Panel on:
Practical Applications of Combustion Kinetics

Premise

Combustion kinetics provides a basis for computing ignition phenomena, pollutant formation, flame behavior, etc., and can be useful to industry for product design and modifications

Topics for discussion

What are the gaps between fundamental studies/detailed mechanisms vs. practical applications?

What level of detail is required?

Are detailed mechanisms acceptable? If not, how much reduction is desired?

What computational costs are acceptable?

Examples of recent successes?

What are the future directions/needs?

Can we work around proprietary concerns?

Panel Members
Both Industry and Academia Represented

Industry

Jenny Larfeldt
Siemens

Howard Levinsky
DNV GL Oil and Gas

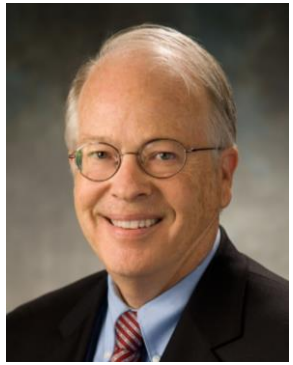
Gautam Khalghatgi
Saudi Aramco, ret.

Academia

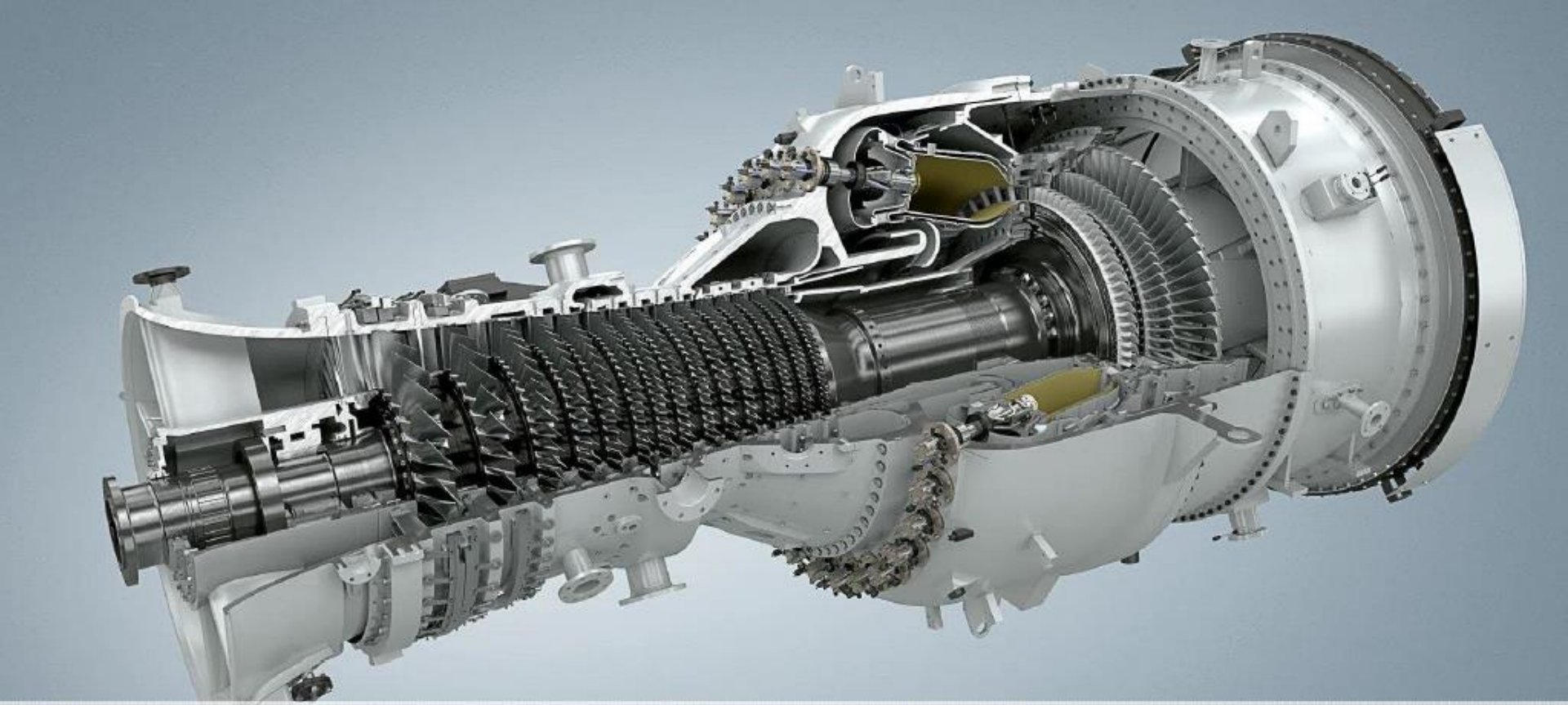
Jim Driscoll
Univ. of Michigan

Fred Dryer, Princeton
Univ. of South Carolina

Moderator



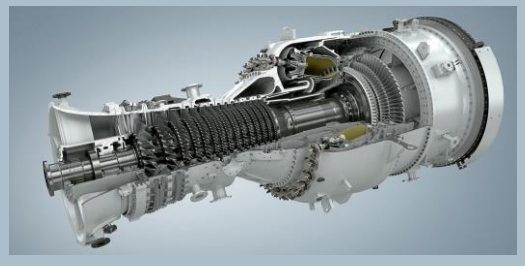
Med Colket,
United Technologies, ret



Dublin, 2nd of August 2018

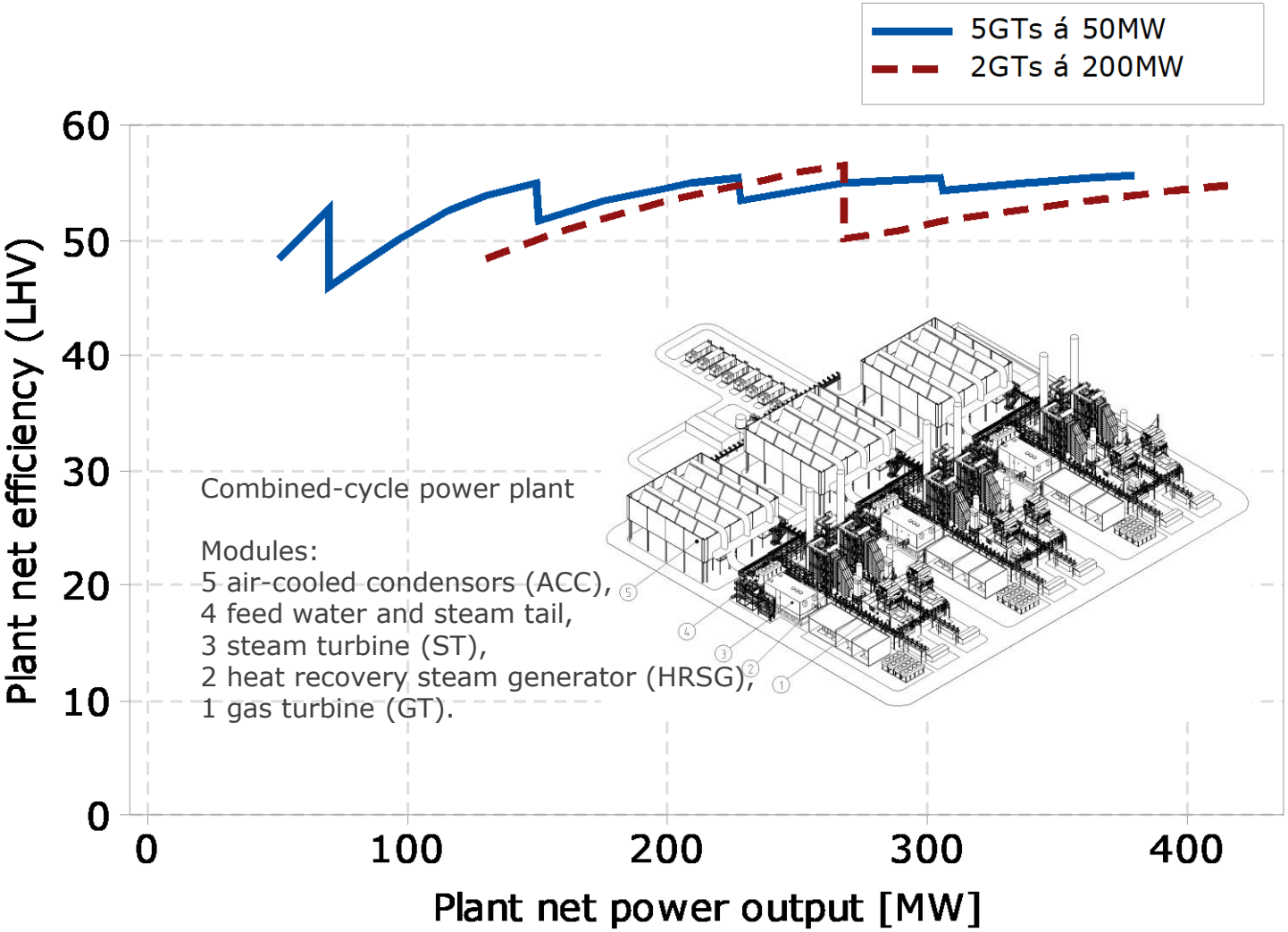
Jenny Larfeldt

Industrial Gas Turbines



SIEMENS

Jenny Larfeldt



Gas turbines can:

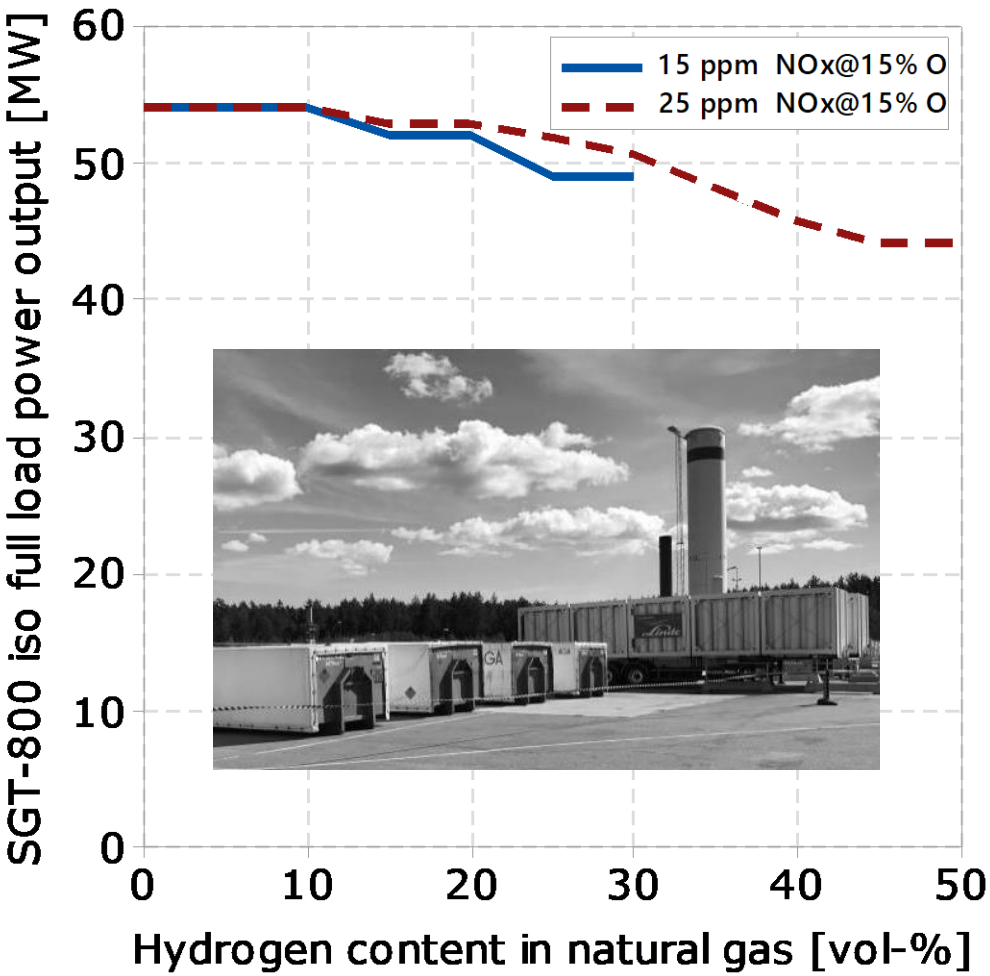
Balance fluctuating renewable energy sources

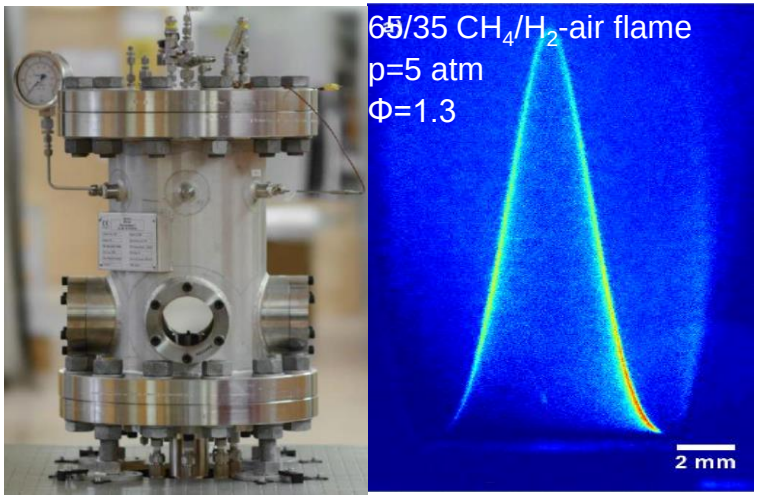
Generate both power and heat/steam

Be co-fired/fired with green fuels

Hydrogen co-firing in industrial gas turbines

Jenny Larfeldt





"Experimental and modeling study of hydrogen-methane combustion in premixed laminar flames"

Adding 80vol-% H2 in NG at 1 bar = moving from 1 bar to high pressure conditions.

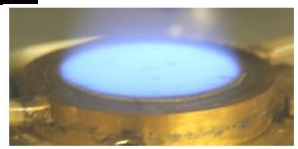
Adding H2 at high pressure conditions is less pronounced due to a change in reaction pathways…

WIPP -> Brackmann, Gao, Abou-Taouk, Kim, Nilsson, Li, Larfeldt, Aldén

Future needs and challenges for gaseous fuels combustion kinetics related to industrial gas turbines

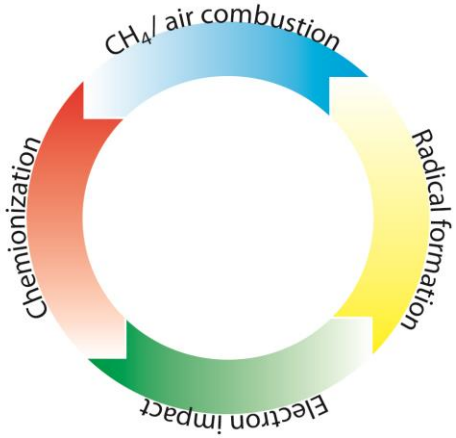
SIEMENS

Jenny Larfeldt



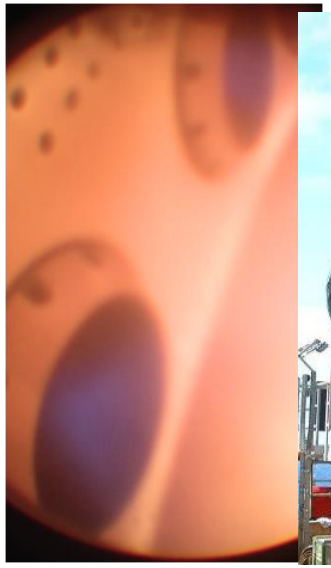
Chemical kinetics of mixtures of "green" fuels (H2, NH3, methanol) and CH4, CO, CO2, N2, C2-4 at gas turbine relevant conditions (20-40 bar pressure and lean conditions with air preheat 350-500 °C)

Chemical kinetics of electrically stimulated flames including influence from chemionization and the electron impact.



Skeletal Methane–Air Reaction Mechanism for Large Eddy Simulation of Turbulent Microwave-Assisted Combustion
Larsson, Zettervall, Hurtig, Nilsson, Ehn, Petersson, Alden, Larfeldt, Fureby. *Energy Fuels*, **2017**

Reduced chemical kinetics enabling simulations of:
- gas turbine burner retrofit designs (FB and LBO).
- flame position -> better combustor heat load and emissions formation comparisons.



