Modeling Strategies for Advanced Automotive Engine and Fuels Research

Workshop on
Chemkin in Combustion

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This is a very exciting period for combustion modeling

- Computer power is growing rapidly
  - Combustion models on supercomputers
  - Single CPU capabilities are growing
- Multi-dimensional combustion codes are including more detail in more submodels
- Chemical kinetic mechanisms are being published for fuels of much greater complexity and size than ever

Practical combustion problems are complex

- Engines are 3D, complicated
- 3D CFD calculations are expensive
- Chemical kinetics calculations are expensive
- Radiation transport calculations are expensive
- Liquid spray, multiphase problems are expensive
- Particulate, soot calculations are expensive

- Expensive means computer time, computer size, model development time
- Usually significant model simplifications are made

Combustion Modeling Challenges

- Many past models have avoided a full 3D, multiphase, detailed kinetics, radiation transport, complex geometry, treatment
- We have emphasized detailed kinetics of fuel reactions, with 0D (ignition) or 1D (laminar flame) geometry.
- Clever formulation of these 0D and 1D problems has answered some very challenging engine questions
- We have extended chemical models to mechanisms many times more complex than in the past

Causes and implications of flammability limits

- Law and Egolfopoulos for atmospheric pressure flames
- Basic concept is competition between 2 reactions

$$H + O_2 = O + OH \qquad R1$$
$$H + O_2 + M = HO_2 + M \qquad R2$$

Rates of these reactions have different temperature and pressure dependence, and for atmospheric pressure, lean limit occurs at adiabatic flame temperature where R2 becomes faster than R1

Currently a topic of considerable attention at high pressure

Chemical classes being modeled in combustion
モデル化の対象となる化学物質の系統

Hydrocarbons

Methane, ethane, paraffins through decane

Natural gas

Alcohols (e.g., methanol, ethanol, propanol

Other oxygenates (e.g., dimethyl ether, MTBE, aldehydes)

Automotive primary reference fuels for octane and cetane ratings

Aromatics (e.g., benzene, toluene, xylenes, naphthalene)

Others

Oxides of nitrogen and sulfur (NOx, SOx)

Metals (Aluminum, Sodium, Potassium, Lead)

Chlorinated, brominated, fluorinated species

Silane

Air toxic species

Chemical warfare nerve agents

Kinetic modeling covers a wide range of systems

Types of systems studied

Flames
Shock tubes
Detonations
Pulse combustion
Flow reactors
Stirred reactors
Supercritical water oxidation
Engine knock and octane sensitivity
Flame extinction
Diesel engine combustion
Combustion of metals
CW agent chemistry
Catalytic combustion
Material synthesis
many others . . . .

Waste incineration
Kerogen evolution
Oxidative coupling
Heat transfer to surfaces
Static reactors
Ignition
Soot formation
Pollutant emissions
Cetane number
Liquid fuel sprays
HE & propellant combustion
Gasoline, diesel, aviation fuels
CVD and coatings
Chemical process control

Laminar flames in quenching problems

- Bulk quenching in direct injection stratified charge (DISC) engine
- Bulk quenching due to volume expansion in lean mixtures
- Flame quenching at lean and rich flammability limits
- Flame quenching on cold walls and unburned hydrocarbon emissions from internal combustion engines
- Flame inhibition
- Soot production and reduction

Combustion chemistry modeling needs

- Chemistry models for transportation fuels
- Extend chemistry models for these fuels by adding complexity and realism with new chemical components
- Our chemistry modeling needs are somewhat incremental, and we must validate each new component species as it is added to the overall model

Chemical Kinetic Model

Contains a large database of:

- Thermodynamic properties of species
- Reaction rate parameters

Size of mechanism grows with molecular size:

Fuel:	H_2	CH_4	C_3H_8 (Propane)	C_6H_{14} (Hexane)	$C_{16}H_{34}$ (Cetane)
Number of species:	7	30	100	450	1200
Number of reactions:	25	200	400	1500	7000

Most fuels of interest consist of complex mixtures of many chemical species

- Natural gas
- Gasoline
- Diesel
- Jet fuel
- Rocket fuel
- These fuels contain many components that do not have detailed mechanisms
  - Gasoline, diesel and jet fuel have hundreds of components (even natural gas)

and JP5. The fuel vapors had average molecular weights ranging from 114 to 132 and hydrogen to carbon ratios ranging from 1.90 to 196. The LEL equivalence ratios of jet fuel vapors are similar to those of pure hydrocarbons of equal molecular weight. The fuel tank explosion hazard is still significant when the vapor-space to liquid-fuel ratio is as high as 400.

