Designing Future Combustion Systems for Renewable Fuels

NSTD Presentation

Student Seminar

August 2, 2007

Joanna McFarlane

Alternative fuels for transportation are key to US security and global climate change

"It is in our vital interest to diversify America's energy supply – and the way forward is through technology."—Pres. Bush, 23-Jan-2007

"We need to press on with battery research for plug-in and hybrid vehicles, and expand the use of clean diesel vehicles and biodiesel fuel."

" …new methods of producing ethanol…" "…35 billion gallons of renewable and alternative fuels by 2017…"

"---help us confront the serious challenge of global climate change."

"Tonight I ask Congress to join me in pursuing a great goal."

"…reduce gasoline usage in the United Stat years"

TWENTY IN TEN

OAK RIDGE National Laboratory

Interest in alternative fuels is not new.

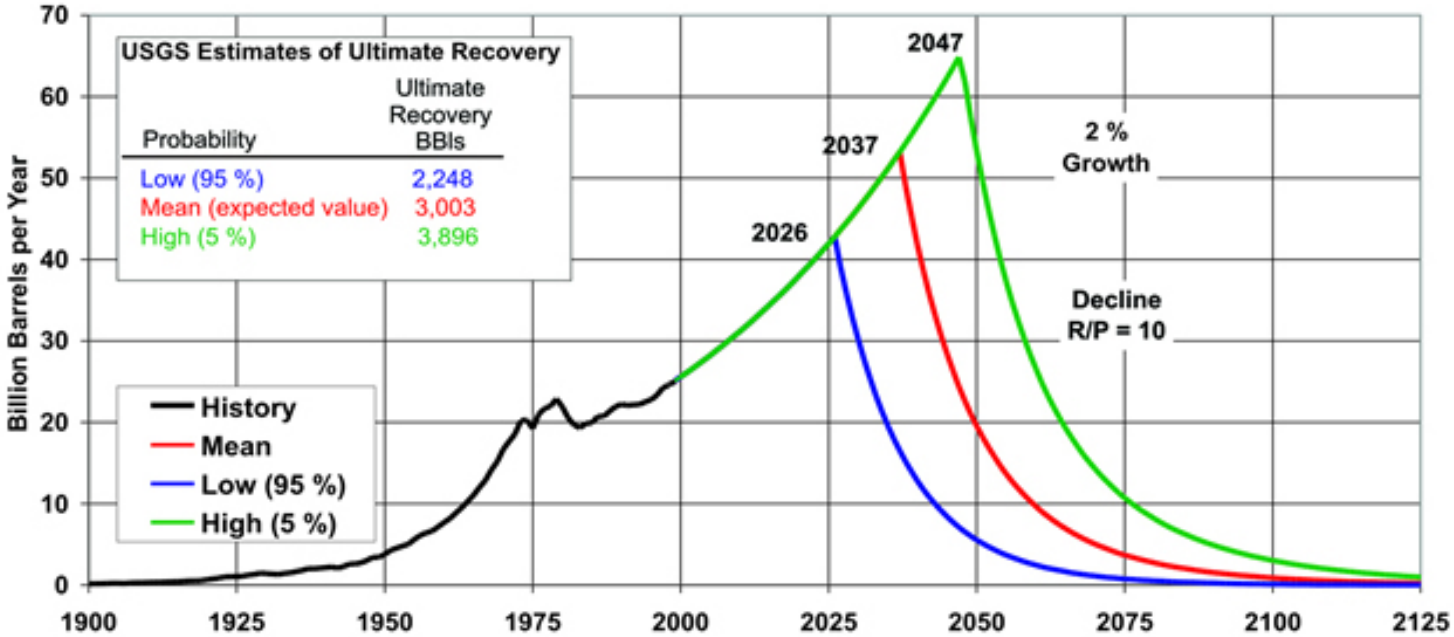
- **1970's – spike in oil prices**
- **Clear Air Act amendments in 1990's**
  - **Regulate air quality, ozone, CO, Pb, NO2, SO2, particulates**
- **Energy Policy Act 1992**
  - **Energy security in wake of 1st Iraq war**
- **Alternative fuels (0.1% US road use)**
  - **included propane (97.4%), compressed natural gas, methanol/gasoline in CA, some government ethanol/gasoline demos, electric (tiny #) and biodiesel (no fleet vehicles)**
- **Replacement fuels excluding alternatives (1.4%)**
  - **MTBE accounts for 2/3, ethanol other 1/3**

DOE/EIA-0585/O 1994

Why? Economics

- **Cost of fuel not likely to return to mid-90's levels**
- **Conventional oil will become more scarce and worldwide consumption will increase**

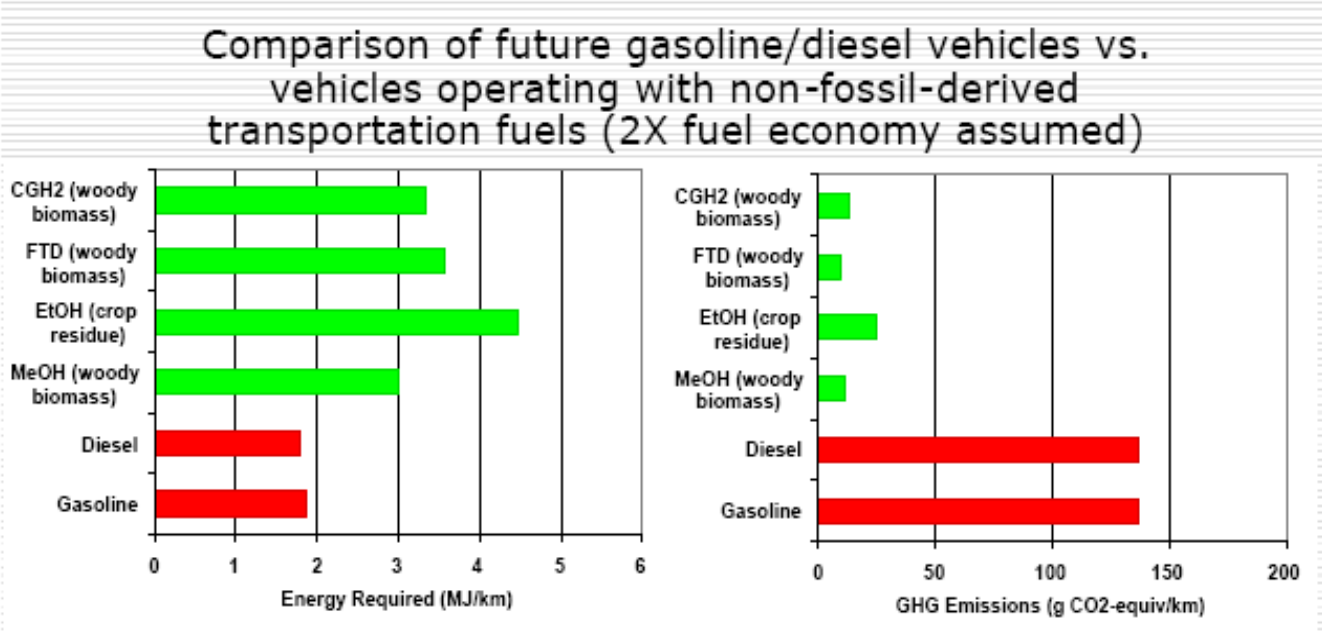
Figure 2. Annual Production Scenarios with 2 Percent Growth Rates and Different Resource Levels (Decline R/P=10)



Source: Energy Information Administration
Note: U.S. volumes were added to the USGS foreign volumes to obtain world totals.

EIA August 18, 2004, Wood, Long, Morehouse

Why? Environment

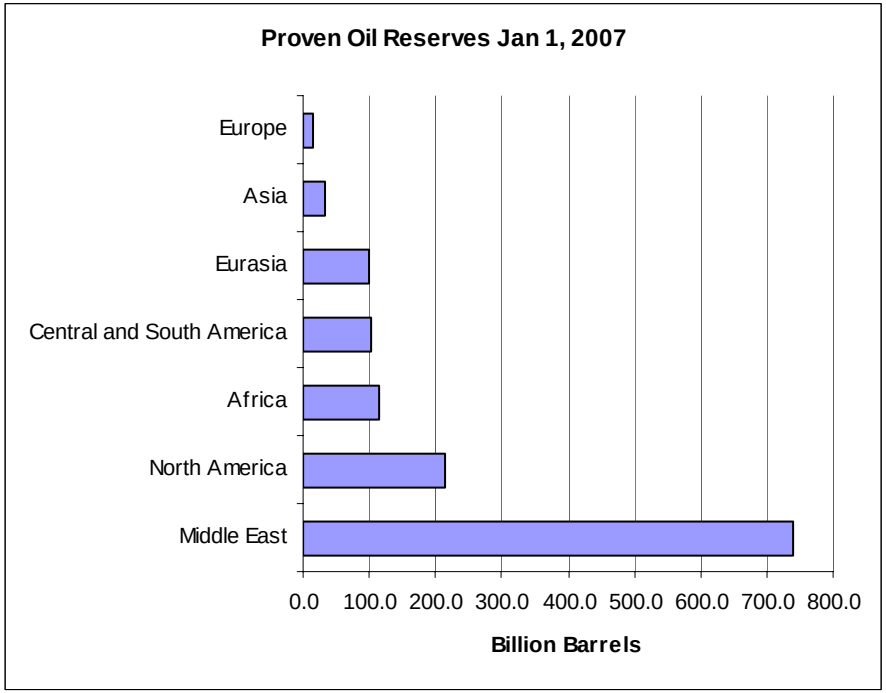


EPA, Matthew Brusster 2005

- **Lowered CO_2 emissions relative to conventional fuel**
- **Oxygen content in ethanol, esters promotes combustion and reduces emissions, eliminates need for MTBE**

Why? National Security

- **Most oil reserves in middle east**
- **Oil prices reflect costs for securing supply**
- **Ethanol and biodiesel are being manufactured in the US**
- **Supportive of US agriculture, small communities**



Worldwide Look at Reserves and Production
04, 47, 24-25

HOUSTON BUSINESS JOURNAL

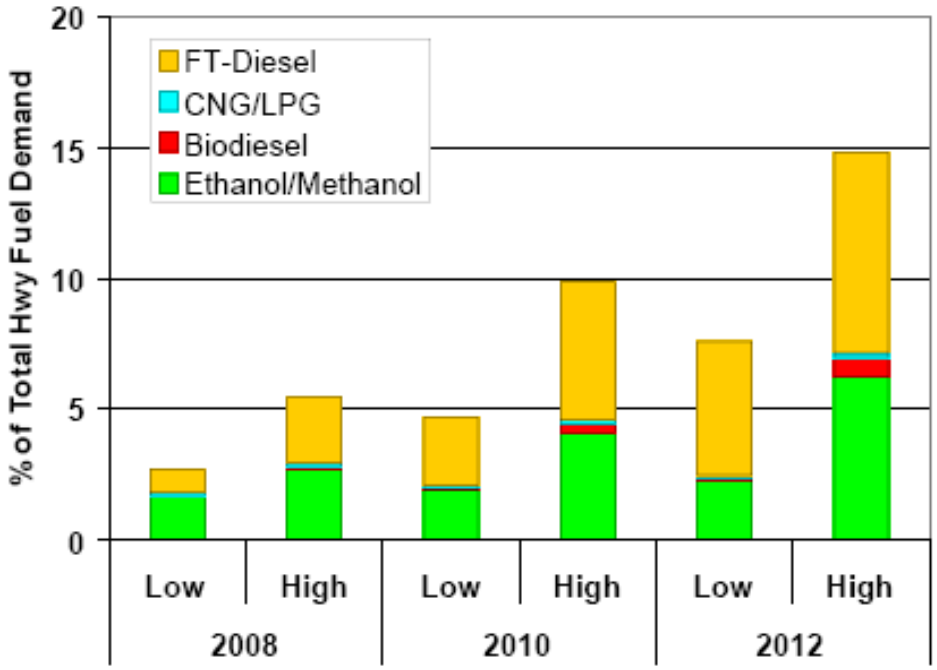
BUSINESS PULSE SURVEY: Would you rather work for a small company

Biofuels Power fires up biodiesel plant in Montgomery Co.

