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Lecture 8: Non-premixed combustion

AAE-E3030 Numerical Modeling of Multiphase Flows
2019

Combustion, Warnatz, J., Maas, U., and Dibble, R. W., 2nd edition, ISBN 3-540-65228-0, 1999.

Turbulent Combustion, Norbert Peters, ISBN 0-951-66082-3, 2000.

D.Sc (Tech) Ossi Kaario

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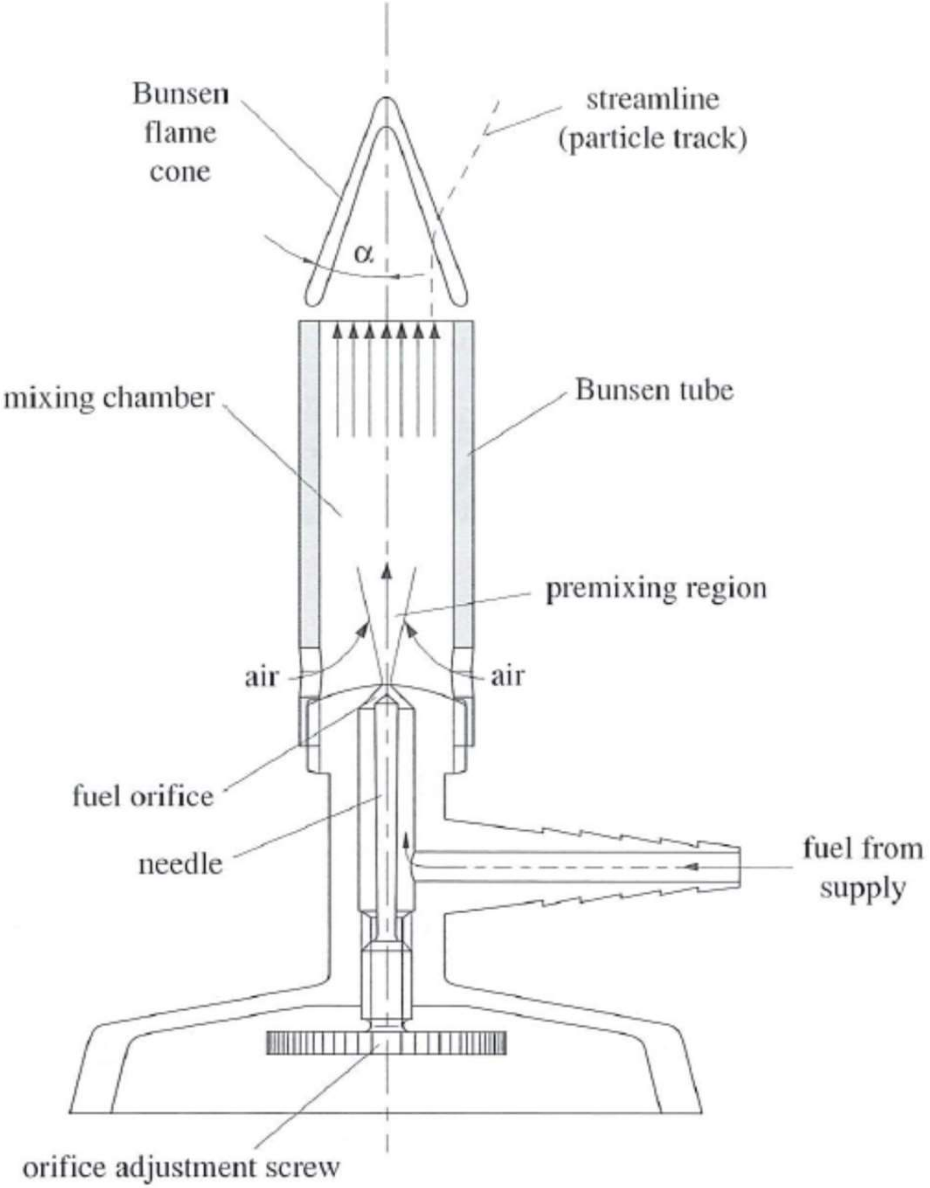
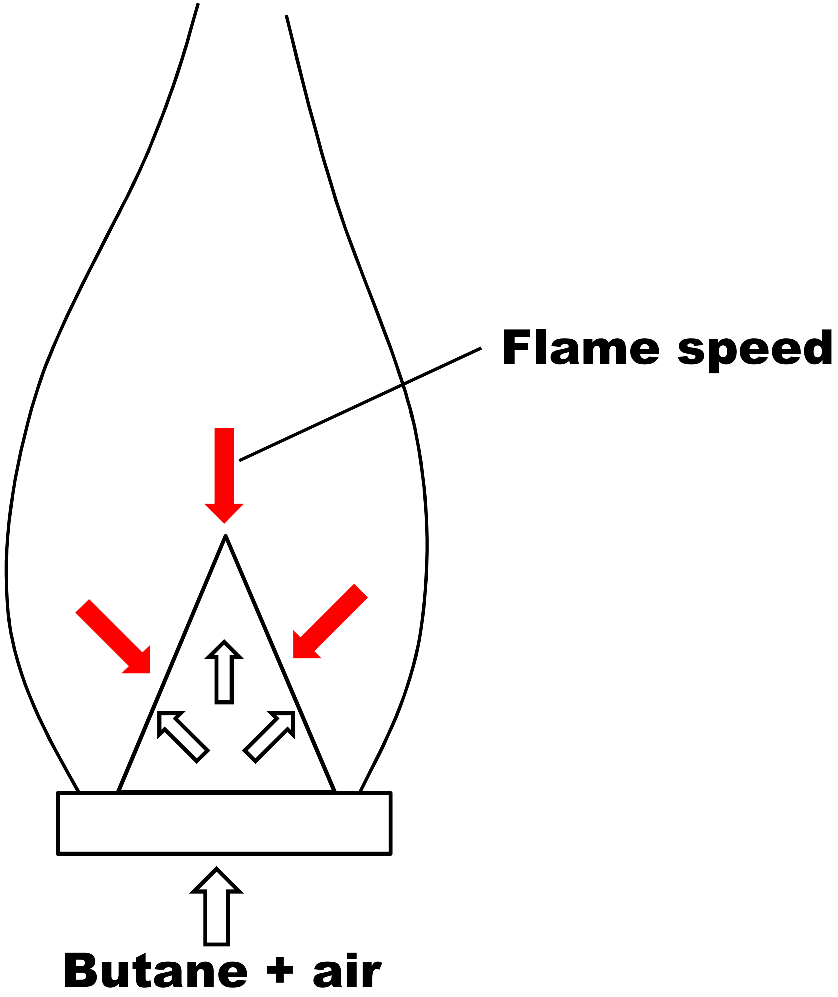
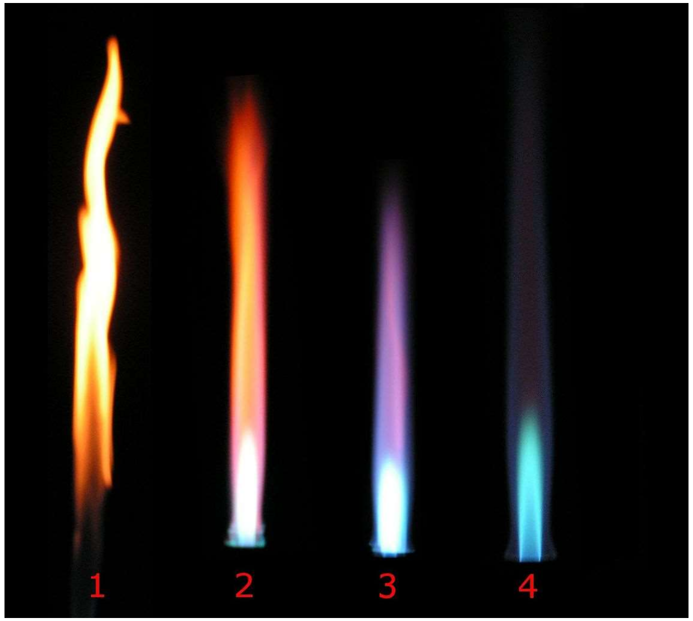
Bunsen burner



Premixed Bunsen flame

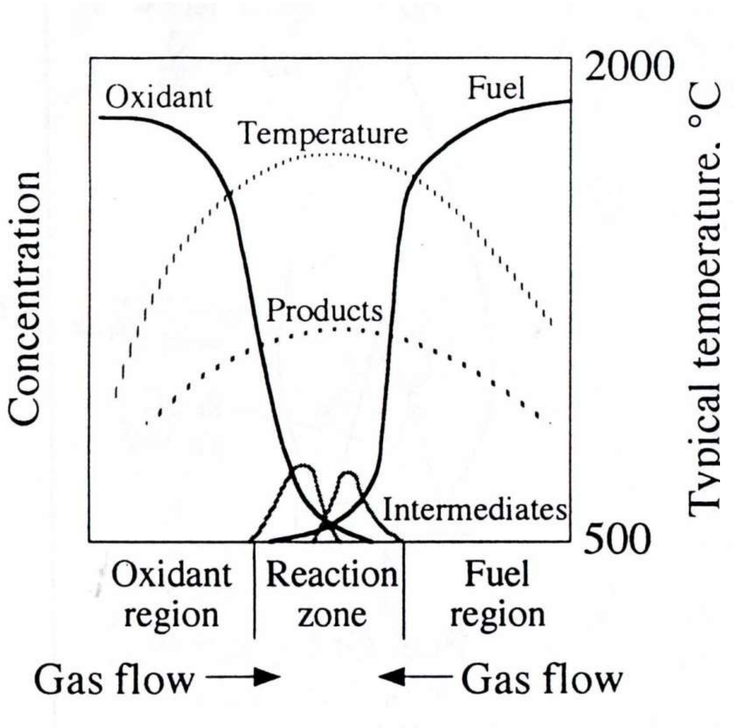




Diffusion ---- premixed combustion

Fundamental gas flames

Non-premixed flame



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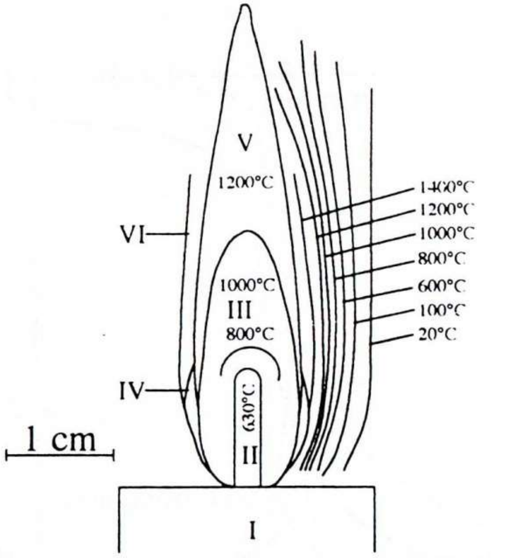
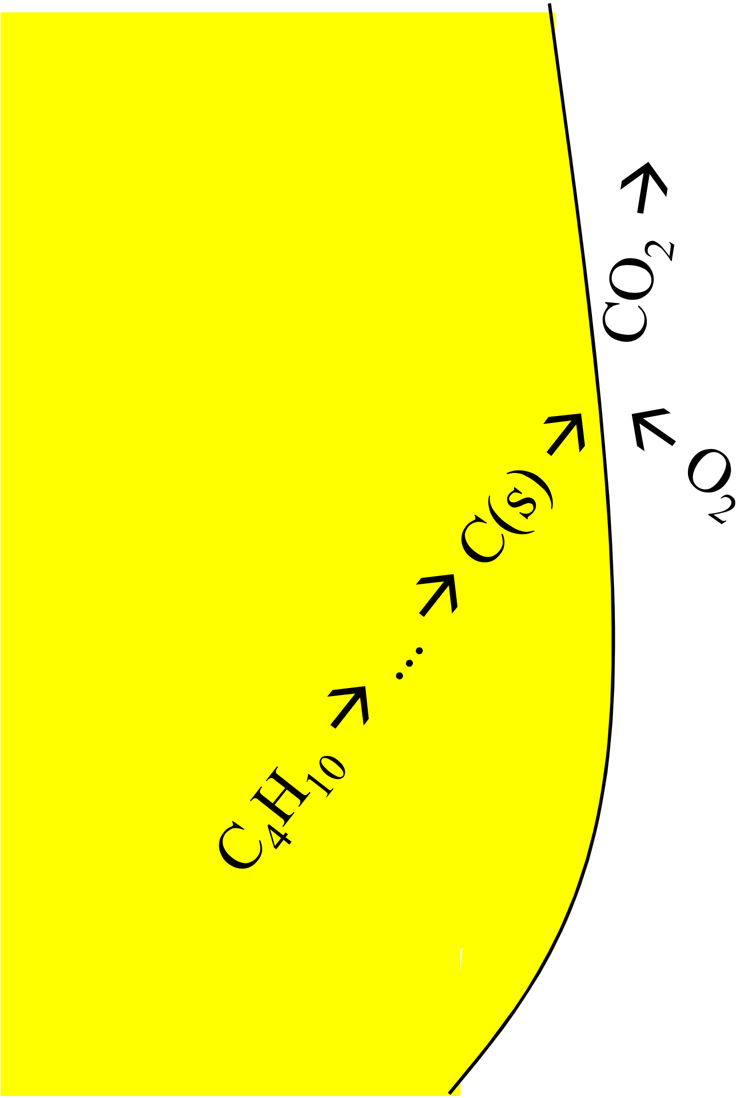


