Flame ignition - basic concepts

- Experiments (Lewis & von Elbe, 1987) show that a minimum energy ($E_{\text{min}}$) (not just minimum $T$ or volume) required for ignition
- $E_{\text{min}}$ lowest near stoichiometric (typically 0.2 mJ) but minimum shifts to richer mixtures for higher HCs (why? Stay tuned…)
- Prediction of $E_{\text{min}}$ relevant to energy conversion and fire safety
Flame ignition - basic concepts

- $E_{\text{min}}$ related to need to create flame kernel with dimension ($\delta$) large enough that chemical reaction ($\omega$) can exceed conductive loss rate ($\alpha/\delta^2$), thus $\delta > (\alpha/\omega)^{1/2} \sim \alpha/\omega \sim \delta$
- $E_{\text{min}} \sim$ energy contained in volume of gas with $T \approx T_{\text{ad}}$ and radius $\approx \delta = 4\alpha/S_L$

\[
E_{\text{min}} = \frac{4\pi}{3} \delta^3 \rho C_p (T_{\text{ad}} - T_{\infty}) = 0.3 \frac{4\pi}{3} \delta^3 \rho C_p (T_{\text{ad}} - T_{\infty}) = 34\alpha^2 \frac{k(T_{\text{ad}} - T_{\infty})}{S_L^3}
\]

Flame ignition - simple $E_{\text{min}}$ formula

- Since $\alpha \sim P^{-1}$, $E_{\text{min}} \sim P^{-2}$ if $S_L$ is independent of $P$
- $E_{\text{min}} \approx 100,000$ times larger in a He-diluted than SF$_6$-diluted mixture with same $S_L$, same $P$ (due to $\alpha$ and $k$ [thermal conductivity] differences)
- Stoichiometric CH$_4$-air @ 1 atm: predicted $E_{\text{min}} \approx 0.010$ mJ $\approx 30x$ times lower than experiment (due to chemical kinetics, heat losses, shock losses …)
- ... but need something more (Lewis number effects):
  - 10% H$_2$-air ($S_L \approx 10$ cm/sec): predicted $E_{\text{min}} \approx 0.3$ mJ $= 2.5$ times higher than experiments
  - Lean CH$_4$-air ($S_L \approx 5$ cm/sec): $E_{\text{min}} \approx 5$ mJ compared to $\approx 5000$ mJ for lean C$_3$H$_8$-air with same $S_L$ - but prediction is same for both
Flame ignition - simple $E_{\text{min}}$ formula

- $E_{\text{min}} \sim \delta^3 \rho_{\infty}$
- $\delta$ hard to measure, but quenching distance ($\delta_q$) (min. tube diameter through which flame can propagate) should be $\sim \delta$ since Peclet number at extinction [to be discussed later] $Pe_{\text{lim}} = S_{\text{L,lim}} \delta_q / \alpha \sim \delta_q / \delta \approx 40 \approx$ constant, thus should have $E_{\text{min}} \sim \delta_q^3 P$
- Correlation so-so

Flame ignition - Lewis number effects

- Recall flame ball solution – use $R_z$ instead of $\delta$ to capture Le effects?

$$ \frac{R}{\delta} = \frac{1}{Le} \exp \left( \frac{\beta(1)}{2(\theta - 1)} \right) $$

- Energy requirement very strongly dependent on Lewis number!
- 10% increase in Le: 2.5x increase in $E_{\text{min}}$ ($R_z$: 2.2x (Tromans & Furzeland))
Flame ignition - Lewis number effects

- Why does minimum MIE shift to richer mixtures for higher HCs?
  - \( L_{\text{effective}} = \frac{\alpha_{\text{effective}}}{D_{\text{effective}}} \)
  - \( D_{\text{eff}} = D \) of stoichiometrically limiting reactant, thus for lean mixtures \( D_{\text{eff}} = D_{\text{O}_2} \)
  - Rich mixtures \( D_{\text{eff}} = D_{\text{O}_2} \)

- Lean mixtures - \( L_{\text{effective}} = L_{\text{fuel}} \)
  - Mostly air, so \( \alpha_{\text{eff}} \approx \alpha_{\text{air}} \); also \( D_{\text{eff}} = D_{\text{fuel}} \)
  - Higher HCs: \( D_{\text{fuel}} < D_{\text{O}_2} \), thus \( L_{\text{eff}} < 1 \), much higher MIE

- Rich mixtures - \( L_{\text{effective}} = L_{\text{O}_2} \)
  - \( CH_4: \alpha_{\text{CH}_4} > \alpha_{\text{air}} \) since \( M_{\text{CH}_4} < M_{\text{N}_2&O_2} \), so adding excess \( CH_4 \) INCREASES \( L_{\text{eff}} \)
  - Higher HCs: \( \alpha_{\text{fuel}} < \alpha_{\text{air}} \) since \( M_{\text{fuel}} > M_{\text{N}_2&O_2} \), so adding excess fuel DECREASES \( L_{\text{eff}} \)
  - Actually adding excess fuel decreases both \( \alpha \) and \( D \), but decreases \( \alpha \) more

\[
\alpha_{\text{eff}} = \alpha_{\text{mix}} \sim \sqrt{\frac{\text{Const}_1 \cdot M_{\text{O}_2}}{M_{\text{mix}}}} \cdot D_{\text{O}_2} \sim \sqrt{\frac{\text{Const}_2 \cdot M_{\text{O}_2}}{M_{\text{mix}}}} + \frac{\text{Const}_3}{M_{\text{O}_2}}
\]

