Optimization of the Molecular Structure of Low-Greenhouse-Gas-Emission Synthetic Oxygenated Fuels for Improved Combustion and Pollutant Emission Characteristics of Diesel Engines

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Optimization of Synthetic Oxygenated Fuels

(a.k.a The Oxyfuels Project)

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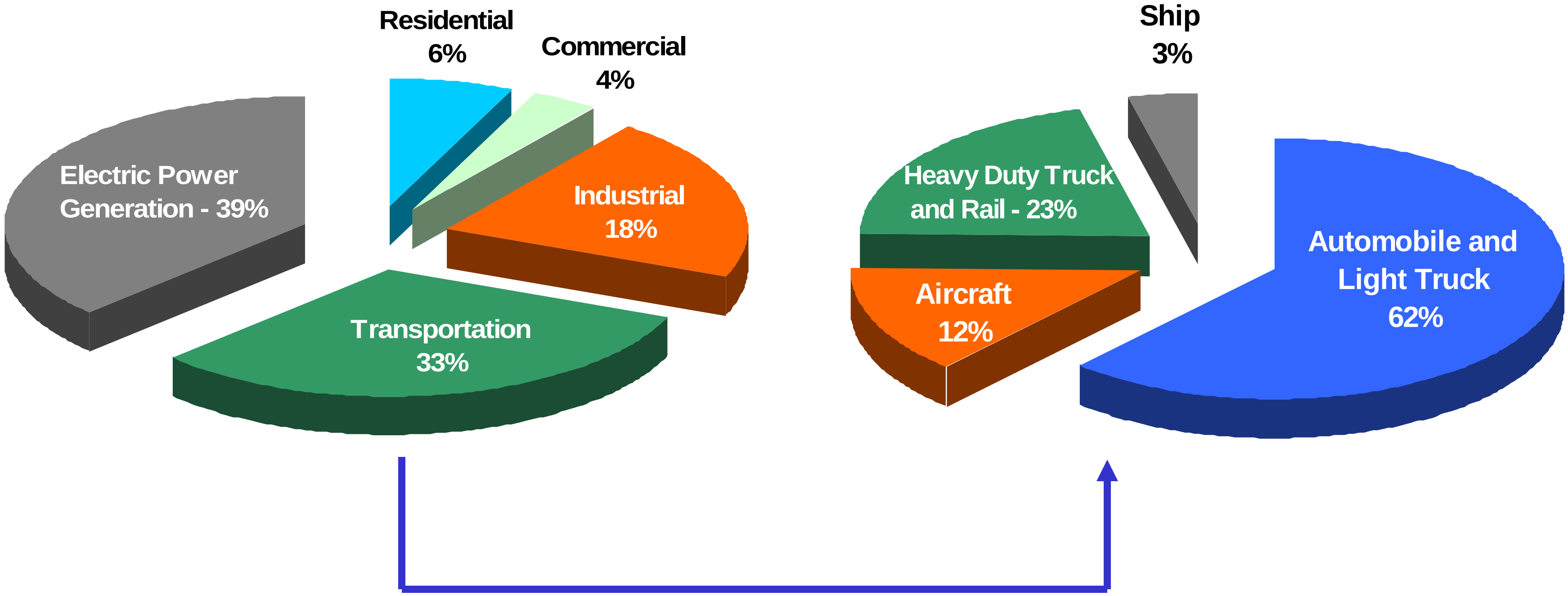
Presentation Outline

- Background and Motivation – Why Oxyfuels?
- Project Goals
- Research Tasks and Approach
- Results

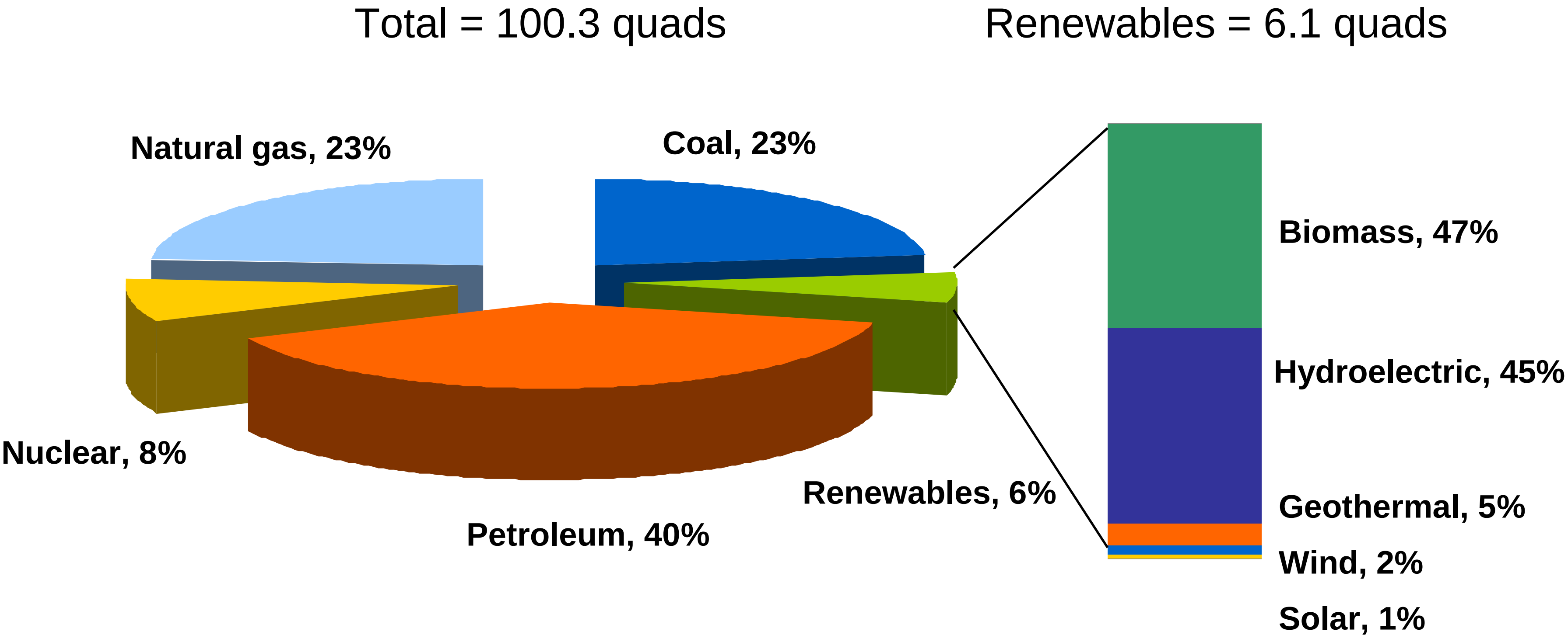
U. S. Combustion-Generated CO_2 Emissions

Total = 1631 x 10^9 kg C/yr (2005)

