Serendipity and Contrarianism in Research: Hit 'em where they ain't

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Today's message

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- Most great scientific and technological discoveries are the result of accidents
- Must be so, because if the result was consistent with expectation, nothing new was learned
- My experience: *compared to a generation ago, researchers today are*
  - *More likely to adopt "follow me" research plans*
  - *More trusting of current "wisdom"*
- Goal of today's lecture
  - Develop an appreciation of serendipity and contrarianism
  - Give personal examples
  - Provide some basic rules and guidelines for exploiting your own S&C

Examples of serendipitous discovery

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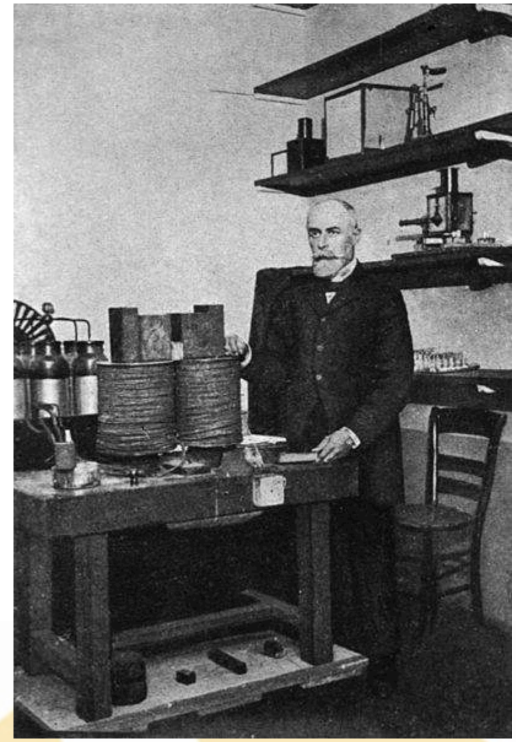
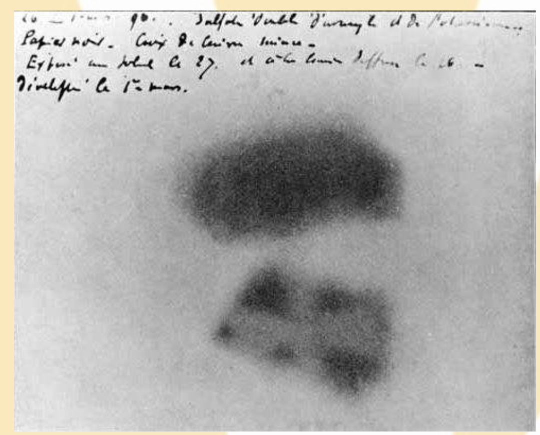
- Radioactivity (Henri Becquerel, 1896)
- Thought that phosphorescent materials could emit penetrating X-rays when illuminated by intense light
- Wrapped photographic plates in thick black paper, covered them with various phosphorescent materials, illuminated them with sunlight
- No penetrating rays found until he used uranium salts
- … and by developing plates exposed on a cloudy day, found that uranium worked even in the dark!
- His student Marie Curie then isolated other radioactive elements – polonium, thorium, radium





Examples of serendipitous discovery

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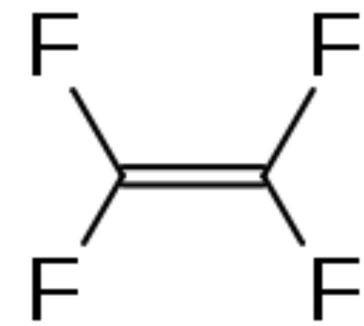
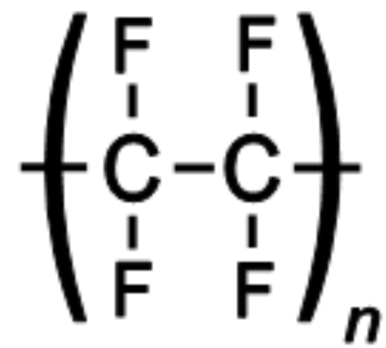
- **Teflon** (Roy Plunkett, 1938)
- Working for Kinetic Chemicals (joint venture between DuPont and General Motors)
- Was looking for a new refrigerant for automotive air conditioning systems
- One morning, opened a cylinder of tetrafluoroethylene (C_2F_4) only to find it had no pressure but still the same mass (i.e. no gas had leaked out)
- Sawed open the cylinder to find a white powder – iron on cylinder walls had acted as a catalyst to polymerize C_2F_4!





Examples of serendipitous discovery

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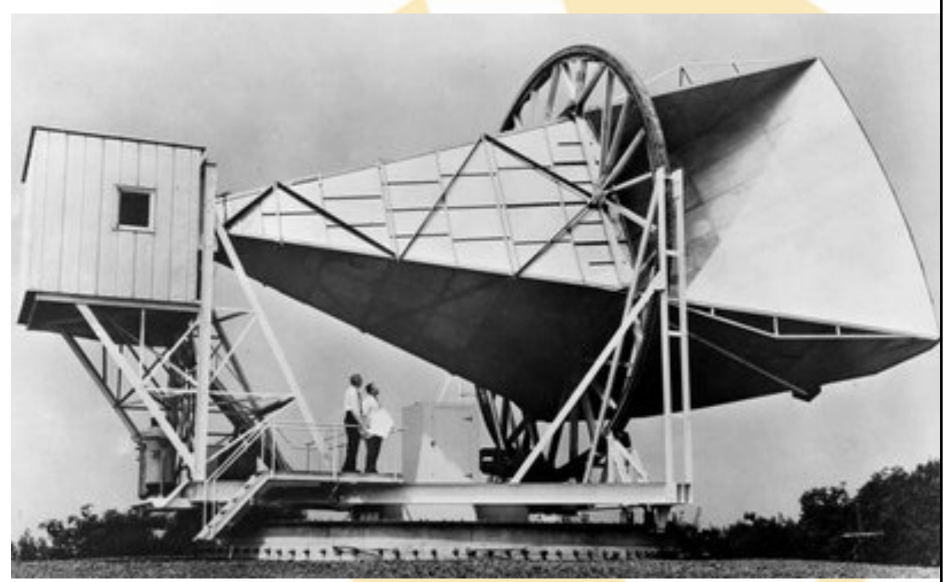
- **The Big Bang** (Arno Penzias & Robert Wilson, 1964)
- At Bell Labs, experimenting with sensitive horn antenna to detect radio waves reflected off of balloon satellites to be used for communications
- Even using liquid helium (4K) detector to minimize thermal noise, still found noise **coming equally from all directions at all times, day & night**
- Intensity corresponded to blackbody radiation at 2.7K
- Concluded it was from deep space, a fossil remnant of the Big Bang theorized by others



Examples of serendipitous discovery

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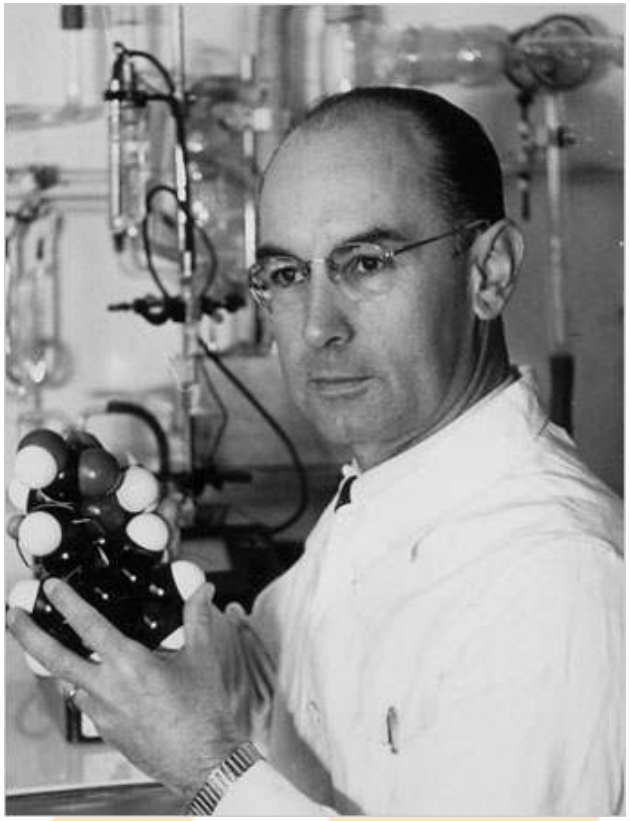
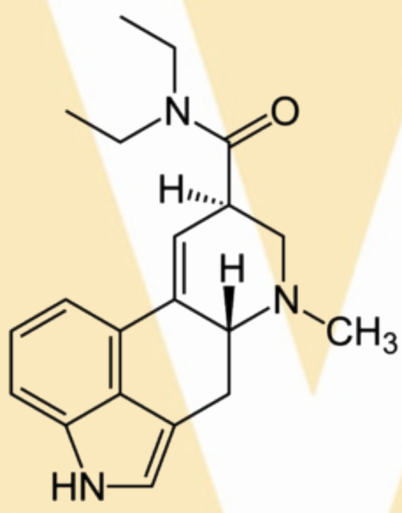
- LSD (Albert Hofmann, 1943)
- Pharmaceutical chemist, looking for respiratory and circulatory system stimulant that would not affect the uterus
- Synthesized in 1938, but set aside until 1943 when he accidentally absorbed a small amount through his fingertips
- Experienced "uninterrupted stream of fantastic pictures, extraordinary shapes with intense, kaleidoscopic play of colors"
- Continued studying (and testing) hallucinogens, lived to be 102!





Examples of serendipitous discovery

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- Microwave oven (Percy Spencer, 1945)
- Radar engineer with Raytheon, noticed that a chocolate bar in his shirt pocket melted
- Radar frequency happened to correspond to one at which water molecules would rotate back and forth due to its dipole moment
- Tested popcorn and eggs in radar set, then purposefully built a shielded box which rapidly heated food inside

Examples of serendipitous discovery

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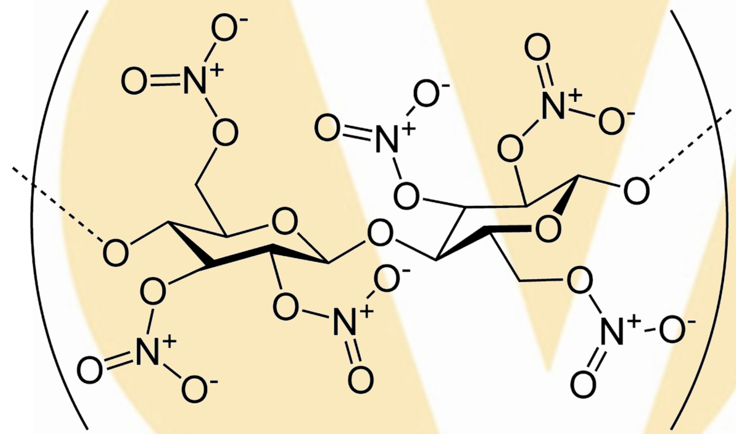
- Nitrocelluose (Christian Schönbein, 1846)
- At home, spilled a mixture of nitric and sulfuric acids, wiped it up with a cotton apron and hung it to dry over a stove
- When dry, the apron exploded!
- Recognized it as a gunpowder alternative by Schönbein and even Jules Verne, though not reduced to practice until 1884
- Schönbein also discovered ozone (serendipitously, of course!) and invented the fuel cell



Examples of serendipitous discovery

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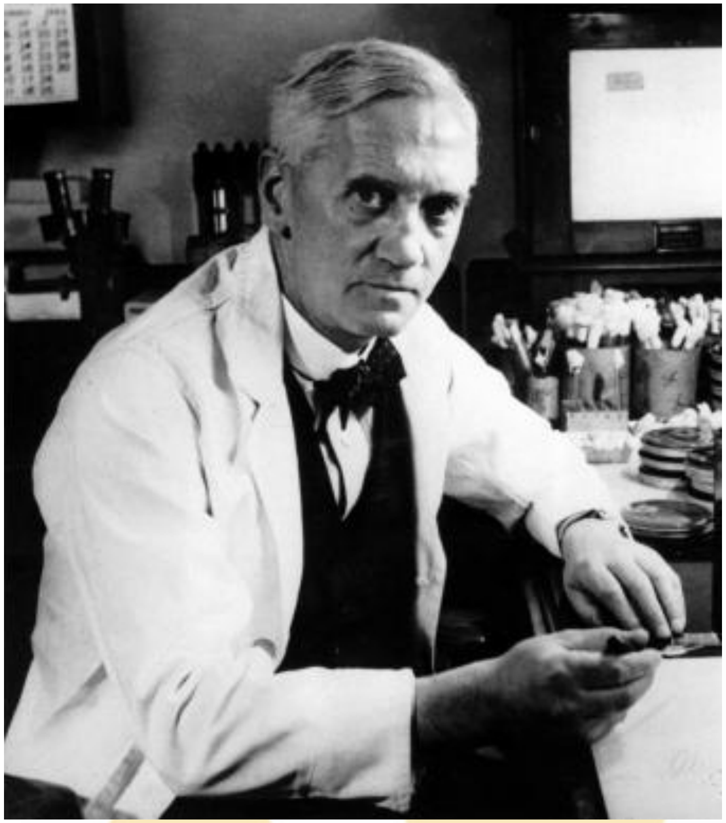

- Penicillin (Alexander Fleming, 1928)
- Was already famous for discovering lysozyme enzyme, but known to be untidy
- Left petri plates containing staphylococci unwashed when he went on summer vacation
- When he returned, one plate had grown moldy; colonies of staphylococci nearby were dead, farther away unaffected
- Isolated mold and showed it affected many disease-causing bacteria

Examples of contrarianism

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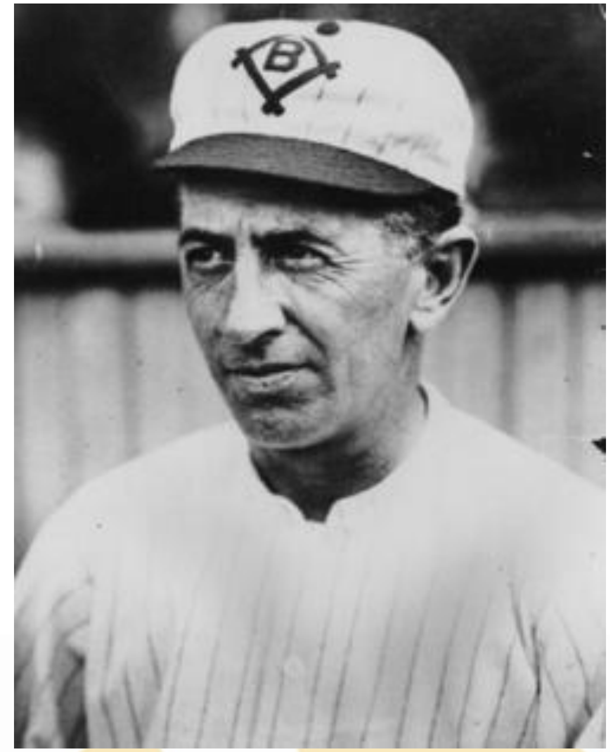
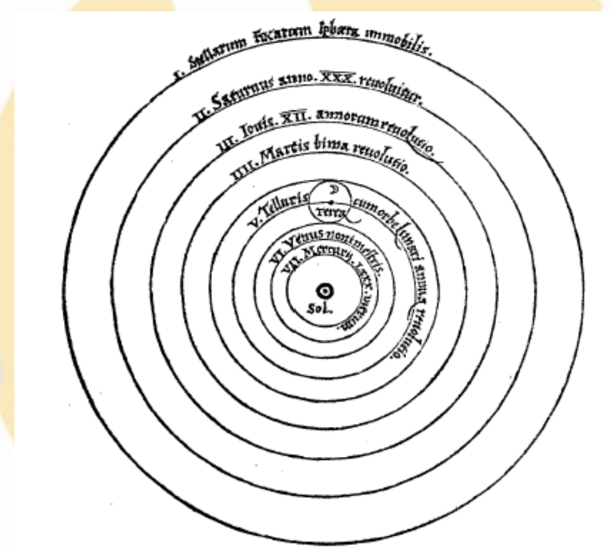
- Willie Keeler - professional baseball player (1892 – 1910) with extraordinary hitting statistics despite being only 5’5” tall and weighing 140 pounds:

  "Keep your eye clear, and hit 'em where they ain't”

- Famous examples
  - Heliocentrism (Copernicus, 1543),
  - Evolution of species (Darwin, 1838)
  - Relativity (Einstein, 1905)
  - Quantum mechanics (many, late 1800s – early 1900s)
  - Extinction of the dinosaurs due to meteorite impact (Alvarez, 1980)
  - Human-caused climate change (ongoing)
- Popular in investing strategies (e.g. Fidelity Contrafund™, $61 billion)





Examples of contrarianism

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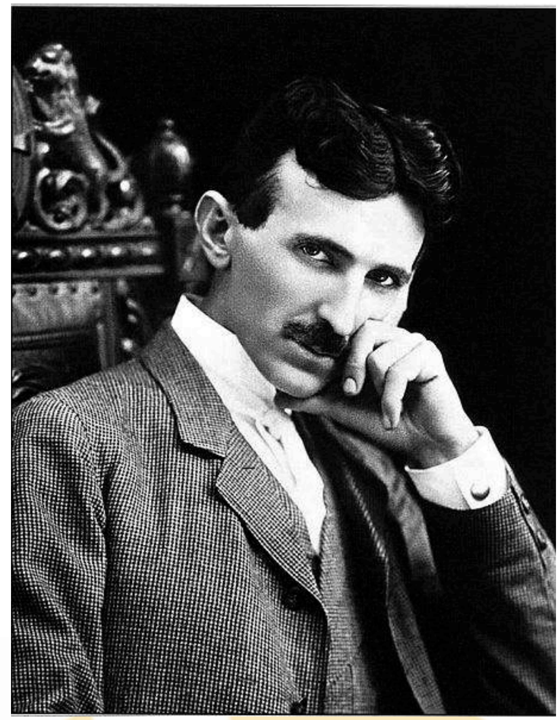
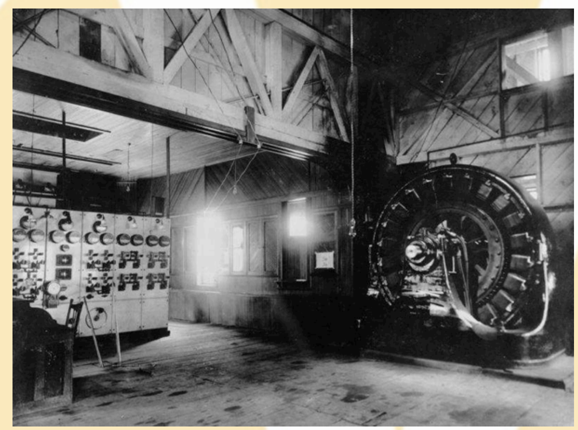
- Alternating current (Nikola Tesla, 1887)
- Edison championed direct current power grid – because that's the system he invented
- DC operated at low voltages / high currents, thus huge losses, because there was no efficient way to step-up DC voltages
- Tesla showed that AC generation + step-up & step-down transformers was far more efficient
- Westinghouse (using Tesla's patents) finally won competition to bring hydroelectric power from Niagara Falls, signaling the end of DC for large-scale power transmission





Examples of contrarianism

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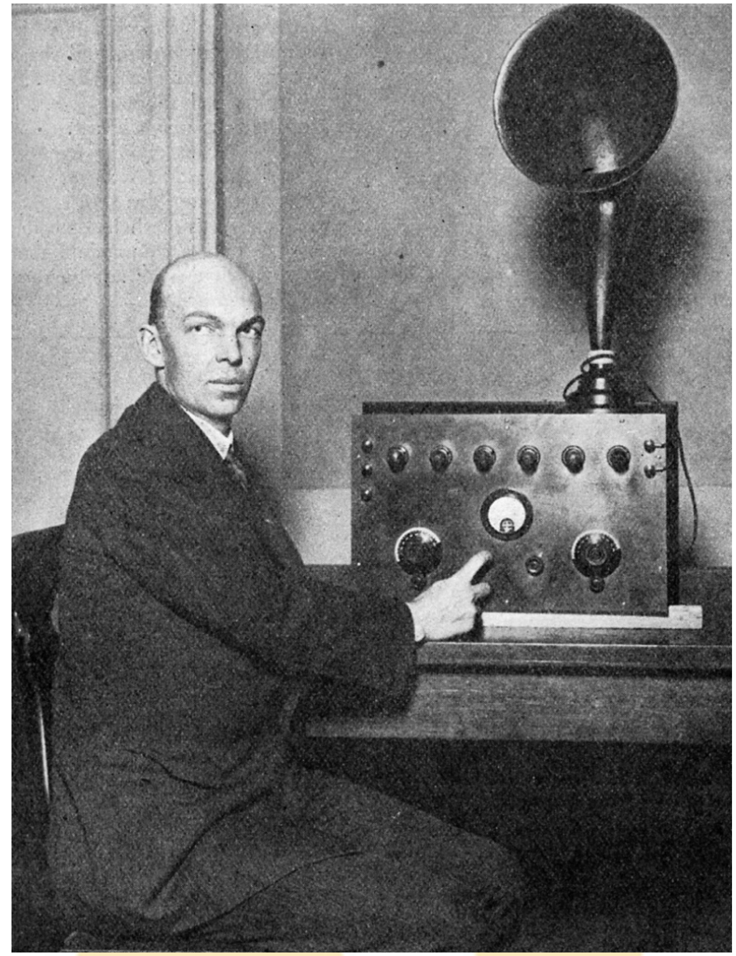
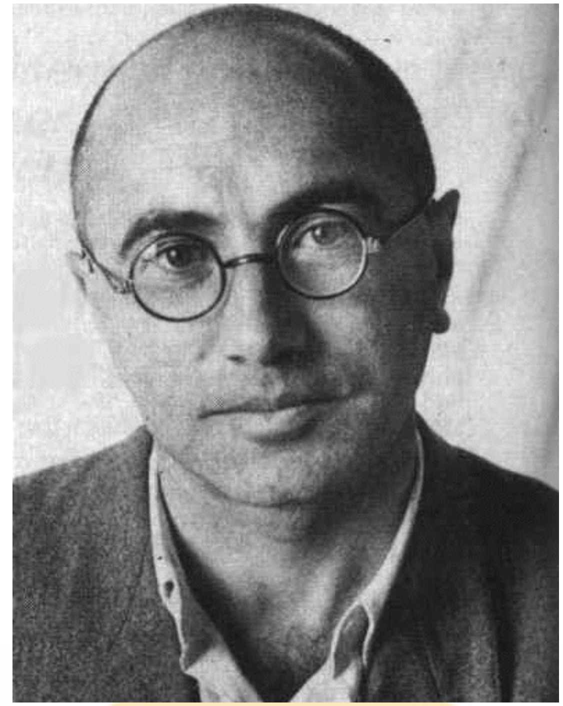
- **Frequency Modulation (Edwin Armstrong, 1934)**
- **Had already made major contributions to radio frequency circuit design before FM**
- **Developed FM and demonstrated its superior resistance to noise/ interference compared to AM**
- **RCA and others had vested interests in preserving the AM standard**
- **Fierce legal battles with RCA**
- **Committed suicide at age 63, never received royalties for his work (though his heirs did many years later after much litigation)**



PDR's serendipity #1



- Flame balls (1984)
- Zeldovich, 1944: stationary, spherical, diffusion-controlled combustion possible
- $\nabla^2 T$ & $\nabla^2 C = 0$ have solutions for *unbounded* domain in spherical geometry
- $T(r) = C_1 + C_2/r$ - bounded as $r \rightarrow \infty$
- Not possible for cylinder or plane
- Perfectly valid steady solution to the governing equations for energy & mass conservation for any combustible mixture but…

Flame balls - history

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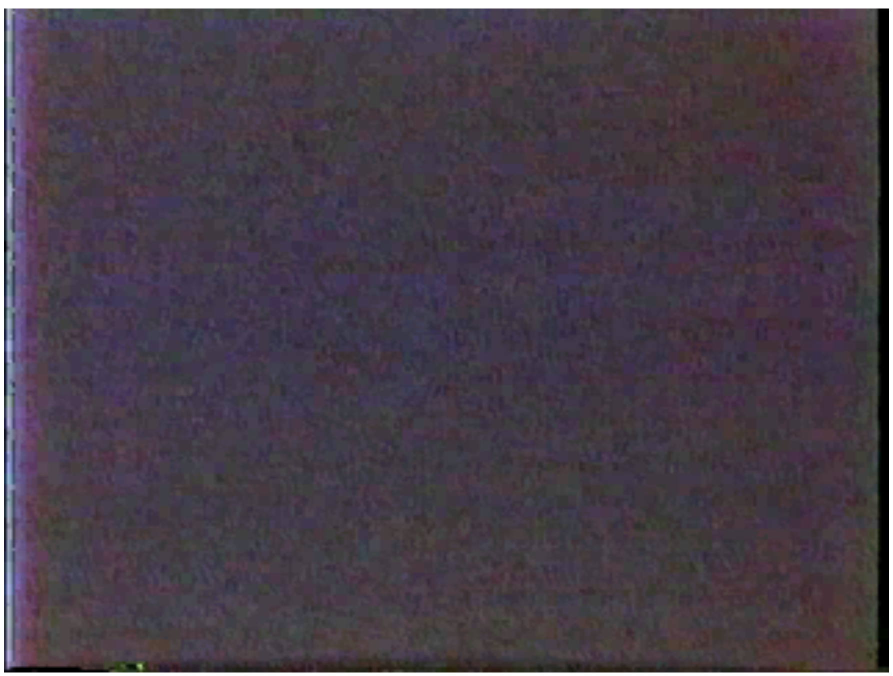
- Zeldovich, 1944; Joulin, 1985; Buckmaster, 1985: adiabatic flame balls are *unstable*
- Ronney (1990): seemingly stable, stationary flame balls ***accidentally*** discovered in very lean H_2-air mixtures in drop-tower experiment
- Farther from limit - expanding cellular flames
- Actually, the whole concept of microgravity research was "contrarian" at the time



Far from limit

Close to limit

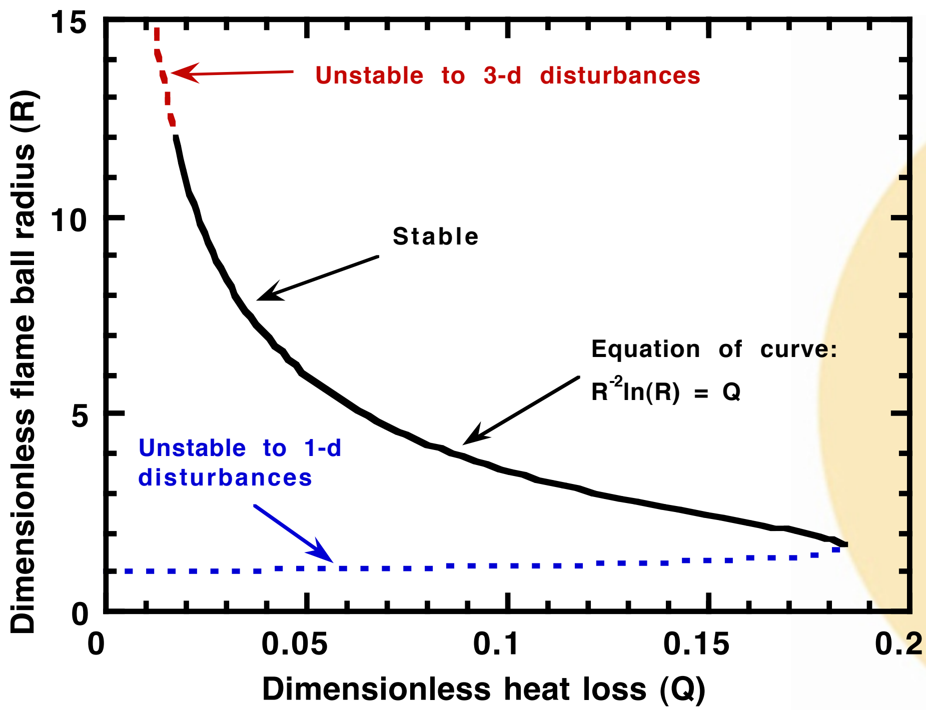
Flame balls - history

- **Buckmaster, Joulin, *et al.*: window of *stable* conditions with (1) radiative loss near-limit, (2) low gravity & (3) low Lewis number (2 of 3 is no go!)**

$$\text{Impact of heat loss} \sim \frac{\text{Heat loss}}{\text{Heat release}} \sim \frac{T_{flame}^2}{e^{-E/RT_{flame}}} \Uparrow \text{ as } T_{flame} \text{ (thus fuel \%)} \Downarrow$$

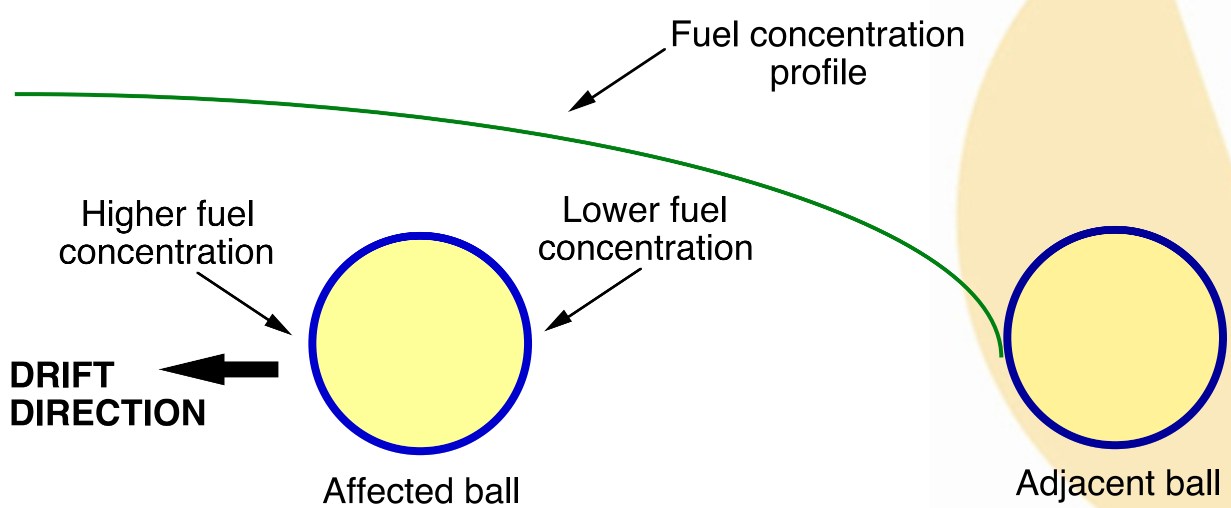
$$\text{Le} \equiv \frac{\text{Thermal diffusivity of the bulk mixture } (\alpha)}{\text{Mass diffusivity of scarce reactant into the bulk mixture (D)}}$$