Houston Business Journal - March 5, 2007

Biofuels Power Corp. said Monday that it has begun to produce and sell electricity from its biodiesel-powered generating plant in Oak Ridge North, in south Montgomery Co.

Alternative fuel consumption in the US projected to triple in the next 5 years



Note: From non- coal/shale feedstocks; biomass sources not included

Source: EPA In-house staff sensitivity projections.

- **Ethanol and biodiesel are manufactured in the US**
- **Economically competitive as oil prices projected to remain high**
- **US has large reserves of coal and the technology for coal-to-liquids**
- **FT fuels can be tailored to meet specific needs**

Issues with Unconventional Fuels

- **Lower heat content**
- **Physical properties can affect engine performance**
- **Stability of biofuels**
- **Purity of feedstocks**
- **Non-centralized processing**
- **Distribution difficulties**

Lower Heating Values
(ΔH Vap H_2O neglected)

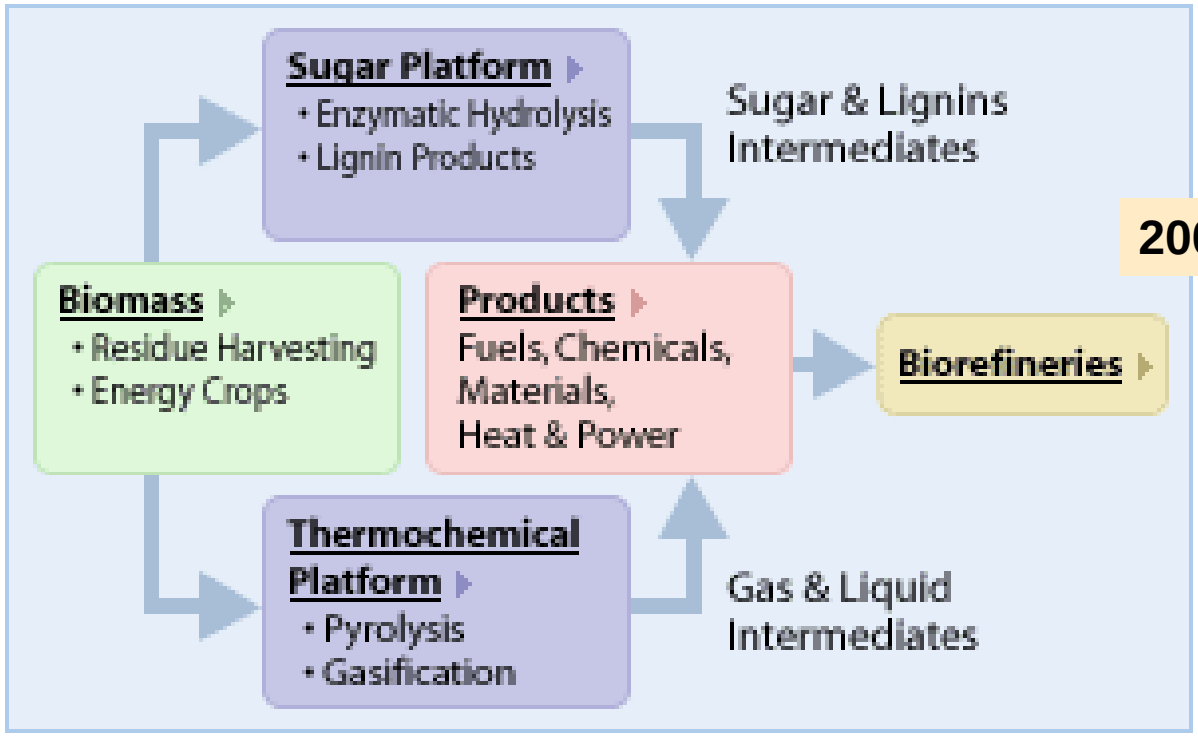
Gasoline	**32 MJ/liter**
Diesel	**36.4 MJ/liter**
Ethanol	**21.1 MJ/liter**
Biodiesel	**33.3 - 35.7 MJ/liter**
Natural Gas	**34.6 MJ/m3**

www.bioenergy.ornl.gov

Fuels are addressed by the DOE Biomass Program

http://www1.eere.energy.gov/biomass/

375M$ bioenergy centers



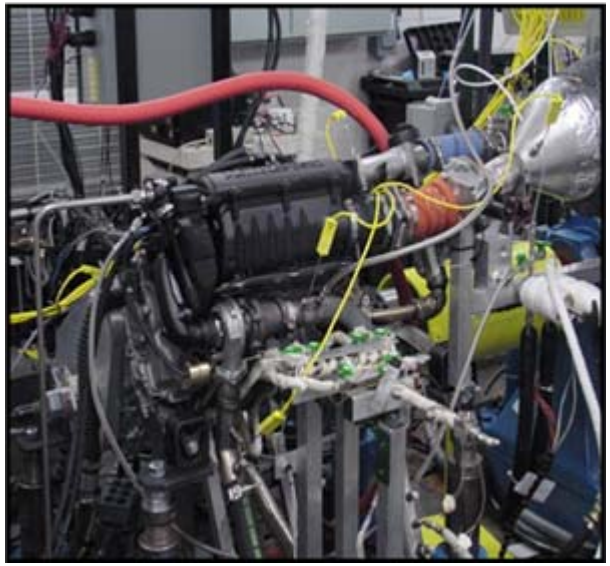
200M$ cellulosic biorefineries

23M$ cellulosic ethanol

18M$ biofuels/bioproducts, joint with USDA

To achieve twenty in ten

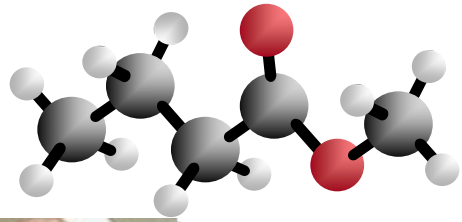
FreedomCAR program at DOE includes



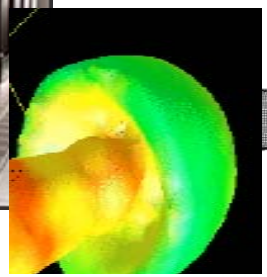
- **Fuel cells**
  - **325 W/kg, 60% peak energy efficiency**
- **Electric vehicles**
  - **55 kW for 18s**
  - **Electric drivetrain energy storage**
- **Clean energy efficient vehicles running on HC and bio fuels**
- **Hydrogen fuels,**
  - **refueling, onboard storage, drivetrain**
- **Lightweight vehicles**

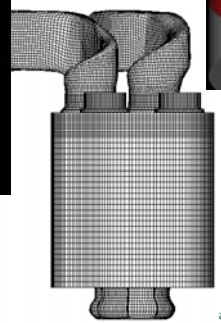
http://www1.eere.energy.gov/vehiclesandfuels/

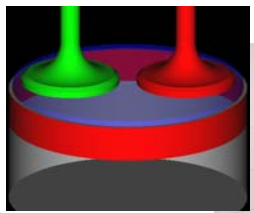
ORNL has combined resources to develop modern solutions to the President's challenge.



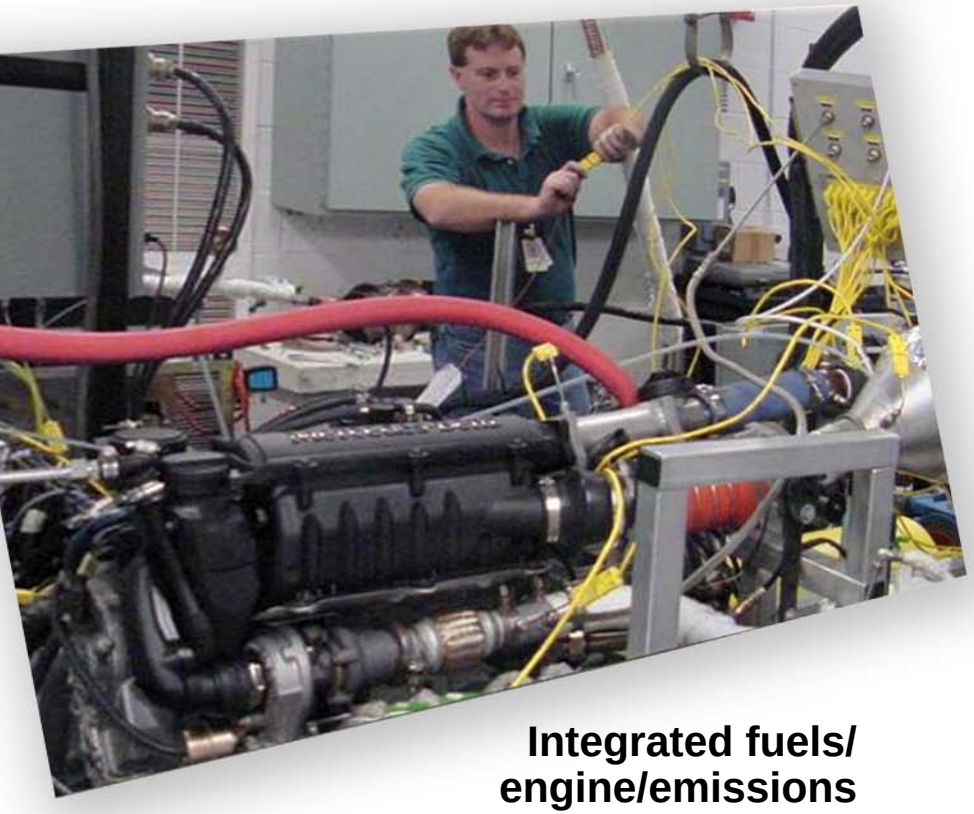
State-of-the-art fuel chemistry and high-performance computational fluid dynamics combine with strengths in advanced engine technologies for a *predictive* capability for innovation in development of alternative fuels and design of novel efficient, environmentally sound combustion systems.