Flame ignition - dynamic analysis

- \( R_z \) is related (but not equal) to an ignition requirement
- Joulin (1985) analyzed unsteady equations for Le < 1

\[
\chi(\sigma) \ln(\chi(\sigma)) + \frac{q(\sigma)}{2} = \chi(\sigma) \int_0^\sigma d\chi(s) \frac{ds}{\sqrt{\sigma - s}}
\]

\[
\chi = \frac{R(\sigma)}{R_z}; \sigma \equiv 4\pi \left( \frac{\theta^2}{1 - \varepsilon} \right) \frac{Le}{1 - \sqrt{Le}} \left( \frac{\alpha a}{R_z^2} \right) q \equiv \frac{\Theta}{4\pi \lambda R_z T_{\text{ad}} \theta^*}
\]

\( (\chi, \sigma \) and \( q \) are the dimensionless radius, time and heat input) and found at the optimal ignition duration

\[
E_{\text{min}} = 14\beta \left( \frac{1 - \varepsilon}{\varepsilon} \right) \left( \frac{1 - \sqrt{Le}/\theta^* Le}{\theta^* \theta^*} \right) \rho_{\text{ad}} C_p (T_{\text{ad}} - T_\infty) R_z^3
\]

which has the expected form

\[
E_{\text{min}} \sim \{\text{energy per unit volume} \} \times \{\text{volume of minimal flame kernel} \} \sim \{\rho_{\text{ad}} C_p (T_{\text{ad}} - T_\infty)\} \times (R_z)^3
\]
Flame ignition - dynamic analysis

- Joulin (1985)

Radius vs. time

Minimum ignition energy vs. ignition duration

Flame ignition - effect of spark gap & duration

- Expect “optimal” ignition duration ~ ignition kernel time scale ~ $R^2/\alpha$
- Duration too long - energy wasted after kernel has formed and propagated away - $E_{\text{min}} \sim t^1$
- Duration too short - larger shock losses, larger heat losses to electrodes due to high T kernel

- Expect “optimal” ignition kernel size ~ kernel length scale ~ $R_Z$
- Size too large - energy wasted in too large volume - $E_{\text{min}} \sim R^3$
- Size too small - larger heat losses to electrodes
Flame igniton - effect of flow environment

- Mean flow or random flow (i.e. turbulence) (e.g. inside IC engine or gas turbine) increases stretch, thus $E_{\text{min}}$

Mean flow or random flow (i.e. turbulence) (e.g. inside IC engine or gas turbine) increases stretch, thus $E_{\text{min}}$. Ballal and Lefebvre, 1975

Flame igniton - effect of ignition source

- Laser ignition sources higher than sparks despite lower heat losses, less asymmetrical flame kernel - maybe due to higher shock losses with shorter duration laser source?

Laser ignition sources higher than sparks despite lower heat losses, less asymmetrical flame kernel - maybe due to higher shock losses with shorter duration laser source? Lim et al., 1996
Flammability and extinction limits

- Too lean or too rich mixtures won't burn - flammability limits
- Even if mixture is flammable, still won't burn in some environments
  - Small diameter tubes
  - Strong hydrodynamic strain or turbulence
  - High or low gravity
  - High or low pressure
- Understanding needed for combustion engines & industrial combustion processes (leaner mixtures \( \Rightarrow \) lower \( T_{ad} \) \( \Rightarrow \) lower NO\(_x\));
  - fire & explosion hazard management, fire suppression, ...
- Limits occur for mixtures that are thermodynamically flammable - theoretical adiabatic flame temperature (\( T_{ad} \)) far above ambient temperature (\( T_\infty \))
- Limits characterized by finite (not zero) burning velocity at limit
- Models of limits due to losses - most important prediction: burning velocity at the limit (\( S_{L,lim} \)) - better test of limit predictions than composition at limit

2 limit mechanisms, (1) & (2), yield similar fuel % and \( T_{ad} \) at limit but very different \( S_{L,lim} \)
Flammability limits in vertical tubes

- Most common apparatus - vertical tube (typ. 5 cm in diameter)
- Ignite mixture at one end of tube, if it propagates to other end, it's "flammable"
- Limit composition depends on orientation - buoyancy effects