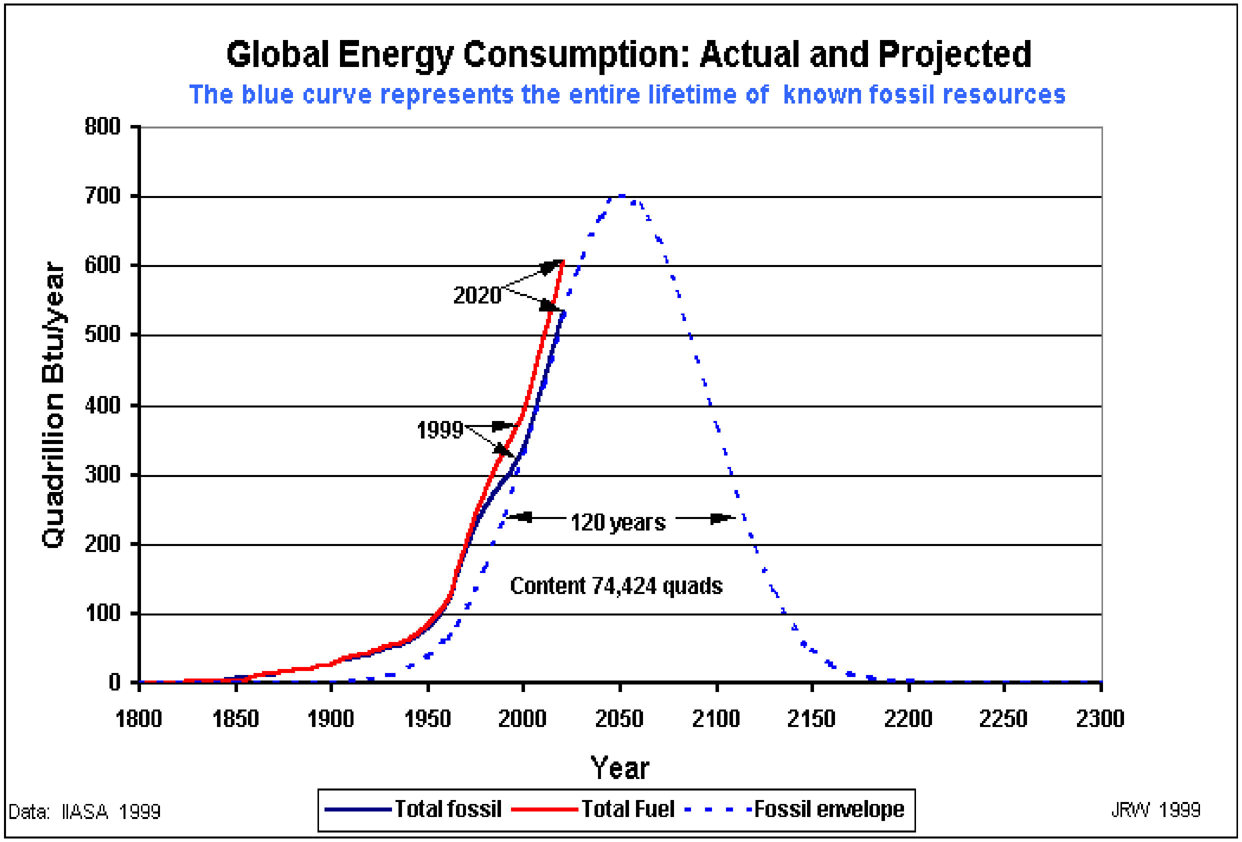


EIA 2006

U.S. Energy Consumption 2004

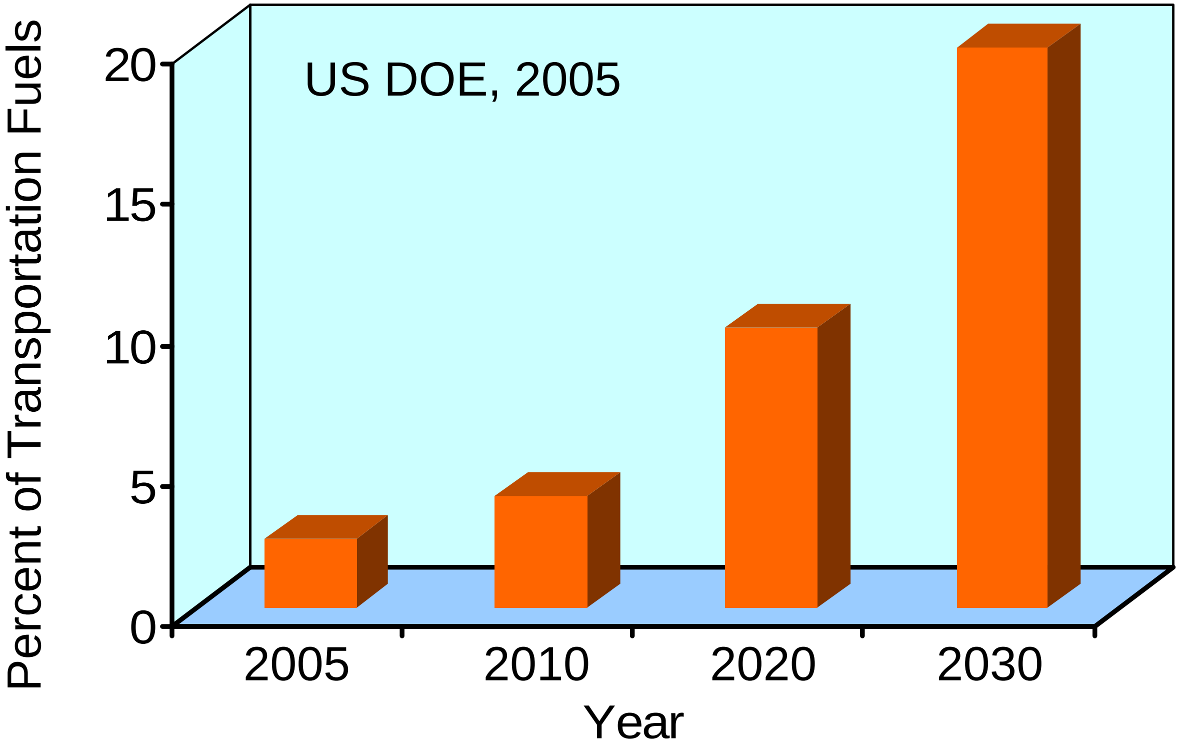


EIA, 2005



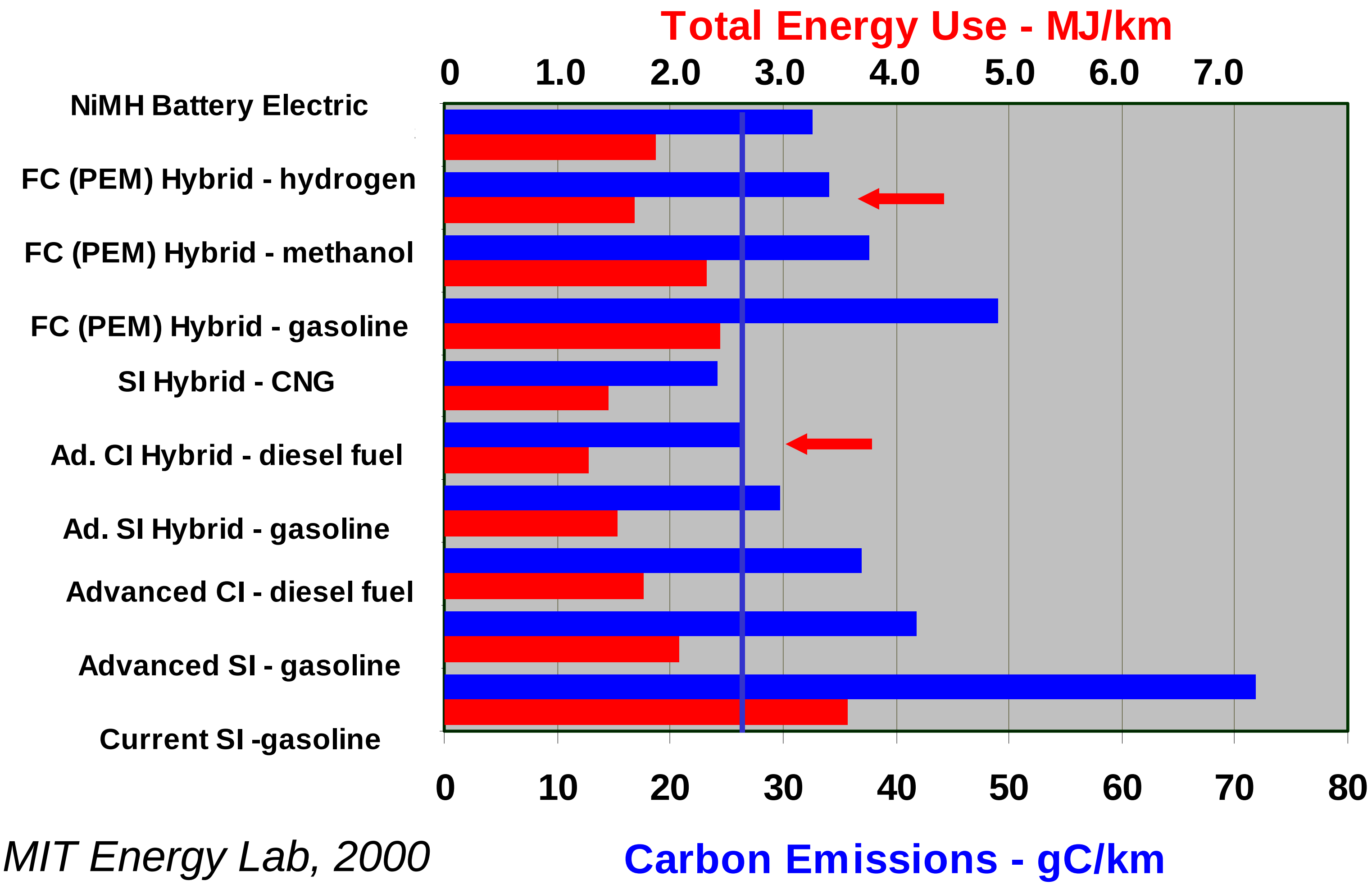
