@ 慶應義塾大学　12月5日　2011年

アルコール燃料の
高温・低温反応機構のモデリング

独立行政法人産業技術総合研究所
新燃料自動車技術研究センター
Research Center for New Fuels and Vehicle Technology NFV

○　辻村　拓

Acknowledgments

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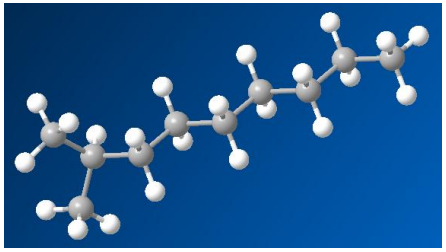
- コネチカット大学：Sung教授ら・・・・・・・・・急速圧縮膨張装置実験
- サンディア国立研究所：Dec氏ら・・・・・・・・・・HCCIエンジン実験

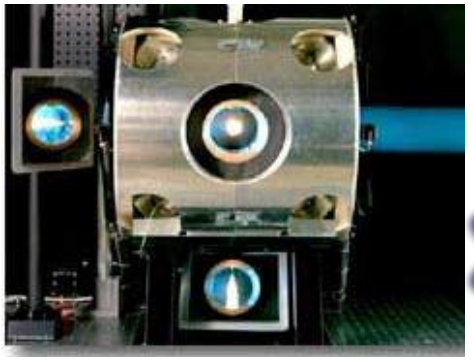
Combustion Chemistry Research From Fundamental

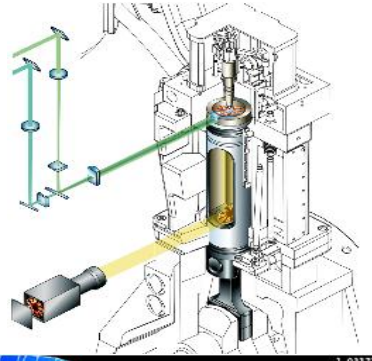
This slide is given by courtesy of Sarathy M.

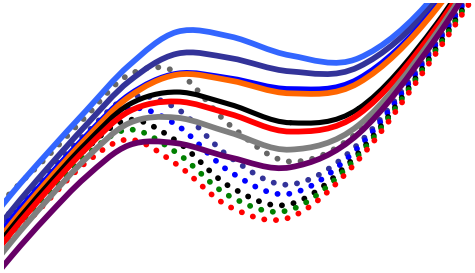
Zigler et al., NREL's DOE Merit Review, June 2010
Pickett et al., Sandia, 2010
Mueller et al., Sandia DOE Merit Review, Jun 2010
Amsden, KIVA 3V- LANL, 2010

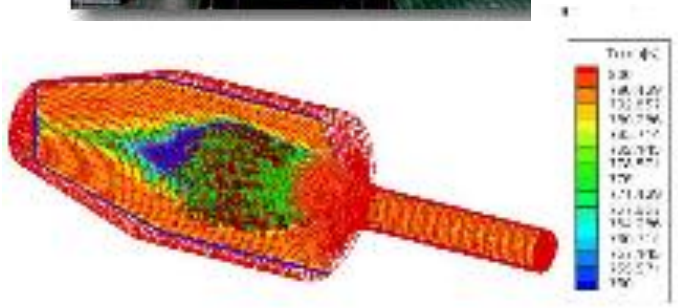
- Develops fundamental kinetic models that aid in developing advanced engine technologies

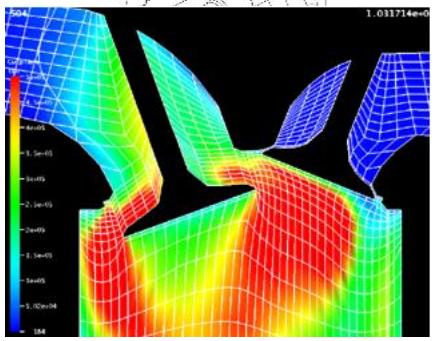










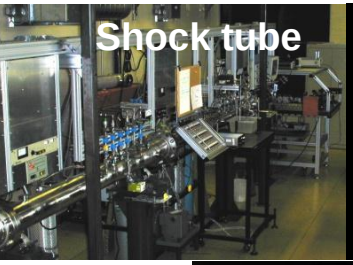


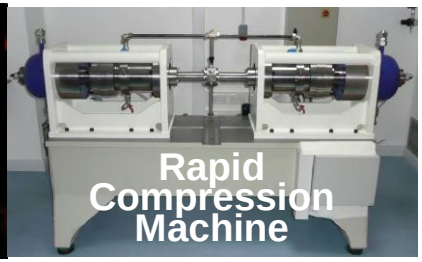
Fundamental 0-D/1-D Combustion Modeling and Experiments → 2D Combustion Modeling in Experimental Systems → 3D Combustion Modeling in Practical Engine Systems

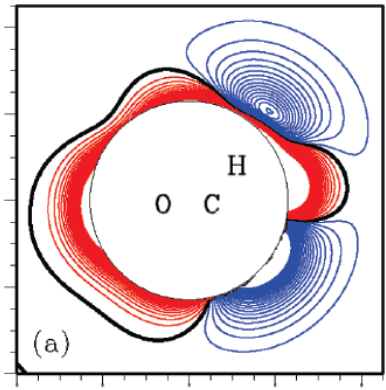
Detailed Chemical Kinetic Models → Skeletal Kinetic Models → Reduced Kinetic Models

Development of Chemical Kinetic Models for Fuels

Arranged the presentation file made by Pitz W.J. for WS on Techniques for High-Pressure Combustion, Aug 2011.







