INTRODUCTION

What is combustion?
Why combustion?
Statistics
Chemical Kinetics and Modeling
Global fuel properties
Composition of Fuels

EXPERIMENTAL TECHNIQUES FOR KINETIC MODELS ASSESSMENT

Introduction
Shock-tubes and rapid compression machines
Flow reactors: Tubular Flow Reactors and Stirred Reactors
Flames
Some conclusions and perspectives

MODELING

Modeling: General information
Temperature dependencies of elementary reactions
Pressure dependencies
Kinetic analyses
Sensitivity analyses
Pressure/Temperature dependencies and reaction pathways
Oxidation at low-T
Pyrolysis and high-T oxidation
Single-fuel vs. multi-fuel components

4/ POLLUTANTS: NOx formation (thermal, prompt, N₂O, NNH) and reduction (SNCR, reburning)
   NOx formation
   NOx reduction
   UHC and soot
   Effect of trace species on ignition: NOx, ozone

5/ COMMERCIAL FUELS, SURROGATES, BIOFUELS
   Gasoline
   Diesel
   Jet fuel
   Biofuels
Part 1
INTRODUCTION

La Guerre du Feu, Jean-Jacques Annaud, 1981
Where is combustion?
**What is combustion? (1/2)**

The **oxidation** of a fuel, ultimately leads to the formation of carbon dioxide, water, and heat in the case of organic fuels (e.g. hydrocarbons).

Other definition: an exothermic redox reaction between a fuel (reductant) and an oxidant (e.g., oxygen from air)

Incomplete combustion yields UHC and soot. ⚠️

NOx resulting from nitrogen oxidation can also be released. ⚠️
What is combustion? (2/2)

Combustion involves chemical reactions, thermochemistry, kinetics, heat and mass transfer, radiation...

The overall/global chemical equation, e.g. $2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O}$, $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$, is a mass balance that does inform on the reaction pathways to products.

**Equivalence ratio and excess air:**

$$\varphi = \frac{[\text{Fuel}]/[\text{O}_2]}{[\text{Fuel}]/[\text{O}_2]} \text{ at stoichiometry}$$

$$\lambda = 1/\varphi$$

$2 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O}$ \hspace{1cm} $\varphi=1$ and $\lambda = 1$ (stoichiometric mix)

$3 \text{H}_2 + \text{O}_2 = 2 \text{H}_2\text{O} + \text{H}_2$ \hspace{1cm} $\varphi>1$ and $\lambda < 1$ (fuel-rich, excess of fuel, some left over)

$2 \text{H}_2 + 2 \text{O}_2 = 2 \text{H}_2\text{O} + \text{O}_2$ \hspace{1cm} $\varphi<1$ and $\lambda > 1$ (fuel-lean, excess of oxygen, some left over)

The combustion of methane involves a long sequence of elementary reactions (*initiation, propagation, branching, and termination*). They involve stable species and labile species (*atoms, radicals*). These reactions proceed with reaction rates ranging from slow (e.g., $\text{RH} + \text{O}_2$) to very fast (R+R’).
**Why combustion?**

Transport accounts for ca. 20% of the total global primary energy consumed, ca. 23% of CO$_2$ emissions, ca. 7 billion tons of CO$_2$, ca. from livestock farming.

> 99.9% Transport is powered by I.C. engines (land and marine) and air transport by GT.

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**Table 2**

<table>
<thead>
<tr>
<th>Aircraft</th>
<th>Maximum Take-off Weight (MTOW), kg</th>
<th>Volume of fuel, liters</th>
<th>Weight of fuel$^a$, kg</th>
<th>Energy content of fuel (ECF)$^b$, MWh</th>
<th>Weight of battery pack with the same ECF$^b$ (WBP), kg</th>
<th>WBP/MTOW</th>
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<td>Embraer 135 [41]</td>
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<td>5146</td>
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<td>Airbus A320 Neo [42]</td>
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The global demand for transport energy is ca. 105 TWh of liquid fuel energy/day (**38,325 TWh/year**)

In 2016 the consumption of wind and solar energy together reached **1,292 TWh/year**.

In 2016 the consumption of electricity reached almost **25,000 TWh/year**. ⚠️
World electricity production

From Global Energy Statistical Yearbook 2018
What do we burn?

IEA, 2009

98% transport fuels are oil-derived
Primary Energy Use

2010 World marketed energy use
500 quadrillion Btu (12,603 Mtoe)

Renewables 10%
Nuclear 6%
Coal 26%
Liquids 35%
Natural Gas 23%

Source: U.S. Energy Information Administration
(Report #DOE/EIA-0484(2010))

Figure 2. World marketed energy use by fuel type

Source: U.S. Energy Information Administration
(Report #DOE/EIA-0484(2010))
Sustainability:

We need to burn cleaner

We need more efficient combustion (energy production)
EU regulations

HCCI (Homogeneous Charge Compression Ignition)
Sources of particulates: industry, agriculture, air and ground transportation (soot, tires, brakes), homes, wild fires, volcanoes, soil erosion and hurricanes/tornados, sea salts…
PARTICULATES

Concentration of particulate matter with an aerodynamic diameter of 10 μm or less (PM10) in nearly 3000 urban areas*, 2008–2015

The boundaries and names shown and the designations used on this map do not imply the expression of any opinion whatsoever on the part of the World Health Organization concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries. Dotted and dashed lines on maps represent approximate border lines for which there may not yet be full agreement.

Data Source: World Health Organization
Map Production: Information Evidence and Research (IER)
World Health Organization
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See also https://www.conserve-energy-future.com/causes-and-effects-of-particulate-matter.php
PARTICULATES and health

- Pollen
- Mold Spores
- House Dust Mite Allergens
- Bacteria
- Cat Allergens
- Viruses
- Heavy Dust
- Settling Dust
- Suspended Atmospheric Dust
- Cement Dust
- Fly Ash
- Oil Smoke
- Smog
- Tobacco Smoke
- Soot
- Gas Molecules

Size in µm

Combustion Institute Summer School, Princeton June 2021
PARTICULATES and health

Source: produits.xpair.com

N.B. PM1 (< 1 μm or 1000 nm)
PARTICULATES from i.c. engines

PARTICULATES

TEM image of soot particles generated by CAST

Source: [http://www.sootgenerator.com](http://www.sootgenerator.com)

Source: H. Bockhorn (1986)
GHG: CO₂

http://www.worldclimatereport.com
GHG: CO₂

Fossil Fuel Usage per Capita

(world’s 20 largest populations)

Annual Tonnes Carbon Emitted / Person

United States
Russia
Germany
Japan
France
Iran
Mexico
Thailand
Turkey
China
Egypt
Brazil
Indonesia
India
Philippines
Viet Nam
Pakistan
Nigeria
Bangladesh
Ethiopia
GHG

Transport 14%

Rest of Global GHGs 86%

Road 72%

Domestic Air 5%
Int’l Air 6%
Int’l Marine 8%
Other 8%

REDUCE CO$_2$ EMISSIONS

[1] China’s target reflects gasoline vehicles only. The target may be higher after new energy vehicles are considered.
Chemical Kinetics and Modeling

\[ \text{RH} + \text{OH} \rightleftharpoons \text{R} + \text{H}_2\text{O} \]
\[ \text{R} + \text{O}_2 \rightleftharpoons \text{RO}_2 \]
\[ \text{RO}_2 + \text{NO} \rightleftharpoons \text{RO} + \text{NO}_2 \]
\[ \text{HO}_2 + \text{NO} \rightleftharpoons \text{OH} + \text{NO}_2 \]
\[ 2\text{RO}_2 \rightleftharpoons 2\text{RO} + \text{O}_2, \ldots \]
\[ \text{RO}_2 + \text{HO}_2 \rightleftharpoons \text{RO}_2\text{H} + \text{O}_2, \ldots \]
\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}; \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 \]
Experimental data ↔ Model

Constrain the model by using

- **Global parameters:** Ignition delays (initiation reactions, R+O₂)
  Burning velocities (H fluxes)

- **Detailed information:** Species concentrations (~ all processes)

### Initiations:
- RH ⇌ R + H
- RH ⇌ R’ + R”
- RH + O₂ ⇌ R + HO₂

### Propagations:
- RH + X ⇌ R + HX (X= H, O, OH, HO₂, CH₃, HCO, …)

### Terminations:
- R + H ⇌ RH
- R’ + R” ⇌ RH

- **Different types of ‘reactors’:** ST, PF, PSR, Flames (laminar premixed, opposed flow), RCM, engines
Global vs. detailed chemistry

$H_2 + \frac{1}{2} O_2 = H_2O$: mass balance; misrepresents reaction pathways

Global Rate = $A T^n \exp\left(-\frac{E}{RT}\right) [\text{Fuel}] [O_2]^{\frac{1}{2}}$

In reality, many more reactions:

\begin{align*}
H + H + M &\rightarrow H_2 + M \\
O + O + M &\rightarrow O_2 + M \\
O + H + M &\rightarrow OH + M \\
H_2 + O_2 &\rightarrow 2 OH \\
H + OH + M &\rightarrow H_2O + M \\
H_2 + O &\rightarrow 2 OH \\
OH + OH &\rightarrow O + H_2O
\end{align*}

\begin{align*}
H_2 + O_2 &\rightarrow HO_2 + H \\
H + O_2 &\rightarrow OH + O \\
H_2 + OH &\rightarrow H_2O + H \\
H_2 + O &\rightarrow OH + H \\
H + O_2 &\rightarrow HO_2 \\
2 HO_2 &\rightarrow H_2O_2 + O_2 \\
H_2O_2 &\rightarrow 2 OH
\end{align*}

The value of $k_i$ indicates how fast the reaction can proceed

Such sets of reactions constitute a “chemical kinetic reaction mechanism”
Kinetics

Forward reaction \[ A + B \rightarrow C + D \]

Rate = \(-d[A]/dt = \k_+ [A][B] = A_+ T^n \exp[-\frac{E}{RT}][A][B]\)

Reverse reaction \[ C + D \rightarrow A + B \]

Rate = \(-d[C]/dt = \k_- [C][D] = A_- T^n' \exp[-\frac{E'}{RT}][C][D]\)

Equilibrium constant computed from thermochemistry \[ K_{eq} = \frac{\k_+}{\k_-} \]

\(k_+ \) and/or \(k_- \) are determined experimentally or computed

K can be obtained in tabulations (JANAF, NASA …)
Thermodynamics

As H approaches F₂, the F-F bond extends and electron density moves from that F-F bond into the newly forming F-H bond. This involves an increase in potential energy.

1\textsuperscript{st} law: The energy U of an isolated system is constant
\[ dU = dQ + dW; \quad Q = \text{heat absorbed by the system}; \quad w = \text{work done on system} \]

2\textsuperscript{nd} law: Mechanical energy can be transferred completely into heat but heat cannot be transformed completely into mechanical energy
\[ dS \geq dQ/T; \quad S = \text{entropy} \]
\[ dS = dQ_{\text{rev}}/T \text{ and } dS > dQ_{\text{irrev}}/T \]

3\textsuperscript{rd} law: The entropy of a perfectly crystalline substance at 0\textdegree K is 0
\[ S = 0 \text{ at } T = 0\textdegree K \left( \lim_{T \to 0} (S) = 0 \right) \]
Thermodynamics

Gibbs energy: \( G = H - TS \)

At constant \( T \), \( \Delta G = \Delta H - T\Delta S \)

Equilibrium occurs at minimum \( G \) (at constant \( T, P \))

Equilibrium constant: \( \Delta G^\circ = -RT \ln(K) \) \(^\circ\) refers to the standard state

Heat capacities (\( p \) at constant pressure; \( v \) at constant volume):

\[ C_v = \frac{\partial U}{\partial T}_v \quad C_p = \frac{\partial U}{\partial T}_p \quad C_p = C_v + R \text{ (ideal gas)} \]

\[ H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p \,dT \]

\[ \Delta_r H(T_2) = \Delta_r H(T_1) + \int_{T_1}^{T_2} \Delta_r C_p \,dT \]
Gibbs Energy \((G)\) indicates the spontaneity of a reaction

\[ G = H - TS \]

\(\Delta_r G < 0\) for spontaneous reaction

\(\Delta_r G > 0\) for non-spontaneous reaction
Global fuels properties

Cetane number, Octane number

Cool flame  High-T

S.I. engines: ON=100 for iso-octane and ON=0 for n-heptane (C₈H₁₈)
C.I. engines: CN=100 for n-hexadecane (C₁₆H₃₄) and CN=0 for 1-methylnaphtalene (C₁₁H₁₀)

piston damaged by strong knock (LLNL)

Fuel concentration vs. temperature

CN=0 : ON>100

Concentration

Temperature/K

500  ~650  ~800

NTC
**FIGURE 6** Carbon monoxide and carbon dioxide maximum mole fraction at low temperature, as a function of RON.