Chemical kinetics of flammability limits

- Lean hydrocarbon-air flames: recall main branching reaction (promotes combustion) is (in units of moles, cm^2, s, cal)
  \[ H + O_2 \rightarrow OH + O; \quad \frac{d[H]}{dt} = -10^{18.7} T^{-0.4} [H][O_2]e^{-16500/RT} \]
  Depends on P^2 since [ ] ~ P, strongly dependent on T
- Why important? Only energetically viable way to break O=O bond (120 kcal/mole), even though [H] is small
- Main H consumption reaction
  \[ H + O_2 + M \rightarrow HO_2 + M; \quad \frac{d[H]}{dt} = -10^{15.2} T^0 [H][O_2][M]e^{1000/RT} \]
  for M = N_2 (higher rate for CO_2 and especially H_2O)
  Depends on P^3, nearly independent of T
- Why important? Inhibits combustion by replacing H with much less active HO_2
- Branching or inhibition may be faster depending on T and P
### Chemical kinetics of flammability limits

- Rates equal ("crossover") when 
  \[ [M] = 10^{1.5} T^{-0.8} \exp^{-17500/RT} \]
- Ideal gas law: \( P = [M]RT \) thus 
  \[ P = 10^{3.4} T^{0.2} \exp^{-17500/RT} \text{ (P in atm)} \]
  \( \Rightarrow \) crossover at 950K for 1 atm, higher T for higher P
- …but this only indicates that chemical mechanism may change and perhaps overall reaction rate \( \omega \) will drop rapidly
- Computations show no limits without losses – no purely chemical criterion (Lakshmisha et al., 1990; Giovangigli & Smooke, 1992) - for steady planar adiabatic flames, \( S_L \) decreases smoothly to zero as fuel conc. decreases (domain sizes up to 10 m, \( S_L \) down to 0.02 cm/s)
- …but as \( S_L \) decreases, \( \delta \) increases - need larger computational domain or experimental apparatus
- Also more buoyancy & heat loss effects as \( S_L \) decreases …. 

### Aerodynamic effects on premixed flames

- Aerodynamic effects occur on a large scale compared to the transport or reaction zones but affect \( S_L \) and even existence of the flame
- Why only at large scale?
  - Re on flame scale \( \approx S_L \delta/\nu \) (\( \nu \) = kinematic viscosity)
  - \( \text{Re} = (S_L \delta/\alpha)/(\alpha/\nu) = (1)(1/Pr) \approx 1 \) since \( Pr \approx 1 \) for gases
  - \( \text{Re}_{\text{flame}} \approx 1 \Rightarrow \text{viscosity suppresses flow disturbances} \)
- Key parameter: stretch rate (\( \Sigma \)) 
  \[ \Sigma = \frac{1}{A} \frac{dA}{dt} \text{ (A = flame area)} \]
- Generally \( \Sigma \sim U/d \)
  - \( U \) = characteristic flow velocity
  - \( d \) = characteristic flow length scale
Aerodynamic effects on premixed flames

- Strong stretch ($\Sigma \geq \omega \sim S_L^{2/\alpha}$ or Karlovitz number $Ka = \Sigma \alpha/S_L^2 \geq 1$) extinguishes flames
- Moderate stretch strengthens flames for $Le < 1$

$$Le = \frac{\text{Thermal diffusivity of the bulk mixture (}\alpha)}{\text{Mass diffusivity of scarce reactant into the bulk mixture (D)}}$$

Buckmaster & Mikolaitis, 1982a, cold reactants against adiabatic products

Lewis number tutorial

- $Le$ affects flame temperature in curved (shown below) or stretched flames
- When $Le < 1$, additional thermal enthalpy loss in curved/stretched region is less than additional chemical enthalpy gain, thus local flame temperature in curved region is higher, thus reaction rate increases drastically, local burning velocity increases
- Opposite behavior for oppositely curved flames
Time scales - premixed-gas flames

- Chemical time scale
  \[ t_{\text{chem}} \approx d/S_L \approx (\alpha/S_L)/S_L \approx \alpha/S_L^2 \]

- Conduction time scale
  \[ t_{\text{cond}} \approx T_{ad}/(dT/dt) \approx d^2/16\alpha \]
  \( d \) = tube or burner diameter

- Buoyant transport time scale
  \[ t \sim d/V; \quad V \approx (gd/\rho)^{1/2} \approx (gd)^{1/2} \]
  \( g = \text{gravity}, \quad d = \text{characteristic dimension} \)

  - Inviscid: \( t_{\text{inv}} \sim d/(gd)^{1/2} \)
  - Viscous: \( d \sim \sqrt{V} \Rightarrow t_{\text{vis}} \approx (V/g)^{1/3} \)

- Radiation time scale
  \[ t_{\text{rad}} \approx T_{ad}/(dT/dt) \approx T_{ad}/(L/r_Cp) \]
  \( L = \text{radiative heat loss per unit volume} \)

  - Optically thin radiation: \( \Lambda = 4\sigma_T(T_{ad}^4 - T_{\infty}^4) \)
  - \( \sigma_T = \text{Planck mean absorption coefficient} \) [typ. 2 m\(^{-1}\) at 1 atm]
  - \( \Lambda \approx 10^6 \text{ W/m}^2 \text{ for HC-air combustion products} \)
  - \( t_{rad} \sim P/\sigma_T(T_{ad}^4 - T_{\infty}^4) \sim P^0, \quad P = \text{pressure} \)