DNV·GL

OIL & GAS

Combustion kinetics of gaseous fuels

The devil is in the details

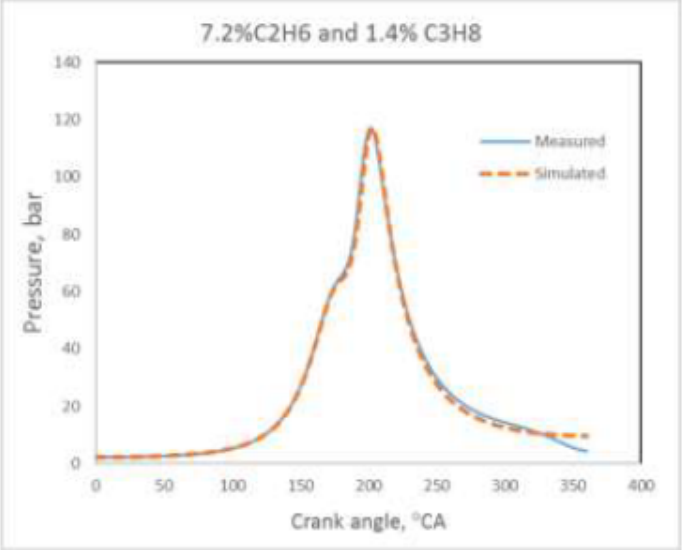
Howard Levinsky

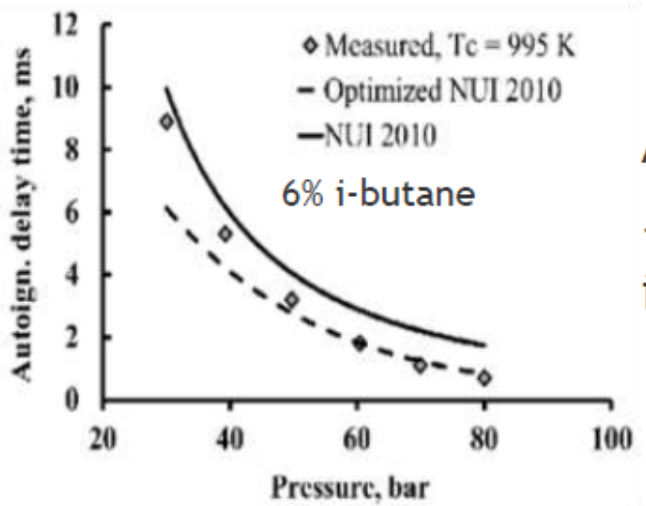
How do we use kinetics?

- DNV GL (our group):
  - develops, and supports development, of combustion equipment for gaseous fuels (natural gas, hydrogen, syngas, biogas…and their mixtures)
  - Analyzes the impact of changing fuel composition on performance of combustion equipment
- Clients: OEMs, fuel suppliers, governments
- Use and develop numerical tools to analyze underlying combustion phenomena responsible for equipment behavior; emphasis on changing fuel composition
  - Flame stability (flashback/lift) → burning velocities
  - Engine knock → burning velocities and autoignition delay times
  - Pollutant formation → kinetics/mechanism of formation
- Successes:
  - Stability: lift of biogases, flashback for hydrogen addition to natural gas (in government regulations); de Vries, et al., Appl. Energy 2017
  - *Engine knock: new method to characterize impact of fuel composition; Gersen, et al., SAE 2016*

Impact fuel composition on engine knock

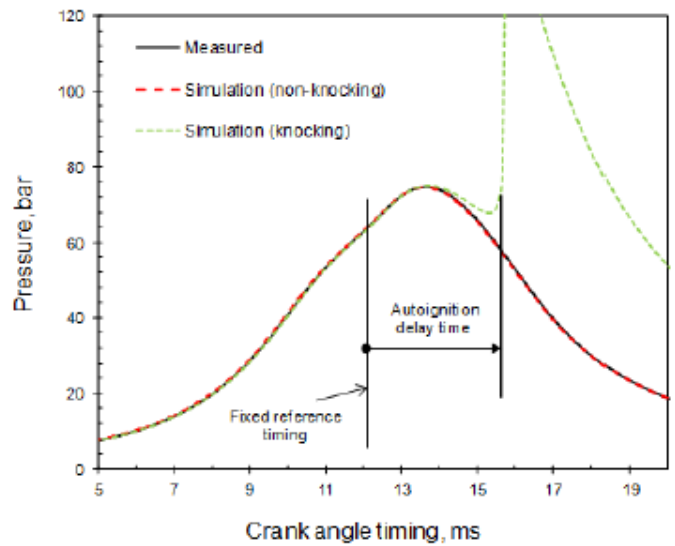
- Analysis couples 2 modules:
  - 1-D burning velocity (laminar) for phasing
  - O-D for occurrence of autoignition
  - Put autoignition chemistry in P/T history to get knock
- Must get P/T history right → USC Mech
- Must also get autoignition right → NUIG (adapted to RCM data at 80 bar)





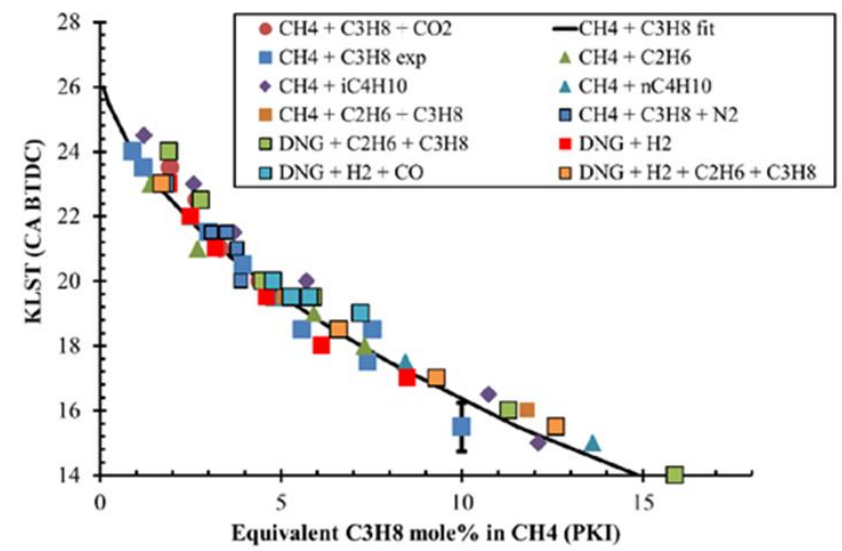
Adapted ~20 rxns

- C2, C3, C4, C5, H2 in C1 mechanism

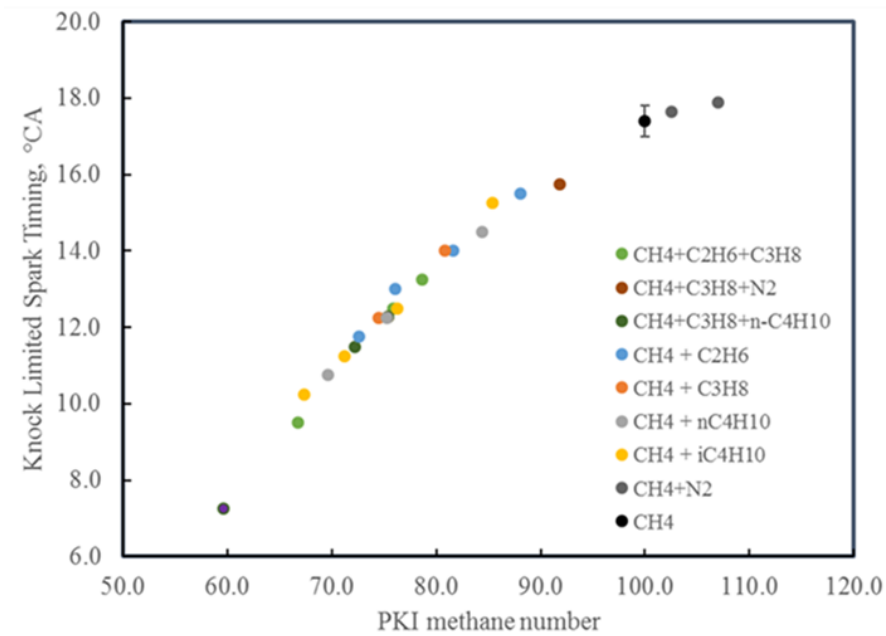


Impact fuel composition on engine knock

- After many steps, put results on a propane scale, similar to octane number
- Compare predictions of knock with measurements (knock limited spark timing) on engines for which we have the phasing…