Relative temperatures in a candle flame from thermocouple measurements: I - Body of candle, II - Wick, III - Dark zone, IV - C_2 and Cl zone, V - Luminous zone, VI - Main reaction zone

Diffusion flame

Diffusion flame chemistry



$C(s) + O_2 \rightarrow CO_2$

Properties of premixed and diffusion combustion processes

Premixed	Diffusion
-No soot	-Sooting flame
-Poor radiator	-Good raditive heat transfer
-Chemical reactions determine reaction rate	-Mixing determine reaction rate
-flame speed can be determined	-Cannot define burning velocity

-applications (stove, furnace..)
-safety issues

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Discuss

Discuss with the person next to you

1. **Differences between premixed and non-premixed flames**
2. **Where does fuel-air mixing take place for each flame type**
3. **Why the other flame type is sooting**

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Stoichiometry

- Stoichiometric: Fuel-Oxygen ratio such that both are entirely consumed when combustion to CO_2 and H_2O is completed
- Global reaction describing combustion of a single component hydrocarbon fuel C_mH_n (subscript F for fuel)

$$v'_F C_m H_n + v'_{O_2} O_2 = v''_{CO_2} CO_2 + v''_{H_2O} H_2O \qquad (1)$$

- Stoichiometric coefficients are

$$v'_F = 1 \qquad v'_{O_2} = m + \frac{n}{4} \qquad v''_{CO_2} = m \qquad v''_{H_2O} = \frac{n}{2}$$

where $v'_F = 1$ may be chosen arbitrarily to unity

Stoichiometric Mass Ratio

- Mole number ratio for stoichiometric condition

$$\frac{n_{O_{2,u}}}{n_{F_u}}|st = \frac{v'_{O_2}}{v'_F}$$

or in terms of mass fractions

$$\boxed{\frac{Y_{O_{2,u}}}{Y_{F,u}}|st = \frac{v'_{O_2}W_{O_2}}{v'_F W_F} = v}$$

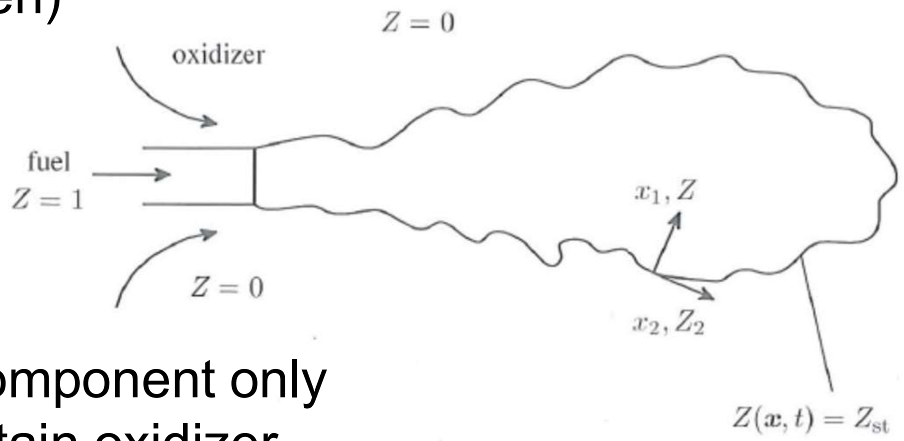
where v is called the stoichiometric mass ratio

- Typical value: Methane v = 4
- Mass ratio v : Fuel and oxidixer are both consumed when combustion is completed

The mixture fraction

- Mixture fraction quantifies local the state of mixing in non-premixed combustion.

- Consider two separate feed streams of
  - Fuel
  - Oxidizer (air, pure oxygen)
- Streams mix and burn



- Fuel stream
  - Often consists of one component only
  - In general does not contain oxidizer
- Oxidizer stream
  - Generally does not contain fuel

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The mixture fraction

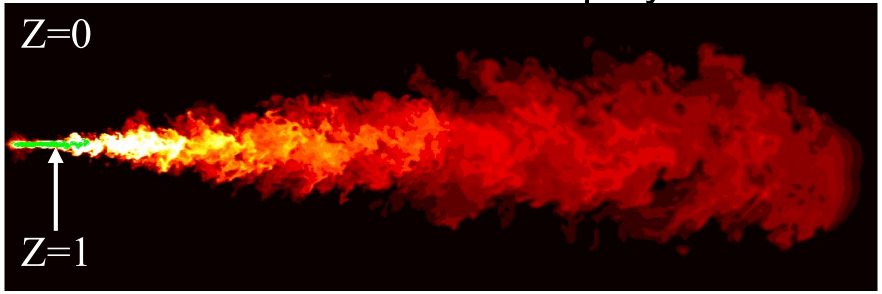
- In the following:
  - Fuel stream: Subscript 1
  - Oxidizer stream: Subscript 2
- Defining mixture fraction
- Mass fraction of the fuel stream in the mixture:

$$Z = \frac{m_1}{m_1 + m_2}$$

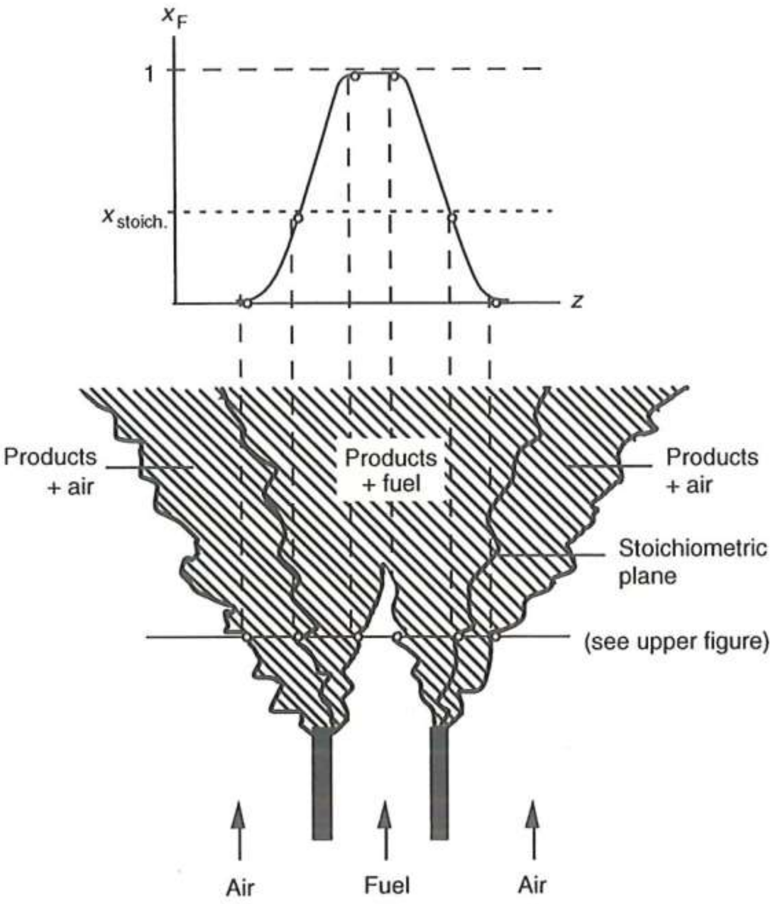
where m_1 and m_2 are the local masses originating from the individual streams.

- Mixture fraction is always between zero and one
- Fuel stream: Z=1
- Oxidizer stream: Z=0

Mixture fraction field in a spray case



The mixture fraction



Turbulent non-premixed jet flame

Figure: Combustion by Warnatz, Maas, and Dibble

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The mixture fraction

- Mass fraction of fuel in the fuel stream: $Y_{F,1}$
- Mass fraction of oxygen in the oxidizer stream: $Y_{O_2 2}$

- If we assume equal diffusivities of fuel, oxygen, and inert substances, the local mass fraction $Y_{F,u}$ of fuel in the unburned mixture is related to the mixture fraction Z as

$$Y_{F,u} = Y_{F,1} Z$$

- Similarly, since $(1 - Z)$ represents the mass fraction of the oxidizer stream locally in the unburned mixture, we obtain the local mass fraction of oxygen as

$$Y_{O_{2,u}} = Y_{O_2 2}(1 - Z) \qquad (Y_{O_2 2} = 0.232 \text{ for air})$$

The mixture fraction

- In a single step global reaction

$$v'_F C_m H_n + v'_{O_2} O_2 = v''_{CO_2} CO_2 + v''_{H_2O} H_2O$$

the reaction equation relates the changes of mass fractions of oxygen dY_{O_2} and fuel dY_F to each other by

$$\frac{dY_{O_2}}{v'_{O_2} W_{O_2}} = \frac{dY_F}{v'_F W_F}$$ where W_i:s are the molecular weights.

- This may be integrated to obtain

$$vY_F - Y_{O_2} = vY_{F,u} - Y_{O_2 u} \qquad (2)$$

The mass fractions Y_F and Y_{O_2} correspond to any state of combustion between the unburned and the burned state.

The mixture fraction

- Combining $vY_F - Y_{O_2} = vY_{F,u} - Y_{O_2u}$ with $Y_{F,u} = Y_{F,1}Z$

  and $Y_{O_2u} = Y_{O_22}(1 - Z)$

- We get

$$\mathrm{Z} = \frac{vY_F - Y_{O_2} + Y_{O_22}}{vY_{F,1} + Y_{O_22}} \qquad v = \frac{v'_{O_2}W_{O_2}}{v'_F W_F}$$

which relates the mixture fraction Z to the mass fractions of Y_F and Y_{O_2}

- For stoichiometric composition, the first two terms have to cancel out

$$Z_{st} = \frac{Y_{O_22}}{vY_{F,1}+Y_{O_22}} \text{ or } \boxed{Z_{st}= \left(1 + v\frac{Y_{F,1}}{Y_{O_22}}\right)^{-1}}$$

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Relation of mixture fraction and equivalence ratio

- Fuel-air equivalence ratio is

$$\phi = \frac{Y_{F,u}/Y_{O_{2,u}}}{\left(Y_{F,u}/Y_{O_{2,u}}\right)_{st}} = \frac{vY_{F,u}}{Y_{O_{2,u}}}$$

- Introducing $Y_{F,u} = Y_{F,1}Z,\;\; Y_{O_2u} = Y_{O_22}(1-Z)$, and

$$Z_{st}= \left(1 + v\frac{Y_{F,1}}{Y_{O_22}}\right)^{-1}$$

- We obtain a relationship between Z and ϕ as

$$\boxed{\phi = \frac{Z}{1-Z}\frac{(1-Z_{st})}{Z_{st}}}$$

- This suggests that mixture fraction can be interpreted as a normalized fuel-air equivalence ratio

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Simple Mixture Fraction Eq.

- In CFD, simple equation for the calculation of Z: we only need to know the N_2 field
- Often accurate enough is the following mixture fraction definition

$$Z = \frac{Y_{N_2} - Y_{N_2 2}}{Y_{N_{2\_fuel}} - Y_{N_2 2}}$$

$Y_{N_2 2}$	Initial N2 massfraction
$Y_{N_{2\_fuel}}$	N2 massfraction in the fuel

Additional material

Mixture fraction definition by Bilger

- Let Z_C, Z_H, and Z_O denote the element mass fractions of C, H, and O, and W_C, W_H, and W_O their molecular weights, respectively. Setting the stoichiometric coefficient v'_F of the global reaction (1) to unity, we obtain the element mass fractions

$$\frac{Z_C}{mW_C} = \frac{Z_H}{nW_H} = \frac{Y_{F,u}}{W_F}, \qquad Z_O = Y_{O_2,u}$$

where $$Z_j = \frac{m_i}{m} = \sum_{1}^{n} \frac{a_{ij} W_j}{W_i} Y_i$$

a_{ij} is the number of atoms of element j in a molecule of species i

W_j is the molecular weight of atom j

Additional material

Mixture fraction definition by Bilger

- We can now formulate a coupling function

$$\beta = \frac{Z_C}{mW_C} + \frac{Z_H}{nW_H} - 2\frac{Z_O}{v'_{O_2}W_{O_2}}$$

which vanishes under stoichiometric combustion, and corresponds to the original definition of Burke and Schumann (1928) of a conserved scalar. It can be normalized between 0 and 1

$$Z = \frac{\beta - \beta_2}{\beta_1 - \beta_2}$$ or

$$Z = \frac{Z_C/(mW_C) + Z_H/(nW_H) + 2\left(\left(Y_{O_2,2} - Z_O\right)/\left(v'_{O_2}W_{O_2}\right)\right)}{Z_{C,1}/(mW_C) + Z_{H,1}/(nW_H) + 2\left(Y_{O_2,2}/\left(v'_{O_2}W_{O_2}\right)\right)}$$

- This formula is often used to determine mixture fraction experiments or numerical results.

