5X %

Gasoline ICE

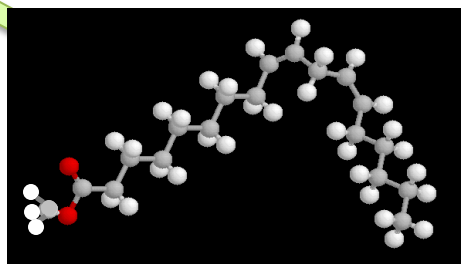


John E. Dec, 2008

Research Thrusts of Combustion EFRC for Quantitative Prediction of Biofuel Combustion



Biodiesel



Questions?

- How different are the size, reactivity, and bond dissociation energies of ester function groups in affecting burning properties and emissions of biodiesel?
- How to address the knowledge gaps in large biodiesel molecules?
- Can we use quantum computation and kinetic experiments to build a better, predictive model?

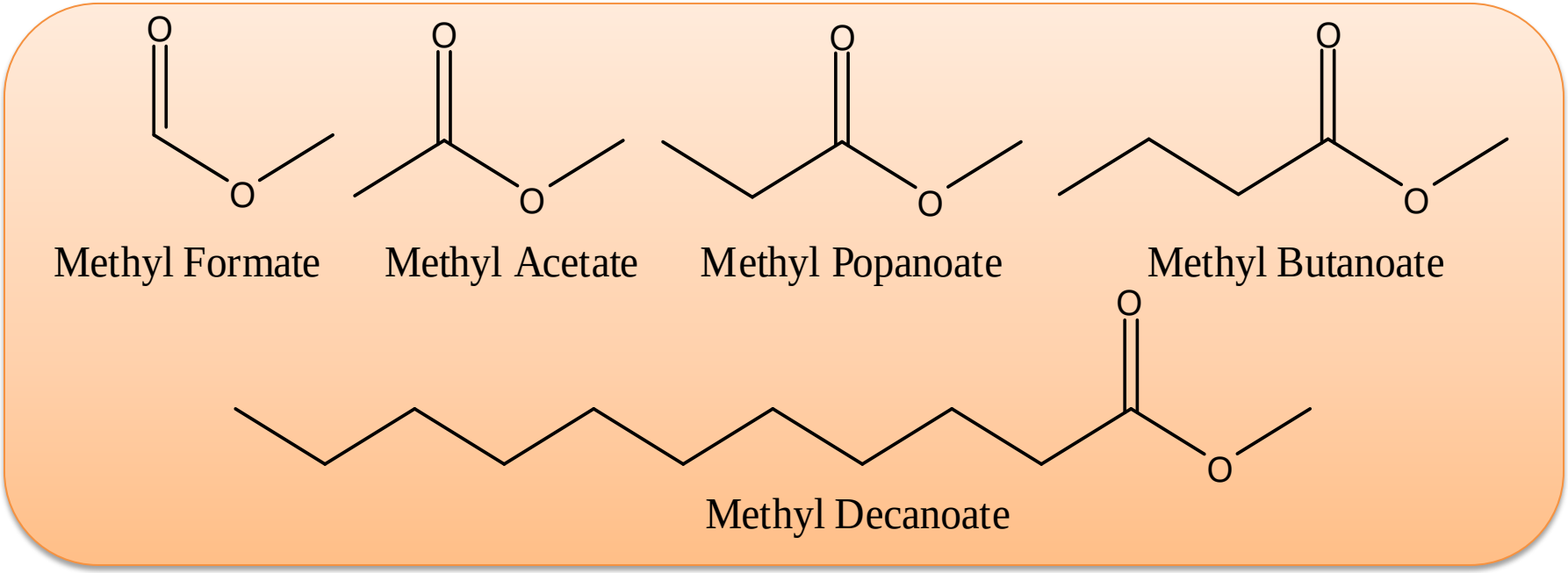
Research Objectives

- **Advance the understanding of combustion and emission kinetics of biodiesel combustion.**

- **Develop a validated, comprehensively reduced kinetic mechanism to model oxidation and pyrolysis of biodiesel at extreme combustion conditions.**

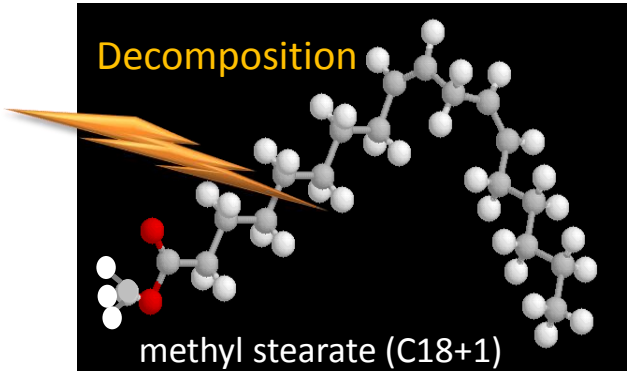
- **Challenge: Biodiesel fuel molecules are very large (C16-19), few models and experiments are available!**

Research Methodology: A Bottom Up Approach for Biodiesel



•Gaining knowledge from small esters

•Similarity between Small/Large Esters?



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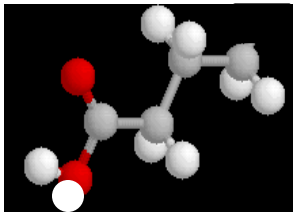
Methyl Butanoate (C1-4+1)



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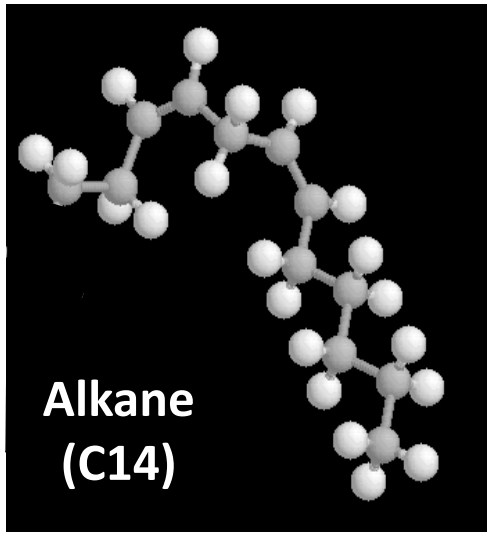
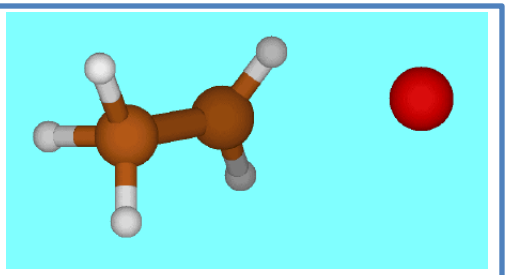


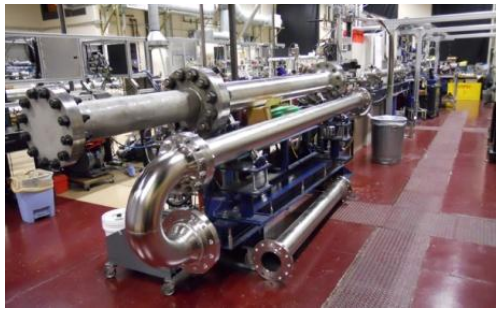
Roadmap for Biodiesel Mechanism Development