*Dagaut et al., CST 103:1-6, 315-336 (1994).*
S.I. engines: ON=100 for iso-octane and ON=0 for n-heptane ($C_8H_{18}$)

C.I. engines: CN=100 for n-hexadecane ($C_{16}H_{34}$) and 0 for 1-methylnaphtalene ($C_{11}H_{10}$)
### Hydrocarbons

#### Paraffins

<table>
<thead>
<tr>
<th>Name</th>
<th>CN</th>
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<td>2-Méthylpentane</td>
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## Hydrocarbons

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<tr>
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<td>90,9</td>
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</tr>
<tr>
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<td>98,0</td>
<td>83,0</td>
</tr>
<tr>
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<td>77,1</td>
</tr>
<tr>
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</tr>
<tr>
<td>Hept-2-ène</td>
<td>73,4</td>
<td>68,8</td>
</tr>
</tbody>
</table>
Composition of Fuels

- **NG**: methane + higher alkanes (ca. C\textsubscript{8})
- **LPG**: region-dependent; C\textsubscript{3}–C\textsubscript{4} alkanes and alkenes
- **Gasoline**: C\textsubscript{4}–C\textsubscript{12} hydrocarbons. Mixture of paraffins (alkanes), olefins (alkenes), cycloalkanes (naphthenes), aromatics
- **Kerosene (Jet A-1 fuel)**, standard AFQRJOS (Aviation Fuel Quality Requirements for Jointly Operated Systems): C\textsubscript{6}–C\textsubscript{16} hydrocarbons. Mixture of paraffins (alkanes), cycloalkanes (naphthenes), aromatics and <2% alkenes.
- **Diesel**: C\textsubscript{6}–C\textsubscript{28} hydrocarbons. Mixture of paraffins (alkanes), olefins (alkenes), cycloalkanes (naphthenes), aromatics, naphteno-aromatics
- **Additives**: EtOH, ETBE
GC analysis of a NG sample

Retention time / min

Oxygen
Nitrogen
CO₂
Air
Carbon Dioxide
Ethane
Propane
i-Butane
n-Butane
i-Pentane
n-Pentane

(https://www.thermofisher.com/)
GC analysis of a US LGP sample

Retention time / min

1. Methane
2. Ethane
3. Ethylene
4. Propane
5. Cyclopropane
6. Propylene
7. Isobutane
8. Acetylene
9. n-Butane
10. Propadiene
11. trans-2-Butene
12. 1-Butene
13. Isobutylene
14. cis-2-Butene
15. Isopentane
16. n-Pentane
17. Propyne
18. 1,3-Butadiene
19. 1-Pentene

(https://gassite.com/)
GC analysis of a gasoline sample

Retention time / min

(https://www.sigmaaldrich.com)
GC analysis of a Jet fuel sample

(Dagaut et al., CNRS)
GC analysis of a GtL sample

(Egolfopoulos et al., USC)
GC analysis of a diesel fuel sample

(Dagaut et al., CNRS)
GC analysis of a B20 diesel fuel sample

1. Nonane (C9)
2. Decane (C10)
3. Undecane (C11)
4. Dodecane (C12)
5. Tridecane (C13)
6. Tetradecane (C14)
7. Pentadecane (C15)
8. Hexadecane (C16)
9. Heptadecane (C17)
10. Octadecane (C18)
11. Nonadecane (C19)
12. Eicosane (C20)
13. Heneicosane (C21)
14. Docosane (C22)
15. Hexadecanoate (C16:0)
16. Tricosanoate (C23)
17. Tetracosane (C24)
18. Pentacosane (C25)
19. Octadecanoate (C18:0)
20. Oleate (C18:1)
21. Linoleate (C18:2)
22. Linolenate (C18:3)
23. Eicosanoate (C20:0)

(https://www.sigmaaldrich.com)
Summary

What is combustion? The oxidation of a fuel, ultimately leads to the formation of carbon dioxide, water, and heat in the case of organic fuels (e.g. hydrocarbons). Other definition: an exothermic redox reaction between a fuel (reductant) and an oxidant (e.g., oxygen from air). Incomplete combustion yields UHC and soot. NOx resulting from nitrogen oxidation can also be released.

Why combustion? Transport accounts for ca. 20% of the total global primary energy consumed, ca. 23% of CO₂ emissions, ca. 7 billion tons of CO₂, ca. from livestock farming. > 99.9% Transport is powered by I.C. engines (land and marine) and air transport by GT.

Chemical Kinetics and Modeling. Feed and feedback: Experimental data ↔ Model. Global parameters: Ignition delays (initiation reactions, R+O₂), Burning velocities (H fluxes) vs. Detailed information: Species concentrations (~ all processes). Different types of ‘reactors’: ST, PF, PSR, Flames (laminar premixed, opposed flow), RCM, engines; provide complementary data.

Global fuel properties: Cetane number, Octane number (S.I. engines: ON=100 for iso-octane and ON=0 for n-heptane; C.I. engines: CN=100 for n-hexadecane and CN=0 for 1-methylnaphtalene.

Composition of Fuels. NG: methane + higher alkanes (ca. C₈); LPG: region-dependent; C₃–C₄ alkanes and alkenes; Gasoline: C₄–C₁₂ hydrocarbons. Mixture of paraffins (alkanes), olefins (alkenes), cycloalkanes (naphthenes), aromatics; Kerosene (Jet A-1 fuel), C₆–C₁₆ hydrocarbons. Mixture of paraffins (alkanes), cycloalkanes (naphthenes), aromatics and <2% alkenes; Diesel: C₆–C₂₈ hydrocarbons. Mixture of paraffins (alkanes), olefins (alkenes), cycloalkanes (naphthenes), aromatics, naphteno-aromatics; Additives: EtOH, ETBE.
Part 2

EXPERIMENTAL TECHNIQUES FOR KINETIC MODELS ASSESSMENT
1. Introduction

Chemical kinetic reaction mechanisms for combustion, either hand-written or automatically generated, rely on experimental data obtained over a large range of conditions. However, combustion is a complex, generally exothermic, phenomenon involving strongly coupled chemical processes (reaction kinetics) and physical processes (diffusion and heat transfer). Thus, in order to better assess chemical kinetic reaction mechanisms, it is preferable to design experiments were the complexity of physical processes is minimized and the accuracy of the data is maximized.

This is the case for ideal reactors such as plug-flow reactors, perfectly stirred reactors, and shock-tubes.

In practice, the experiments should be performed under conditions were ideal reactor models can be used, e.g., operating a JSR under highly diluted conditions, under near-isothermal conditions).
Indeed, such kinetic reaction mechanisms need to be validated through extensive comparison of modeling predictions and experimental results obtained under well-defined conditions. A wide range of experimental facilities can provide such data which are usually described as ‘global’ and ‘detailed’. By combining data obtained from several techniques and conditions, one can check their consistency and use them to constrain chemical kinetic reaction mechanisms.

**Global data** include ignition delay times which can be obtained using shock-tubes, rapid compression machines, or plug-flow reactors, and laminar burning velocities or flame speeds determined using several types of experiments such as spherical flames in combustion vessels, Bunsen burners, stagnation-flow flames, counter-flow flames, or heat-flux burners. Ignition experiments are particularly useful for probing initiation and termination reactions and reactions of molecular oxygen with radicals whereas they are usually less useful for probing the kinetics of propagation reactions involving atoms and radicals.
Initiations reactions:

\[
\text{RH} (+\text{M}) \rightleftharpoons \text{R} + \text{H} (+\text{M}), \quad \text{RH} (+\text{M}) \rightleftharpoons \text{R'} + \text{R''} (+\text{M}), \quad \text{and} \quad \text{RH} + \text{O}_2 \rightleftharpoons \text{R} + \text{HO}_2
\]

Propagation reactions:

\[
\text{RH} + \text{X} \rightleftharpoons \text{R} + \text{HX} (\text{X}= \text{H, O, OH, HO}_2, \text{CH}_3, \text{HCO, ...}) \text{ and radicals reactions, e.g., }
\]

\[
\text{R} + \text{O}_2 \rightleftharpoons \text{R} + \text{HO}_2, \quad \text{R} \rightleftharpoons \text{olefin} + \text{R'}, \quad \text{R} \rightleftharpoons \text{olefin} + \text{H}
\]

Termination reactions:

\[
\text{R} + \text{H} (+\text{M}) \rightleftharpoons \text{RH} (+\text{M}) \text{ and } \text{R'} + \text{R''} (+\text{M}) \rightleftharpoons \text{RH} (+\text{M}).
\]
The paramount importance of H-atoms has been recognized long ago (Tanford, C., J. Chem. Phys., 1947. 15(7): p. 433-439). Burning velocity experiments are very valuable for probing reactions involving H-atoms such as RH (+M) ⇌ R + H (+M) and R (+M) ⇌ product + H (+M). Burning velocities are also very sensitive to the main branching reaction in combustion, i.e., H+O₂ ⇌ OH + O

Detailed data are mostly concentration profiles of stable and unstable chemical species observed during the oxidation and combustion of fuels. Many reactors in conjunction with sampling methods and analytical techniques have been used to acquire such data.

Analytical techniques are often used after gas sampling performed using a range of probes (e.g., low-pressure, cooled, molecular beam) or traps (cold trap, bubblers, traps containing absorbents). These probes should stop chemical reactions and transfer a chemical sample to appropriate analyzers without changing its composition. This assumption needs to be verified. Low-pressure probes reduce reactions rates by lowering molecular concentrations and temperature after gas expansion.

Cooled probes reduce reaction rates which are exponentially temperature-dependent, according to the Arrhenius equation.

Probes are responsible for disturbance of the reaction medium (flow, temperature) which can result in additional complications for interpreting the experimental results.
Many cool traps can be used to collect the condensible compounds at the temperature of the trap (water ice: 273 K; CO₂ dry ice: 194.65 K; liquid nitrogen: 77.2 K). The use of liquid nitrogen traps oxygen (O₂ boiling temperature = 90.2 K) and requires particular care to prevent hazards.

Nowadays, the most popular experimental techniques used are flow reactors (jet-stirred reactors, tubular flow reactors), burner stabilized laminar flames (premixed low-pressure flames, opposed flow diffusion flames), and shock-tubes. These techniques by themselves are useful because they cover a wide range of conditions (temperature, pressure, equivalence ratio, initial concentrations, residence time, recirculation rate) allowing to probe the complexity of combustion chemical kinetics. But this is through their coupling to a large range of analytical techniques that one can acquire the data needed to validate detailed kinetic combustion models.
Among these **analytical techniques**, some are very popular whereas others are less frequently used:

Gas chromatography (with thermal conductivity detector, flame ionization detector, mass spectrometry), molecular-beam mass spectrometry, Fourier transform infrared spectrometry are commonly used. They are commercially available, reliable, and easy to use.

Other **spectroscopy techniques** are also used in laboratory experiments. They are mostly used to measure radicals, atoms, and unstable molecular species in the UV or the infrared. Recent coupling of synchrotron-sourced photoionization with mass spectrometry allowed very detailed probing of oxidation and combustion processes. Several mass spectrometry techniques are used in laboratory experiments. They mostly differ by the use of different types of mass separation (time-of-flight, quadrupole, ion trap, Orbitrap®), and ionization mode (electronic, chemical, photonic).

By combining the above-mentioned laboratory experiments, one can cover a very broad range of conditions relevant to practical applications such as internal combustion engines and gas turbines.
By combining shock-tubes and RCM experiments, one can probe fuels ignition under internal combustion engine conditions. The measurements of burning velocities and flame structures are limited to about 10 bar. Whereas individual reactor experiments have limited operating ranges, by combining them, one can provide detailed data over almost the entire range of pressure and temperature pertinent to I.C. engines and GT.
2. Shock-tubes and rapid compression machines

Shock-tubes and RCM are **batch reactors** which can provide both global and detailed combustion data, i.e., ignition delay times and speciation.