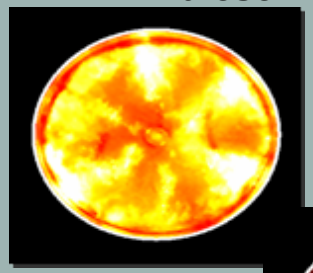


ORNL is developing energy-efficient, low-emissions engine technologies

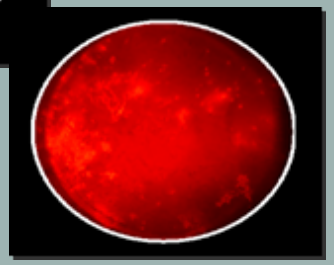


Integrated fuels/ engine/emissions testing at NTRC

Conventional diesel



Low-temperature combustion



Photos courtesy of Caterpillar

Demonstration of advanced combustion regime with reduced emissions

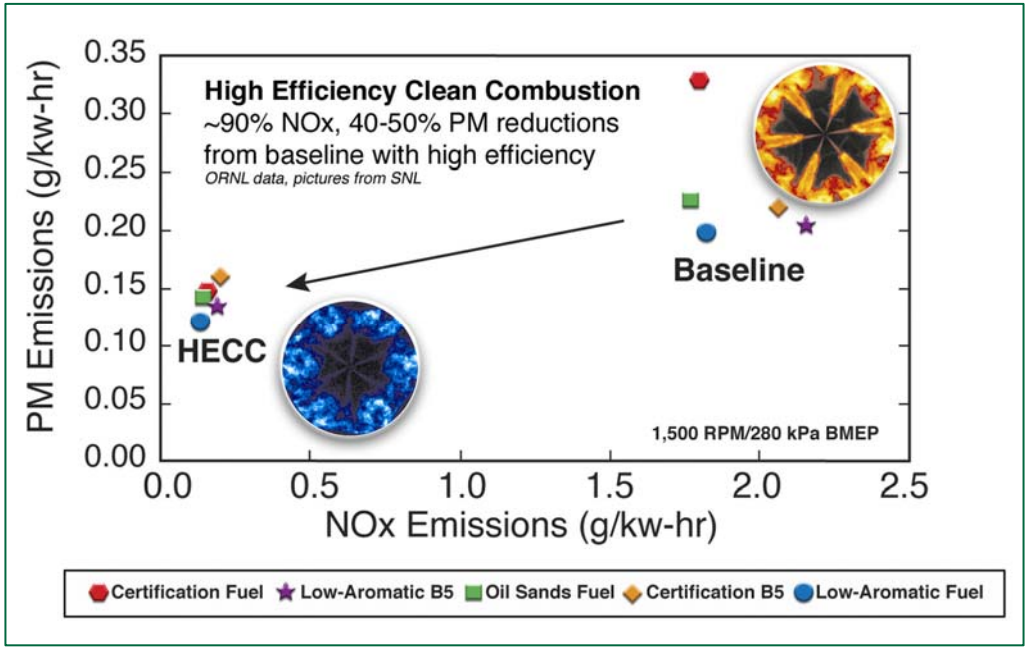
- **Soot: reduced 2x**
- **NO_X: reduced 10x**

Without fuel efficiency penalty

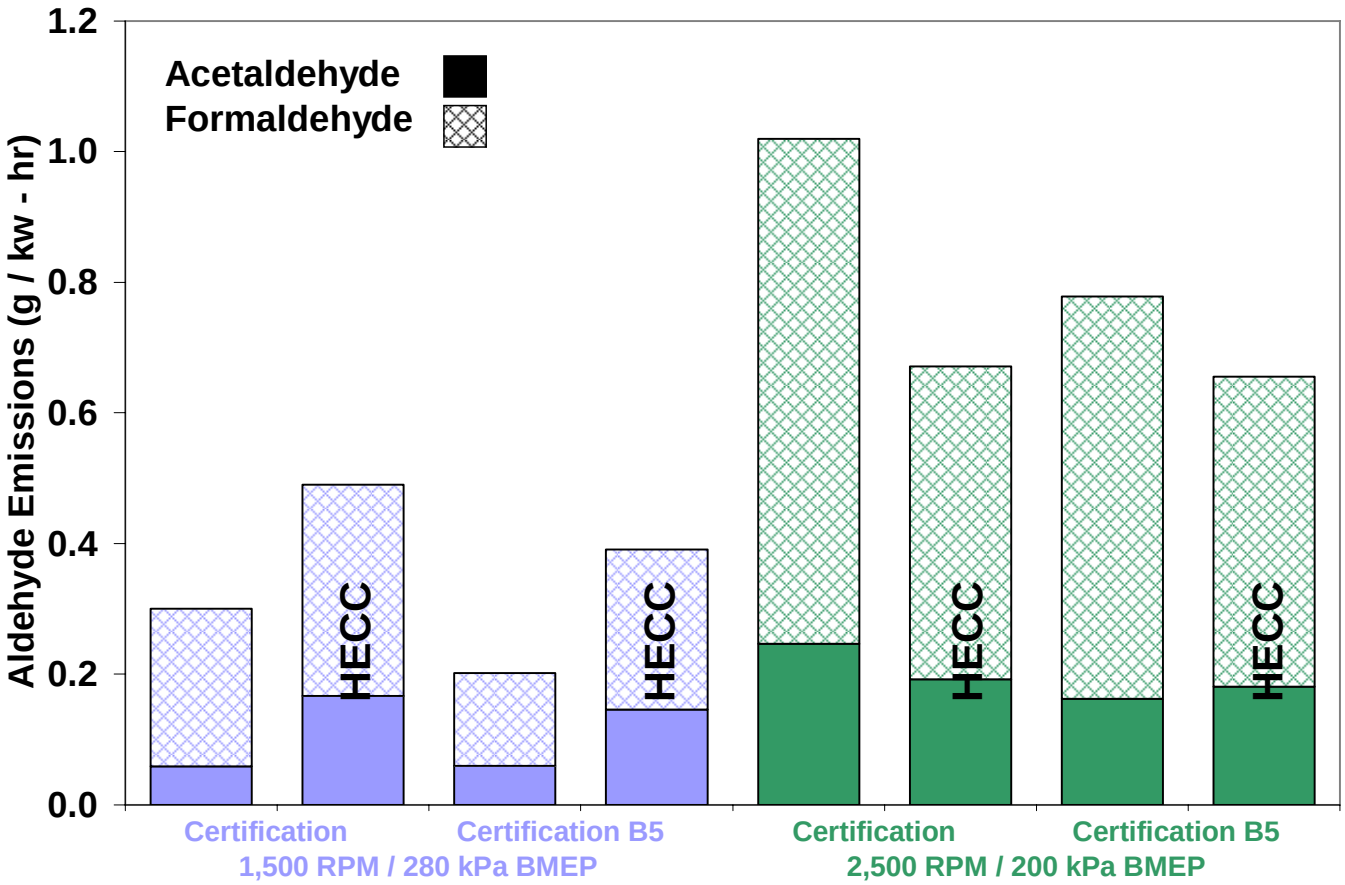
ORNL/FEERC and U Wisconsin/ERC are collaborating to study effects of fuel under HECC conditions

Advanced combustion modes will be used on some level in all future transportation engines

- **Advanced combustion characterized by low temperature combustion (LTC) processes: low emissions and improved efficiency.**
- **Typically less stable than conventional forms of combustion (i.e., sensitive to air-fuel charge conditions including fuel properties).**



Adding biodiesel changes emissions of HC, NOx, and aldehydes (Data from FEERC*).



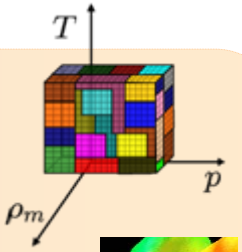
* Fuels, Engines and Emissions Research Center
National Transportation Research Center, ORNL

Predictive modeling assists development of advanced engines using alternative fuels

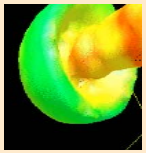
Fuel Chemistry

- Molecular modeling & measurements
- Development of reaction mechanisms
- Automated mechanism analysis

Advanced computing

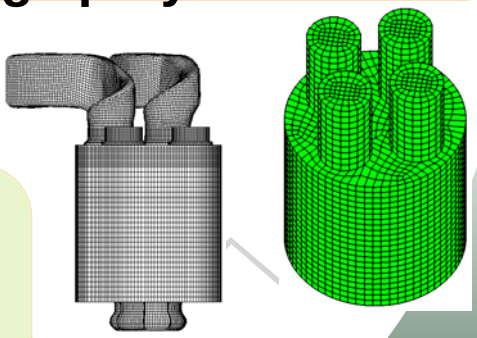


- Next Generation CFD
- Parallel Implementation
- Unstructured mesh
- Interface tracking spray model



Engine Experiments

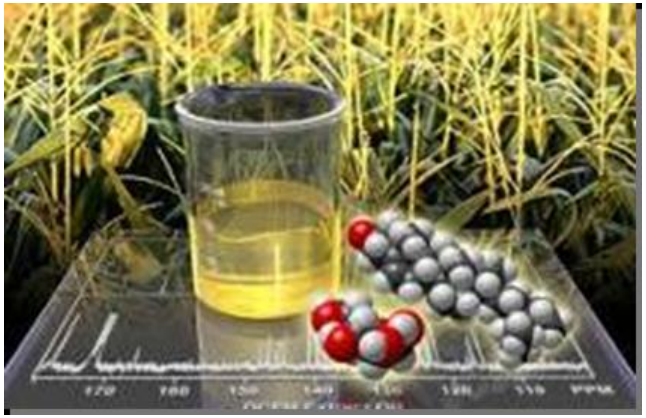
- Advanced Combustion
- Validation of models
- Novel fuel formulations

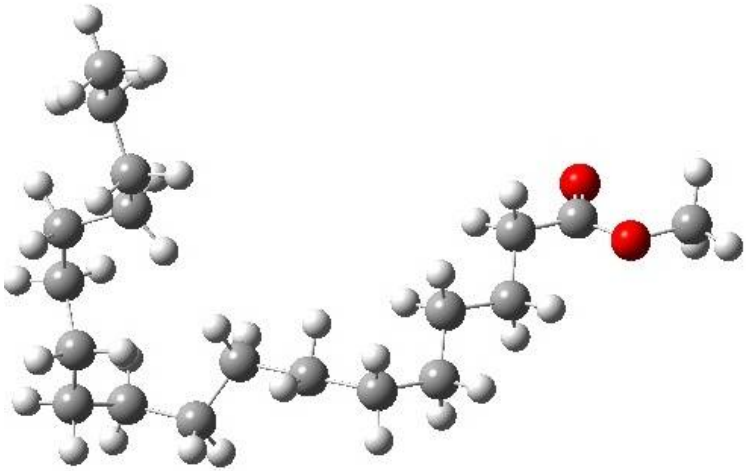


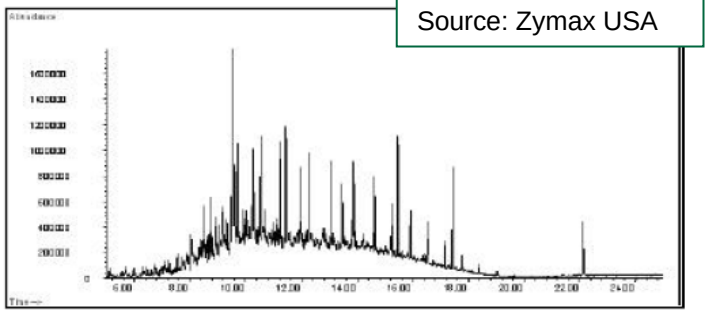
Prediction of fuel performance

Molecular modeling used to derive alternative fuel properties required for predictive models

- **Necessary for phenomenological modeling of fuel spray characteristics**
- **Molecular modeling for structure and property determination for CFD & kinetic simulations**
- **Cluster computing – NWChem**
  - **S. Elseroad**
- **Can simulate performance of non-ideal mixtures, especially above critical point**