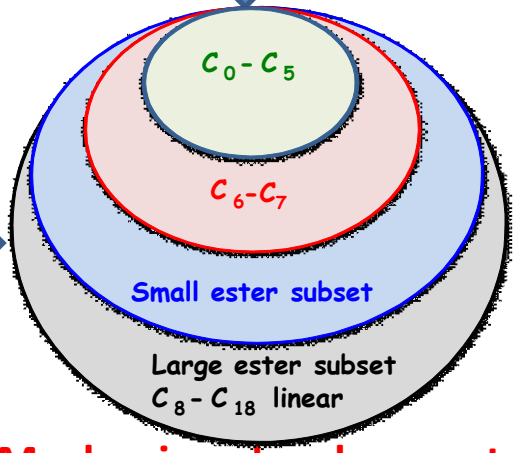
Quantum chemistry computation

- Bond dissociation energy
- Potential energy surface
- Reaction rates



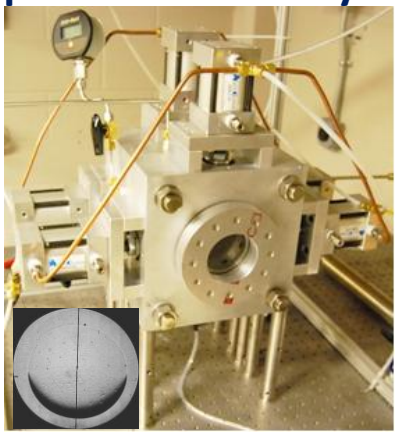
Elementary reaction rates

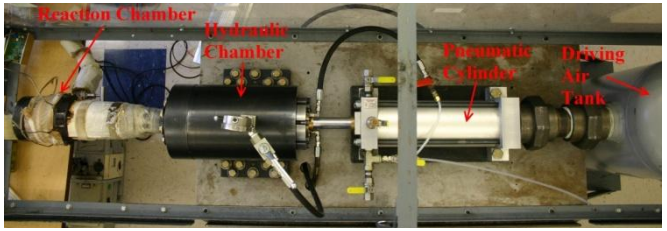




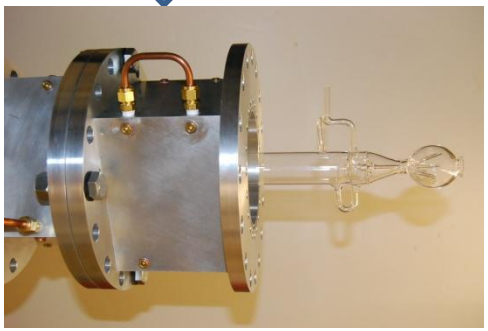
Mechanism development

High pressure flame dynamics

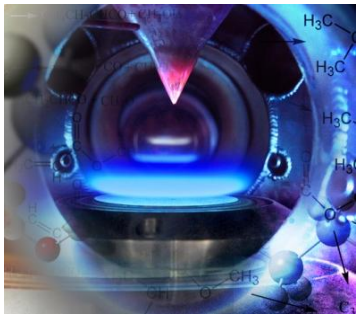




Rapid Compression Machine Ignition chemistry

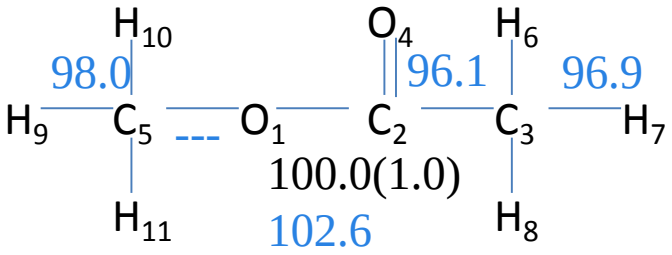


High pressure JSR: speciation



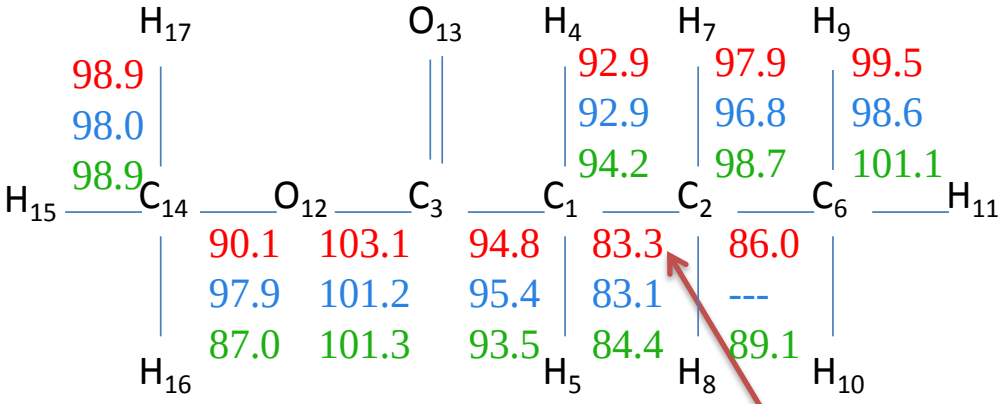
Advanced Light source

1. Bond dissociation energies and H abstraction reactions



Methyl Acetate

KEY: Experiment
MRSDCI//HF/cc-pVDZ
MRSDCI//B3LYP/6-311G(2d,p)
CBS-QB3 of El-Nahas et al.



Methyl Butanoate

Weakest bond

A. M. El-Nahas et al., J. Phys. Chem. A **111** (19), 3727 (2007).

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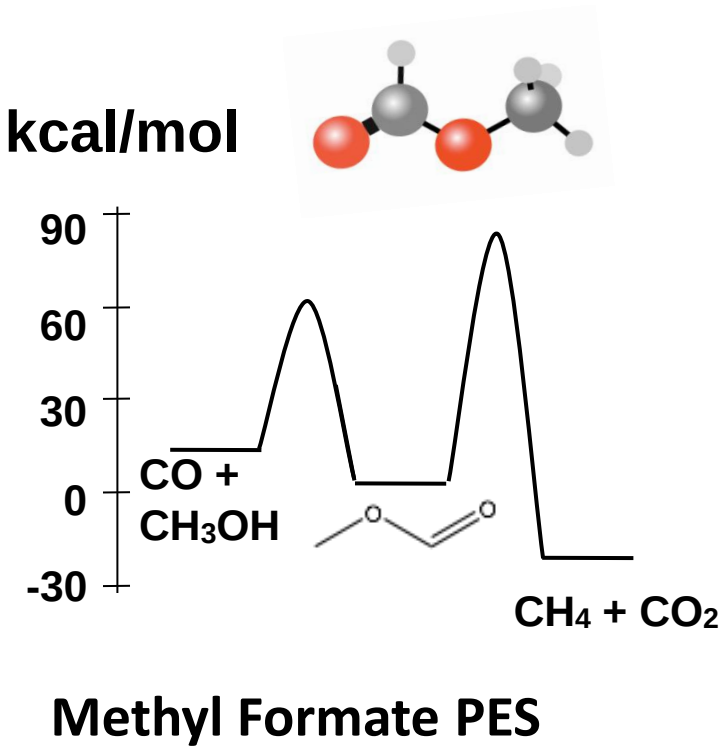
Carter et al.

Quantum calculations of PES & radical decomposition for methyl formate



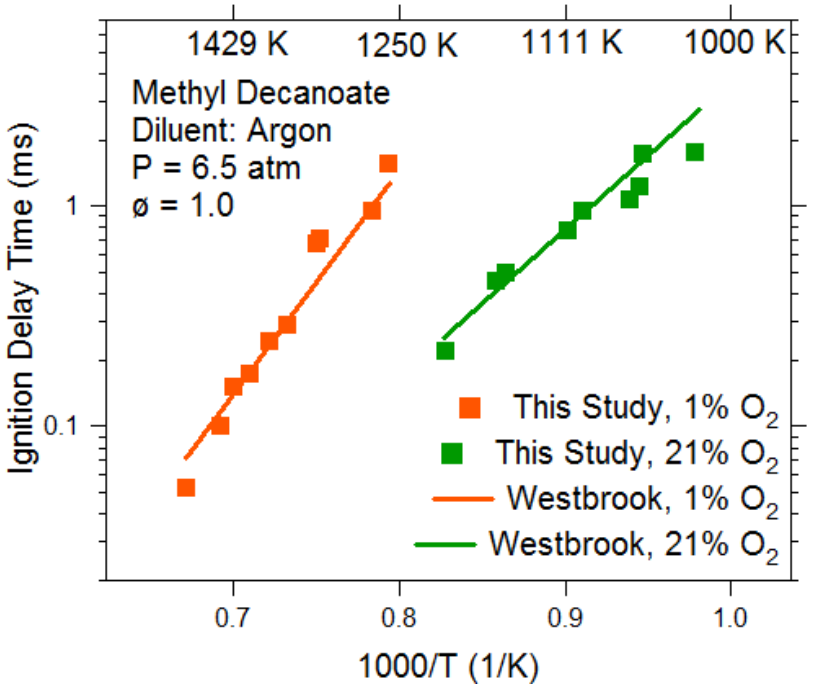
Methyl Formate PES

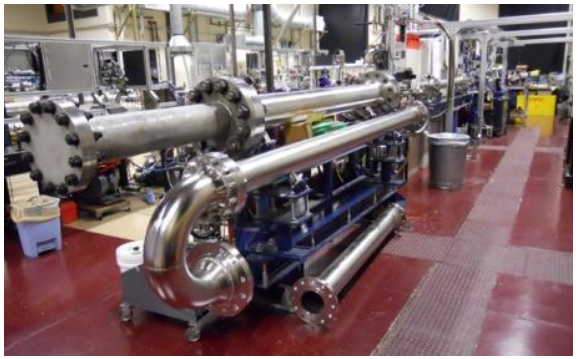
- RQCISD(T)/CBS//B3LYP/6-311++G(d,p) with hindered rotor scans calculated with B3LYP/6-31+G(d,p)

(MIT, Green et al. 2011)

2A. Shock Tube Ignition and Speciation Data: Ignition Delay Times of Large Methyl Esters

Methyl Decanoate





Campbell et al. (2011)

