Chemical Engineering 522

Combustion Processes

Kinetics 2

H_2-O_2 System

Initiation

$H_2 + M \rightarrow H + H + M$
$H_2 + O_2 \rightarrow HO_2 + H$

First is active at only high temperatures

Chain Reactions

$H + O_2 \rightarrow O + OH$
$O + H_2 \rightarrow H + OH$
$H_2 + OH \rightarrow H_2O + H$
$O + H_2O \rightarrow OH + OH$

Radicals break down O_2, H_2, or H_2O
Three of these are chain branching
Three create OH, which reacts with $H_2 \rightarrow H_2O$

Chain Termination

$H + H + M \rightarrow H_2 + M$
$O + O + M \rightarrow O_2 + M$
$H + O + M \rightarrow OH + M$
$H + OH + M \rightarrow H_2O + M$

Three-body termination
Two produce reactants
Third creates radical but kills two
Last produces product H_2O

Also have reactions for HO_2 and H_2O_2

H_2-O_2 Mechanism (Yetter)

"Full" mechanism: 8 species: H_2, O_2, H_2O, OH, O, H, HO_2, H_2O_2

1) O2 + H <=> OH + O
2) H2 + O <=> OH + H
3) OH + H2 <=> H + H2O
4) 2 OH <=> H2O + O
5) H2 + M <=> 2 H + M
6) 2 O + M <=> O2 + M
7) H + O + M <=> OH + M
8) OH + H + M <=> H2O + M
9) O2 + H + M <=> HO2 + M
10) H + HO2 <=> O2 + H2
11) H + HO2 <=> 2 OH
12) O + HO2 <=> OH + O2
13) OH + HO2 <=> O2 + H2O
14) 2 HO2 <=> O2 + H2O2
15) H2O2 + M <=> 2 OH + M
16) H + H2O2 <=> OH + H2O
17) H + H2O2 <=> H2 + HO2
18) O + H2O2 <=> HO2 + OH
19) OH + H2O2 <=> H2O + HO2

$CO\text{-}O_2$ Mechanism

CO with H_2O

$CO + O_2 \rightarrow CO_2 + O$
$O + H_2O \rightarrow OH + OH$
$CO + OH \rightarrow CO_2 + H$
$H + O_2 \rightarrow OH + O$

Slow, but initiates
CO is slow without Hydrogen
CO + OH is the fast step
Two of these steps just make OH

CO with H_2

$H_2 + O \rightarrow OH + H$
$OH + H_2 \rightarrow H_2O + H$

Add these to the above

$CO + HO_2 \rightarrow CO_2 + OH$

... and this one for good measure!

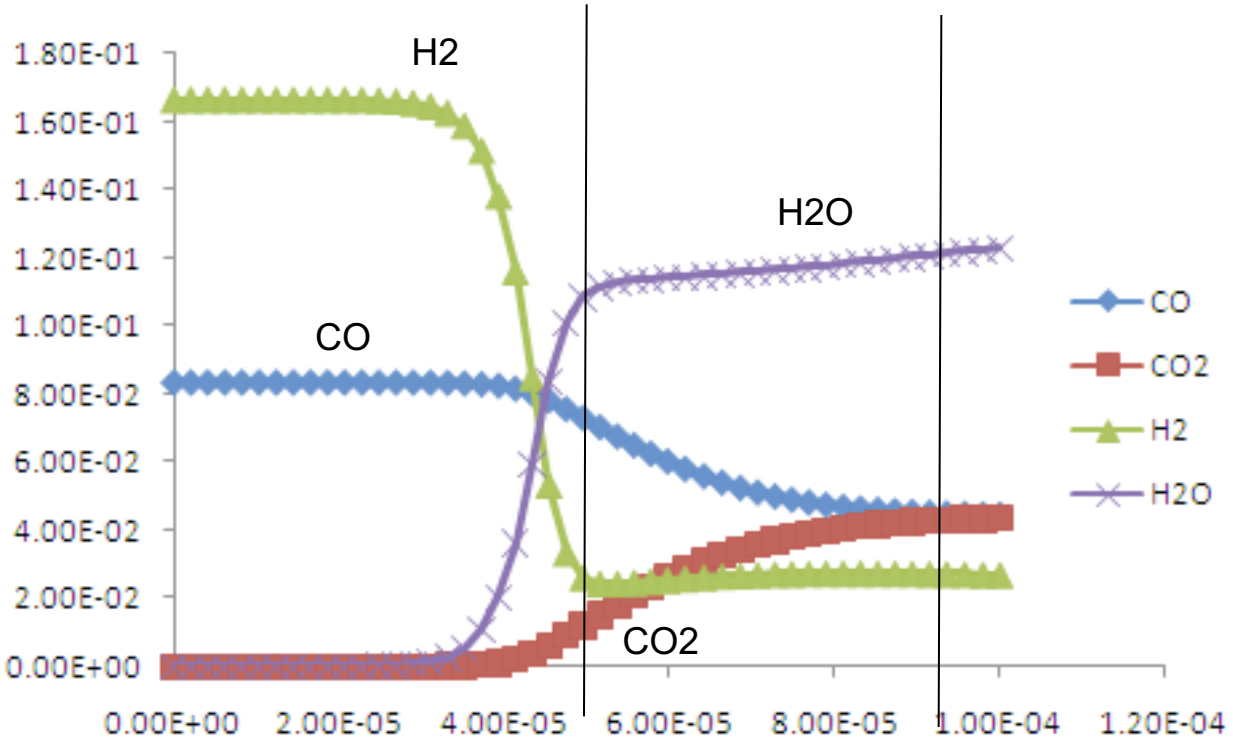
With H and O in the system, include all the hydrogen mechanism too.