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Discuss

Discuss and calculate with the person next to you

1. For Methane combustion, what is Z_{st} ?
   Assume $Y_{F,1} = 1$ and $Y_{O_2 2} = 0.232$
2. If $Y_{N_2 2} = 0.77$ and $Y_{N_2} = 0.73$ what is Z ?
3. What is mixture fraction ? What does it mean ?

Diffusion flame structure at complete conversion

- Stoichiometric composition

$$Z_{st} = \frac{Y_{O_2 2}}{vY_{F,1}+Y_{O_2 2}}$$

- If Z < Z_{st} then the mixture is lean (fuel is deficient)
- Combustion terminates when $Y_{F_b} = 0$
- Remaining oxygen mass fraction is calculated from

$$\mathrm{Z} = \frac{vY_F - Y_{O_2} + Y_{O_2 2}}{vY_{F,1} + Y_{O_2 2}}$$

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Diffusion flame structure at complete conversion

$$Y_{O_2} = Y_{O_2,2}\left(1 - \frac{Z}{Z_{st}}\right), \quad Y_F = 0, \text{ for } Z \leq Z_{st}$$

- $Z > Z_{st}$ mixture is rich (oxygen deficient)
- Combustion terminates when all oxygen is consumed $Y_{O_{2,b}} = 0$

$$Y_F = Y_{F,1}\frac{Z - Z_{st}}{1 - Z_{st}}, \qquad Y_{O_2} = 0, \text{ for } Z \geq Z_{st}$$

Diffusion flame structure at complete conversion

$$Y_{CO_2} = Y_{CO_2,st}\frac{Z}{Z_{st}} \; ; \qquad Y_{H_2O} = Y_{H_2O,st}\frac{Z}{Z_{st}} \qquad Z \le Z_{st}$$

$$Y_{CO_2} = Y_{CO_2,st}\frac{1-Z}{1-Z_{st}} \; ; \; Y_{H_2O} = Y_{H_2O,st}\frac{1-Z}{1-Z_{st}} \qquad Z \ge Z_{st}$$

where

$$Y_{CO_2,st} = Y_{F,1}Z_{st}\frac{mW_{CO_2}}{W_F} \qquad Y_{H_2O,st} = Y_{F,1}Z_{st}\frac{nW_{H_2O}}{W_F}$$

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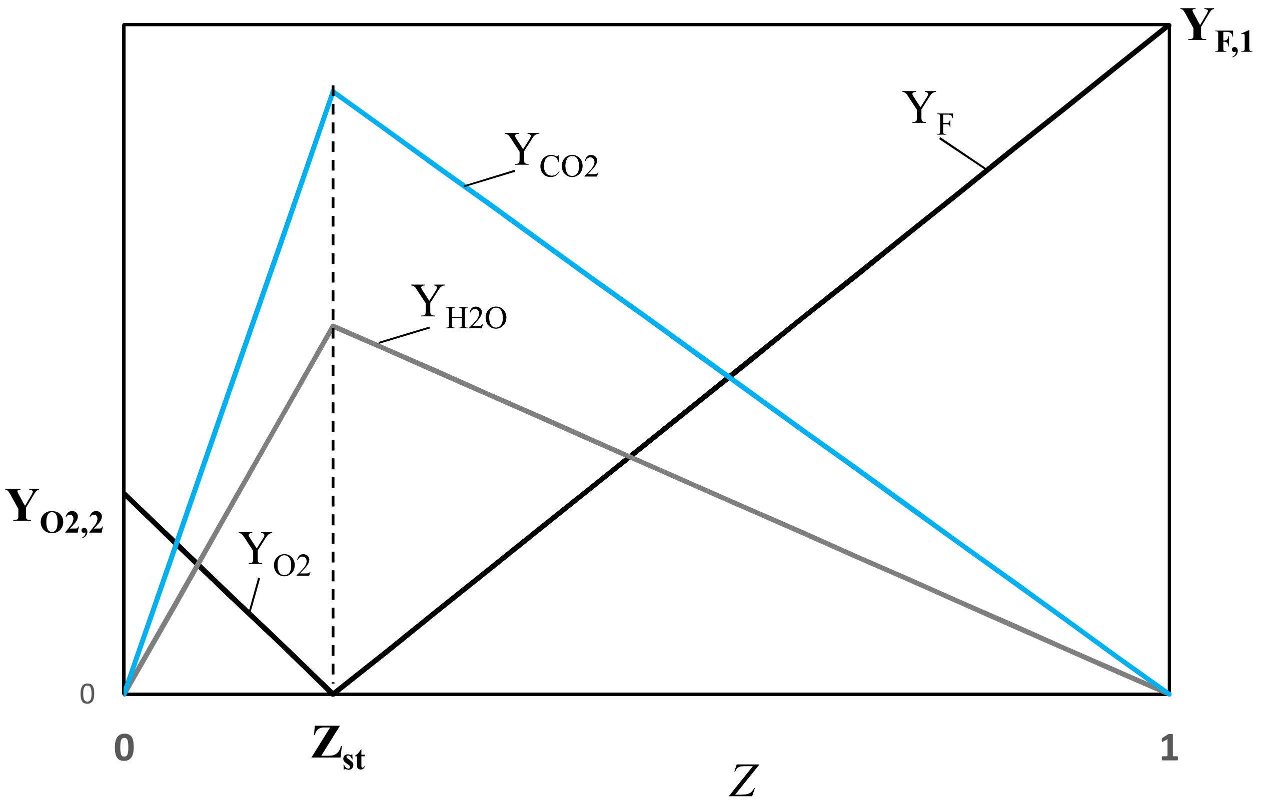
The Burke-Schumann solution



The Burke-Schumann solution

- Concerning temperature, if all c_p:s are assumed equal and constant, pressure is constant, Le=1 for all species, and heat transfer due to radiation is neglected, temperature equation may be written

$$\rho \frac{\partial T}{\partial t} + \rho u \cdot \nabla T = \nabla \cdot (\rho D \nabla T) + w_T \qquad w_T = -\frac{1}{c_p} \sum_{1}^{n} h_i w_i$$

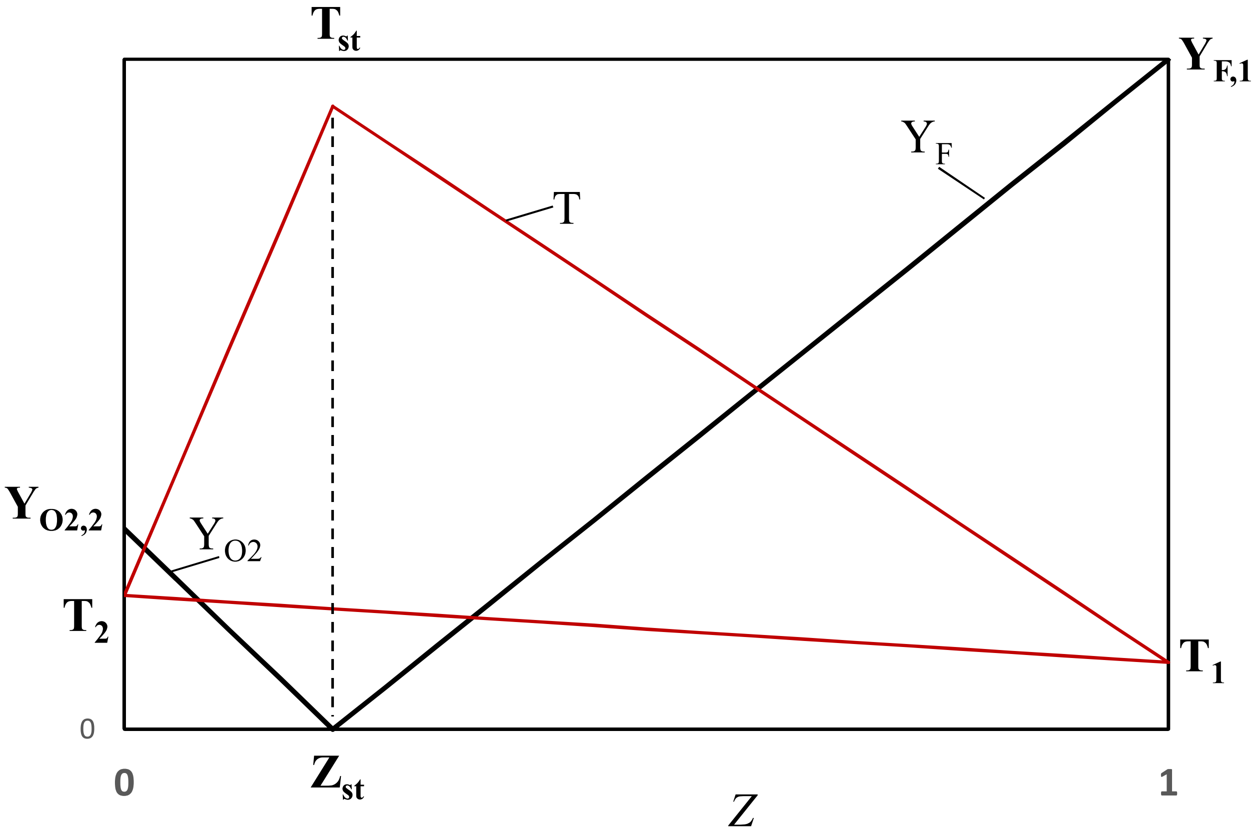
- Then heat release rate w_T may be written as $w_T = \frac{Q}{c_p} w$, where w is the Arrhenius reaction rate and Q is the fuel heating value.
- Under these assumptions, temperature is also a piecewise linear function of Z:

$$T_u(Z) + \frac{QY_{F,1}}{c_p v_F' W_F} Z, \qquad Z \leq Z_{st}$$

$$T_u(Z) + \frac{QY_{O,2}}{c_p v_{O_2}' W_{O_2}} (1 - Z), \qquad Z \geq Z_{st}$$

$$T_u(Z) = T_2 + Z(T_1 - T_2)$$

The Burke-Schumann solution



Temperature, O_2 and Fuel profiles assuming fast chemistry and equal mass diffusivities