These techniques have been used for several decades. In 1890, Vieille started using compression driven shock tubes (Vieille, P., Comptes Rendus de l’Académie des Sciences, 1890. 111 p. 639-641).

In 1906, Falk used a RCM to determine ignition temperatures (Falk, K.G., J. Am. Chem. Soc., 1906. 28 p. 1517).

2.1 Ignition data from RCM and ST.

RCM are limited to the investigation of relatively long ignition delays (5–100’s ms) at moderate-T, c.a. 1000 K, and to P < 100 bar, shock-tubes can operate over a wider range of P (up to 100’s bar) and to very high-T (1000’s K) where ignition delays are rather short (ca. 1–100’s ms).

Experimental (symbols) and modeled (lines) ignition delay times for a φ = 0.5 NG/air mix measured using a RCM (open symbols) and a shock-tube (closed symbols) at 8–10 atm (black) and 19–20 atm (red). From Sung, C.J. and H.J. Curran, Using rapid compression machines for chemical kinetics studies. Progress in Energy and Combustion Science, 44: p. 10, 2014.
However, modelers must be aware of a complication when trying to combine ignition data obtained in a shock-tube and a RCM. At first, they can look irreconcilable. In fact, it is necessary to consider facility-dependent effects before combining ignition delay times measured in shock-tubes and RCMs.

These have been described with great details in several publications and have been reviewed recently (Sung, C.J. and H.J. Curran, PECS, 2014. 44: p. 1-18).

Up to now, a large set of data is available for the ignition of fuels ranging from hydrogen to practical fuels such as jet fuels or biodiesel (Dagaut, P., et al., CNF, 2014. 161(3): p. 835-847; Ramirez-Lancheros, H.P., et al., CNF, 2012. 159(3): p. 996-1008). These data have been extensively used to propose detailed and simple kinetic models.
2.2 Species measurements from ST and RCM.

Whereas speciation in shock-tubes has received much attention (studies concern both oxidation and pyrolysis), a more limited database is available from RCM experiments.


Hanson and co-workers have recently reported laser-absorption-based measurements in shock-tubes of time-histories of reactants, small-radicals, stable intermediates, and combustion products:
Such data are particularly useful for improving kinetic reactions schemes. This is also true for data coming from single-pulse shock-tube experiments with gas-sampling and GC analyses (Sivaramakrishnan, R. et al., PROCI, 2005. 30(1): p. 1165-1173):

Toluene oxidation at $\phi = 1$ and 610 bar in a shock-tube. (●) Experimental data $C_6H_5CH_3$; (▲) Expt. CO; (□) KBG model $C_6H_5CH_3$; (◇) KBG model CO; (○) STB model $C_6H_5CH_3$; (△) STB model CO; (⋯) fit to KBG model predictions; and (—) fit to STB model predictions. From Sivaramakrishnan, R., R.S. Tranter, and K. Brezinsky, A high pressure model for the oxidation of toluene. Proceedings of the Combustion Institute, 30(1), p. 1169, 2005
More recent developments:

A miniature with high-repetition rate shock-tube was recently introduced by Tranter (Tranter, R.S. and P.T. Lynch, Rev. Sci. Instr., 2013. 84(9): p. 094102) who used it to probe pyrolysis chemistry of dimethyl ether at high temperature (1400 –1700 K) and high pressure (3 –16 bar) with a tunable synchrotron-generated photoionization time-of-flight mass spectrometer (Lynch, P.T. et al., Analytical Chemistry, 2015. 87(4): p. 2345-2352). This new set-up opens up new horizons for chemical kinetics.

Data obtained with shock-tubes have been extensively used to propose detailed and simple kinetic models for the oxidation of fuels ranging from hydrogen to large hydrocarbons and practical fuels (gasoline and jet fuel, Zhu, Y. et al., in 53rd AIAA Aerospace Sciences Meeting. 2015; Li, Y., Ph.D., School of Chemistry. 2017, Nat. Univ. of Ireland: Galway; Javed, T. et al., CNF, 2017. 185(Sup. C): p. 152-159).

**Advantages:**

Can be run with very little fuel compared to flames and reactors experiments.

A wide range of operating conditions, in terms of $P$, $T$, and $\phi$, is covered by combining these techniques.

**Limitations/weaknesses:**

Batch reactor experiments are time consuming because they involve mixture preparation, pumping after each ignition experiment, replacement of the shock-tube diaphragm (needing disassembling / reassembling).

Also, pressure history must be well characterized to allow accurate kinetic modeling.
3. Flow reactors: Tubular Flow Reactors and Stirred Reactors

Flow reactors are particularly useful for measuring the concentration of reactants, intermediates species, and final products of fuels oxidation or pyrolysis or interaction of fuels with other species, e.g., NOx, SOx, CO$_2$, H$_2$O.

They usually operate at temperatures below 1500 K and pressure less than 50 bar.

They are particularly useful for studying the low-T oxidation chemistry of fuels. In most of the experiments, high fuel dilution (100–1000’s ppm) is used to avoid flame occurrence and large temperature gradients. Nevertheless, experiments are also performed with higher initial fuel concentrations (1–few mole %).
Whereas in **tubular flow reactors**, ideally called plug-flow reactors (PFRs), one can observe chemical reactions along the reactor axis; in jet-stirred reactors the chemical composition is ideally homogeneous. Flow reactors are usually heated by external ovens. Temperature measurements are of great importance for running accurate modeling. In tubular reactors, this means that measurements must be made along the reactors axis.

In **JSR**, temperature homogeneity is usually verified along the reactor main axis and measurements used as input in isothermal perfectly stirred reactor model. Compared to flame experiments, flow reactors are not limited to flammability limits. As shock-tubes, they allow studying fuel-lean oxidation to pyrolysis. Although this is not very common, tubular-flow reactors operating under plug-flow conditions can be used to determine ignition delays, as presented in Section 3.2.
3.1 Species measurements.


![Diagram of a tubular flow reactor](image)


Whereas most of the currently used PRFs use conventional analytical instruments (e.g., GC, GC-MS, FTIR) to probe the chemistry, molecular-beam mass spectrometry and tunable synchrotron VUV photoionization have been introduced recently (Zhang, T.C. et al., J. Phys. Chem. A, 2008. 112(42): p. 10487-10494), opening new horizons for the understanding and validation of chemical kinetic reaction mechanisms.
Several **jet-stirred reactor** (JSR) geometries have been used (spherical, hemispherical, toroidal, near-conical), but the most popular design is a spherical reactor of less than 50 cm$^3$. This technique potentially allows operation over a wide range of residence time (from few milliseconds to several seconds), depending on the reactor geometry (David, R. and D. Matras, Can. J. Chem. Eng., 1975. 53(3): p. 297-300).


Composition homogeneity was shown to be easier to achieve.

*Picture of a fused-silica JSR used at CNRS Orléans. Stirring is provided by 4 injectors. With this reactor, one can operate from 40 ms to 3s.*
These reactors have been used to provide useful data for modeling the pyrolysis and oxidation of a wide range of fuels, i.e. hydrogen, ammonia, carbon monoxide, syngas, hydrocarbons, oxygenates, and complex fuels such as gasoline, jet-fuels, Diesel-fuels, synthetic fuels, and biodiesel.

Comparison of experimental data obtained from the JSR oxidation of (a) Jet A-1 (closed symbols) and GtL (open symbols) and (b) CtL (closed symbols) and GtL jet fuel (open symbols) at $\phi = 1.0$, 10 bar, and a mean residence time of 1 s. From Dagaut, P., CNF, 2014, 161(3), p. 840.


Recent results have been obtained through the combination of JSRs and high resolution mass spectrometry (Photoionization-MBMS and APCI-Orbitrap MS). They demonstrate that currently accepted reaction schemes for hydrocarbons oxidation are missing reaction pathways leading to the formation of highly oxygenated molecules.

Mass spectra of intermediates with the molecular formula of $C_7H_{10}O_x$ ($x=0-4$). (a) and (b) are for JSR-1 PI-MBMS measurements at $T=530$ K and $600$ K, respectively. Photon energy is 9.6 eV. (c) is for JSR-2 APCI-OTMS measurements at 535 K. (d) is for CFR engine APCI-OTMS measurements. From Wang, Z.D. et al., Combustion and Flame, 187, Supporting information, p.S5, 2018.
Experimental setup

Positive HESI ionization
M + H⁺ => MH⁺

Negative HESI ionization
MH => H⁺ + M⁻

Dagaut et al., MCS 2019
Dagaut et al., MCS 2019
Quantitative measurements using cavity ring-down spectroscopy in the near-IR of HO$_2$ and H$_2$O$_2$ were reported recently (Djehiche, M. et al., JACS, 2014. 136(47): p. 16689-16694; Le Tan, N.L. et al., Fuel, 2015. 158: p. 248-252). The gas mixtures were sampled with a wide angle fused silica nozzle, the tip being located 5 mm inside the reactor. The CRDS cell was kept at low-P (0.3 to 10 mbar), while operating the JSR at 1 atm.

![Graph showing HO$_2$ concentration profile measured by CRDS during the oxidation of 5000ppm of dimethyl ether in a JSR at an equivalence ratio of 0.5 and a mean residence time of 1.5s. The data (symbols) are compared to simulations using three literature mechanisms. From Le Tan, N.L., M. Djehiche, C.D. Jain, P. Dagaut, and G. Dayma,. Fuel, 158, p. 250, 2015.](image)

HO$_2$ concentration profile measured by CRDS during the oxidation of 5000ppm of dimethyl ether in a JSR at an equivalence ratio of 0.5 and a mean residence time of 1.5s. The data (symbols) are compared to simulations using three literature mechanisms. From Le Tan, N.L., M. Djehiche, C.D. Jain, P. Dagaut, and G. Dayma,. Fuel, 158, p. 250, 2015.
JSR and PFR have been combined at MIT (Lam, F.W. et al., Symp. (Int.) Combust., 1989. 22(1): p. 323-332) to allow probing combustion chemistry over a wider range of residence times. The original design was further modified at NIST by Lenhert and Manzello.


Flow reactors advantages:

Operating temperature range and the possibility to investigate pyrolysis to oxidation, whereas flame studies are much more limited.

Reactors are particularly useful for gaining insights into reaction products and intermediates through the use of advanced detection and/or quantification techniques.

Numerous analytical techniques are used after gas sampling achieved using a range of probes for stopping chemical reactions and transferring a chemical sample to the appropriate analyzers. Also, one should be aware of possible complications such as surface reactions.

Flow reactors disadvantages:

Can operate over limited temperature, pressure, and residence time ranges. This is due to material range of use and reachable flow rates.

Experiments need much larger fuel quantities compared to shock-tube and RCM experiments. The quantification of intermediate species by photoionization remains limited due to unknown photoionization efficiency difficult to compute using current theoretical methods.
3.2 Ignition data from PFR

Ignition delays can also be determined using PFRs. Recently an experimental setup was designed for this purpose (Wada, T. et al., CTM, 2013. 17(5): p. 906-936). The 1st-stage ignition is observed as a temperature increase of a few degrees in the reactor. After the first-ignition, strong heat loss to the reactor wall reduces the temperature and stops chemical reactions. The 1st-stage ignition is determined based on the distance between fuel injection and the location of the first T-rise and the flow rate in the reactor.

This set-up was successfully used for measuring first-stage ignition delays of biofuels:

\[
\tau_g \text{ [ms]} = \frac{1}{k} \left( \frac{1}{T} \right)
\]

4. Flames

Laminar flames are used to obtain both global (laminar burning velocity) and detailed (spatial speciation or flame structure) data usable for validating kinetic models. Experiments are currently performed over a wide range of pressure, from ca. 0.04 to 60 bar.

Burning velocities have been obtained from ca. 0.1 to 60 bar whereas flame structures are available up to ca. 10 bar.

