Biodiesel Kinetics and Flame Chemistry

Yiguang Ju, Princeton University

On behalf of CEFRC: Biodiesel Thrust and Flame Chemistry Working Group

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Three Thrusts Unite the Team

Synergistic 2D Research Structure

- Three Thrusts Unite the Team
- Alcohol Chemistry, Modeling, and Applications
- Reaction Mechanisms
- Kinetic Experiments

- Potential energy surfaces
- Rate constants with tunneling
- Laminar flame speeds, extinction and ignition, pollutants
- High-pressure flames, turbulent flames, droplet processes
- Flame chemistry, biodiesel kinetics, model reduction & multi-scale modeling
- Flow reactor experiments: reactivity and species history, $\text{H}_2$, CO, small HC chemistry, DME, small oxygenates
- Mechanisms of butanols, automatic mechanism generation
- Soot: small HC chemistry, transport properties, UQ methods
- Flame species by synchrotron MS, burner-stabilized flames
- Rapid compression machine, high-pressure ignition, thermometry and species
- Shock tube/Laser diagnostics, ignition/species histories, rate constants
- DNS of HCCI/SACI combustion, DNS data for model validation, high pressure turbulence/chemistry interaction
- LES/PDF/ISAT turbulent combustion, turbulence/chemistry interaction
- Low-T combustion engines: HCCI and RCCI CFD modeling, interface with DERC consortium
- Ab initio methods: thermochemical kinetics, ester chemistry
- Potential energy surfaces, reaction rate constants, high pressure theories
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Biodiesel:

- Produced from vegetable oils, animal fats, & waste materials
- Energy density much higher than ethanol
- 28 billion gallons of biodiesel produced in 2010 worldwide
- Large molecules: $C_{16}-C_{18}$ with ester functional group
- Different combustion chemistry/emissions from hydrocarbons
- Large disparities in alkyl chain length and structures

**Motivation**

Biodiesel:

\[
\text{R}_1 \quad \text{O} \quad \text{O} \quad \text{R}_2
\]
Sooting Propensity of Diesel Surrogate and Large Ester Flames

Maximum soot volume fraction measured in a diesel surrogate, \( n \)-decane, methyl decanoate, methyl undecanoate, and methyl 10-undecenoate flames; (\( \bullet \)) diesel surrogate; (\( \triangle \)) methyl 10-undecenoate; (\( \square \)) \( n \)-C\(_{10} \)H\(_{22} \); (\( \bigcirc \)) methyl undecanoate; (\( \blacktriangle \))methyl decanoate.

**Diesel surrogate: 70\% \( n \)-C\(_{10} \)H\(_{22} \) + 30\% 1-methyl naphthalene**  Dagaut and coworkers (2010)
Scientific Questions?

- How to address the knowledge gaps in kinetics of large, oxygenated fuel molecules?
- How can we use quantum chemistry and kinetic experiments to provide a better, predictive model?
- How to address the transport and chemistry interaction in flames?
Research Objectives

- Advance the understanding of combustion kinetics of methyl esters
- Develop a validated kinetic methyl ester kinetic mechanism to model oxidation with quantum chemistry calculations
- Advance understanding of chemistry/transport interaction
1. Biodiesel Kinetics: Hypothesis

Similarity between Small/Large Esters?

Methyl Butanoate (C4+1)

= methyl stearate (C18+1) + Alkane (C14)
The reactivity is strongly affected by the alkyl chain length.
1B. Comparison of Premixed Flame Speeds of Small Methyl-Esters/Air (C$_1$-C$_4$: 1 atm)

- Methyl formate has the highest reactivity
- Methyl propanoate is the second
1C. Comparison of Extinction Limits of Methyl Esters (C$_1$-C$_{10}$)

Extinction limit vs. Transport weighted enthalpy (TWE)

Uniqueness of small methyl esters: methyl formate & methyl propanoate

Similarity of large methyl esters

$T_f = 500$ K, $T_{ox} = 298$ K

- Methyl Formate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Methyl Hexanoate
- Methyl Octanoate
- Methyl Decanoate

• Uniqueness of small methyl esters: methyl formate & methyl propanoate
• Similarity of large methyl esters
1D: BDEs ($D_{298}^{\text{cal/mol}}$) in Biodiesel Methyl Butanoate (MB)

MRSDCI /cc-pV\infty Z // B3LYP
CBS-QB3-Isodesmic*


Weakest bonds: dissociated radicals are resonance stabilized.