- **Predictions consistent with experimental observations**

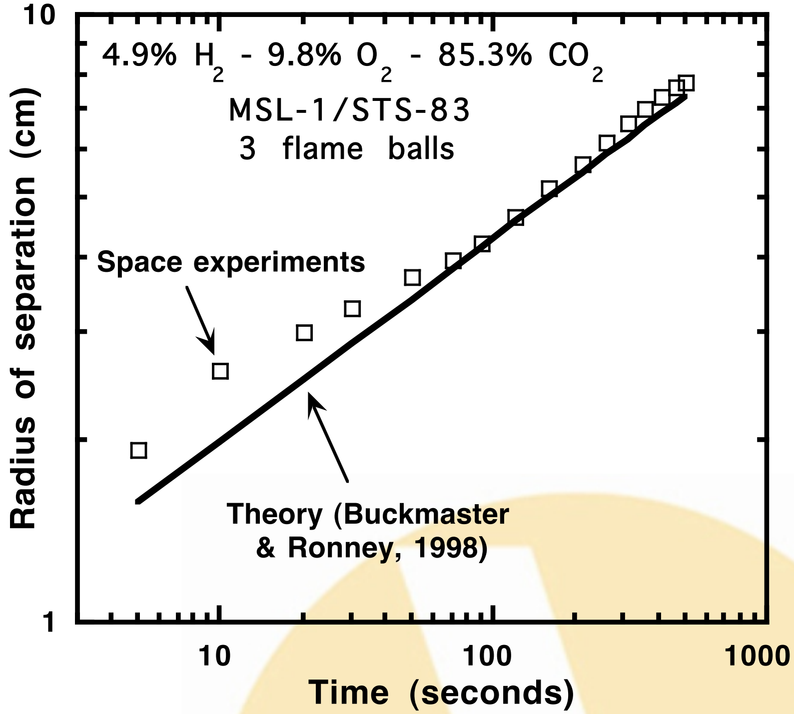


Flame balls

- Results led to space experiments in 1997 & 2003
- One of several surprises seen in space experiments: flame balls always drifted apart at a continually decreasing rate
- Flame balls interact by
  (A) warming each other - attractive
  (B) depleting each other's fuel - repulsive
- Analysis (Buckmaster & Ronney, 1998)
  - Adiabatic flame balls, two effects exactly cancel
  - Non-adiabatic flame balls, fuel effect wins - thermal effect disappears at large spacings due to radiative loss

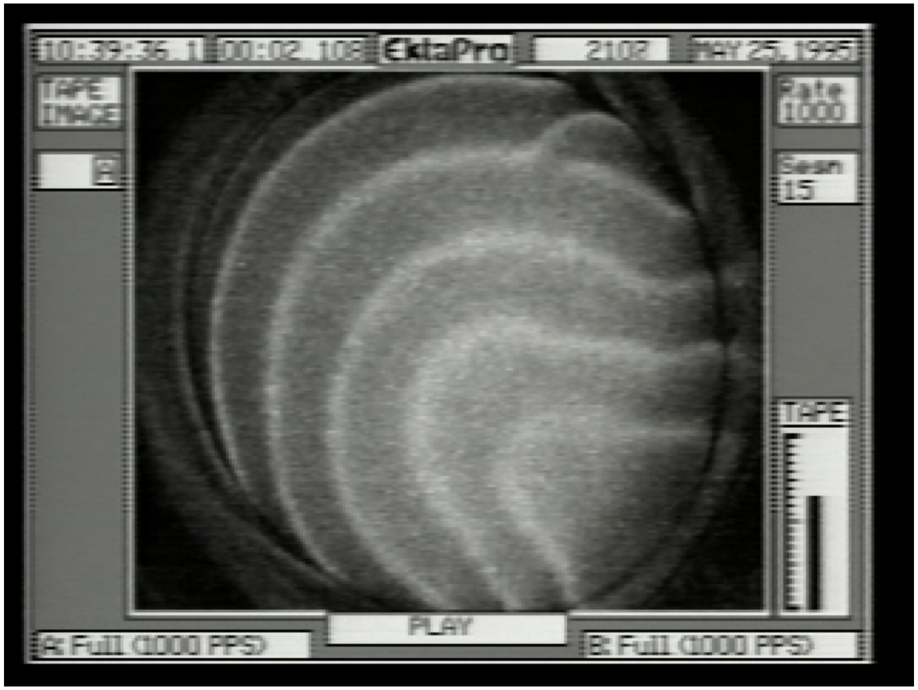


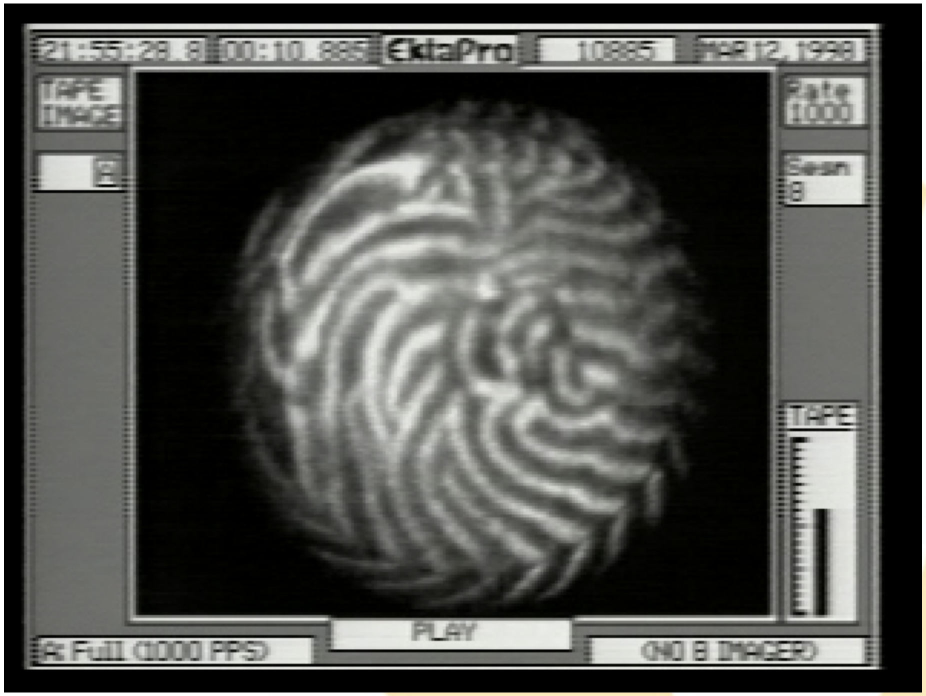
Flame ball drift



PDR's serendipity #2

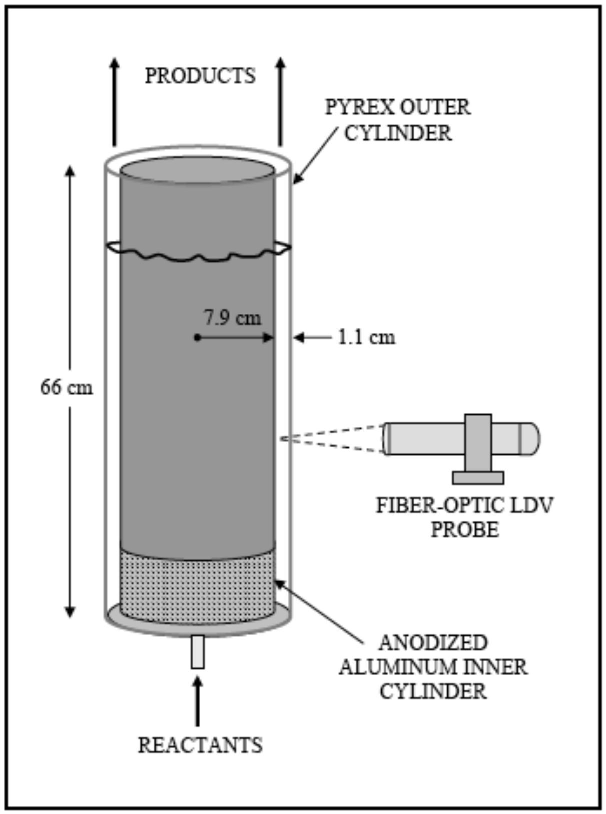
- **Spiral flames (1994)**
- **If low Lewis numbers are good, what about high Le?**
- **Theory predicts pulsating and/or travelling-wave instabilities at high Le – is it true?**
- **Pearlman & Ronney – $C_4H_{10}/O_2/He$ mixtures (Le ≈ 3) traveling down tubes**
- **Showed not only pulsating but also spiral flames!**

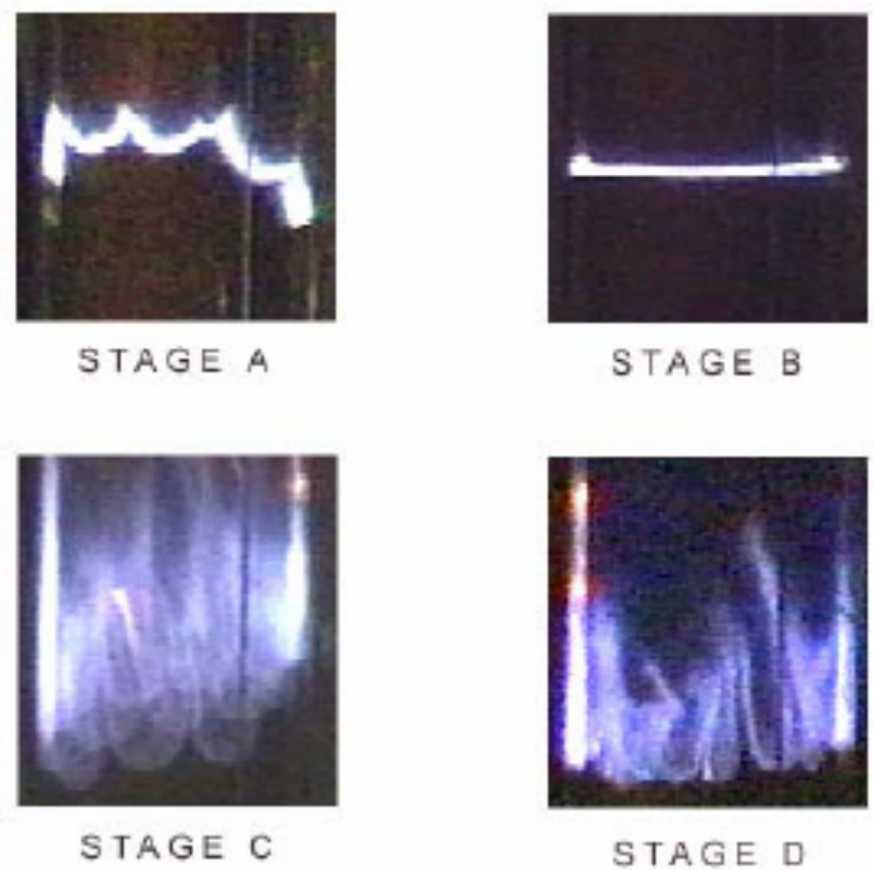




PDR's serendipity #3

- Instabilities of flames in confined channels (1998)
- Aldredge & Ronney studying effects of turbulence in Taylor-Couette cell on flame propagation speeds
- Found the flame was wrinkled, even when cylinders were not moving!





Flames in confined channels

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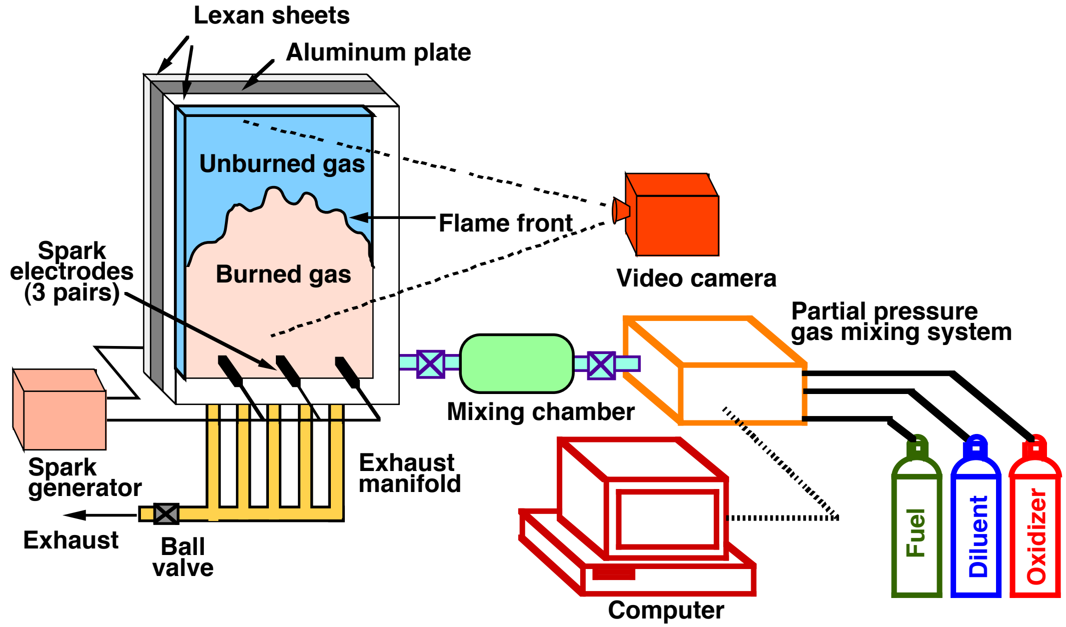
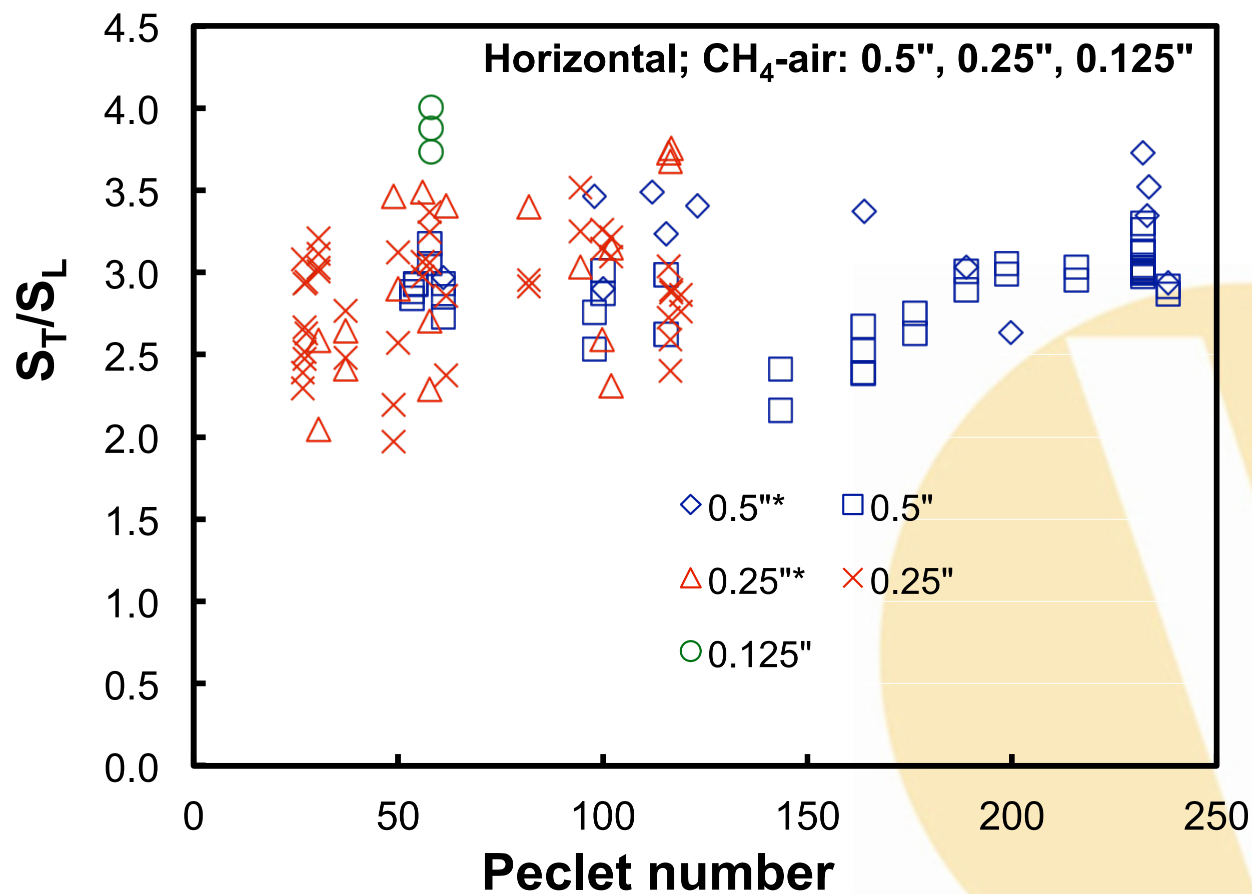
- Built "unwrapped" Hele-Shaw cell
- Again found that flame was wrinkled **even with no turbulence**
- Lewis number affected fine-scale structure but not overall behavior