- Fossil fuels will be a dominant energy carrier in the 21st century.

Projected Growth in Bio-Transportation Fuels

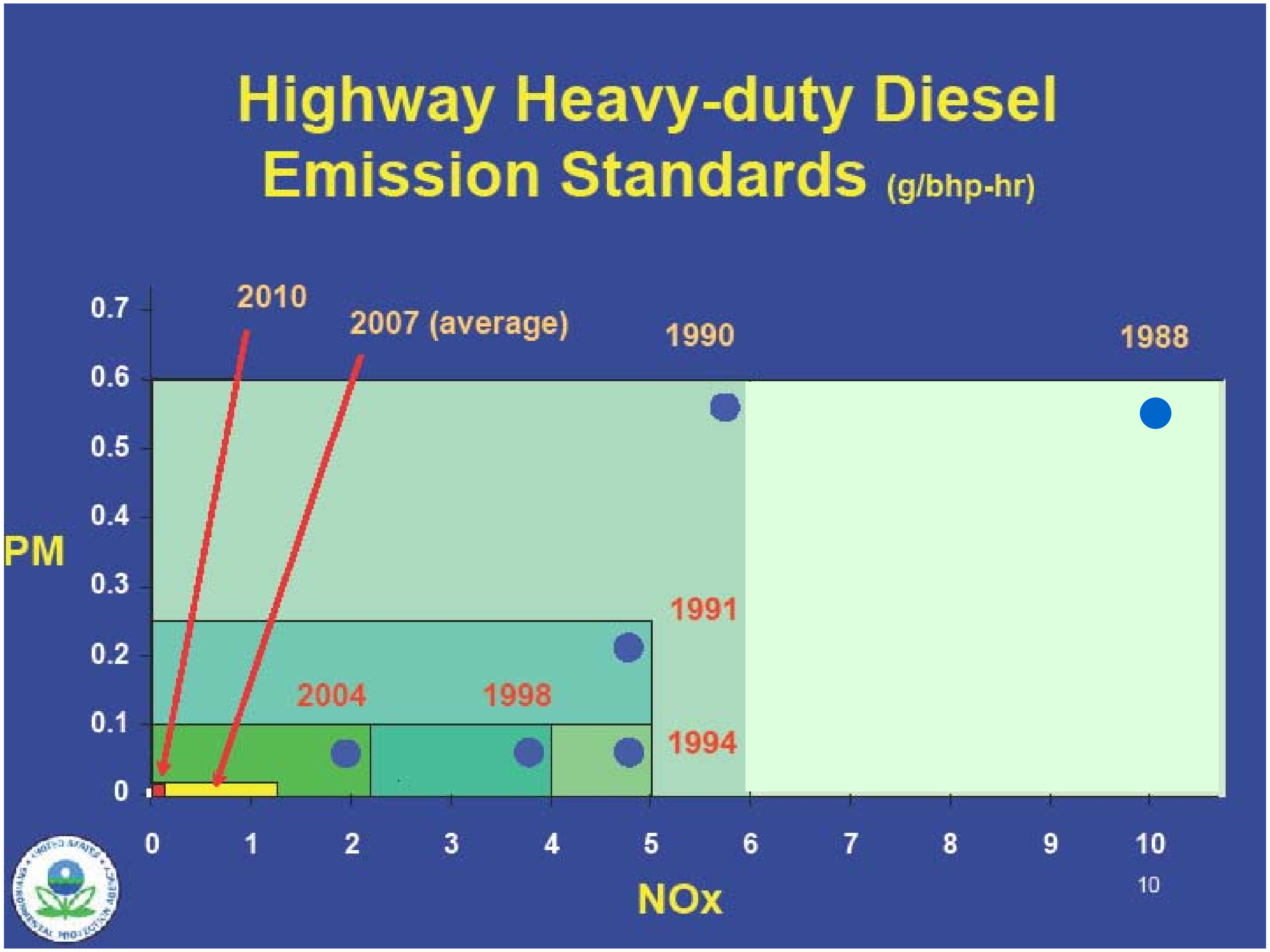


- Biomass may become an increasingly important energy carrier.