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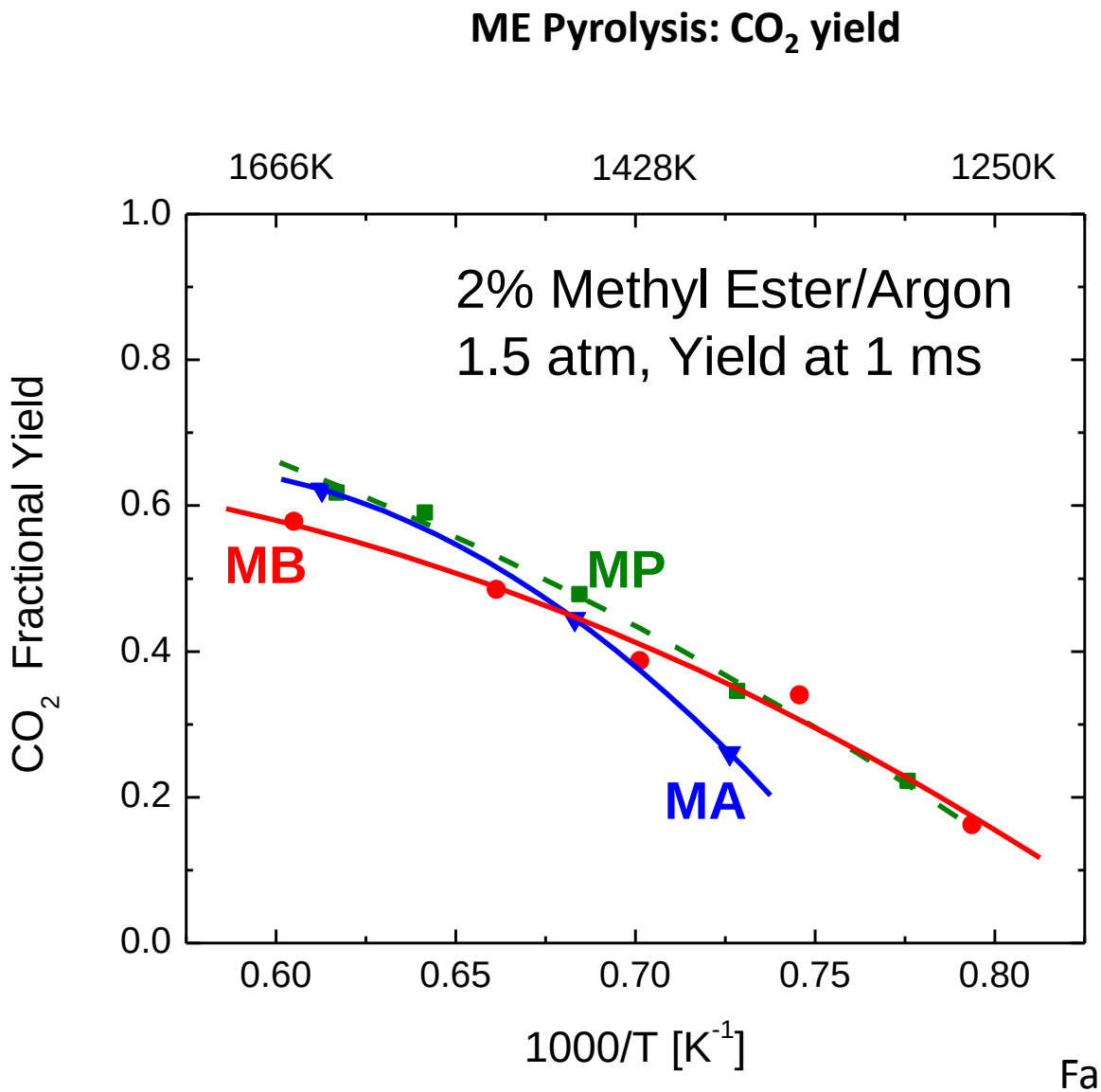
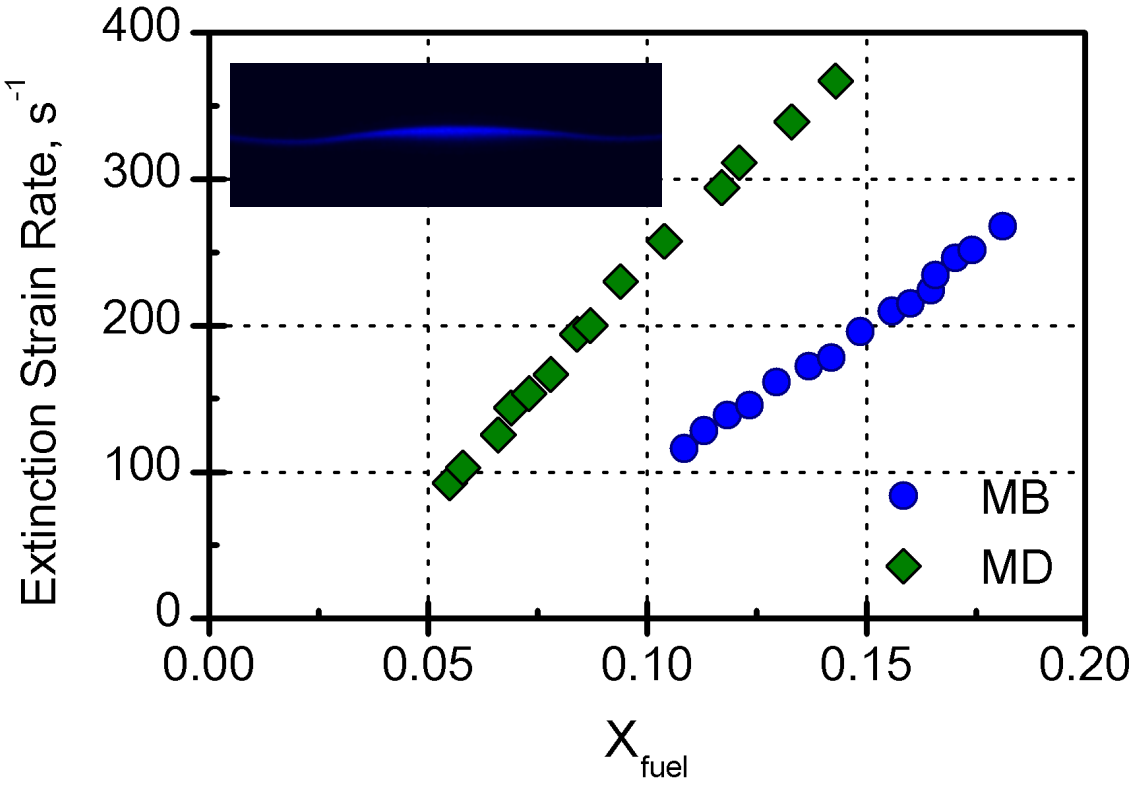
Species Time-Histories via Laser Absorption



Farooq et al. (2008)

3. Diffusion flame extinction limit: Methyl butanoate vs. methyl decanoate



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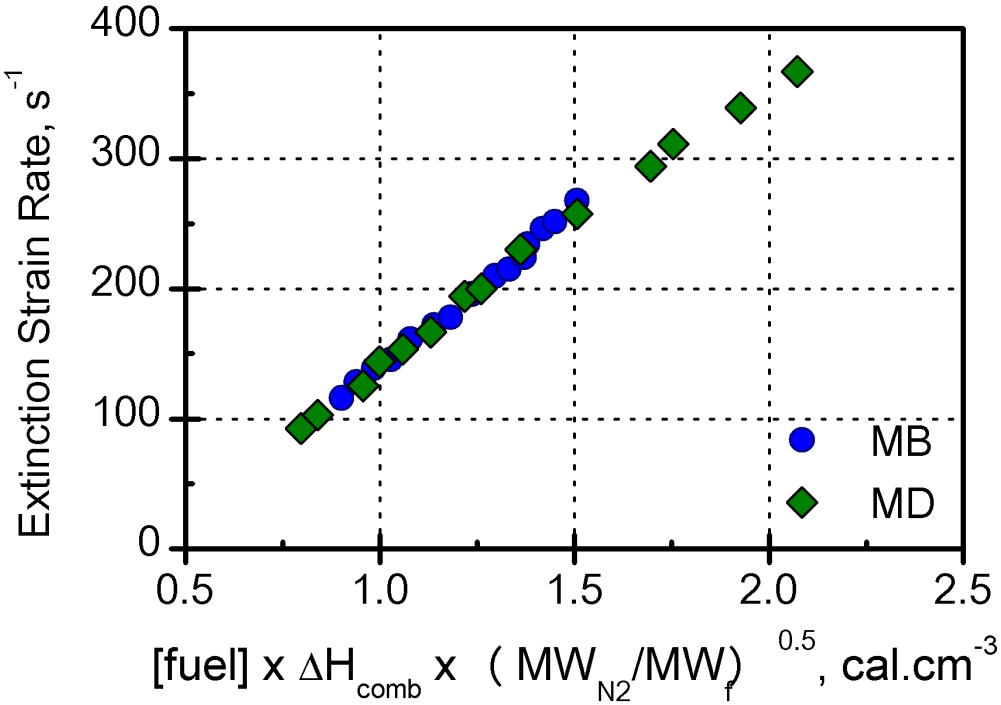
Ju et al.

	ΔH_{comb} (kcal/mol)	MW (g/mol)
MB	-651.6	102.14
MD	-1533.3	186.29

4. Reactivity scaling of small/large methyl esters: Methyl butanoate (C4) vs. methyl decanoate (C10)

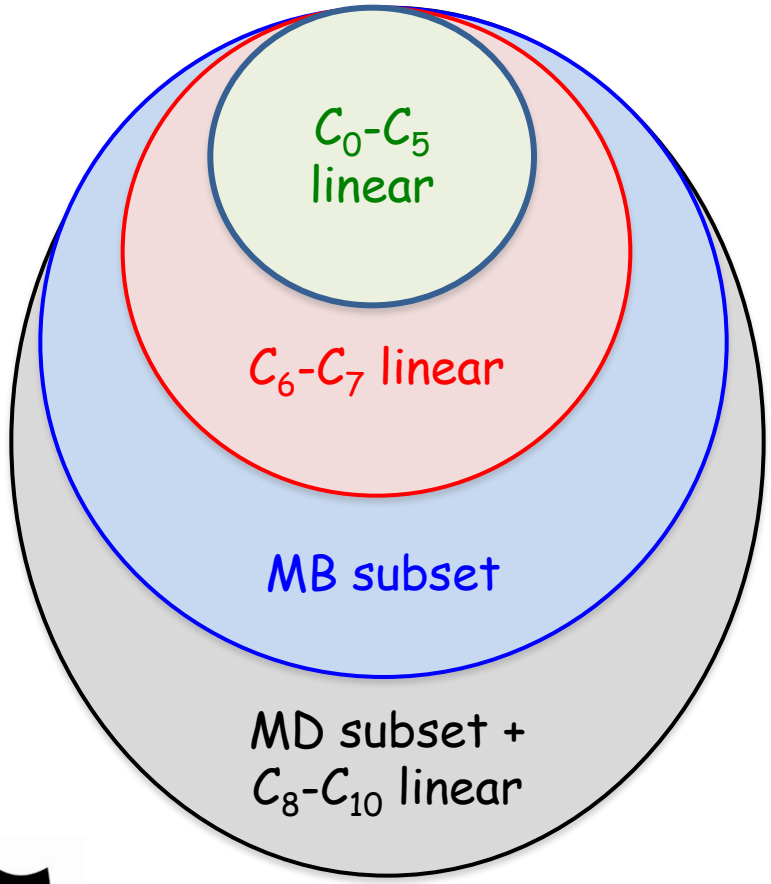


Extinction limit vs. Transport weighted enthalpy flux

Dievart et al. 2011

MB and MD have the same kinetics!