Fundamental experimental measurements

Ab initio calculations

```
oh        7/13/ 0 rucich   1o   1    0    0g   300.000  5000.000 1710.000    01
 2.85376040e+00 1.02994334e-03-2.32666477e-07 1.93750704e-11-3.15759847e-16    2
 3.69949720e+03 5.78756825e+00 3.41896226e+00 3.19255801e-04-3.08292717e-07    3
 3.64407494e-10-1.00195479e-13 3.45264448e+03 2.54433372e+00                   4
```

```
c3h8+oh<=>nc3h7+h2o 1.054e+10 0.970 1.586e+03
```

Base chemistry

Thermodynamic database

Reaction rate constants

Detailed chemical kinetic model for practical fuels

Reaction rate rules

```
reactions
h+o2<=>o+oh 9.65E+14 -0.262 1.62E+04
o+h2<=>h+oh 5.080e+04 2.670 6.292e+03
oh+h2<=>h+h2o 2.160e+08 1.510 3.430e+03
o+h2o<=>oh+oh 2.970e+06 2.020 1.340e+04
h2+m<=>h+h+m 4.577e+19 -1.400 1.044e+05
h2/ 2.5/ h2o/ 12/ co/ 1.9/ co2/ 3.8/
o+o+m<=>o2+m 6.165e+15 -0.500 0.000e+00
h2/ 2.5/ h2o/ 12/ ar/ .83/ co/ 1.9/ co2/ 3.8/ ch4/ 2/ c2h6/ 3/ he/ .83/
o+h+m<=>oh+m 4.714e+18 -1.000 0.000e+00
h2/ 2.5/ h2o/ 12/ ar/ .75/ co/ 1.5/ co2/ 2/ ch4/ 2/ c2h6/ 3/ he/ .75/
```

High temperature mechanism

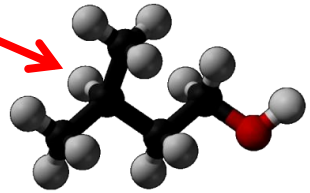
Reaction class 1: Unimolecular fuel decomposition
Reaction class 2: H atom abstractions from fuel
Reaction class 3: Alkyl radical decomposition
Reaction class 4: Alkyl radical + O_2 = olefin + HO_2
Reaction class 5: Alkyl radical isomerization
Reaction class 6: H atom abstraction from olefins
Reaction class 7: Addition of radical species to olefins
Reaction class 8: Alkenyl radical decomposition
Reaction class 9: Olefin decomposition

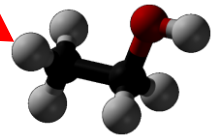
What & Why Isopentanol ?

A Next Generation Bio-Alcohol Fuel:

- Isopentanol (3-Methyl-1-Butanol or 3 Methylbutane-1-ol) is one of biomass derived alcoholic fuel, like Ethanol

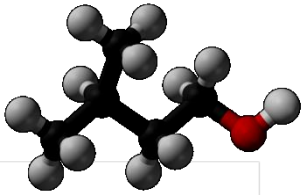
jbei
Joint BioEnergy Institute
http://www.jbei.org/