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	Vapor Concentrations		
HYDROCARBON SPECIES	JP-8 ppm	Jet A ppm	JP-5 ppm
Isobutene	18.69	0.00	0.00
n-Butane	29.59	28.16	5.25
Isobutane	26.14	17.38	5.57
n-Pentane	28.47	17.38	7.35
2,2-Dimethyl Butane	6.51	0.00	0.00
Cyclo-Pentane	6.61	5.11	0.00
2,3-Dimethyl Butane	12.09	4.67	0.00
2-Methyl Pentane	48.71	35.82	7.61
3-Methyl Pentane	35.62	28.16	9.87
n-Hexane	90.12	59.51	22.61
Methyl Cyclo-Pentane	112.27	87.05	20.64
2,4-Dimethyl Pentane	13.37	6.14	0.00
2,2,3-Trimethyl Butane	3.78	0.00	0.00
Benzene	68.01	29.44	10.15
3,3-Dimethyl Pentane	11.13	2.21	0.00
Cyclo-Hexane	238.62	103.82	30.89
2-Methyl Hexane	145.41	107.38	20.36
3-Methyl Hexane	95.79	82.69	14.65
trans 1,3-Dimethyl Pentane	37.78	56.65	7.00
cis 1,3-Dimethyl Pentane	36.24	55.52	7.44
trans 1,2-Dimethyl Pentane	64.02	98.97	17.00
3-Ethyl Pentane	5.68	0.00	0.00
n-Heptane	251.53	185.09	62.63
Methyl Cyclohexane	803.03	401.89	166.21
1,1,3-Trimethyl Cyclopentane	26.39	37.99	7.35
2,2-Dimethyl Hexane	16.63	1.99	0.00
Ethyl Cyclo-Pentane	28.55	37.45	12.27
2,2,3-Trimethyl Pentane	3.31	0.00	0.00
2,5-Dimethyl Hexane	26.75	16.92	4.70
2,4-Dimethyl Hexane	33.73	22.88	6.73
1,2,4-Trimethyl Cyclopentane	30.06	52.77	12.76
3,3-Dimethyl Hexane	18.07	3.74	2.35
1,2,3-Trimethyl Cyclopentane	29.21	57.61	13.70
Iso-Octene	4.87	2.52	2.32
Toluene	410.25	178.89	118.02
Iso-Octene	16.37	15.48	5.06
2,3-Dimethyl Hexane	30.79	20.68	8.49
2-Methyl-3-Ethyl Pentane	6.74	6.65	3.03
2-Methyl Heptane	184.76	136.13	53.82
4-Methyl Heptane	81.35	52.36	24.80
Iso-Octene	0.00	5.93	0.00
Iso-Octene	0.00	4.92	0.00
cis 1,4-Dimethyl Cyclohexane	260.98	159.56	72.60
3-Methyl Heptane	160.82	117.65	43.23
3-Ethyl Hexane	144.10	82.76	38.87
1,1-Dimethyl Cyclohexane	59.14	22.55	13.32
trans 1-Ethyl-3-Methyl Cyclopentane	23.68	32.00	12.81
cis 1-Ethyl-2-Methyl Cyclopentane	18.45	32.60	14.80
cis 1-Ethyl-3-Methyl Cyclopentane	26.17	42.92	24.10
n-Octene -1	6.19	5.72	4.37
trans 1,2-Dimethyl Cyclohexane	154.00	91.66	51.45
Iso-Octene	0.00	3.13	0.00
trans 1,4-Dimethyl Cyclohexane	88.78	82.17	32.08
n-Octane	497.50	241.00	170.96
Iso-Nonene	4.02	6.10	2.85