Flames in confined channels

- Even with no turbulence, burning rate is $3S_L$
- Big problem for turbulent combustion modelers; prediction for no turbulence is $1S_L$
- Results independent of Peclet number, thus heat loss not a factor



PDR's serendipity #4

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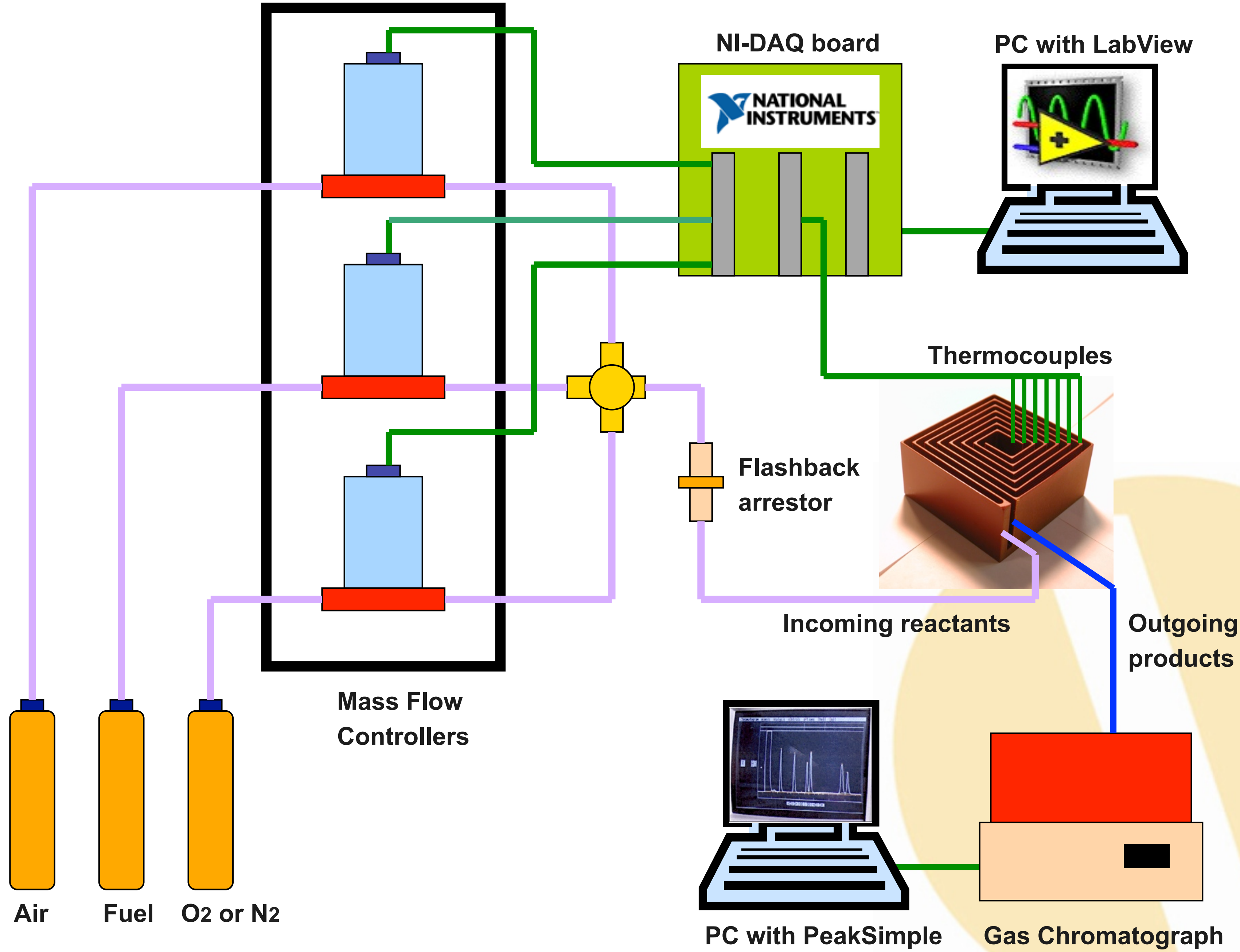
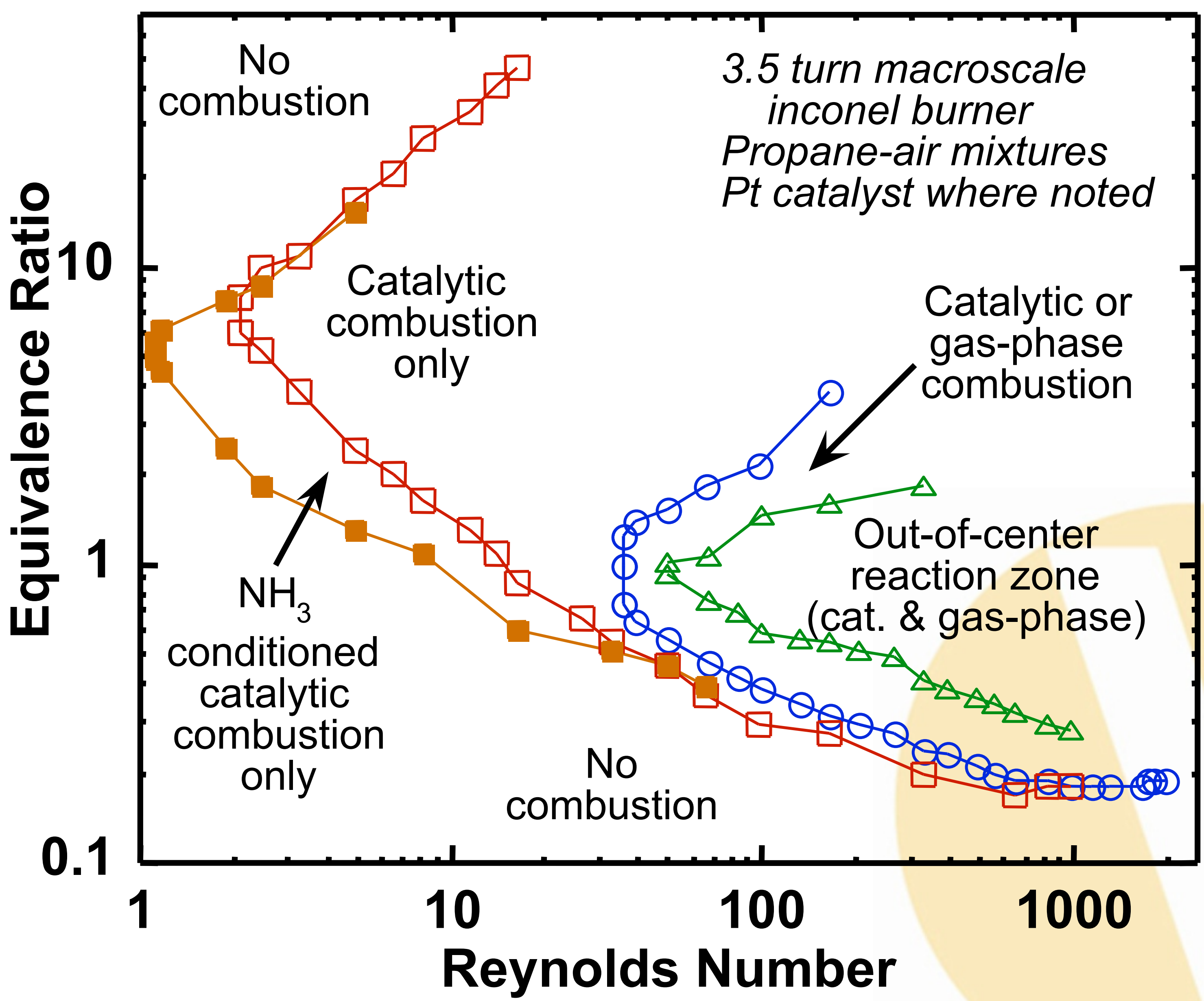
- NH$_3$–treated Pt catalyst for low-temperature hydrocarbon "combustion" (2002)
- Studying combustion in spiral counterflow "Swiss Roll" heat recirculating combustors
- Wanted to use catalyst to minimize flame temperatures, but low-temperature performance was poor
- Well known that O_2 inhibits platinum catalysis at low T because of its high activation energy for desorption
- NH_3 was suggested as a fuel additive because of its known ability to "scrub" O_2 off Pt surfaces
- Test results
  - Started standard test with propane-air mixture
  - Added ≈ 1% NH_3, temperatures skyrocketed
  - Added more NH_3, temperatures dropped
  - Reduced NH_3, temperatures increased again
  - Shut off NH_3, temperature was highest of all
  - Moral: NH_3 is a terrible fuel additive but a fantastic catalyst conditioner

Catalysis experiments



Catalysis experiments



Catalysis experiments

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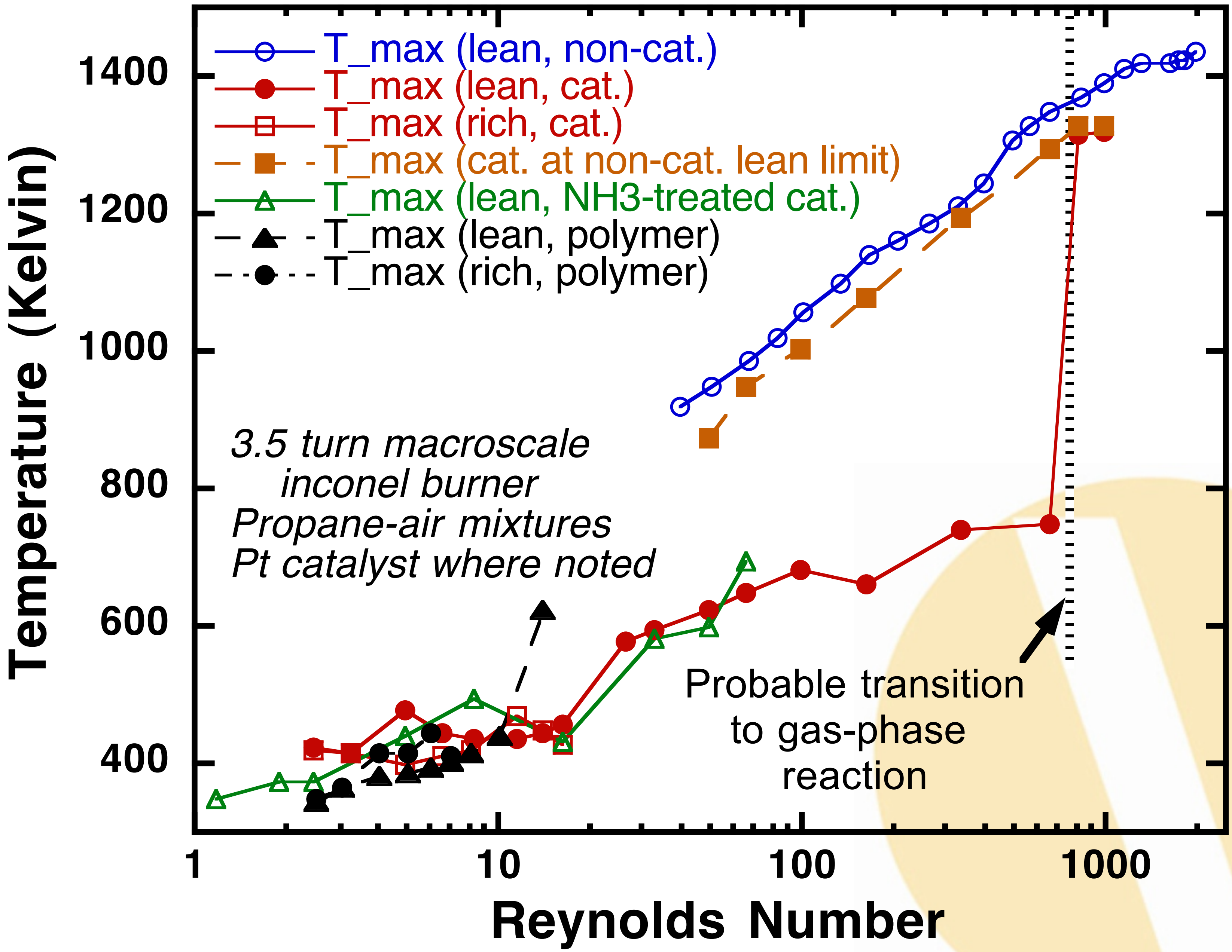