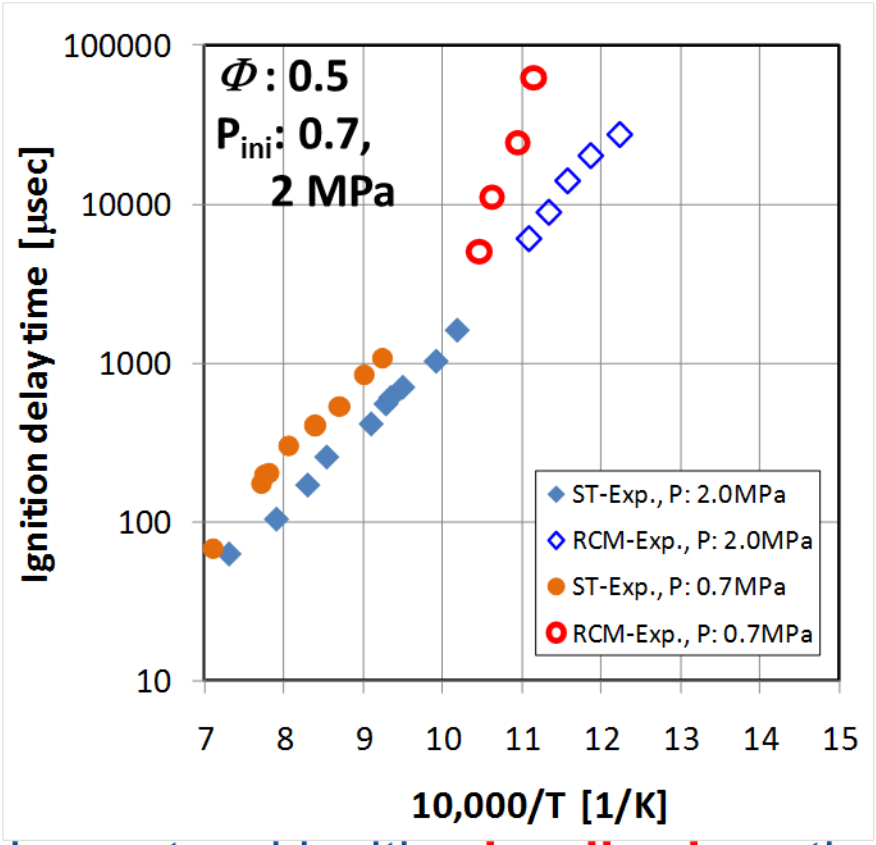


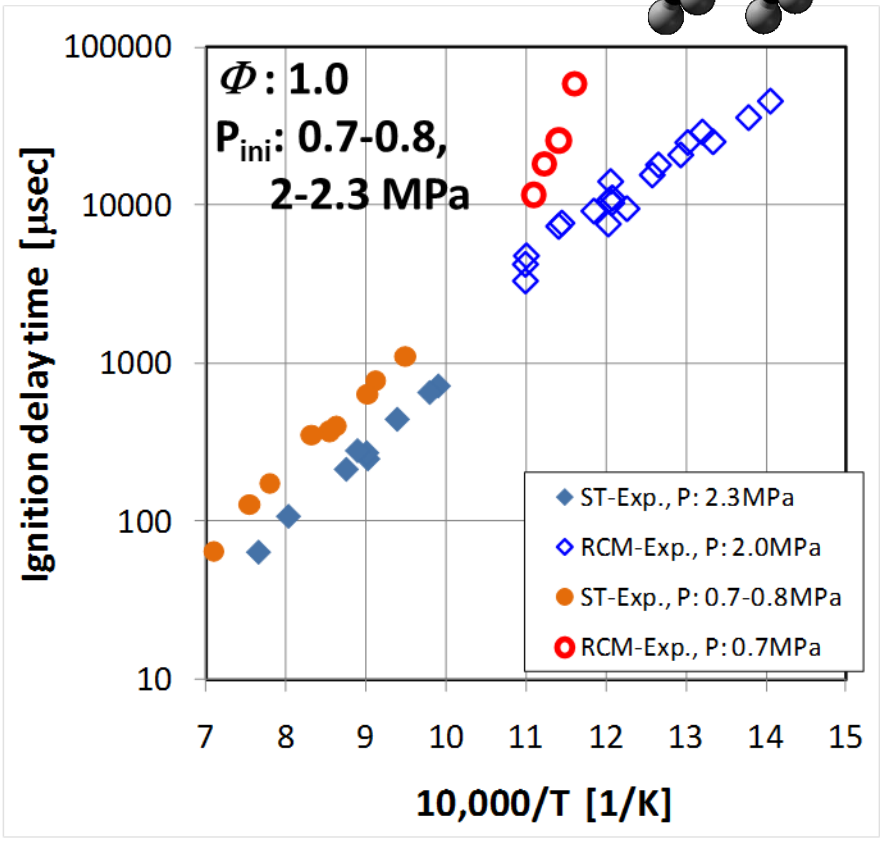


- The challenge of **JBEI**: To convert all monomer sugars (hexoses and pentoses) released from depolymerization of lignocellulosic biomass into transportation fuels and other chemicals. And the **initial targets of JBEI** is ethanol, butanol, **isopentanol**, hexadecane, and geranyl decanoate ester.
- Higher alcohols such as isopentanol has **higher energy density** and **lower hygroscopicity** compared to ethanol.
- Volatility is **moderate** like gasoline, “Not too volatile”

Reaction classes for low temperature reactions







- Isopentanol ignition **hardly show** the **NTC** (Negative Temperature Coefficient) trend like ethanol or 1-butanol, and that's unlike saturate hydrocarbons
- Phi and Pressure dependences appear as well as strong temp. dependence

Shock tube experiments: Kenji Yasunaga, Fiona Gillespie, and Henry Curran (NUI Galway - Ireland)
Rapid compression machine (RCM) experiments: Bryan Weber, Yu Zhou and Chih-Jen Sung (UConn.)

Assign reaction rate rules by reaction classes

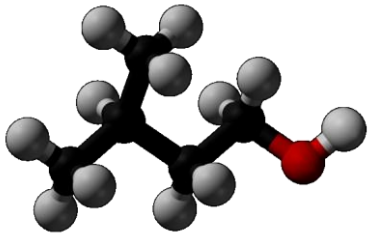
High temperature mechanism

class 1: Unimolecular fuel decomposition
class 2: H atom abstractions from fuel
class 3: Alkyl radical decomposition
class 4: Alkyl radical + O_2 = olefin + HO_2
class 5: Alkyl radical isomerization
class 6: H atom abstraction from olefins
class 7: Addition of radical species to olefins
class 8: Alkenyl radical decomposition
class 9: Olefin decomposition

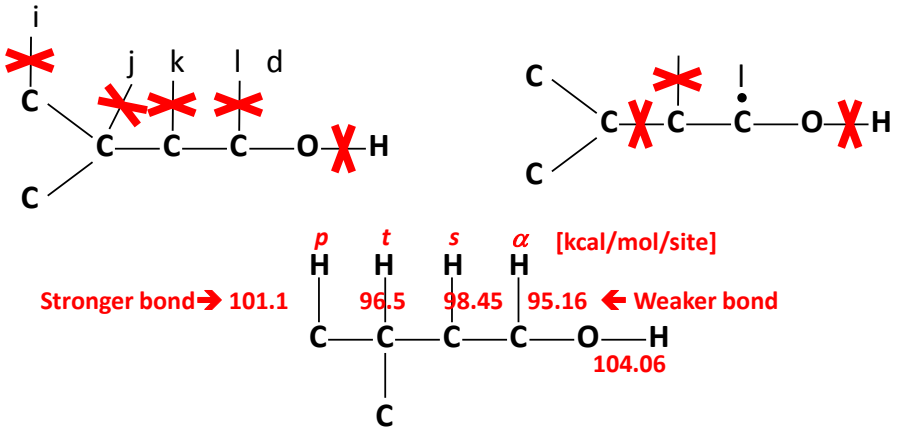
Target Fuel:

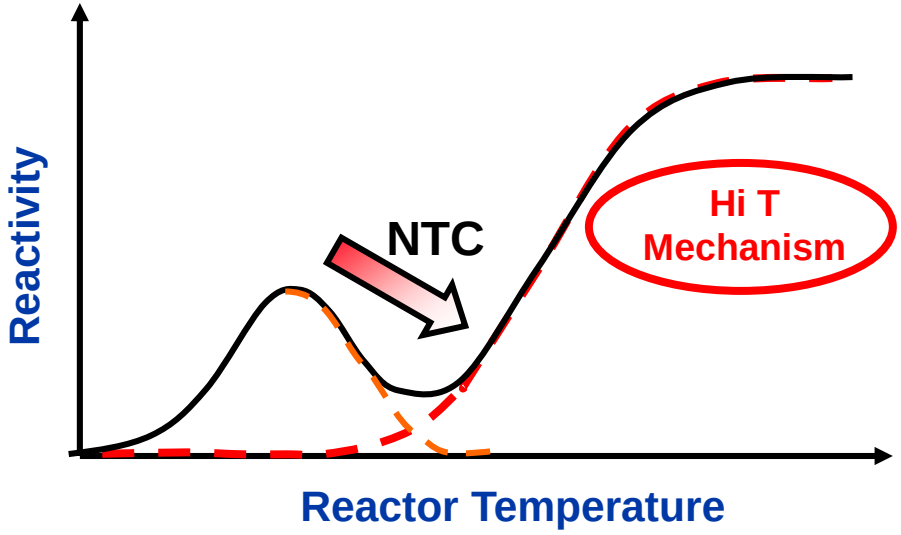
Isopentanol

(3-methyl-1-butanol)