Time scales (hydrocarbon-air, 1 atm)

<table>
<thead>
<tr>
<th>Time scale</th>
<th>Stoich. flame</th>
<th>Limit flame</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry ( t_{\text{chem}} )</td>
<td>0.00094 sec</td>
<td>0.25 sec</td>
</tr>
<tr>
<td>or diffusion ( t_{\text{diff}} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buoyant, inviscid ( t_{\text{inv}} )</td>
<td>0.071 sec</td>
<td>0.071 sec</td>
</tr>
<tr>
<td>Buoyant, viscous ( t_{\text{vis}} )</td>
<td>0.012 sec</td>
<td>0.010 sec</td>
</tr>
<tr>
<td>Conduction ( t_{\text{cond}} ), ( d = 5 \text{ cm} )</td>
<td>0.95 sec</td>
<td>1.4 sec</td>
</tr>
<tr>
<td>Radiation ( t_{\text{rad}} )</td>
<td>0.13 sec</td>
<td>0.41 sec</td>
</tr>
</tbody>
</table>

- Conclusions
  - Buoyancy unimportant for near-stoichiometric flames
    \( (t_{\text{inv}} \& t_{\text{vis}} \gg t_{\text{chem}}) \)
  - Buoyancy strongly influences near-limit flames at 1g
    \( (t_{\text{inv}} \& t_{\text{vis}} < t_{\text{chem}}) \)
  - Radiation effects unimportant at 1g \( (t_{\text{vis}} < t_{\text{rad}}; t_{\text{inv}} < t_{\text{rad}}) \)
  - Radiation effects dominate flames with low \( S_L \)
    \( (t_{\text{rad}} \approx t_{\text{chem}}), \quad \text{but only observable at } \mu g \)
  - Small \( t_{\text{rad}} \) (a few seconds) - drop towers useful
  - Radiation > conduction only for \( d > 3 \text{ cm} \)
  - \( Re \sim Vd/\nu \sim (gd^{3/2})^{1/2} \Rightarrow \text{turbulent flow at 1g for } d > 10 \text{ cm} \)
Flammability limits due to losses

- **Golden rule:** at limit

\[
\frac{\text{Heat loss rate per unit volume}}{\text{Heat generation rate per unit volume}} = \frac{1}{\beta}
\]

- Why $1/\beta$ not 1? $T$ can only drop by $O(1/\beta)$ before extinction - $O(1)$ drop in $T$ means exponentially large drop in reaction rate $\omega$, thus exponentially small $S_L$ (could also say heat generation occurs only in $\delta/\beta$ region whereas loss occurs over $\delta$ region)

\[
\begin{align*}
\text{Heat loss rate per unit volume} & \approx 1 \beta \\
\text{Heat generation rate per unit volume} & \approx 1 \beta \\
\text{Adiabatic flame} & \\
\text{Non-adiabatic flame} & \\
\text{Convective-diffusive zone, } O(\delta) & \\
\text{Reactive-diffusive zone, } O(\delta/\beta) & \\
\text{Convective-loss zone} & \\
\end{align*}
\]

- Heat loss to walls
  - $t_{\text{chem}} \sim t_{\text{cond}} \Rightarrow S_{L,\text{lim}} = (8\beta)^{1/2}a/d$ at limit
  - or $Pe_{\text{lim}} = S_{L,\text{lim}}/\alpha = (8\beta)^{1/2} = 9$
  - Actually $Pe_{\text{lim}} \approx 40$ (USE $Pe_{\text{lim}} \approx 40$ NOT 9) due to temperature averaging - consistent with experiments (Jarosinsky, 1983)

- Upward propagation in tube
  - Rise speed at limit $= 0.3(gd)^{1/2}$ due to buoyancy alone (same as air bubble rising in water-filled tube (Levy, 1965))
    \[
    \Rightarrow Pe_{\text{lim}} \approx 0.28 Ra_d^{1/2}; \quad Ra_d = \text{Rayleigh number} = gd^3/\alpha \nu
    \]
  - Causes stretch extinction (Buckmaster & Mikolaitis, 1982b):
    \[
    t_{\text{chem}} \approx t_{\text{inv}} \quad \text{or} \quad 1/t_{\text{chem}} = \Sigma_{\text{inv}}
    \]
    \[
    \Rightarrow S_{L,\text{lim}} = f(Le)^{\beta} \left( \frac{g\alpha^2}{d} \right)^{1/4} \cdot f(Le) = \exp \left( \frac{\beta}{4} \left( 1 - \frac{T_{\infty}}{T_{\text{ad}}} \right) \left( 1 - \frac{1}{Le} \right) \right)
    \]
    Note $f(Le) < 1$ for $Le < 1$, $f(Le) > 1$ for $Le > 1$ - flame can survive at lower $S_L$ (weaker mixtures) when $Le < 1$
**Difference between $S$ and $S_L$**

Mass conservation: if $S_L =$ constant

$$\rho_\infty S A_{tube} = \rho_\infty S_L A_{flame}$$

$$\frac{A_{flame}}{A_{tube}} = \frac{S}{S_L} = \frac{0.3 \sqrt{gd}}{f} = \frac{0.3}{f} Ra^{1/4}$$

$\Rightarrow$ long flame skirt at high $Ra$ or with small $f$ (low Lewis number, $Le$) (but note $S_L$ not really constant over flame surface!)