Low-T catalyst surface structure

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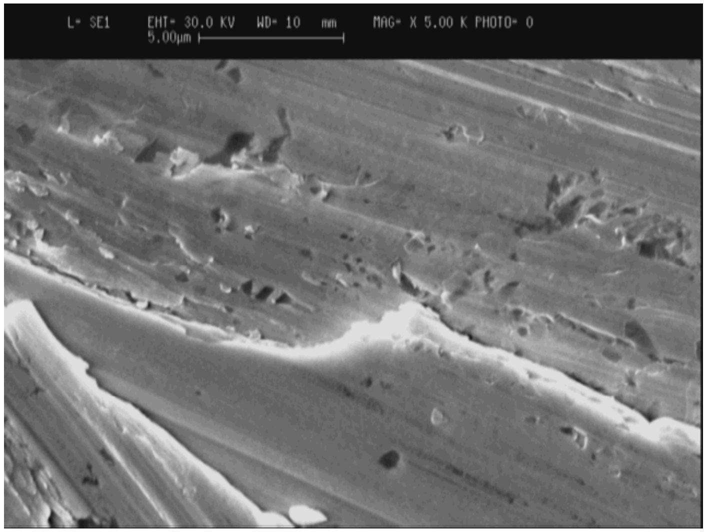
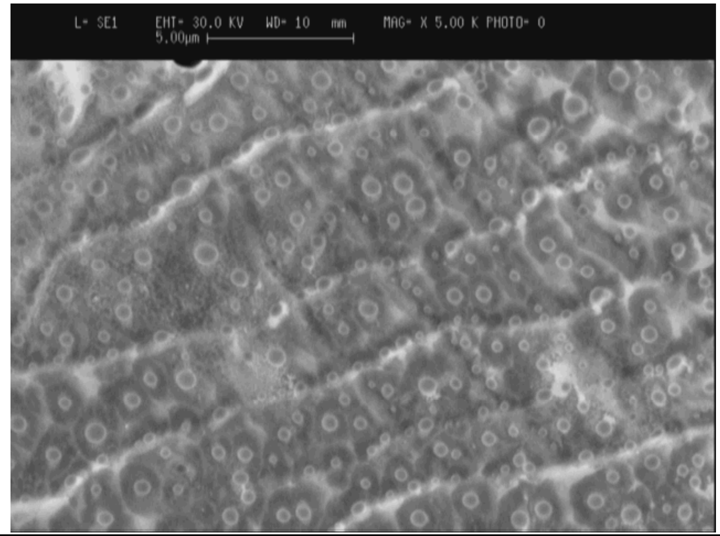
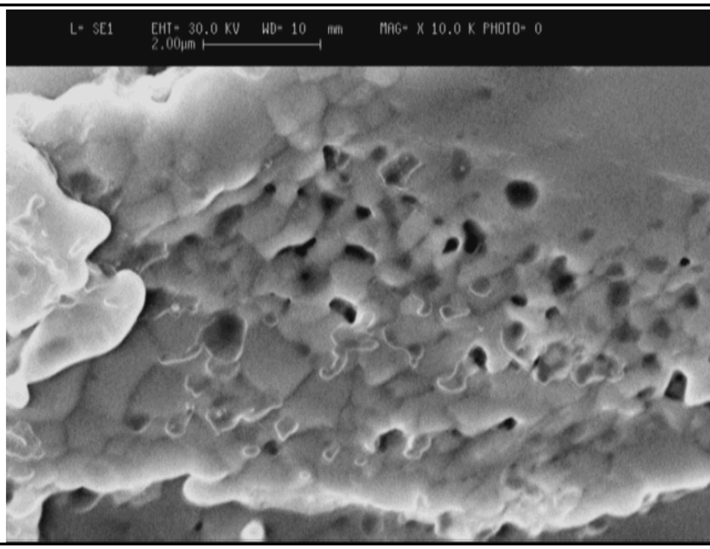


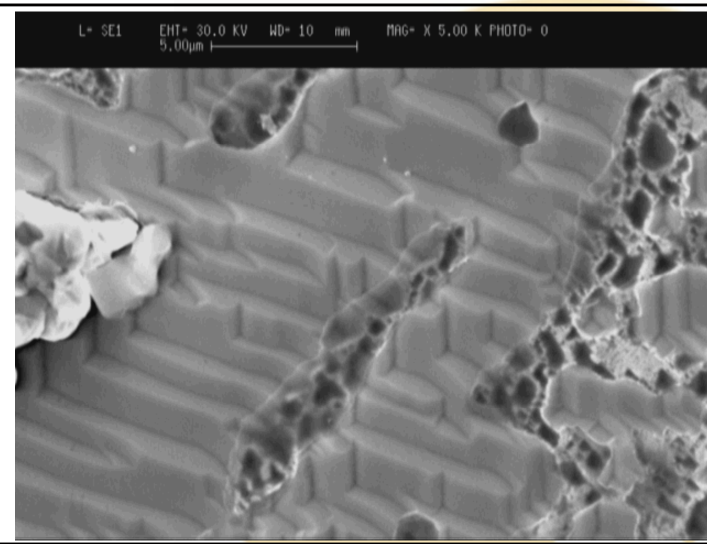
Without NH_3 treatment, before combustion testing (field of view 15 μm x 20 μm)



Without NH_3 treatment, after combustion testing (field of view 15 μm x 20 μm)



With NH_3 treatment, before combustion testing (field of view 6 μm x 8 μm)



With NH_3 treatment, after combustion testing (field of view 15 μm x 20 μm)

NH_3 conditioned Pt catalyst

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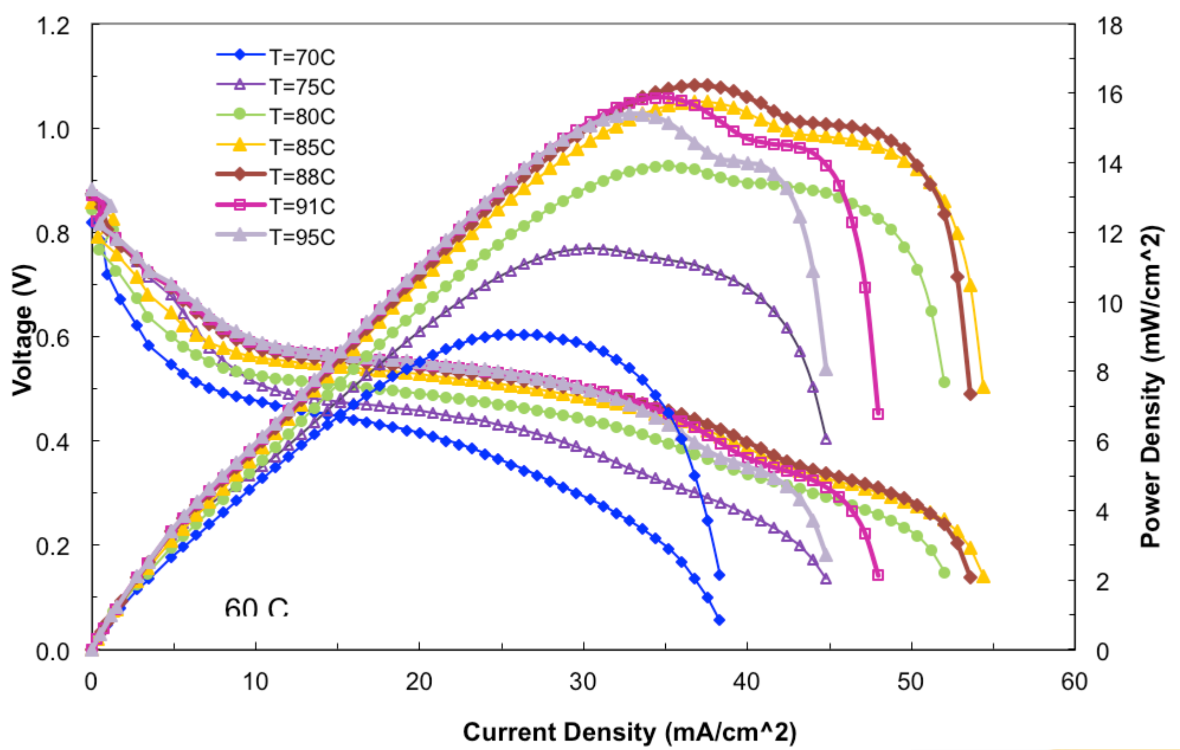
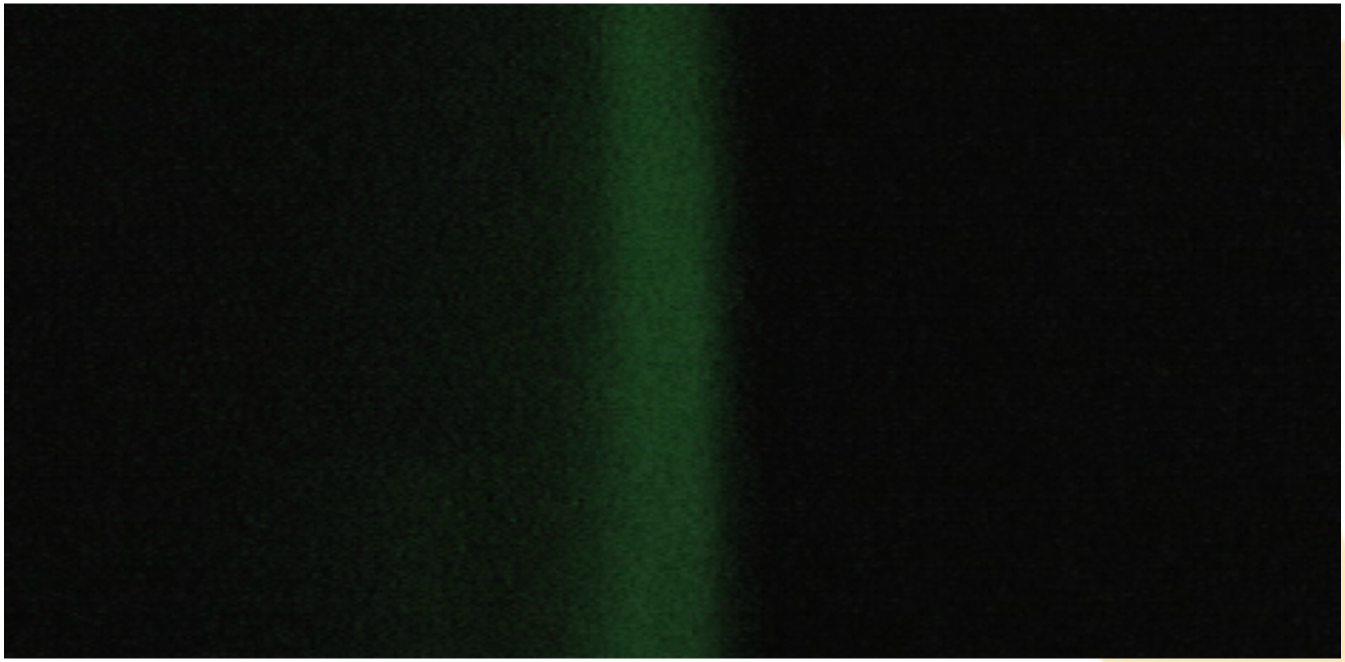
- **Consequences**
  - **World's lowest temperature self-sustaining hydrocarbon flames (70˚C)**
  - **World's lowest temperature hydrocarbon ignition (85˚C)**
  - **Use of NH_3 then N_2H_4 catalyst for the world's first direct hydrocarbon Proton Exchange Membrane fuel cells (with Surya Prakash, USC Dept. of Chemistry)**



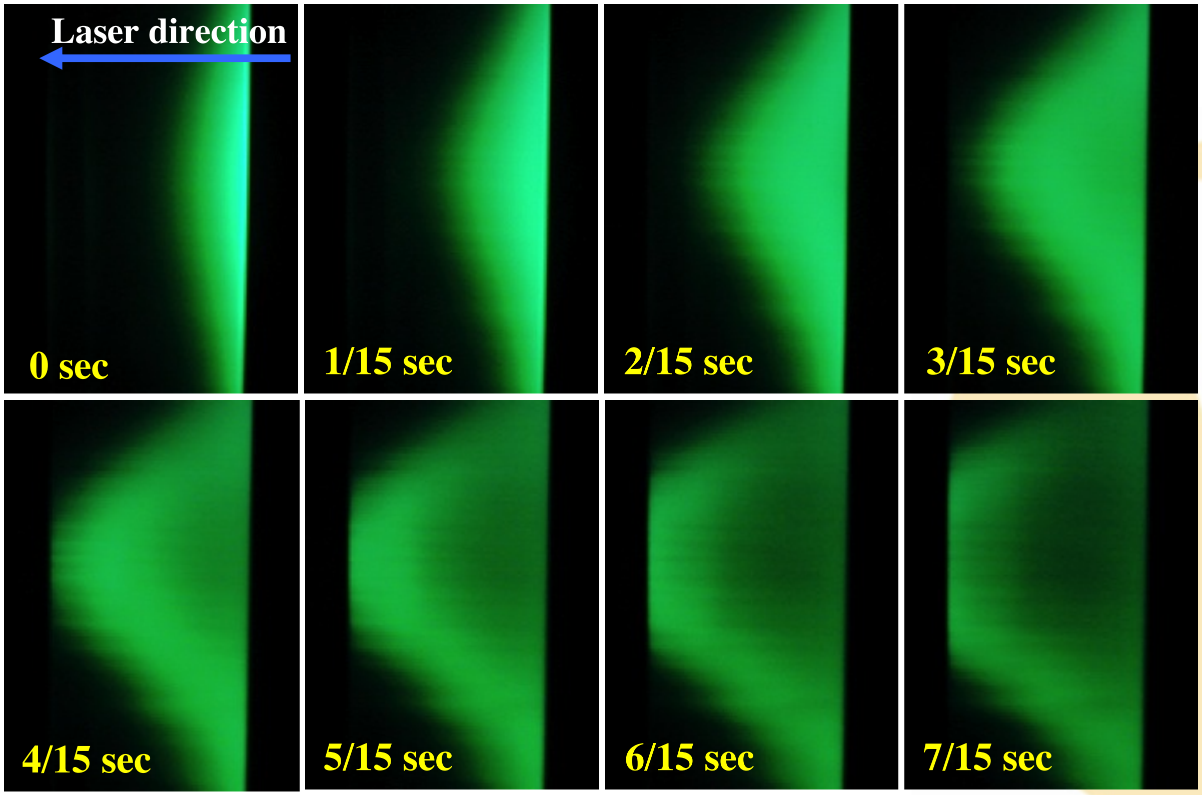
PDR's serendipity #5

- **Photobleaching velocimetry** (2004)
- Found in Taylor-Couette flow that solutions of fluorescein and sodium dithionite ($Na_2S_2O_4$) were non-fluorescent, even at high pH, until cylinders were rotated
- Initially thought it was a shear-rate-sensitive indicator (like bioluminescence) but when laser source or solution is moved slightly, fluorescence re-appears (even if no flow)
- If movement is stopped, fluorescence disappears again



Photobleaching velocimetry

- At high fluorescein concentrations, where significant attenuation of laser sheet occurs within the test section, an advancing wave of photobleaching was observed
- Key factor: $Na_2S_2O_4$ inhibits fluorescence of fluorescein (already known) but (not known)
  - It does not happen in the dark
  - In the presence of light, it occurs at a kinetically limited rate