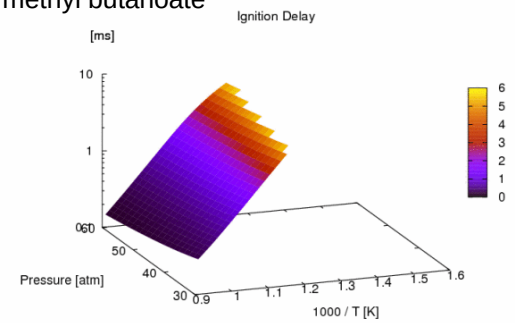


GCMS Trace of Diesel
Source: Zymax USA

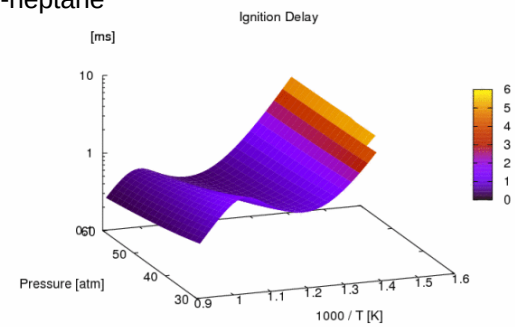
Chemical kinetic studies needed to develop a realistic reaction set for alternative fuels

- **Consider bio-derived mixtures (e.g., methyl esters, alcohols)**
- **Fuel physical properties are required for energy equation**
- **Define reaction mechanisms**
  - **Combustion of real multi-component fuels involves hundreds of species and thousands of reactions (n-heptane, methyl esters, NOx, long chain olefins – C16+)**
- **Evaluate reaction kinetics for use in CFD**
  - **Develop reduced mechanism**
  - **Senkin for sensitivity analysis**
  - **XChemKin exploratory tool**

methyl butanoate

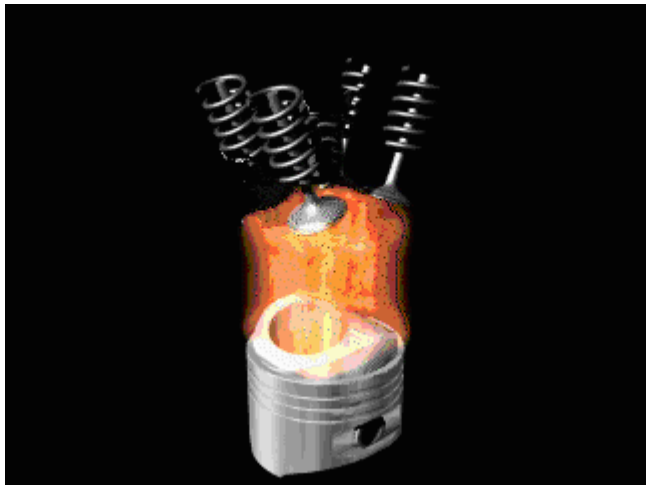


n-heptane

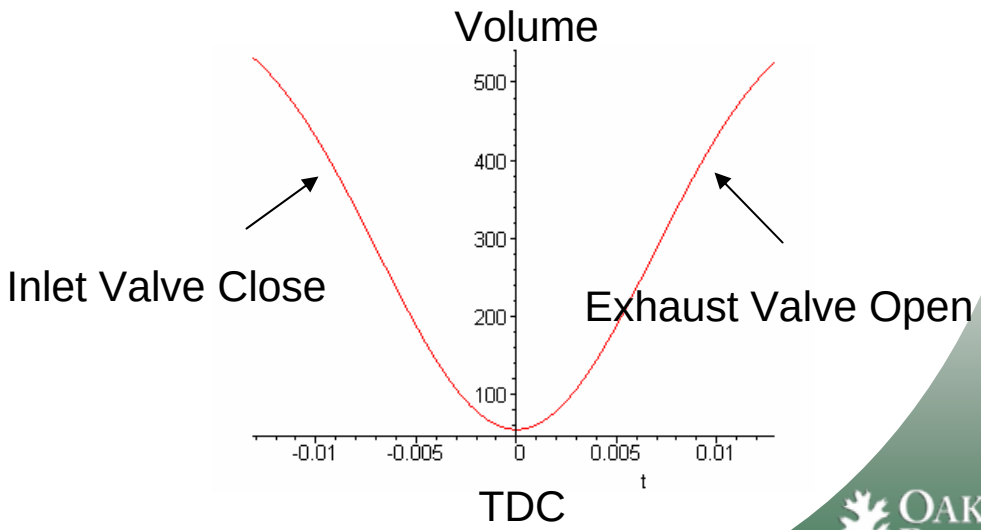


Homogeneous Charge Compression Ignition

- **Mixed fuel/air introduced into cylinder**
- **Compression-induced ignition**
- **Biodiesel and blends up to 50 volume %**
- **Experimental data from Hatz diesel engine at FEERC**



*Animation edited by G. Leung (LLNL)
Original from Mitsubushi Corp



Mixed results from comparison of simulations with HCCI experiments using biodiesel blends

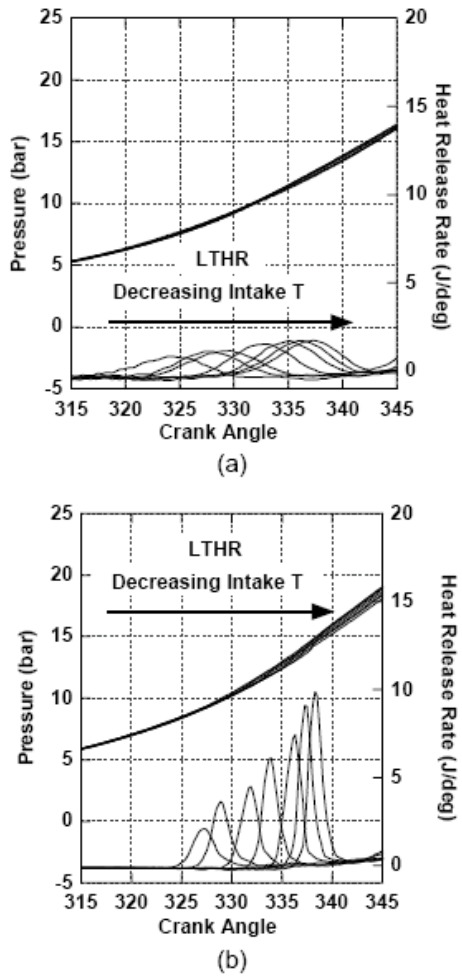


Figure 4. LTHR portion of pressure and heat release traces for intake temperature sweeps for (a) $B0_{exp}$ and (b) $B0_{sim}$.

- **Trends in timing of LTHR and main combustion event reproduced**
- **Trends in magnitude of LTHR reproduced**
- **Duration of LTHR longer in experiment**
- **Heat transfer and stratification are important post-ignition and were not simulated**

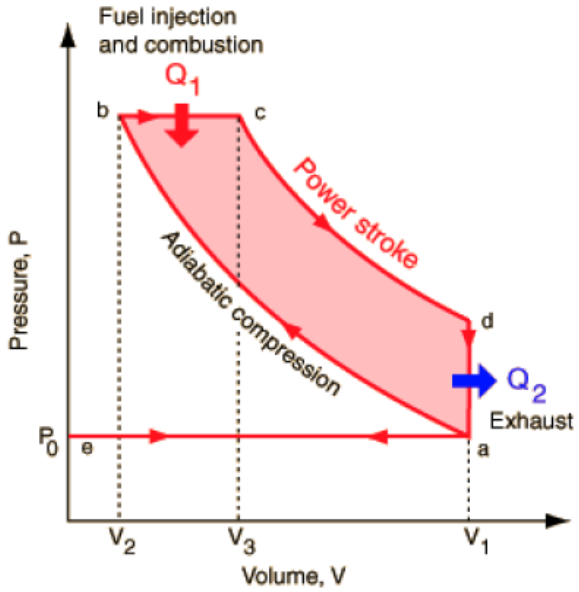
SAE 07FFL-147 draft
Syzbist, McFarlane, Bunting

Heat transfer and multizone models added to CHEMKIN

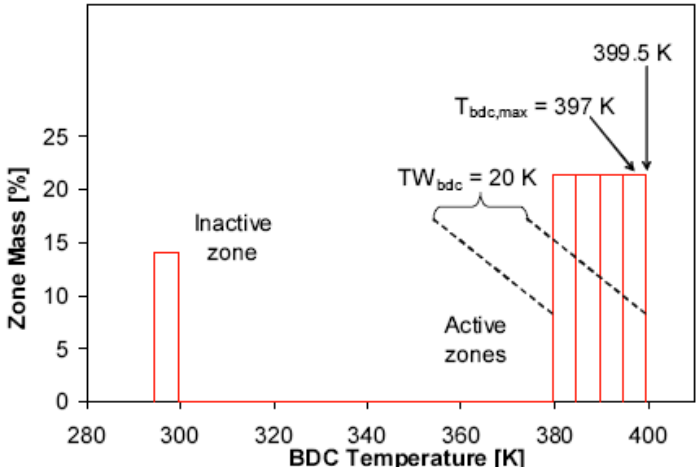
- **Single zone heat transfer in CHEMKIN**
  - **KC Cushman**

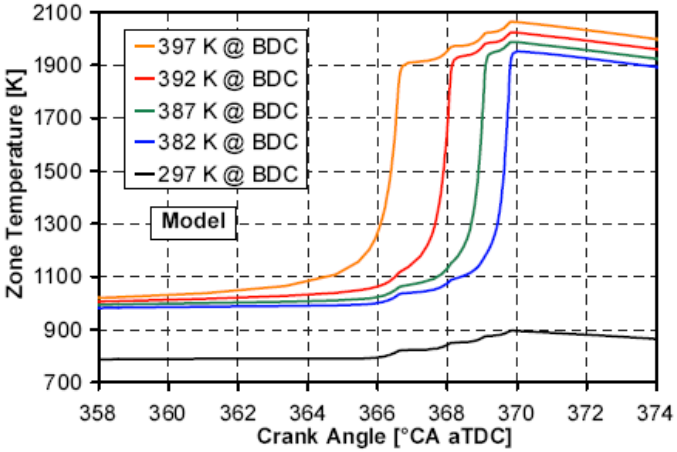
$$\dot{q} = h(T - T_0)$$

- **Multizone Model**
  - **K. Chakravarthy**



Air standard diesel engine cycle





Sjöberg and Dec SAE 2005-01-2125

Chemical kinetics models continue to be improved

- **Need better match for CN, C/O ratio**
- **Longer chain methyl esters, methyl decanoate (LLNL), +++**
- **Ethanol (R. Ahsen)**
  - **Mechanisms dependent on type of experimental data used to derive rate constants**
- **Gasoline –**
  - **n-heptane, iso-octane**
  - **Toluene for aromatics**
- **Chemistry of soot**
  - **PAH**
  - **Role of unburned fuel**
  - **Role of additives**

	$B0_{sim}$	$B10_{sim}$	$B50_{sim}$	Methyl Butanoate
Wt% methyl butanoate	0.00	4.02	19.64	100.00
Wt% C	83.90	82.89	78.97	58.80
Wt% H	16.10	15.85	14.88	9.87
Wt% O	0.00	1.30	6.20	12.00
A/F_{stoich}	15.12	14.87	13.88	8.77
LHV (MJ/kg)	44.56[1]	43.83[1]	40.98[1]	26.30[1]
Cetane Number	56.00[1]	54.55[1]	48.93[1]	20[1]