CO versus H2 reaction rates

- $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$
- $CH_4 + ½\ O_2 \rightarrow CO + 2H_2$
- $CO + 2H_2 + 3/2\ O_2 \rightarrow CO_2 + 2H_2O$

using Modlink

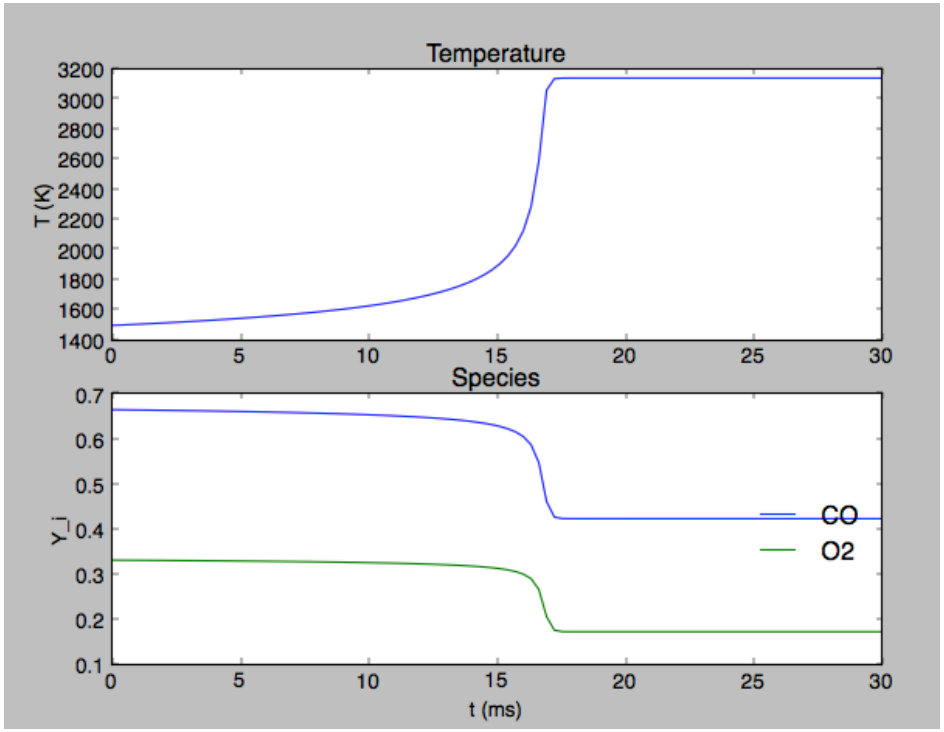
1200 K inlet, adiabatic reaction, CO, 2H2, 1.5O2, 7.52 N2