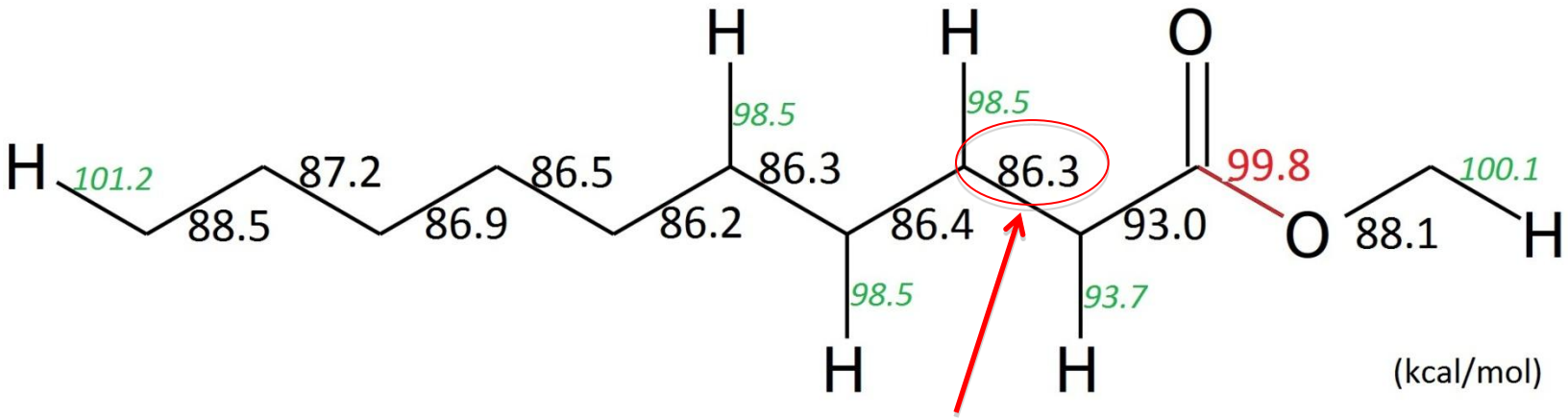
5. Mechanism development and validation (C4, C10 Methyl esters)



- MB: Ester functional group
  Dooley et al., 2008
- **MD subset**
  - **Thermo**: Benson's group additivity method with updated group contributions
  - **Kinetics**: direct analogy from MB for the methyl ester group atoms
- C0-C7: n-heptane model
  Curran et al., 2008, 2010

Detailed model was reduced with Chem-RC (PFA, path flux analysis)

Change of MD bond dissociation energies:

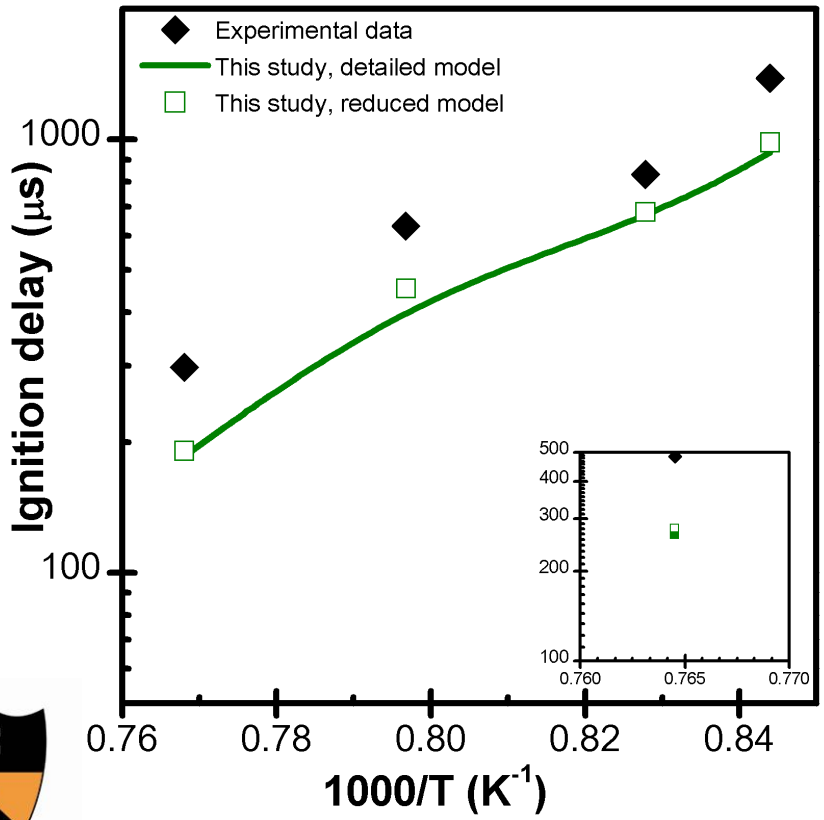


Carter et al.: 83.1-84.4, ± 3 kcal/mol

Seshadri et al. : 80.8 kcal/mol

MODEL VALIDATION (1)

The present model has been tested against ignition delays from Hanson's group (Aerosol Shock Tube, very lean mixtures, highly diluted in argon, ~7.5 atm)



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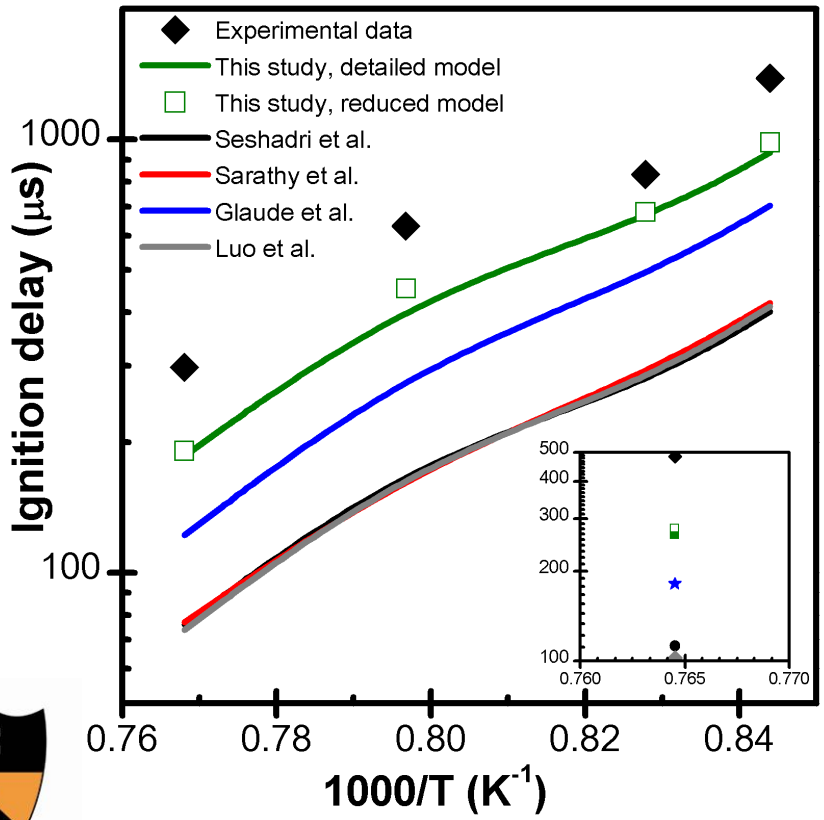


- ✓ Present model in good agreement (35%), whereas literature models strongly overestimate MD oxidation rate (50 to 80%)
- ✓ UFD Pressure Dependence can not entirely explained these discrepancies

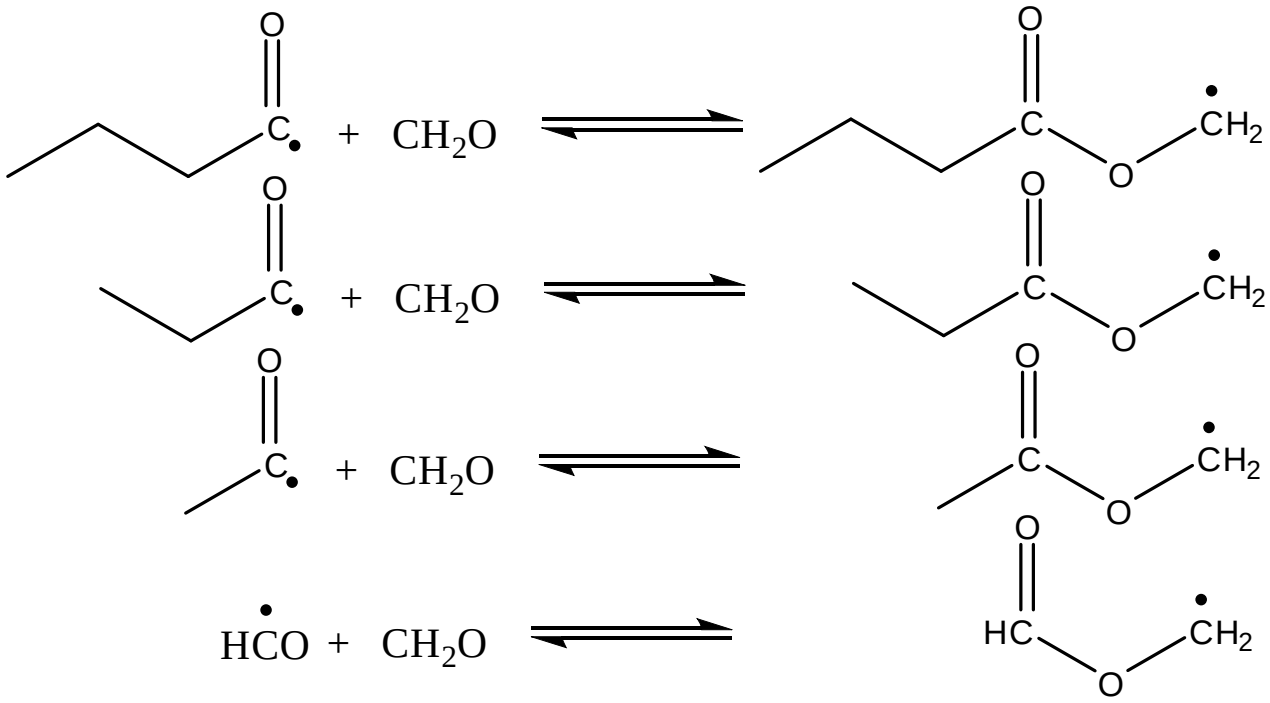
Conclusions

- Bond dissociation energy and H abstract reactions of methyl esters are computed by using MRSDCI.
- Ignition delay, flame speeds, and extinction limits of methy and ethyl esters are experimentally measured.
- Distinctive reactivity of small methyl esters, and similarity of large esters in extinction were demonstrated.
- Bond dissociation energy and branching ratio of methy esters play an important role in reactivity, ignition , flame propagation, and extinction.
- The current mechanism with better estimation of BDEs and branching ratio of ester functional group showed better prediction.

