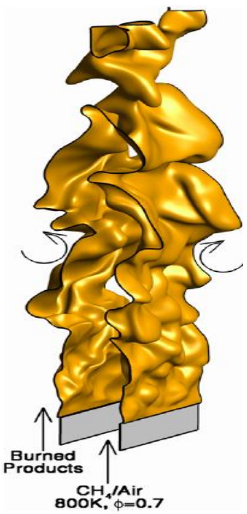
# Thursday: Partially-premixed flames

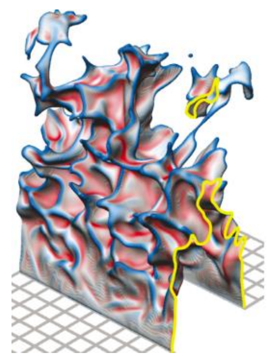
## Turbulent Combustion

### Experiments and Fundamental Models

J. F. Driscoll, University of Michigan




R. Sankaran,
E. Hawkes,
Jackie Chen
T. Lu, C. K. Law
premixed



Bell, Day,
Driscoll
“corregated”
premixed

# Outline for the week

Mon: **Physical concepts** faster mixing, faster propagation, optimize liftoff, flame surface density, reaction rate, PDF

Tues**:** **Kilohertz PLIF, PIV measurements of flame structure** - to assess models

Wed: **Non-Premixed and Premixed flames** - measurements, models gas turbine example

Thurs: **Partially premixed flames -** and some examples

Fri: **Future challenges:** Combustion Instabilities (Growl), Extinction

# Partially Premixed Combustion

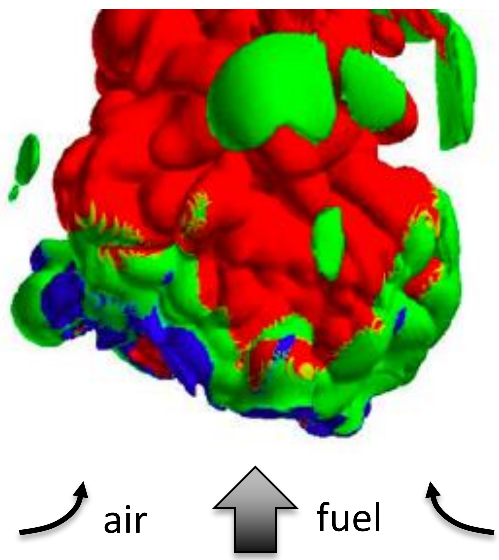
**Partially-premixed combustion** = at a point, sometimes there are premixed flamelets and sometimes there are non-premixed flamelets

**Flame Index** = a quantity that varies from zero (all flamelets are non-premixed) to unity (all flamelets are premixed)

1. Motivation for PPC
2. Models of PPC
3. Measurements of flame index
4. Some results: a) gas turbine combustor
   b) blowout of jet in cross flow

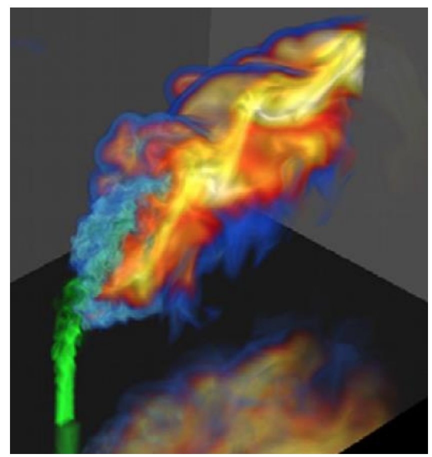
# Examples of partially premixed combustion

Base of a lifted, jet flame that is initially non-premixed



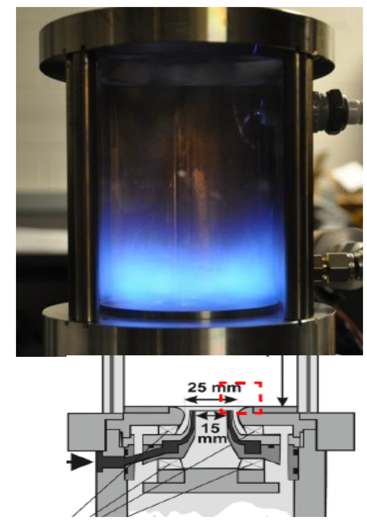

DNS of Mizobuchi, Takeno
red= rich premix, blue = lean premix
green = non-premix
PROCI 30, 2005

Base of a lifted jet in cross flow, initially non-premixed



DNS of Gruber,
JH Chen, PROCI

Base of a lifted Swirl flame in a gas turbine combustor




Rosenberg, Driscoll
Comb Flame 162, 2808

# Motivation - for Partially-Premixed Studies

Lean premixed combustion is the way of the future -

low $NO_x$, CO, soot; GE, Pratt, ground-based electric power from natural gas

"Growl" combustion instabilities - premixed flames difficult to anchor

need kilohertz PIV, PLIF movies, need frequencies, phase angles

Flame Index measurements of fraction of flamelets that are premixed

needed to improve models of partially-premixed combustion in engines

# Gas turbine run on syngas ($H_2$ and CO)

has chemistry and flame speed problems

Auto ignition - likely with preheated air

Sudden flashback events - due to wider flammability limits

Flame anchors too close to wall - Large flame speed

Large diffusivity of hydrogen - Lewis number affects mixing and flame shape

MICHIGAN

# Models of Partially premixed combustion

| | | | RR | PDF | authors |
|---|---|---|---|---|---|
| 1 | **FSD** | Flame surface density, also called F-TACLES = tabulated chemistry LES | FSD eqn w flamelet state relns | bimodal* | Bray, Vervisch Veynante, Fureby Ihme, |
| 2 | **FPV** | Flamelet progress variable | flamelet state relns | Beta fcn** | Moin, Ihme Pitsch, Kempf |
| 3 | **TFM** | Thickened flamelet model | flamelet | | Poinsot |
| 4 | **G-EQ** | G equation | G-Eqn | | Pitsch, Bai |
| 5 | **LEM** | Linear eddy model | G-Eqn | | Menon |

# Good models - of partially premixed combustion

**FSD model:** P. Domingo, L. Vervisch, Combust. Flame 140 (2005) 172–195.
K. Bray, P. Domingo, L. Vervisch, Combust. Flame 141 (2005) 431–437.
P. Domingo, L. Vervisch, K. Bray, Combust. Theor. Model. 6 (2002) 529–551.

**G-equation model:** Knudsen, H. Pitsch, Combust. Flame 156 (2009) 678.
E. Knudsen, H. Pitsch, Combust. Flame 159 (2012) 242–264.
K.J. Nogenmyr, J. Kiefer, Z.S. Li, X.S. Bai, M. Aldén, Comb. Flame 157, 915

**FPV model:** C.D. Pierce, P. Moin, J. Fluid Mech. 504 (2004) 73–97.
M. Ihme, Y.C. See, Combust. Flame 157 (2010) 1850–1862.
M. Ihme, H. Pitsch, Combust. Flame 155 (2008) 90–107.

**TFM model**: B. Franzelli, E. Riber, T. Poinsot, Comb. Flame 159 621

**LEM model:** N. Patel, S. Menon, Combust. Flame 153 (2008) 228–257.

**DNS:** K. Luo, H. Pitsch, M.G. Pai, O. Desjardins, Proc. Combust. Inst. 332, 143
R. Grout, J.H. Chen, PROCI 33, 1629

# Flame Index

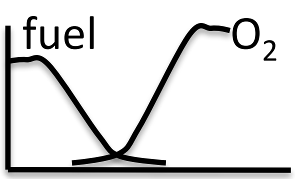
Flame index = fraction of flamelets that are premixed

**Flame Index** (Takeno and Yamashita)

$$\xi = \frac{\nabla Y_{F,max} \cdot \nabla Y_{O2,max}}{\left| \nabla Y_{F,max} \cdot \nabla Y_{O2,max} \right|}$$

$\xi$ = -1 non-premixed

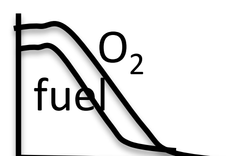
mass fraction




distance

$\xi$ = +1 premixed

mass fraction




distance

# Models require a new PDF - for partially-premixed

Z = mixture fraction, proportional to local fuel-air ratio
c = reactedness, proportional to gas temperature

$$\frac{\partial}{\partial t}(\rho Z) + \frac{\partial}{\partial x_j}(\rho u_j Z) = \frac{\partial}{\partial x_j}\left(\rho \mathscr{D}_Z \frac{\partial}{\partial x_j}(Z)\right),$$

$$\frac{\partial}{\partial t}(\rho C) + \frac{\partial}{\partial x_j}(\rho u_j C) = \frac{\partial}{\partial x_j}\left(\rho \mathscr{D}_C \frac{\partial}{\partial x_j}(C)\right) + \rho \dot{\omega}_C$$

LES
Subgrid
Reaction
Rate

$$\widetilde{\dot{\omega}}_C = \int_Z \int_C \dot{\omega}_C(Z, C)\widetilde{P}(Z, C)\, dZ\, dC$$