Major improvements of the methods have been made over the years, allowing the acquisition of very valuable data for kinetic modelers over a very wide range of conditions and for many fuels (Ranzi, E. et al., PECS, 2012. 38(4): p. 468-501; Egolfopoulos, F.N. et al., PECS, 2014. 43: p. 36-67).
4.1 Burning velocities

The laminar flame speed is defined as the propagation speed of a steady, laminar, one-dimensional, planar, stretch-free, and adiabatic flame. It is an important fundamental property of a flammable mixture, being a measure of its reactivity, diffusivity, and exothermicity. It constitutes an important validation target for kinetic models and a key parameter in turbulent combustion.
Burning velocity can be extracted from a range of experimental configurations, e.g., soap bubble method, flames in tubes, flat flame burner method, conical flames (Bunsen type), heat flux method, spherical flames in constant volume chamber, and stagnation flame/opposed-flow method:

\[ S_u = V_u \sin \alpha \]

Determination of the burning velocity \( S_u \) by applying the cone angle method \( (S_u=V_u \sin \alpha) \).

Spherical flames in constant volume chamber:

<table>
<thead>
<tr>
<th>0 ms</th>
<th>3.3 ms</th>
<th>5 ms</th>
<th>6.7 ms</th>
<th>8.3 ms</th>
<th>10 ms</th>
</tr>
</thead>
</table>

Shadowgraphs of the temporal evolution of an ethyl propanoate/air flame front at $P = 1$ bar, $T_u = 423$ K and $\phi = 0.9$. The temporal increase of the flame radius is used to compute the stretched laminar burning velocity. The unstretched burning velocity is obtained after extrapolation to zero-stretch using proposed methods in the literature. From Dayma, G., F. Halter, F. Foucher, C. Mounaim-Rousselle, and P. Dagaut, Laminar Burning Velocities of C(4)-C(7) Ethyl Esters in a Spherical Combustion Chamber: Experimental and Detailed Kinetic Modeling. Energy & Fuels, 26(11), p. 6670, 2012.
Nowadays spherical flames in constant volume chamber and stagnation flame/opposed-flow method are the most widely used.


High pressure and temperature conditions are hardly reachable using Bunsen flames, counter-flow flames or heat flux burner. Most of the results reported at elevated pressures were obtained with spherical expanding flames. One limitation of this method comes from the fact that the spherical flame surface is changing during propagation inducing stretch effects which must be accounted for using extrapolation methods. Until the work of Wu and Law (Symp. (Int.) Combust., 1985. 20(1): p. 1941-1949), undetermined stretch effects led to lots of scatter in measurements.

Burning velocities for simple to complex fuels have been published. An example of such results is given here for the combustion of synthetic jet-fuels.

4.2 Species measurements.


These techniques have been reviewed recently ([Egolfopoulos, F.N. et al., PECS, 2014. 43: p. 36-67]). Samples are extracted from the flame using a probe and sent to analyzers (gas chromatography, mass spectrometry).

Molecular beam-mass spectrometry has been used extensively.

Schematic of a low-pressure McKenna burner experimental set-up. Gases from the flame are sampled through a fused-silica probe (picture) into a time-of-flight mass spectrometer where chemicals are photo-ionized by synchrotron-generated vacuum-ultraviolet radiation. From Taatjes, C.A. et al. Physical Chemistry Chemical Physics, 10(1), p. 22, 2008.
Fused-silica probe can cause significant perturbations to the flame, making difficult to model and interpret the experiments, as demonstrated in a recent study by Hansen et al. ([CNF, 2017. 181: p. 214-224]).

Also, the use of a thermocouple for measuring temperature profiles in the flame can alter the flow fields and temperature profiles ([Skovorodko, P.A. et al., CTM, 2013. 17(1): p. 1-24; CNF, 2012. 159(3): p. 1009-1015]), although these effects are small compared to sampling probe perturbations.

Nevertheless, a wide range of fuels have been studied in flames. Examples of concentration profiles of C$_2$–C$_{14}$ species measured in low-pressure premixed flames of toluene next.
Experimental (symbols) and simulated (lines) mole fraction profiles of acetylene (C$_2$H$_2$), propargyl (C$_3$H$_3$), vinylacetylene (C$_4$H$_4$), cyclopentadienyl (C$_5$H$_5$), benzene (A1), benzyl (A1CH$_2$), phenylacetylene (A1C$_2$H), ethylbenzene (A1C$_2$H$_5$), indenyl (C$_9$H$_7$), indene (C$_9$H$_8$), naphthalene (A2) and phenanthrene (A3) in the premixed flames of toluene at five equivalence ratios (0.75 to 1.75). The data were obtained by MB-MS with photoionization by synchrotron-sourced vacuum-UV radiation. From Yuan, W.et al.,CNF 162(1), p. 36, 2015.
Temperature profiles in the present ethylene/O\textsubscript{2}/Ar flame. Open diamonds and open circles represent the T\textsubscript{pert} and T\textsubscript{unpert} profiles, respectively. Shadows represent the scaled T\textsubscript{pert} profiles considering the uncertainties of maximum T\textsubscript{pert} values.

Measured (symbol) and predicted (lines) mole fraction profiles of C\textsubscript{2}H\textsubscript{5}OOH in the present ethylene/O\textsubscript{2}/Ar flame. The solid and dashed lines represent the predicted results with the T\textsubscript{pert} and T\textsubscript{unpert} profiles, respectively. Shadows represent the predicted results considering the uncertainties of T\textsubscript{pert}.

ROP analysis with the Hashemi model* by using the T\textsubscript{pert} profile at (a) d = 0 mm (T = 555 K) and (b) d = 0.98 mm (T = 755 K).


Whereas time-of-flight mass spectrometry with photoionization by synchrotron-generated vacuum-ultraviolet radiation are very useful for detecting intermediate species, the differentiation between isomers can be difficult when photoionization energies are too close.

Dias et al. (CST, 2004. 176(9): p. 1419-1435) have introduced a useful method consisting of a conventional EI-MBMS setup where a portion of the sample is sent to a GC-MS through a capillary, allowing separation of isomers of stable products that could not be differentiated based on their ionization energies or mass.

Other workers also combined EI-MBMS measurements with GC-MS measurements to get better characterization of isomers (Bourgeois, N. et al., PROCI, 2017. 36(1): p. 383-391).
5. Some conclusions and perspectives

The most common experiments for kinetic mechanism assessment have been presented. It was shown that shock-tube and RCM are very useful for determining fuel ignition properties but also to measure chemical products. Recent advances in CFD modeling of RCM (Bourgeois, N. et al., PROCI, 2017. 36(1): p. 383-391; CNF, 2018. 189: p. 225-239) are expected to facilitate the use of RCM ignition data for kinetic model validation. Tubular flow reactors and jet-stirred reactors are commonly used. Their coupling with advanced analytical techniques is able to provide unique data for kinetic models assessment. However, current limitations due to unknown photoionization efficiency for many intermediates must be addressed, possibly through the use of advanced theoretical methods. Flames can also provide valuable data in terms of burning velocities and speciation, although, limiting perturbations by conventional large sampling probes remains a major challenge for future work.

Summary

Shock-tubes and rapid compression machines. Shock-tube and RCM are very useful for determining fuel ignition properties but also to measure chemical products.

Flow reactors: Tubular Flow Reactors and Stirred Reactors. Commonly used. Their coupling with classical (GC, MS, FTIR) and advanced analytical techniques is able to provide unique data for kinetic models’ assessment.

Flames. They provide valuable data in terms of burning velocity and speciation. Beware of probe perturbations.
Part 3
MODELING
Modeling: General information

Need accurate kinetics, thermochemistry, and transport data

Use inputs from theory and measurements and also estimations by analogy, tabulations

Need accurate data that are used to constrain the model
Modeling

Chemkin computer package.

Kinetic reaction mechanism with modified Arrhenius equation, $k = A T^b \exp(-E/RT)$; $k(P,T)$.

Reaction mechanism with strong hierarchical structure.

The core-mechanism is $\text{H}_2/\text{O}_2$ ($\text{H}$, $\text{O}$, $\text{OH}$, $\text{HO}_2$, $\text{H}_2\text{O}_2$, $\text{O}_2$, $\text{O}_3$, $\text{H}_2$).
Modeling: Hierarchical structure of chemical kinetic schemes
Modeling: Size of chemical kinetic schemes

## Modeling: reaction scheme

**REACTIONS** \( k = A \cdot T^n \cdot \exp(-E/RT) \)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A (cc, molecule, second)</th>
<th>E (cal, molecule)</th>
<th>Ref</th>
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<td>H+ H+ M = H2+ M</td>
<td>7.310E+17</td>
<td>-1.00</td>
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<tr>
<td>O+ O+ M = O2+ M</td>
<td>1.140E+17</td>
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<td>6260.0</td>
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Modeling: thermochemistry

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<td>O2</td>
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<td></td>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>

(a_{1,k}...a_{7,k}) to calculate thermodynamics over the range 1000 - 5000 K and (a_{8,k}...a_{14,k}) over the range 300 - 1000 K.

\[
\frac{C_{r,k}}{R} = a_{1,k} + a_{2,k} T + a_{3,k} T^2 + a_{4,k} T^3 + a_{5,k} T^4; \quad \frac{H^0}{RT} = a_{1,k} + a_{2,k} \frac{T}{2} + a_{3,k} \frac{T^2}{3} + a_{4,k} \frac{T^3}{4} + a_{5,k} \frac{T^4}{5} + a_{6,k} \frac{1}{T}
\]

\[
\frac{S^0}{R} = a_{1,k} \ln T + a_{2,k} T + a_{3,k} \frac{T^2}{2} + a_{4,k} \frac{T^3}{3} + a_{5,k} \frac{T^4}{4} + a_{7,k}
\]

\[
G^0 = H^0 - TS^0; \quad \Delta G^0 = G^0_{prod} - G^0_{react} = -RT \ln(K_p); \quad \frac{K_c}{k_{rev}} = K_p \left( \frac{P}{RT} \right) \sum v_{prod} - \sum v_{react}
\]

Combustion Institute Summer School, Princeton June 2021
Modeling: transport

<table>
<thead>
<tr>
<th>SPECIES</th>
<th>STRUCTURE</th>
<th>L-J POTENTIAL WELL</th>
<th>L-J COLLISION DIAM.</th>
<th>DIPOLE MOMENT</th>
<th>POLARIZABILITY</th>
<th>ROTATIONAL RELAX COLL NBR</th>
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<td>2.750</td>
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<td>H2O2</td>
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<td>107.400</td>
<td>3.458</td>
<td>0.000</td>
<td>0.000</td>
<td>3.800</td>
</tr>
</tbody>
</table>

Structure: 0= atom; 1= linear; 2= non-linear


Modeling: Temperature dependencies of elementary reactions

In 1889, Svante Arrhenius proposed the Arrhenius equation from direct observations of the plots of rate constants vs. temperature: \[ k = A \exp\left(-\frac{E_a}{RT}\right) \]

Later, modified Arrhenius expression: \[ k = A T^n \exp\left(-\frac{E_a}{RT}\right) \]
\[ \text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$

\[ T / \text{K} \]

\[ 1000 \quad 500 \quad 300 \quad 200 \]

\[ -12 \quad -11 \quad -10 \quad -9 \]

\[ \log(\frac{k}{\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}}) \]

-12 -11 -10 -9

0 1 2 3 4 5

$10^3 T^{-1} / \text{K}^{-1}$

-10

-9

-8

-7

-6

-5

-4

-3

-2

-1

0

1

2

3

4

5

\[ \text{Friswell and Sutton 1972} \]
\[ \text{Hochanadel et al. 1972} \]
\[ \text{Peeters and Mahnen 1973} \]
\[ \text{DeMore and Tschuikow-Roux 1974} \]
\[ \text{Burrows et al. 1977} \]
\[ \text{Chang and Kaufaman 1978} \]
\[ \text{Hack et al. 1978} \]
\[ \text{Burrows et al. 1979} \]
\[ \text{DeMore 1979} \]
\[ \text{Hochanadel et al. 1980} \]
\[ \text{Lii et al. 1980} \]
\[ \text{Burrows et al. 1981} \]
\[ \text{Cox et al. 1981} \]
\[ \text{Kuryle 1981} \]
\[ \text{Thrush and Wilkinson 1981} \]
\[ \text{Braun et al. 1982} \]
\[ \text{DeMore et al. 1982} \]
\[ \text{Sridharan et al. 1982} \]
\[ \text{Temps and Wagner 1982} \]
\[ \text{Rozenshtein et al. 1984} \]
\[ \text{Sridharan et al. 1984} \]
\[ \text{Dransfield and Wagner 1987} \]
\[ \text{Keyser 1988} \]
\[ \text{Goodings and Hayhurst 1988} \]
\[ \text{Schwab et al. 1989} \]
\[ \text{Hippler et al. 1990} \]
\[ \text{Hippler et al. 1995} \]
\[ \text{This Evaluation} \]
Modeling: Pressure dependencies