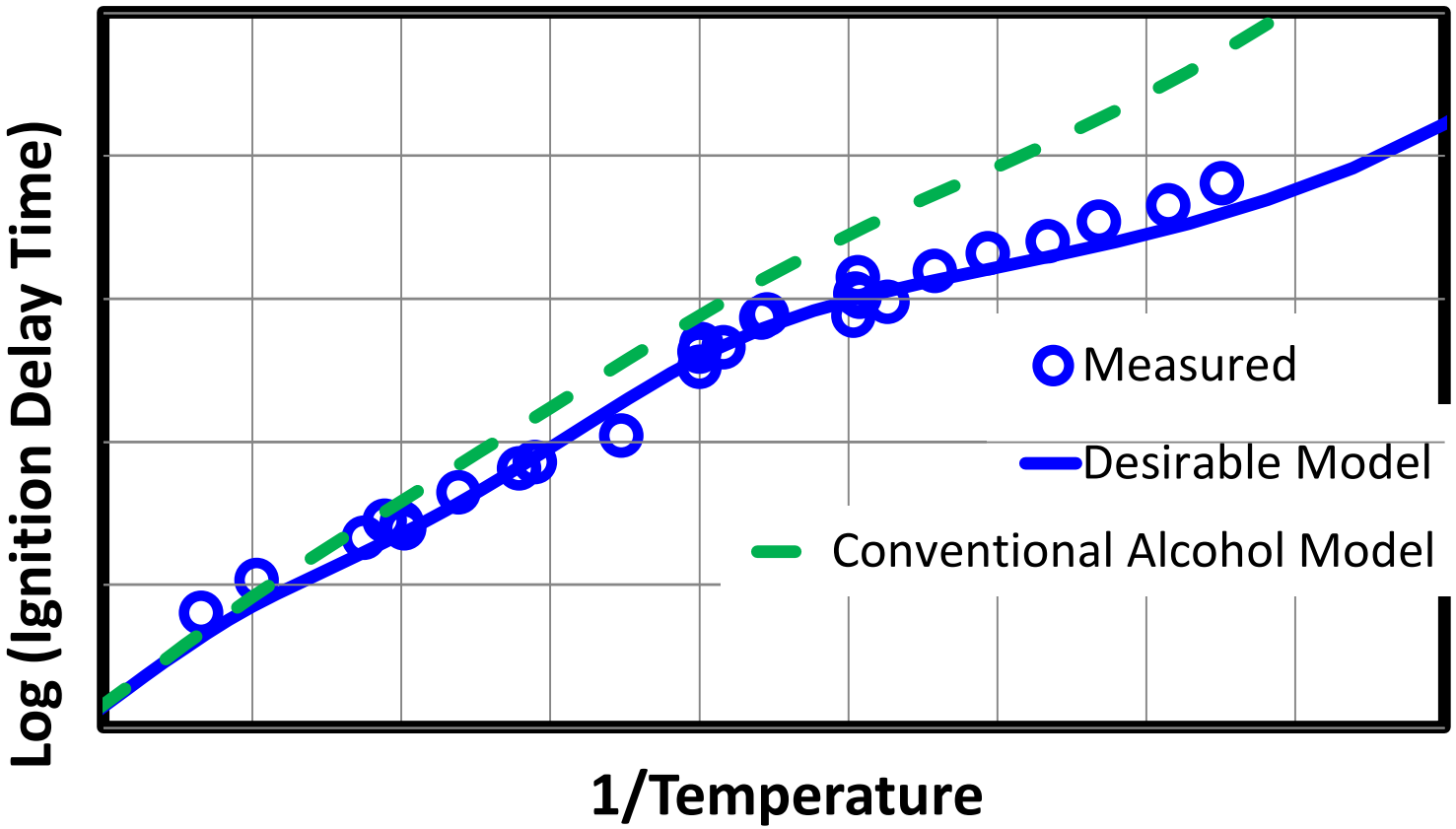


jbei Joint BioEnergy Institute http://www.jbei.org/





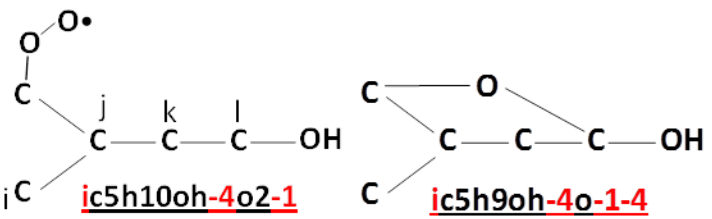
Model Formula of Isopentanol Reaction

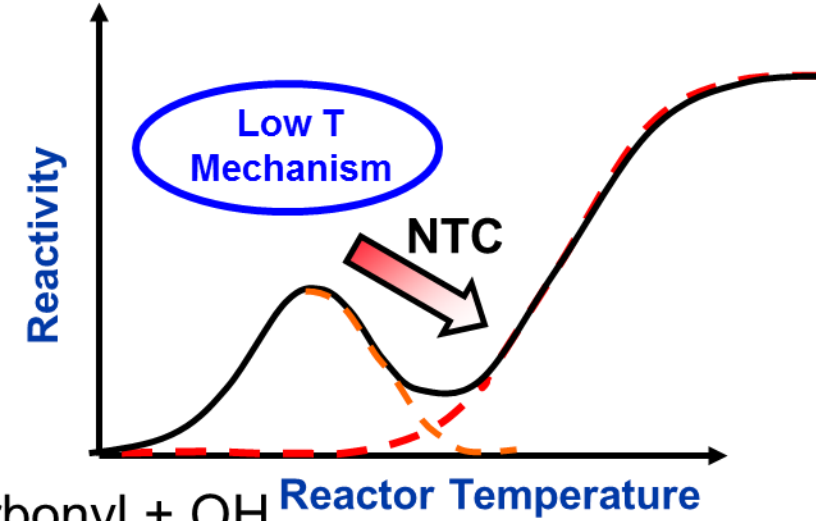


Reaction classes for low temperature reactions

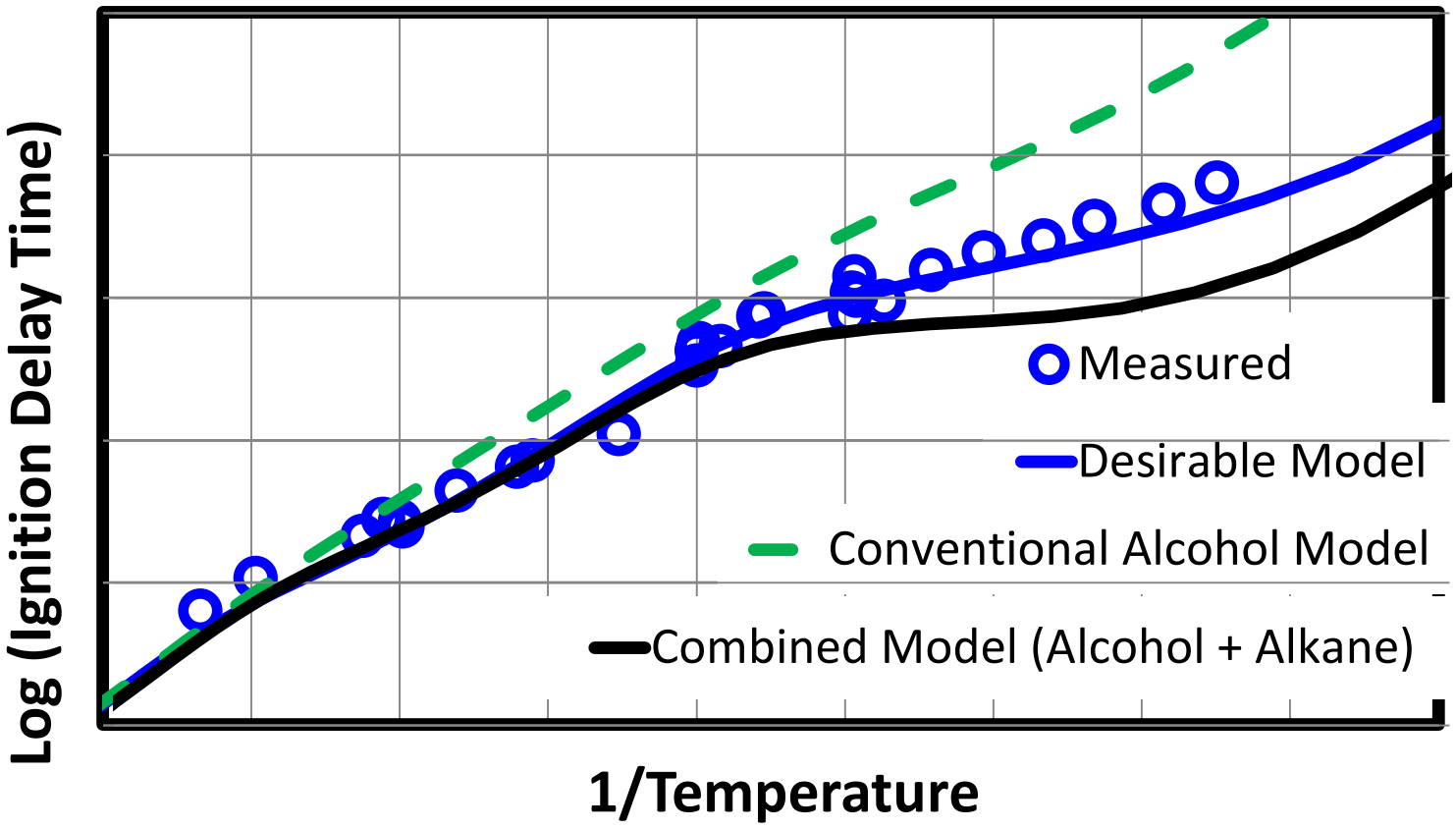
Low temperature mechanism

class 10: Alkyl radical addition to O_2 ($R + O_2$)
class 11: $R + R'O_2 = RO + R'O$
class 12: Alkylperoxy radical isomerization
class 13: $RO_2 + HO_2 = ROOH + O_2$
class 14: $RO_2 + H_2O_2 = ROOH + HO_2$
class 15: $RO_2 + CH_3O_2 = RO + CH_3O + O_2$
class 16: $RO_2 + R'O_2 = RO + R'O + O_2$
class 17: ROOH = RO + OH
class 18: RO Decomposition