PDF must include probabilities of premixed vs. non-premixed flamelets

# Partially premixed models

Knudsen Pitsch, Combust Flame 156, 678
Domingo, Bray, Comb Theory Model 6, 529

within an LES computational cell:

fraction of flamelets in LES cell that are premixed

Reaction rate of premixed flamelets

$$\overline{\dot{\omega}_{CH4}} = P(\xi = 0)\,[\overline{\dot{\omega}_{CH4}}]_{nonpremixed} + P(\xi = 1)\,[\overline{\dot{\omega}_{CH4}}]_{premixed}$$

Fuel Reaction rate

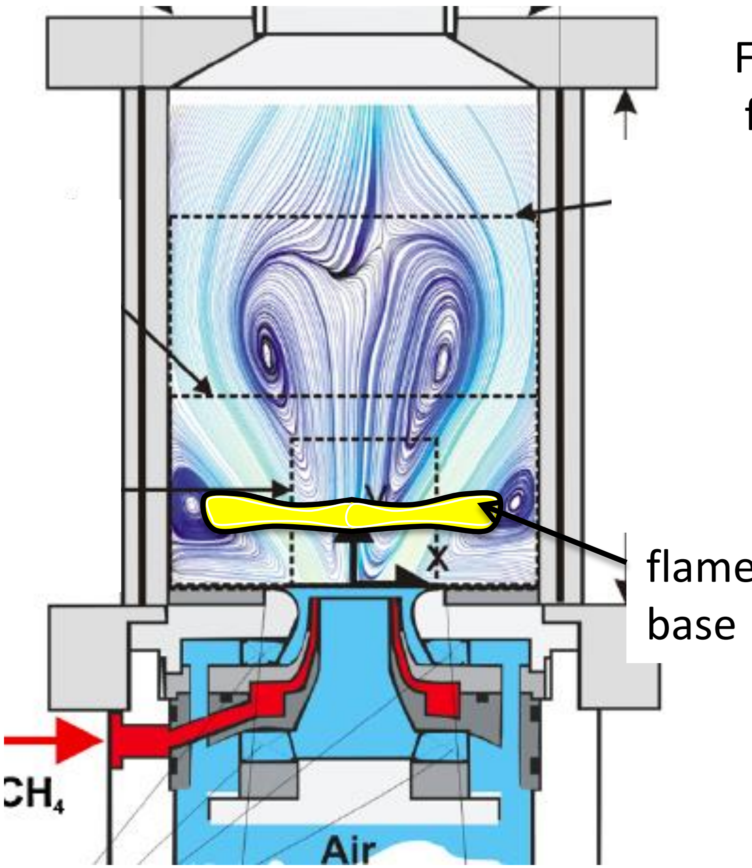
fraction of flamelets in LES cell that are non-premixed

reaction rate of non-premixed flamelets

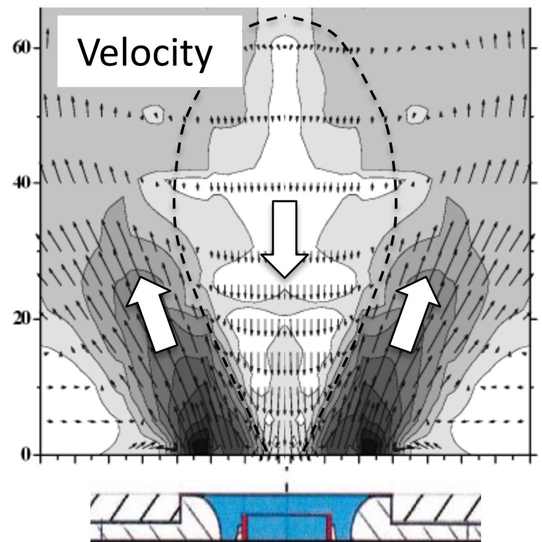
$P(\xi)$ is bimodal

# What is a good “canonical” partially premixed experiment ?

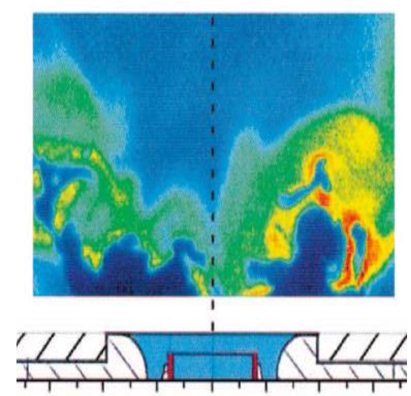
DLR  GTMC =  Gas Turbine Model Combustor of Meier



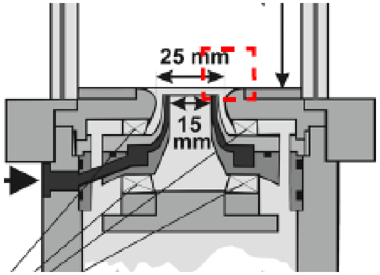

Fuel and air are injected separately, but
flame base is lifted and **is partially-premixed**

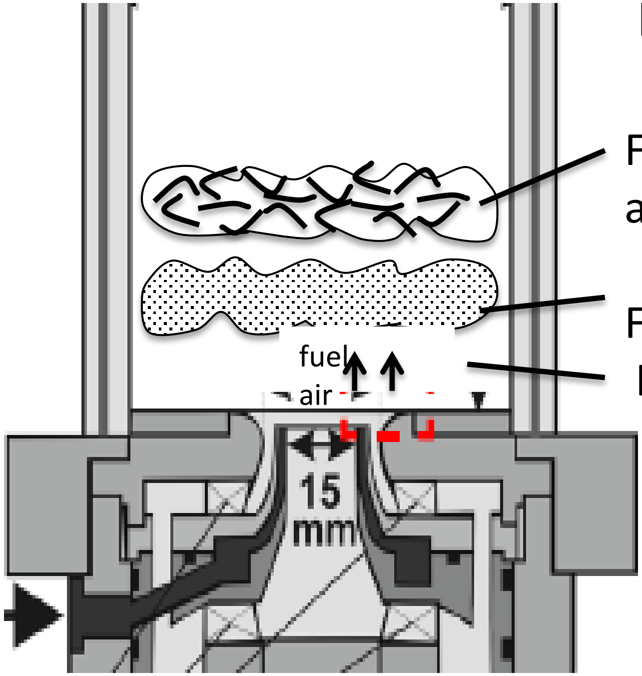



Temperature



# DLR gas turbine flame - is partially-premixed




Lifted flame base

Flamelets – premixed and non-premixed

Fuel-air mixing region
Initially not premixed

# A new method to measure Flame Index

Rosenberg, Driscoll, Comb Flame 162, 2808

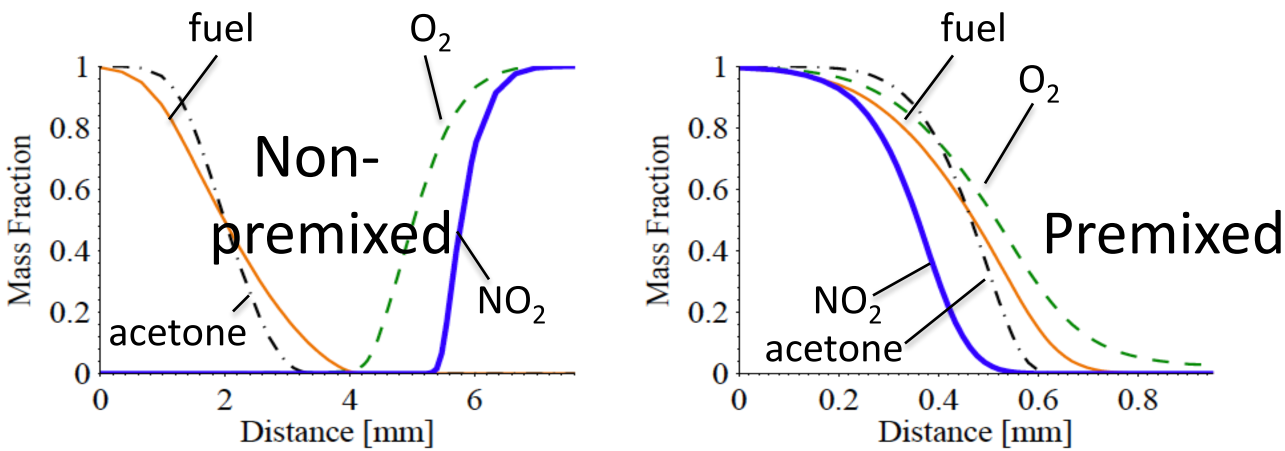
Add acetone tracer gas to fuel

Add $NO_2$ tracer gas to air

Both gases fluoresce

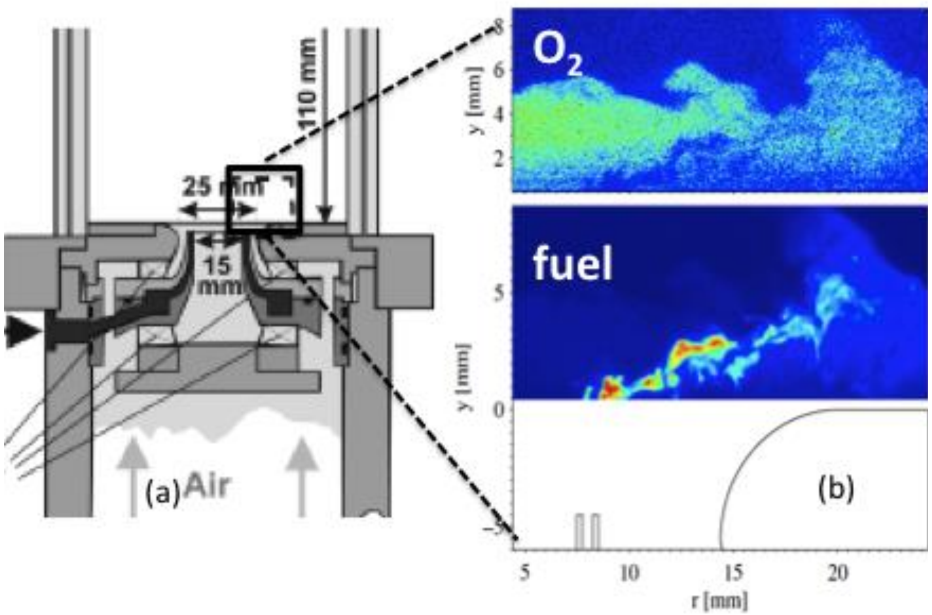
Acetone faithfully tracks the propane fuel