The Burke-Schumann solution

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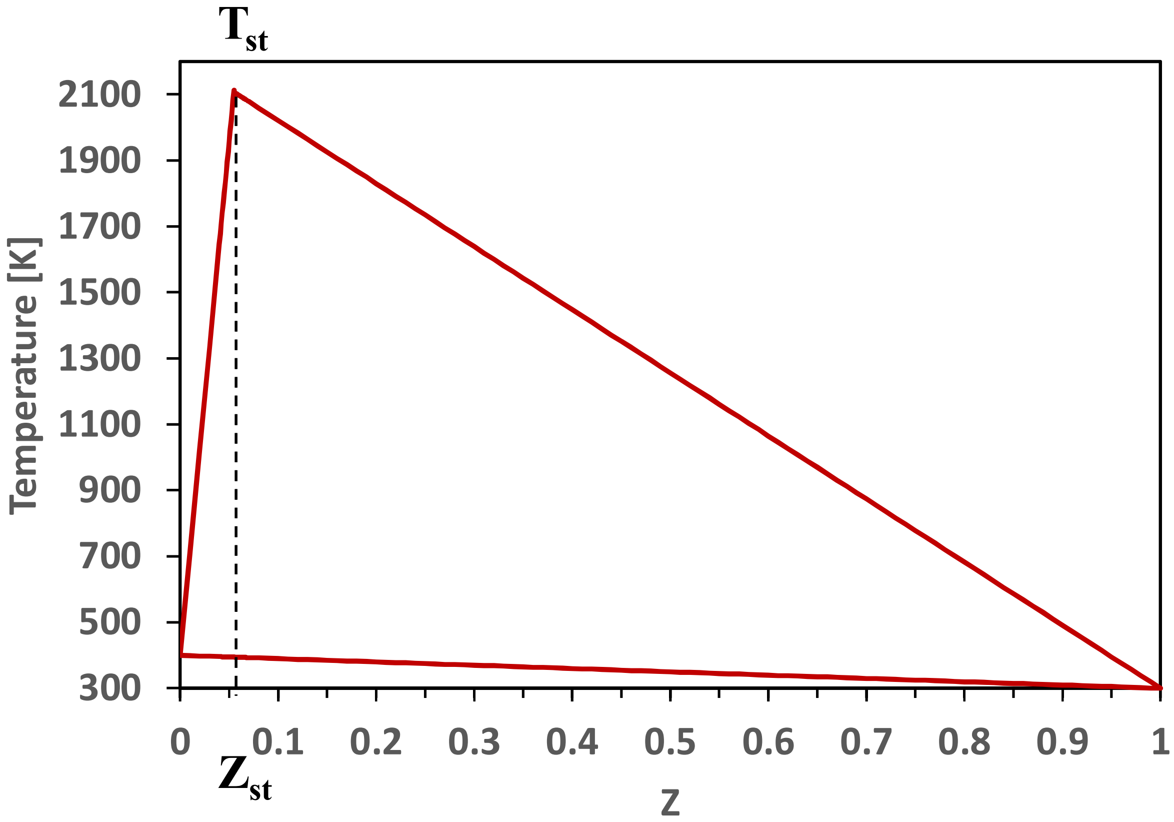
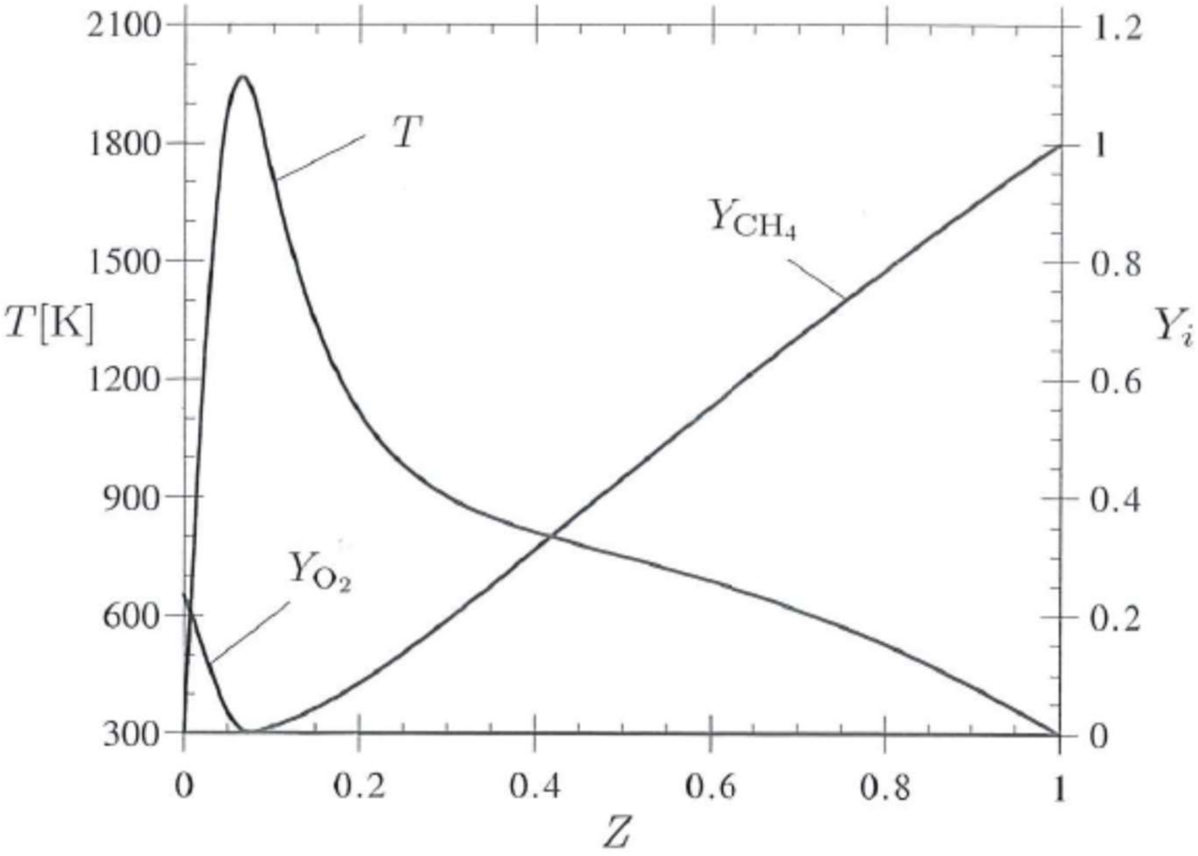


Temperature profile for methane-air combustion with realistic values for c_p, Q, and initial temperatures.

The Equilibrium solution



Methane-air combustion with fast-chemistry assumption but with reversible reactions (N. Peters, 2006)

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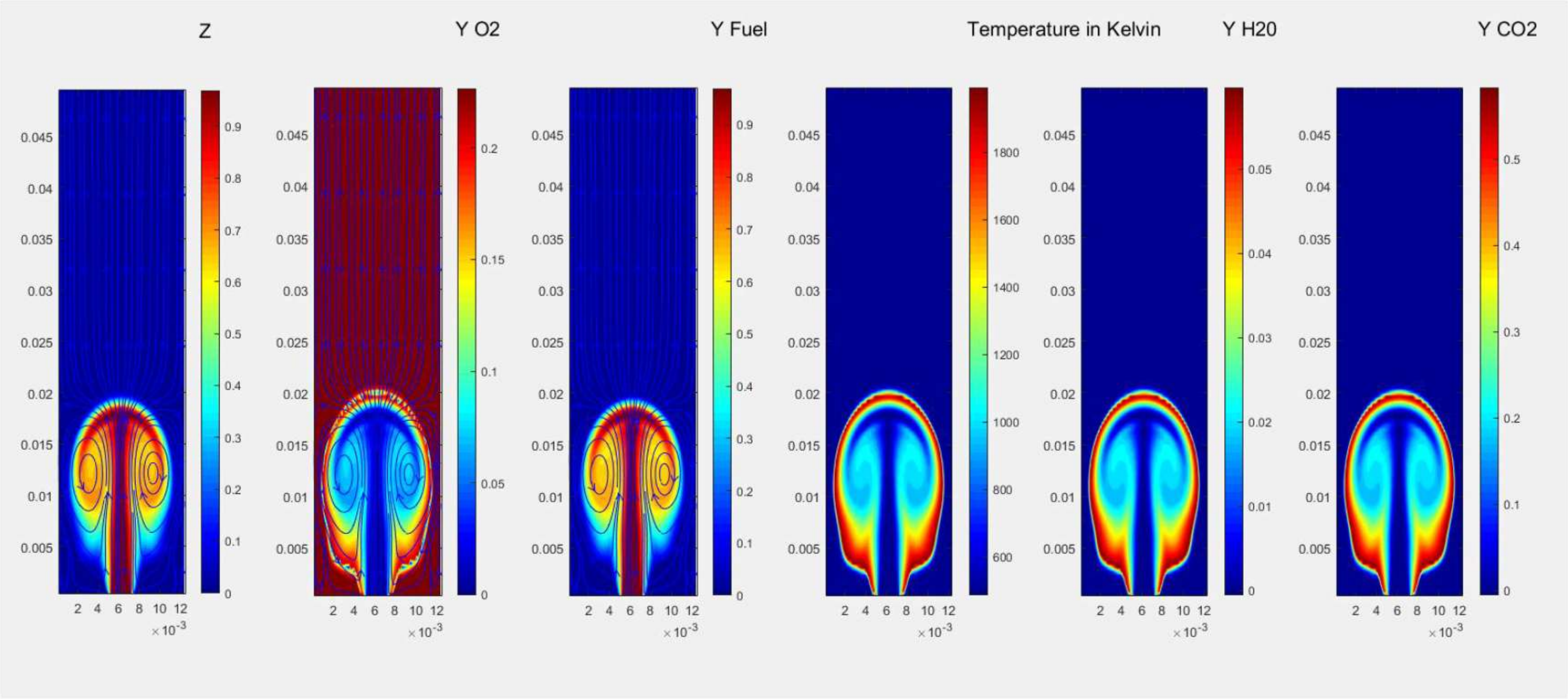
The Equilibrium solution



Burke-Schuman solution for a 2D gas jet
(Navier-Stokes solver)

Modeling of non-premixed combustion

- There are different kinds of simplifications that can be done to model combustion. Here, three modeling approaches are presented.

1. Mixed is burned –approach. Typically eddy break-up –type of models. Single step chemistry which basically neglegts the chemistry totally.
2. Flamelet model based on Flamelet Generated Manifold (FGM)
3. Direct Chemistry

A Turbulent Mixing Limited Approach

- **Eddy Break-Up approach**

$$S_{Fu} = C_m \bar{\rho} \frac{\varepsilon}{k} \min\left(\tilde{m}_{Fu}, \frac{\tilde{m}_{O_2}}{r}, \frac{\tilde{m}_{\mathrm{Pr}}}{1+r} \right)$$

A Turbulent Mixing Limited Approach

- **The Laminar and Turbulent Characteristic Time (LaTCT) combustion model**

$$\tau_c = \tau_{ch} + f\,\tau_\varepsilon$$

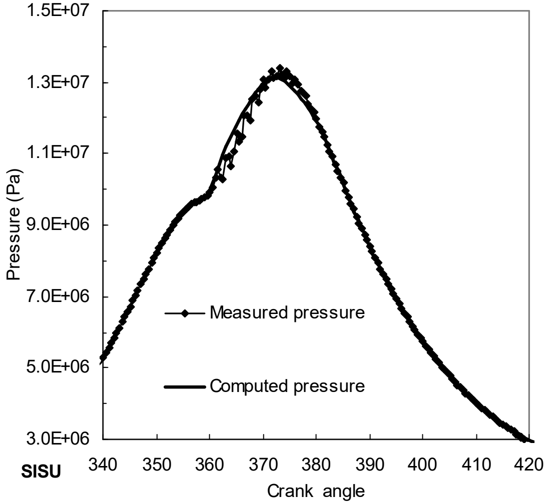
$$\tau_\varepsilon = C_M\,\bar{\rho}\,\frac{\varepsilon}{k}\min\left(\tilde{m}_{Fuel}, \frac{\tilde{m}_{O_2}}{r}\right) \qquad \tau_{ch} = A^{-1}[Fuel]^{0.75}[O_2]^{-1.5}\exp\left(E/RT\right)$$

$$f = \left(1 - e^{-p}\right)/0.632 \qquad p = \frac{\tilde{m}_{CO_2} + \tilde{m}_{H_2O} + \tilde{m}_{CO} + \tilde{m}_{H2}}{1 - \tilde{m}_{N_2}}$$

- **Reaction rate** $$\frac{dY_i}{dt} \sim \frac{1}{\tau_c}$$

- **The model can be used, in principle, when chemistry is either very fast compared to mixing or when chemistry is very slow compared to mixing**

Some results with the Eddy Breakup model



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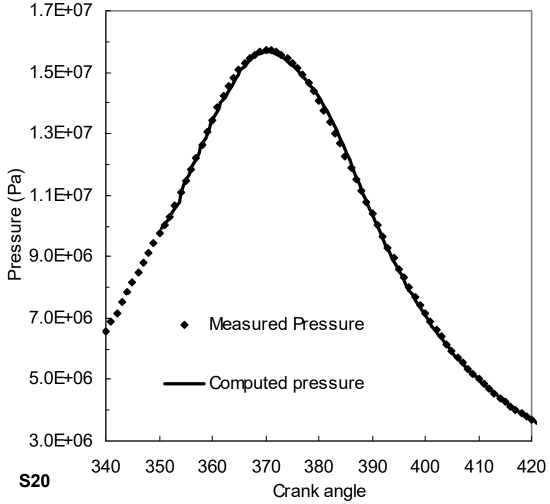
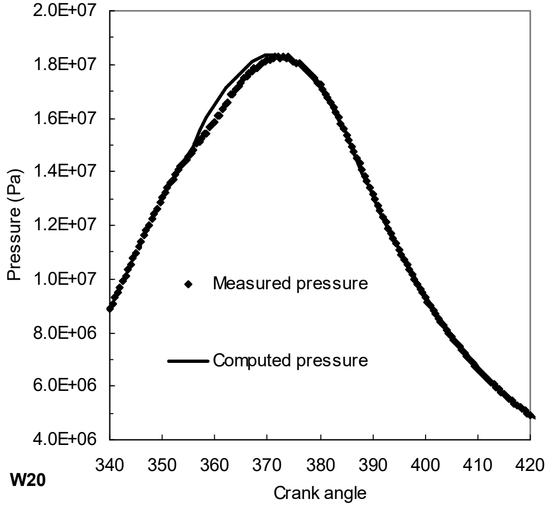


B) Sulzer 20



C) Wärtsilä 20

Flamelet Generated Manifolds (FGM)

- Consider a simplyfied combustion configuration

$$CH_4 + 2O_2 + N_2 \rightarrow CO_2 + 2H_2O + N_2$$

CH_4
O_2
N_2

CO_2
H_2O
N_2

Flamelet:

- Laminar
- 1-dimensional
- Detailed computation of transport processes
- Detailed chemical reactions
- Full set of species and reactions