**Flammability limits in vertical tubes**

- Downward propagation – sinking layer of cooling gases near wall outruns & "suffocates" flame (Jarosinsky et al., 1982)
  - $t_{chem} \approx t_{vis}$ \Rightarrow $S_{L,lim} \approx 1.3(g\alpha)^{1/3}$
  - $Pe_{lim} \approx 1.7 Ra^{1/3}$
  - Can also obtain this result by equating $S_L$ to sink rate of thermal boundary layer $= 0.8(gx)^{1/2}$ for $x = \delta$
  - Consistent with experiments varying $d$ and $\alpha$ (by varying diluent gas and pressure) (Wang & Ronney, 1993) and $g$ (using centrifuge) (Krivulvin et al., 1981)
Flammability limits in vertical tubes

- **Upward propagation**
  - Buoyancy-induced flame stretch
  - Direction of flame propagation
  - Flame front
  - Tube walls

- **Downward propagation**
  - Cooling combustion products near wall cause sinking boundary layer
  - Direction of flame propagation
  - Tube walls

Flammability limits in vertical tubes graph:

- Peclet number at limit
- Rayleigh number
- Le = 0.17, 0.3, 0.71, 0.86, 0.96, 1.46, 3.2
- Pe = 0.28 Ra^{1/2}

Upward propagation - Wang & Ronney, 1993
Flammability limits in vertical tubes

Downward propagation - Wang & Ronney, 1993

Flammability limits due to heat losses

- Big tube, no gravity – what causes limits?
- Radiation heat loss \((t_{\text{rad}} \approx t_{\text{chem}})\) (Joulin & Clavin, 1976; Buckmaster, 1976)

\[
S_{L,\text{lim}} = \frac{1}{\rho_{\infty} C_p} \sqrt{\frac{1.2 \beta \Lambda k_{ad}}{T_{ad}}}
\]

- What if not at limit? Heat loss still decreases \(S_L\), actually 2 possible speeds for any value of heat loss, but lower one generally unstable

\[
S^2 \ln S^2 = -Q; \quad S = \frac{S_{L(\text{non-ad})}}{S_{L(ad)}}, \quad Q = \frac{\beta \Lambda \alpha^2}{k(T_{ad} - T_{\infty}) S_{L(ad)}^2}
\]
Doesn't radiative loss decrease for weaker mixtures, since temperature is lower? NO!

Impact of heat loss ~ \( \frac{\text{Heat loss rate}}{\text{Heat release rate}} \sim \frac{T^2}{e^{-E/RT}} \) as \( T \downarrow \)

Predicted \( S_{L,\text{lim}} \) (typically 2 cm/s) consistent with \( \mu \)g experiments (Ronney, 1988 [below]; Abbud-Madrid & Ronney, 1990)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Pressure, Torr</th>
<th>Composition (see legend)</th>
<th>Estimated ( E_a ) kcal/mole</th>
<th>( S_{L,\text{calc}} ) measured, cm/sec</th>
<th>( S_{L,\text{meas}} ) measured, cm/sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_4 )</td>
<td>1500</td>
<td>0.532</td>
<td>47.4</td>
<td>1.30</td>
<td>1.04</td>
</tr>
<tr>
<td></td>
<td>760</td>
<td>0.513</td>
<td>43.6</td>
<td>1.73</td>
<td>1.47</td>
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<tr>
<td></td>
<td>250</td>
<td>0.474</td>
<td>31.6</td>
<td>2.46</td>
<td>2.02</td>
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<tr>
<td></td>
<td>100</td>
<td>0.441</td>
<td>27.8</td>
<td>3.48</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0.418</td>
<td>26.2</td>
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<tr>
<td>( \text{CH}_4 )</td>
<td>760</td>
<td>0.25, 54.7%</td>
<td>43.6</td>
<td>1.71</td>
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<td>0.75, 81.5%</td>
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<td>1.75</td>
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<td>1.50, 73.4%</td>
<td>55.7</td>
<td>2.48</td>
<td>2.15</td>
</tr>
<tr>
<td></td>
<td>760</td>
<td>2.00, 82.5%</td>
<td>55.7</td>
<td>5.73</td>
<td>2.70</td>
</tr>
</tbody>
</table>

Is radiation always a loss mechanism?
- **Reabsorption** may be important when \( a_P^{-1} < d \)
- Small concentration of blackbody particles - decreases \( S_L \) (more radiative loss)
- More particles - reabsorption extend limits, increases \( S_L \)