Thank you!

Future work

- Update thermochemistry data (BDEs)
- Provide bench mark rate constants to determine branching ratio
- Elementary rate constants and speciation measurements



Biodiesel (Methyl Esters) Research Plan

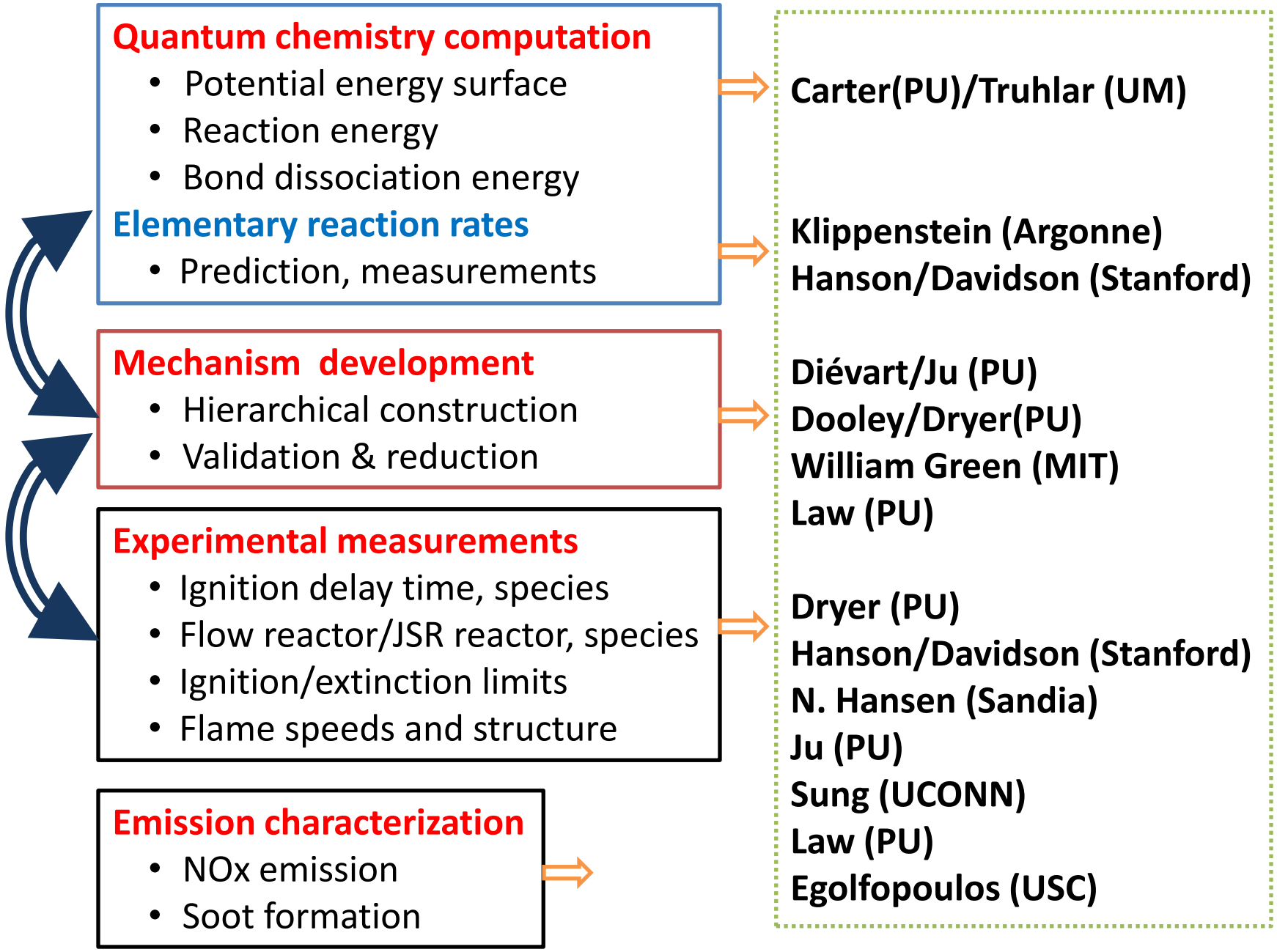
Deliverables :

- Obtain new experiment data of elementary reaction rates, ignition delay time, extinction limit, and speciation.
- Develop quantum computational methods for prediction of reaction rate, activation energy, and bond energy.
- Advance understanding of oxidation mechanism of molecules with methyl ester functional group
- Develop models to understand the impact of the ester functional group on kinetics, ignition, and flame propagation and extinction.
- Develop a validated kinetic mechanism for biodiesel.

Current gaps in knowledge of biodiesel combustion

- **Biodiesel contains many different kinds of large (C_{16}-C_{20}) saturated and unsaturated methyl esters, which are too difficult to be studied in computation and experiments.**
- **Models of MD and MB over-predict ignition and extinction limits.**
- **For high temperature flames, MB and MD have similar oxidation chemistry.**
- **Current kinetic models fail to predict CH_2O formation from ester functional group correctly.**
- **Rate constants of β-scission and isomerization of methyl ester radicals have large uncertainties.**
- **Rigorous thermochemistry and transport data are not available.**
- **Experimental data of ignition, flames, and speciation are rare.**
- **……**

Biodiesel research tasks and team structure



Emily Carter (Quantum chemistry computation)

1. Method developments and validation

Development of an effective quantum chemical method that approaches the "chemical accuracy" by a proper treatment of electronic correlation (both static and dynamic correlation), and at the same time retains feasibility for application to large molecules.

a. Set up of a model chemistry approach based on MRCI / L-MRCI / L-MRACPF.
b. Validation on small molecules (C1-C5) against available experimental data.

2. Applications to biodiesel surrogate molecules

Calculations of **bond dissociation energies** (BDEs), **barrier heights** (activation energies) and **reaction energies** for

Reactions:

- ***hydrogen abstraction by radical species, ·H, ·OH, and ·OOH.***
- ***Isomerization reactions of RO2 (intramolecular hydrogen abstraction).***
- ***beta scission reactions of methyl esters.***

Species:

- ***model systems (oxygenated species), methyl formate, and methyl acetate (< C4)***
- ***Biodiesel surrogate for high temperature, methyl butanoate, $CH_3CH_2CH_2COOCH_3$ (MB)***
- ***Biodiesel surrogate for low temperature, methyl decanoate, $CH_3(CH_2)_8COOCH_3$ (MD)***
- ***BDEs in methyl esters with increasing alkyl tail length, from methyl formate to methyl stearate (C2-C18)***
- ***unsaturated molecules, starting from methyl crotonate, $CH_3CHCHCOOCH_3$***

Stephen Klippenstein
(Elementary rate computation)

- Key reaction rates of small methyl-esters,
- Highly activated reaction rates at high pressure

Nils Hansen

(Intermediate species measurements in flames)

- Flame speciation: Syncrotron/molecular beam sampling
- Laser diagnostics:

Hanson/Davidson

(Elementary reaction rates, ignition delay time, and speciation)

1) Ignition delay times, Aerosol Shock Tube methodology

Targeted fuel molecules (methyl palmitate, methyl stearate, methyl oleate, methyl linoleate, methyl linolenate, methyl decanoat,e and small ester molecules from methyl formate)

2) Species concentration time-histories

Species time-histories during oxidation and pyrolysis of these methyl esters. (target species: OH, C_2H_4, CO_2 and H_2O, and hopefully CO and CH_2O,)

3) Direct determination of rate constants for targeted elementary reactions

Decomposition reaction rates and X +OH elementary reaction rate constants

Jackie Sung

(Autoignition dealy time, Speciation, and Sooting Tendency)

- Autoignition delay time (RCM)
- Speciation
- Sooting Tendency measurements

Fokion Egolfopoulos

(Ignition, flames, and emissions)

1. Focus: C1-C10 methyl and ethyl esters fuels at various degrees of fuel branching and saturation. C1-C4 and C10 methyl and ethyl esters.
2. Experimental and modeling work on flame ignition, propagation, and extinction,
3. NOx profiles and soot volume fractions.

Chung K. Law

(flame speeds, ignition temperature, soot)

- Measurements of high-pressure flame speeds and ignition temperature
- droplet combustion, soot mitigation
- Mechanism reduction for blended fuels

Stephen Dooley/Fred Dryer

(Flow reactor speciation and mechanism development)

- High pressure flow reactor experiments for fuel oxidation and speciation
- Mechanism development and validation

Pascal Dievart/Yiguang Ju

(Fuel pyrolysis and oxidation, extinction, mechanism development)

- Low temperatures fuel pyrolysis and oxidation: intermediate species measurements in JSR.
- Measurements of flame speeds, speciation, and extinction limits
- Low temperature flame chemistry modeling.
- Mechanism development and validation

William Green

Automatic mechanism generation for large methyl ester molecules

Milestone of Biodiesel mechanism development

Mechanism will be updated once a year before the annual review meeting and posted at EFRC webpage

Year 1: High temperature MD/MB-MF mechanism
Year 2: Low temperature MD/MB-MF mechanism
Year 3: Updated MD/MB-MF mechanism and a surrogate model for biodiesel modeling

Year 1 Targets: Elementary reaction kinetics

Emily
Don

H abstraction reactions and thermal chemistry:

MY(Y=B,D…)+ X(HO2, CH3, OH, H…)= Radicals — **Theory**

Ron

Shock tube elementary rate measurements — **Exp.**

Emily
Stephen

Radical Decomposition and isomerization reactions

Methyl ester radical_A= Methyl ester radicals_B

Methyl ester radical = Radical_1 +Radical_2

Methyl ester = Radical_1 +Radical_2 — **Theory**

Nils
Yiguang
Fred

ALS MBMS radical measurements in flames

MBMS pyrolysis measurement in JSR

GCMS flow reactor — **Exp.**

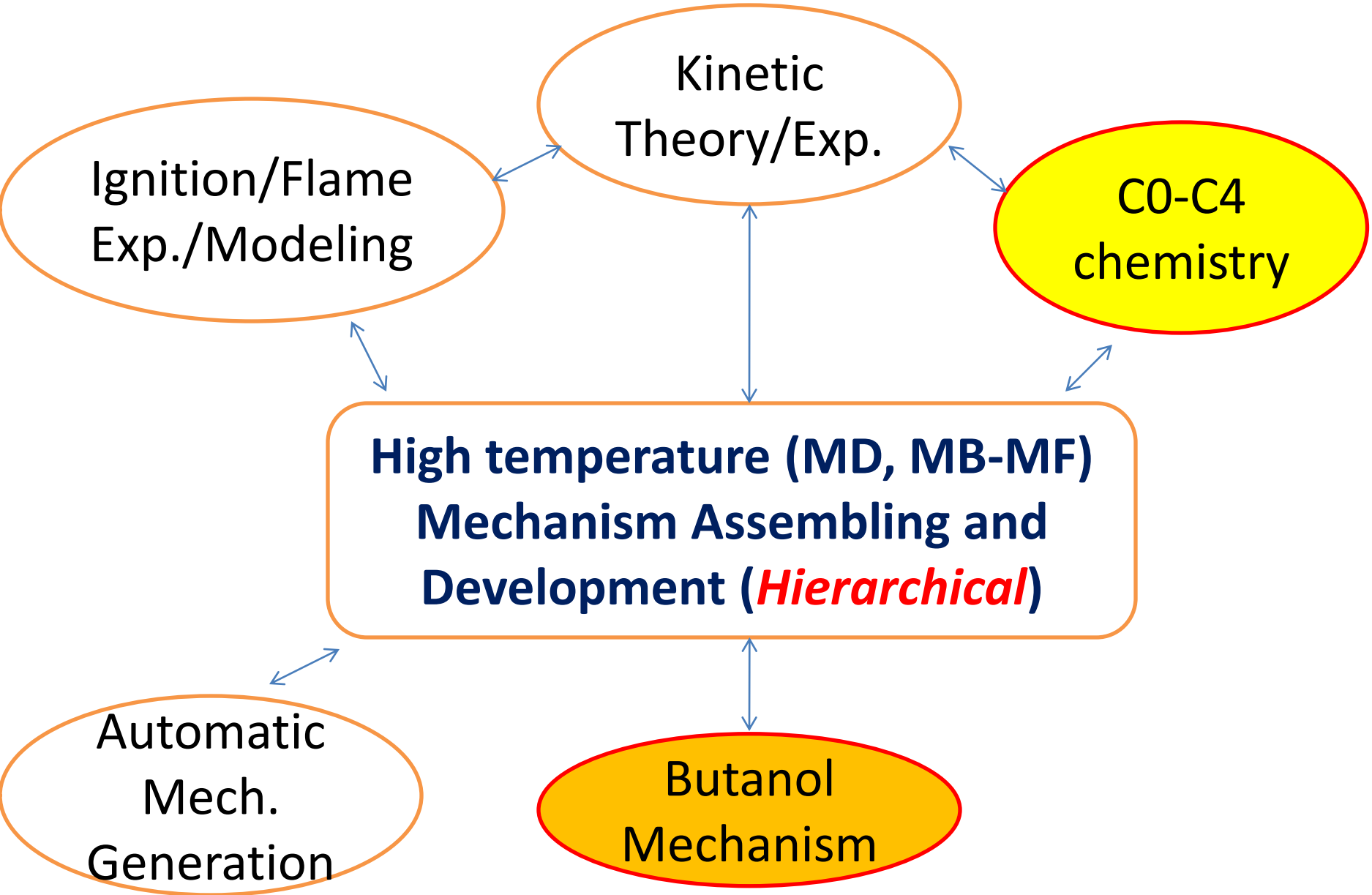
Year 1 Targets: Ignition, flame, and emissions

Ron Jackie Fokion/Ed	**Ignition/speciation** MY(Y=B,D…), 700-1300 K Shock tube RCM Counterflow	Exp. Modeling Sens.

Yiguang Ed Fokion Hai	**Flame (Speed, extinction, and structure (1200-2500 K)** Diffusion flame structure (CO, CO2, CH2O, aldehydes…) Flame speeds/extinction Low temperature flames (Temp. Effect) Transport properties	Exp. Modeling Sens.

Jackie/ Ed/Fokion	**NOx/Soot** Diffusion flames	Exp. Modeling

Year 1 Targets: Methyl-ester mechanism development



Contact information of Biodiesel mechanism development

Contact information:

Pascal Di**é**vart (MD):
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Stephen Dooley (MB and below):
E-mail: dooleys@Princeton.EDU

Year 1 Targets: Elementary kinetics

- **Thermochemistry** : methyl ester species (MF, MB, MP2D, MB3D and their radicals)
  - Derived accurate group contributions (Benson's additivity method) for ester group and surrounding carbon atoms

- **H atom abstraction reactions**: 1st step of the oxidation process at low and intermediate temperature

  - *Emily Carter and Donald Truhlar*

    MB + X = MBiJ + HX i = M, 2, 3,4 and X = OH, H, HO2, O, CH3

    Branching ratio for the formation of the first radicals

    Then extension to MD (or whatever larger methyl ester) to confirm that H abstraction in position M and 2 are independent of the ester size

  - *Ronald Hanson*

    Measure experimentally rate constants for reaction of MF, MB (and MP2D ?) with OH

    Comparison with and validation of the computed rate constants

Year 1 Targets: Elementary kinetics

- **Reaction pathways of methyl ester radicals**:
  Branching ratio between Isomerization and beta-scission reactions
  Needed to predict correctly the formation of formaldehyde CH2O

- *Isomerization*: cyclic transition state involving the ester group
  MBMJ = MB2J
  MBMJ = MB3J
  MBMJ = MB4J
  MB2J = MB4J
  MB2J = MB3J
- β-*scission reactions* : main target is reverse rate constant (recombination of a radical and a unsaturated species)
  CH2O + HCO = CH2OCHO
  CH2O + CH3CO = CH3COOCH2
  CH2O + C3H7CO = MBMJ
  CH3OCO + C3H6 = MB3J
  C2H4 + ME2J = MB4J (Comparison with same rate constants for n-alkanes)
  MP2D + CH3 = MB2J

- **Unimolecular Fuel Decomposition (MB, MD)**:
- Pressure and temperature dependence for MB and MD
- Tools to easily extrapolate to higher methyl esters

Year 1 Targets: Experiments (High T)

- **Shock Tube**:
  - Pyrolysis and oxidation of MB, MF: time profile of CO, CH2O, CO2, C2H4
  - Ignition delays of small methyl esters: MB, MF (low and high pressure, different fuel loading,…)

- **RCM:**
  - Ignition delays of MB
  - Species profiles (radicals ?)

- **Flame:**
  - Speciation of diffusion and premixed flames (MB, MF,…)
  - Extinction limits of MB, MF, MD,…
  - Flame speeds (MB, MF,…) at different pressures

- **Flow reactors:**
  - Pyrolysis and oxidation of MB, MF, MD
  - Rate constant determination

CH_2O should systematically be detected and quantified !

Year 1 Targets: Experiments (High T)

- **Transport properties**:
  - Determination of binary diffusion coefficients of important methyl esters
  - Derivation of Lennard-Jones coefficients

- **Database compilation**

Year 1 Targets: Modeling

- **Release of the intial model** (benchmark, v. 0.1)
  - Determination of binary diffusion coefficients of important methyl esters
  - Derivation of Lennard-Jones coefficients

- **Model refinement**
  - Use of the last release of the C0-C4 subset
  - Sensitivity analysis (=> identify/ modify the targets for years 2 and 3)
  - Deliver version 0.2 of the model (CEFRC webpage)

	Year 1			Year 2				Year 3			
	2011			2012				2013			
	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1
Model initial release (v 0.1)	X	X										
Thermo data (MB, MF,… and group contribution)	X	X										
H atom abstraction rate constants (MB, MF,…)	X	X	X	X								
Methyl esters radicals decomposition and isomerization	X	X	X	X								
Unimolecular fuel decomposition (MB, MD)	X	X	X	X								
Shock Tube time profiles (MB, MF)	X	X	X									
Shock Tube rate constants (RH+OH)	X	X	X	X								
Shock Tube and RCM ignition delays (MB, MD, …)	X	X	X	X								
Flame speeds	X	X	X									
Flame (diffusion, premixed, laminar) and flow reactors speciation	X	X	X	X								
Extinction limits												
Transport properties	X	X	X									
Model refinement (v0.2)			X	X	X							

Year 2 Targets: Elementary kinetics (Low T)

- **Thermochemistry** : RO2, QOOH, cyclic ethers (MB and MD)
  - Derive accurate group contributions (Benson's group additivity method)

- **Low Temperature oxidation pathways**:

  - *O2 addition*
  - *RO2 isomerization*
  - *RO2 and HO2 concerted elimination*
  - *QOOH reactions: branching ratio between cyclic ether formation, second O2 addition, decomposition and HO2 elimination*

Year 2 Targets: Experiments (Low T)

- **Shock Tube**:
  - Ignition delays MB, MF (low and high pressure, different fuel loading,…)

- **RCM:**
  - Ignition delays of MD
  - Species profiles (radicals ?)

- **Flames:**
  - Low Temperature flame (?)