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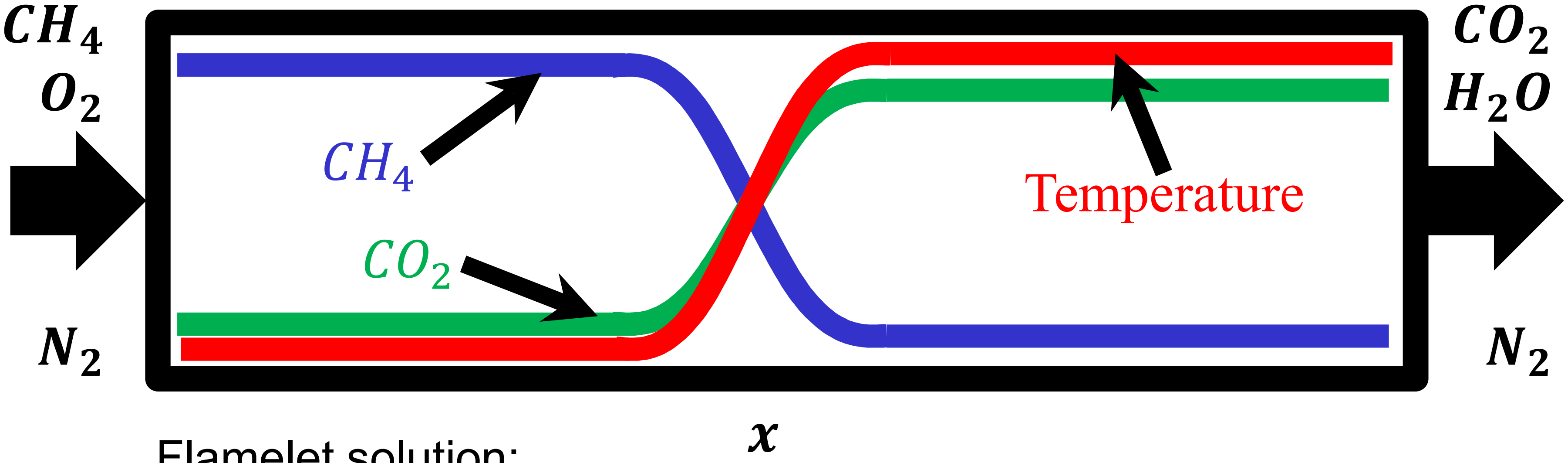
Flamelet Generated Manifolds (FGM)

- Consider a simplyfied combustion configuration

$$CH_4 + 2O_2 + N_2 \rightarrow CO_2 + 2H_2O + N_2$$



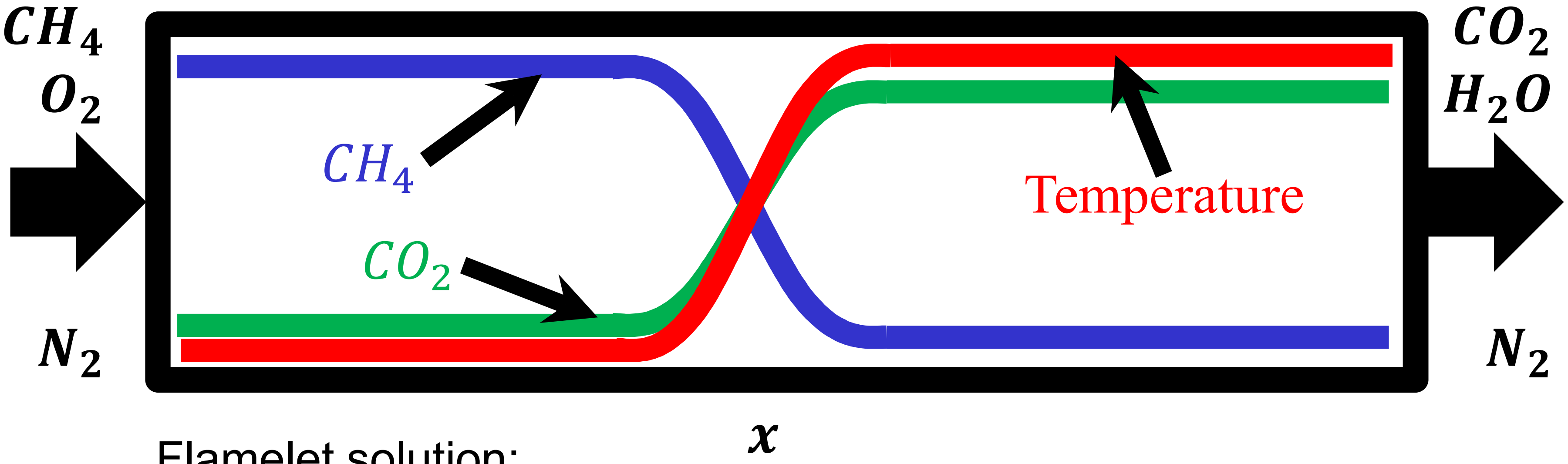
Flamelet solution:

- $T(x)$
- $\rho(x)$
- $CH_4(x)$
- $O_2(x)$
- $CO_2(x)$
- $\dots$

Flamelet Generated Manifolds (FGM)

- Consider a simplyfied combustion configuration

$$CH_4 + 2O_2 + N_2 \rightarrow CO_2 + 2H_2O + N_2$$



Flamelet solution:

- $T(x) \quad \rightarrow \quad T(CO_2)$
- $\rho(x) \quad \rightarrow \quad \rho(CO_2)$
- $CH_4(x) \quad \rightarrow \quad CH_4(CO_2)$
- $O_2(x) \quad \rightarrow \quad O_2(CO_2)$
- $CO_2(x)$
- $\dots$

Flamelet Generated Manifolds (FGM)

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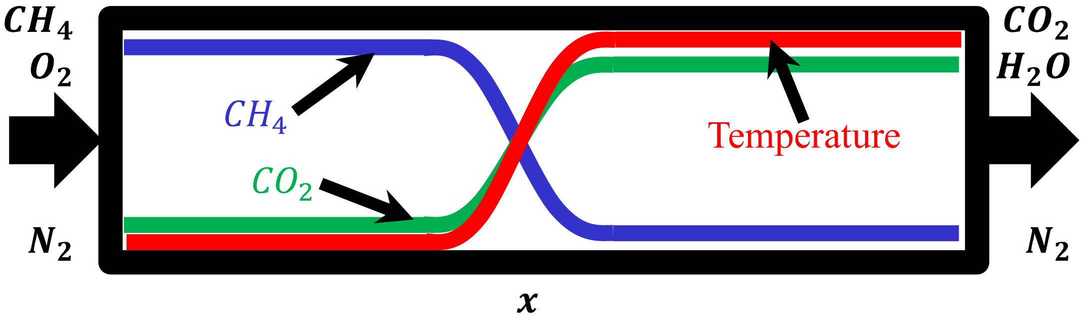
- **Combustion computation with FGM**
- **Conservation equations**
  - Mass ρ
  - Momentum u
  - Enthalpy h
  - CO_2
- **Chemical reaction rate for CO2 and all other species mass fractions are obtained from the flamelet solution**



FGM Tables

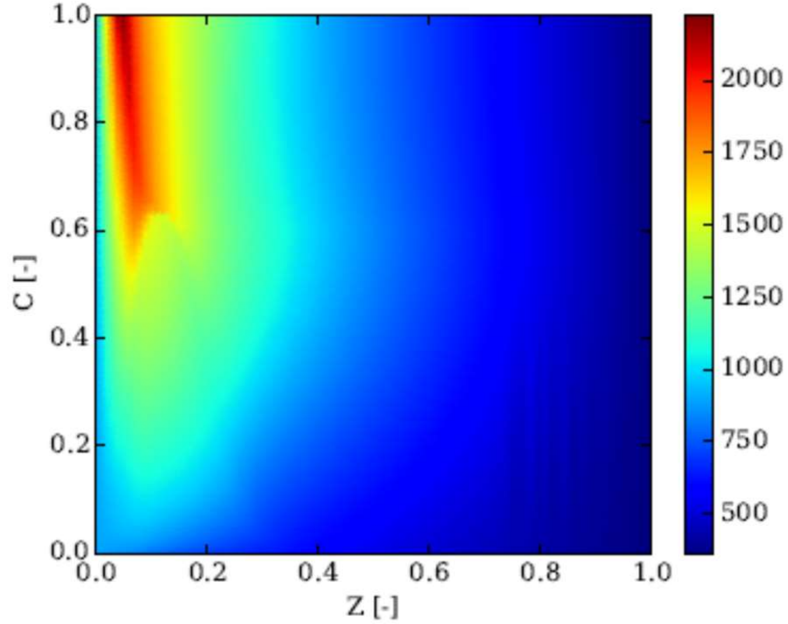


Figure : Temperature

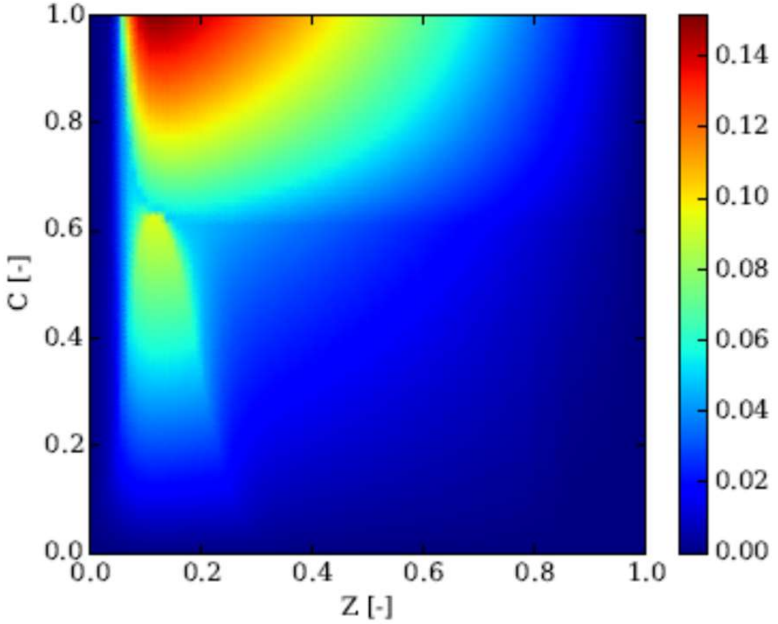


Figure : CO mass fraction

Chemistry parametrized by mixture fraction *Z* and the reaction progress variable *C*

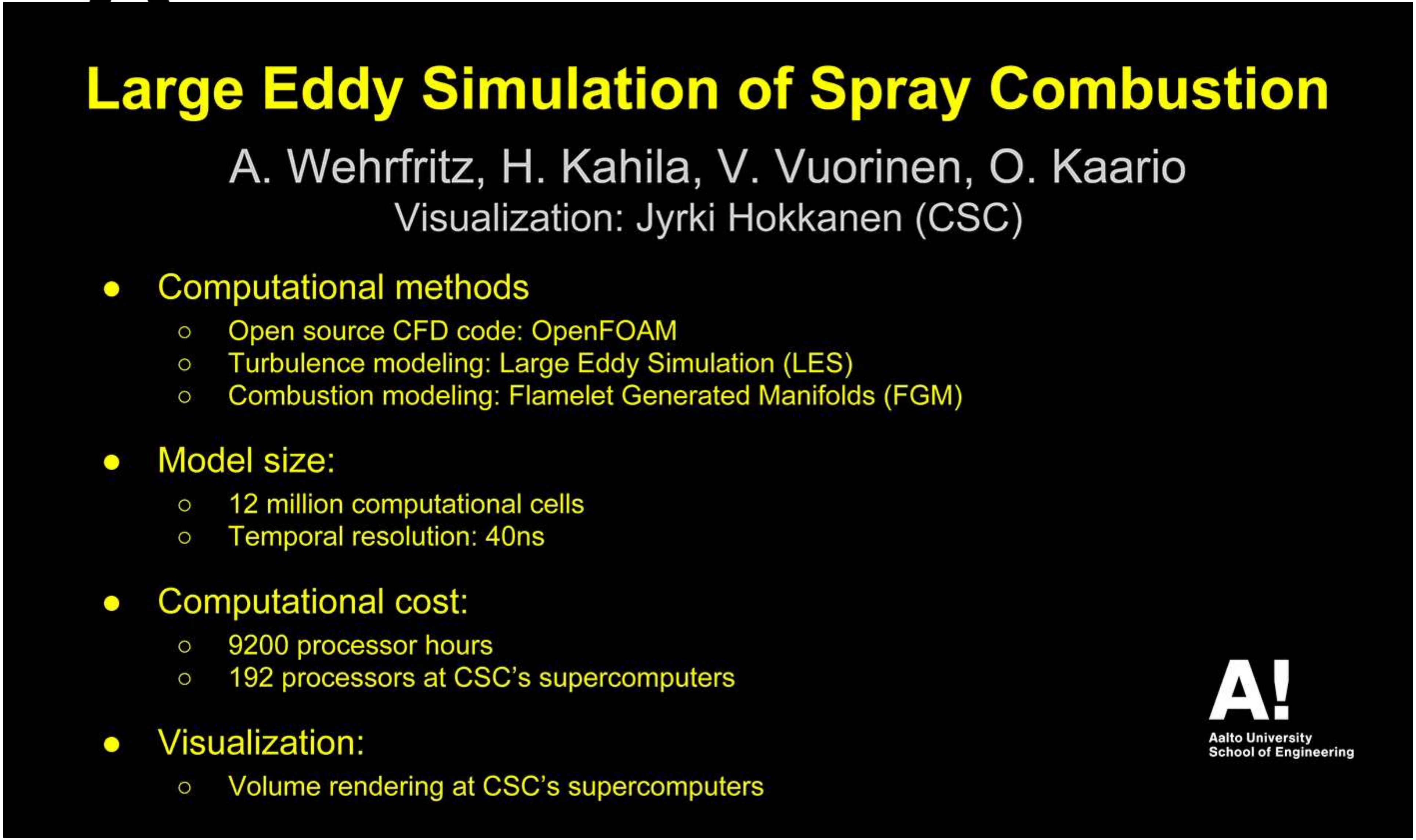
Spray combustion simulation

- **Objectives:**
  - Investigate the ignition characteristics and early flame structure using Large Eddy Simulation and Flamelet Generated Manifold (FGM)
  - **Case: ECN Spray A** (Engine Combustion Network)
  - Constant volume combustion vessel T = 900 K
  - P_amb 6MPa Rhoo_amb = 22:8 kg/m3
  - 15% O2 Pinj = 150MPa