![Graph showing pressure dependencies](image)
$\text{CH}_3 + \text{CH}_3 (+ \text{Ar}) \rightarrow \text{C}_2\text{H}_6 (+ \text{Ar})$

![Graph showing the reaction rate coefficient and Ar concentration for various temperatures.](image)

- Glänzer et al. 1977 ($T = 1350$ K)
- Hippler et al. 1984 ($T = 296$ K)
- Slagle et al. 1988 ($T = 296$ K)
- MacPherson et al. 1985 and Slagle et al. 1988 ($T = 296$ K)
- Slagle et al. 1988 ($T = 577$ K)
- MacPherson et al. 1985 and Slagle et al. 1988 ($T = 577$ K)
- Slagle et al. 1988 ($T = 906$ K)
- MacPherson et al. 1985 and Slagle et al. 1988 ($T = 906$ K)
- Walter et al. 1990 ($T = 200$ K)
- Walter et al. 1990 ($T = 300$ K)
- Hwang et al. 1990 ($T = 1200$ K)
- Hwang et al. 1990 ($T = 1400$ K)
- Du et al. 1996 ($T = 1350$ K)
- Du et al. 1996 ($T = 1523$ K)

This Evaluation
Modeling: Pressure dependencies

Lindemann-Hinshelwood (1/2)

Assume every collision leads to stabilization

\[
\begin{align*}
A + M & \rightarrow A^* + M \quad k_1(T) \\
A^* + M & \rightarrow A + M \quad k_2(T) \\
A^* & \rightarrow \text{product} \quad k_3(T)
\end{align*}
\]

The quasi-steady state approximation (QSSA) for \(A^*\): \(\frac{d[A^*]}{dt}=0\)

Steady state for \([A^*]\): \([A^*] = \frac{k_1 [A] [M]}{(k_2 [M] + k_3)}\)

\[Rate = k_3 [A^*] = \frac{k_3 k_1 [A] [M]}{(k_2 [M] + k_3)} = k_{uni} [A]\]

High Pressure limit ([M] → ∞, k_2 [M] >> k_3):

\[Rate = k_3 [A^*] = \frac{k_3 k_1 [A] [M]}{(k_2 [M] + k_3)} = k_{uni} [A]\]

\[Rate = \frac{k_1 k_3 [A]}{k_2} = k_{uni} [A] \Rightarrow k_{uni} = \frac{k_1 k_3}{k_2}\]
Modeling: Pressure dependencies
Lindemann-Hinshelwood (2/2)

Steady state for \([A^*]\): \([A^*] = k_1 [A] [M] / (k_2 [M] + k_3)\)

\[Rate = k_3 [A^*] = k_3 k_1 [A] [M]/(k_2[M] + k_3) = k_{uni} [A]\]

Low Pressure limit ([M] \(\to 0\), \(k_2 [M] \ll k_3\)):

\[Rate = k_3 [A^*] = k_3 k_1 [A] [M]/(k_2[M] + k_3) = k_{uni} [A]\]

\[Rate = k_1 [A] [M] = k_0 [A]; \Rightarrow k_{uni} = k_1 [M]\]
Troe fitting

\[ k(T,p) = \frac{k_0[M]k^\infty}{k^\infty + k_0[M]} F \]

\[ \log_{10} F = \frac{\log_{10} F_{cent}}{1 + \left[ \frac{\log_{10}(p^*) + c}{N - d(\log_{10}(p^*) + c)} \right]^2} \]

\[ d = 0.14 \]

\[ p^* = \frac{k_0[M]}{k^\infty} \]

\[ c = -0.4 - 0.67 \log_{10} F_{cent} \]

\[ N = 0.75 - 1.27 \log_{10} F_{cent} \]

\[ F_{cent} = (1 - a)\exp\left(-T/T^{**}\right) + a\exp\left(-T/T^*\right) + \exp\left(-T^{**}/T\right) \]
Troes Formalism in CHEMKIN format

\[ F_{cent} = (1 - a) \exp\left(-\frac{T}{T^{**}}\right) + a \exp\left(-\frac{T}{T^{*}}\right) + \exp\left(-\frac{T^{**}}{T}\right) \]

CHEMKIN uses 3- or 4-Troe parameters (in the order: a, T^{***}, T^{*}, T^{**})

\[ \text{OH + OH (+M) = H}_2\text{O}_2 (+M) \ 7.224E+13 -0.37 0.0 !(94BAU/COB) \]

\[ \text{High-Pres rate cst} \]

\[ \text{LOW / 2.211E+19 -0.76 0.0/} \]

\[ \text{low-P rate cst} \]

\[ \text{TROE / 0.5 1.0E+08 1.0e-06/} \]

\[ \text{a, T^{***}, T^{*} (T^{**} not used here)} \]
Modeling: Kinetic analyses

1- Reaction pathways

   How reactions proceed?
   How reactants and intermediates are consumed?
   How products are formed?

ROP(Product1):
   reaction rate (R1)/(sum of reaction rates yielding Product1)

ROC(Product1):
   reaction rate (R1)/(sum of reaction rates consuming Product1)

Net rate of production= (total rate of production) – (total rate of consumption)
What are the important routes for NO-reduction?

Fig. 3. The influence of temperature on the main reaction paths involved in the reduction of NO by propane at 1 atm (\( \varphi = 1.25; \, \tau = 0.12 \, s; \, 1000 \, ppm \) of NO; 2930 ppm of propane). Reactions: \( \text{NH} + \text{NO} \rightleftharpoons \text{N}_2\text{O} + \text{H} \) (16); \( \text{HNO} + \text{H} \rightleftharpoons \text{NO} + \text{H}_2 \) (50); \( \text{NO} + \text{HO}_2 \rightleftharpoons \text{NO}_2 + \text{OH} \) (65); \( \text{NO} + \text{H} + \text{M} \rightleftharpoons \text{HNO} + \text{M} \) (67); \( \text{NO} + \text{HCO} \rightleftharpoons \text{HNO} + \text{CO} \) (68); \( \text{NO}_2 + \text{H} \rightleftharpoons \text{NO} + \text{OH} \) (70); \( \text{CH}_2 + \text{NO} \rightleftharpoons \text{HCN} + \text{OH} \) (90); \( \text{HCCO} + \text{NO} \rightleftharpoons \text{HCNO} + \text{CO} \) (93); \( \text{HCCO} + \text{NO} \rightleftharpoons \text{HCN} + \text{CO}_2 \) (94); \( \text{HCNO} + \text{O} \rightleftharpoons \text{NO} + \text{HCO} \) (96); \( \text{HCNO} + \text{OH} \rightleftharpoons \text{NO} + \text{CH}_2\text{O} \) (97).
How PRF100 reactions pathways are modified by ozone injection?

\[ [O_3] = 0 \]

\[ [O_3] = 10 \text{ ppm} \]

Reaction pathway analysis from rates of consumption (at the bottom) for iso-octane (PRF100) at initial temperature of 800 K, initial pressure of 50 bar and equivalence ratio of 0.3. From Masurier et al. Energy Fuels 2013, 27, 5495–5505.
How reactions pathways are modified by ozone injection?

How reactions pathways are modified by ozone injection?
2-Brute force method and 1st order sensitivity analyses

What is the impact of a variation of a given parameter (e.g., A-factor, \( \Delta H_f \)) on the model predictions?

What reactions influence the prediction of the formation/consumption of the product 1?

Initial \( k \rightarrow [\text{product1}]_0 \)

\( k*\varepsilon \rightarrow [\text{product1}]_+ \)

\( k/\varepsilon \rightarrow [\text{product1}] \).

\[ S = \frac{[\text{product1}]_{\text{ini}} - [\text{product1}]_{\text{mod}}}{[\text{product1}]_{\text{ini}}}; \text{e.g., } [\text{product1}]_{\text{mod}} = \text{conc. after } k_j \times 5: \]
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$k/\varepsilon \Rightarrow [\text{product1}]$.

$S = [\text{product1}]_{\text{ini}}/ [\text{product1}]_{\text{mod}}$; e.g., $[\text{product1}]_{\text{mod}} = \text{conc. after } k_j / 5$

$s = \frac{\partial n_i}{\partial \pi_i}$

$s' = \frac{(\partial n_i/n_i)}{(\partial \pi_i/\pi_i)}$

where $n_i$ is the response of the model and $\pi$ is a model parameter (A-factor, $\Delta H_f$), e.g., $s_{i,j} = (\partial c_i/c_i) / (\partial A_j/A_j)$ for conc. of species in reaction j:
1st order sensitivity analysis

Sensitivity analysis of the present model at $\varphi = 0.35$ (575 K, 1 atm) and $\varphi = 4.0$ (625 K, 1 atm) in JSR oxidation of propanal. From New insights into propanal oxidation at low temperatures: Experimental and kinetic modeling study. X. Zhang et al., Proc. Combust. Inst (2019)
Modeling: Pressure/Temperature dependencies and reaction pathways

Explosion Limits of a $\Phi=1$ H$_2$-O$_2$ Mixture

![Graph showing explosion limits](image-url)
Modeling: Pressure dependencies

Explosion Limits of a $\Phi=1$ H$_2$-O$_2$ Mixture

- $\text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{OH}$
- $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ (3)
- $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$ (2)
- $\text{H}_2 + \text{O}_2 \rightarrow \text{H} + \text{HO}_2$
- $\text{H} + \text{H} + \text{S} \rightarrow \text{H}_2 + \text{S}$ (1)
- $\text{D} \downarrow$ $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$
- Diffusion $\text{D} \sim P^{-1}$