- **Flow reactors:**
  - Low-temperature oxidation of MD and MB
  - Detection of specific low-temperature species (conjugated olefins, cyclic ethers, …)

Year 2 Targets: Modeling

- **Release of the second version of MB and MD model** (v. 0.2)

- **Model reduction**
  - Diffusion flame validation
  - DNS or LES simulations

- **Refinement of the model**
  - Low-temperature update
  - Sensitivity analysis to identify the gaps in the models and the rate constant that need to be revised (High-temperature)

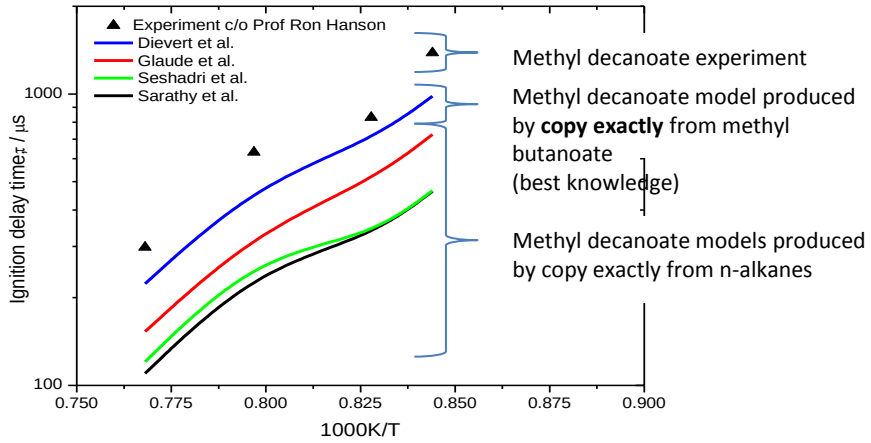
	Year 1			Year 2				Year 3			
	2011			2012				2013			
	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1
Thermo data (RO2, QOOH, cyclic ehers and group contribution)					X	X						
Low-T reaction rate constants (O2 addition, RO2 isomerization, HO_2 concerted elimination,…) (MB, MD)					X	X	X	X	X			
Shock Tube and RCM ignition delays (MB, MD, …)					X	X	X					
Flow reactor data (Low temperature)					X	X	X					
Combustion (experimental data and rate constant) database (CEFRC access)												
Model refinement (v0.3)							X	X				

Basic Energy Research on Methyl Esters, Stephen Dooley/Princeton University

Summary of philosophy and progress to date

•Systematic experimental/kinetic modeling study of small methyl esters to yield iterative rate constant data on biodiesel oxidation processes, presently best knowledge is of methyl butanoate.

•Accurate chemical models can be built by extendibility of kinetic terms generated and tested for small molecules, no need for detailed study of largest methyl esters, Dievert et al.



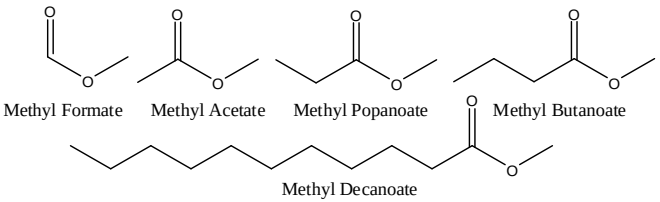
Dievert et al. AIAA 2011 Ignition delay of methyl decanoate/oxygen/argon at ~8 atm (c/o Prof. Ron Hanson).

•better performance of existing methyl ester models is limited by information on elementary processes of methyl ester radical decomposition vs isomerisation and of methyl ester pyrolysis.

•Strategy

=> Develop and test methods for estimation of kinetic modeling parameters at small ester level, extend to larger esters.

=> Little value in study of molecules larger than methyl decanoate.



Limiting knowledge gaps and suggested work plan

•Compute rate *k*s which dictate **important branching ratios,** do so in a manner which allows for the accurate estimation of other similar processes of the oxygenate hydrocarbon sub model.

•Focus initially on high temperature oxidation as system is simpler and validation data is much more available.

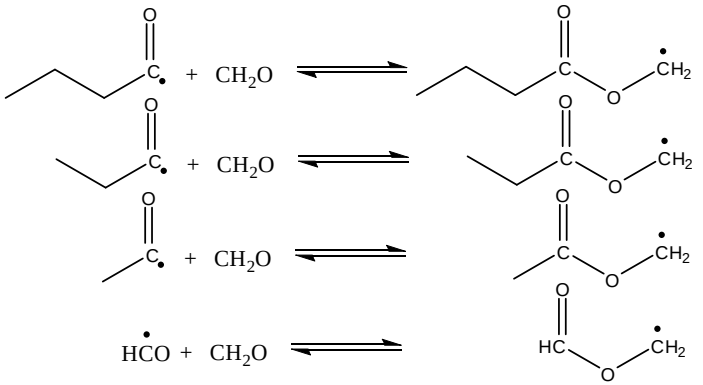
2 Exemplar suggestions (there are more)

1) Methyl ester radical beta scission vs isomerization

•Compute rate *k*s for addition of carbonyl centered radicals to O atom of formaldehyde (utility for addition to C atom?)

• Provide bench mark rate *k*s for reverse (decomposition) reactions, this is important to test rate *k*s produced by detailed balancing through thermochemistry as is frequently used by modelers.

e.g.



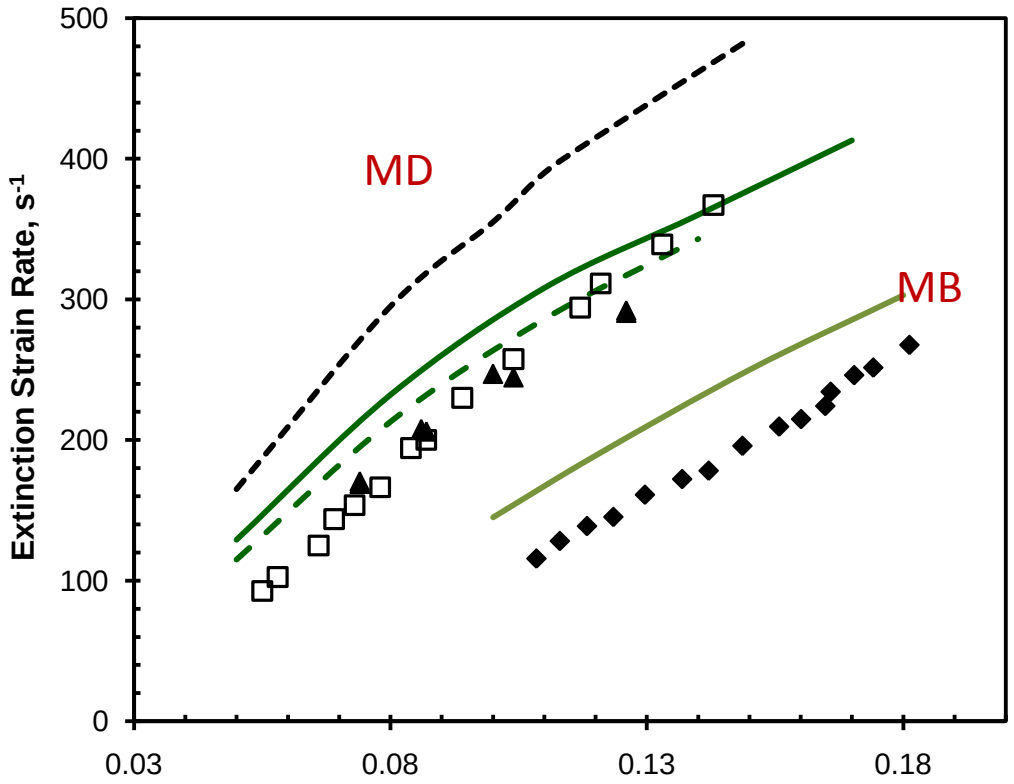
2) Methyl ester pyrolysis kinetics

•Better knowledge of unimolecular ester decomposition kinetics, is important for model fidelity in (diffusion) flames and high temperature ignition.

•Pyrolysis kinetics of methyl esters are not known. Can we measure CO, CO_2, CH_2O and C_2H_4 for pyrolysis of methyl butanoate? Can anyone compute rate ks of unimolecular fission processes?

•Test generated rate *ks* by experiment through kinetic modeling of small methyl esters, (beware unimolecular elimination!)