Computational Methods

- Flow solver
  - Implicit Large Eddy Simulation
  - Lagrangian Particle Tracking
  - OpenFOAM 2.2.x
  - Advanced thermodynamic/transport models (i.e. Wilke/Mathur mixture models)
- Flamelet Generated Manifolds (FGM)
  - Tabulated chemistry model
  - State of combustion is parametrized by a few control variables (here, mixture fraction and a reaction progress variable)
  - Chemistry data obtained from 1D igniting/steady counterflow diffusion flames (i.e. flamelets)
  - Detailed chemical kinetics (253 species, 1437 reactions)

Results



Large Eddy Simulation of Spray Combustion

A. Wehrfritz, H. Kahila, V. Vuorinen, O. Kaario

Visualization: Jyrki Hokkanen (CSC)

- Computational methods
    - Open source CFD code: OpenFOAM
    - Turbulence modeling: Large Eddy Simulation (LES)
    - Combustion modeling: Flamelet Generated Manifolds (FGM)
- Model size:
    - 12 million computational cells
    - Temporal resolution: 40ns
- Computational cost:
    - 9200 processor hours
    - 192 processors at CSC's supercomputers
- Visualization:
    - Volume rendering at CSC's supercomputers

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Results

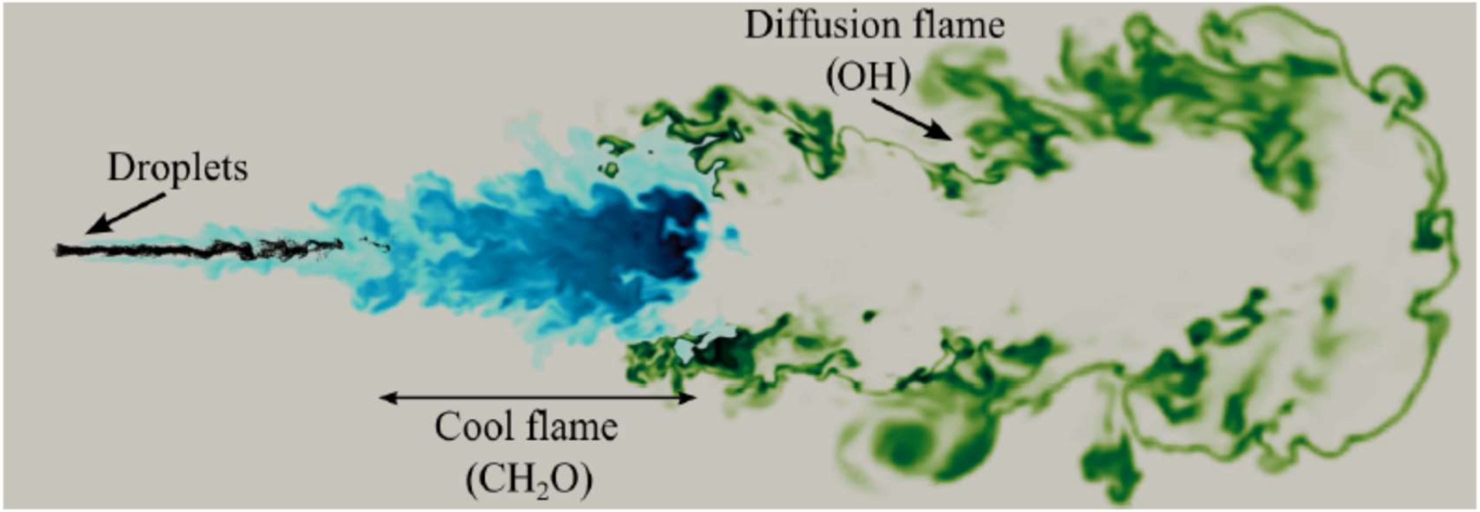

Figure 8: Spatial CH_2O and OH fields for the 100 MPa case at $t = 1.5$ ms.

H. Kahila et al., 2017

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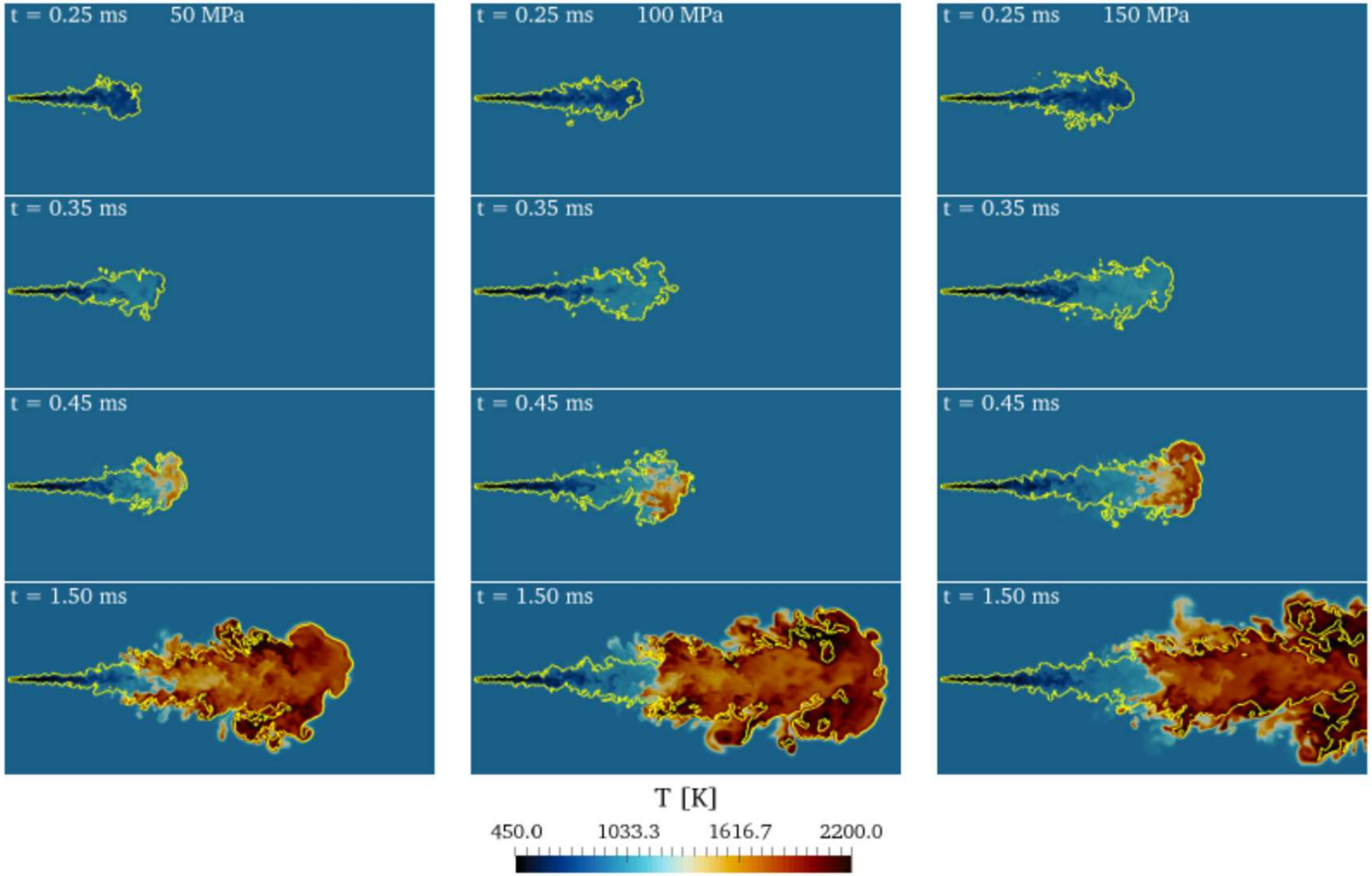
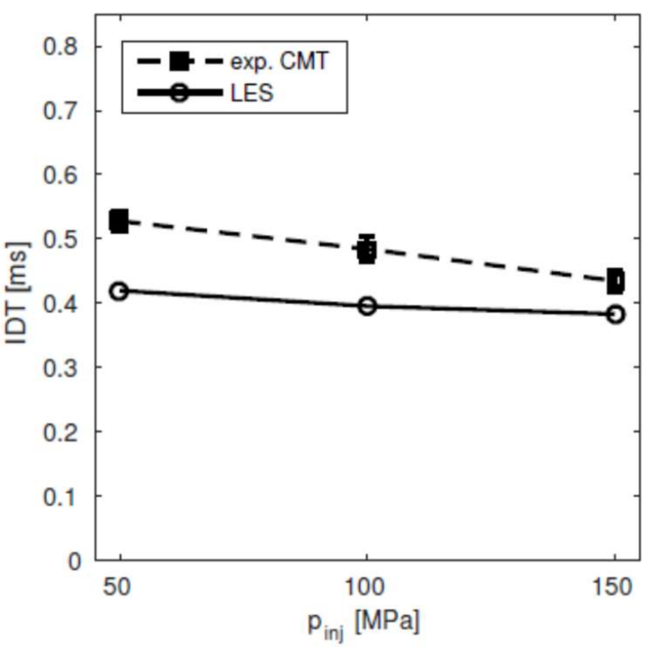
Results

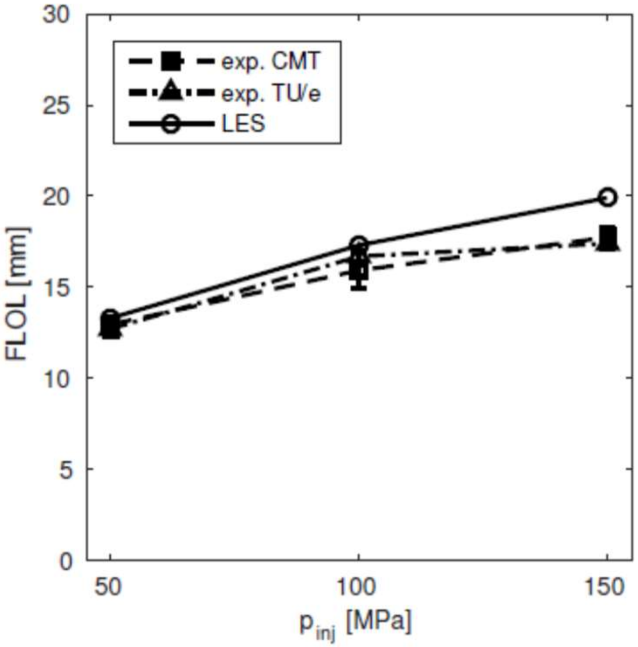


H. Kahila et al., 2017

Results



Ignition delay time



Flame lift off lenght

H. Kahila et al., 2017

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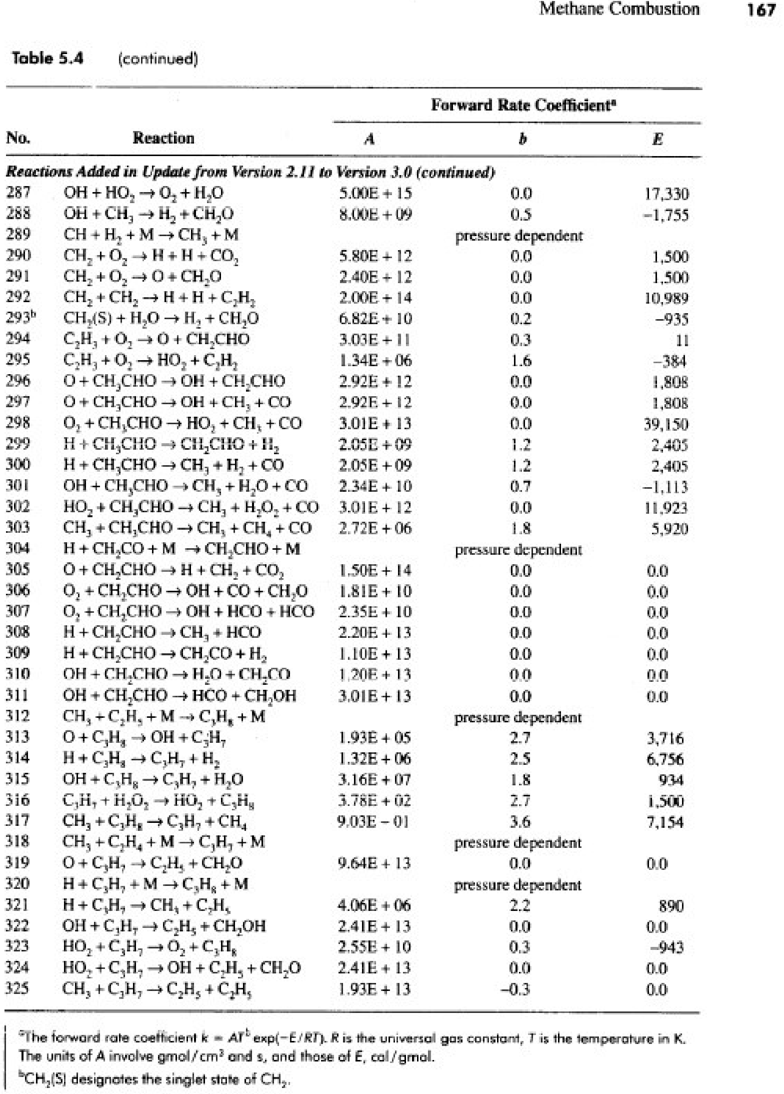
Direct Chemistry