class 19: QOOH = Cyclic Ether + OH
class 20: QOOH = Olefin + HO_2
class 21: QOOH = Olefin + Aldehyde or Carbonyl + OH
class 22: Addition of QOOH to molecular oxygen O_2
class 23: O_2QOOH isomerization to carbonylhydroperoxide + OH
class 24: Carbonylhydroperoxide decomposition
class 25: Reactions of cyclic ethers with OH and HO_2

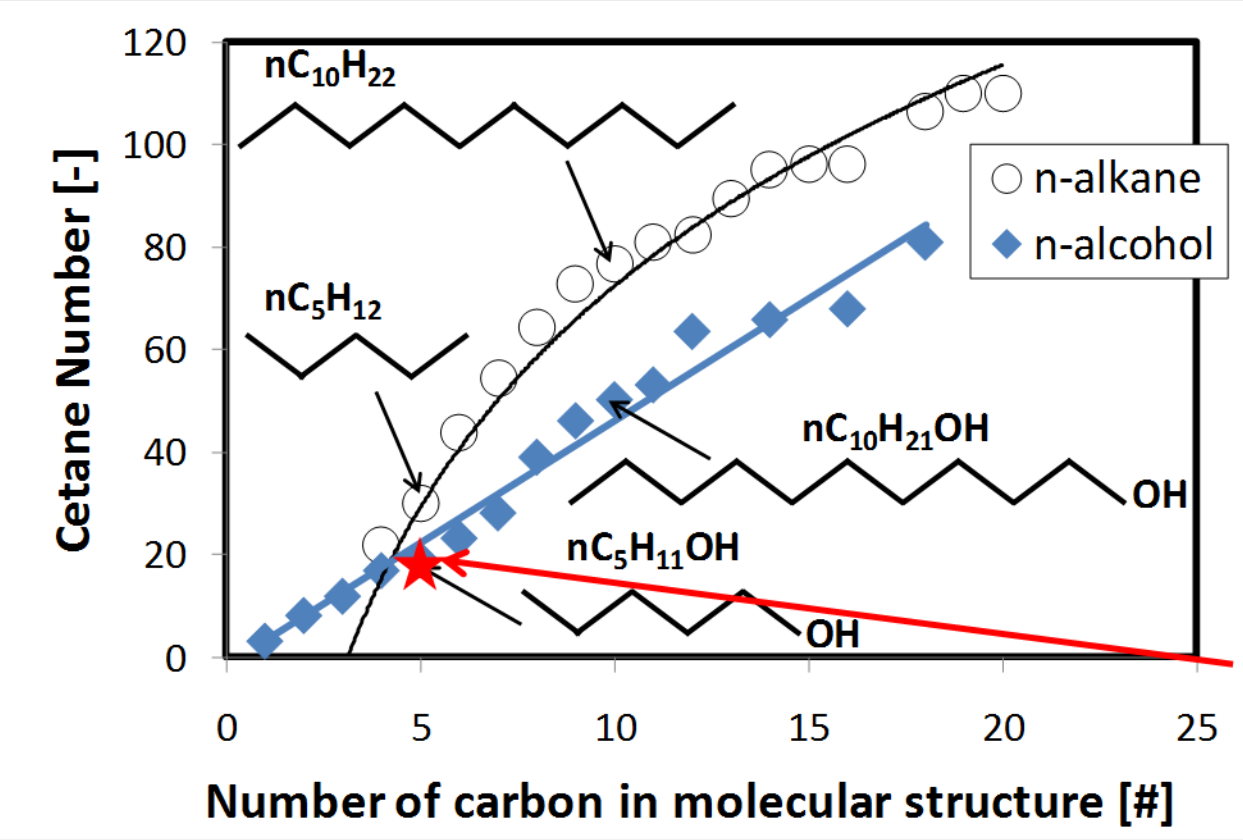




Model Formula of Isopentanol Reaction



Reactivity of Straight-Chain Alkanes and Alcohols

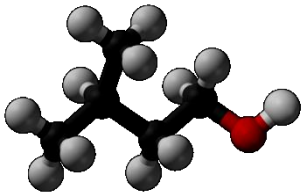


Murphy, M., et al., "Compendium of Experimental Centane Number Data," Subcontractor Report, NREL/SR-540-36805, 2004. URL: http://www.nrel.gov/vehiclesandfuels/pdfs/sr368051.pdf