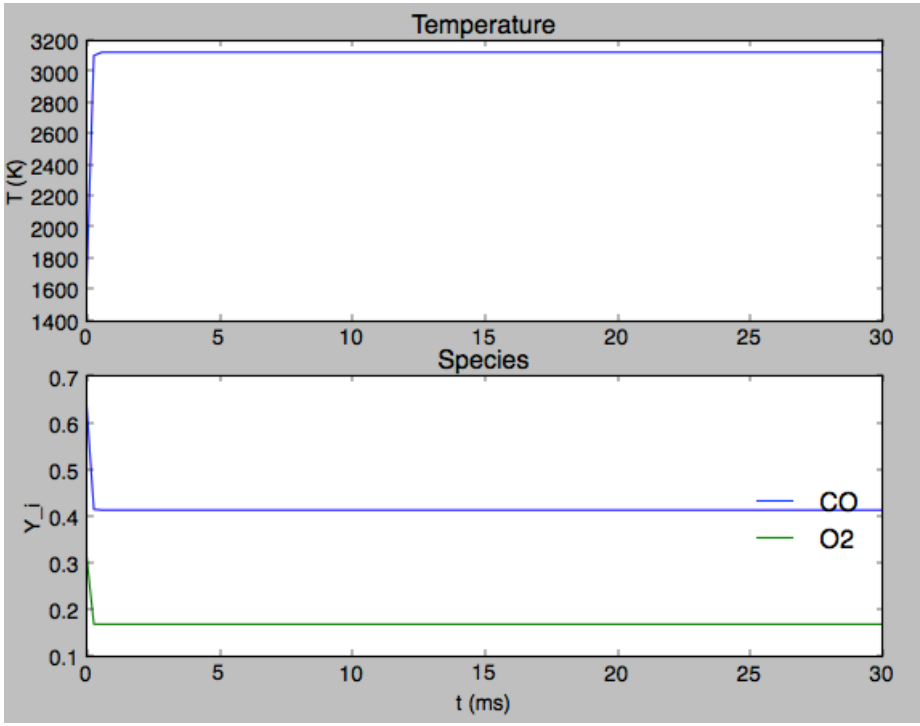
CO reaction speeds

T0 = 1500, adiabatic PFR, Compare effect of Hydrogen on CO reaction

Moles CO, O2, H2O =
1, 0.5, 0

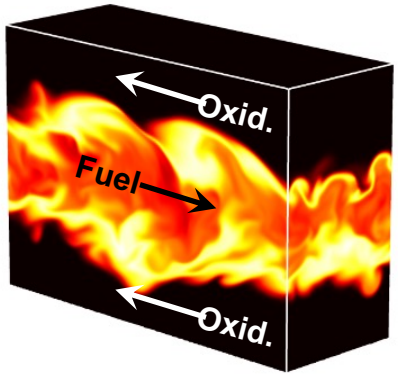


Moles CO, O2, H2O =
1, 0.5, 0.01

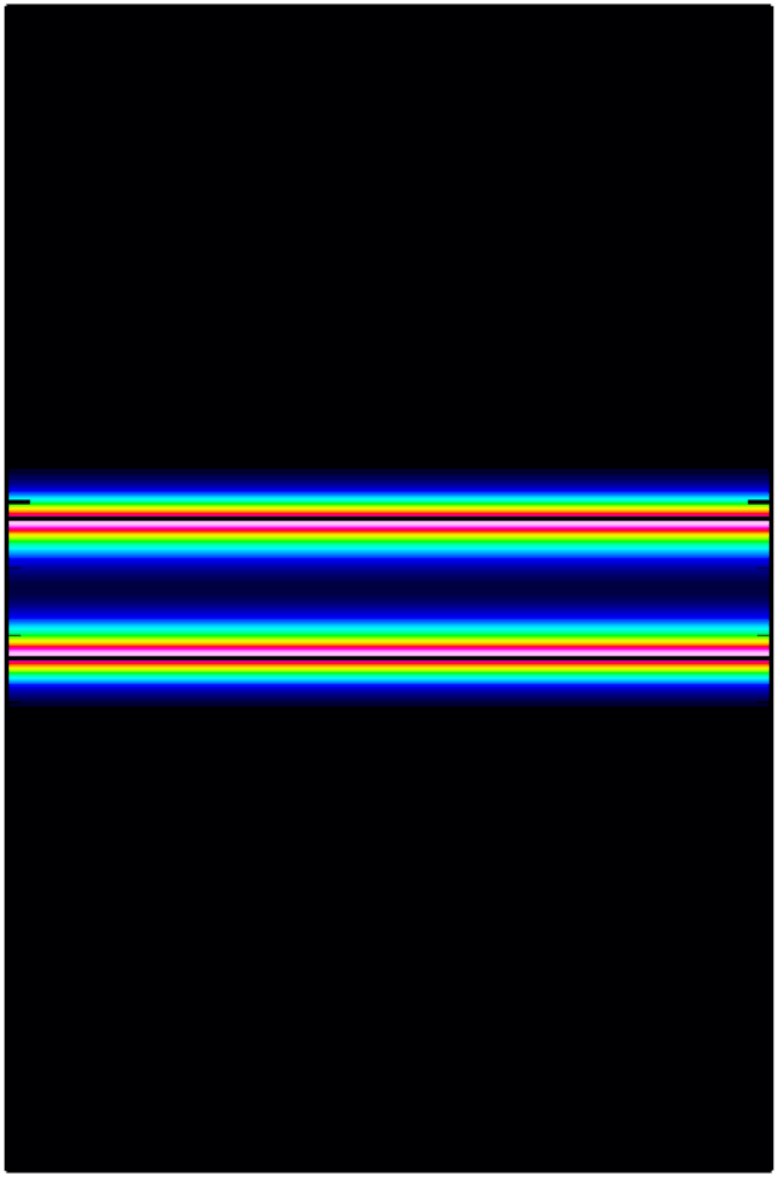


Cantera Solution

Global Mechanism Example—DNS



- DNS is expensive (2 MM CPU hrs).
- Run preliminary tests with cheap chemistry (one-step) instead of the normal 19 species, 167 reaction mechanism



One-Step Mechanisms

$$C_xH_y + (x + y/4)O_2 \xrightarrow{k_G} xCO_2 + (y/2)H_2O$$

$$\frac{d[C_xH_y]}{dt} = -A \exp(-E_a/R_uT)[C_xH_y]^m[O_2]^n$$

$$[=] \text{ gmol/cm}^3\text{-s},$$

Table 5.1 Single-step reaction rate parameters for use with Eqn. 5.2 (Adapted from Ref. [6])