1. Estimate values. Direct measurements will be included in final draft.

Development of a reduced mechanism for biodiesel using sensitivity analysis

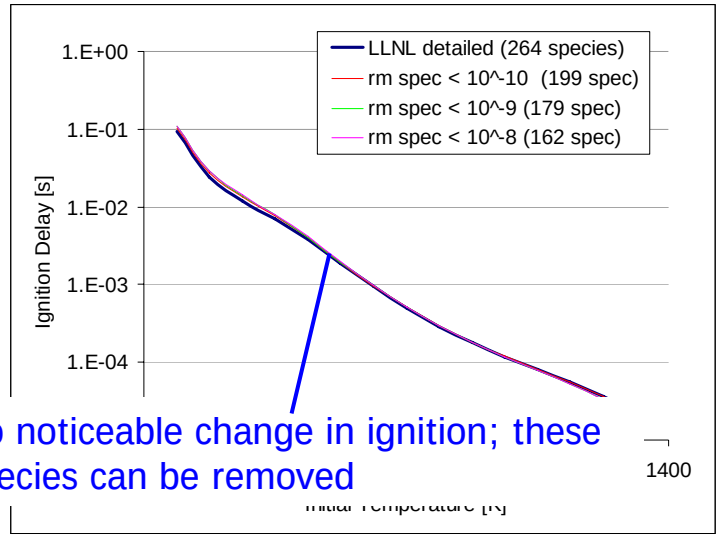
(J. Brakora – U. Wisconsin)

LLNL methyl butanoate (MB)*

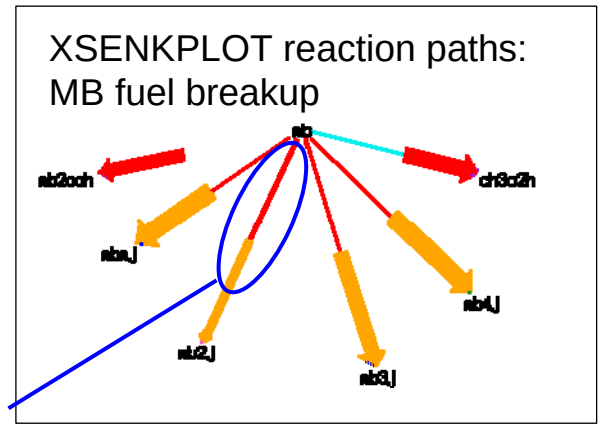
- Surrogate to represent the large methyl esters in biodiesel
- MB chemical formula: $C_5H_{10}O_2$
- *264 species, 1219 reactions*

Mechanism Reduction Method

- SENKIN constant volume analysis
- Identify key species and reaction paths based on ignition timing
  - Peak concentration: remove low concentration species (-112 species)
  - XSENKPLOT reaction flux analysis to identify key reaction pathways, remove less important paths (-111 species)
- Adjust rate constants for key reactions to optimize ignition timing



No noticeable change in ignition; these species can be removed

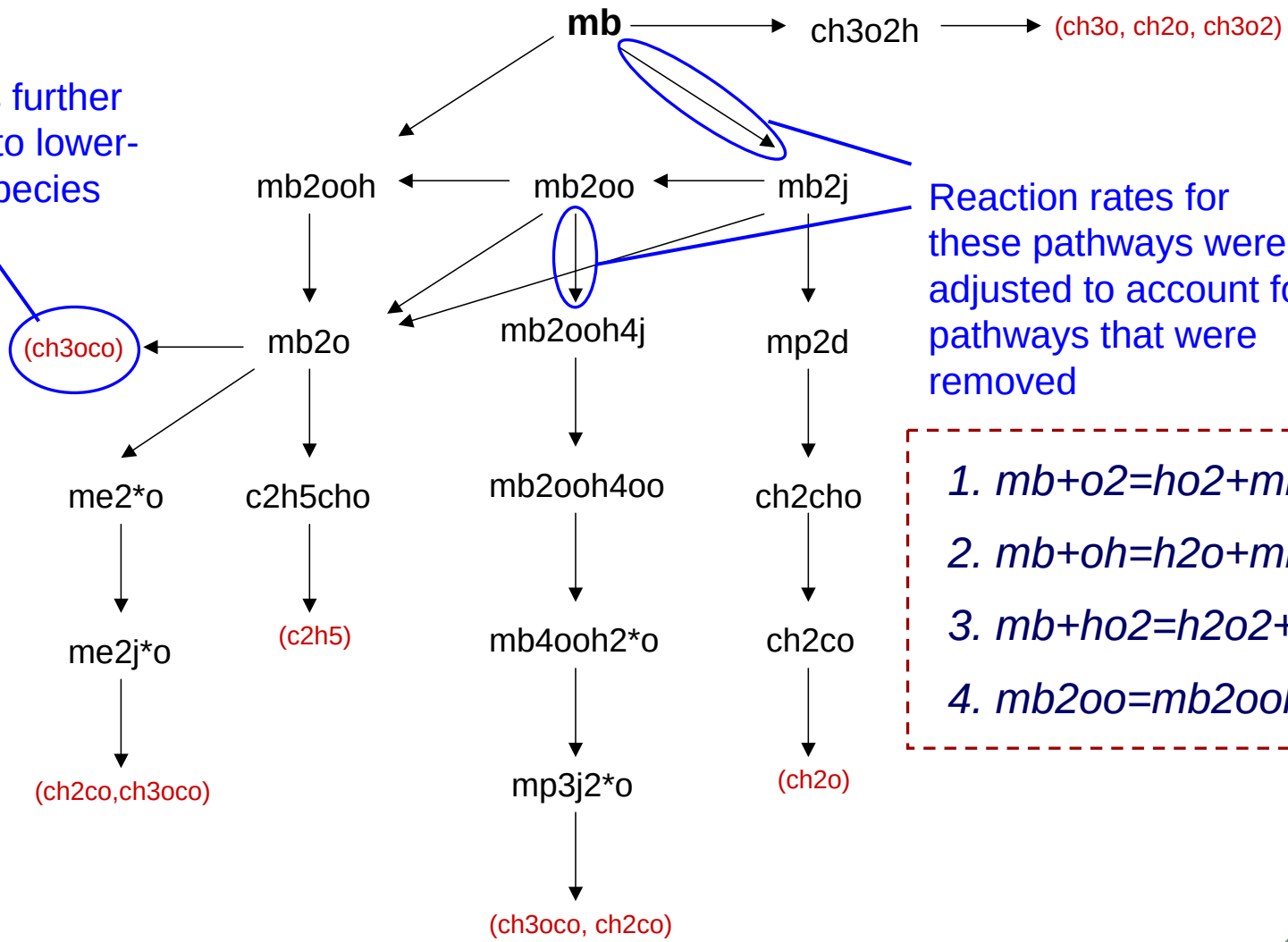


Large flux to "mb2j" ($C_5H_9O_2$); test removal of other paths

*Proc. Comb. Inst., Vol 28, 2000/pp.1579-1586

Generation of a reduced methyl butanoate kinetic mechanism for CFD simulations

These species further break down into lower-level carbon species



Reaction rates for these pathways were adjusted to account for pathways that were removed

1. *mb+o2=ho2+mb2j*
2. *mb+oh=h2o+mb2j*
3. *mb+ho2=h2o2+mb2j*
4. *mb2oo=mb2ooh4j*

Developed a graphical tool for reaction analysis & mechanism reduction.

$$\partial_t(\rho u) + \cancel{\mathrm{div}_x(\rho v u)} = -p\,\mathrm{div}_x v + \tau \bullet \nabla_x u - \cancel{\mathrm{div}_x q} + \dot{Q}^c + \cancel{\dot{Q}^*}$$

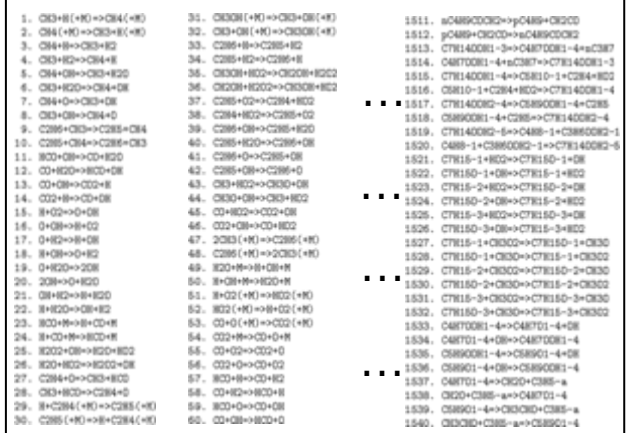
$$\partial_t \rho_m + \cancel{\mathrm{div}_x(\rho_m v)} = \cancel{\mathrm{div}_x(\rho D\ \nabla_x(\rho_m \rho^{-1}))} + \dot{\rho}_m^c + \cancel{\rho^* \delta_{m1}}$$

Model
(CHEMKIN III)

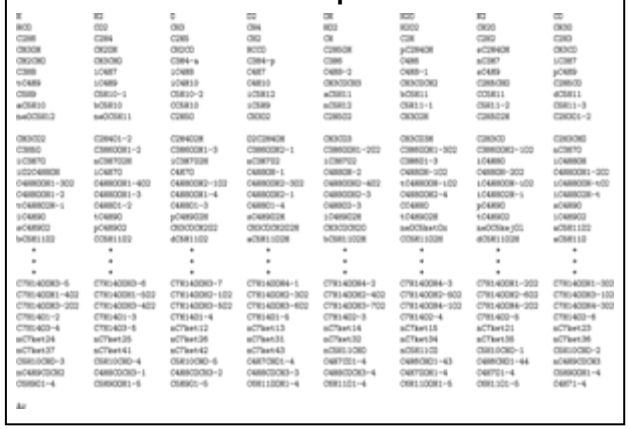
XChemKin

Mechanism

3000+ reactions

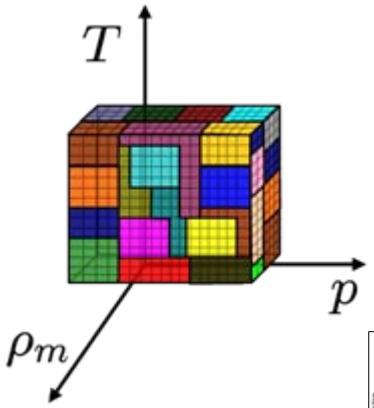


300+ species

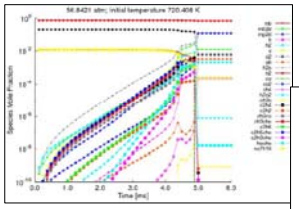


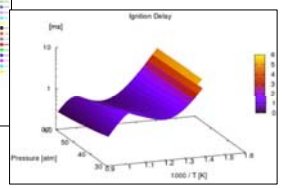
Parallel Computing

Phase Space Partitioning



Data Mining:
Statistical
Analysis
Graphical

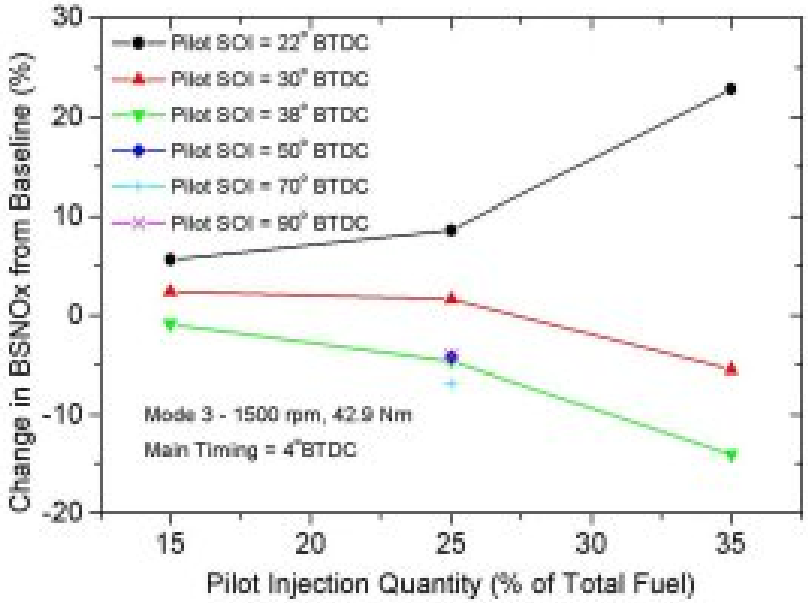




OAK RIDGE National Laboratory

Pre-Mixed Charge Compression Ignition (PCCI) is an example of advanced combustion