Acknowledgement:
Matthew Ratcliff and colleagues @ NREL recently took the data of Derived Centane Number (DCN) of isopentanol.
DCN=18.35 (Range:14-22)

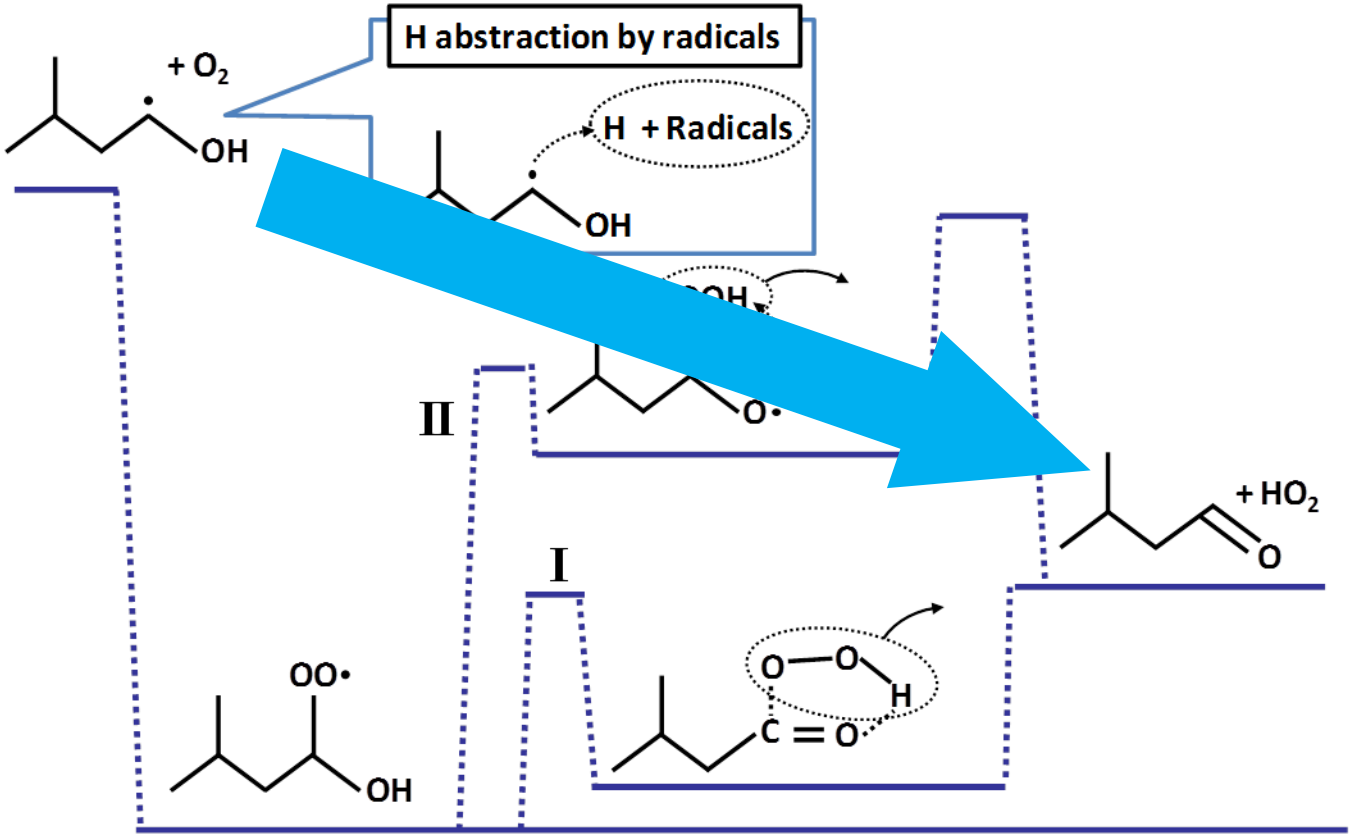
Large differences of CN between straight-chain fuels;
Why alcohols have so less reactivity?
Obvious difference of fuel structure ➔ W or W/O OH-group