Fuel	Pre-exponential Factor, A^a	Activation Temperature, E_a/R_u (K)	m	n
CH_4	$1.3 \cdot 10^8$	24,358[b]	−0.3	1.3
CH_4	$8.3 \cdot 10^5$	15,098[c]	−0.3	1.3
C_2H_6	$1.1 \cdot 10^{12}$	15,098	0.1	1.65
C_3H_8	$8.6 \cdot 10^{11}$	15,098	0.1	1.65
C_4H_{10}	$7.4 \cdot 10^{11}$	15,098	0.15	1.6
C_5H_{12}	$6.4 \cdot 10^{11}$	15,098	0.25	1.5
C_6H_{14}	$5.7 \cdot 10^{11}$	15,098	0.25	1.5
C_7H_{16}	$5.1 \cdot 10^{11}$	15,098	0.25	1.5
C_8H_{18}	$4.6 \cdot 10^{11}$	15,098	0.25	1.5
C_8H_{18}	$7.2 \cdot 10^{12}$	20,131[d]	0.25	1.5
C_9H_{20}	$4.2 \cdot 10^{11}$	15,098	0.25	1.5
$C_{10}H_{22}$	$3.8 \cdot 10^{11}$	15,098	0.25	1.5
CH_3OH	$3.2 \cdot 10^{12}$	15,098	0.25	1.5
C_2H_5OH	$1.5 \cdot 10^{12}$	15,098	0.15	1.6
C_6H_6	$2.0 \cdot 10^{11}$	15,098	−0.1	1.85
C_7H_8	$1.6 \cdot 10^{11}$	15,098	−0.1	1.85
C_2H_4	$2.0 \cdot 10^{12}$	15,098	0.1	1.65
C_3H_6	$4.2 \cdot 10^{11}$	15,098	−0.1	1.85
C_2H_2	$6.5 \cdot 10^{12}$	15,098	0.5	1.25

[a] Units of A are consistent with concentrations in Eqn. 5.2 expressed in units of gmol/cm^3, i.e., $A[=]$ (gmol/cm^3)$^{1-m-n}$/s.

[b] $E_a = 48.4$ kcal/gmol.

[c] $E_a = 30$ kcal/gmol.

[d] $E_a = 40$ kcal/gmol.

One-Step Mechanism

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

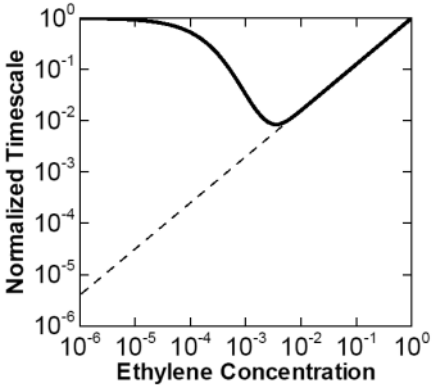
$$\frac{d[C_2H_4]}{dt} = -k(T)[C_2H_4]^{0.1}[O_2]^{1.65}$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$$[C_2H_4]^{0.1} \rightarrow [C_2H_4]^{0.1+0.9\exp(-800Y_{C2H4})}$$

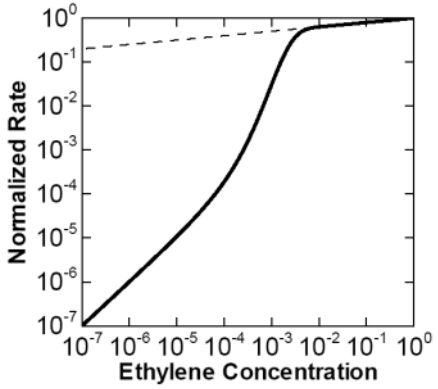
- ***Problem:*** Very Stiff Explicit ODE integration
  - Very small timestep sizes required.
  - Takes too many steps.
  - Why?
- Apply Characteristic Timescale

$$\tau = \frac{\Delta[C_2H_4]_{max}}{\left|\frac{d[C_2H_4]}{dt}\right|_{max}} \qquad \tau = \frac{[C_2H_4]}{[C_2H_4]^{0.1}} = [C_2H_4]^{0.9}$$