Automotive Engine/Fuel Performance



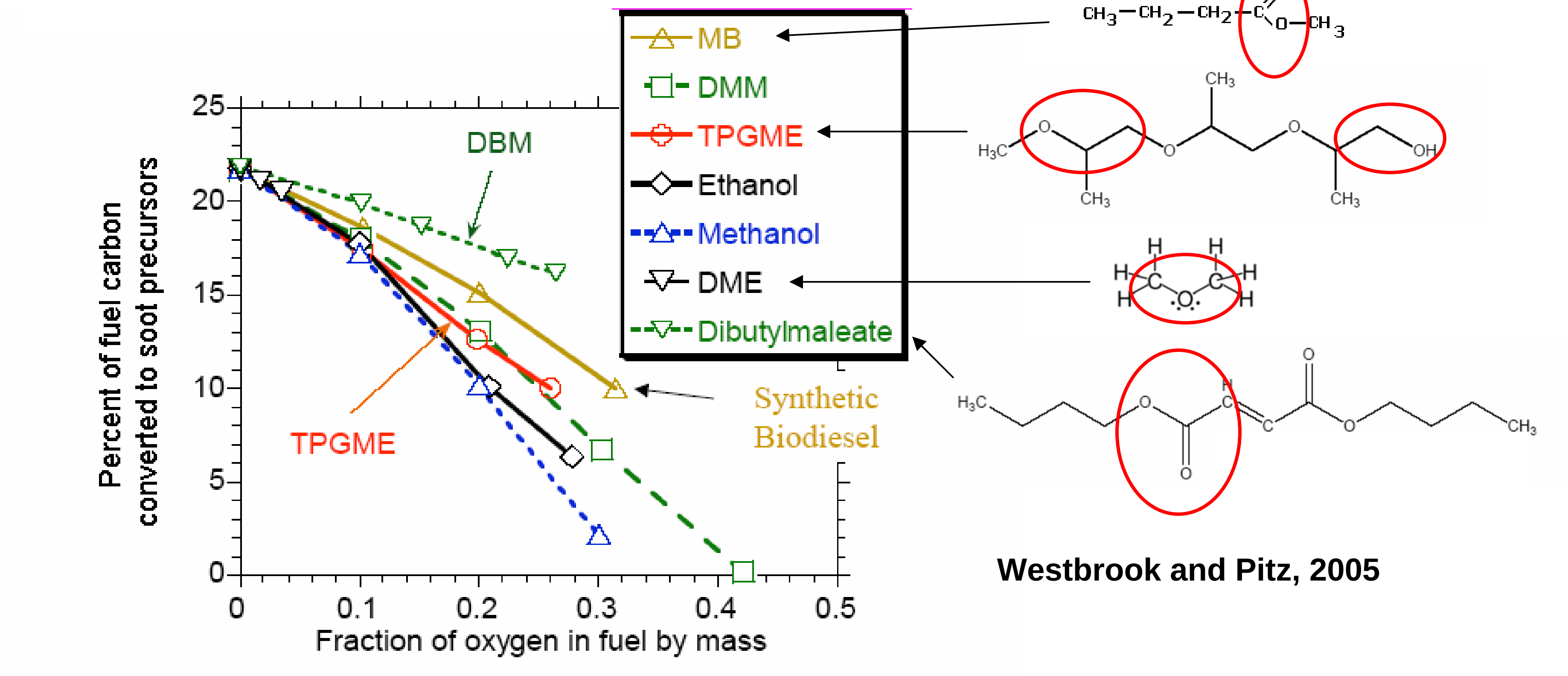
MIT Energy Lab, 2000


Highway Heavy-duty Diesel Emission Standards (g/bhp-hr)
2010
2007 (average)
1990
1988
1991
2004
1998
1994
PM
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
5
6
7
8
9
10
NOx
10

Mitigation of GHG emissions from transportation sources will require implementation of a variety of strategies:

- improvements in overall efficiency of vehicle/fuel systems, such as hybrid and new high-efficiency diesel engines
- use of synthetic or renewable fuels to replace or supplement petroleum-based fuels or as performance-improving additives

- An attractive class of synthetic fuels is oxygenated liquid fuels that may be synthesized from a variety of feedstocks.
- Oxygenated fuels are especially attractive for use in advanced diesel engines and diesel-hybrids because of the inherently high thermal efficiencies of these engines.
- In addition, these fuels offer significant potential for reduction in particulate emissions from diesel engines.



Westbrook and Pitz, 2005

- How well an oxygenated fuel works to reduce soot depends on its molecular structure.

Project Goals

- Explore the impact of oxygenated fuel structure on combustion and emissions performance under diesel combustion conditions
  - determine fuel structures that will minimize pollutant emissions (especially soot) and provide suitable ignition properties
  - identify processing strategies to produce synthetic oxygenated hydrocarbons from various feedstocks on a refinery scale

Research Tasks

- Task 1a: Experimentally investigate the combustion and emissions characteristics of oxygenated fuels using two high-pressure combustion facilities – shock tube and flow reactor.
- Task 1b: Develop and validate detailed chemical kinetics models for these fuels to provide insight into the mechanisms by which fuel structure impacts combustion behavior.

Research Tasks

- Task 2: Use advanced CFD models to examine effects of fuel structure and in-cylinder processes on soot and NO_x formation and ignition in diesel engine environments.

- Task 3: Identify functionalities most suitable for clean-burning diesel fuels.

- Task 4: Explore strategies for production of candidate oxygenated fuels on a large-scale basis from a variety of feedstocks.