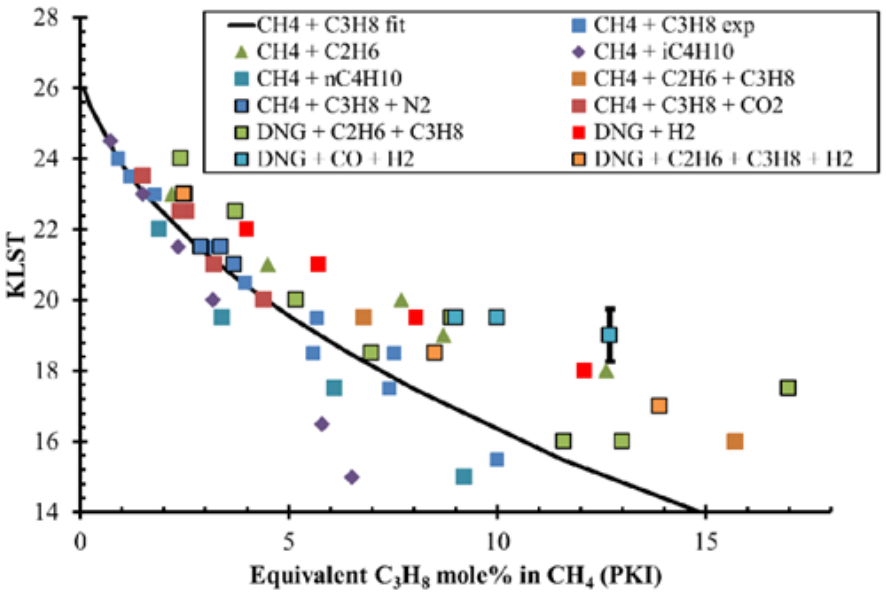
Lean burn

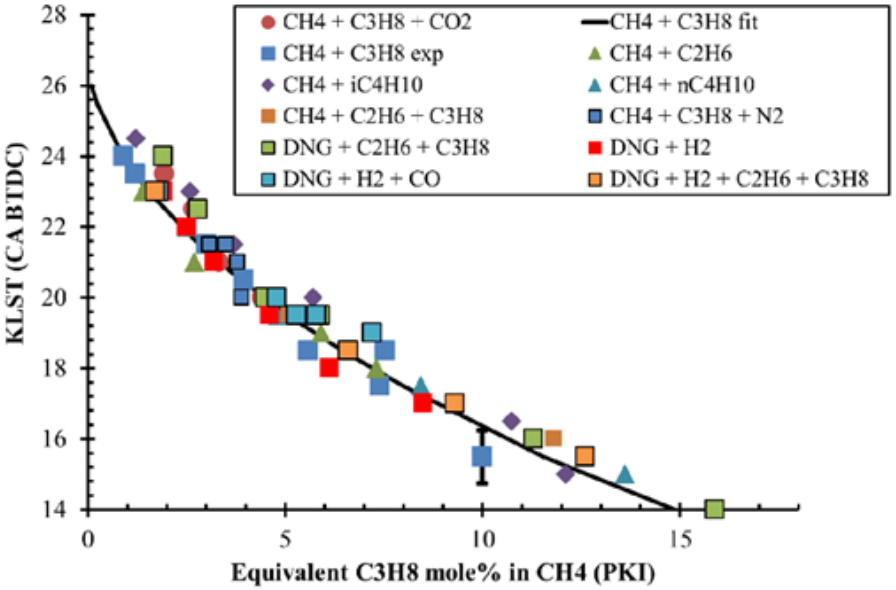


stoichiometric

- *Ultimate tool is result of thousands of simulations of phasing and autoignition*

The main point





40% difference with RCM measurements at 75 bar

15% difference with RCM measurements at 75 bar

Engine can ‘see’ the difference!

Conclusions and research needs

- *Simulation of practical equipment can see the accuracy of kinetic models*
- Needs for engine analysis of gaseous fuels:
  - Accurate ignition data under engine conditions (T/P) for:
    - *Isomers* of C_6^+ (particularly low fractions in methane, well-head gas), trace N- and S-containing compounds (biogas), odd species in methane carrier (DME?)
  - Burning velocities for odd species in a methane carrier
- Reduction?
  - Need thousands of accurate simulations
  - Reduced mechanism is fine, only if it is as accurate across the full range of conditions (15%) compared with measurements
  - Question: who says accuracy of a more complex physical model (e.g., turbulent) with reduced chemistry is better than a simpler model with detailed chemistry?
- **'Druthers': At present, I druther have an accurate detailed chemical mechanism**

Combustion kinetics of gaseous fuels

Howard Levinsky

Howard.levinsky@dnvgl.com

+31 6 155 103 72

www.dnvgl.com

SAFER, SMARTER, GREENER

Practical applications of chemical kinetics in SI engines

Gautam Kalghatgi

- Kalghatgi, G.T. 2015 " Auto-ignition quality of practical fuels and implications for fuel requirements of future SI and HCCI engines", SAE 2005-01-0239
- Gautam Kalghatgi, 2018 "Knock onset, knock intensity, superknock and preignition in SI engines" International J of Engine Research, Vol. 19(1): 7–20)
- Kalghatgi, G.T., Babiker, H. and Badra, J.,2015 "A simple method to predict knock using toluene, iso-octane, n-heptane blends (TPRF) as gasoline surrogates", SAE 2015-01-0757, SAE Int. J. Engines 8(2):505-519
- Kalghatgi, G.T. and Bradley, D., "Pre-ignition and super-knock in turbo-charged spark ignition (SI) engines", International Journal of Engine Research 2012 13: 399
- Kalghatgi, G.T., Algunaibet, I. and Morganti, K. " On knock Intensity and Superknock in SI Engines", SAE Int. J. Engines; 10(3):SAE 2017-01-0689
- Gautam Kalghatgi, Kai Morganti and Ibrahim Algunaibet. "Some insights on the stochastic nature of knock and the evolution of hot spots in the end-gas during the engine cycle from experimental measurements of knock onset and knock intensity", SAE 2017-01-2233

Knock in SI engines- stochastic phenomenon

Primary operating principle in SI engines is to avoid knock which limits engine efficiency and is caused by autoignition in the end-gas

- Though fuel/air are fully premixed, end-gas is not homogeneous because of turbulent mixing of hot gases with cold charge
- Autoignition occurs in hot spots
- Combustion and knock are marked by cycle-to-cycle variations and are stochastic phenomena
- Most knock studies focus on onset of knock which is triggered by autoignition in a hot spot
- Knock intensity is determined by the evolution of the pressure wave set off by knock onset

Assumptions are necessary and can be reasonably made to get practically useful results

Ignition delay and the Livengood - Wu integral

- Ignition delay (ID) as a function of pressure and temperature – to be generated from chemical kinetic calculations
- Pressure in the end-gas measured or modelled but flame development is stochastic!
- Temperature in the hot spot develops stochastically but needs to be estimated!
- Then Livengood-Wu integral can be estimated