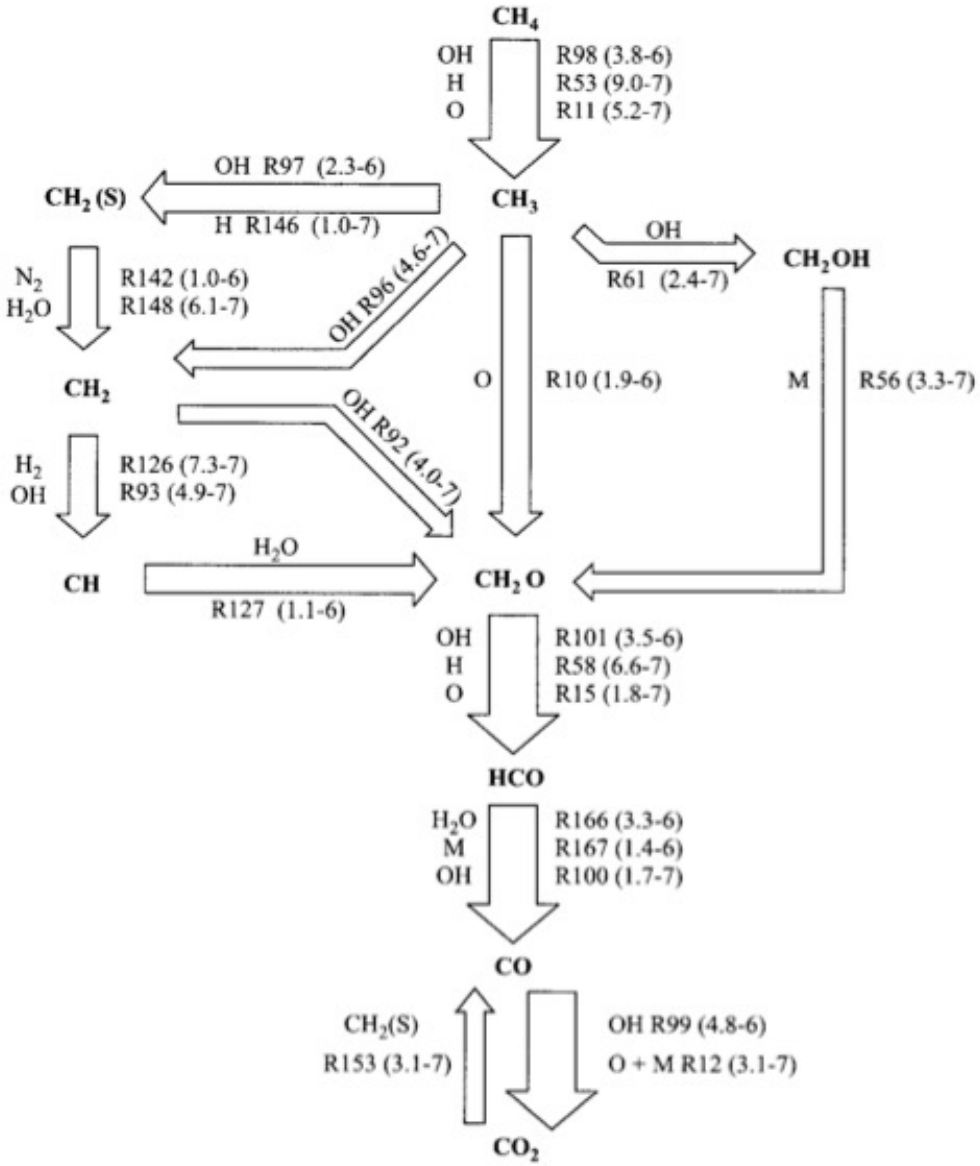


- As [C_2H_4] becomes small, τ becomes small.
- The small reaction order is the culprit.
- Fix: As [C2H4] becomes small, increase reaction order.