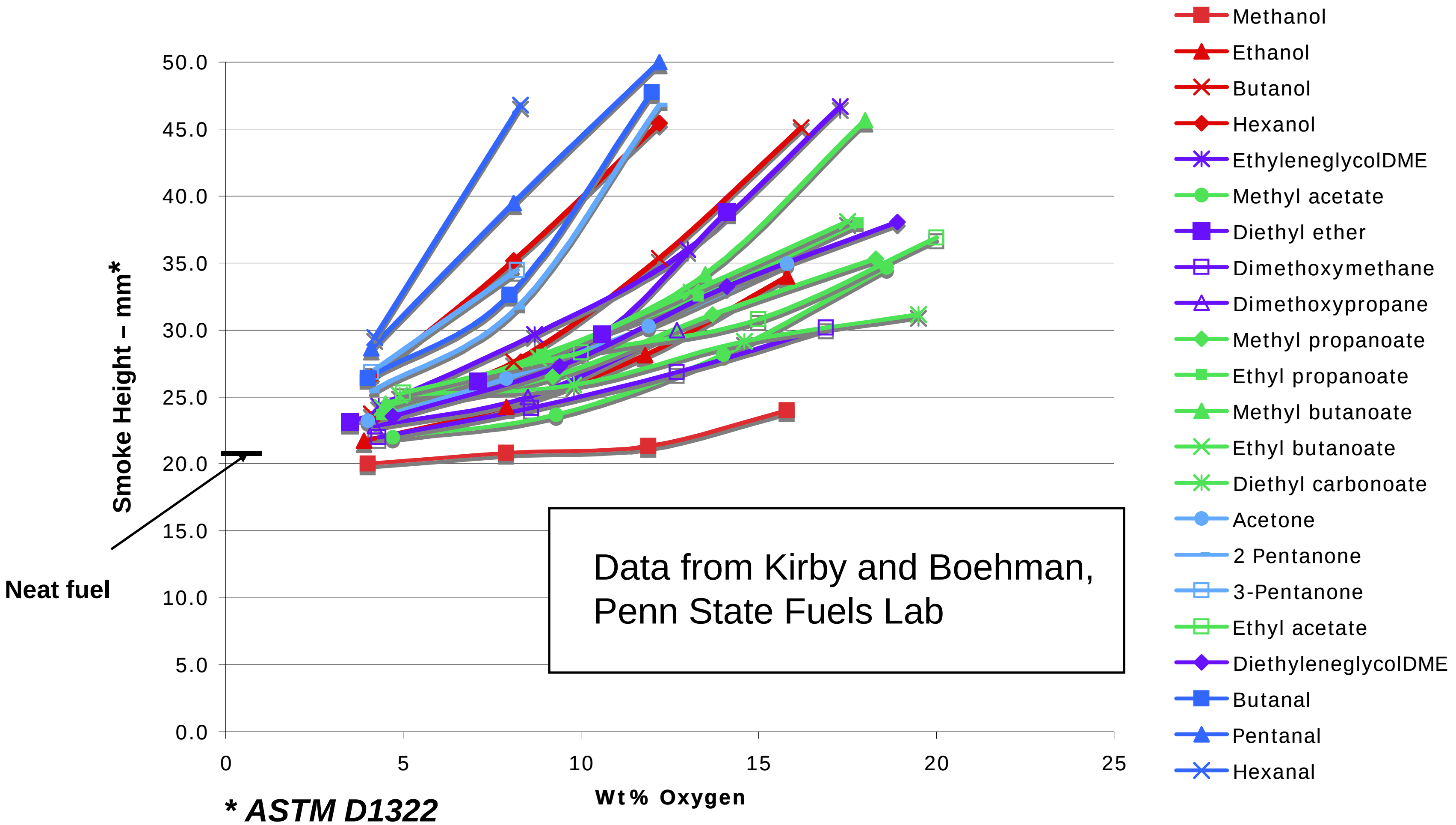
Screening Structures for Effectiveness in Soot Suppression

	Compound	C	H	O	N	MW	MW/O
Alcohols							
1	Methanol	1	4	1	0	32	32
2	Ethanol	2	6	1	0	46	46
3	Butanol	4	10	1	0	74	74
4	Hexanol	6	14	1	0	102	102
5	Octanol	8	18	1	0	130	130
Ethers							
6	Dimethyl ether	2	6	1	0	46	46
7	Diethyl ether	4	10	1	0	74	74
8	Dimethoxymethane	3	8	2	0	76	38
9	2,2-Dimethoxy propane	5	12	2	0	104	52
10	Ethyleneglycol dimethyl ether	4	10	2	0	90	45
11	Diethyleneglycol methyl ether	5	12	3	0	120	40
12	Triehtyleneglycol methyl ether	7	16	4	0	164	41
Esters							
13	Methyl acteate	3	6	2	0	74	37
14	Methyl propanoate	4	8	2	0	88	44
15	Ethyl propanoate	5	10	2	0	102	51
16	Methyl butanoate	5	10	2	0	102	51
17	Ethyl butanoate	6	12	2	0	116	58
18	Diethyl carbonoate	5	10	3	0	118	39.7
19	Methyl soyate						

	Compound	C	H	O	N	MW	MW/O
Ketones							
20	Acetone	3	6	1	0	58	58
21	3-Pentanone	5	10	1	0	86	86
22	2-Pentanone	5	10	1	0	86	86
23	Acetophenone	8	8	1	0	120	120
Aldehydes							
24	Butanal	4	8	1	0	72	72
25	Pentanal	5	10	1	0	86	86
26	Hexanal	6	12	1	0	100	100
Misc.							
27	2-Ethylhexyl nitrate	8	17	3	1	161	53.7
28	Di-t-butyl peroxide	8	18	2	0	146	73
29	2-Nitropentane	5	11	2	1	103	51.5
30	Amyl nitrate	5	11	3	1	119	39. 7
31	Amyl nitrite	5	11	2	1	103	51.5

Task 1

Screening Structures for Effectiveness in Soot Suppression



Data from Kirby and Boehman, Penn State Fuels Lab

*** ASTM D1322***

Task 1

Screening Structures for Effectiveness in Soot Suppression

- Effectiveness of soot suppressing additives depends on the mass of oxygen in the fuel blend and on molecular structure