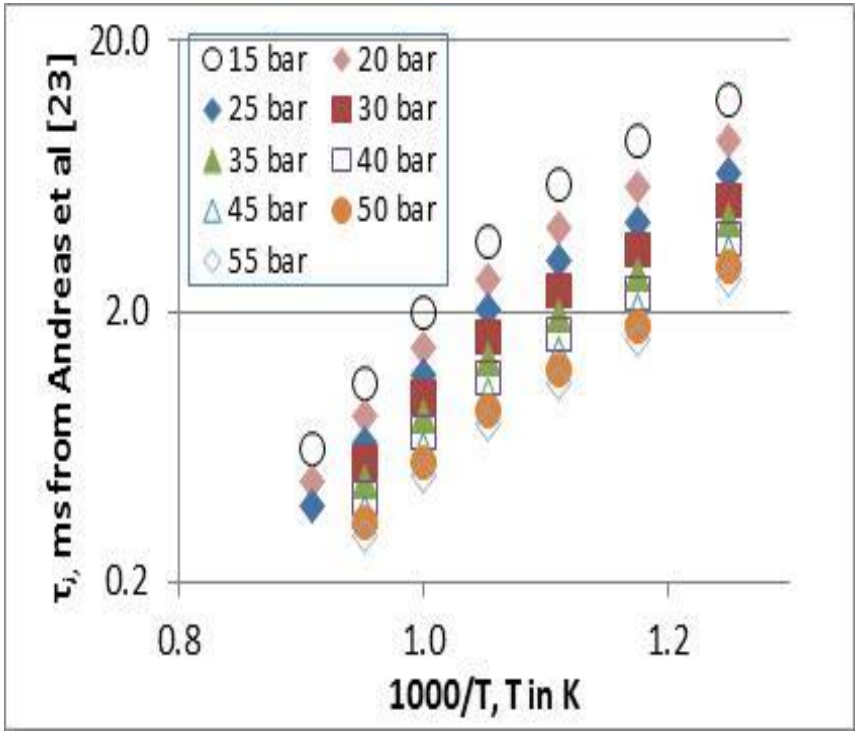
$$I = \int (1/\tau).dt = 1$$

Surrogate fuel for gasoline but which surrogate?

– A Toluene/PRF mixture of the same RON and MON

- Use the method, based on extensive experiments, from e.g,. SAE 2015-01- 0757 to fix the composition of surrogate
- Use a chemical kinetic model to calculate ID for different pressures and temperatures for a fixed surrogate

Further simplifications



IDs for one gasoline surrogate 95/86

- We can ignore large IDs
- At 1500 RPM, 15 ms is 135 crank angle degrees (CAD)
- 1 CAD step contributes little (1/135) to Livengood-Wu integral
- Simpler equation - $\tau_i = Aexp(\frac{B}{T})P^{-n}$
- From kinetic calculations for different surrogates of different RON and MON, A, B and n as functions of RON and MON

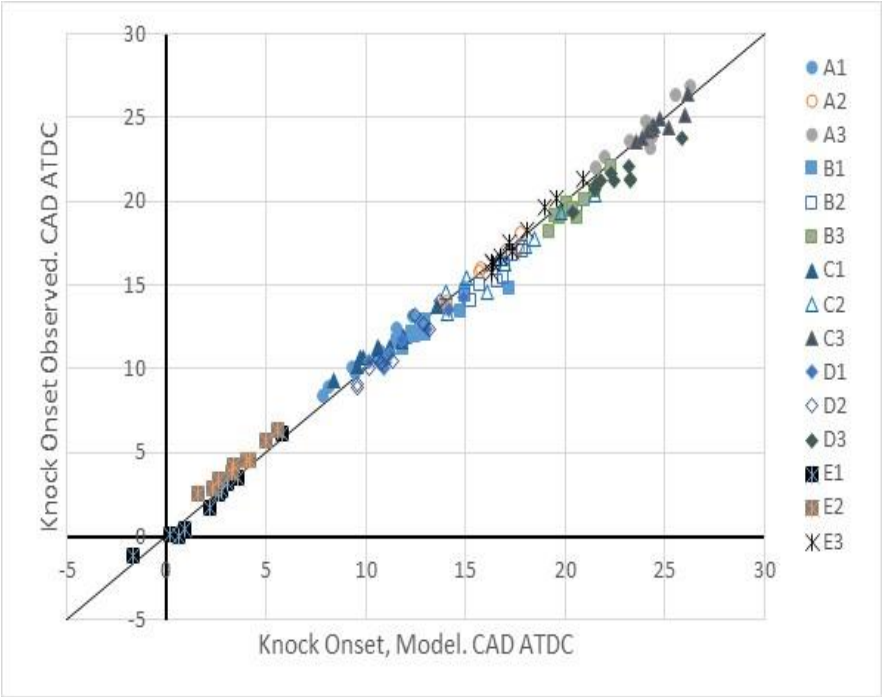
Gautam Khalghatgi

Experimental Validation

- Use measured pressures on each cycle

Temperature Estimation in the hot spot

- Estimate bulk gas temperature, T_{comp15}, from P=nRT, at 15 bar
- Assume hot spot temperature at 15 bar to be ($T_{comp15}+\Delta T$)
- At any other pressure, P, T assuming adiabatic compression
- Predict knock onset angle from Livengood-Wu integral and compare with experimental observation



150 cycles- 5 fuels, 3 operating Conditions

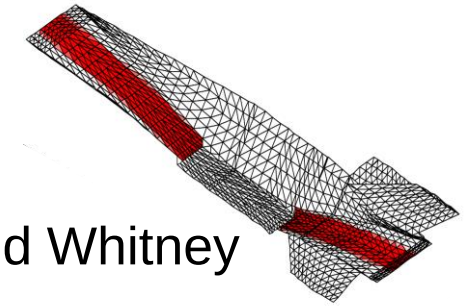
- Once the model is validated for your engine/fuel, it can be used for other variations

Of course you don't know how accurate your ID model or your temperature estimation are! But the combination can be good enough with suitable assumptions

- Practical problem of superknock should only be described in probabilistic terms but a theoretical framework is useful for understanding

Jim Driscoll Professor of Aerospace Engineering
University of Michigan

Some new challenges - identified by industry



1. **Hypersonics** - Boeing, Kevin Bowcutt, Pratt and Whitney

chemistry of JP-7 highly preheated
low pressure and high pressure chemistry
0.2 atm – 20 atm **heat transfer** need chemistry
of many gas species

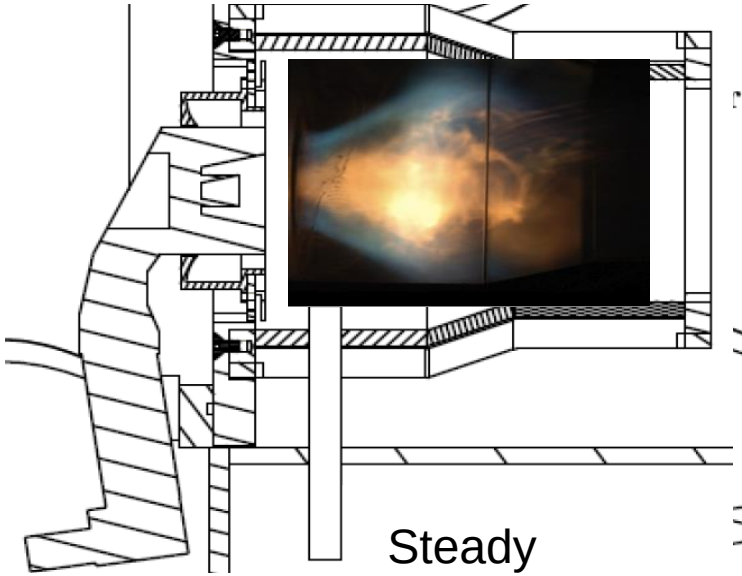
2. **Combustion Instabilities** LPP, flex fuels (GE, Siemens, Pratt)

predictive model of flame stabilization with complex fuels flame-flame interactions: Pilot and Main flames tradeoffs between low NOx and instabilities

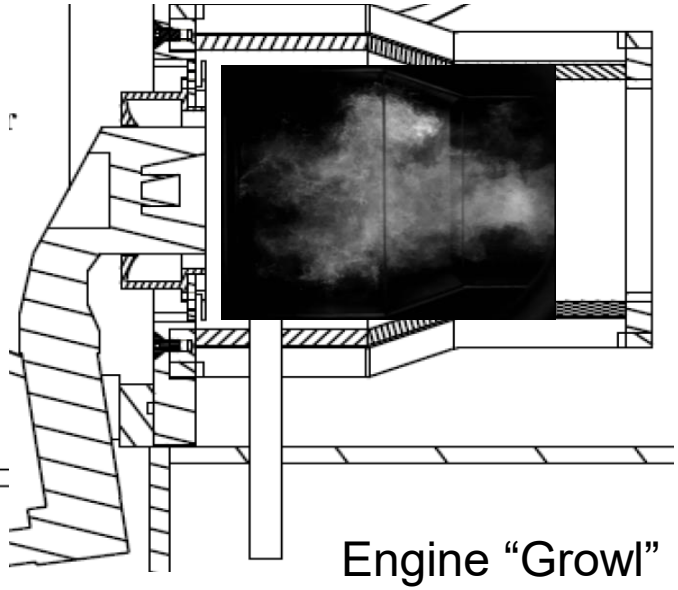
One Example:

U. Michigan project funded by General Electric

Combustor Growl studies - for off-design conditions
of a Lean Premixed Prevaporized (LPP)
Gas Turbine Fuel Injector of Jet-A Fuel Spray



Steady

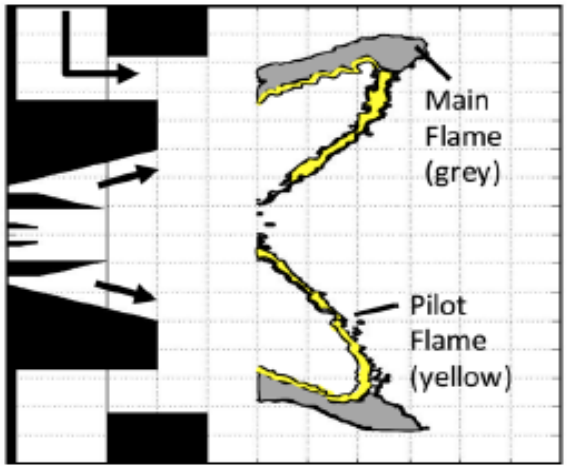


Engine "Growl"

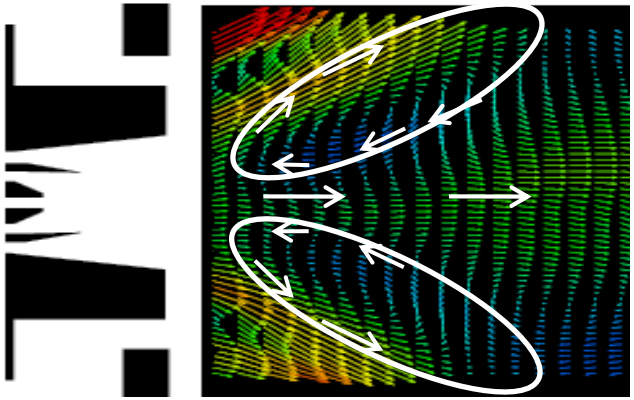
Rayleigh criterion –we must know where flame is located

Jim Driscoll

GE TAPS



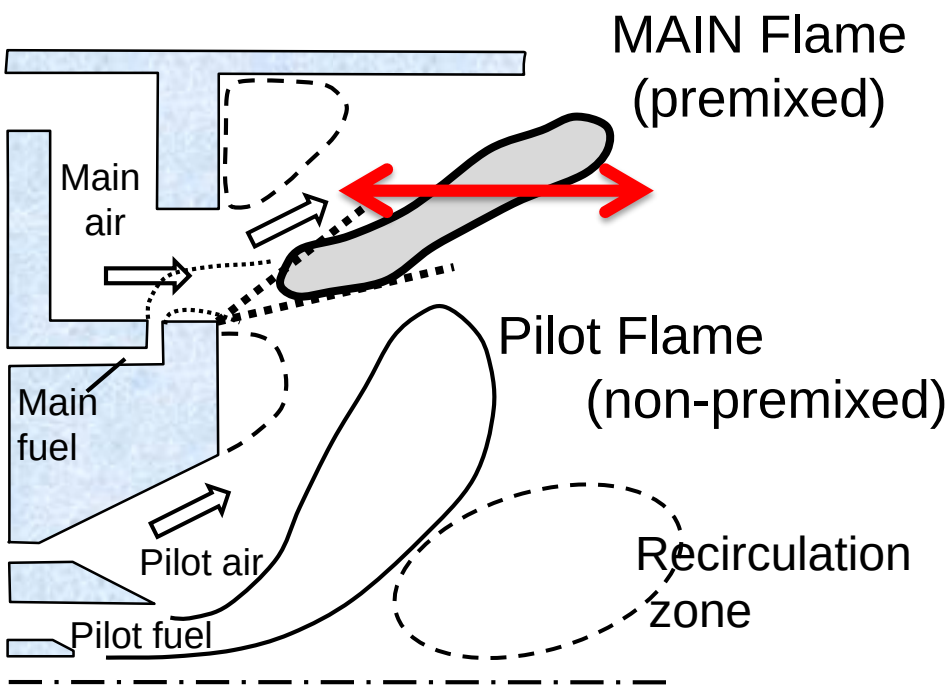
Flame locations – from formaldehyde PLIF gradient



Velocity (PIV)

Lifted premixed flames – low NOx - but not well-anchored

Jim Driscoll



Issues

Proprietary results versus student must publish to get a job !

Industry needs answers now versus student learning curve

Laser diagnostics / advanced CFD only at universities

Industry requires real operating conditions
(liquid fuel, elev. pressure, temp. large mass flows)

Intermittent funding / management changes

Some Remarks on Combustion Kinetics and Real Fuel Applications

Frederick L. Dryer

Professor Emeritus
Mechanical & Aerospace Engineering
Princeton University
Princeton NJ 08544

Distinguished Research Professor
Mechanical Engineering
University of South Carolina
Columbia SC 29208

37th International Symposium on Combustion
Dublin Ireland
28 July – 4 August, 2018

"Sustainable Energy"

Current Fossil Fuel Based Energy Drivers

- ***Public health – Air pollutants – nmHC, CO, NO_x, PM_{10}, SO_x => Ground level O_3, "Smog", PAH, Upper atmospheric ozone layer***
- ***Finiteness of fossil resources (not really)***
- ***Energy Security***
- ***$PM_{2.5}$, Toxics, Carcinogens, "Green House gases"/Particulate Emissions & Climate Change!***

Define a "Sustainable" energy future! Eliminate Fossil Use!

Non-fossil power – photovoltaic, solar thermal, wind, sea, geo-thermal, *nuclear*, etc.

Fuels generated primarily from biomass – net cycle carbon emission reduction Carbon capture/storage=>zero/negative carbon cycle emissions

Hydrogen as the energy carrier – essentially eliminate all but water as an emission

"Solar Fuels" – "fuels" from renewable (or fusion) energy, water, and CO_2 (*from air?*)

Electric vehicles – eliminate liquid-fueled transportation/local emissions (marine/*air?)*

Phase out non-hybrid combustion engine technologies by 2030
Reduce carbon emissions of aircraft sector by 50% from 2005 numbers by 2050
G7 – June 2015: phase out fossil fuels by 2100! (and also mitigate world poverty!)

"Sustainable Energy"

Current Fossil Fuel Based Energy Drivers

- ***Public health – Air pollutants – nmHC, CO, NO_x, PM_{10}, SO_x => Ground level O_3, "Smog", PAH, Upper atmospheric ozone layer***
- ***Finiteness of fossil resources (not really)***
- ***Energy Security***
- ***$PM_{2.5}$, Toxics, Carcinogens, "Green House gases"/Particulate Emissions & Climate Change!***

Define a "Sustainable" energy future!

Non-fossil power – photovoltaic, solar thermal, wind, sea, geo-thermal, *nuclear*, etc.