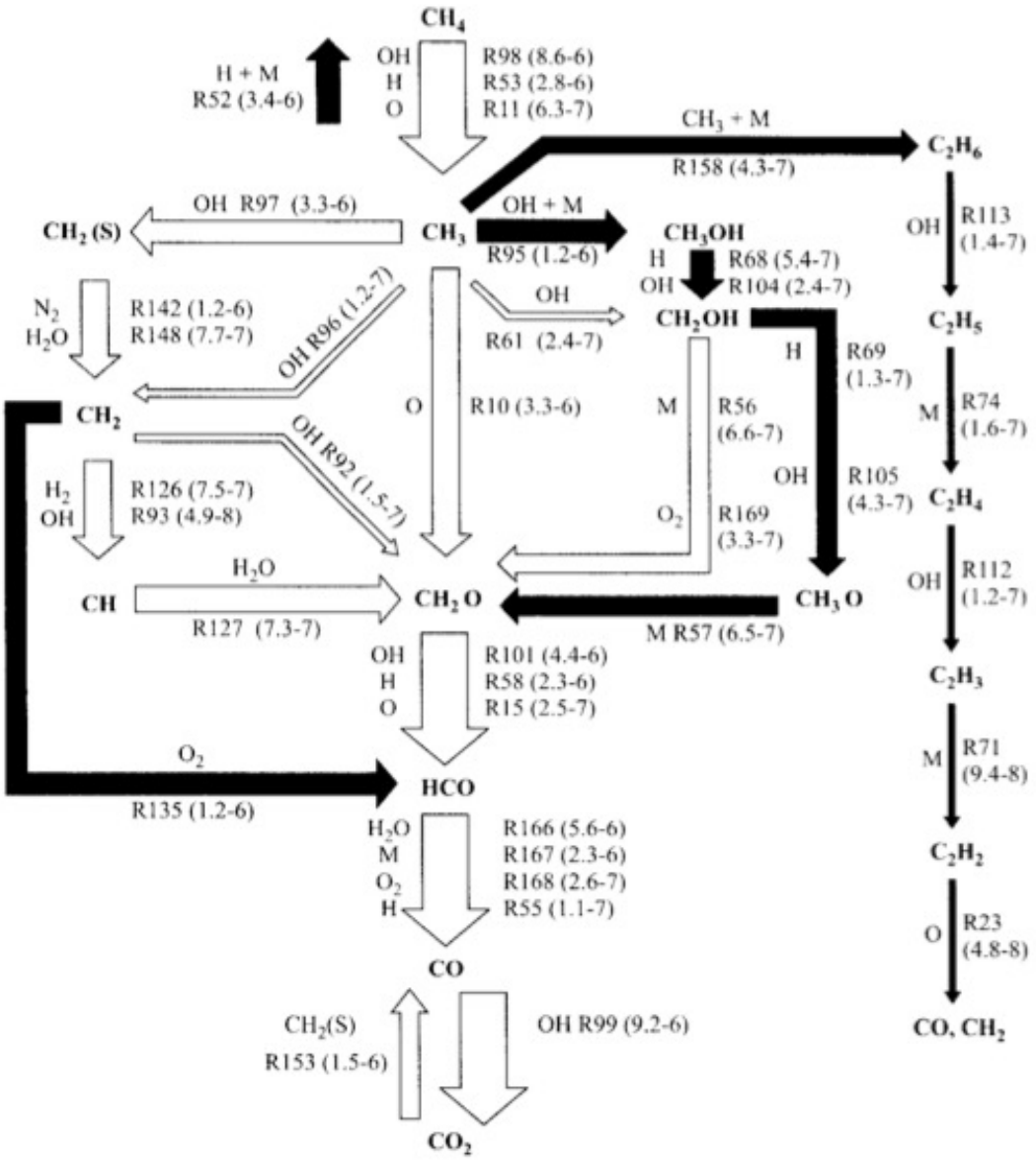
$$\tau_{new} = [C_2H_4]^{0.9[1-\exp(-800Y_{C2H4})]}$$