Photobleaching velocimetry

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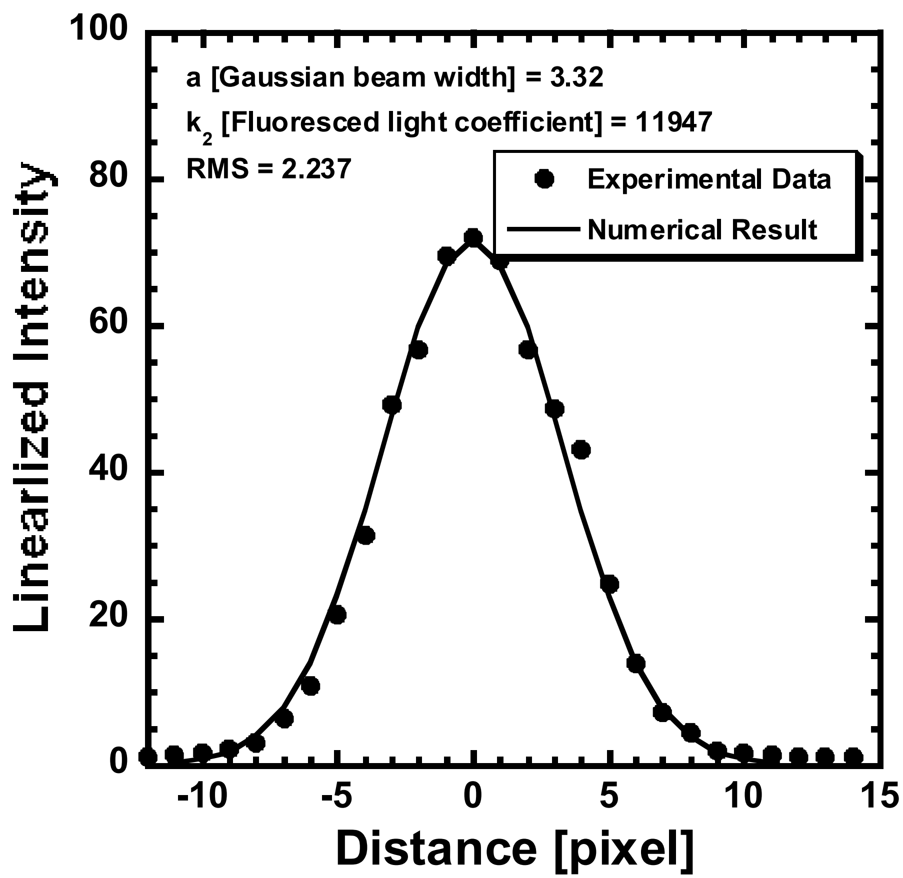
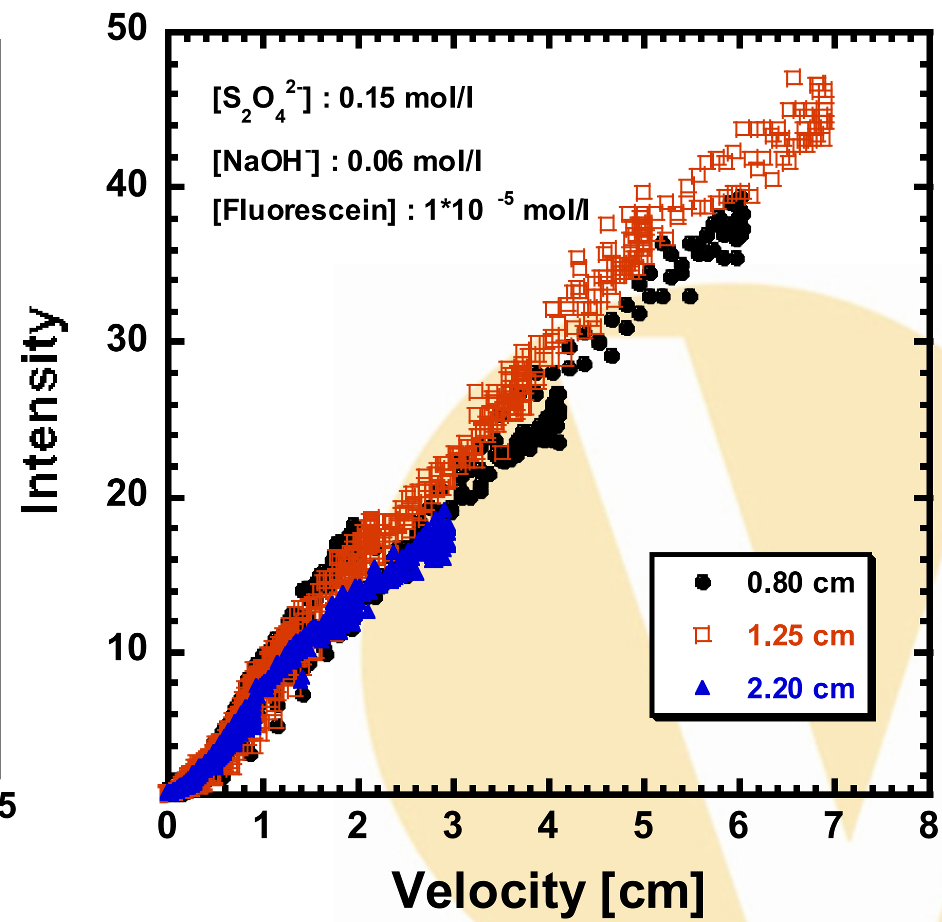
- Can use this for velocimetry – velocity = f(intensity)
- Extremely simple alternative to LDV/PIV
- Reversible – after ≈ 10 min darkness, fluorescence response returns to initial state





PDR's contrarianism #1

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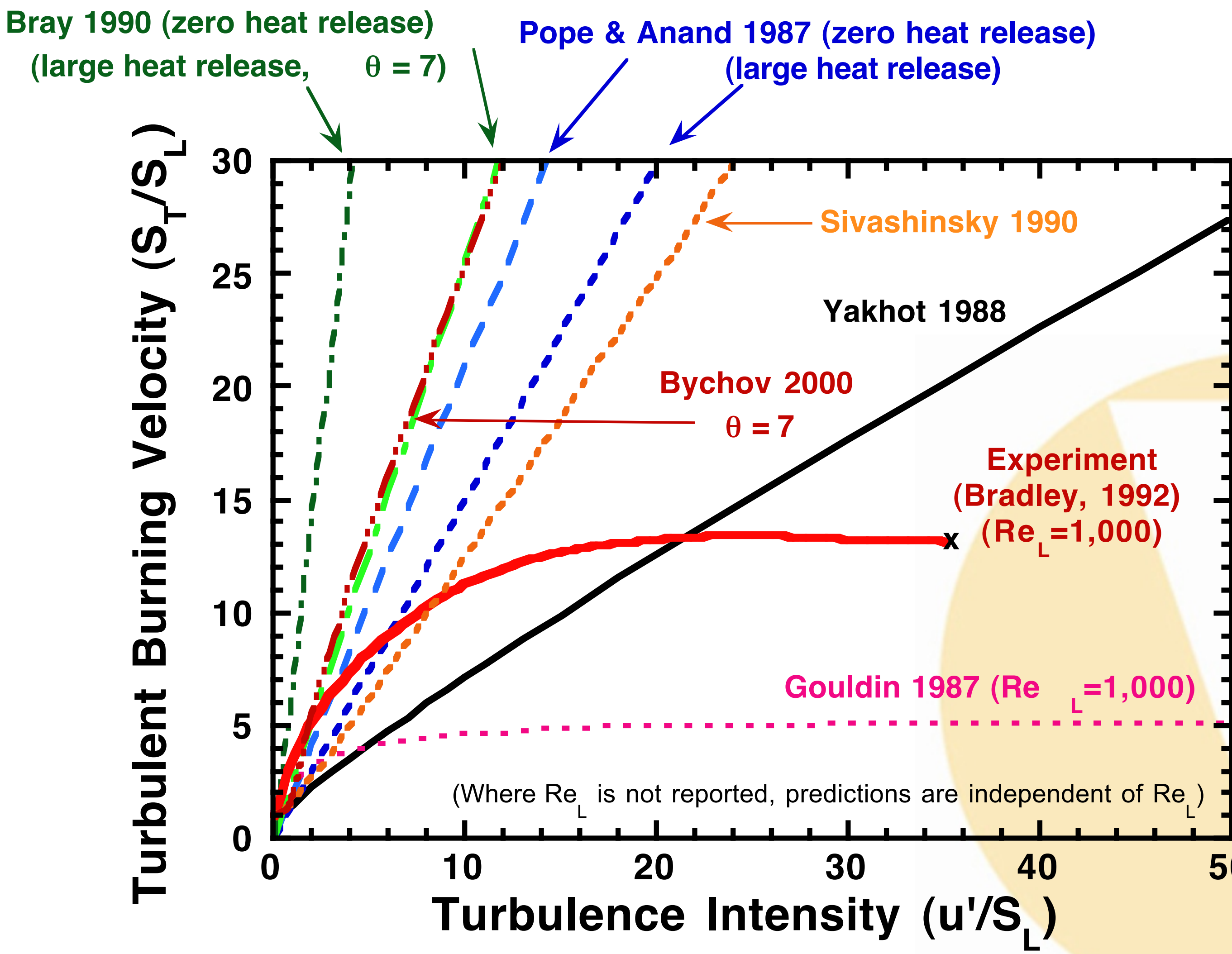
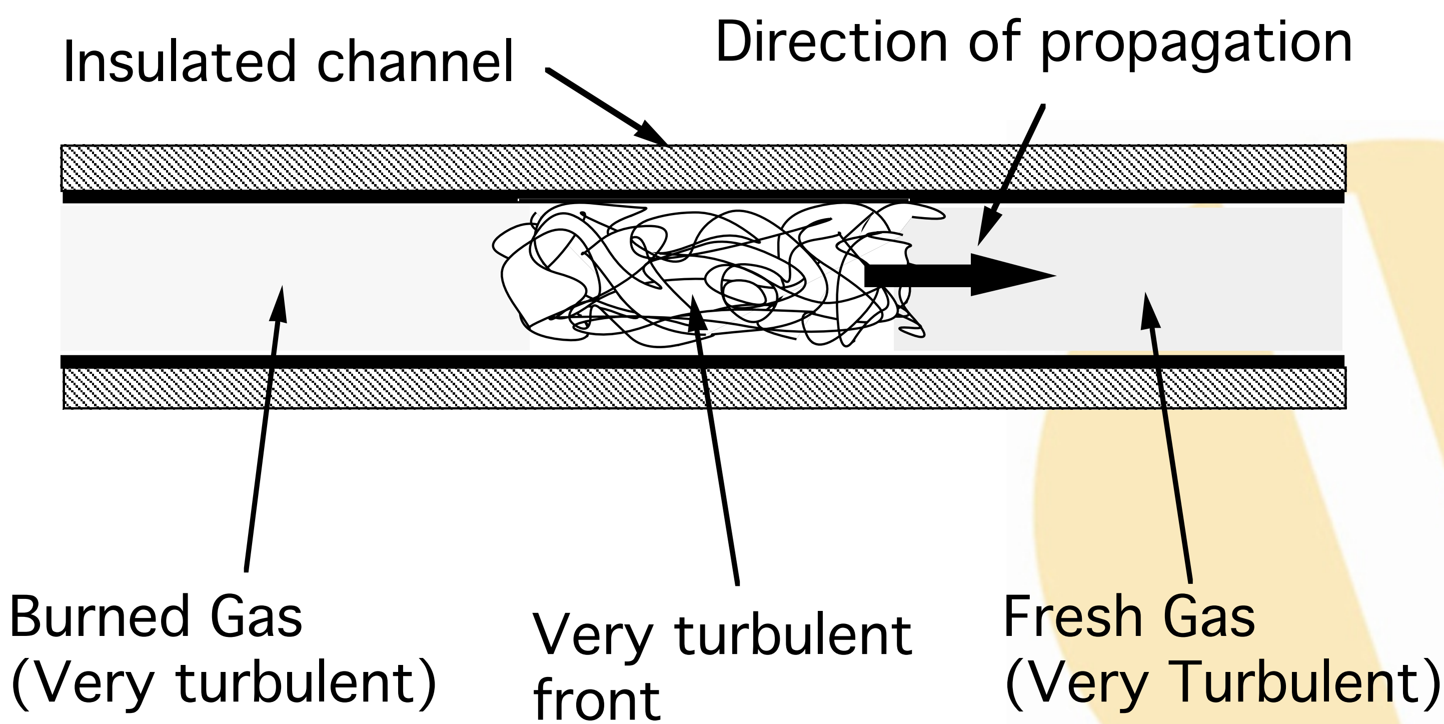
- "Liquid flames" (1992)
- Models of burning velocities of premixed turbulent flames don't agree with experiments nor each other!



Quenching by turbulence

- Why does strong turbulence quench flames?
- Attributed to mass-extinguishment of flamelets by <u>zero-mean</u> turbulent strain
- Hypothetical system: flammable mixture in adiabatic channel with arbitrary <u>zero-mean</u> flow disturbance

  ∴ Propagating front will always exist (???)



"Liquid flame" idea

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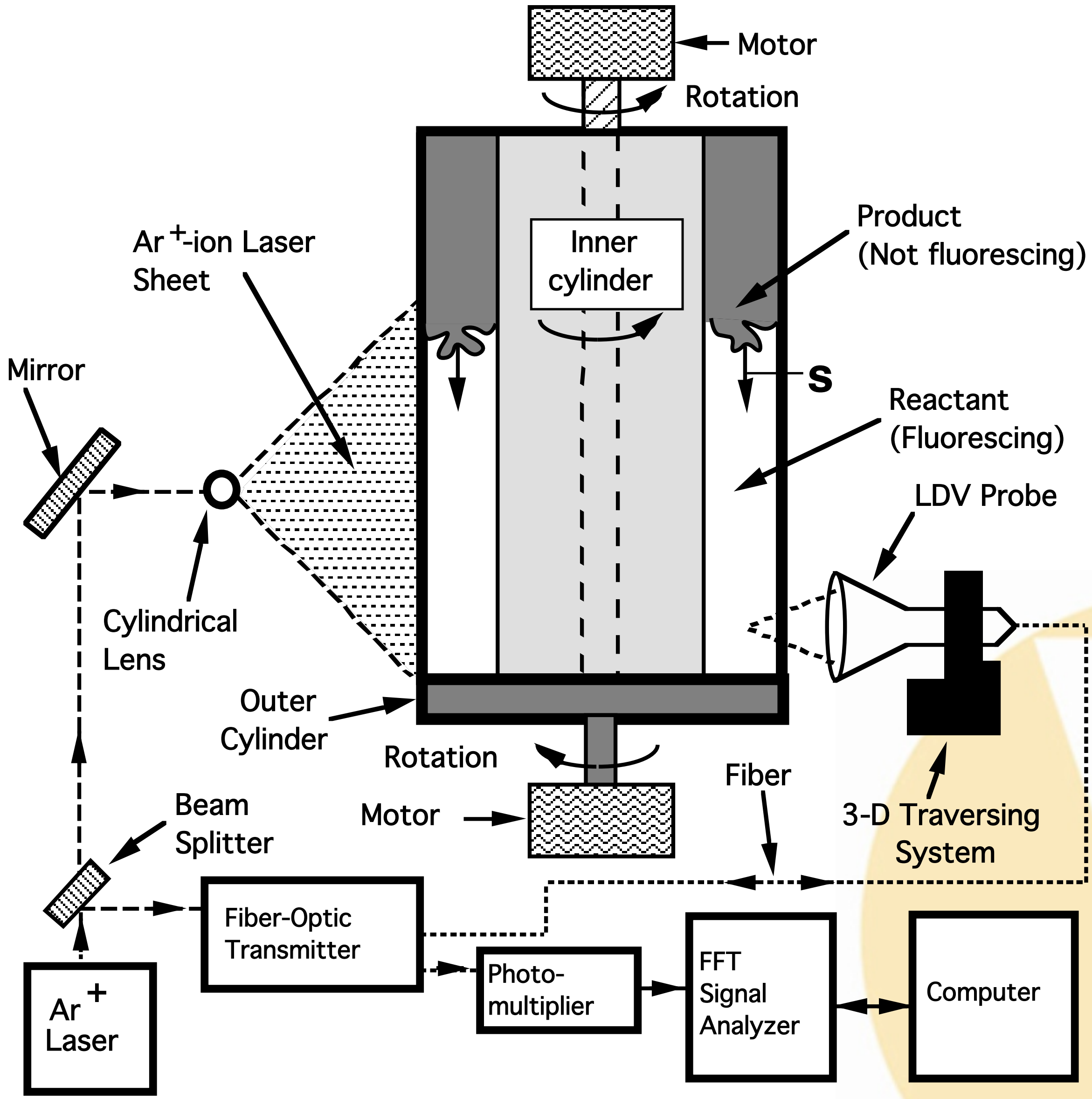
- **Use propagating acidity fronts in aqueous solution**
- **Generic form**