EXTINCTION LIMITS



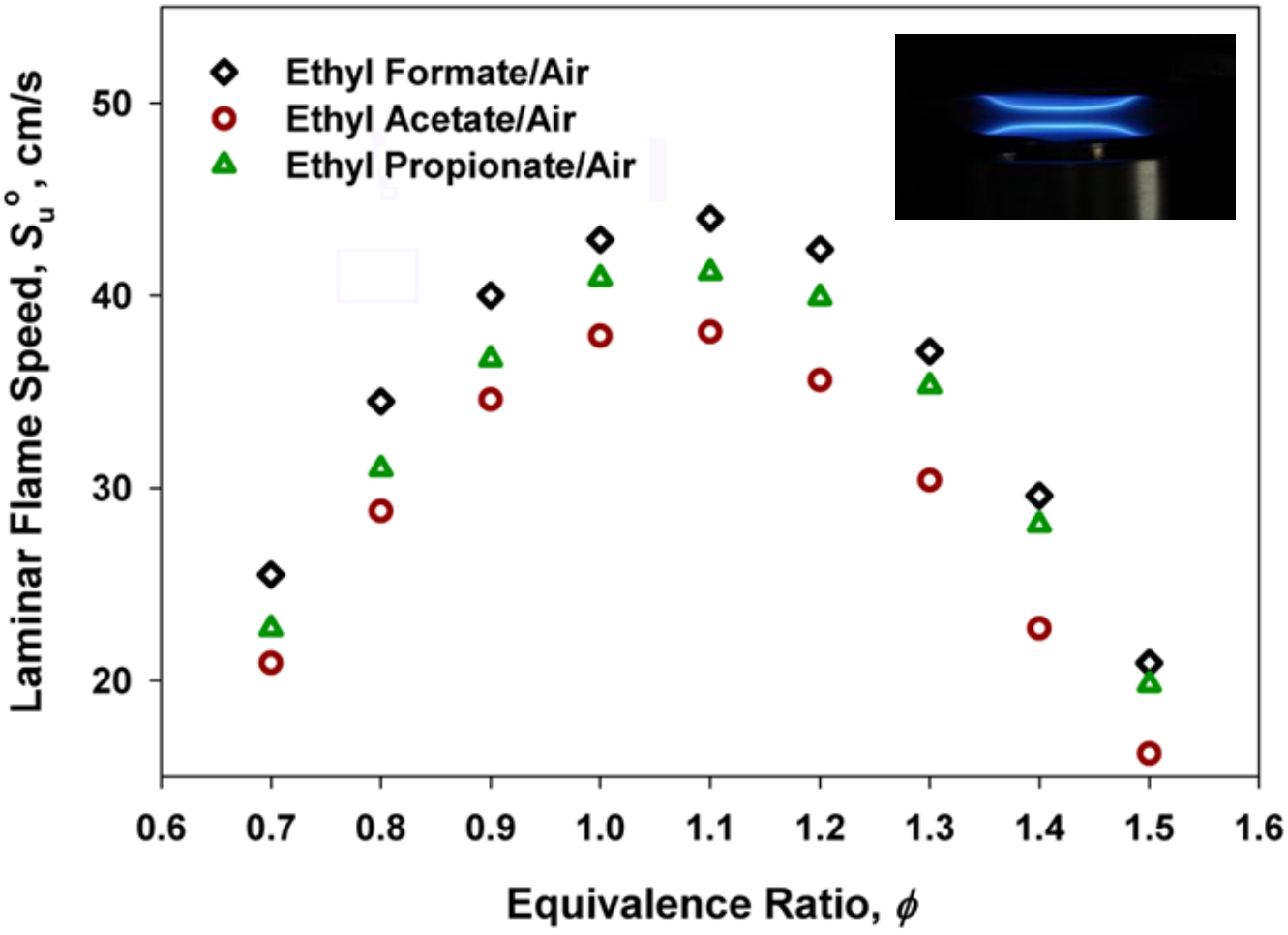
Model over-predicts extinction limit

Dievert et al. AIAA 2011.

◆ MB data, 500 K, Uddi et al.
□ MD data, 500 K
Δ MD data, 468 K, Seshadri et al.

MB computations, 500 K (present MD model)
MD computations, 500 K (present MD model)
MD computations, 468 K (present MD model)
MD computations, 500K, Seshadri et al.

3. Premixed flame speeds of ethyl-esters/air (C1-C4: 1 atm)



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Egolfopoulos et al.

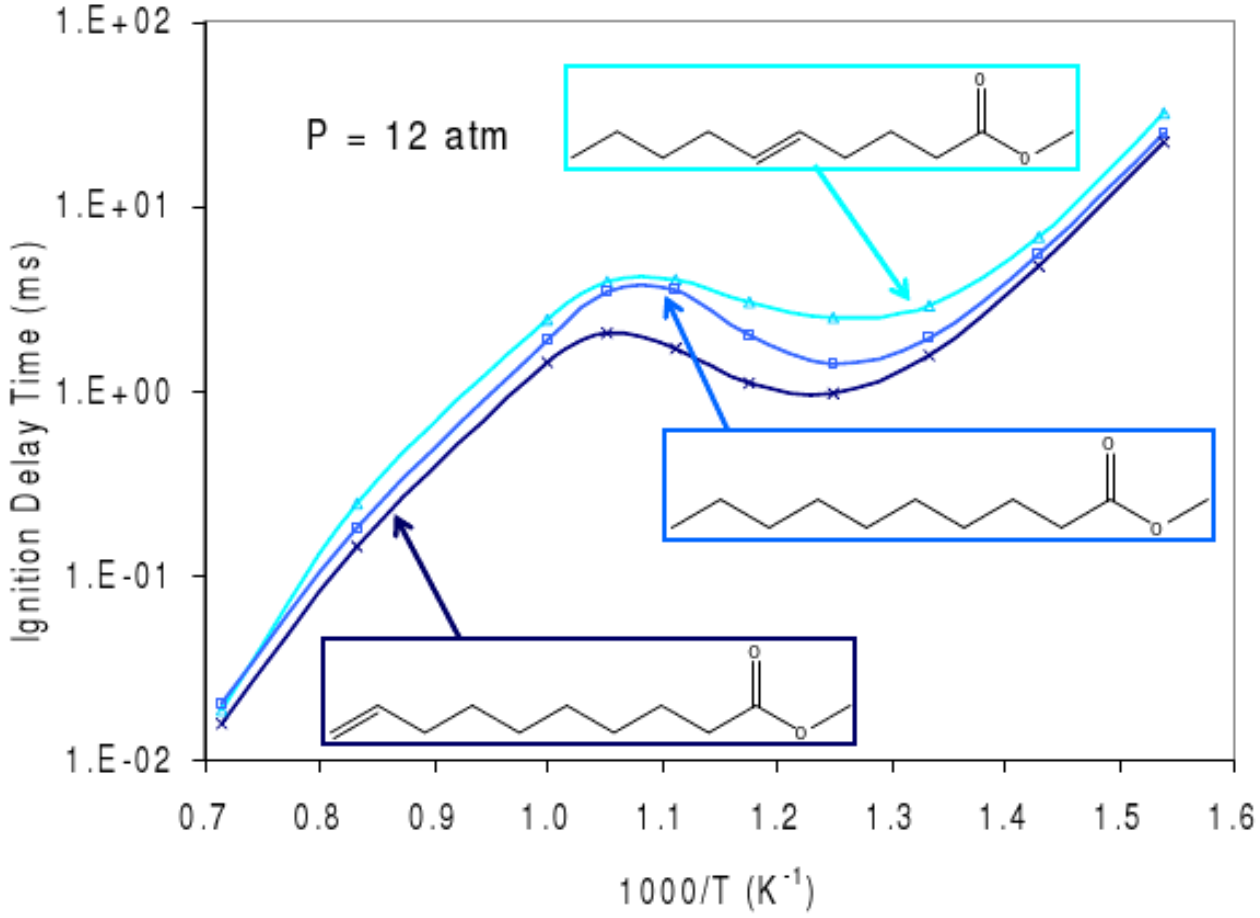
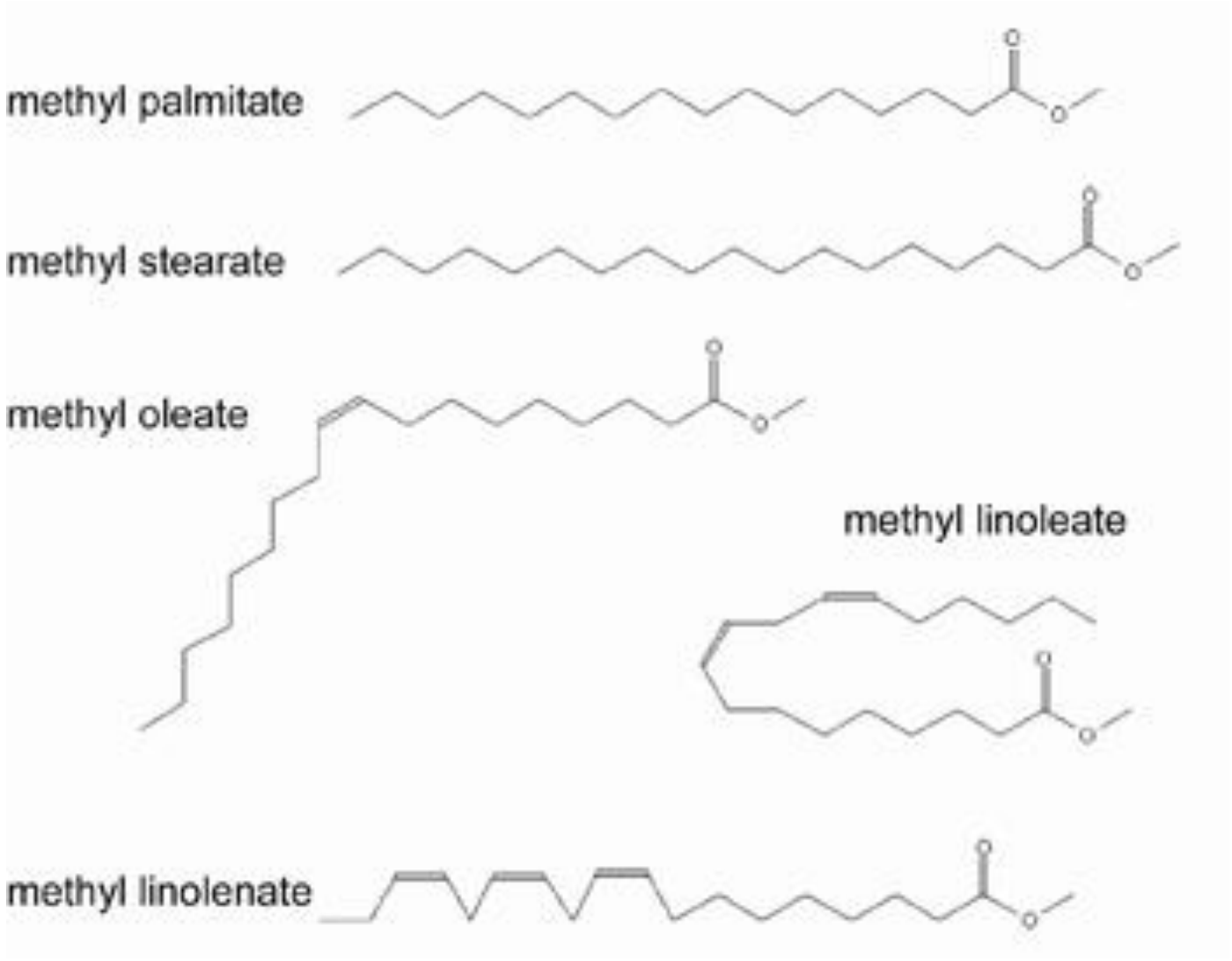


Figure 2: Ignition behavior of saturated and unsaturated methyl esters for stoichiometric, fuel-air mixtures at 12 atm. The top and bottom methyl ester components are isomers of decenoate and the middle structure is methyl decanoate.

W. J. PItz, C. K. Westbrook, O. Herbinet, 2009, LLNL-TR-410103
Chemical Kinetic Modeling of Advanced Transportation Fuels


methyl palmitate
methyl stearate
methyl oleate
methyl linoleate
methyl linolenate