Specific Reaction Step for Alcohol Fuel

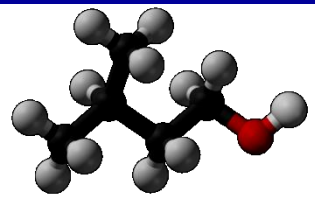


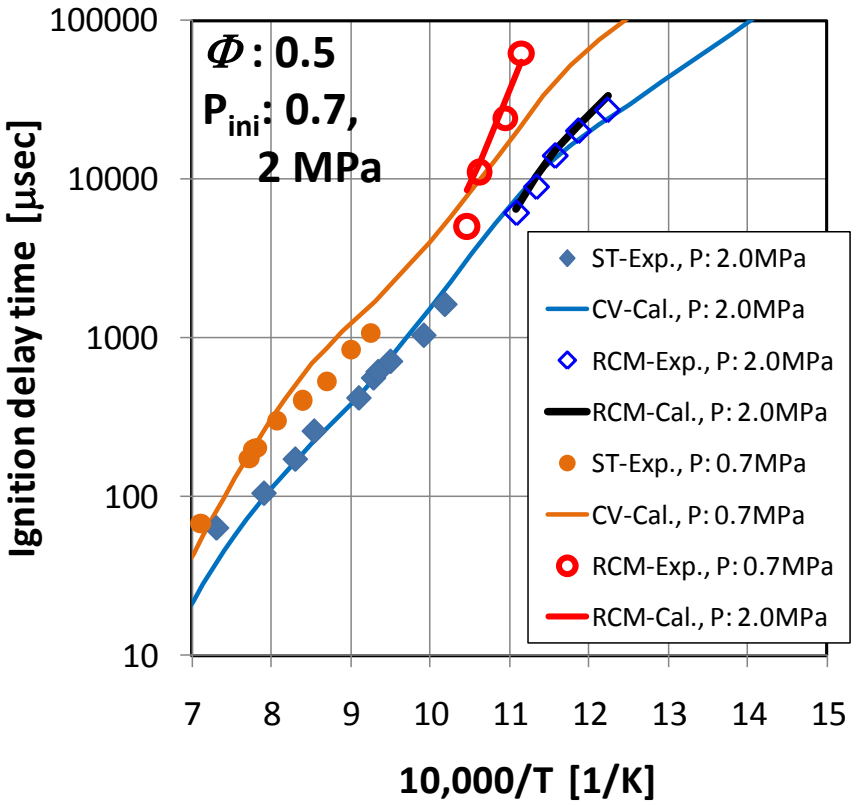
Concerted elimination of HO_2:

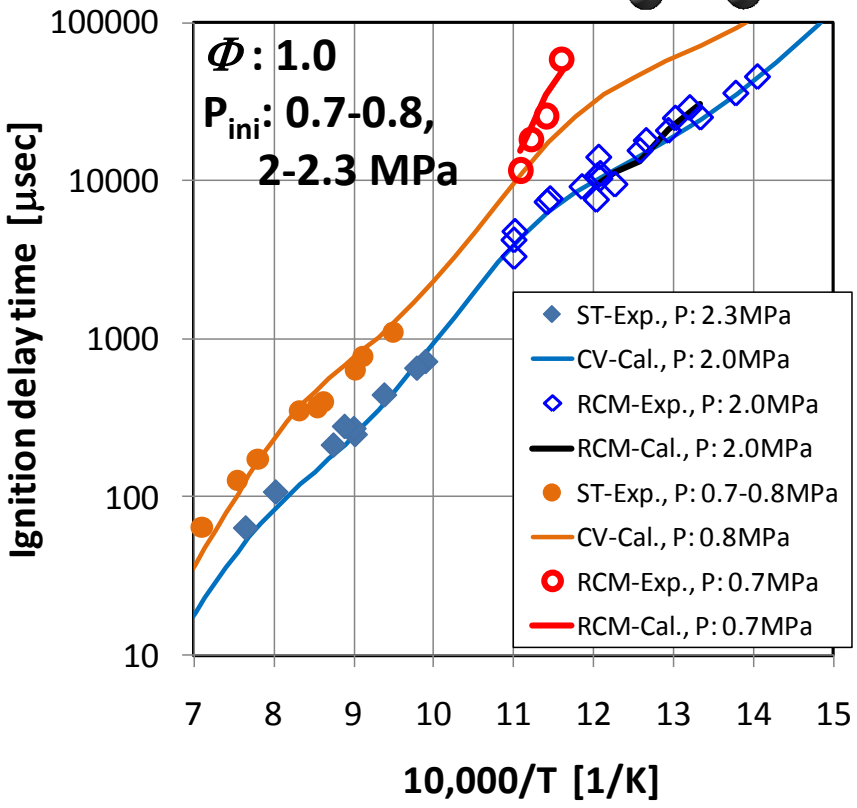
- Concerted elimination forming aldehyde and HO_2 from RO_2 is so fast that low temperature reactions would be slowed down



Validations of Reaction Mechanism







- Isopentanol model developed in this study can reproduce the experimental data which were acquired under various Φ, T, and P conditions with a shock tube and an RCM

Shock tube experiments: Kenji Yasunaga, Fiona Gillespie, and Henry Curran (NUI Galway - Ireland)
Rapid compression machine (RCM) experiments: Bryan Weber, Yu Zhou and Chih-Jen Sung (UConn.)

Concluding Remarks

A study on the chemical kinetic modeling for isopentanol, a prospective next-generation biofuels was conducted.

- A detailed kinetic model for isopentanol was developed. The model consists of low- and high-temperature chemistry and the HO_2 elimination mechanism.
- The model consists of butanol basis high-T chemistry and isooctane basis low-T chemistry. Concerted HO_2 elimination should be additionally taken into consideration.
- The model is precisely validated for the given basic experimental conditions of a shock tube and an rapid compression expansion machine (**T: 652 - 1457 K, P: 0.7 - 6.2 MPa, ϕ: 0.5, 1.0, 2.0**).
- The model is able to reproduce flame speed (**P: 1 atm, ϕ: 0.75 - 1.5**), and fuel oxidation (**T: 740 - 1220 K, P: 5 atm, ϕ: 0.35 - 4.02**).

Thank You for Kind Attention!!!