  A + nB → (n+1)B - *autocatalytic*
- **$\Delta\rho/\rho \ll 1$ - no self-generated turbulence**
- **Aqueous fronts not affected by heat loss!!!**
- **Results**
  - **S_T/S_L in <u>4 different flows</u> consistent with Yakhot model**

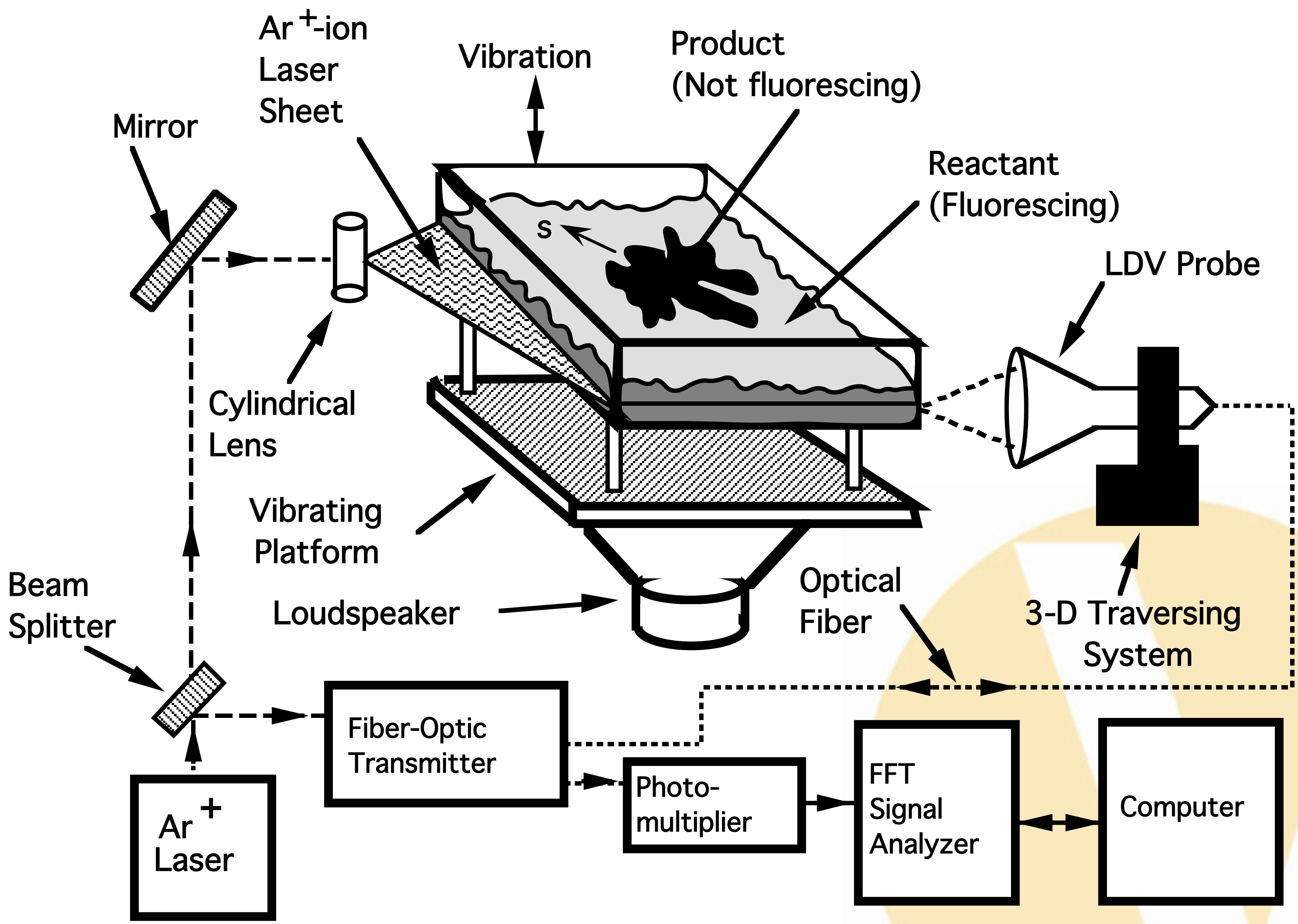
$$\frac{S_T}{S_L} = \exp\left(\frac{\left(u'/S_L\right)^2}{\left(S_T/S_L\right)^2}\right)$$

  - **No quenching observed, even at non-dimensional turbulence levels 1000x greater than that required to extinguish gaseous flames**

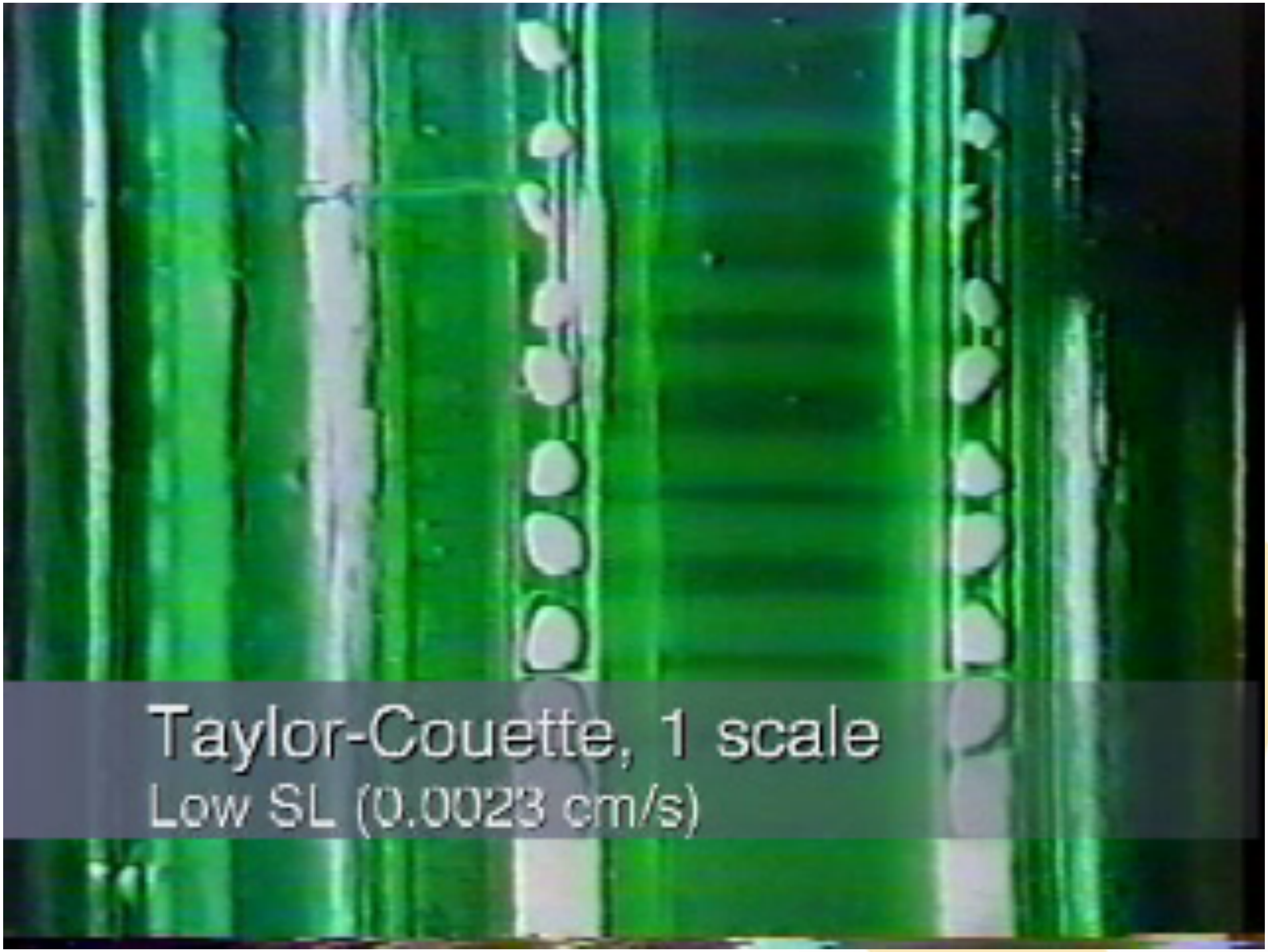
Taylor-Couette apparatus



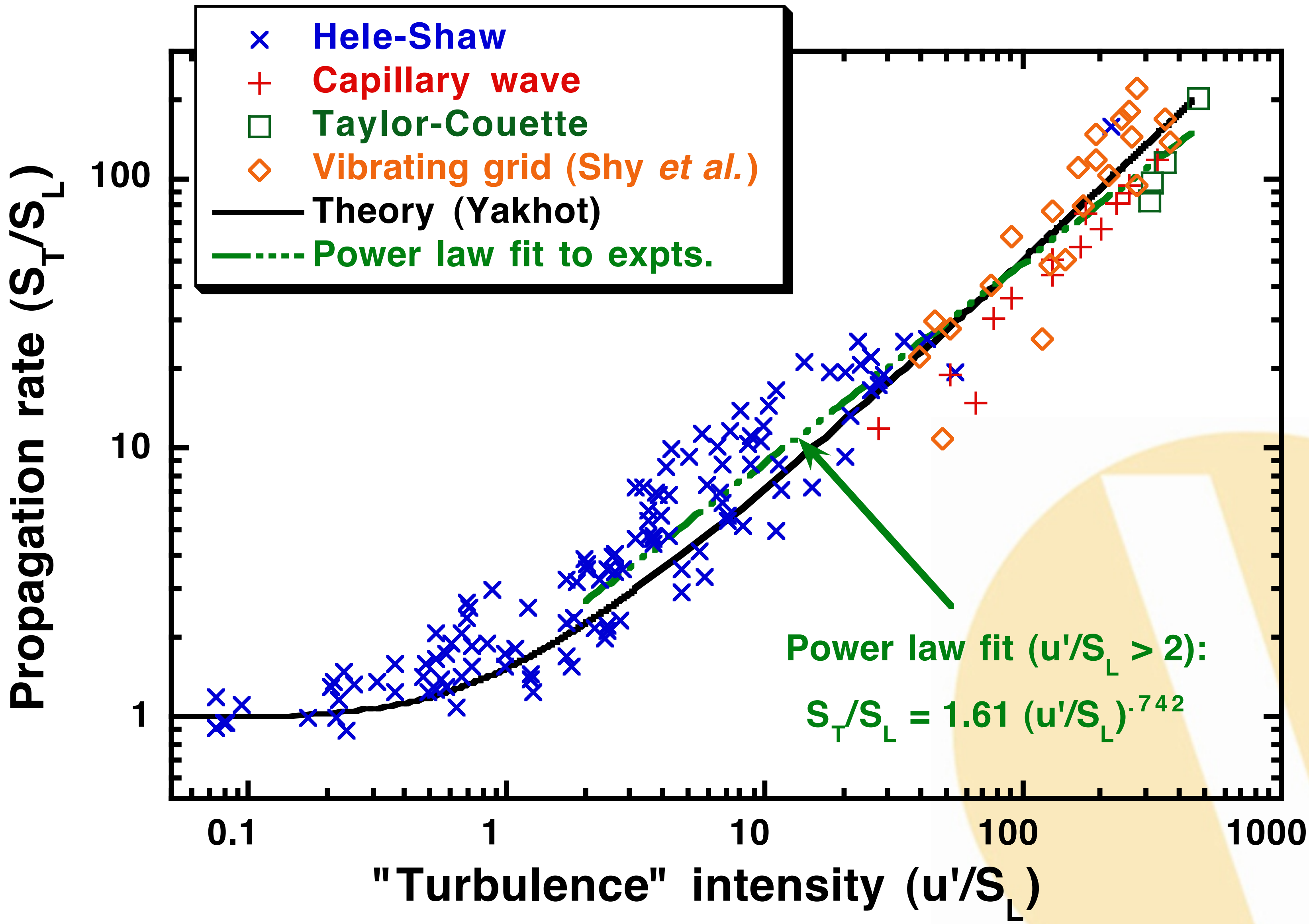
Capillary-wave apparatus



Results - liquid flames



Liquid flames - comparison to Yahkot (1988)



PDR's contrarianism #2

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- Concurrent-flow flame spread (2000)
- Models predict inherently unsteady spread due to continually growing flame length

Fuel Type	Buoyant convection	Forced convection
Thermally thin	$S_{f,con} \sim t^3$, $L \sim t^4$	$S_{f,con} \sim t^1$, $L \sim t^2$
Thermally thick	$S_{f,con} \sim t^1$, $L \sim t^2$	$S_{f,con} \sim t^0$, $L \sim t^1$

- Unlikely that the flame length (L) can grow indefinitely due to heat and momentum losses!
- Hypotheses
  - For narrow beds, flame length grows until boundary-layer thickness ≈ sample width, where transverse heat and momentum losses will limit flame length and spread rate
  - For wide fuel beds, radiative losses from the fuel bed limit spread rate when radiative loss = heat generation rate
- Enormous amount of data explained by these hypotheses