$P$/mBar vs $T$/K

Combustion Institute Summer School, Princeton June 2021
<table>
<thead>
<tr>
<th>REACTIONS  $k=A \times T^n \times \exp(-E/RT)$</th>
<th>A/cc,mole,s</th>
<th>n</th>
<th>E/cal/mol</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H^+ + H^+ \rightarrow H_2^+ + M$</td>
<td>7.310E+17</td>
<td>-1.0</td>
<td>0.0</td>
<td>(BAULCH 76)</td>
</tr>
<tr>
<td>$O^+ + O^+ \rightarrow O_2^+ + M$</td>
<td>1.140E+17</td>
<td>-1.0</td>
<td>0.0</td>
<td>(BAULCH 76)</td>
</tr>
<tr>
<td>$O^+ + H^+ \rightarrow OH^+ + M$</td>
<td>6.200E+16</td>
<td>-0.6</td>
<td>0.0</td>
<td>(DIXON-LEWIS 81)</td>
</tr>
<tr>
<td>$H_2^+ + O_2 \rightarrow OH^+ + OH$</td>
<td>1.700E+13</td>
<td>0.0</td>
<td>47780.0</td>
<td>(MILLER 77)</td>
</tr>
<tr>
<td>$O^+ + H_2 \rightarrow OH^+ + H$</td>
<td>3.870E+04</td>
<td>2.7</td>
<td>6260.0</td>
<td>GRI</td>
</tr>
<tr>
<td>$H^+ + O_2 \rightarrow OH^+ + O$</td>
<td>4.400E+14</td>
<td>-0.12</td>
<td>16812.0</td>
<td>Nicolle 2004</td>
</tr>
<tr>
<td>$H^+ + O_2^+ \rightarrow HO_2^+ + M$</td>
<td>8.000E+17</td>
<td>-0.8</td>
<td>0.0</td>
<td>(WARNATZ 84)</td>
</tr>
<tr>
<td>$H^+ + OH^+ \rightarrow H_2O^+ + M$</td>
<td>8.615E+21</td>
<td>-2.0</td>
<td>0.0</td>
<td>(BAULCH 76)</td>
</tr>
<tr>
<td>$H_2^+ + OH \rightarrow OH^+ + H$</td>
<td>2.161E+08</td>
<td>1.51</td>
<td>3430.0</td>
<td>(MICHAEL 88)</td>
</tr>
<tr>
<td>$H_2O^+ + O = OH^+ + OH$</td>
<td>1.500E+10</td>
<td>1.14</td>
<td>17260.0</td>
<td>(WARNATZ 84)</td>
</tr>
<tr>
<td>$HO_2^+ + OH \rightarrow H_2O^+ + O_2$</td>
<td>2.890E+13</td>
<td>0.0</td>
<td>-497.0</td>
<td>(KEYSER 88)</td>
</tr>
<tr>
<td>$HO_2^+ + O = OH^+ + O_2$</td>
<td>1.810E+13</td>
<td>0.0</td>
<td>-400.0</td>
<td>(JPL 87-41)</td>
</tr>
<tr>
<td>$H^+ + HO_2 \rightarrow H_2^+ + O_2$</td>
<td>4.280E+13</td>
<td>0.0</td>
<td>1411.0</td>
<td>(94BAU/COB)</td>
</tr>
<tr>
<td>$H^+ + HO_2 \rightarrow OH^+ + OH$</td>
<td>1.690E+14</td>
<td>0.0</td>
<td>874.0</td>
<td>(94BAU/COB)</td>
</tr>
<tr>
<td>$H^+ + HO_2 \rightarrow H_2O^+ + O$</td>
<td>3.010E+13</td>
<td>0.0</td>
<td>1721.0</td>
<td>(BAULCH 92)</td>
</tr>
<tr>
<td>$HO_2^+ + HO_2 \rightarrow H_2O_2^+ + O_2$</td>
<td>4.075E+02</td>
<td>3.32</td>
<td>1979.0</td>
<td>(HIPPLER 90)</td>
</tr>
<tr>
<td>$OH + OH (+M) \rightarrow H_2O_2 (+M)$</td>
<td>7.224E+13</td>
<td>-0.37</td>
<td>0.0</td>
<td>(94BAU/COB)</td>
</tr>
<tr>
<td>$H_2O_2^+ + OH \rightarrow HO_2^+ + H_2O$</td>
<td>5.800E+14</td>
<td>0.0</td>
<td>9557.0</td>
<td>(92HIP/TRO)</td>
</tr>
<tr>
<td>$H_2O_2^+ + H = HO_2^+ + H_2$</td>
<td>1.700E+12</td>
<td>0.0</td>
<td>3750.0</td>
<td>(BAULCH 72)</td>
</tr>
<tr>
<td>$H_2O_2^+ + H = H_2O^+ + OH$</td>
<td>1.000E+13</td>
<td>0.0</td>
<td>3590.0</td>
<td>(WARNATZ 84)</td>
</tr>
<tr>
<td>$H_2O_2^+ + O = HO_2^+ + OH$</td>
<td>2.800E+13</td>
<td>0.0</td>
<td>6400.0</td>
<td>(ALBERS 71)</td>
</tr>
</tbody>
</table>
Modeling: Hydrocarbons oxidation

Fuel concentration vs. temperature

Cool flame  High-T

NTC
Modeling: Multiple cool flames

Modeling

Ignition diagram for fuel concentration within the flammable range. Moving from A to B can yield to strong ignition.
Modeling

- Olefin + HO₂ → R
- RH + X → XH
- RO₂ → R' + Olefin
  H + Olefin
- RO₂ → RO + RO + O₂
- ROOH → RO + OH
- RO + OH → RO₂
- Cyclic Ether + OH → O₂
- OOQOOH → HOOQ'OOH
- OOQ'OOH + OH → OQ'O + OH
- Decomposition → OQ'O + OH
- Cyclic Ether + OH → O₂
Modeling

\[
\begin{align*}
\text{CH}_3\text{OCH}_3 + &\overset{(\text{OH})}{\longrightarrow} \text{CH}_3\text{OCH}_2. \\
\text{CH}_2\text{O} + &\text{CH}_3. \overset{\text{CH}_3\text{OCH}_2.}{\longrightarrow} \overset{\text{CH}_3\text{OCH}_2\text{OO}.}{\longrightarrow} \overset{\text{CH}_2\text{OCH}_2\text{OOH}}{\longrightarrow} 2 \text{CH}_2\text{O} + \overset{\text{(OH)}}{\longrightarrow} \\
\text{O}_2 \overset{\text{CH}_2\text{OCH}_2\text{OOH}}{\longrightarrow} \overset{\text{O}_2}{\overset{\text{OOCH}_2\text{OCH}_2\text{OOH}}{\longrightarrow} \overset{\text{HOOCH}_2\text{OCHO}}{\longrightarrow} \overset{\text{OCH}_2\text{OCHO}}{\longrightarrow} \overset{\text{(OH)}}{\longrightarrow} \text{CH}_2\text{O} + \text{OCHO.}
\end{align*}
\]
Modeling

Branching reactions: multiplication of the number of active species

**Low-T**

$$R + O_2 \rightarrow RO_2; \ RO_2 \rightarrow \text{QOOH} \rightarrow O_2\text{QOOH} \rightarrow >3 \text{ radicals}$$

**Medium-T**

$$H + O_2 + M \rightarrow HO_2 + M; \ RH + HO_2 \rightarrow R + H_2O_2; \ H_2O_2 + M \rightarrow 2 \ OH + M$$

$$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$$

**High-T**

$$H + O_2 \rightarrow \text{OH} + O$$
Korcek mechanism

γ-Ketohydroperoxides decompose to a carbonyl and a carboxylic acid
Waddington mechanism

\[ R-\text{CH}=\text{CH}-R' + \text{OH} \rightarrow R-\text{CH}-\text{CH}-R' + \text{OH} \]

\[ R-\text{CH} - \text{CH} - R' \rightarrow R-\text{CH} - \text{CH} - R' \]

\[ \text{OH} + R-\text{CH} \rightarrow R-\text{CH} \]
More reaction pathways at low-T

Example: di-n-propyl ether oxidation

\[ R + O_2 \rightleftharpoons RO_2 \rightleftharpoons QOOH \]

\[ QOOH + O_2 \rightleftharpoons OOQOOH \]

\[ OOQOOH \rightleftharpoons HOOPOOH \] (alternative H-transfer, not from HC-OOH)

3\(^{rd}\) \(O_2\) addition:

\[ HOOPOOH + O_2 \rightleftharpoons (HOO)_2POO \rightleftharpoons (HOO)_2P'OOH \rightarrow OH + (HOO)_2P'=O \ (C_6H_{12}O_6) \]

4\(^{th}\) \(O_2\) addition:

\[ (HOO)_2P'OOH + O_2 \rightleftharpoons (HOO)_3P''OO \rightleftharpoons (HOO)_3P''OOH \rightarrow OH + (HOO)_3P''=O \ (C_6H_{12}O_8) \]

5\(^{th}\) addition …
Dipropyl ether oxidation
Reaction pathways to ketohydroperoxides

HOMs formation mechanism
OOQOOH ⇌ HOOPPOOH (alternative H-transfer, not from HC-OOH)

3rd O₂ addition:
HOOPPOOH + O₂ ⇌ (HOO)₂P'O'O + (HOO)₂P'O'O => OH + (HOO)₂P'O'O (C₆H₁₂O₆)

4th O₂ addition:
(HOO)₂P'O'O + O₂ ⇌ (HOO)₃P'O'O + (HOO)₃P'O'O => OH + (HOO)₃P'O'O (C₆H₁₂O₆)

Korcek mechanism

Major KHP isomer:

UHPLC analyses

Propanoic acid

Dagaut et al., MCS 2019
Reaction pathways to highly oxygenated products considered in atmospheric chemistry (a) and recently extended reaction pathways in combustion (b)

(a)

\[
\begin{align*}
\text{C}_{10}H_{16} & \xrightarrow{-H} \text{C}_{10}H_{15} & \xrightarrow{+O_2} \text{C}_{10}H_{15}O_2 & \xrightarrow{\text{RO}_2} \text{C}_{10}H_{15}O_3 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_5 & \xrightarrow{+O_2} \text{C}_{10}H_{15}O_7 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_9 & \xrightarrow{+O_2} \text{C}_{10}H_{15}O_{11} \\
\text{Limonene} & & (\text{R}^\prime) & (\text{RO}_2^\prime) & (\text{HOOQ}^\prime(\text{OH})\text{OO}^\prime) & (\text{HOO}_2\text{P}(\text{OH})\text{OO}^\prime) & (\text{HOO}_2\text{P}^\prime(\text{OH})\text{OO}^\prime) & (\text{HOO}_4\text{P}^\prime(\text{OH})\text{OO}^\prime) \\
\text{RO}_2 & \xrightarrow{+O_2} \text{C}_{10}H_{15}O_3 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_4 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_6 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_8 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_{10} \\
\text{Q}^\prime\text{OH} & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_2 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_4 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_6 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_8 & \xrightarrow{\text{H-shift}} \text{C}_{10}H_{15}O_{10} \\
\end{align*}
\]

(b)

\[
\begin{align*}
\text{R}^\prime & \xrightarrow{+O_2} \text{ROO}^\prime & \xrightarrow{\text{H-shift}} \text{QOOH} & \xrightarrow{+O_2} \text{OOQOQOH} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} & \xrightarrow{+O_2} \text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} \\
\text{ROO}^\prime & \xrightarrow{\text{H-shift}} \text{QOOH} & \xrightarrow{+O_2} \text{OOQOQOH} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} & \xrightarrow{+O_2} \text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} \\
\text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} & \xrightarrow{+O_2} \text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} & \xrightarrow{+O_2} \text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} & \xrightarrow{\text{H-shift}} \text{HOOQ'O} \\
\end{align*}
\]
Pyrolysis and high-T oxidation

```
              ALCANE
             +H, O, OH -H2, OH, H2O

                    RADICAL ALKYLE
                   +M -ALCENE

                        RADICAL ALKYLE
                       +M -ALCENE

                           H, CH3, C2H5
```
n-Octane pyrolysis

In R': radical position #1 => ethylene
In R': radical position #2 => propene
In R': radical position #3 => butene, heptane
In R': radical position #4 => pentene, hexene
# Bonds dissociation energies

<table>
<thead>
<tr>
<th>Bond ⇋</th>
<th>Bond</th>
<th>Bond-dissociation energy at 298 K (kcal/mol) ⇋ (kJ/mol) ⇋ (eV/Bond) ⇋</th>
</tr>
</thead>
<tbody>
<tr>
<td>I–I</td>
<td>Iodine</td>
<td>36 151 1.57</td>
</tr>
<tr>
<td>Br–Br</td>
<td>Bromine</td>
<td>46 192 1.99</td>
</tr>
<tr>
<td>Cl–Cl</td>
<td>Chlorine</td>
<td>58 242 2.51</td>
</tr>
<tr>
<td>O=CH₂</td>
<td>Formaldehyde</td>
<td>179 748 7.75</td>
</tr>
<tr>
<td>N≡N</td>
<td>Nitrogen</td>
<td>226 945 9.79</td>
</tr>
<tr>
<td>O–H</td>
<td>in α-tocopherol (an antioxidant)</td>
<td>77 323 3.35</td>
</tr>
<tr>
<td>O–H</td>
<td>in methanol</td>
<td>105 440 4.56</td>
</tr>
<tr>
<td>O=CO</td>
<td>Carbon dioxide</td>
<td>127 532 5.51</td>
</tr>
<tr>
<td>C–Cl</td>
<td>in CH₃Cl</td>
<td>83.7 350 3.63</td>
</tr>
<tr>
<td>C–C</td>
<td>in typical alkane</td>
<td>83–90 347–377 3.60–3.90</td>
</tr>
<tr>
<td>H–H</td>
<td>Hydrogen</td>
<td>104 436 4.52</td>
</tr>
<tr>
<td>O=O</td>
<td>Oxygen</td>
<td>119 498 5.15</td>
</tr>
<tr>
<td>C≡O</td>
<td>Carbon monoxide</td>
<td>257 1077 11.16</td>
</tr>
<tr>
<td>H–F</td>
<td>Hydrogen fluoride</td>
<td>136 569 5.90</td>
</tr>
<tr>
<td>O–H</td>
<td>in water</td>
<td>119 497 5.15</td>
</tr>
</tbody>
</table>
# Bonds dissociation energies