Fuels generated primarily from biomass – net cycle carbon emission reduction Carbon capture/storage=>zero/negative carbon cycle emissions

Hydrogen as the energy carrier – essentially eliminate all but water as an emission

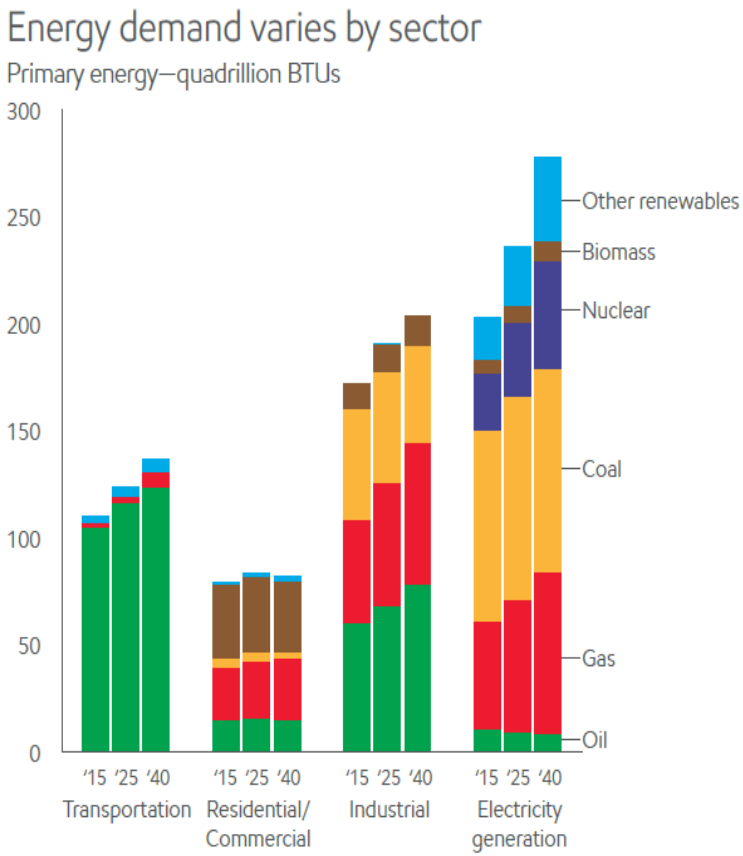
"Solar Fuels" – "fuels" from renewable (or fusion) energy, water, and CO_2 (*from air?*)

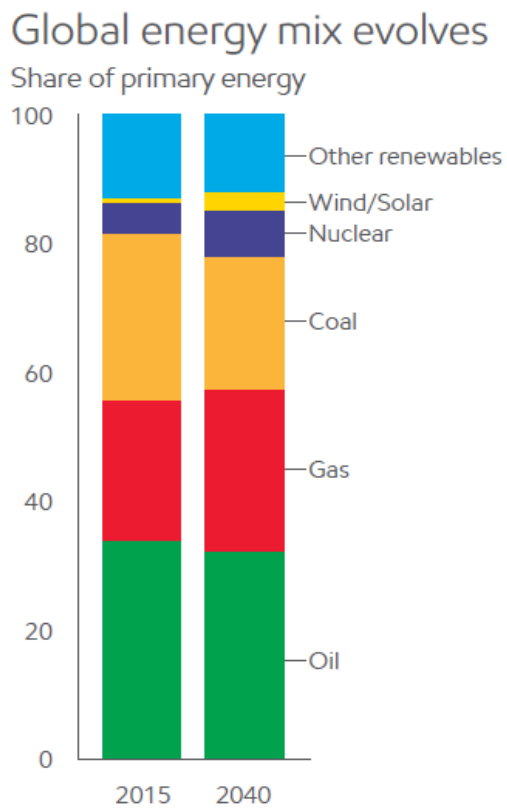
Electric vehicles – eliminate liquid-fueled transportation/local emissions (marine/*air?)*

Fundamental science discoveries will be important in developing the technical road maps for and ultimate long term impacts of each of these ideas.

But in the near-term (next several decades), integrated sustainable technologies and optimized utilization of fossil energy and combustion are central to supplying global energy needs and reducing carbon emissions!

Global Energy Projections through 2040





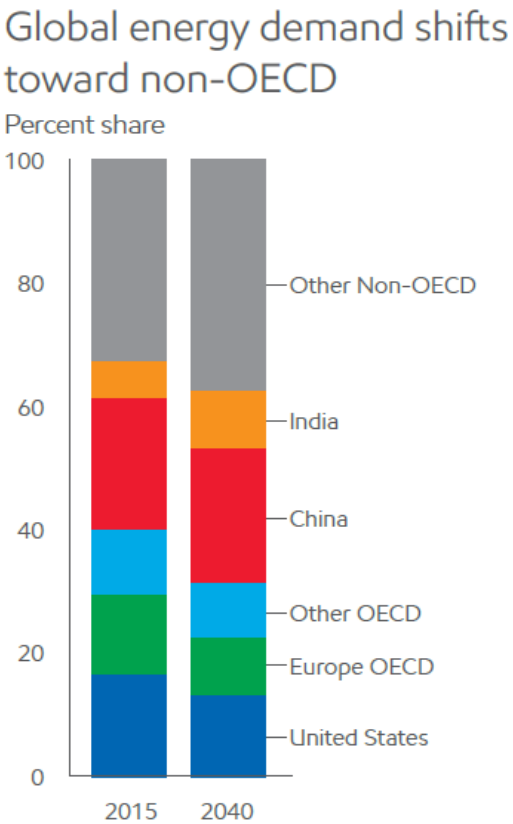


Chart Data from 2017 ExxonMobil Energy Outlook

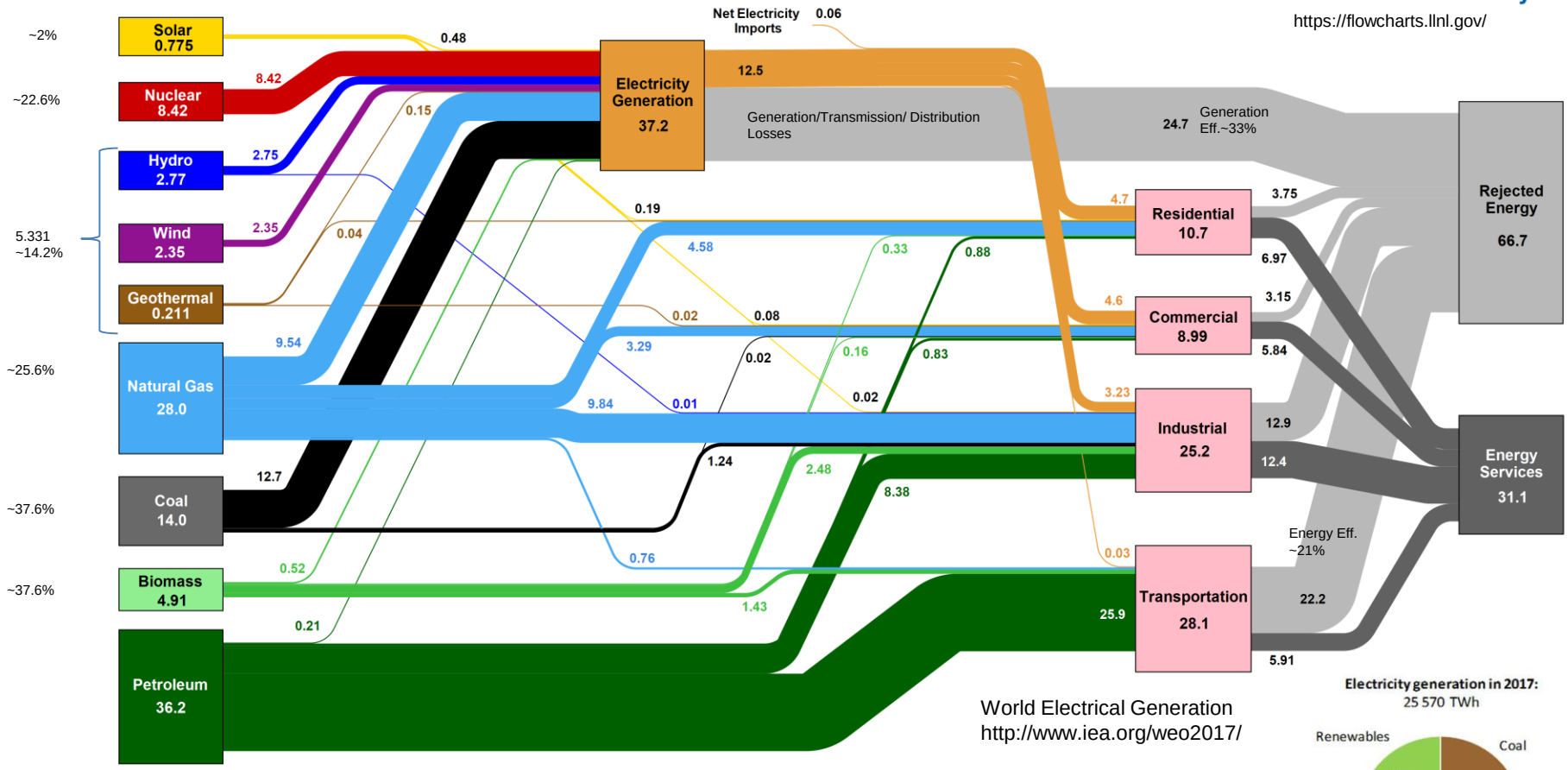
My Opinions -

- **There is little likelihood of severely limiting fossil energy use over this century**
- **Natural gas/petroleum will continue to be a major player in the power and transportation sectors**
- **Every possible means to augment fossil energy use will be needed to raise global living standards**
- **Carbon capture, recycling/storage technologies are going to be essential to our future**