---

**Flammability limits due to heat losses**

**Radiation absorption effects**

Abbud-Madrid & Ronney (1993)
Radiation absorption effects

- Why do limits exist even when reabsorption effects are considered and the ambient mixture includes absorbers?
  - Spectra of product H$_2$O different from CO$_2$ (Mechanism I)
  - Spectra broader at high T than low T (Mechanism II)
  - Some radiation reaches upstream boundary due to "gaps" in spectra - product radiation that cannot be absorbed upstream
  - As a result, dramatic difference in $S_L$ & limits compared to optically thin (Ju et al., 1998)

Modeling of reabsorption effects (Ju et al., 1998)

- CHEMKIN, steady planar 1D energy & species cons. equations
- 18-species, 58-step CH$_4$ oxidation mechanism (Kee et al.)
- Boundary conditions
  - Upstream - T = 300K, inflow velocity $S_L$ at x = $L_1$ = -30 cm
  - Downstream - zero gradients of T & composition at x = $L_2$ = 400 cm
- Radiation model
  - CO$_2$, H$_2$O and CO; Wavenumbers ($\omega$) 150 - 9300 cm$^{-1}$
  - Statistical Narrow-Band model for overlapping absorption lines (see Excel spreadsheet)
  - 300K black walls at upstream & downstream boundaries
- Mixtures CH$_4$ + {0.21O$_2$+(0.79-$\gamma$)N$_2$+ $\gamma$ CO$_2$} - substitute CO$_2$ for N$_2$ in "air" to assess effect of absorbing ambient
- Practical applications
  - Combustion at high pressures and in large furnaces
    - IC engines: 40 atm - Planck mean absorption length $\approx$ 4 cm for combustion products $\approx$ cylinder size
    - Furnaces - $L_P$ $\approx$ 1.6 m - comparable to boiler dimensions
  - Exhaust-gas recirculation - absorbing CO$_2$ & H$_2$O in unburned mixture
Radiation absorption effects - flame structure

- Adiabatic flame (no radiation)
  - The usual behavior
- Optically-thin
  - Volumetric loss always positive
  - Maximum $T < \text{adiabatic}$
  - $T$ decreases "rapidly" in burned gases
  - "Small" preheat convection-diffusion zone - similar to adiabatic flame
- With reabsorption
  - Volumetric loss negative in reactants - indicates net heat transfer from products to reactants via reabsorption
  - Maximum $T > \text{adiabatic}$ due to radiative preheating
  - $T$ decreases "slowly" in burned gases - heat loss reduced
  - "Small" preheat convection-diffusion zone PLUS "huge" convection-radiation preheat zone

Flame zone detail

Radiation zones (large scale)

Mixture: $\text{CH}_4$ in "air", 1 atm, equivalence ratio ($\phi$) = 0.70; $\gamma = 0.30$ ("air" = 0.21 $\text{O}_2 + 0.49 \text{N}_2 + 0.30 \text{CO}_2")
**Radiation absorption effects - spectra**

- Flux at upstream boundary shows spectral regions where radiation can escape - "gaps" due to mismatch between radiation emitted at the flame front and that which can be absorbed by the reactants.
- Depends on "discontinuity" (as seen by radiation) in T and composition at flame front - doesn't apply to downstream radiation because T gradient is small.
- Behavior cannot be predicted via simple mean absorption coefficients - critically dependent on compositional & temperature dependence of spectra.

![Spectrally-resolved radiative flux at upstream boundary for a reabsorbing flame](image)

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**Reabsorption effects - burning velocities**

- CH₄-air ($\gamma = 0$)
  - Minor differences between reabsorption & optically-thin.
  - But $S_{L,lim}$25% lower with reabsorption; since $S_{L,lim} \sim$ (radiative loss)$^{1/2}$, if net loss halved, then $S_{L,lim}$ should be $1 - 1/\sqrt{2} = 29%$ lower with reabsorption.
  - $S_{L,lim}/S_{L,ad} \approx 0.6$ for both optically-thin and reabsorption models - close to theoretical prediction ($e^{-1/2}$).
  - Interpretation: reabsorption eliminates downstream heat loss, no effect on upstream loss (no absorbers upstream); classical quenching mechanism still applies.
  - All experiments lie below predictions - are published chemical mechanisms accurate for very lean mixtures?
- $\gamma = 0.30$ (38% of N₂ replaced by CO₂)
  - Massive effect of reabsorption.
  - $S_{L}$ much higher with reabsorption than with no radiation!
  - Lean limit much leaner ($\phi = 0.44$) than with optically-thin radiation ($\phi = 0.68$).
Reabsorption effects - burning velocities

\[ \gamma = 0 \text{ (no CO}_2\text{ in ambient)} \quad \gamma = 0.30 \]

Reabsorption effects of \( \gamma \) (CO\(_2\) substitution)

- \( \phi = 1.0 \): little effect of radiation;
- \( \phi = 0.5 \): dominant effect - why?
  1. \( \phi = 0.5 \): close to radiative extinction limit - large benefit of decreased heat loss due to reabsorption by CO\(_2\);
  2. \( \phi = 0.5 \): much larger Boltzmann number (defined below) (B) (≈127) than \( \phi = 1.0 \) (≈11.3); B ~ potential for radiative preheating to increase \( S_L \)