- **Fuel/air mixture injected into cylinder before main fuel injection event (pilot)**
- **More of the combustion happens under lean conditions so that temperatures are lower and NOx is reduced**
- **Lead to smaller and lighter emissions control equipment**
- **Expect that fuel physical properties will have effect on combustion, diffusion controlled**



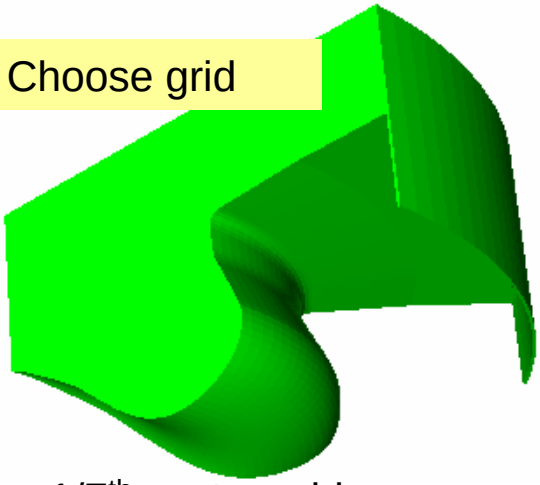
Effect of Single Pilot Injection Timing and Quantity on NOx at 1500 rpm

Southwest Research Institute: Neely and Ryan
http://www.swri.edu/3pubs/IRD2003/Synopses/039281.htm

Parameters used in computation study of effect of biodiesel properties on PCCI – Y. Ra (U. Wisconsin)

Engine conditions	
Bore x Stroke [mm]	**82 x 90.4**
Connecting rod length [mm]	**161**
Compression ratio [mm]	**16.6 and 19.5**
Intake valve closure [deg ATDC]	**-132**
Exhaust valve open [deg ATDC]	**112**
Engine speed [rev/min]	**2000**
Swirl ratio	**2.2**
Pivc [bar]	**1.926**
Tivc [K]	**357.18**
External EGR ratio [%]	**0**
Injection conditions	
number of nozzle	**7**
Injection pressure [bar]	**860**
Included angle [degree]	**155**
Initial composition @ IVC	
O2	**0.206170**
N2	**0.777881**
CO2	**0.007443**
H2O	**0.008506**

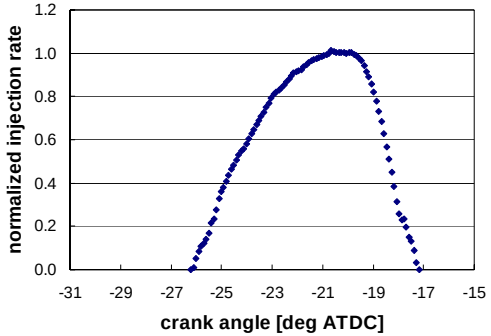
Choose grid



1/7th sector grid

# of cells @ BTDC =32656

Injection Shape



Used computed physical properties for biodiesel

Diesel (C14H30) versus Biodiesel Properties as a function of temperature

index	property	Diesel*	Biodiesel*
1	Density [g/cm^3]	0.7625	0.8837
2	vapor pressure [dyne/cm^2]	22.244	0.00061 (0.01180)
3	surface tension [dyne/cm]	26.83	24.87
4	liquid viscosity [dyne-s/cm^2]	0.0314	0.091
5	liquid thermal conductivity [erg/cm-s-K]	1.4430E+4	1.0020E+4
6	latent heat [erg/g]	3.6E+9	3.379E+9**
7	vapor specific heat [kcal/mol-K]	0.1536#	0.2026#
8	vapor diffusion coefficient [cm^2/s]	8.50E-2	9.441E-3
9	vapor viscosity [dyne-s/cm^2]	1.00E-4#	1.21E-4**#
10	vapor thermal conductivity [erg/cm-s-K]	4344.7#	2601.9#
11	liquid specific heat [J/g-K]	2.270182	2.0128153