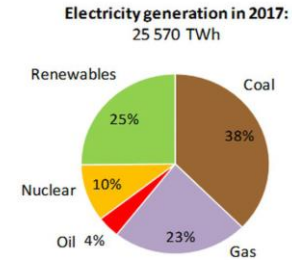
Estimated U.S. Energy Consumption in 2017: 97.7 Quads

Lawrence Livermore National Laboratory

https://flowcharts.llnl.gov/



World Electrical Generation
http://www.iea.org/weo2017/



1Quad = 1.055 Joules 10^{18}J

Overall
EU (2016) ~44% Fossil, ~25% Nuclear, ~28% Renewable, ~3% Solar
US (2017) ~75.8% Fossil, ~8.6 Nuclear, ~10.8% Renewable, ~0.8% Solar

- **Moving significantly toward electrification of ground transportation requires re-distribution in fossil fuel use paradigms from transportation into electrical generation!**
- **Current rejected energy in both power and transportation sectors suggest potential for very large energy efficiency gains yet to be realized=> *potential for large carbon emission reductions!***

Critical Gas Turbine ICE Needs

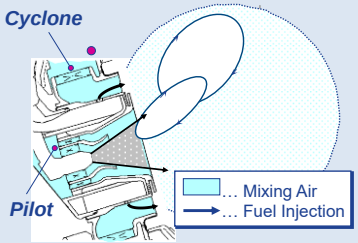
Base load power generation dynamics to accommodate renewables

Fuel Reference Indicators –
No autoignition Indicator, distillation curve, liquid density, Lower Heating Value (LHV), thermal stability, viscosity, freezing point, Smoke point (*SP*),
Composition limits: e.g. sulfur, naphthenes, vanadium, ash components, etc.
Emissions –Particulate NOx , SOx, H_2O Particulates (mass, size)

Aircraft Applications

GE - Lean Premixed/Prevaporized (LPP) aircraft gas turbine designs produce substantial reductions in NOx and particulate emissions at increased efficiency over other current (Rich/Quench/Lean (RQL) combustor designs.

International Fuel Certification essential



Twin Annular Premixing Swirler-stabilized (TAPS) Arrangement

Figure courtesy of H. Mongia

Stationary Power Generation

GE H-Frame natural gas power generation in combined cycle configuration. **62.2% thermal efficiency** in generating 605 megawatts with full power operation in under 30 minutes on natural gas.

28 April 2016, Bouchain Fr

Comparative thermal efficiency for all Rankine Cycle steam power plants: ~<40%

GE H-Frame power generation in combined cycle configuration in Saudi Arabia firing Arabian Super-Light crude oil at 60+% thermal efficiency. Avoids refining losses in producing typical liquid fuels for gas turbine applications.

March 2015, SA

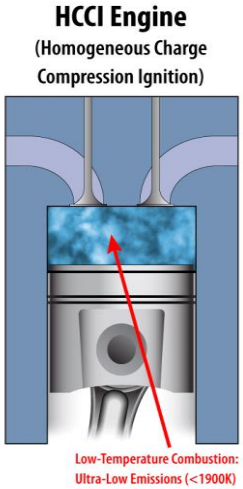
(~ 25% refining energy savings for producing refined turbine fuel)

Overall fuel flexibility is very important! Marine applications?

C_nH_m real fuel & emissions models for multi phase physical chemical coupled combustion systems remain inadequate

RCCI Engine Sensitive to Fuel Properties

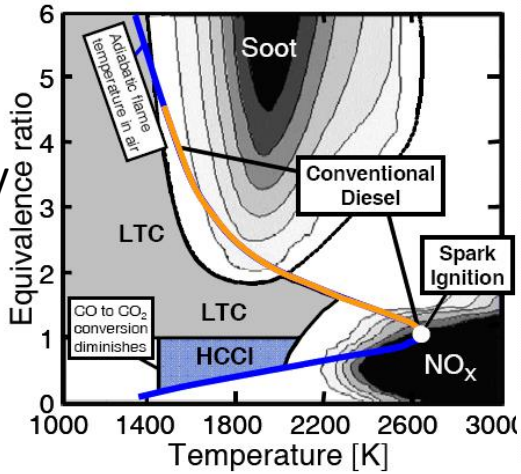
RCCI
Optimize Timing & Heat release rate for HCCI by controlling fuel charge chemical kinetic properties! (currently using "dual fuel" concepts)

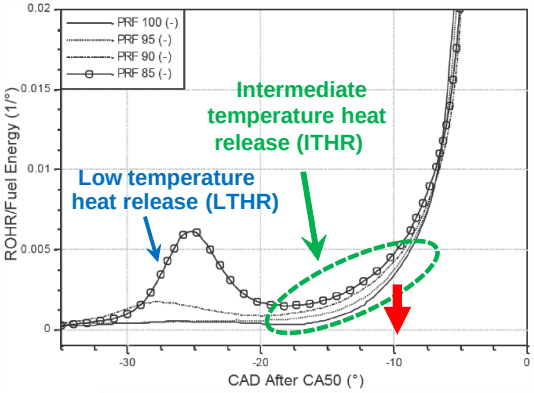


Kinetic Related Issues

- ***Optimized fuel properties?***
- ***Replication of fuel kinetic effects on heat release coupling?***
- ***Low temperature HC/CO oxidation catalysts?***
- ***Single fuel operation by fuel reforming?***
- ***Lubricant LSPI assessments?***
- ***Hybrid integration?***

Because the engine cycle operates at much lower temperatures, it has very low NOx, low particulates, and primarily only HC/CO emissions, **but 20 -30% higher fuel efficiency than other piston engine operating concepts.**
(Values as high as 60⁺% in the lab)





Magnified heat release profiles for various fuels at 1.4 bar intake pressure, ϕ = 0.4, and CA50 = 6 °aTDC.

Vuilleumier et al. SAE 2013-01-2622

Kinetic-Related Needs

In Late 70's, early 1980's

- Urgent need for fundamental elementary kinetic data, comprehensively validated detailed models, even for single species
  - Westbrook and Dryer (1981) 18th Int. Combust. Symp.
- Empirical approaches to provide an engineering solution, based on available fundamental experimental foundation e.g. Westbrook and Dryer (1981) Combust. Sci. Tech.

Similar multi-step empiricisms still commonly used in CFD parametric design today!

Since 1990's - Present

- Incredible advances in chemical kinetic validation experiments, theory, stiff solvers, parallel computing (Moore's law advances)
- The fundamental kinetic paradigm - creation of "EXTREME" high-dimensionality, even for single species, state of art fundamental research!
  - Generally impractical for CFD Engineering Design tools – even for single species fuels
  - Describing real fuel properties important for LTC applications has advanced, but remains complicated.
  - Models for complex mixtures for multi-phase applications typically represent real fuel as C_nH_m (Physical/chemical property CFD representations improving but remain limited)
  - Emissions chemistry predictions improving in fidelity; coupling with HC kinetics advancing
  - Numerical reduction results in high fidelity smaller dimensional models still too large

What kind of applications driven improvements would be most impacting?

- **High fidelity descriptions for real fuel compositions that include coupled pollutant and fuel chemistry, higher fidelity modeling of multi-phase physical/chemistry effects**
- **Comprehensive lower dimensional results that can support CFD design specific models of less than 10-15 species.**
- **Optimization of real fuel models based upon chemical functional characteristics in nominating molecular surrogate species and composition => compact modeling methodologies**

Fundamental research that improves fidelity of Industrial CFD parametric engineering design for LTC and advanced power cycles

Panel on:
Practical Applications of Combustion Kinetics

Premise

Combustion kinetics provides a basis for computing ignition phenomena, pollutant formation, flame behavior, etc., and can be useful to industry for product design and modifications

Topics for discussion

What are the gaps between fundamental studies/detailed mechanisms vs. practical applications?

What level of detail is required?

Are detailed mechanisms acceptable? If not, how much reduction is desired?

What computational costs are acceptable?

Examples of recent successes?

What are the future directions/needs?

Can we work around proprietary concerns?