- **Methane chemistry**
- Detailed methane (CH_4) chemistry involves 53 species and 325 reaction (GRI 3.0 mechanism)
- Or reduced n-dodecane mechanism by Ranzi et al. Involving 96 species and 993 reactions



Methane Combustion 167

Table 5.4 (continued)

No.	Reaction	Forward Rate Coefficient[a] A	b	E
Reactions Added in Update from Version 2.11 to Version 3.0 (continued)				
287	$OH + HO_2 \rightarrow O_2 + H_2O$	5.00E + 15	0.0	17,330
288	$OH + CH_3 \rightarrow H_2 + CH_2O$	8.00E + 09	0.5	−1,755
289	$CH + H_2 + M \rightarrow CH_3 + M$		pressure dependent	
290	$CH_2 + O_2 \rightarrow H + H + CO_2$	5.80E + 12	0.0	1,500
291	$CH_2 + O_2 \rightarrow O + CH_2O$	2.40E + 12	0.0	1,500
292	$CH_2 + CH_2 \rightarrow H + H + C_2H_2$	2.00E + 14	0.0	10,989
293[b]	$CH_2(S) + H_2O \rightarrow H_2 + CH_2O$	6.82E + 10	0.2	−935
294	$C_2H_3 + O_2 \rightarrow O + CH_2CHO$	3.03E + 11	0.3	11
295	$C_2H_3 + O_2 \rightarrow HO_2 + C_2H_2$	1.34E + 06	1.6	−384
296	$O + CH_3CHO \rightarrow OH + CH_2CHO$	2.92E + 12	0.0	1,808
297	$O + CH_3CHO \rightarrow OH + CH_3 + CO$	2.92E + 12	0.0	1,808
298	$O_2 + CH_3CHO \rightarrow HO_2 + CH_3 + CO$	3.01E + 13	0.0	39,150
299	$H + CH_3CHO \rightarrow CH_2CHO + H_2$	2.05E + 09	1.2	2,405
300	$H + CH_3CHO \rightarrow CH_3 + H_2 + CO$	2.05E + 09	1.2	2,405
301	$OH + CH_3CHO \rightarrow CH_3 + H_2O + CO$	2.34E + 10	0.7	−1,113
302	$HO_2 + CH_3CHO \rightarrow CH_3 + H_2O_2 + CO$	3.01E + 12	0.0	11,923
303	$CH_3 + CH_3CHO \rightarrow CH_3 + CH_4 + CO$	2.72E + 06	1.8	5,920
304	$H + CH_2CO + M \rightarrow CH_2CHO + M$		pressure dependent	
305	$O + CH_2CHO \rightarrow H + CH_2 + CO_2$	1.50E + 14	0.0	0.0
306	$O_2 + CH_2CHO \rightarrow OH + CO + CH_2O$	1.81E + 10	0.0	0.0
307	$O_2 + CH_2CHO \rightarrow OH + HCO + HCO$	2.35E + 10	0.0	0.0
308	$H + CH_2CHO \rightarrow CH_3 + HCO$	2.20E + 13	0.0	0.0
309	$H + CH_2CHO \rightarrow CH_2CO + H_2$	1.10E + 13	0.0	0.0
310	$OH + CH_2CHO \rightarrow H_2O + CH_2CO$	1.20E + 13	0.0	0.0
311	$OH + CH_2CHO \rightarrow HCO + CH_2OH$	3.01E + 13	0.0	0.0
312	$CH_3 + C_2H_5 + M \rightarrow C_3H_8 + M$		pressure dependent	
313	$O + C_3H_8 \rightarrow OH + C_3H_7$	1.93E + 05	2.7	3,716
314	$H + C_3H_8 \rightarrow C_3H_7 + H_2$	1.32E + 06	2.5	6,756
315	$OH + C_3H_8 \rightarrow C_3H_7 + H_2O$	3.16E + 07	1.8	934
316	$C_3H_7 + H_2O_2 \rightarrow HO_2 + C_3H_8$	3.78E + 02	2.7	1,500
317	$CH_3 + C_3H_8 \rightarrow C_3H_7 + CH_4$	9.03E − 01	3.6	7,154
318	$CH_3 + C_2H_4 + M \rightarrow C_3H_7 + M$		pressure dependent	
319	$O + C_3H_7 \rightarrow C_2H_5 + CH_2O$	9.64E + 13	0.0	0.0
320	$H + C_3H_7 + M \rightarrow C_3H_8 + M$		pressure dependent	
321	$H + C_3H_7 \rightarrow CH_3 + C_2H_5$	4.06E + 06	2.2	890
322	$OH + C_3H_7 \rightarrow C_2H_5 + CH_2OH$	2.41E + 13	0.0	0.0
323	$HO_2 + C_3H_7 \rightarrow O_2 + C_3H_8$	2.55E + 10	0.3	−943
324	$HO_2 + C_3H_7 \rightarrow OH + C_2H_5 + CH_2O$	2.41E + 13	0.0	0.0
325	$CH_3 + C_3H_7 \rightarrow C_2H_5 + C_2H_5$	1.93E + 13	−0.3	0.0

[a] The forward rate coefficient $k = AT^b \exp(-E/RT)$. R is the universal gas constant, T is the temperature in K. The units of A involve gmol/cm³ and s, and those of E, cal/gmol.

[b] $CH_2(S)$ designates the singlet state of CH_2.

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Solve a transport equation for each species

$$\frac{\partial \rho Y_k}{\partial t} + \frac{\partial \rho u_j Y_k}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho D_k \frac{\partial Y_k}{\partial x_j}\right) + w_k$$

Reaction rates for each species from rate law and Arrhenius reaction rates

$$aA + bB \rightarrow dD + eE \ldots$$

$$\frac{d[A]}{dt} = -k[A]^a[B]^b$$

$$k = A \cdot e^{-E_a/RT}$$

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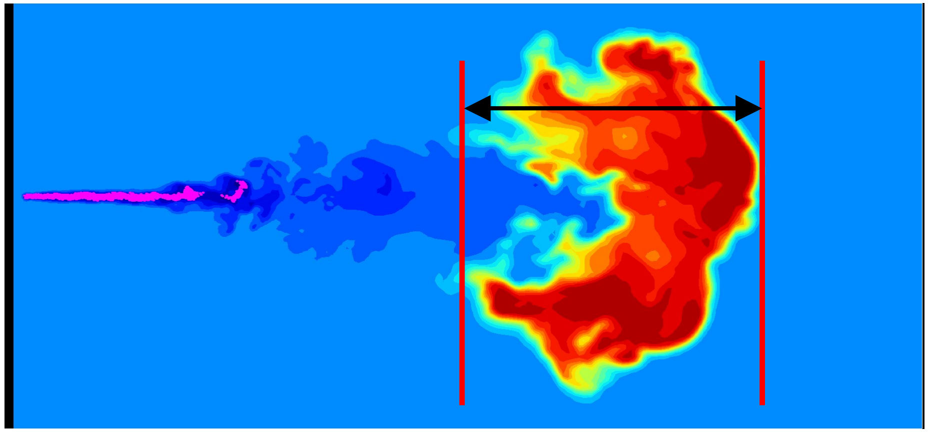
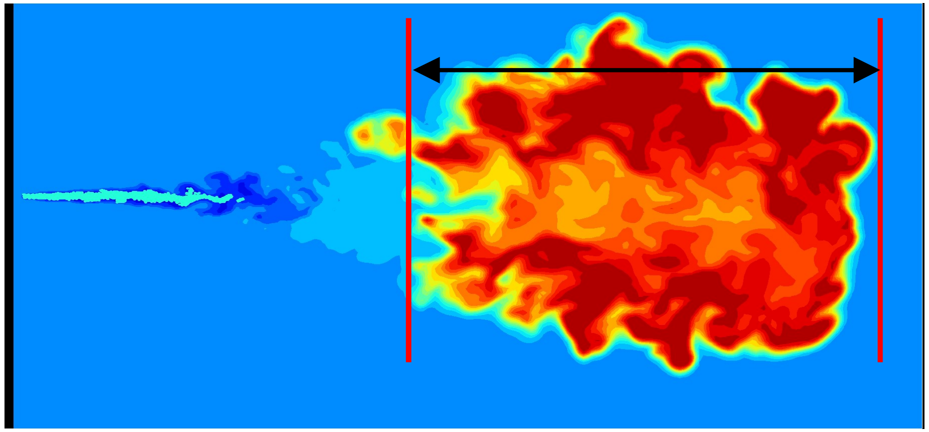
n-dodecane - methanol



n-dodecane



t = 1.6 ms

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Emissions: NOx and soot

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NO$_x$ emissions

- NO + NO2 = NOx
- Nitric oxide + nitrogen dioxide = nitrogen oxides
- Typically >95% is NO, rest is NO2
- Environmental effects of NOx
  - Precursor of acid rain
  - Photochemical smog in the presence of unburned hydrocarbons and sunlight

- Nitrous oxide
  - Pollutant N_2O
    - Ozone depletion
    - Greenhouse gas

NO_x emissions

- The different types of NO_x emissions:

  - Thermal NO_x
  - Prompt NO
  - NO produced via N_2O
  - Fuel bound nitrogen

Thermal NO

- **Or Zeldovich-NO (1946)**

$$O + N_2 \xrightarrow{k_1} NO + N \qquad k_1 = 1.8 \cdot 10^{14} \exp\left(-318 kj\, mol^{-1} /(RT)\right)$$

$$N + O_2 \xrightarrow{k_2} NO + O \qquad k_2 = 9 \cdot 10^{9} \exp\left(-27 kj\, mol^{-1} /(RT)\right)$$

$$N + OH \xrightarrow{k_3} NO + H \qquad k_3 = 2.8 \cdot 10^{13}$$

First reaction has high activation energy and hence it has relevant reaction rates only at high temperatures. It is the rate limiting step of the mechanism.