There are 10 more pages of species concentrations

Iso-Nonene	4.00	8.73	2.06
2,2,4-Trimethyl Hexane	0.00	1.46	0.00
2,3,5-Trimethyl Hexane	6.41	5.20	2.49
2,2-Dimethyl Heptane	7.22	0.00	0.00
cis 1,2-Dimethyl Cyclohexane	3.32	13.66	5.37
2,4-Dimethyl Heptane	29.10	4.90	3.75
Iso-Nonene	32.04	22.11	11.47
Iso-Nonene	43.24	30.41	17.23
Unidentified	6.28	5.71	1.75
Ethyl Cyclo-Hexane	266.85	175.58	140.31
2-Methyl-4-Ethyl Hexane	3.50	2.03	0.00
2,6-Dimethyl Cyclohexane	91.75	61.64	47.64
Iso-Nonene	0.00	8.35	0.00
1,1,3-Trimethyl Cyclohexane	88.04	105.67	64.05
Nonene	25.45	20.80	10.54
2,5-Dimethyl Heptane	86.97	46.78	23.50
Iso-Nonene	34.41	9.67	6.26
Iso-Nonane	0.00	13.95	6.48
3,3-Dimethyl Heptane	10.84	25.34	11.52
Iso-Nonene	5.26	14.82	6.01
Ethyl Benzene	106.97	74.18	70.47
1,2,4-Trimethyl Cyclohexane	15.52	32.00	20.47
Isononene	65.71	83.73	30.32
2,3,4-Trimethyl Hexane	3.48	5.60	4.72
Isononene	2.48	0.00	0.00
3,3,4-Trimethyl Cyclohexane	3.43	10.54	1.63
meta-Xylene	439.45	134.95	160.21
para-Xylene	124.56	45.32	47.37
2,3-Dimethyl Heptane	69.23	38.37	35.94
3,5-Dimethyl Heptane	8.73	6.46	3.60
3,4-Dimethyl Heptane	39.46	21.67	19.49
3-Methyl-3-Ethyl Hexane	18.52	19.40	8.82
Isononene	2.54	7.41	2.96
4-Methyl Octane	68.02	65.70	37.01
2-Methyl Octane	117.21	87.71	49.14
Iso-Nonane	17.61	17.20	11.67
3-Ethyl Heptane	36.82	45.69	20.15
3-Methyl Octane	126.82	130.04	64.67
1,2,4-Trimethyl Cyclohexane	0.00	3.21	2.66
1,1,2-Trimethyl Cyclohexane	0.00	13.38	0.00
ortho-Xylene	235.28	82.34	112.71
Isononene	0.00	14.75	10.17
Isononene	1.73	17.32	5.58
Isononene	3.79	3.65	1.69
Isononane	22.13	47.40	33.14
1-Ethyl-4-Methyl Cyclohexane	90.36	98.14	58.69
Isononane	73.47	60.57	43.02
Nonene-1	1.85	8.98	6.97
Isobutyl Cyclopentane	6.51	17.66	9.59
Isononane	0.00	1.70	0.00
cis Nonene-3	22.68	10.99	9.51
Isononane	0.00	4.60	1.77
n-Nonane	449.86	313.15	290.63
trans Nonene-2	60.82	78.13	47.69
Isononene	4.16	0.00	30.68
1-Methyl-2-Propyl Cyclopentane	31.60	24.13	23.01
C10 Iso-paraffin	0.00	0.00	3.68
Isopropyl Benzene	22.23	19.95	26.85
t-Butyl Pentane	2.25	2.86	0.00
Isononene	7.92	11.35	6.15
Isononene	44.66	56.22	49.60
Isopropyl Cyclohexane	40.39	37.42	36.42