$NO_2$ faithfully tracks the $O_2$




Flame Index $$\xi = \frac{\nabla Y_{F,max} \cdot \nabla Y_{O2,max}}{|\nabla Y_{F,max} \cdot \nabla Y_{O2,max}|}$$

# Michigan images of fuel and oxygen in GTMC



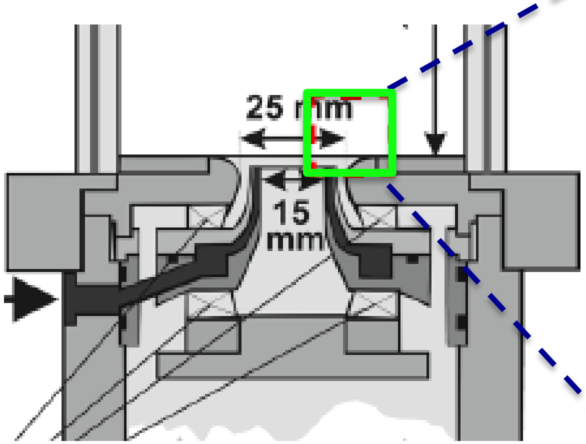

PLIF signal from $NO_2$ tracer gas

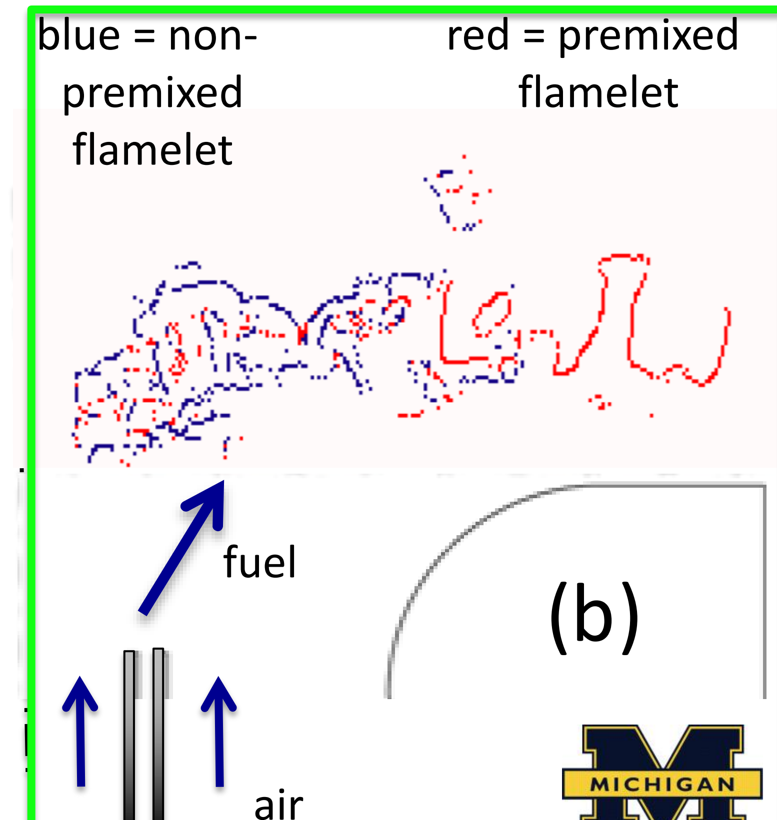
PLIF signal from Acetone tracer gas

# Measure flame index

Premixed flamelet - gradients of fuel and $O_2$ are in same direction
Non-premixed flamelet – gradients of fuel and $O_2$ are in opposite direction

Acetone is one component of fuel
$NO_2$ added to air



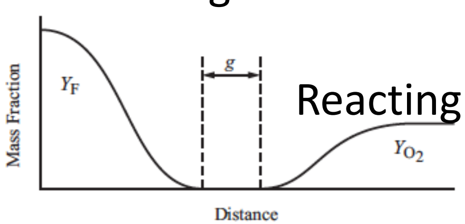
# Analysis of PLIF images - how to measure flame index

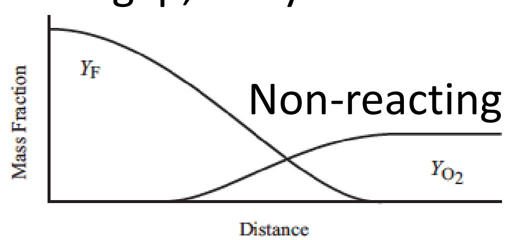
Remove noise from the PLIF images by using a central-differencing method to compute gradients, then apply a Canny edge detection algorithm

Conduct a search to match each acetone gradient layer with its nearest NO2 layer. Start from left side of the image. Proceed to right until a pixel in an acetone layer is identified. Determine the direction of the gradient. The search proceeds along the gradient vector direction until the adjacent NO2 layer is detected.

Values of gradients inserted into equation for Flame index – either +1 (premixed flamelet) or -1 (non-premixed flamelet)

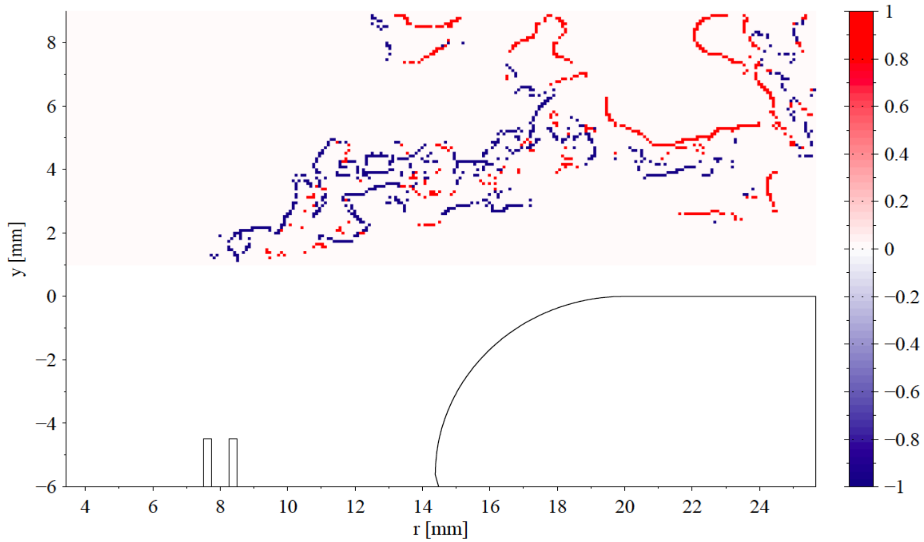
Check that gradients are sufficiently steep and that there is a gap between gradients (indicating reactions occur); throw out about 5% of the gradients that are very weak gradients that have no gap, they must be due to mixing only