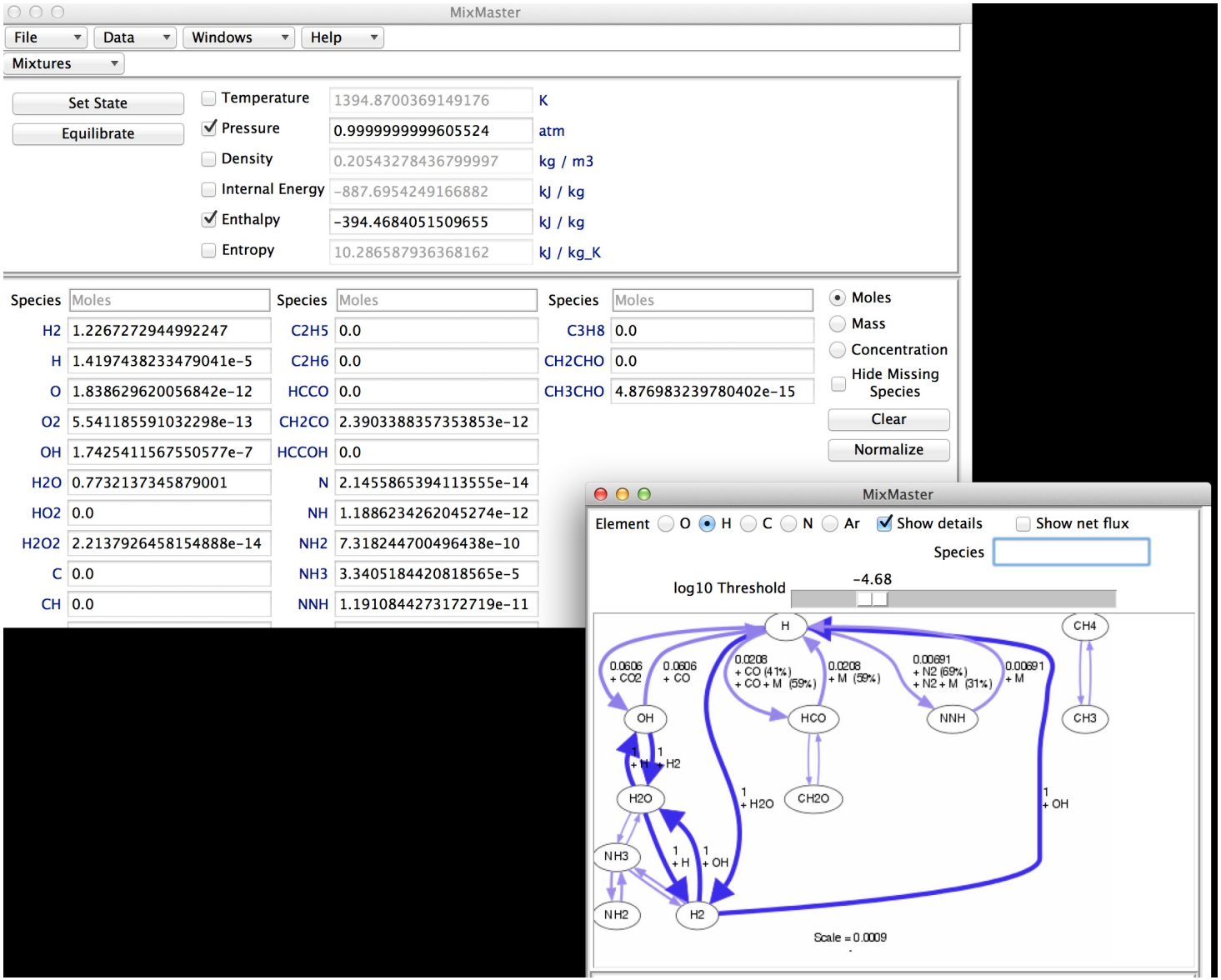
Methane Low Temperature



Methane High Temperature



Mix Master (Cantera)



Complex Fuels

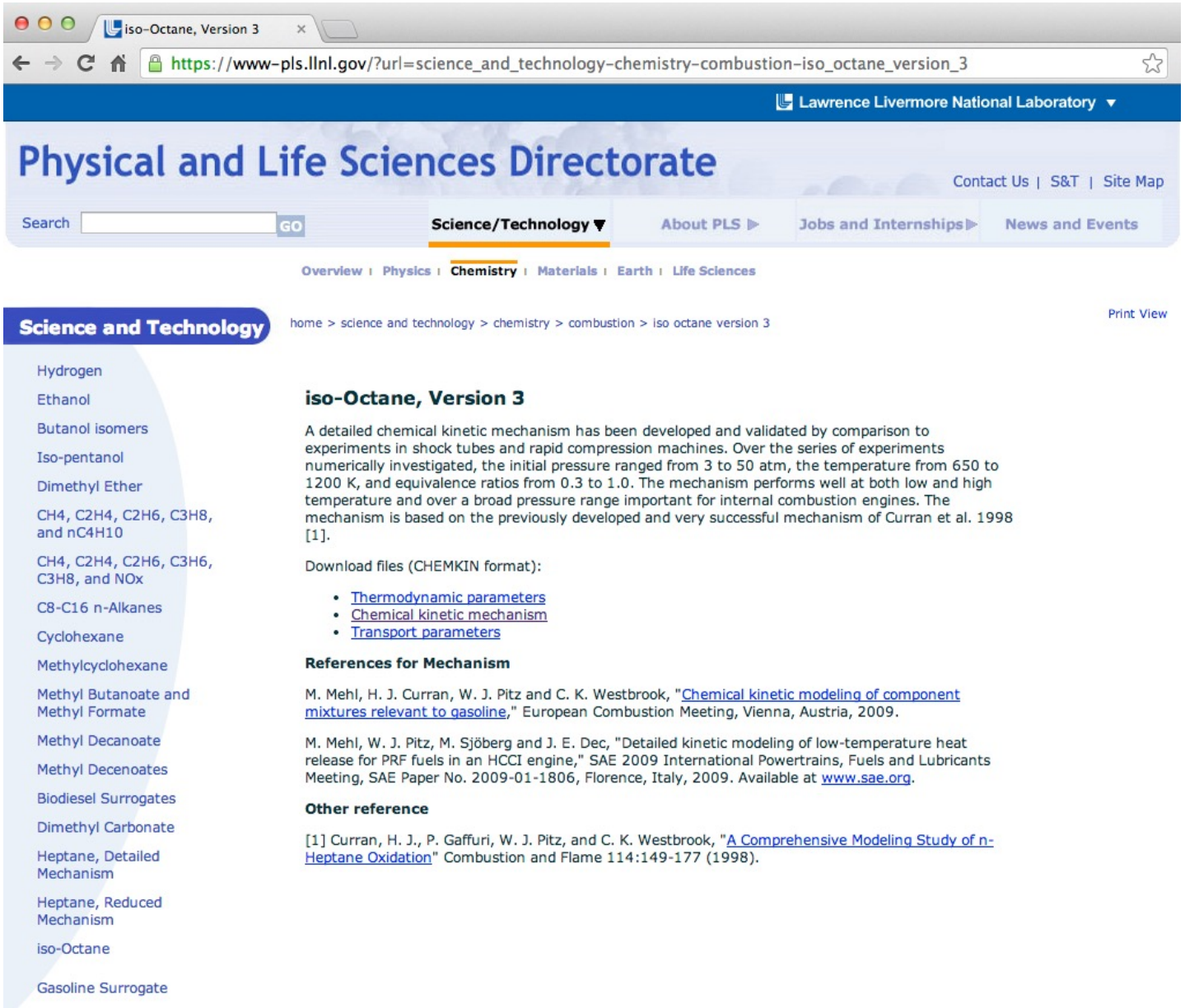
Table 5.3 Chemical kinetic studies targeting real fuel combustion