C-C bonds are weaker than C-H bonds: alkyl fragments allow more structural relaxation than H.
1E. Kinetic Mechanism Development (Ester-MECH: C_2-C_{11} methyl esters)

- MB: Ester functional group
  Dooley et al., 2008
- C_{1}-C_{7}: n-heptane model
  Curran et al., 2008, 2010
- H_2/O_2: PU hydrogen model

Dievart et al., 34th Symposium on Combustion on Comb., 2012
1F. Model Validation: Ignition Delay Time

Ignition delays from Hanson’s group (Aerosol Shock Tube, very lean mixtures, diluted in argon, ~7.5 atm)

- Present model in good agreement (35%), whereas literature models overestimate MD oxidation rate (50 to 80%)

- Bond dissociation energy affects strongly fuel decomposition pathway
Model validation: JSR & Flame speeds

- methyl decanoate
  - high temperature kinetics
  - speciation profiles, flame speeds

Jet-Stirred reactor (Glaude et al., C&F 157, 2010)
\[ P = 1\text{atm}, \tau = 1.5\text{ s} \]

Laminar Flame Speeds
(Wang et al., C&F 158, 2011)
\[ P = 1\text{atm}, T = 403\text{ K} \]
Model comparison in diffusion flame: MD

Present Model

H atom abstraction
unimolecular decomposition

Before extinction
a = 150 s\(^{-1}\)

Seshadri et al. [14]

Before extinction
a = 150 s\(^{-1}\)

Luo et al. [20]

Before extinction
a = 150 s\(^{-1}\)

MD Consumption Ratio (%)
Model validation: Diffusion flame extinction

Dievart et al., 34th symposium on combustion, 2012
Model validation: Species time history

$[H]$, [mol.cm$^{-3}$]

Time [s]

$T = 1333$ K
$P = 0.51$ atm
$X_{\text{fuel}} = 239.1$ ppm

Methyl formate
H abstraction reactions by OH and H: Methyl Formate

- Large deviations between the rate constants calculated by the Carter’s group (J. Phys. Chem. A, 2012) and the previous estimates or calculations.

\[ \text{CH}_3\text{OCHO} + \text{OH} = \text{CH}_3\text{OCO} + \text{H}_2\text{O} \]

\[ \text{CH}_3\text{OCHO} + \text{H} = \text{CH}_3\text{OCO} + \text{H}_2 \]

**Graphs:**

- **Left Graph:**
  - **Blue line:** Ting Tan (Carter)
  - **Red line:** Good and Francisco
  - **Green line:** Current Model
  - **Diamond line:** Szilagyi et al. (2004)
  - Temperature in K from 300 to 1800
  - Rate constant in mol cm\(^{-3}\) s\(^{-1}\)

- **Right Graph:**
  - **Blue line:** Ting Tan (Carter)
  - **Red line:** Good and Francisco
  - **Green line:** Current Model
  - **Black line:** Akih-Kumgeh
  - **Pink line:** Peukert et al. (Argonne)
  - **Magenta line:** Peukert et al.
  - Temperature in K from 300 to 1900
  - Rate constant in mol cm\(^{-3}\) s\(^{-1}\)

**References:**

- Peukert et al., Combustion and Flame, 2012, Vol. 159, pp. 2312-2323
Methyl-Ester Radical Decomposition Reactions
(Collaborative work: Carter, Klippenstein and Ju)

- Decomposition of small methyl ester radicals such as CH$_3$OCO (and C$_2$H$_5$OCO) are key reactions.
- Literature: only high pressure limit rate constant with low level PES is available (e.g. BH&HLYP/CC-PVTZ).
- Present method: MRACPF/CBS//CASPT2/CC-PVTZ method on PES and VARIFLEX for pressure dependence

Collaborative structure of the Biodiesel

Carter
- Thermochemistry
  - H, Cp, S
- Rate constants
  - MF+X, ME+X, MP+X...
  - (OH, H, CH₃, HO₂)

Yang, Raghu, Ju, Klippenstein
- Rate constants
  - CH₃OCO
  - C₂H₅OCO
  - MF, ME, MP...
  - Decomposition

Hanson group
- Rate constants
  - MX+ OH
  - X=F,A,P,B
- Speciation time history

Eggolfopoulos, Ju, Law
- Flame speeds
- Flame structure
- Extinction
- Emissions

Dryer, Hansen and Ju
- Speciation experiments
  - (Flow tube, flames)

Sung and Hanson
- Ignition delay
  - (Shock tube, RCM)
• Data agree within 25% with Structure Activity Relationship (SAR) estimated rate constants (the same rate used in the current model).
Methyl Formate Decomposition Kinetics

Summary Arrhenius Plot $k_1$: MF $\rightarrow$ CO + CH$_3$OH

- Wide T range
- Low data scatter
- Repeatable

$\pm 25\%$

- Experiment, current study
- Westbrook et al. 2009
- Dooley et al. 2010
- Peukert et al. 2012
- Metcalfe et al. 2010