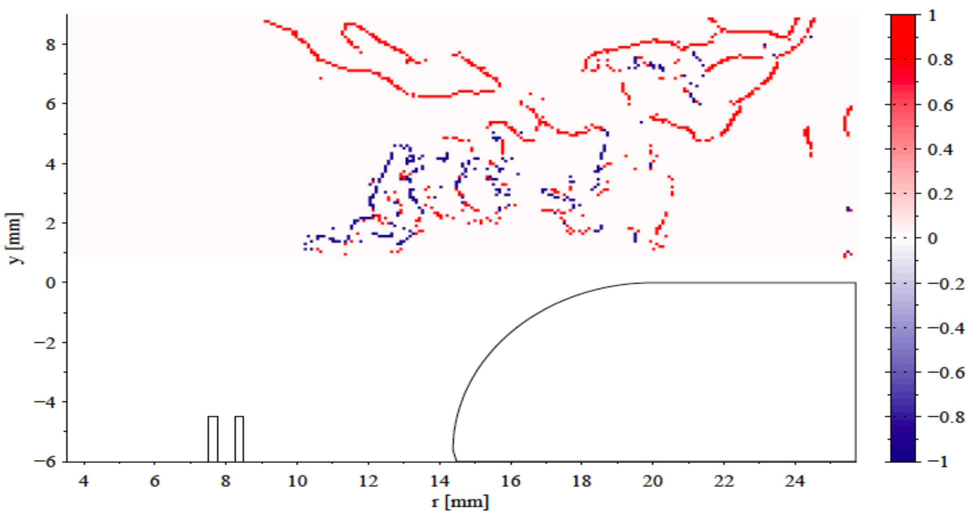



Assess the method first in laminar premixed and non-premixed flames

# Results - instantanous images of Flame Index



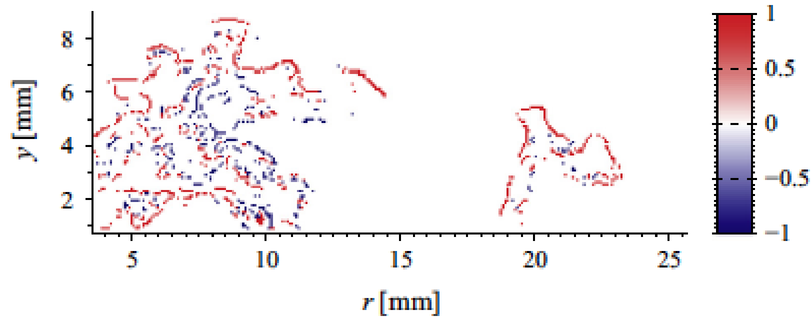

Red = premixed flamelet
flame index = +1

Blue = non-premixed
flamelet
flame index = -1

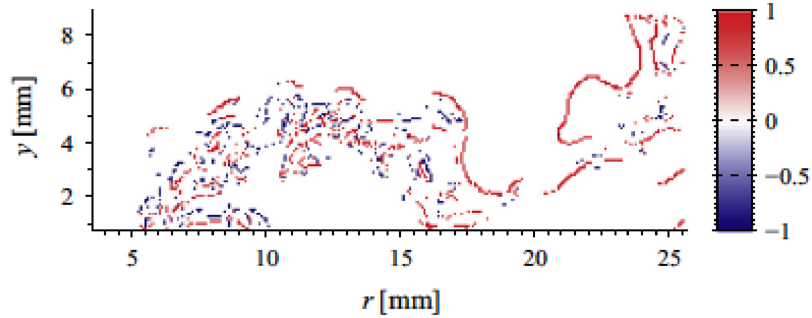
# More images of flame index

Red = premixed flamelets

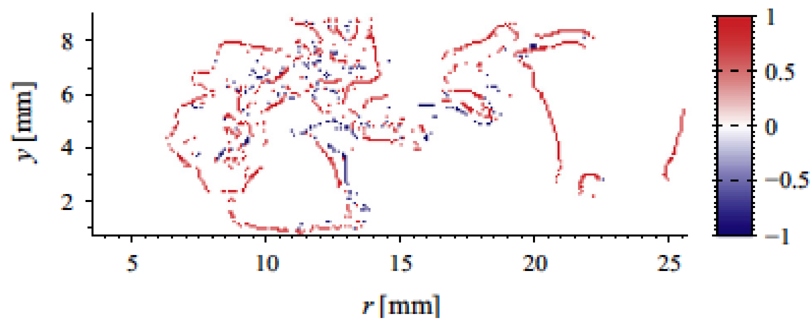
Blue = non-premixed flamelets




(a) Case P-3, fuel-lean equivalence ratio, high velocity ratio, and high flow rate.

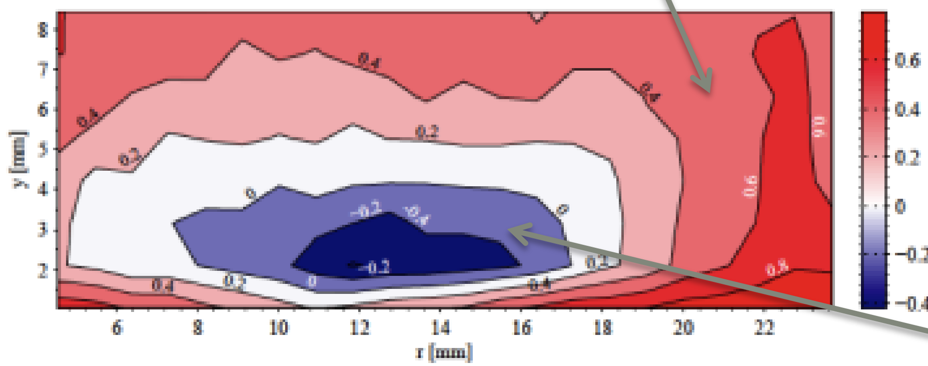



(b) Case P-3, when nearly 50% of flamelets are premixed.

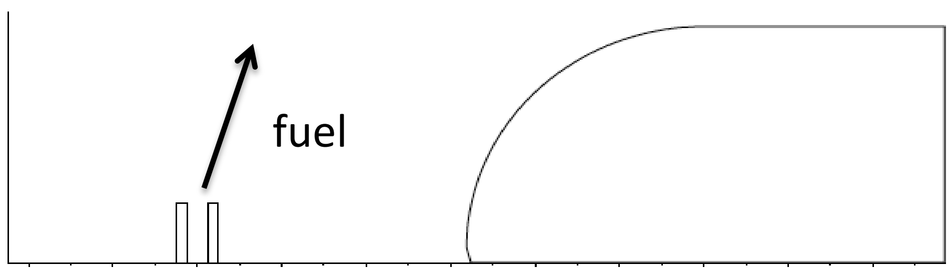


# Fraction of flamelets that are premixed – from statistical averages

RED = large fraction of flamelets are premixed



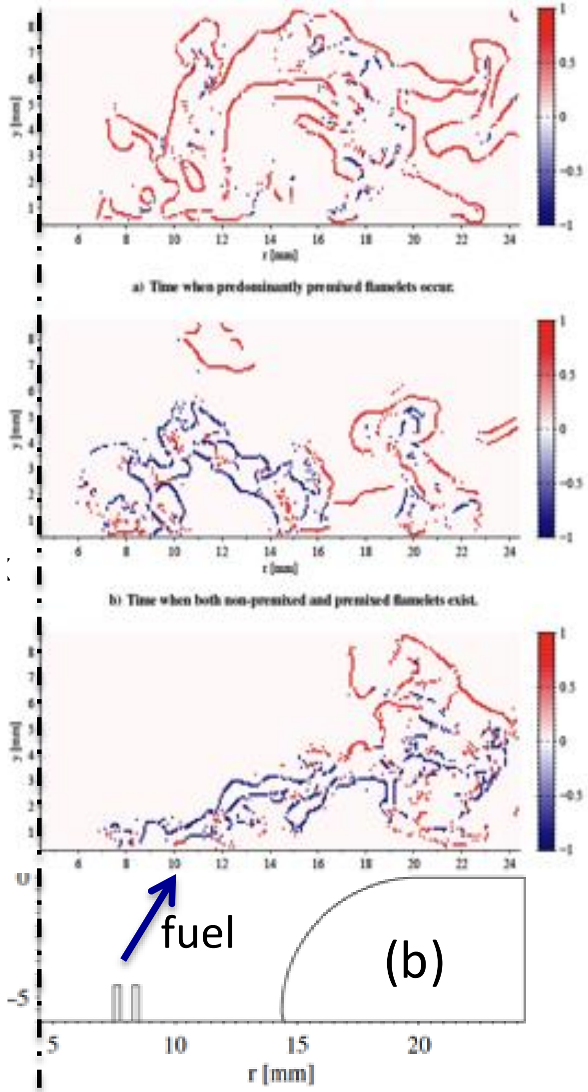

BLUE = mostly Non-premixed flamelets




Compare to subgrid model of Domingo, Bray, Vervisch – in progress

$$\text{Flame index} = (F_z \ \chi_z + F_c \ \chi_c)$$

# Compare our flame index measurements to DNS



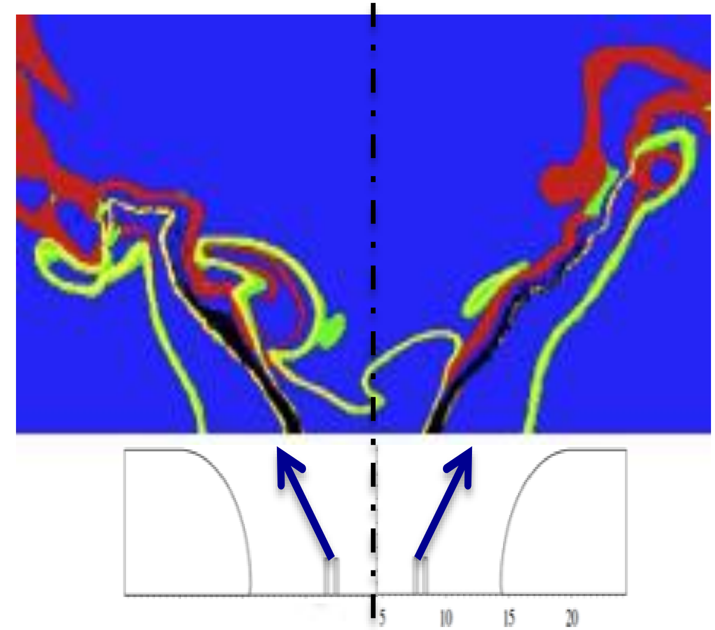

Michigan Experiment

Time when mostly premixed (red)