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond</th>
<th>Bond-dissociation energy at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3\text{C–H}$</td>
<td>Methyl $\text{C–H}$ bond</td>
<td>105 kcal/mol, 439 kJ/mol, 4.550 eV/Bond</td>
</tr>
<tr>
<td>$\text{C}_2\text{H}_5\text{–H}$</td>
<td>Ethyl $\text{C–H}$ bond</td>
<td>101 kcal/mol, 423 kJ/mol, 4.384 eV/Bond</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{CH–H}$</td>
<td>Isopropyl $\text{C–H}$ bond</td>
<td>99 kcal/mol, 414 kJ/mol, 4.293 eV/Bond</td>
</tr>
<tr>
<td>$(\text{CH}_3)_3\text{C–H}$</td>
<td>$t$-Butyl $\text{C–H}$ bond</td>
<td>96.5 kcal/mol, 404 kJ/mol, 4.187 eV/Bond</td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{NCH}_2\text{–H}$</td>
<td>$\text{C–H}$ bond $\alpha$ to amine</td>
<td>91 kcal/mol, 381 kJ/mol, 3.949 eV/Bond</td>
</tr>
<tr>
<td>$(\text{CH}_2)_3\text{OCH–H}$</td>
<td>$\text{C–H}$ bond $\alpha$ to ether</td>
<td>92 kcal/mol, 385 kJ/mol, 3.990 eV/Bond</td>
</tr>
<tr>
<td>$\text{CH}_3\text{C(=O)CH}_2\text{–H}$</td>
<td>$\text{C–H}$ bond $\alpha$ to ketone</td>
<td>96 kcal/mol, 402 kJ/mol, 4.163 eV/Bond</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CH–H}$</td>
<td>Vinyl $\text{C–H}$ bond</td>
<td>111 kcal/mol, 464 kJ/mol, 4.809 eV/Bond</td>
</tr>
<tr>
<td>$\text{HCC–H}$</td>
<td>Acetylenic $\text{C–H}$ bond</td>
<td>133 kcal/mol, 556 kJ/mol, 5.763 eV/Bond</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{–H}$</td>
<td>Phenyl $\text{C–H}$ bond</td>
<td>113 kcal/mol, 473 kJ/mol, 4.902 eV/Bond</td>
</tr>
<tr>
<td>$\text{CH}_2\text{CHCH}_2\text{–H}$</td>
<td>Allylic $\text{C–H}$ bond</td>
<td>89 kcal/mol, 372 kJ/mol, 3.856 eV/Bond</td>
</tr>
<tr>
<td>$\text{C}_6\text{H}_5\text{CH}_2\text{–H}$</td>
<td>Benzyl $\text{C–H}$ bond</td>
<td>90 kcal/mol, 377 kJ/mol, 3.907 eV/Bond</td>
</tr>
<tr>
<td>$\text{H}_3\text{C–CH}_3$</td>
<td>Alkane $\text{C–C}$ bond</td>
<td>83–90 kcal/mol, 347–377 kJ/mol, 3.60–3.90 eV/Bond</td>
</tr>
<tr>
<td>$\text{H}_2\text{C=CH}_2$</td>
<td>Alkene $\text{C=C}$ bond</td>
<td>~170 kcal/mol, ~710 kJ/mol, ~7.4 eV/Bond</td>
</tr>
<tr>
<td>$\text{HCC=CH}$</td>
<td>Alkyne $\text{C≡C}$ triple bond</td>
<td>~230 kcal/mol, ~960 kJ/mol, ~10.0 eV/Bond</td>
</tr>
</tbody>
</table>
## Bonds dissociation energies vs. kinetic parameters

<table>
<thead>
<tr>
<th>Reaction</th>
<th>A</th>
<th>n</th>
<th>E/cal/mol</th>
<th>bond, BDE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄ = CH₃ + H</td>
<td>1.168E+33</td>
<td>-5.43</td>
<td>108732.0</td>
<td>C–H, 105 kcal/mol</td>
</tr>
<tr>
<td>C₂H₆ = C₂H₅ + H</td>
<td>6.684E+33</td>
<td>-5.48</td>
<td>105330.0</td>
<td>C–H, 101 kcal/mol</td>
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<tr>
<td>C₃H₈ = C₂H₅ + CH₃</td>
<td>1.698E+44</td>
<td>-1.77</td>
<td>103004.0</td>
<td>C–C, 88 kcal/mol</td>
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</tbody>
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Single-fuel vs. multi-fuel components
Oxidation of methane and NG-mixtures in a JSR at 1 atm and 140ms.
Summary

Modeling: General information. Need accurate kinetics, thermochemistry, and transport data. Use inputs from theory and measurements and also estimations by analogy, tabulations. Need accurate data that are used to constrain the model. Reaction mechanism has a strong hierarchical structure. The core-mechanism is H_2/O_2 (H, O, OH, HO_2, H_2O_2, O_2, O_3, H_2).

Temperature dependencies of elementary reactions. Modified Arrhenius expression: $k=A T^n \exp(-E_a/RT)$

Pressure dependencies: Lindemann-Hinshelwood, Troe.

Kinetic analyses: ROP, ROC

Sensitivity analyses: Probe how the model responds to variations of the kinetic parameters

Pressure/Temperature dependencies and reaction pathways: cool flames, high-T oxidation (e.g., R+O_2 $\rightarrow$ RO_2 vs. R-H+HO_2)

Oxidation at low-T. More complex than generally considered. Combustion chemistry vs. tropospheric chemistry.

Pyrolysis and high-T oxidation

Single-fuel vs. multi-fuel components. The most reactive components drive the overall oxidation of the complex fuel (e.g., NG vs. methane).
Part 4
POLLUTANTS
1-NOx formation

1-1-Thermal-NO (Zel’dovich, 1946)

\[
\begin{align*}
\text{N}_2+\text{O} & \rightarrow \text{NO}+\text{N} \quad \text{(75.5 kcal/mole)} \\
\text{N}+\text{O}_2 & \rightarrow \text{NO}+\text{O} \\
\text{N}+\text{OH} & \rightarrow \text{NO}+\text{H}
\end{align*}
\]

Global rate (NO formation) = \([\text{N}_2] \times [\text{O}_2] \exp (-133000/RT)\)
1-2-Prompt-NO (Fenimore, 1979)

\[
\begin{align*}
\text{CH}+\text{N}_2 & \rightarrow (\text{HCN}+\text{N}) \text{NCN} + \text{H} \\
\text{CH}_2+\text{N}_2 & \rightarrow \text{HCN}+\text{NH} \\
\text{C}+\text{N}_2 & \rightarrow \text{CN}+\text{N}
\end{align*}
\]

Followed by:

\[
\begin{align*}
\text{HCN}+\text{X} & \rightarrow \text{CN}+\text{HX} \\
\text{NCN}+\text{O} & \rightarrow \text{CN} + \text{NO} \\
\text{NCN} + \text{OH} & \rightarrow \text{HCN} + \text{NO} \\
\text{NCN} + \text{H} & \rightarrow \text{HCN} + \text{N} \\
\text{NCN} + \text{O}_2 & \rightarrow \text{NO} + \text{NCO} \\
\text{NCN} + \text{O}_2 & \rightarrow \text{NO} + \text{CNO}
\end{align*}
\]
1-3-$\text{N}_2\text{O}$ (Malte and Pratt, 1974)

$$\text{N}_2\text{O}(+M) = \text{N}_2\text{O}(+M)$$
$$\text{N}_2\text{O}+\text{H} = \text{N}_2\text{+OH}$$
$$\text{N}_2\text{O}+\text{O} = \text{NO}+\text{NO}$$
$$\text{N}_2\text{O}+\text{O} = \text{N}_2\text{+O}_2$$
$$\text{N}_2\text{O}+\text{OH} = \text{N}_2\text{+HO}_2$$
$$\text{N}_2\text{O}+\text{OH} = \text{HNO}+\text{NO}$$
1-4-NNH (Bozzelli, Dean, *IJCK* 1995)

\[
\begin{align*}
N_2 + H &= NNH \\
NNH + H &= N_2 + H_2 \\
NNH + O &= N_2 O + H \\
NNH + O &= N_2 + OH \\
NNH + O &= NH + NO \\
NNH + OH &= N_2 + H_2 O \\
NNH + O_2 &= N_2 + HO_2 \\
NNH + O_2 &= N_2 + H + O_2 \\
NNH + NH &= N_2 + NH_2 \\
NNH + NH_2 &= N_2 + NH_3 \\
NNH + NO &= N_2 + HNO
\end{align*}
\]
Formation of HCN and NH\textsubscript{3} by pyrolysis of amines, pyridinic compounds or pyrroles followed by oxidation of HCN or NH\textsubscript{3} to NO and N\textsubscript{2}O

(i=1, 2)
Pyridinic-type

- acridine or 2,3,5,6-dibenzo-pyridine
- 1,2-bis (4-pyridyl)-ethane
- 3-pyridol or 3-hydroxypyridine
- nicotinic acid or 3-pyridinecarboxylic acid
- orotic acid or 6-uracilcarboxylic acid
- atrasan acid or 2,6-dihydroxy-4-pyridine-carboxylic acid

Pyrrrole-type

- carbazole or dibenzopyrrole
- dipicolinic acid or 2,6-pyridinedicarboxylic acid
- antipyrine or 2,3-dimethyl-1-phenyl-5-pyrazolone
- 2-pyrolecarboxylic acid
- DL-pyroglutamic acid or DL-5-pyrrolidone-2-carboxylic acid

Amino-type

- urea
- biuret or N-carbamoylurea
- meglumine or N-methyl-D-glucamine
Coal-N → Tar-N

Diagram showing the combustion process involving nitrogen compounds.
2-NOx reduction

2-1-Reduction through combustion modifications

2-1-1-Optimization of burner parameters - BasNOx burners

Burner parameter optimization techniques and lowNOx burners are used to limit NO production during combustion. These burners are specially designed to control the mixing of air and fuel to create more or less turbulent flames stabilized by internal recirculation zones. The temperature of the flame is lowered, thus limiting the production of thermal-NO. This type of burner works as a dual internal staging of fuel and combustion air:

The fuel burns with primary air (70-90%) under fuel-rich conditions. Secondary air (10-30%) is injected over the main combustion zone and completes the oxidation of the fuel. This increases the volume of the flame which decreases the flame temperature and thus the production of thermal-NO.
Low-NOx burner

- Post-combustion
- Primary zone: $\phi > 1.00$
- Internal recirculation
- Air (primary)
- Air (secondary)
- Fuel
2-1-2-Flue gas recirculation (FGR, EGR)

The recirculation of the fumes inside the oven or burner allows a dilution of the flame and therefore a sharp decrease in temperature. Generally, 20 to 30% of the flue gases recirculate and are mixed with the combustion air. The stoichiometry is not modified since the concentration of oxygen in the fumes is negligible. The efficiency is relatively low (<20%) because the contribution of thermal NO does not dominate in installations burning coal.

2-1-3-Fuel staging

Staging of the fuel allows alternation between a fuel-rich zone and a fuel-lean zone which limits the temperature of the flame, improves the distribution of oxygen, and limits NOx formation.
2-2-Chemical reduction of NOx

2-2-1-NOx reduction by SNCR (Lyon, 1974)

Effect of NO initial concentration on its removal by ammonia in lean conditions ($\Phi=0.1$). The initial conditions were: 1000 ppm of NH$_3$, 12500 ppm of O$_2$, residence time=100 ms, 500 ppm of NO (open symbols and dashed lines) or 1000 ppm of NO (closed symbols and solid line). The data (symbols) are compared to the modeling results (lines).
Effect of NH$_3$ initial concentration on NO reduction and N$_2$O formation in lean conditions ($\Phi=0.1$). The initial conditions were: residence time=100 ms, 500 ppm of NO, (i) 500 ppm of NH$_3$ and 6250 ppm of O$_2$ (open symbols and dashed lines), (ii) 1000 ppm of NH$_3$ and 12500 ppm of O$_2$ (closed symbols and solid line). The data (symbols) are compared to the modeling results using the present kinetic reaction mechanism (thin lines) and that of literature (thick lines).
The reduction of NO by ammonia in a plug flow reactor: comparison between the experimental results of Kasuya et al. [F. Kasuya, P. Glarborg, J.E. Johnsson, K. Dam-Johansen, Chem. Eng. Sci. 50 (1995) 1455.] (symbols) and this modeling (line). The initial conditions were: 1000 ppm of NH₃, residence time=(88 K/T) s, 500 ppm of NO, 4% O₂, 5% H₂O, balance N₂.
Ammonia oxidation boosted by NO:

Impact of the initial concentration of NO on NH$_3$ conversion. Experimental results obtained in a JSR at 1 bar, 1000 ppm NH$_3$, $\tau=100$ ms, $\phi=0.1$, 0 ppm (open symbols), 500 ppm (small black symbols), and 1000 ppm (large black symbols) of NO.
Data (symbols) and computed (lines) results for NH$_3$ oxidation in a JSR: 1000 ppm of NH$_3$, $\tau$=100ms; $\varphi$=0.1. Models: (a), (b), (c), and (d).