Thermal NO

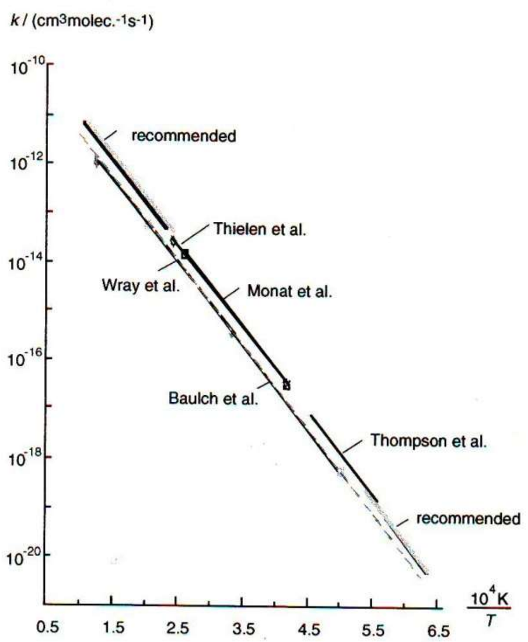
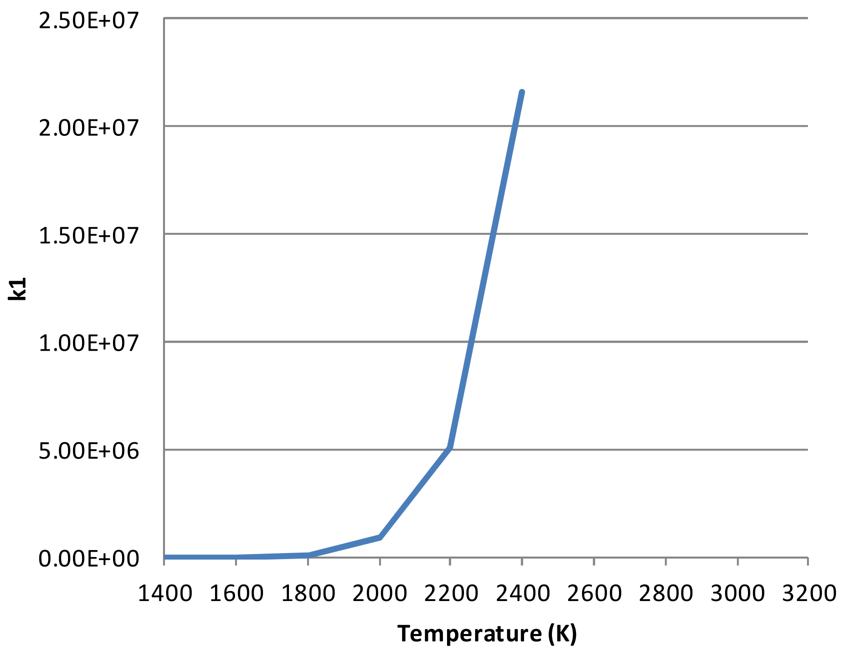


Fig. 17.1. Arrhenius plot $k = k(1/T)$ for the reaction $O + N_2 \rightarrow NO + N$ (Riedel et al. 1992)

Warnatz, Maas, and Dibble 1998



Temperature dependence of the rate coefficient k_1 in the Zeldovich mechanism.

Thermal NO

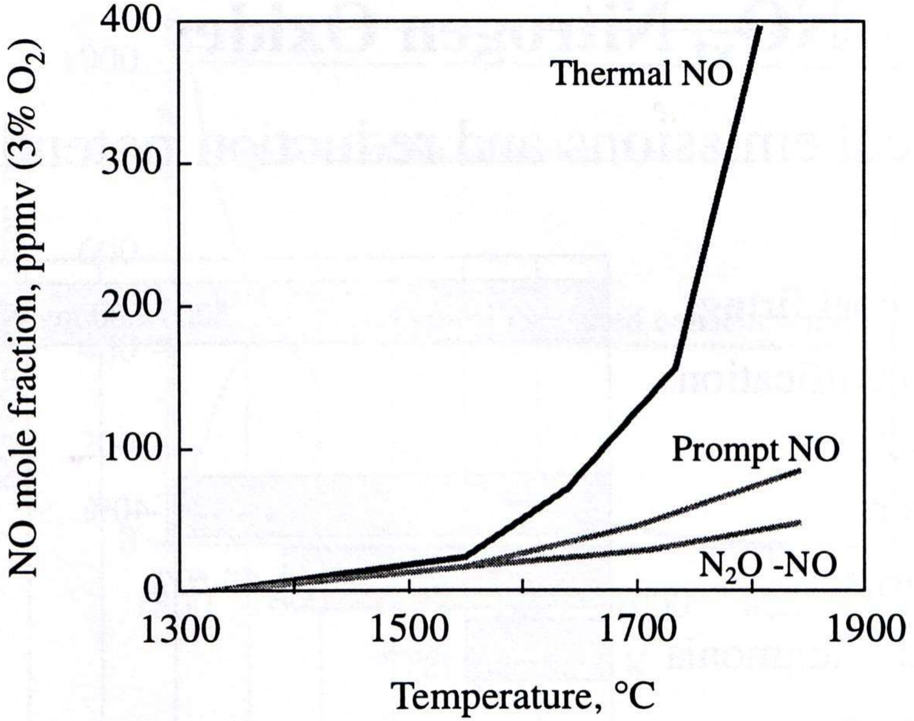
- The thermal NO formation can be approximated by

$$\frac{d[NO]}{dt} = 2k_1[O][N_2]$$

- Consequently, NO formation can be reduced by lowering [O] or [N2] or k_1 (temperature)

NO$_x$ emissions

- **Thermal NO forms only at high temperatures**
- **Thermal NO chemistry “freezes” at lower temperatures**



N_2 Fixation to NO - Effect of Temperature
(CH_4, SR = 1.15, CSTR, 1 atm, 10 ms)

P. Kilpinen 1995

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Soot emissions

- Complicated reaction mechanisms
- Detailed formation mechanisms will be provided in another lecture

- Soot formation starts with the production of polycyclic aromatic hydrocarbons or PAH’s. Most important precursor of PAH is acetylene (C2H2).
- PAH consists of e.g. benzene rings (C6H6).
- PAH grows by acetyle addition

- PAH and acetylene can be found under rich conditions

Soot emissions

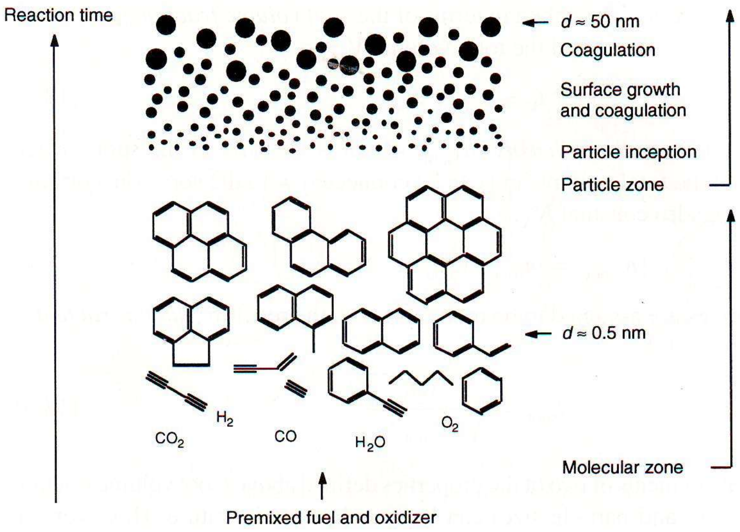

Fig. 18.7. Schematic reaction path leading to soot formation in homogeneous mixtures or premixed flames (Bockhorn 1994); ≡ is an acetylenic triple bond (≡ = acetylene, e. g.)

Warnatz, Maas, and Dibble 1998

Typical soot particle size is between 10-1000 nm and the maximum number density close to 100nm.
Early soot chemistry is fast.

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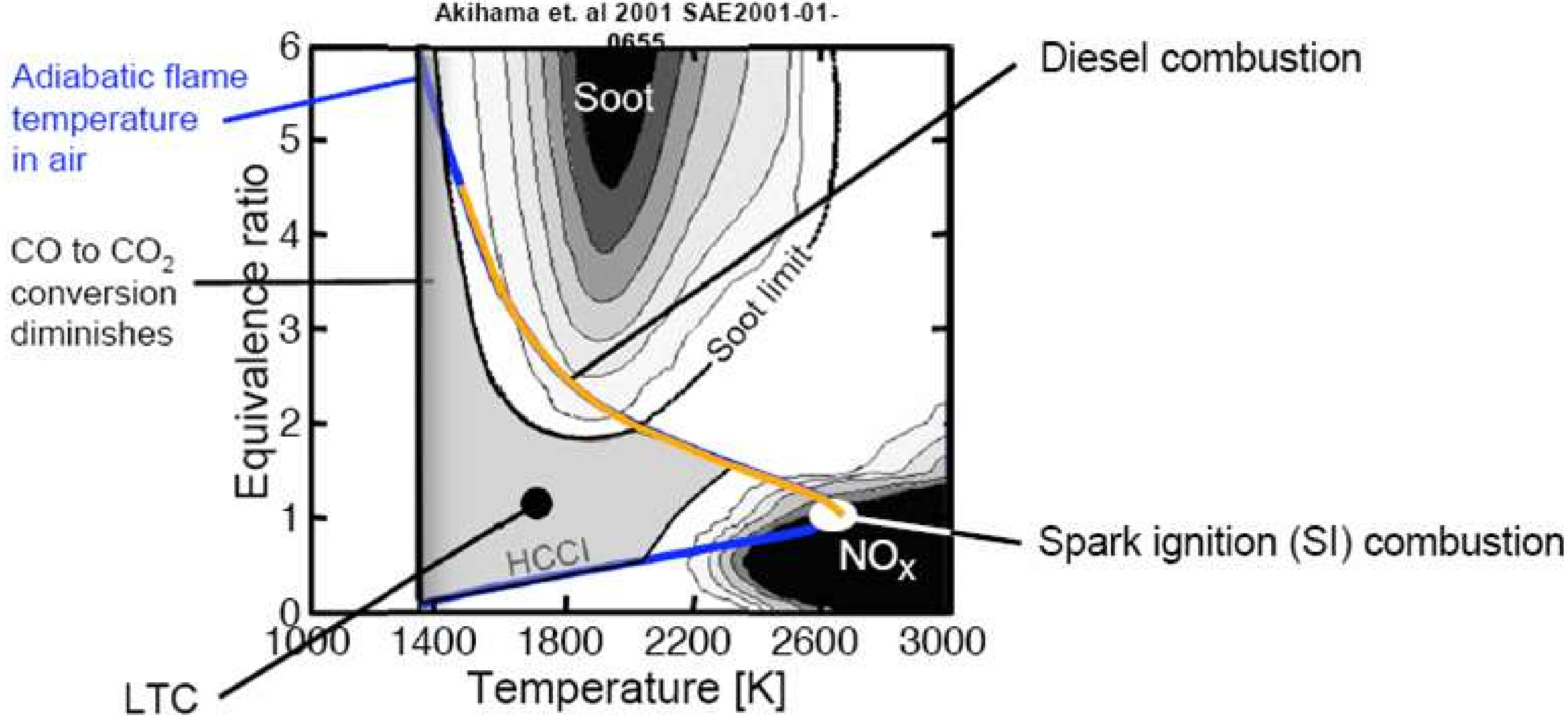
Soot and NO_x formation tendencies during Diesel combustion


Akihama et. al 2001 SAE2001-01-0655

Adiabatic flame temperature in air

CO to CO_2 conversion diminishes

LTC

Diesel combustion

Spark ignition (SI) combustion

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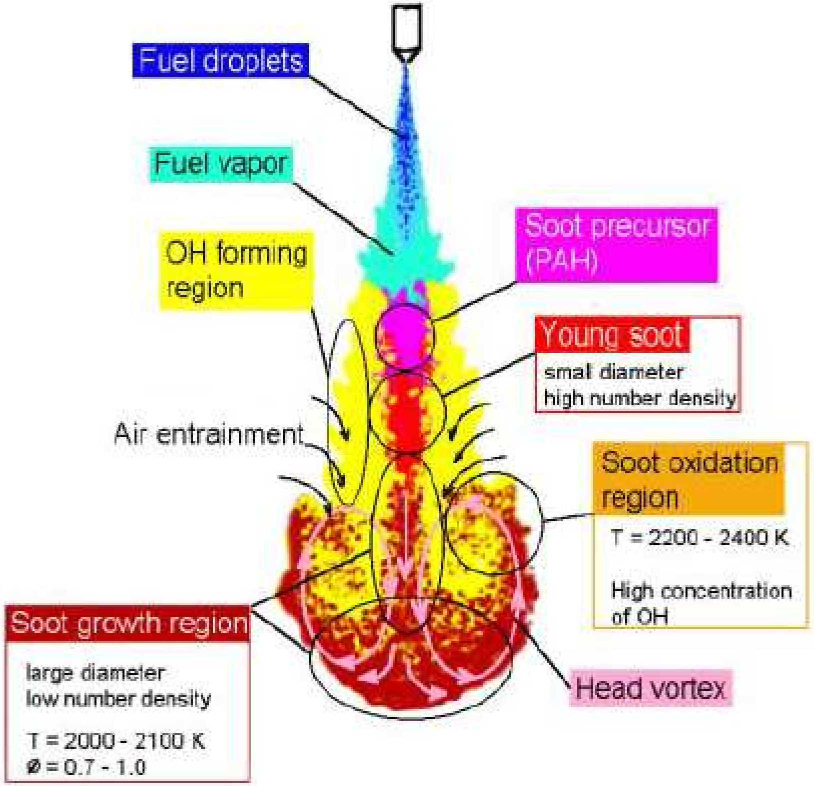
Conceptual model of Diesel combustion: Soot formation and oxidation



T. Aizawa et al. 2002

Additions to Dec's model:
air entrainment details and
inner structures

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Additional Reading

- Combustion, Warnatz, J., Maas, U., and Dibble, R.W., 2nd edition, ISBN 3-540-65228-0, 1999.
- Poltto ja Palaminen, 2. painos, ISBN 951-666-604-3, 2002.
- Turbulent Combustion, Norbert Peters, ISBN 0-951-66082-3, 2000.
- Combustion Physics, Chung Law, ISBN 978-0-521-15421-5, 2006 (paperback 2010)