Time when half premixed

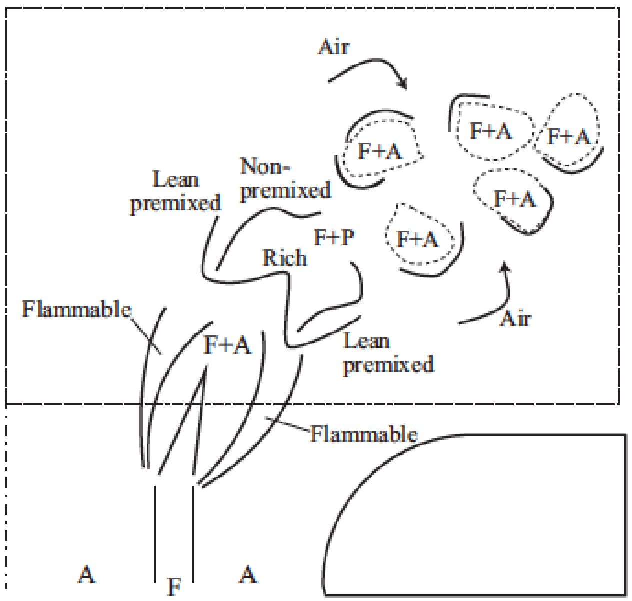
Time when mostly non-premixed (blue)

red = premixed,
green = non-premixed
black = fuel

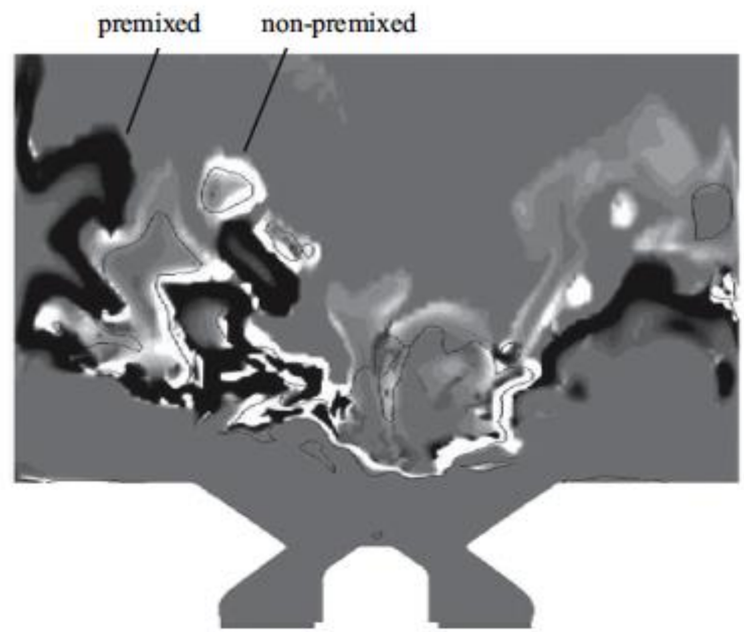


DNS Luo & Pitsch, Stanford
PROCI 33, 2143

# Compare to DNS, continued




Schematic of our measurements
Comb Flame 162, 2808




(b)

DNS of Menon
Comb Flame 153, 228

# <u>Partially -premixed</u> combustion is the way of the future

low NOx, CO, soot;  GE, Pratt, ground-based electric power from natural gas

Partially premixed offers lots of opportunity for future research

- need better models that can be verified vs. experiments
- need better measurements where we know it is partially premixed

Flame Index measurements    of fraction of flamelets that are premixed

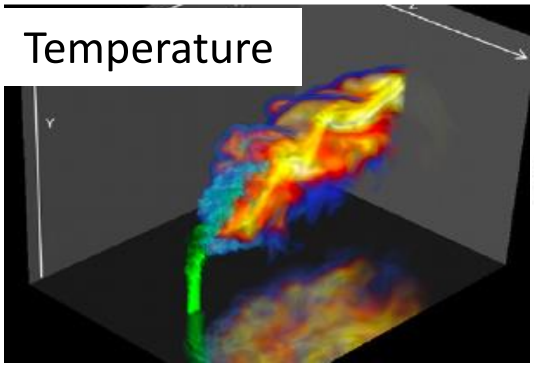
needed to improve models of partially-premixed combustion in engines

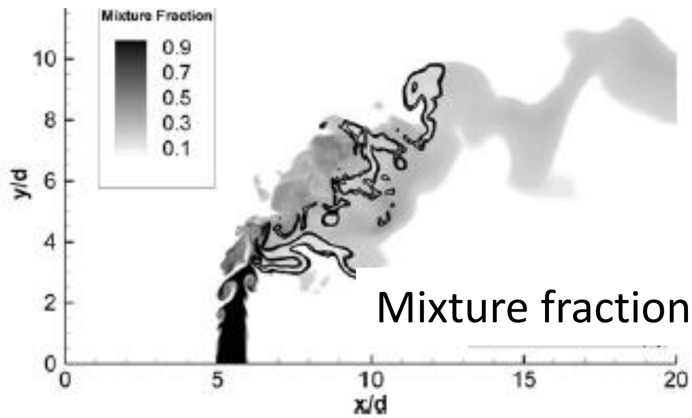
"Growl"  combustion instabilities occur in PPC

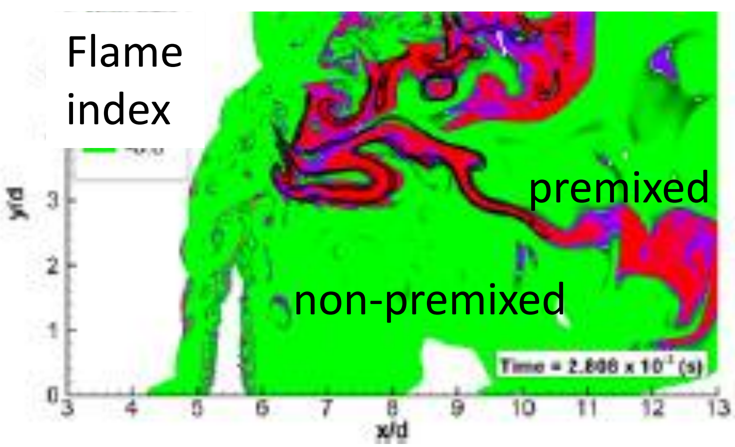
premixed flames  are difficult to anchor  need kilohertz PIV, PLIF movies,
need frequencies of  pressure, velocity, flame oscillations,  phase angles

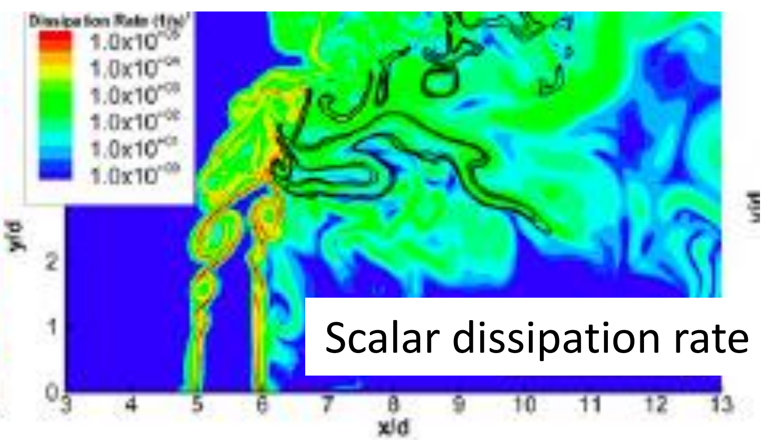
# DNS of Partially premixed – lifted jet in cross flow