PDR's contrarianism #2

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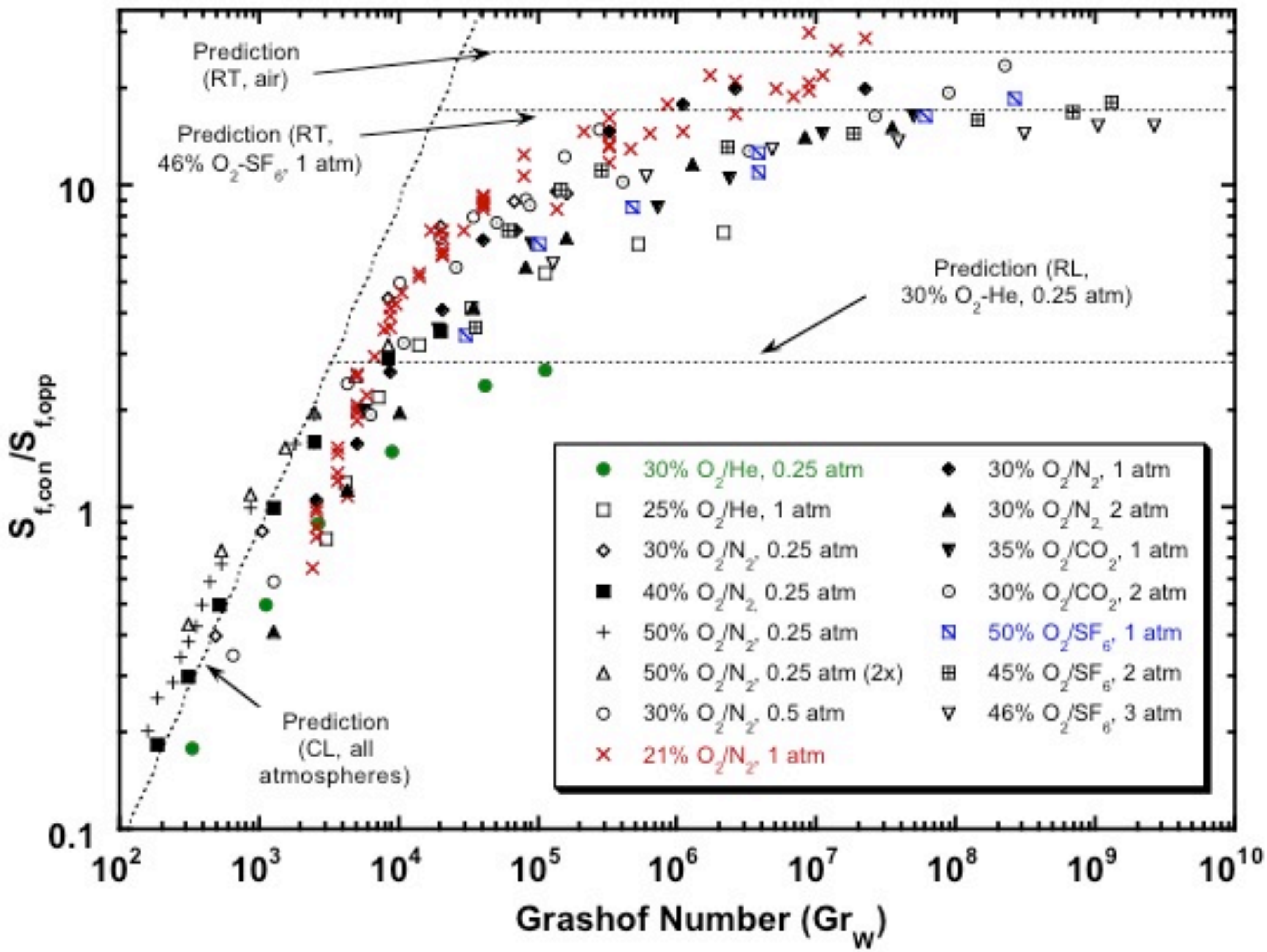

Model - Regimes

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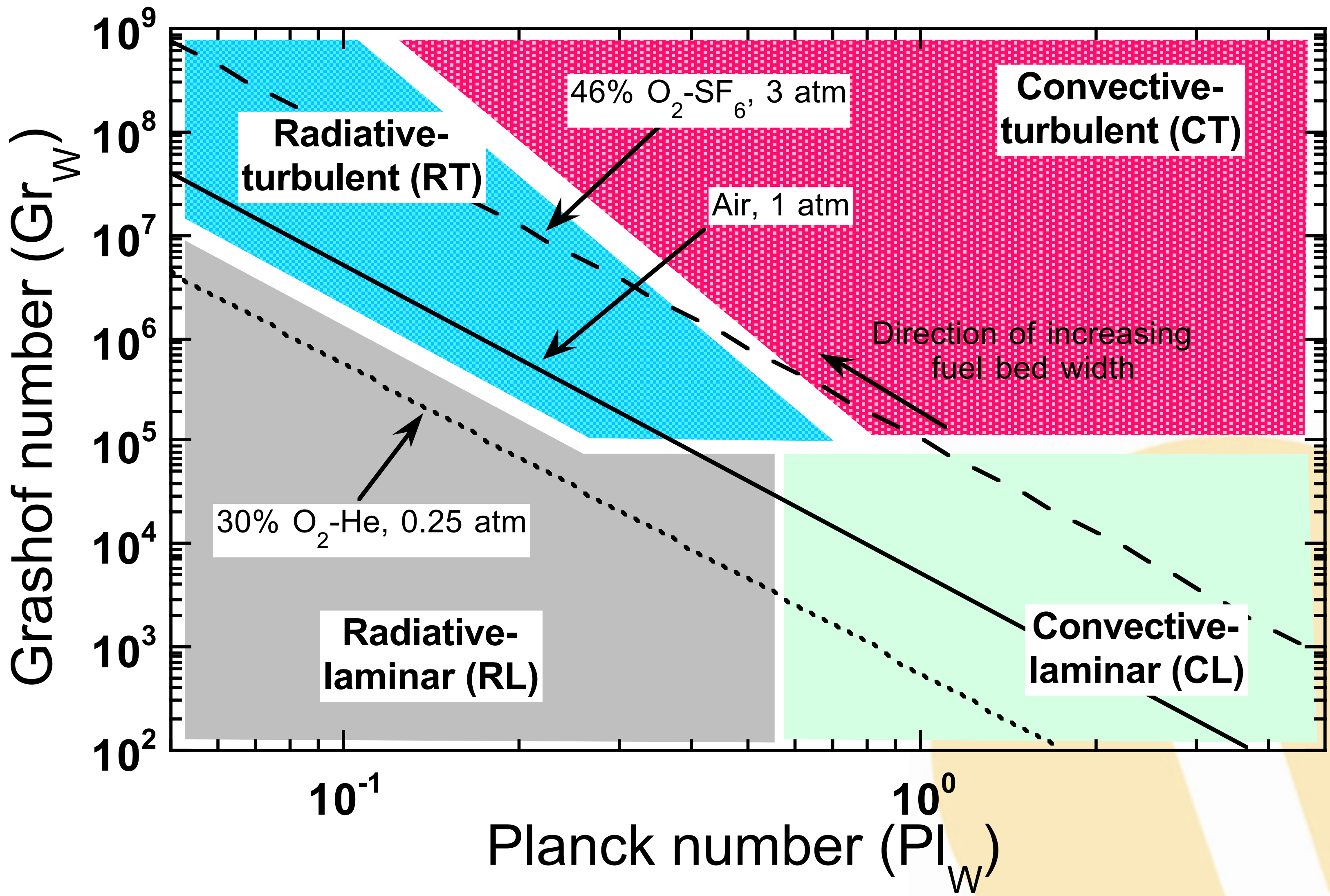

PDR's contrarianism #3

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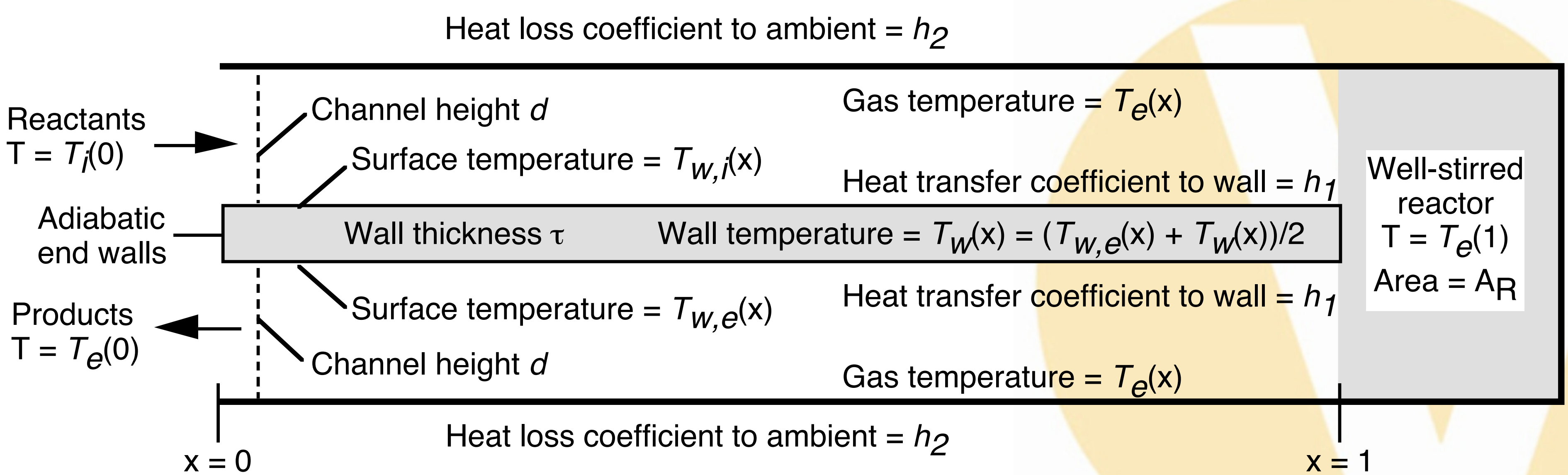
- Simple model of heat-recirculating combustors (2002)
- Existing models of extinction showed no low-velocity limit whereas these limits ALWAYS occurred in experiments
- Initially for my own understanding, developed simple model including
  - (1) heat transfer
  - (2) chemical reaction in well-stirred reactor
  - (3) heat loss to ambient
  - (4) streamwise thermal conduction along wall



Effect of wall thermal conduction

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- Reduces to a single 4th order ODE + 1 nonlinear algebraic equation

$$\frac{M^2}{BH(1+H)}\frac{d^4\tilde{T}_w}{d\tilde{x}^4} - \left[\frac{M^2}{H(1+H)} + \frac{1+H}{BH}\right]\frac{d^2\tilde{T}_w}{d\tilde{x}^2} + \tilde{T}_w = 1 \quad M = Da\left(\frac{\Delta\tilde{T}}{\tilde{T}_e(1) - \tilde{T}_i(1)} - 1\right)\exp\left(-\frac{\beta}{\tilde{T}_e(1)}\right)$$

- Manuscript initially rejected: "too simple… like a student's exercise"
- Eventually published (P. D. Ronney, Combustion & Flame 135 (2003) 421–439) (2nd most cited paper (out of >8000) in any combustion journal with same or later publication date) – why?
  - "Hot topic" – Micropower generation
  - Simple, easily understood message – heat conduction along the wall critical to extinction at low velocity
  - Supported by experiments and later computations

Effect of wall thermal conduction

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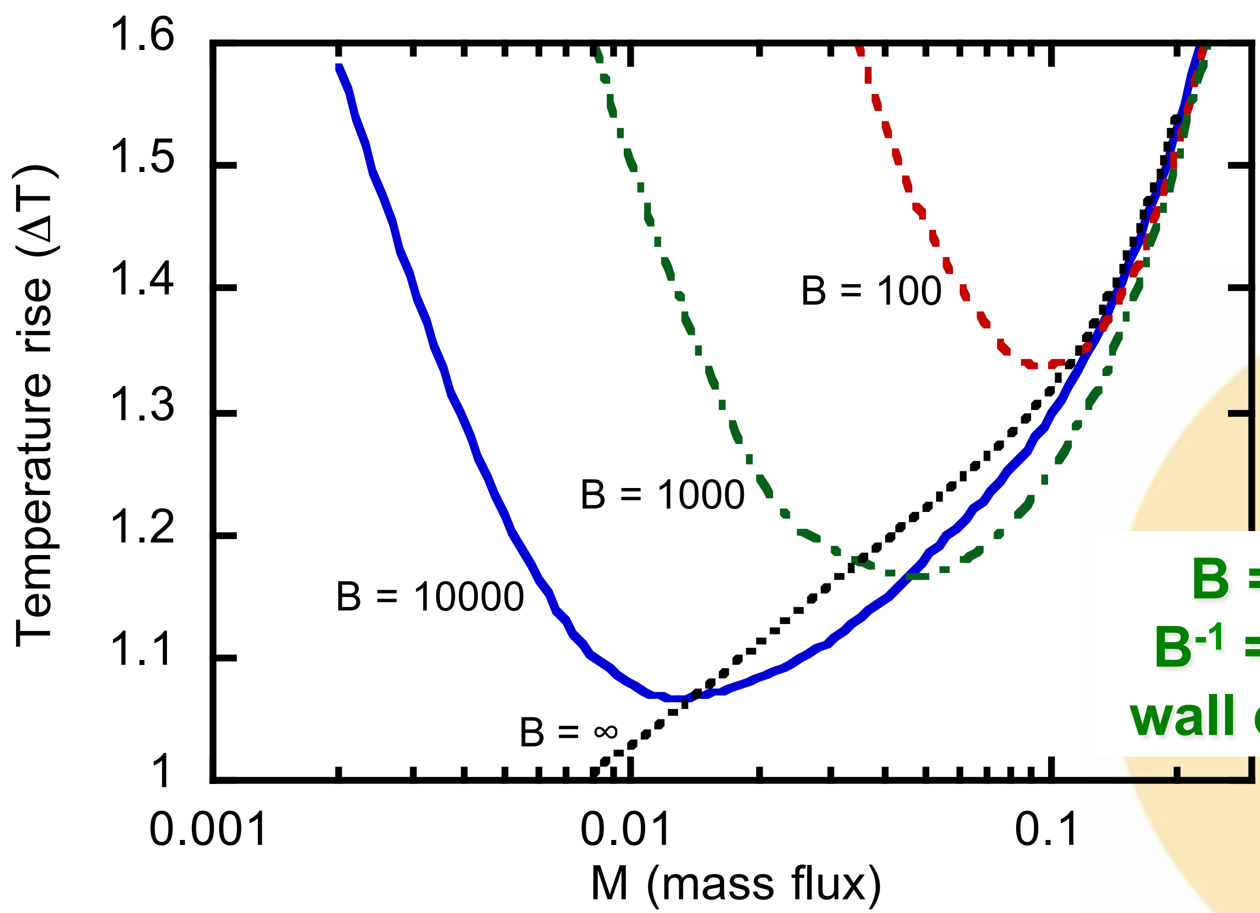
- **Low-velocity limit requires heat loss (H > 0) <u>and</u> wall heat conduction (B < ∞) - counterintuitive: lower k is better - heat transfer across wall is easy, need to minimize streamwise conduction**
- **Suggests the use of plastic combustors (very low k) for better performance – confirmed by experiments**



B = Biot number;
B^{-1} = dimensionless wall conduction effect

Conclusions

- Common traits of serendipity
  - Researchers were looking for something unrelated to the actual discovery
  - Chance favors the prepared mind
  - Focused and perhaps obsessed with discovery and creation
  - Not one-hit wonders, most had very prolific careers (e.g. Percy Spencer had over 300 patents)
  - Not just young upstarts, average age of examples = 39
- Recommendations
  - Look at what everyone else is doing… and do something else (maybe "orthogonalism" not "contrarianism")
  - Turn the knobs as far to the left and right as you (safely!) can
  - Pursue odd results more than expected ones
  - Do not implicitly trust current wisdom and understanding – "trust but verify"
  - Stand up for what you still believe after careful and self-critical deliberation

Conclusions