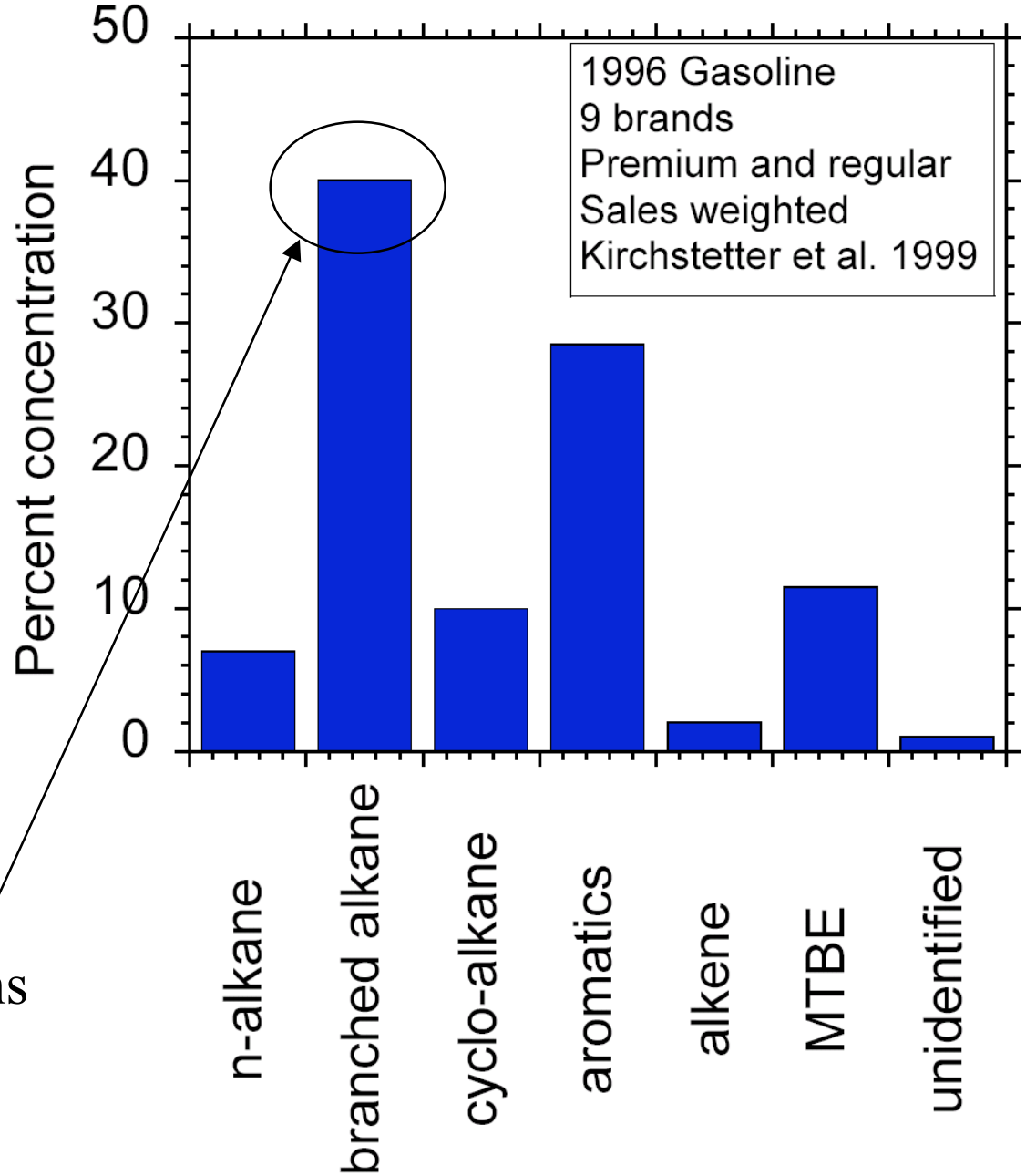
2,2-Dimethyl Octane	29.59	32.22	19.33
2,4-Dimethyl Octane	27.45	20.14	16.91
Isodecane	0.00	6.38	1.50
1-Methyl-4-Isopropyl Cyclohexane	3.65	2.71	2.67
s-Butyl Cyclopentane	13.08	28.59	13.99
2,6-Dimethyl Octane	23.57	28.04	11.37
2,5-Dimethyl Octane	74.50	78.06	79.83
Isodecane	10.88	21.48	11.69
Butyl Cyclopentane	12.93	17.87	6.46
Propyl Cyclohexane	22.75	35.18	26.79
Isodecane	0.00	16.27	9.11
3,5-Dimethyl Octane	51.42	89.34	70.09
1-Methyl-2-Ethyl Cyclohexane	24.76	18.15	20.74
Isodecane	6.83	6.11	8.63
Isodecene	5.57	29.31	10.88
n-Propyl Benzene	55.70	70.21	69.12
3,6-Dimethyl Octane	36.82	63.33	50.22
3-Methyl-5-Ethyl Heptane	0.00	12.57	6.60
Isodecene	6.33	18.01	10.24
Isodecene	5.11	11.47	5.66
meta Ethyl Toluene	83.33	72.54	74.71
para Ethyl Toluene	46.13	64.58	50.25
1,3,5-Trimethyl Benzene	123.63	140.06	111.93
2,3-Dimethyl Octane	3.20	14.85	1.40
Isodecane	1.81	22.95	13.16
5-Methyl Nonane	19.22	48.92	21.85
4-Methyl Nonane	37.93	85.43	54.49
2-Methyl Nonane	41.16	91.11	53.04
ortho Ethyl Toluene	23.71	26.83	43.66
3-Ethyl Octane	3.78	3.73	4.12
Napthene	9.86	28.20	13.57