R. Grout, A. Gruber, C.S. Yoo , J.H. Chen  PROCI  33, 1629



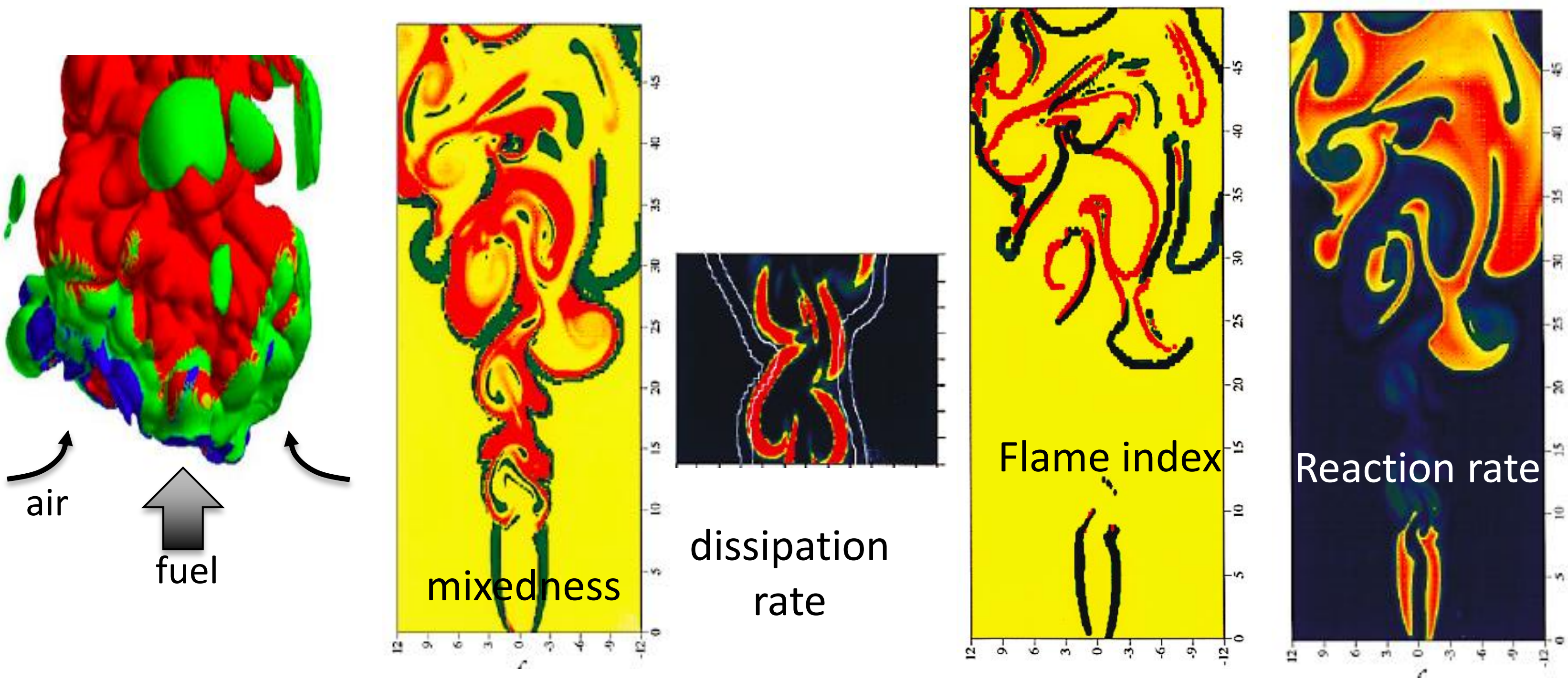




Conclude:    stratified, broken premixed flamelets occur

# DNS of a lifted jet flame      Yamashita, PROCI 26, p. 27




Proof that fuel and air are mixing
In the liftoff region, but
no reactions due to high strain

Flame is lifted - because it cannot propagate upstream any farther into the high dissipation rate region near the fuel jet tube

# Partially premixed LES combustion model of Domingo and Bray

Domingo, Bray, Comb Theory Model 6, 529
the reaction rate, averaged over a computational cell is:

$$\overline{\dot{\omega}_{CH4}} = A \; [\overline{\dot{\omega}_{CH4}}]_{nonpremixed} + B \; [\overline{\dot{\omega}_{CH4}}]_{premixed}$$

*A* = fraction of flamelets that are non-premixed in cell at (x,y,z) at time t

$$A = \int P(\xi = 0)d\xi \;=\; F_Z(\tilde{c},\tilde{Z})\,\frac{\widetilde{Z'^2}}{\tau} + F_c(\tilde{c},\tilde{Z})\,\frac{\tilde{c}\,(1-\tilde{c})}{\tau}$$

All quantities on RHS are determined from resolved-scale values

*B = 1 - A*

$[\overline{\dot{\omega}_{CH4}}]_{nonpremixed}$

$[\overline{\dot{\omega}_{CH4}}]_{premixed}$

Lookup tables for non-premixed and for premixed flamelets

Need to solve conservation equations for mean c and Z

# Partially premixed LES combustion model - FPV of Pitsch

Knudsen, Pitsch, Comb Flame 156, 678 A general flamelet transformation useful for distinguishing between premixed and non-premixed modes of combustion

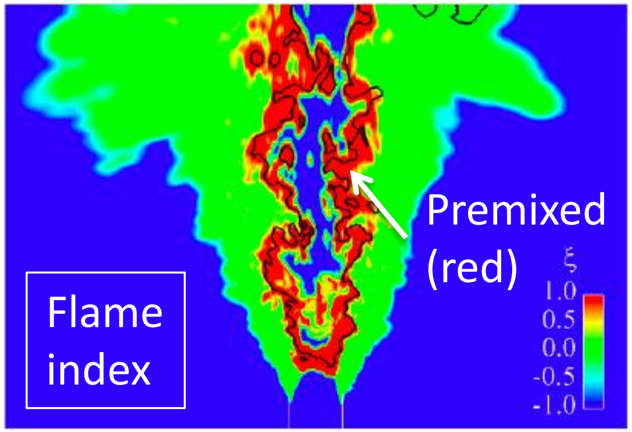
$$\overline{\dot{\omega}_{CH4}} = P(\xi = 0)\,[\overline{\dot{\omega}_{CH4}}]_{nonpremixed} + P(\xi = 1)\,[\overline{\dot{\omega}_{CH4}}]_{premixed}$$

Compute subgrid flame index ξ

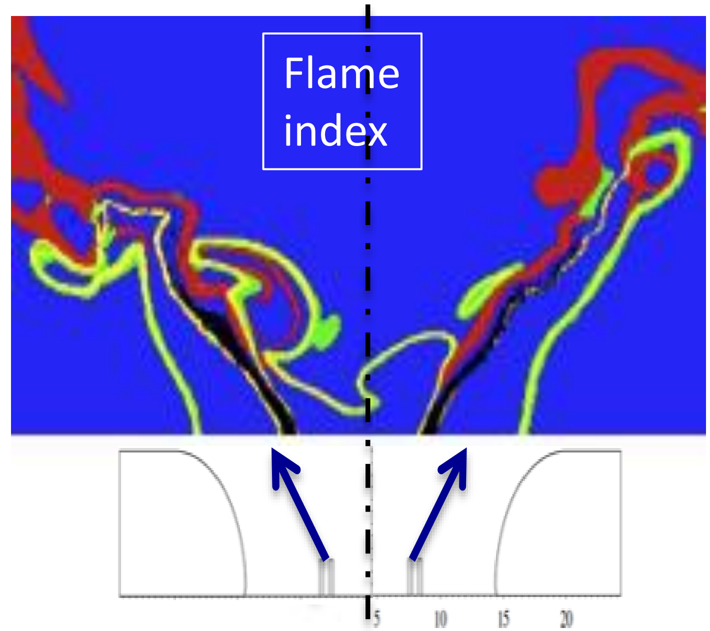
if x = +1 a premixed flamelet lookup table should be called, based on laminar premixed flamelet state relation

if x = -1 a non-premixed flamelet lookup table should be called, based on laminar non-premixed flamelet state relation

## Knudsen, Pitsch model of a lifted swirl flame




red = premixed,
green = non-premixed
black = fuel




auto-ignition dominated regimes
are inherently included in the formulation

DNS Luo & Pitsch,
Stanford
PROCI 33, 2143

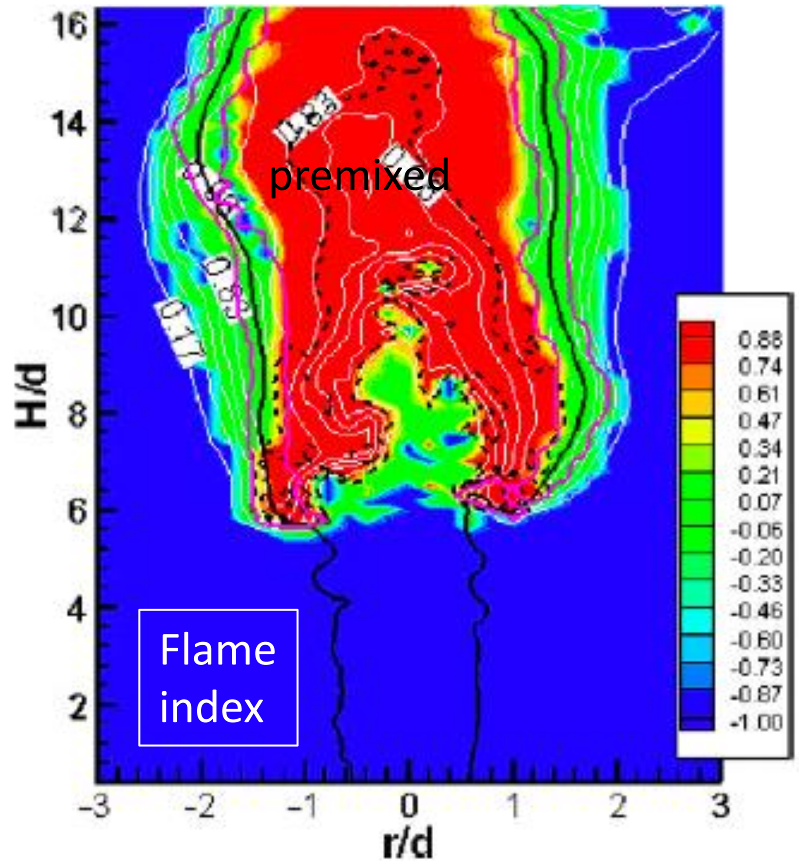
# Partially Premixed Combustion LES model of Domingo