Target Fuel	Surrogate Blend[1]	Reference	Comment
Natural gas	Methane (CH_4) Ethane (C_2H_6) Propane (C_3H_8)	Dagaut [11]	—
Kerosene (Jet A-1)	*n*-Decane ($C_{10}H_{22}$)	Dagaut [11]	Single-component model fuel
Kerosene (Jet A-1)	74% *n*-Decane ($C_{10}H_{22}$) 15% *n*-Propylbenzene 11% *n*-Propylcyclohexane	Dagaut [11]	207 species and 1,592 reactions
Diesel fuel	36.5% *n*-Hexadecane ($C_{16}H_{24}$) 24.5% Isooctane (C_8H_{18}) 20.4% *n*-Propylcyclohexane 18.2% *n*-Propylbenzene	Dagaut [11]	298 species and 2,352 reactions
JP-8 (Jet fuel)	10% Isooctane 20% Methylcyclohexane (C_7H_{14}) 15% *m*-Xylene (C_8H_{10}) 30% *n*-Dodecane (C_7H_{14}) 5% Tetralin (C_7H_{14}) 20% Tetradecane ($C_{14}H_{30}$)	Cooke *et al.* [12] Violi *et al.* [13] Ranzi *et al.* [14] Ranzi *et al.* [15] Ranzi *et al.* [16]	221 species and 5,032 reactions
Gasoline	Isooctane (neat) (C_8H_{18}) Isooctane (C_8H_{18}) – *n*-Heptane (C_7H_{16})	Curran *et al.* [17] Curran *et al.* [18]	Single-component model fuel and two-component surrogates; 860–990 species and 3,600–4,060 reactions
Gasoline	63–69% (liq. vol.) Isooctane (C_8H_{18}) 14–20% (liq. vol.) Toluene (C_7H_8) 17% (liq. vol.) *n*-Heptane (C_7H_{16}) and 62% (liq. vol.) Isooctane (C_8H_{18}) 20% (liq. vol.) Ethanol (C_2H_5OH) 18% (liq. vol.) *n*-Heptane (C_7H_{16}) and 45% (liq. vol.) Toluene (C_7H_8) 25% (liq. vol.) Isooctane (C_8H_{18}) 20% (liq. vol.) *n*-Heptane (C_7H_{16}) 10% (liq. vol.) Diisobutylene (C_8H_{16})	Andrae *et al.* [19] Andrae [20]	Octane numbers of blends match standard European gasoline.
Biodiesel	Methyl decanoate ($C_{10}H_{22}O_2$, i.e., $CH_3(CH_2)_8COOCH_3$)	Herbinet *et al.* [21]	3,012 species and 8,820 reactions

[1]Compositions given in mole percent unless otherwise noted.

LLNL Mechanisms

google. "llnl mechanisms"



iso-Octane, Version 3

https://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion-iso_octane_version_3

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Print View

- Hydrogen
- Ethanol
- Butanol isomers
- Iso-pentanol
- Dimethyl Ether
- CH4, C2H4, C2H6, C3H8, and nC4H10
- CH4, C2H4, C2H6, C3H6, C3H8, and NOx
- C8-C16 n-Alkanes
- Cyclohexane
- Methylcyclohexane
- Methyl Butanoate and Methyl Formate
- Methyl Decanoate
- Methyl Decenoates
- Biodiesel Surrogates
- Dimethyl Carbonate
- Heptane, Detailed Mechanism
- Heptane, Reduced Mechanism
- iso-Octane
- Gasoline Surrogate

iso-Octane, Version 3

A detailed chemical kinetic mechanism has been developed and validated by comparison to experiments in shock tubes and rapid compression machines. Over the series of experiments numerically investigated, the initial pressure ranged from 3 to 50 atm, the temperature from 650 to 1200 K, and equivalence ratios from 0.3 to 1.0. The mechanism performs well at both low and high temperature and over a broad pressure range important for internal combustion engines. The mechanism is based on the previously developed and very successful mechanism of Curran et al. 1998 [1].

Download files (CHEMKIN format):

- Thermodynamic parameters
- Chemical kinetic mechanism
- Transport parameters

References for Mechanism

M. Mehl, H. J. Curran, W. J. Pitz and C. K. Westbrook, "Chemical kinetic modeling of component mixtures relevant to gasoline," European Combustion Meeting, Vienna, Austria, 2009.

M. Mehl, W. J. Pitz, M. Sjöberg and J. E. Dec, "Detailed kinetic modeling of low-temperature heat release for PRF fuels in an HCCI engine," SAE 2009 International Powertrains, Fuels and Lubricants Meeting, SAE Paper No. 2009-01-1806, Florence, Italy, 2009. Available at www.sae.org.

Other reference

[1] Curran, H. J., P. Gaffuri, W. J. Pitz, and C. K. Westbrook, "A Comprehensive Modeling Study of n-Heptane Oxidation" Combustion and Flame 114:149-177 (1998).