Ammonia oxidation boosted by NO:

Reaction pathway analyses were performed to delineate the mechanism responsible for the mutual sensitization of ammonia and nitric oxide. The computations show that it occurs via several reaction pathways leading to OH production, which is the main species involved in ammonia oxidation. In the present conditions HO$_2$ is mainly produced via:

\[
\text{NNH} + \text{O}_2 \rightarrow \text{N}_2 + \text{HO}_2
\]

and

\[
\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}.
\]

The production of OH results from a sequence of reaction including

\[
\text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH}
\]

\[
\text{NNH} \rightarrow \text{N}_2 + \text{H}
\]

\[
\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}
\]

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}.
\]
Computed (lines) and literature experimental (symbols) results for NH₃-air flames at 1 atm.

The kinetics of the reactions \( \text{NH}_2 + \text{H} \rightarrow \text{NH} + \text{H}_2 \) and \( \text{HNO} + \text{H} \rightarrow \text{NO} + \text{H}_2 \) were updated (Otomo et al., 2018) to better simulate burning velocities of ammonia in air.

(Dagaut, CST 2019, [https://doi.org/10.1080/00102202.2019.1678380](https://doi.org/10.1080/00102202.2019.1678380))
Perturbation by sulfur dioxide

Effect of SO$_2$ initial concentration on NO removal by ammonia in lean conditions (Φ=0.1). The initial conditions were: 500 ppm of NH$_3$, 6250 ppm of O$_2$, residence time=100 ms, 500 ppm of NO (open symbols and dashed lines) and 1000 ppm of SO$_2$ (closed symbols and solid line). The data (symbols) are compared to the modeling results (lines).
Effect of SO$_2$ initial concentration on NO removal by ammonia in lean conditions ($\Phi=0.1$). The initial conditions were: 1000 ppm of NH$_3$, 12500 ppm of O$_2$, residence time=200 ms, 1000 ppm of NO (open symbols and dashed lines) and 1000 ppm of SO$_2$ (closed symbols and solid line). The data (symbols) are compared to the modeling results (lines).
Effect of SO$_2$ initial concentration on NO removal by ammonia in fuel-rich conditions (Φ=2). The initial conditions were: 1000 ppm of NH$_3$, 625 ppm of O$_2$, 200 ms, 1000 ppm of NO (open symbols and dashed lines) and 1000 ppm of SO$_2$ (closed symbols and solid line). The data (symbols) are compared to the modeling results (lines).
NH₂ production:

\[
\text{NH}_3 + \text{OH} \rightarrow \text{NH}_2 + \text{H}_2\text{O}, \quad R(\text{NH}_2) = 0.863 \quad (149)
\]

\[
\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}, \quad R(\text{NH}_2) = 0.124 \quad (150)
\]

NH₂ reacts with NO via (161) and (162),

\[
\text{NH}_2 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O}, \quad R(\text{NO}) = -0.544 \quad (161)
\]

\[
\text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH}, \quad R(\text{NO}) = -0.322 \quad (162)
\]

Under conditions, OH radicals are produced via

\[
\text{NH}_2 + \text{NO} \rightarrow \text{NNH} + \text{OH}, \quad R(\text{OH}) = 0.41 \quad (162)
\]

\[
\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}, \quad R(\text{OH}) = 0.187 \quad (-74)
\]

\[
\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}, \quad R(\text{OH}) = 0.157 \quad (99)
\]

\[
\text{NH}_3 + \text{O} \rightarrow \text{NH}_2 + \text{OH}, \quad R(\text{OH}) = 0.142 \quad (149)
\]
O-atoms are produced by reaction (-74),

\[ H + O_2 \rightarrow OH + O, \ R(O)=0.997 \quad (-74) \]

SO\textsubscript{2} contributes moderately to the removal of O-atoms through reaction (7):

\[ \text{SO}_2 + O (+M) \rightarrow \text{SO}_3 (+M), \ R(O)=-0.03 \quad (7) \]

The model indicates that SO\textsubscript{2} reacts mostly through 3 reactions:

\[ \text{SO}_2 + O (+M) \rightarrow \text{SO}_3 (+M), \ R(\text{SO}_2)=-0.173 \quad (7) \]

\[ H + \text{SO}_2 +M \rightarrow \text{HOSO} + M, \ R(\text{SO}_2)=-0.204 \quad (57) \]

\[ \text{SO}_2 + \text{NH}_2 \rightarrow \text{NH}_2\text{SO}_2, \ R(\text{SO}_2)=-0.43 \quad (72) \]

HOSO formed in reaction (57) recycles SO\textsubscript{2} via reaction (13):

\[ \text{HOSO} + O_2 \rightarrow \text{HO}_2 + \text{SO}_2, \ R(\text{HOSO})=-0.999 \quad (13) \]
The sequence of reactions (13) + (57)

\[
\text{HOSO} + \text{O}_2 \Rightarrow \text{HO}_2 + \text{SO}_2 \quad (13)
\]

\[
\text{H} + \text{SO}_2 + \text{M} \Rightarrow \text{HOSO} + \text{M} \quad (57)
\]

is equivalent to \( \text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M} \Rightarrow \) reduction of the radical pool since the fraction of H atoms reacting in (57) will not produce OH and O via reaction (-74) and OH via reaction (100), \( \text{NO}_2 + \text{H} \Rightarrow \text{NO} + \text{OH} \).

Thus, under such conditions, introducing 1000 ppm of \( \text{SO}_2 \) reduces the rate of production of O by a factor of 1.8 and that of OH by a factor of 1.75. Since O and OH are the major agents of oxidation of \( \text{NH}_3 \), via reactions (149) and (150), the rate of ammonia oxidation is reduced by a factor of 1.7, resulting in the reduction of the rate of \( \text{NH}_2 \) production by a factor of 1.7 and in a reduction of 42% of NO-consumption rate.
Summary

Under fuel-lean conditions, the addition of SO₂ inhibits the process via $H + SO_2 + M = HOSO + M$ followed by $HOSO + O_2 = HO_2 + SO_2$ equivalent to the equation $H + O_2 + M = HO_2 + M$.

Under fuel rich conditions, the addition of SO₂ inhibits the process via $H + SO_2 + M = HOSO + M$ followed $HOSO + H = H_2 + SO_2$ and via $H + SO_2 + M = HOSO + M$ followed by $HOSO + O_2 = HO_2 + SO_2$.

SO₂ does not reduce the efficiency of the thermal de-NOx process but shifts the optimal temperature to higher values.
Further inhibiting effects of SO$_2$

The effect of SO$_2$ on the oxidation of a CO/H$_2$ mixture in a plug-flow reactor. Initial conditions: (a) CO = 1.0%, H$_2$ = 1.0%, O$_2$ = 1.0%, H$_2$O = 2.0%, balance N$_2$, without and with SO$_2$ = 1.2%, residence time is 192.7/T or 192.3/T; (b) CO = 1.0%, H$_2$ = 1.0%, O$_2$ = 0.5%, H$_2$O = 2.0%, balance N$_2$, without and with SO$_2$ = 0.3%, residence time is 192.7/T or 192.3/T. Inhibition is due to H+SO$_2$+M=HOSO+M followed by HOSO+H=H$_2$+SO$_2$. From Dagaut et al., Int J Chem Kinet 35: 564–575, 2003.
2-2-2-NOx reduction by reburning)

1. Thermal-NO production in near-stoichiometric conditions;
2. Fuel-rich zone, NO + HC → N₂, HCNOₓ;
3. Excess-air, HCNOₓ oxidation → NO
FIGURE 11  The effect of equivalence ratio on the reburning of NO by a CH₈/C₂H₆ (10:1) mix at 1 atm (φ ~ 0.12 s; 1000 ppm of NO; 727 ppm of CH₄; 728 ppm of C₂H₆). Comparison between experimental data (symbols) and modeling (lines): NO, □--; HCN,△--; TPN, *--; (a) 1250 K, (b) 1400 K; (c) 1350 K; (d) 1400 K; (e) 1450 K.
**FIGURE 9 (Continued)**

**FIGURE 10** The oxidation of a CH₄/C₃H₆ (10:1) mix in a JSR at t₀ = 0.12 s; 7272 ppm of CH₄, 728 ppm of C₂H₆, 8546 ppm of O₂; φ = 2. Comparison between experimental data (symbols) and modeling (lines); (a) CH₄; □; CO₂, △; CO₂, ◊; (b) O₂; ■; H₂, △; (c) C₂H₆, ■; C₃H₆, △; C₂H₂, ◊.
TFN (NO+HCN) vs eq. ratio; 1300 K, 1000ppm NO, 8800 ppm C, 0.12s. Reburn fuels: NG-blend ■; ethane *; ethylene ○, acetylene ●; NG △; propene □; propane ◊; n-butane Δ; i-butane ▲.

TFN (NO+HCN) vs. T for 8 reburn fuels: NG-blend ■; ethane *; ethylene ○, acetylene ●; NG △; propene □; propane ◊; n-butane Δ; i-butane ▲. Stoichiometric mix, 1000ppm NO, 8800 ppm C, t: 0.12-0.16s
HCCO production

\[ \text{Mole Fraction of HCCO} \]

\[ \Phi = 1 \]

- CH\(_4\)/C\(_2\)H\(_6\) 10:1
- C\(_2\)H\(_6\)
- C\(_2\)H\(_4\)
- C\(_2\)H\(_2\)

\[ T / \text{K} \]

\[ 1050 \quad 1100 \quad 1150 \quad 1200 \quad 1250 \quad 1300 \]

\[ 1 \times 10^{-8} \]

\[ 2 \times 10^{-9} \]

- C\(_2\)H\(_6\)
- CH\(_4\)-C\(_2\)H\(_6\) 10:1
Inhibiting effect of SO$_2$ on NO-reburning using 2 reburn fuels at 1300K

\[
\gamma(\text{NO}) = \frac{X(\text{NO})_{\text{w, SO}_2}}{X(\text{NO})_{\text{w/o SO}_2}}
\]

residual of NO increased in presence of sulfur dioxide
### 3-UHCs and Soot

#### Organic compounds in the troposphere

<table>
<thead>
<tr>
<th>Class</th>
<th>Compound</th>
<th>Formula</th>
<th>Typical Source</th>
<th>Sink</th>
<th>Concentration Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkanes</td>
<td>Methane</td>
<td>CH₄</td>
<td>Microbial processes, natural gas</td>
<td>OH</td>
<td>1.7 ppm</td>
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<tr>
<td></td>
<td>Ethane</td>
<td>C₂H₆</td>
<td>Motor vehicles</td>
<td>OH</td>
<td>0–100 ppb</td>
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<tr>
<td></td>
<td>Hexane</td>
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<td>Motor vehicles</td>
<td>OH</td>
<td>0–30 ppb</td>
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<tr>
<td>Alkenes</td>
<td>Ethene</td>
<td>C₂H₄</td>
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<td>OH, O₃</td>
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<td>OH</td>
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Oxidation of organic compounds in the troposphere
Terpenes to HOMs and Secondary Organic Aerosols (SOAs)

From Belhadj et al. ICCK, 2019
Additional pathways to HOMs by Wang et al. PNAS (2017)