Ferraris, Comb Flame 150, 320
heat release rate is:

$$\overline{\dot{Q}_T} = \bar{\xi}_P \overline{\dot{Q}_P} + (1 - \bar{\xi}_P)\overline{\dot{Q}_d}$$

$$\bar{\rho}\left(\frac{\partial \tilde{Z}}{\partial t} + \frac{\partial(\tilde{u}_j \tilde{Z})}{\partial x_j}\right) = -\frac{\partial}{\partial x_j}\left(\overline{\rho u_j Z} - \bar{\rho}\tilde{u}_j \tilde{Z}\right) + \frac{\partial}{\partial x_j}\left(\overline{\rho D \frac{\partial Z}{\partial x_j}}\right),$$

$$\frac{\partial(\rho C)}{\partial t} + \frac{\partial(\rho u_j C)}{\partial x_j} = \frac{\partial}{\partial x_j}\left(\rho D \frac{\partial C}{\partial x_j}\right) + \dot{Q}_C + \left(\frac{2}{Y_{F,0}Z - Y_F^{\mathrm{EQ}}(Z)}\right) \times \left(Y_{f,0} - \frac{\mathrm{d}Y_F^{\mathrm{EQ}}(Z)}{\mathrm{d}Z}\right)\rho \chi_{Z,C}$$




Correctly predicts liftoff height and Sees triple flame structure

# Role of fuel type - and Lewis number

Most turbulent combustion imaging work done with methane or hydrogen,
need to study Jet-A, heptane, octane
New aspects: pyrolysis of fuel into simpler fuels, effect of Lewis number

$Le = \alpha / D_{def}$ = thermal diffusivity of reactant mixture / mass diffusivity of the deficient reactant (fuel if mixture is fuel-lean)

Measurements of Law, Egolfopoulos of stretched flame laminar burning velocity SL,
Divided by unstretched flame laminar burning velocity:

$S_L / S_{L0} = 1 - Ka\ Ma$

Ka = Karlovitz number = stretch rate / ( $S_L^2 / \alpha$)

Ma =Markstein number = slope of the curve when you plot above equation
Ma is related to Lewis number

# Lewis number effects do not go away at high Reynolds number

Rich hydrogen-air premixed jet flames = very tall, not very wrinkled, have low turbulent burning velocity

Lean hydrogen-air premixed jet flames = short and very wrinkled, have high turbulent burning velocity

For the same laminar burning velocity $S_L$ and same turbulence level u'

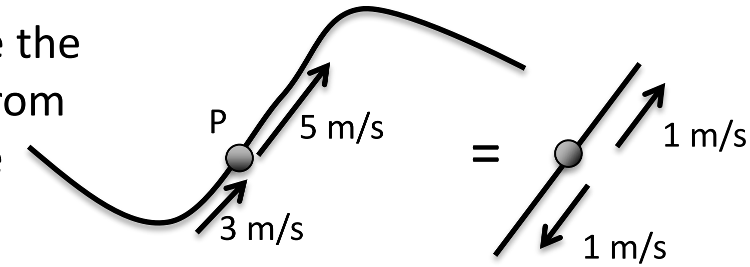
Several examples: one is Wu, Driscoll, Faeth, "Preferential Diffusion Effects on the Surface Structure of Turbulent Premixed Hydrogen/Air Flames," <u>Comb. Sci. Technol.</u> 78:69-96, 1991.

Why does molecular differential diffusion remain important ?

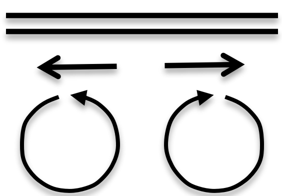
Molecular diffusivity (D) is small compared to turbulent diffusivity ($D_T$)
But turbulence may not get into reaction layers, so there is no turbulent diffusivity near the reaction region to dominate the molecular diffusivity

# Stretched laminar premixed flames (C. K. Law, Princeton)

Near point P in a turbulent premixed flame the tangential velocity of reactants increases from 3 m/s to 5 m/s in the same direction as the tangential velocity, as shown

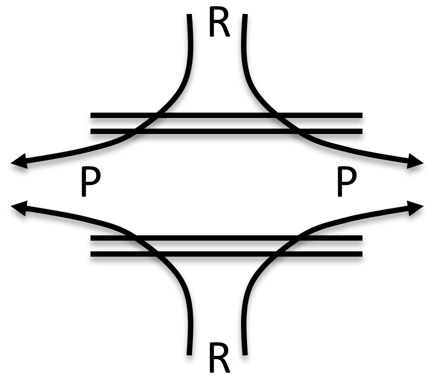



A constant tangential velocity does nothing to the flame equations, so we add a -4 m/s velocity vector to each of these vectors to get the counterflow arrangement on the right



extensive strain from two eddies thins flame

=




Twin counter flow premixed flames

Counterflow is irrotational
Turbulent flow has vorticity

# Stretch rate of flame surface (K)

$$K = \frac{1}{A}\frac{dA}{dt} = K_s + K_c$$

$$= strain + curvature\ components$$

$$K_s = -\boldsymbol{n}\cdot(\boldsymbol{n}\cdot\boldsymbol{\nabla})\,\boldsymbol{V} + \boldsymbol{\nabla}\cdot\boldsymbol{V}$$

$$K_c = \frac{S_L}{R_c}$$

A = flame surface area
n = normal to flame surface
pointing toward reactants
V = gas velocity vector
$R_c$ = radius of curvature of flame
surface

Example: spherical premixed flame of radius $R_f$ propagating radially outward

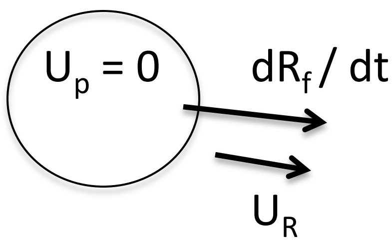
$A = 4\pi R_f^2$ so $K = 1/A\,(dA/dt) = (1/(4\pi R_f^2))\,(4\pi)\,(2 R_f\, dR_f/dt) = (2/R_f)\,(dR_f/dt)$

Spherical flame has positive stretch since area is increasing in time

Spherical flame has contributions from both $K_s$ and $K_c$

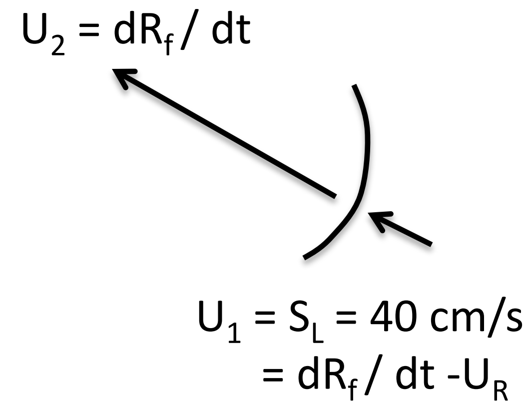
## Spherical flame, continued, reactants are pushed radially outward at 200 cm/s

Given: $\rho_1 = 1.2\ \mathrm{kg/m^3}$, $\rho_2 = 0.2\ \mathrm{kg/m^3}$
$S_L = 40$ cm/s, and $U_P = 0$




LAB frame of reference

Add a radially inward velocity vector at 240 cm/s to every point




FLAME frame of reference

in flame frame (steady) $\rho_1 U_1 = \rho_2 U_2$ Solve this eqn to find $U_2 = 240$ cm/s
$U_2$ must equal $dR_f/dt$ and $U_1$ must equal $dR_f / dt - U_R$

# Stretched laminar flamelet concept

- Segments of curved premixed laminar flames (such as spherical) and strained turbulent flames are similar to counterflow premixed laminar flames, for the same stretch rate (K) and fuel type.  Same for non-premixed too
-

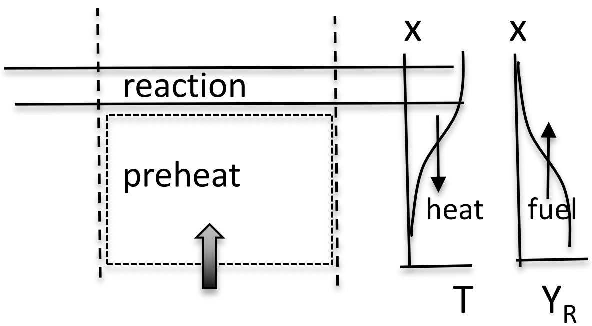
$$K = (1/A)(dA/dt)$$

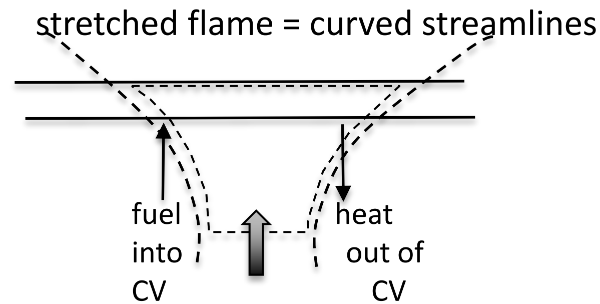
- Stretch rate = has strain rate component, proportional to dV/dy, and a curvature component, proportional to (1/R), R is flame radius of curvature. R is positive for spherically expanding flame, is negative at bunsen tip

- For a counterflow premixed or non-premixed flame, the velocity gradient (which determines the strain rate) is proportional to the scalar gradient, so the scalar gradient (dissipation rate) often is used instead of the strain rate (velocity gradient)

# Theory of Flame Stretch C.K. Law Comb Flame 72, 325

Consider a counter flow lean laminar premixed flame – fuel is the deficient reactant




In the unstretched flat flame, heat diffuses upstream, reactants diffuse downstream and nothing leaves through the vertical sides of the control volume, as shown

For the stretched case, streamlines are curved, control volume shape is shown.