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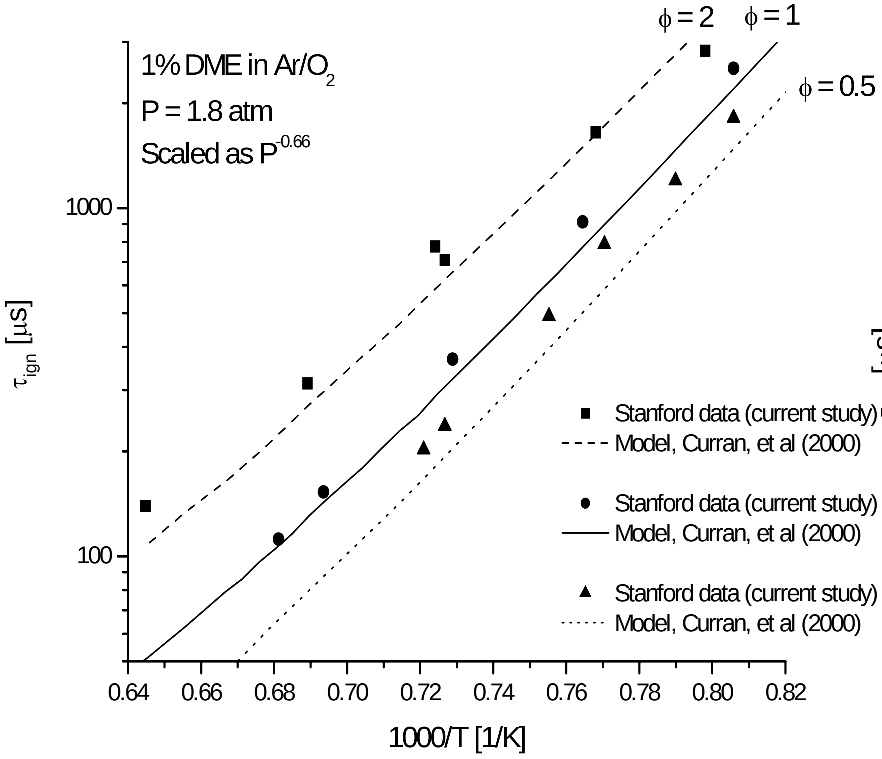
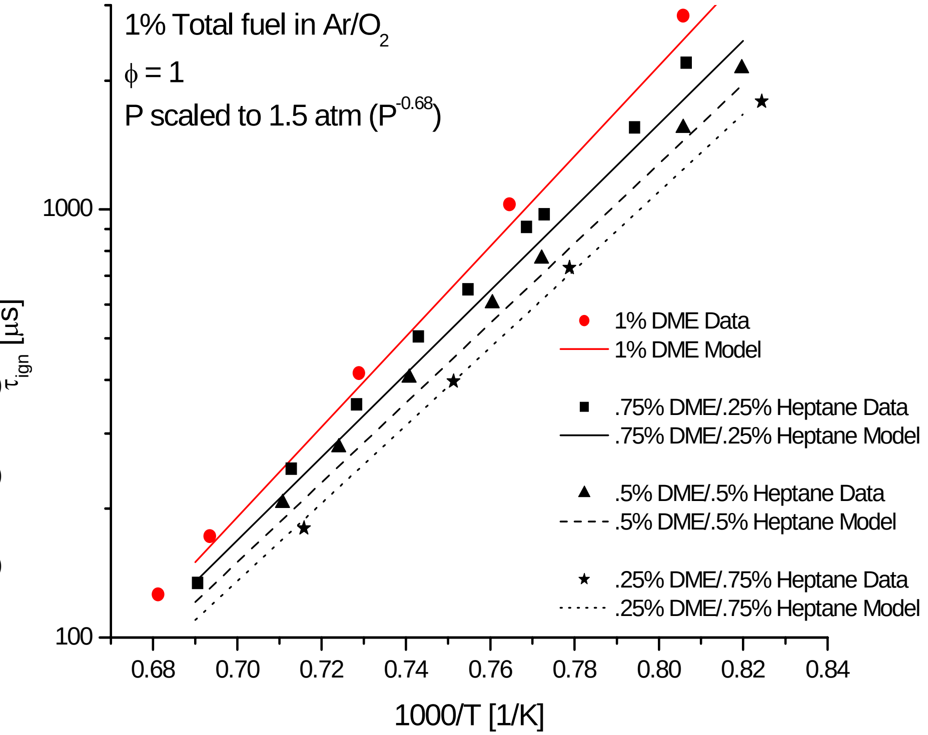
- Effectiveness of soot suppressing additives depends on the mass of oxygen in the fuel blend and on molecular structure

- The smoke point tests indicate that:
  - for a given oxygen functionality the effectiveness increases with chain length
  - effectiveness scales as aldehydes >> ketones > ethers ≈ esters > alcohols