Isodecane	2.44	5.22	9.43
Isodecane	2.28	0.00	0.00
3-Methyl Nonane	48.31	105.77	66.17
Isodecane	0.00	23.16	20.20
Isodecene	8.04	10.99	3.79
Isodecane	15.59	31.17	26.52
Isodecane	4.82	14.17	8.20
1,2,4-Trimethyl Benzene	103.36	116.35	114.54
Isodecane	16.85	41.84	33.94
Isodecane	11.77	33.82	33.89
Isodecane	18.24	42.34	40.71
Isobutyl Cyclohexane	1.98	16.90	10.48
Isodecane	4.34	7.71	9.02
Isodecane	2.22	14.52	10.86
Decene-1	2.23	8.96	7.61
Isodecane	1.75	2.41	3.42
C10 Aromatic	5.74	18.07	14.39
Napthene	14.80	23.20	28.46
1-Methyl 2-Propyl Cyclohexane	0.00	3.76	0.00
n-Decane	179.98	281.60	379.89
Iso-undecane	0.00	2.06	2.14
Iso-undecane	2.26	1.71	3.24
Iso-undecane	0.00	5.59	2.35
Iso-undecane	1.51	1.87	1.81
1,2,3-Trimethyl Benzene	43.58	55.87	77.07
Iso-undecane	4.98	15.21	16.31
para-Isopropyl Toluene	8.90	13.40	20.89
Iso-undecane	8.34	26.23	23.52
Iso-undecane	2.33	5.65	5.32
Iso-undecane	1.07	8.14	6.66
Indan	13.49	34.27	30.80
Iso-undecane	2.24	7.84	10.14
Isobutyl Cyclohexane	34.20	87.01	130.81
Iso-undecane	0.00	0.00	2.35
Iso-undecane	2.31	1.72	3.64
ortho-Isopropyl Toluene	6.94	19.90	15.78