- Note with reabsorption, only 1% CO\(_2\) addition nearly doubles \( S_L \) due to much lower net heat loss!

\[ B = \frac{\text{Blackbody radiative heat flux at } T_{ad}^{\text{ad}}}{\text{Convective enthalpy flux through flame front } \partial \ln(T_{ad})} = \frac{\sigma(T_{ad}^{\text{ad}} - T_{eq}^{\text{ad}})}{\rho_s S_{L,ad} C_p T_{ad}^{\text{ad}} 2} \]

Effect of CO\(_2\) substitution for \( N_2 \) on \( S_L \)
Reabsorption - comparison to analytic theory

- Joulin & Deshaies (1986) - analytical theory
  \[
  \left( \frac{S_L}{S_{L,ad}} \right) \ln \left( \frac{S_{L,ad}}{S_L} \right) = B
  \]
- Comparison to computation - poor
- Better without H₂O radiation
  (mechanism (I) suppressed)
- Slightly better still without T
  broadening (mechanism (II)
  suppressed, nearly adiabatic)
- Good agreement when \( L(\omega) = L_P = \) constant - emission & absorption
  across entire spectrum rather than
  just certain narrow bands.
- Drastic differences between last two
cases, even though both have no net
heat loss and have same Planck
mean absorption lengths!

Reabsorption - comparison with experiment

- No directly comparable expts., BUT...
  - CH₄ + (0.21O₂ + 0.79 CO₂) (\( y = 0.79 \))
  - Counterflow twin flames, extrapolated to
    zero strain
  - \( L_1 = L_2 \approx 0.35 \) cm chosen since 0.7 cm
    from nozzle to stagnation plane
  - No solutions for adiabatic flame or
    optically-thin radiation (!)
  - Moderate agreement with reabsorption
- Abbud-Madrid & Ronney (1990)
  - (CH₄ + 4O₂) + CO₂
  - Expanding spherical flame at \( \mu g \)
  - \( L_1 = L_2 \approx 6 \) cm chosen (≠ flame radius)
  - Optically-thin model over-predicts limit
    fuel conc. & \( S_{L,lim} \)
  - Reabsorption model underpredicts limit
    fuel conc. but \( S_{L,lim} \) well predicted - net
    loss correctly calculated
Combined stretched & heat loss

- Spherical expanding flames, Le < 1: stretch allows flames to exist in mixtures below radiative limit until flame radius \( r_f \) is too large & curvature benefit too weak (Ronney & Sivashinsky, 1989)

\[
\Sigma \equiv \frac{1}{A} \frac{dA}{dt} = \frac{1}{4\pi r_f^2} \frac{d}{dt} (4\pi r_f^2) = \frac{2}{r_f} \frac{dr_f}{dt} \implies \frac{dS}{dR} + S^2 \ln S^2 = \frac{2S}{R} - Q
\]

- Adds stretch term \((2S/R)\) (\( R = \) scaled flame radius; \( R > 0 \) for Le < 1; \( R < 0 \) for Le > 1) and unsteady term \((dS/dR)\) to planar steady equation

- Dual limit: radiation at large \( r_f \), curvature-induced stretch at small \( r_f \) (ignition limit)

Theory (Ronney & Sivashinsky, 1989)

Experiment (Ronney, 1985)
More on flammability limits in tubes

- Experiments show that the flammability limits are wider for upward than downward propagation, corresponding to $S_{L,\text{lim,\;down}} > S_{L,\text{lim,\;up}}$ since $S_L$ is lower for more dilute mixtures.
- ...but note according to the models, $S_{L,\text{lim,\;down}} > S_{L,\text{lim,\;up}}$ when $Ra < 10,000 f^{12}$.
- but also need $Pe > 40$ (not in heat-loss limit).
  - $Ra > 18,000$
  - $Ra < 10,000 f^{12}$, upward limits may be narrower than downward limits (?!?)
- Never observed, but appropriate conditions never tested - high Le, moderate Ra.

Turbulent limit behavior?

- Burned gases are turbulent if $Re > 2000$.
  - Upward limit: $Re \approx S_L (\rho_f / \rho_{ad}) d/\nu \Rightarrow Ra > 300 \times 10^6$
  - Downward limit: $Re \approx S_L (\rho_f / \rho_{ad}) d/\nu \Rightarrow Ra > 40 \times 10^9$ - not accessible with current apparatus.
- "Standard" condition (5 cm tube, air, 1 atm):
  - $Ra \approx 3.0 \times 10^6$ : always laminar!
Approach

- Study limit mechanisms by measuring $S_{b,\text{lim}}$ for varying
- Tube diameter
- $\alpha = \alpha(\text{diluent, pressure})$
- $Le = Le(\text{diluent, fuel})$
- and determine scaling relations ($Pe_{\text{lim}}$ vs. $Ra$ & $Le$)