Some heat diffuses upstream and out of the control volume, across the curved sides
Some reactants diffuse down stream and into the control volume across the curved sides. For every kg/s of fuel that diffuse in about 44,000 kJ/sec of extra heat is added

If more kJ/s of heat diffuses OUT than the kJ/s coming IN with the added reactants, then the flame will propagate slower and extinguish

# Theory of Flame Stretch - Law and Sung

For the stretched flame geometry on last slide, they write balance equations for enthalpy and mass fraction for deficient reactant $Y_F$ (= fuel, assuming fuel-lean) for a hypothetical one step reaction rate: RR = $Y_F$ B exp ($-T_A/T$) where $T_A$ = activation temperature and $q_c$ = heat released per kg fuel

$$(\rho_u\, S_L\, A_u)\, c_p\, (T_b - T_u) = \boxed{\overset{\text{negative}}{k\, \frac{dT}{dx}\, (A_u - A_b)}} + A_b\;\; q_c \int_{xf}^{xf+} Y_F\, \mathrm{B}\exp\left(-\frac{T_A}{T}\right)\, dx$$

$$(\rho_u\, S_L\, A_u)\, Y_F \;=\; \boxed{\overset{\text{positive}}{\rho\, D\, \frac{dY_F}{dx}\, (A_u - A_b)}} + A_b \int_{xf}^{xf+} Y_F\, \mathrm{B}\exp\left(-\frac{T_A}{T}\right)\, dx$$

This is similar to the Le Chatlier-Mallard theory for a flat laminar flame, but due to stretch, it now contains different areas $A_u$ and $A_b$ on unburned and burned side
Replace ( $A_b$-$A_u$) / $A_u$ = Karlovitz number (Ka) = positive for counterflow on last slide

Lewis number Le = $(k/\rho_u c_p)/D_{def}$: if Le >1 heat loss dominates reactant gained → extinction

# Law's theory of flame stretch correctly predicts burning velocity and burned gas temperature

$$S_L / S_{L,0} = 1 - Ka \ Ma \qquad \text{and:}$$

$$T_b = T_{bo} + (T_{b0} - T_u)\,(Le^{-1} - 1)\ Ka$$

Ka = nondimensional stretch rate = (stretch rate K) / $(S_{L,02}/\alpha_0)$
= proportional to the velocity gradient
$T_b$ = Burned gas temperature with stretch
Ma = Markstein number for the reactants selected, related to Lewis number
Lean mixtures of light fuels (methane, hydrogen) have Ma <0, Le >1
Lean mixtures of heavy fuels (propane, butane) have Ma>0, Le<1

Conclude:
Bunsen flame tip for lean methane: Ka = negative, Ma=negative>1, Le <1
so stretch causes smaller $S_L$, lower $T_b$ : we observe an "open tip"
Spherically expanding flame, lean methane: Ka = +, Ma = 1
→so opposite trend; it burns faster

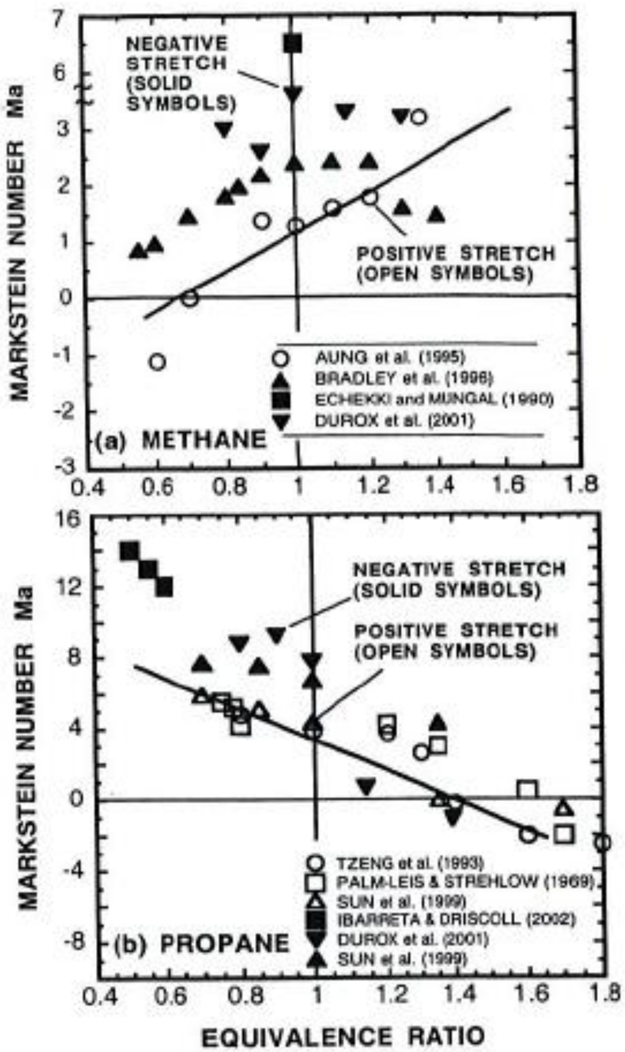
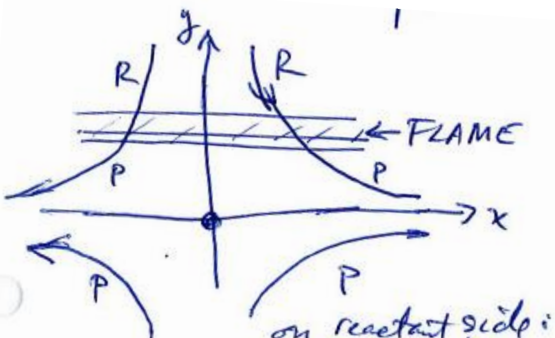



Fig. 1. Markstein numbers measured and computed by previous investigators, showing that larger values of Ma occur for cases of negative stretch. a) methane-air; b) propane-air; reactants at 300 K, 1 atm.

End

# Stretch rate of a counterflow premixed flame




in reactants, assume:

$$\bar{V} = \underbrace{(\epsilon x)}_{u}\vec{i} - \underbrace{(\epsilon y)}_{v}\vec{j}$$

$\epsilon$ = aerodynamic strain rate = constant in reactants

on reactant side: constant density

note: mass is conserved $\quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} = 0 \quad \Rightarrow \epsilon + (-\epsilon) = 0$

flow is irrotational $\quad \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y} = 0 \quad\quad 0 + 0 = 0$

hyperbolas

$$K_s = ? = \bar{\nabla}\cdot\bar{V} - \bar{n}\cdot(\bar{n}\cdot\bar{\nabla})\bar{V} \qquad \bar{n} = \bar{j}$$

$$= \underbrace{\left(\frac{\partial \overset{(\epsilon x)}{u}}{\partial x} + \frac{\partial \overset{(-\epsilon y)}{v}}{\partial y}\right)}_{0} - \underbrace{\vec{j}\cdot\left(\frac{\partial}{\partial y}\right)(u\vec{i}}_{\vec{j}\cdot\vec{i}=0} + V\vec{j})$$

$$\boxed{K_s = -\frac{\partial v}{\partial y}}$$

strain rate is a velocity gradient, since

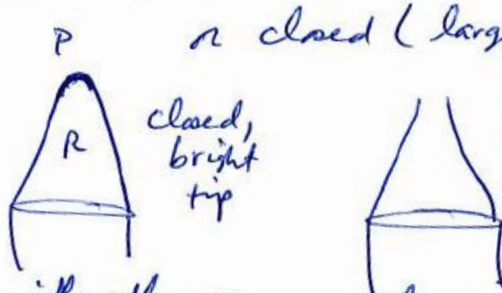
$\therefore \boxed{K_s = \epsilon}$

$V = -\epsilon y$ then;

1-12

# Stretch rate of the tip of a bunsen flame

observe: tip of bunsen burner can be open (small $S_L$)
or closed (large $S_L$)




closed, bright tip

open, extinguished tip

rich methane or lean propane

lean methane or rich propane

bunsen tip: $Ka$ = negative $\Rightarrow$ curvature is concave toward reactants

if rich methane $Ma = +$

$$(S_L / S_{L0}) = 1 - \underset{-}{Ka} \cdot \underset{+}{Ma} = \; > 1 \; !$$

bright tip!