Gasoline has many components

Types by Carbon Number

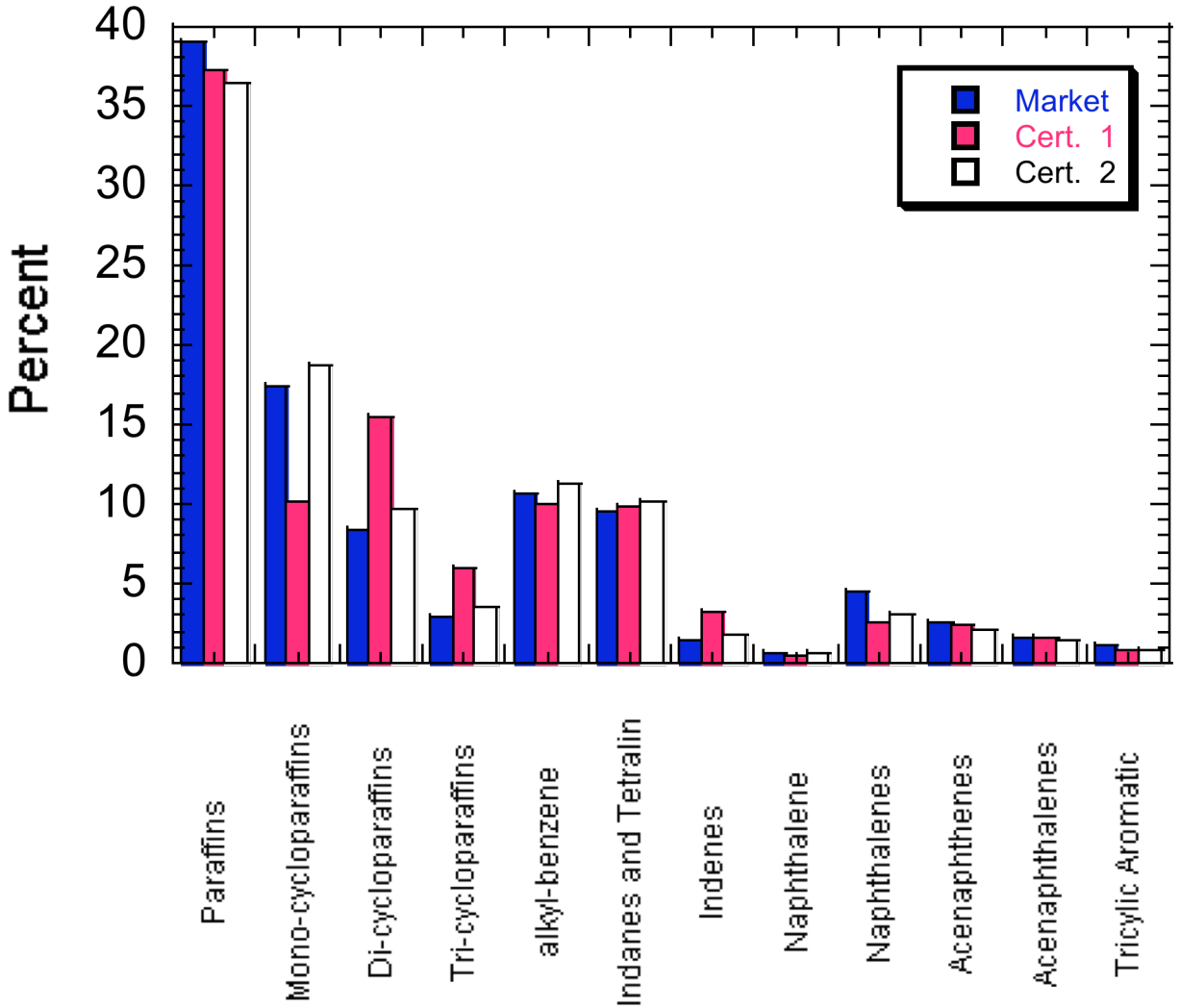
		Wt %	Vol %	Mol %
Paraffins:	C1	0.000	0.000	0.000
	C2	0.000	0.000	0.000
	C3	0.000	0.000	0.000
	C4	0.762	1.008	0.658
	C5	1.809	2.214	1.258
	C6	0.736	0.855	0.428
	C7	0.317	0.356	0.159
	C8	0.186	0.203	0.082
	C9	0.104	0.111	0.041
	C10	0.071	0.074	0.025
	C11	0.112	0.116	0.036
	C12	0.007	0.007	0.002
	C13	0.000	0.000	0.000
Iso-paraffins:	C4	0.022	0.030	0.019
	C5	0.143	0.183	0.100
	C6	3.372	3.926	1.963
	C7	3.280	3.701	1.642
	C8	4.581	5.054	2.012
	C9	0.309	0.326	0.121
	C10	0.598	0.624	0.211
	C11	0.347	0.354	0.112
	C12	0.070	0.071	0.020
	C13	0.000	0.000	0.000
Aromatics:	C6	0.856	0.746	0.550
	C7	5.084	4.493	2.768
	C8	3.425	3.023	1.618
	C9	6.130	5.376	2.561
	C10	2.714	2.361	1.016
	C11	0.610	0.531	0.207
	C12	0.406	0.349	0.125
	C13	0.000	0.000	0.000
Naphthenes:	C5	0.281	0.269	0.187
	C6	0.209	0.207	0.125
	C7	0.642	0.649	0.328
	C8	0.735	0.730	0.329
	C9	0.594	0.582	0.239
	C10	0.365	0.364	0.138
	C11	0.049	0.047	0.016
	C12	0.000	0.000	0.000
	C13	0.000	0.000	0.000
Olefins:	C2	0.000	0.000	0.000
	C3	0.000	0.000	0.000
	C4	0.157	0.197	0.140
	C5	8.071	9.323	5.888
	C6	1.867	2.053	1.116
	C7	2.892	2.885	1.499
	C8	1.002	1.045	0.451
	C9	0.011	0.012	0.005
	C10	0.013	0.013	0.005
	C11	0.028	0.029	0.009
	C12	0.094	0.095	0.028
	C13	0.000	0.000	0.000