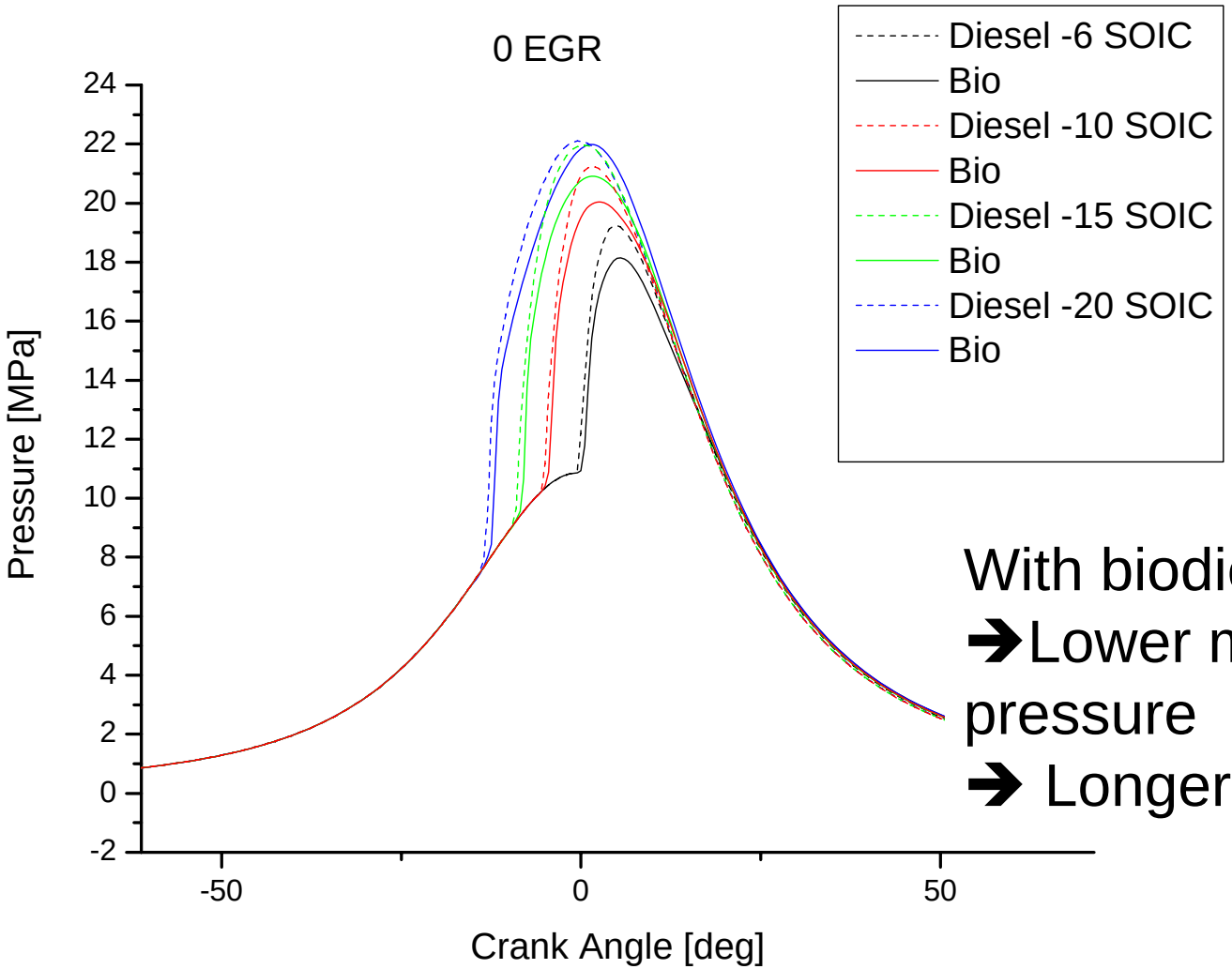
J. McFarlane, J. Griffin

* Values at 300 K

** Methyl Oleate

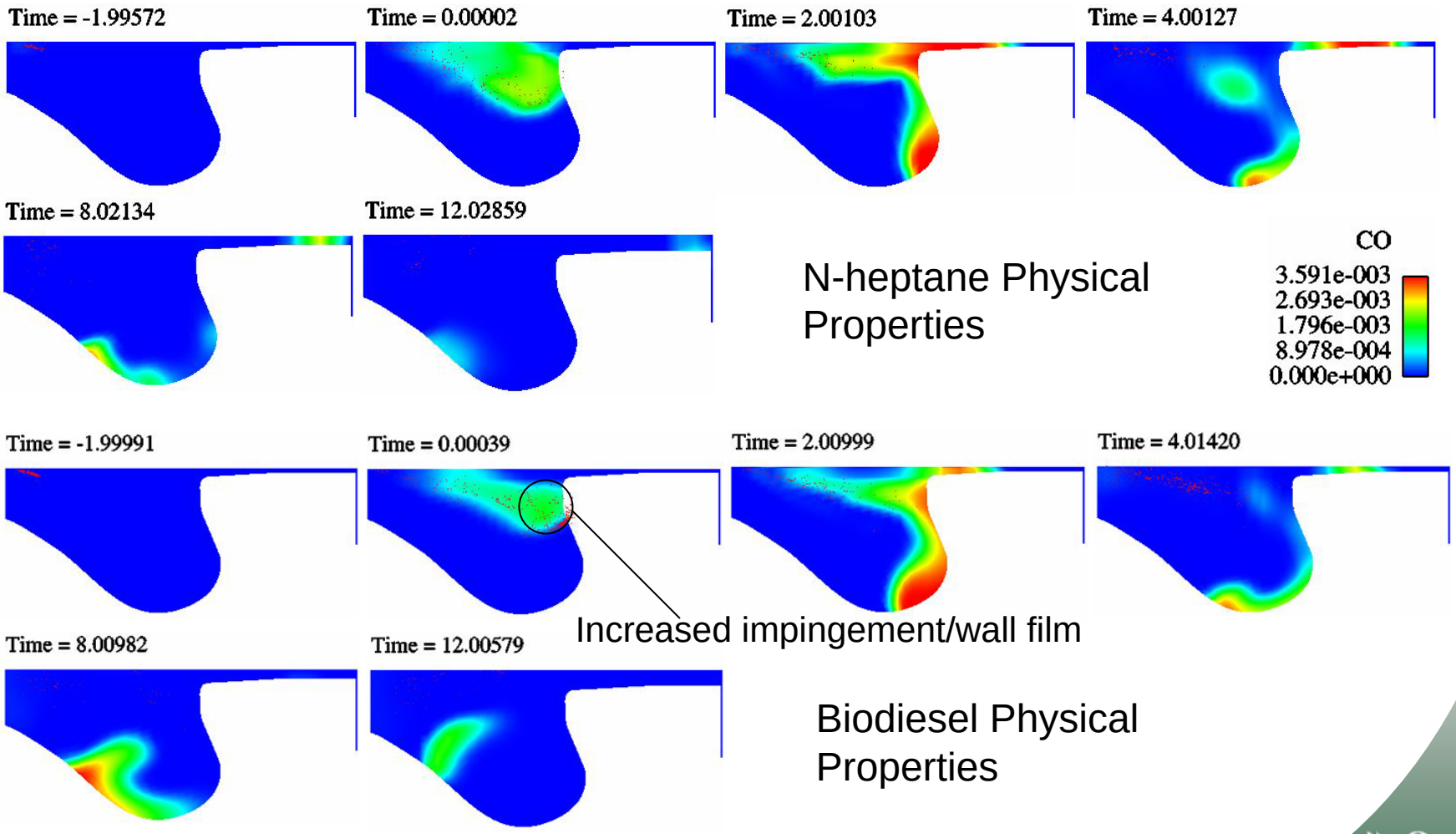
@ 700 K

Changes in pressure profiles predicted with biodiesel

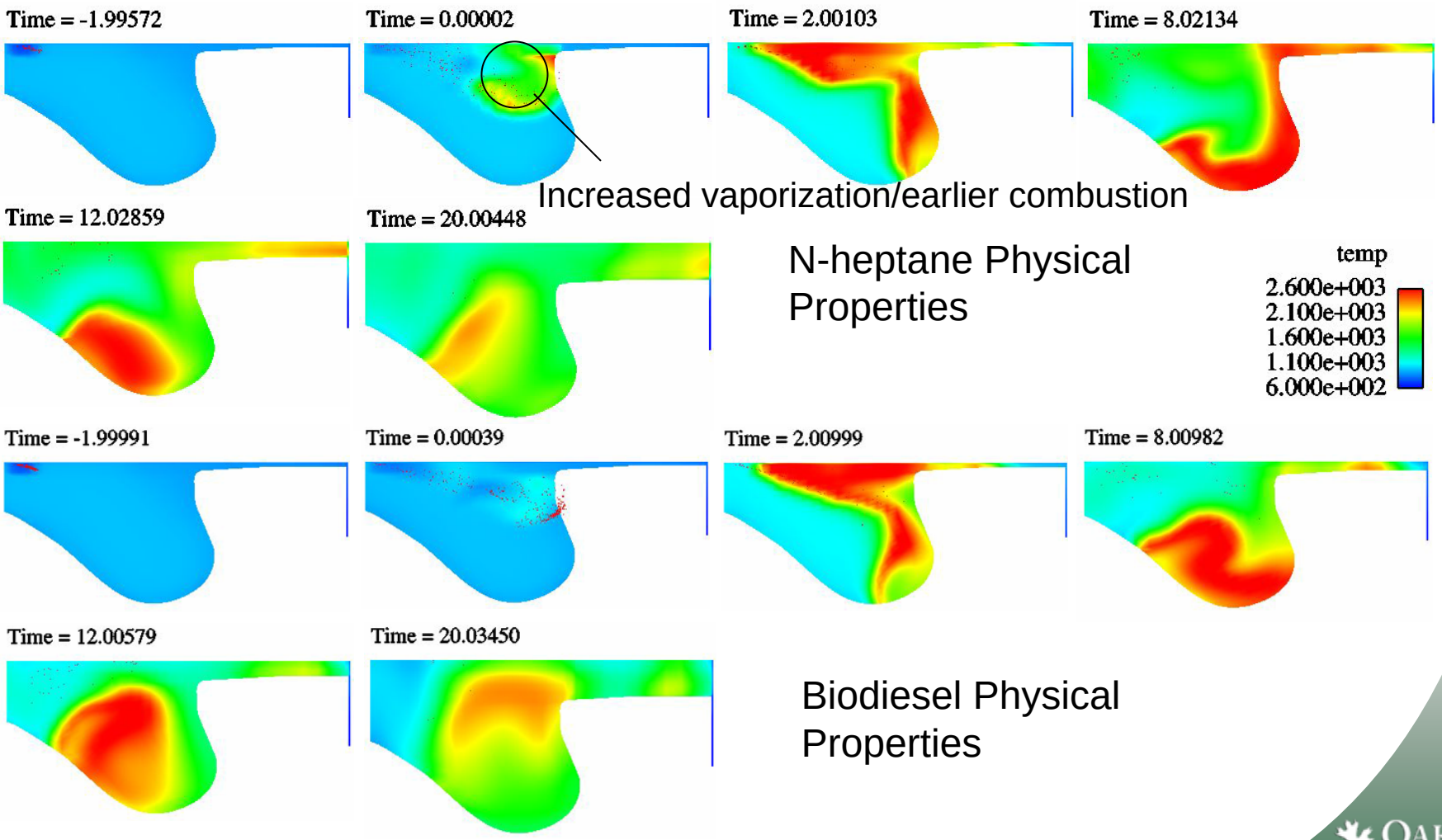


With biodiesel
➔Lower maximum pressure
➔ Longer ignition delay

Comparison of CO distributions shows increased impingement on the wall



Comparison of temperatures shows slower vaporization of biodiesel



Development of DOE Computational Fluid Dynamics (CFD) code for engine simulation

LANL KIVA Code Evolution

- Version 2 (1989)
  - In-cylinder, 3-D, multi-species, chemically reactive, turbulent, "confined", gas flow
  - Single-specie, multi-component discrete fuel spray particle
  - Single-block structured mesh
  - Fuel library
- Version 3 (1993)
  - Block-structured mesh
  - Cylinder side inlet/outlet ports
- Version 3V (1997), Release 2 (1999)
  - Vertical and canted valves
  - Particle-based liquid wall film model
  - Soot model
- Version 4 (available on request to the developer)
  - Unstructured mesh
  - Multiple fuel species evaporation

U. Wisconsin ERC has developed submodels for spray droplet formation, soot formation

Submodels increase data requirements

Need Data
For Fuels:
Physical properties
Combustion kinetics
For Engine: Mesh

Modeling Components

1. Multi-species Gas Flow
2. Chemical Reactions
3. Spray Droplets
4. In-Cylinder
5. Sub-models

coupled

Building the next generation of modeling and simulation tools – V. de Almeida

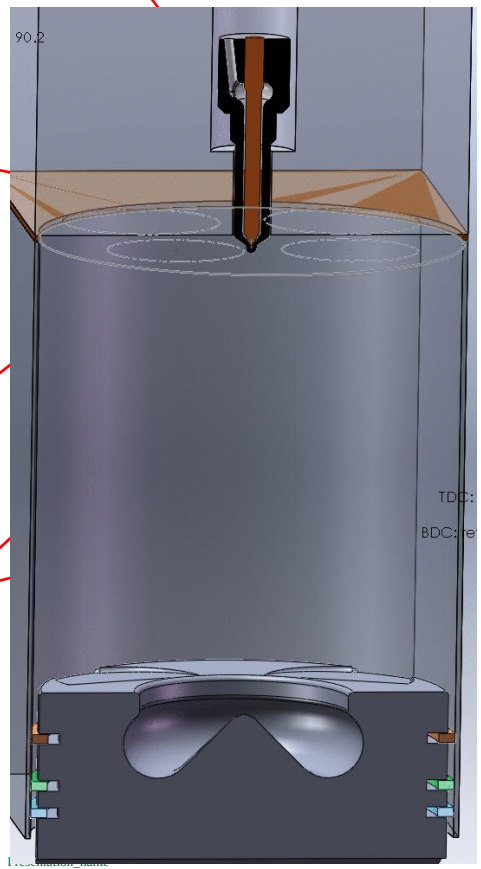
- ***Realistic geometry***
  - + *Moving parts (piston & valves)*
  - + *Stationary parts (cylinder, injector, exhaust manifold)*
  - + *Adaptive, unstructured meshing*

- ***3-D, transient fluid flow***
  - + *Gas-phase multi-species*
  - + *Turbulent*
  - + *Reactive (exothermic)*
  - + *Transport properties*

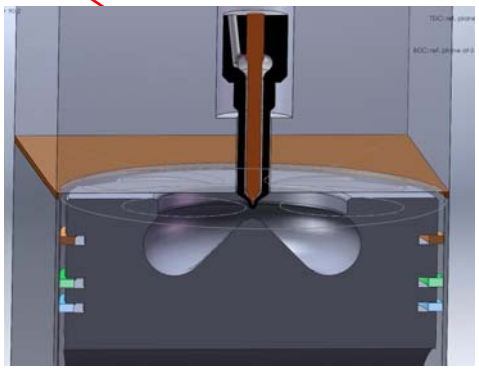
- ***Coupled detailed chemical reactions***
  - + *Reaction mechanisms*
  - + *Thermodynamic data*

- ***Boundary conditions***
  - + *Turbulent film models*

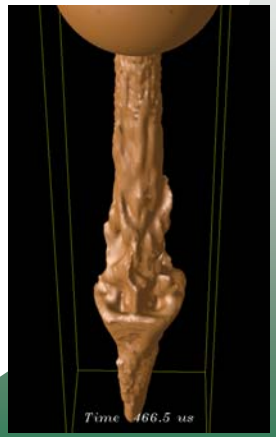
- ***Experimental validation***
  - + *Prototype engine*
  - + *Modern automatic data acquisition*



- ***Spray fuel injection***
  - + *Multi-component fuel*
  - + *Gas-fuel interface prediction*
  - + *Evaporation*
  - + *Physical properties*