Task 1

Ignition Behavior of DME and DME-Heptane mixtures

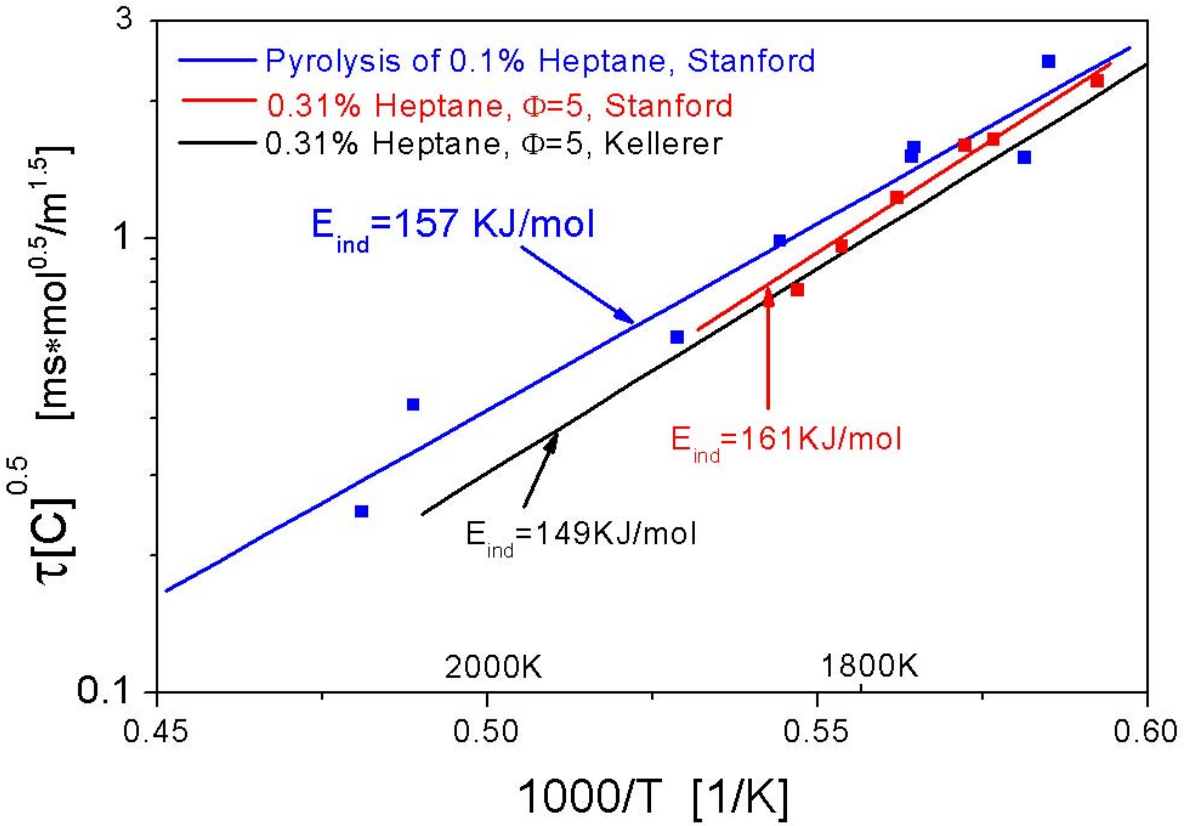




Task 1

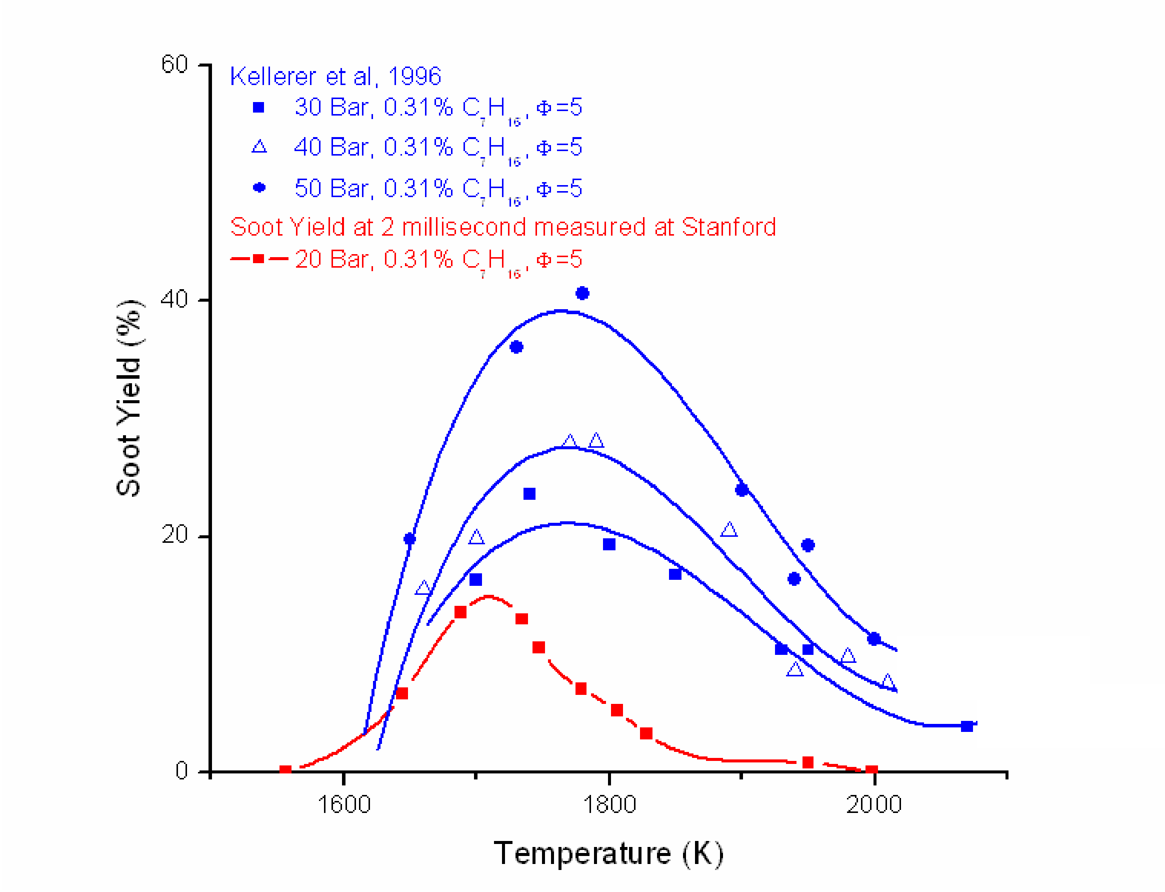
Sooting Characteristics of Heptane and DME-Heptane Mixtures

Soot Induction Times



Sooting Characteristics of Heptane and DME-Heptane Mixtures

Fraction of Fuel Carbon Converted to Soot



Task 2

CFD Modeling of Diesel Engine Combustion

- Assess effect of fuel structure on emissions in Diesel engine combustion and examine fuel optimization
- Required computational capabilities
  - LES and RANS
  - Immersed boundary method for complex geometry
  - Surrogate fuels
  - Advanced combustion models
  - Advanced soot models

Task 2

CFD Modeling of Diesel Engine Combustion

Strategy

Based on existing LES codes

- Required accuracy and numerical methods
- Multi-phase models in place

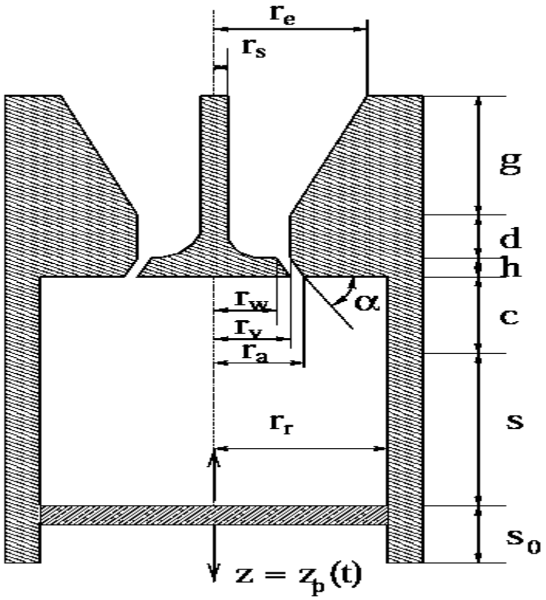
- Strategy for moving and complex geometry
  - Moving meshes for moving piston
  - Immersed boundary for valves and possibly piston bowl

Task 2

CFD Modeling of Diesel Engine Combustion

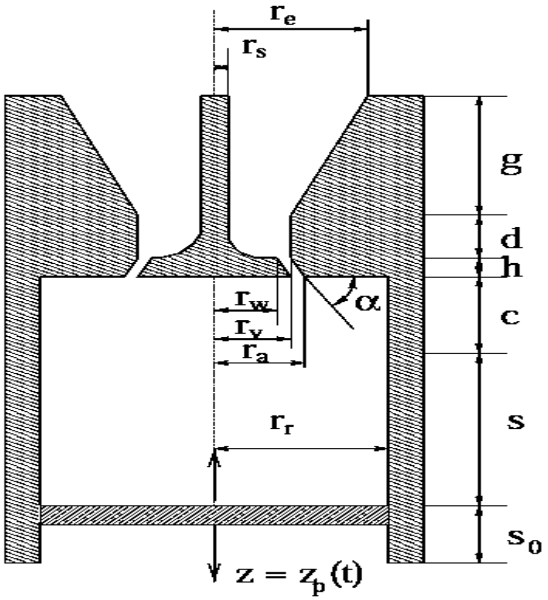
Current Work

- Interfacing IB implementation with STL files
  - STereoLithography: Industry standard for geometry representation
- Finalize compressible solver
- More test cases: Realistic engine simulations