Measurement: 1.45-1.7 atm
Calculation: 1.5 atm
Advanced diagnostics - high pressure reactors at low and intermediate temperatures

MBMS/mid-IR with flow reactor/jet stirred reactor

In air, 60 Torr, 293 K

$\text{CH}_4$, $\text{H}_2\text{O}$

$\text{H}_2\text{O}_2$ Measurements, DME/O$_2$/He
(2 sec, 1 atm (0.02/0.1/0.88)
2. Flame Chemistry: Kinetic & Transport Interaction

- Interaction of Transport and Chemistry on Flame Extinction
- Low Temperature Ignition and New Flame Regimes
2A. Diffusion Flame Extinction Limits: From Methyl Formate to Methyl Decanoate

\[ T_f = 500 \, \text{K}, \quad T_{ox} = 298 \, \text{K} \]

- Methyl Formate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Methyl Hexanoate
- Methyl Octanoate
- Methyl Decanoate

How to separate chemistry from transport and fuel heating value?

<table>
<thead>
<tr>
<th>Fuel</th>
<th>( \Delta H_{\text{comb}} ) (kcal/mol)</th>
<th>MW (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MB</td>
<td>-651.6</td>
<td>102.14</td>
</tr>
<tr>
<td>MD</td>
<td>-1533.3</td>
<td>186.29</td>
</tr>
</tbody>
</table>
A generic correlation for extinction limit: Transport weighted Enthalpy & radical index

Theoretical analysis of Extinction Damkohler number

\[
\frac{1}{Da_E} = \left[ \frac{2}{e} \frac{\tilde{Y}_{O,\infty}}{\tilde{Y}_{F,-\infty}} \right]^2 Le_F^3 P(\eta_F, Le_F, Le_O) L(\eta_F, Le_F) \left[ \frac{1}{\tilde{T}_f - \tilde{T}_{-\infty}} \left( \frac{\tilde{T}_f}{\tilde{T}_a} \right)^3 \exp \left( -\frac{\tilde{T}_a}{\tilde{T}_f} \right) \right]
\]

Extinction Strain Rate

\[
a_e \propto \frac{1}{\sqrt{M_F / M}} \frac{Y_{F,-\infty} Q_F}{C_p(T_f - T_{-\infty})} \ast R_i
\]

Fuel chemistry
Radical production rate

Transport
Heat release/heat loss

Transport weighted Enthalpy *Radical index

Won et al. CNF 159 (2012)
Reactivity Scaling of Small/Large Methyl Esters: From Methyl Formate (C₁) to Methyl Decanoate (C₁₀)

Extinction limit vs. Transport weighted enthalpy (TWE) flux

$T_f = 500 \text{ K, } T_{ox} = 298 \text{ K}$,

- Methyl Formate
- Methyl Ethanoate
- Methyl Propanoate
- Methyl Butanoate
- Methyl Pentanoate
- Methyl Hexanoate
- Methyl Octanoate
- Methyl Decanoate

• Uniqueness of small methyl ester
• Similarity of large methyl ester
Impact of alkyl chain length on methyl ester reactivity

Methyl Formate, R0C

Methyl Acetate, R1C

Higher reactivity

H abstraction reactions,
Fuel, CH3OCO, and CH3OC(O)CH2 decomposition reaction rates

Lower reactivity

Diévart et al, 2012
to presented on Monday at 34th Symposium
Extinction Limit: n-Alkanes, iso-Alkanes, Aromatics

\[ \text{Fuel mole fraction } X_f \]

\[ a_E = \frac{1}{s} \]

How to separate chemistry from transport?

What is the ranking high temperature reactivity?

\[ T_f = 500 \text{ K and } T_o = 300 \text{ K} \]
A General Correlation of Hydrocarbon Fuel Extinction vs. TWE and Radical Index

\[ R^2 = 0.97 \]

Extinction strain rate \( a_E \) [1/s]

- n-decane
- n-nonane
- n-heptane
- iso-octane
- n-propyl benzene
- toluene
- 1,2,4-trimethly benzene
- 1,3,5-trimethly benzene

\( T_f = 500 \text{ K and } T_o = 300 \text{ K} \)

\[ \text{Ri} \times [\text{Fuel}] \times \Delta H_c \times \left( \frac{MW_{\text{fuel}}}{MW_{\text{nitrogen}}} \right)^{-1/2} \text{ [cal/cm}^3] \]
Radical Index for Screening of Alternative Fuels

- Extinction limits of diffusion flames for pure fuel samples have been completely measured and compared by using TWE
  - Heat of combustion, $\Delta H_c$ has been re-estimated based on H/C ratio correlation.
  - Re-evaluation of $\Delta H_c$ might be necessary.
- High temperature reactivity based on Radical index
  - $\text{SPK} \geq \text{HRJ camelina} \geq \text{HRJ Tallow} > \text{JP8} \geq \text{IPK (iso-octane)}$
  - Similar order to DCN measurements, IPK must be heavily isomerized.