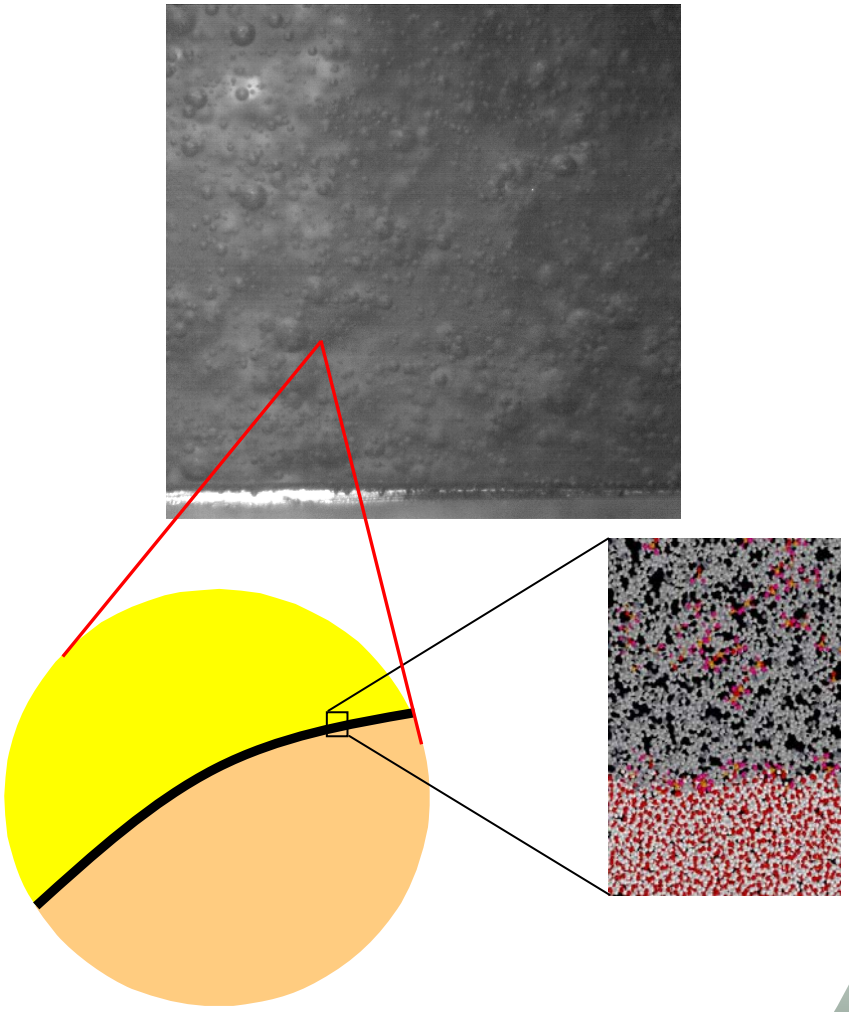


- Parallel KIVA-4
- Front tracking spray
- SciDAC



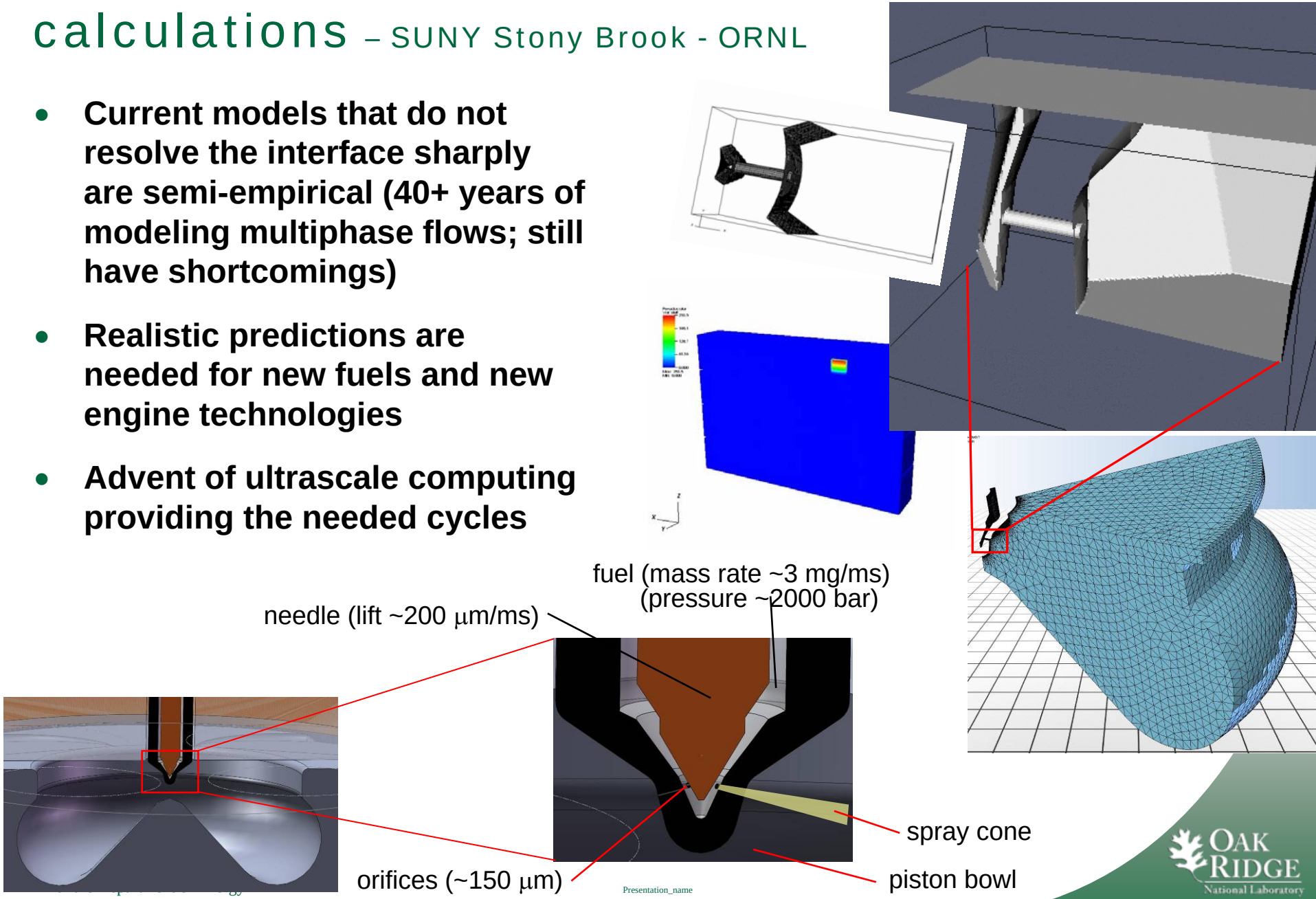
Sharp Interface Dynamics is Ubiquitous in Multiphase Flows

- **Bubbly flows; particulate flows**
- **Jet break-up; drop interactions**
- **Mixing; phase change ….**
- **A sharp interface is a mathematical surface representation of a 3-D region between two fluids**
- **As computing power grows, the evolution of a deforming surface, and the surrounding flow can be computed directly**



Ultrascale computation applied to engineering calculations – SUNY Stony Brook - ORNL

- **Current models that do not resolve the interface sharply are semi-empirical (40+ years of modeling multiphase flows; still have shortcomings)**
- **Realistic predictions are needed for new fuels and new engine technologies**
- **Advent of ultrascale computing providing the needed cycles**



Design of future engines and alternative fuels will be coupled

INTERNATIONAL
Herald Tribune

Military looks at synthetic fuel for bombers and fighters

By Don Phillips
Sunday, June 17, 2007

WASHINGTON: The U.S. Air Force has decided to push development of a new type of fuel to power its bombers and fighters, mixing conventional jet fuel with nonpetroleum-based fuels that could eventually end military dependence on foreign sources of oil.

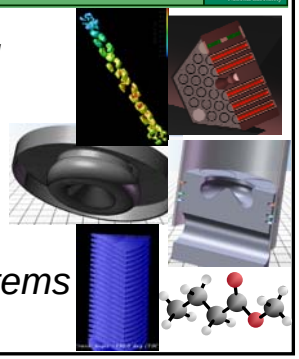
Advanced Engines & Designs
Advanced Fuels
- Available
- Economical
- Efficient
- Low Environmental Impact

Collaborative Team

http://dcpl.ornl.gov

Digital Chemical Processes Laboratory

Modeling and simulation of transport processes w/ emphasis on chemical systems



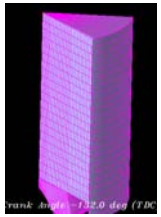
ORNL Research Staff:
Valmor de Almeida
Joanna McFarlane
Bill Steele

- Two national laboratories
- Two universities
- One DOE research center

http://www.erc.wisc.edu

Engine
Research
Center

Coupled modeling and experimental program for IC engines



Prof. Rolf Reitz
Youngchul Ra (post-doc)
Jessica Brakora (grad student)

http://feerc.ornl.gov

Fuels, Engines, and Emissions Research Center

Detailed IC engines characterization facility

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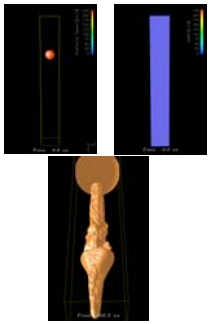
Scott Sluder
Kalyan Chakravarthy
Stuart Daw

http://frontier.ams.sunysb.edu

Front tracking computational fluid dynamics. Emphasis on diesel spray simulation

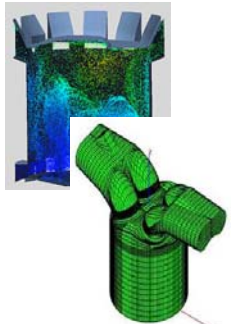


Profs. Xiaolin Li & Jim Glimm
Xingtao Liu & Wurigen Bo(students)

http://www.lanl.gov/orgs/t/t3/codes

Los Alamos National Laboratory
T-3 Computational Fluid Dynamics

CFD Kiva-4 development for IC engines



LANL Research Staff:
David Torres

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Student participants in Summer 2007

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Gohkan Yesilyurt
KC Cushman
Refuyat Ashen

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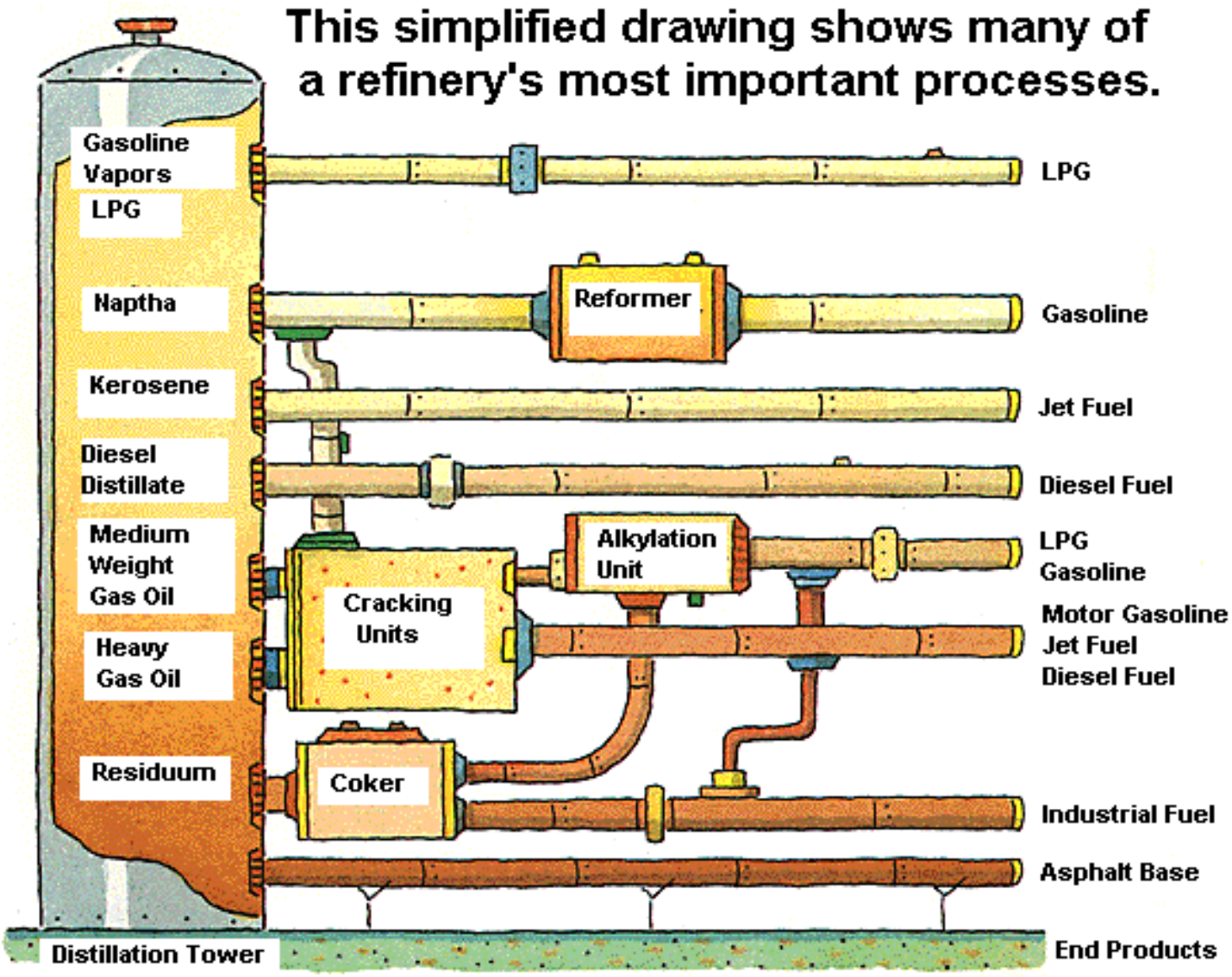

http://www.eia.doe.gov/kids/energyfacts/sources/non-renewable/refinery.html