Task 2

CFD Modeling of Diesel Engine Combustion

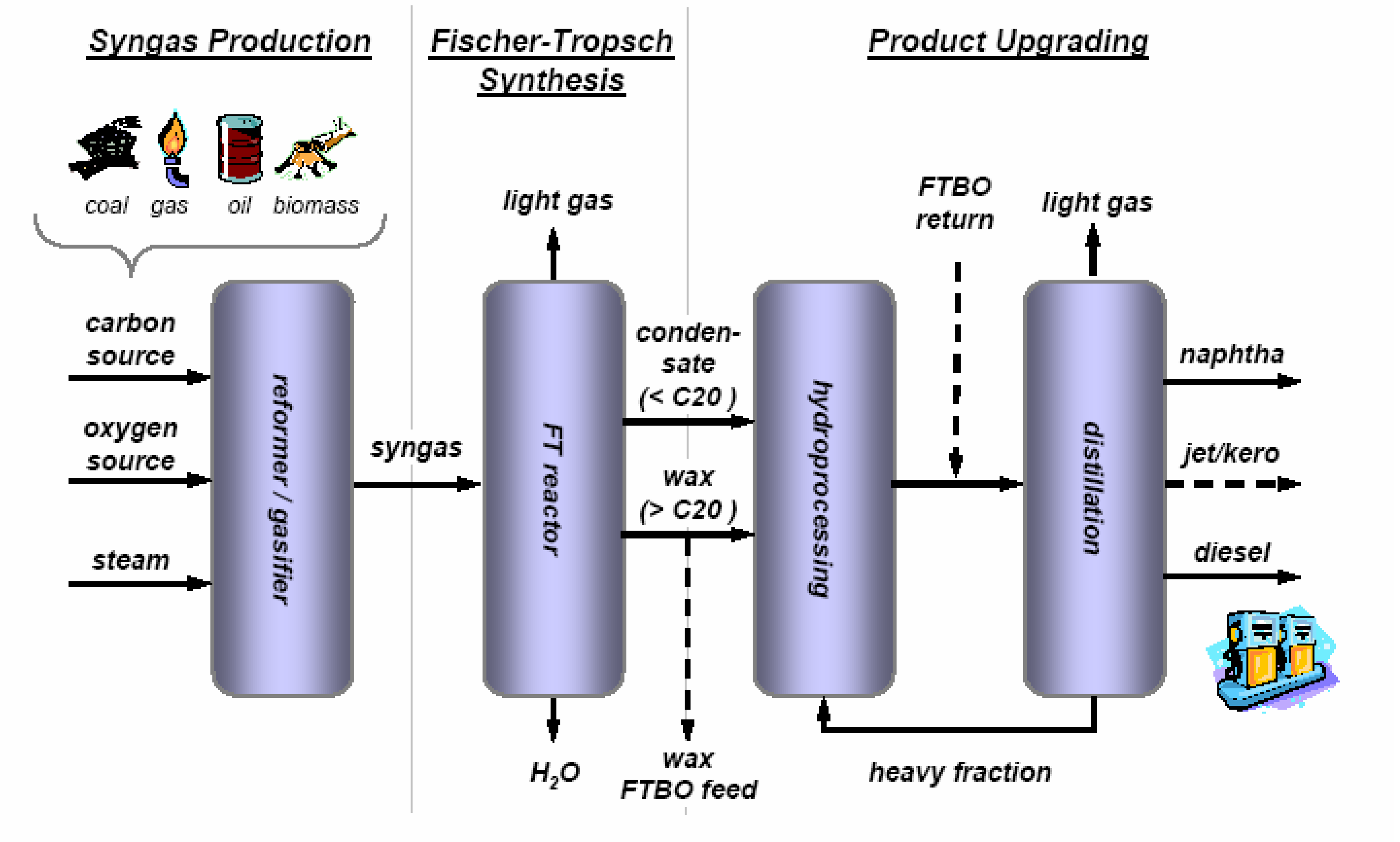


Posters

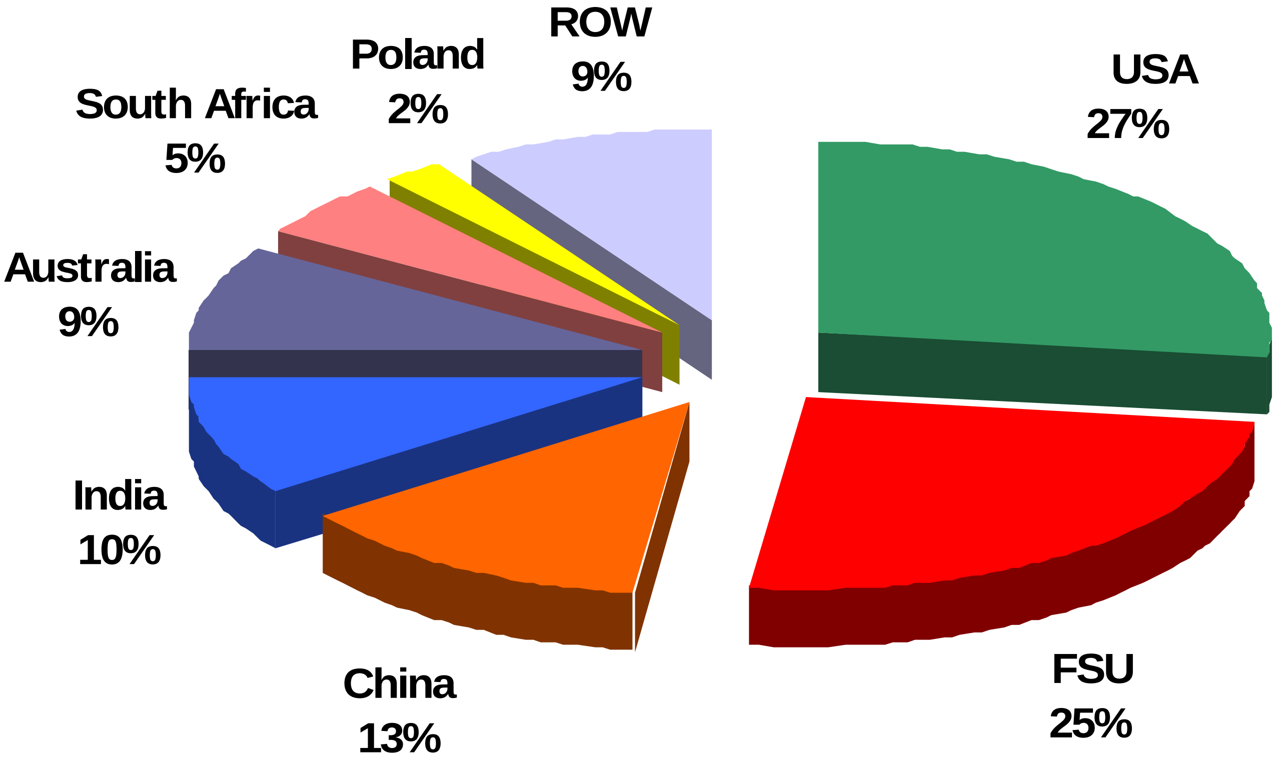
- Effect of Pressure on the Oxidation of Hydrocarbon Fuels under Flameless Oxidation Conditions – Walters and Bowman: #9
- Shock Tube Studies of Soot Formation in Heptane-Air and Heptane-DME-Air Mixtures - Hong, Davidson and Hanson: #2
- Ignition Delay Times of DME/O_2/Ar and DME/Heptane/O_2/Ar Mixtures – Cook, Davidson and Hanson: #1
- Advanced Modeling and Optimization of Diesel Engines – Shashank, Wang, Iyengar and Pitsch: #10

"The use of vegetable oils for engine fuels may seem insignificant today. But such oils may become in the course of time as important as the petroleum and coal tar products of the present time"
Rudolph Diesel, 1912

Generic RTL Synfuels Process



Estimated Recoverable Coal Reserves
(1,000 billion tons)



BP Global 2005