### Table: Radical Index and DCN for Various Fuels

<table>
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<tr>
<th>Fuel</th>
<th>Radical Index</th>
<th>DCN</th>
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</thead>
<tbody>
<tr>
<td>JP8 POSF 6169</td>
<td>0.78</td>
<td>47.3</td>
</tr>
<tr>
<td>SHELL SPK POSF 5729</td>
<td>0.85</td>
<td>58.4</td>
</tr>
<tr>
<td>HRJ Camelina POSF 7720</td>
<td>0.82</td>
<td>58.9</td>
</tr>
<tr>
<td>HRJ Tallow POSF 6308</td>
<td>0.8</td>
<td>58.1</td>
</tr>
<tr>
<td>SASOL IPK POSF 7629</td>
<td>0.76</td>
<td>31.3</td>
</tr>
</tbody>
</table>

**Won et al. CNF 159 (2012)**

**Extinction of diffusion flame in counterflow configuration**

$T_f = 500 \text{ K}$ and $T_{\text{air}} = 300 \text{ K} @ 1 \text{ atm}$
2B. Effects of Transport on Low Temperature Ignition in Non-premixed Counterflow Flames
Law’s group

- NTC behavior extensively observed for homogeneous systems
- Corresponding non-monotonic behavior signaling NTC chemistry in steady state strained has not been well studied in flows (e.g. counterflow), Seshadri et al., CF 2009.
- Reason: Reduced residence time => higher ignition temperature => shifting away from NTC temperature regime
- Explore possible existence of NTC behavior for flows
  - with low strain rates
  - at high pressures

Heptane/air flames

\[ t_{\text{NTC}} > t_{\text{conv}} \]

No NTC at 1 atm, 200/s

\[ t_{\text{NTC}} \sim t_{\text{conv}} \] ?

NTC temp. ↑ as pressure ↑
**n-Heptane vs. Air in Counterflow Ignition**

- **Decrease k**
  - 1 atm, k=200/s
  - Single ignition
  - High-T Chemistry

- **Decrease P**
  - 1 atm, k=100/s
  - 2nd ignition, High-T chemistry

- **Increase k**
  - 10 atm, k=200/s
  - 2nd ign, high-T
  - 1st ign, low-T chemistry

- **Increase P**
  - 10 atm, k=100/s
  - Single ignition
  - Low-T chemistry
Unsteady Flow Perturbation on Low Temperature Ignition in Diffusion Flame

6.17 ms at 74 Hz

• Rise from 72 to 73 Hz

Rise

850 K
30 atm
100 s⁻¹

Normalized ignition delay time

Frequency (Hz)

0 Hz (left)
72 Hz (left)
73 Hz (left)
2000 Hz (left)
0.008
0.006
0.004
0.002
0.00
0
0.002
0.004
0.006
Time (s)

Reaction rate of reaction 3 (mole/cm³/s)

Reaction 2: \( \text{RO}_2 = \text{R'O}_2\text{H} \)

Reaction 3: \( \text{H}_2\text{O}_2 + \text{M} = 2\text{OH} + \text{M} \)

- No effect on initial \( \text{RO}_2 \) formation,
- \( \text{H}_2\text{O}_2 \) decomposition is delayed by heat loss at high strain rate.

Shan et al., 2012
Multi Flame Regimes in HCCI Ignition n-Heptane: Flame Initiation by a Spark at 40 atm, T=700 K

Low temperature ignition

Low temperature flame dominated double flame (decoupled)

S_f = 27.5 cm/s

Transition

High temperature flame dominated double flame (coupled)

S_f = 15.3 cm/s

Single high temperature flame front

S_f = 25.6 m/s

LTI at wall

Hot ignition

Movie

Ju et al., 33rd symposium on Comb., 2011
Conclusions

- Combustion properties, species, and kinetic data methyl esters are experimentally measured by a collective effort.

- An updated methyl ester (C₂-C₁₁) kinetic mechanism is developed and partially validated.

- Large uncertainties in elementary rate constant and species time history.

- Flame theory to correlate flame extinction with TWE and radical index. Uniqueness and similarity of high temperature reactivity of methyl esters are demonstrated.

- Significant impacts of low temperature ignition on ignition and flame propagation are demonstrated. New flame regimes are identified.
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