Apparatus

- Tubes with $0.5 \text{ cm} < D < 20 \text{ cm}$; open at ignition end
- He, Ne, $N_2$, $CO_2$, $SF_6$ diluents
- $0.1 \text{ atm} < P < 10 \text{ atm}$
- $2 \times 10^2 < Ra < 2 \times 10^9$
- Absorption tank to maintain constant $P$ during test
- Thermocouples

Procedure

- Fixed fuel:O$_2$ ratio
- Vary diluent conc. until limit determined
- Measure $S_{b,\text{lim}}$ & temperature characteristics at limit

Results - laminar flames

- Upward limit
  - Low $Ra$
    - $Pe_{\text{lim}} \approx 40 \pm 10$ at low $Ra$
    - Highest $T$ near centerline of tube
  - High $Ra$
    - $Pe_{\text{lim}} \approx 0.3 Ra^{1/2}$ at high $Ra$
    - Highest $T$ near centerline (low $Le$)
    - Highest $T$ near wall (high $Le$)
    - Indicates strain effects at limit
- Downward
  - $Pe_{\text{lim}} \approx 40 \pm 10$ at low $Ra$
  - $Pe_{\text{lim}} \approx 1.5 Ra^{1/3}$ at high $Ra$
- Upward limits narrower than downward limits at high $Le$ & moderate $Ra$, e.g. lean $C_3H_8$-$O_2$-$Ne$, $P = 1 \text{ atm}$, $D = 2.5 \text{ cm}$, $Le \approx 2.6$, $Ra \approx 19,000$: fuel up / fuel down $\approx 0.83$
\[ f = \exp\left(\frac{\beta}{4}(1-\varepsilon)(1-Le^{-1})\right) \]

Limit regimes - upward propagation

- Laminar
- Turbulent
- Flamelet combustion ?
- Distributed combustion
- Boiling tip

Limit regimes - downward propagation

- Laminar
- Turbulent ?
- Heat loss to walls
- SFLT
- Buoyancy (upward wider)
- Buoyancy (downward wider)
Flamelet vs. distributed combustion

- Abdel-Gayed & Bradley (1989): distributed if $Ka > 0.3$
  \[ Ka \approx 0.157 \frac{Re_T^{-1/2}U^2}{Re} \equiv u'L_U, \ U \equiv u'/S_L \]
  \[ L_I \equiv \text{integral scale of turbulence} \]
- Estimate for pipe flow
  - $u' \approx 0.05S(r_\infty/r_{ad}-1)$; $L_I \approx d$
  - $S_{lim}$ from Buckmaster & Mikolaitis (1982) model
  \[ Ka \approx 0.0018/f^2 \frac{Ra^{1/4}}{Ra} \approx 0.3/f^2 \text{ at } Ra = 700 \times 10^6 \]
- Distributed combustion probable at high $Ra$, moderate $Le$
- Away from limit - wrinkled, unsteady skirt

Limit flame - distributed combustion

$C_3H_8-O_2-CO_2$, $P = 2.5 \text{ atm}$, $d = 10 \text{ cm}$, $Le \approx 1.3$, $Ra \approx 6 \times 10^6$
Farther from limit - wrinkled skirt

C$_3$H$_8$-O$_2$-CO$_2$, $P = 2.5$ atm, $d = 10$ cm, $Le \approx 1.3$, $Ra \approx 6 \times 10^8$

Lower Le - boiling tip, no tip opening

C$_3$H$_8$-O$_2$-SF$_6$, $P = 2.5$ atm, $d = 10$ cm, $Le \approx 0.7$, $Ra \approx 5 \times 10^9$
**Turbulent flame quenching**

- Why does distributed flame exist at $\delta \approx 4d$, whereas laminar flame extinguishes when $\delta \approx 1/40 d$ (Pe = 40)?
- Analysis
  - $\text{Nu} = \frac{hd}{k} \approx 0.023 \text{Re}^8 \text{Pr}^3$ (turbulent heat transfer in pipe)
  - $Q_{\text{loss}} = hA\Delta T$; $A = \pi d\delta$; let $\delta = nD$ (n is unknown)
  - $Q_{\text{gen}} = \rho_0 S_b \pi d^2 C_p \Delta T$; $S_b = 0.3(gd)^{1/2}$
  - $Q_{\text{loss}}/Q_{\text{gen}} \approx 1/\beta$ at quenching limit
  - $n \approx 5Gr^{0.1}/\beta$ at quenching limit
- $Gr = 600 \times 10^6$, $\beta = 10 \Rightarrow n = 3.9$ at limit !!!
- But low Le $\Rightarrow S_L$ low at tip opening $\Rightarrow n > 4$ at tip opening $\Rightarrow$ distributed flame not observable

**Conclusions**

- Probable heat loss & buoyancy-induced limit mechanisms observed
- Limit behavior characterized mainly by Lewis & Rayleigh numbers
- Scaling analyses useful for gaining insight
- Transition to turbulence & distributed-like combustion observed
- High-Ra results may be more applicable to "real" hazards (large systems, turbulent) than classical experiments at low Ra
References


References