Gasoline composition



Many branched paraffins

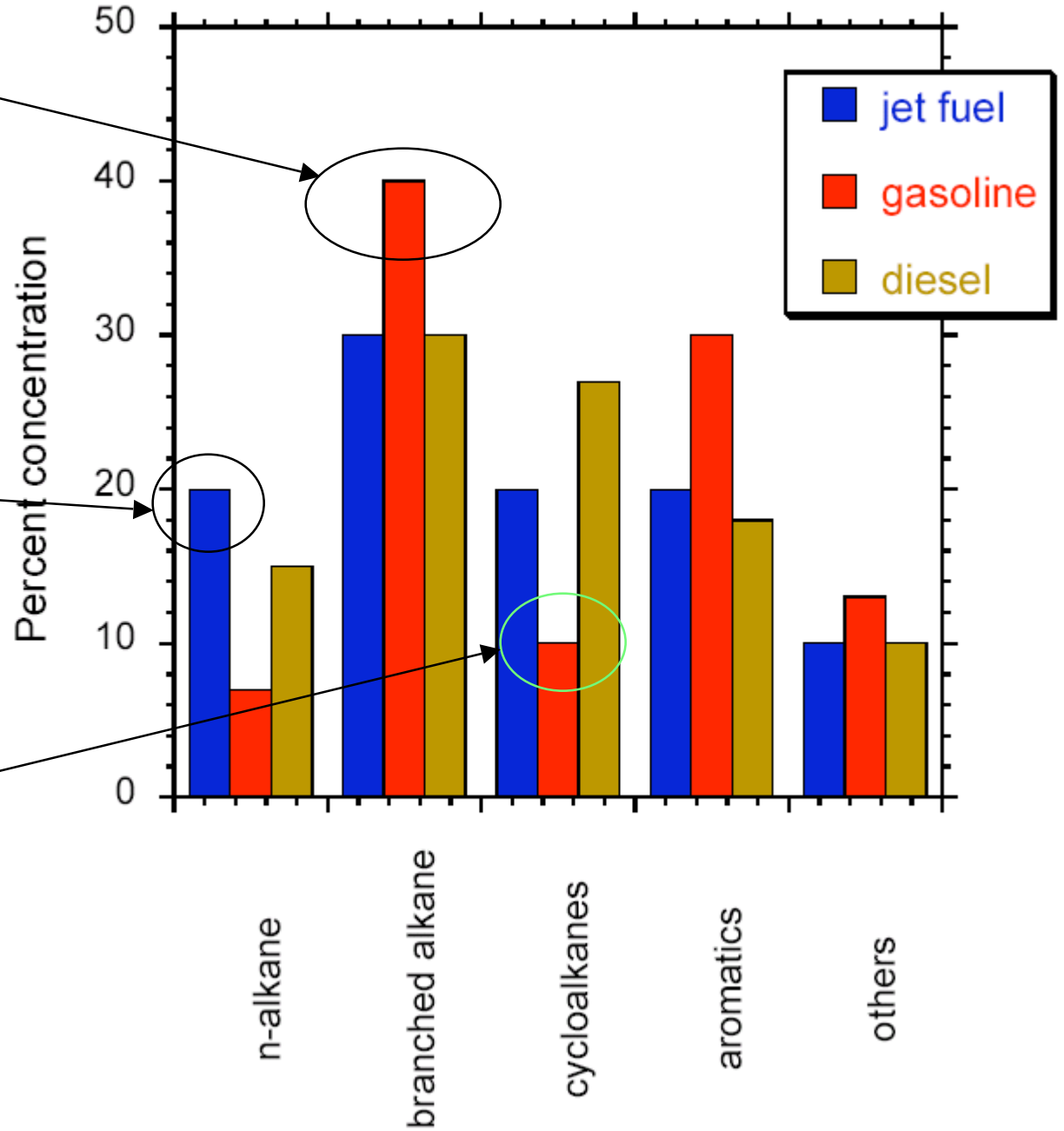
Diesel Composition



Gasoline has many branched alkanes

Jet fuel has the highest n-alkane

Gasoline is lower in cycloalkanes



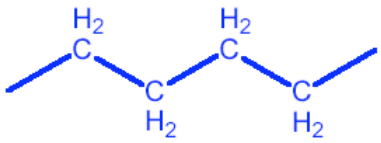
Natural gas is the easiest case

- For natural gas, simplified fuels are generally accepted (e.g. 95% methane, 4 % ethane, 1 % n-butane)
- For liquid fuels, choosing a substitute is more difficult:
  - Gasoline
  - Diesel
  - Jet fuel

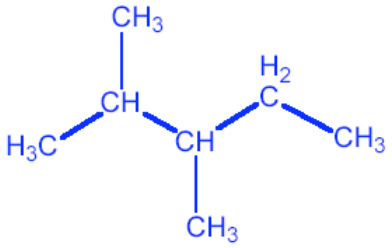
Development of a Simplified Fuel Mechanism for Simulations

Classes of compounds in gasoline and diesel fuel:

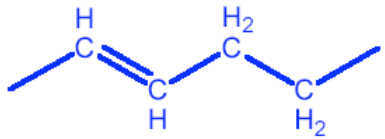
n-paraffin

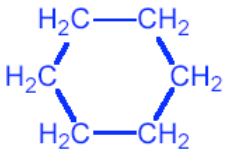


iso-paraffin

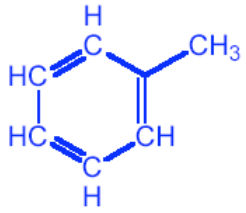


olefin

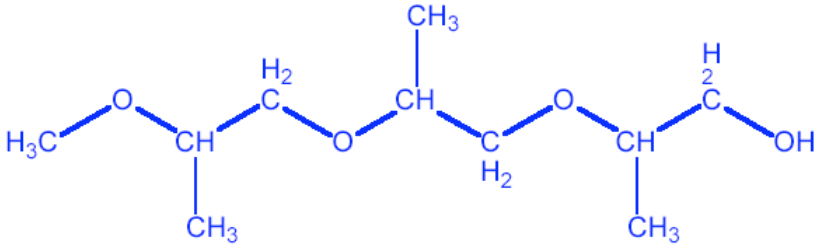




cyclo-alkane



aromatic



oxygenate

Approaches to Surrogate fuels

- Have one or more fuel components to represent each chemical class of components
- Surrogate fuel should be able to predict desired combustion and physical properties, e.g.:
  - Ignition properties
  - Flame speeds
  - Sooting tendency
  - Others ???
- Produce reduced kinetic model as needed

Need to add new species for specific applications and conditions

- Larger hydrocarbon molecules, with their significantly larger reaction mechanisms
- New species for liquid fuels, use existing techniques
- Mechanisms for individual species must each be validated thoroughly (Comprehensive mechanism)
  - Purely kinetic tests, including shock tubes, flow reactors, flame speeds, stirred reactors
  - Applied tests in application environments
- Relevant pressure and temperature ranges identified for each type of application

Prior simplified versions of diesel/gasoline

- n-heptane: frequently used to represent diesel fuel. Has similar cetane no. (55) to diesel fuel

- n-heptane/iso-octane: primary reference fuels for gasoline. Some success as a substitute for gasoline under HCCI conditions and engine knock, some problems too

Work in progress

Teams of kinetics modeling researchers are working to produce these surrogate fuel models

Recent example:

Violi et al., CST 174, 399 (2002), surrogates for JP-8

a. iso-octane, MCH, m-xylene, dodecane, tetralin and tetradecane
b. iso-octane, MCH, toluene, decane, dodecane, tetradecane

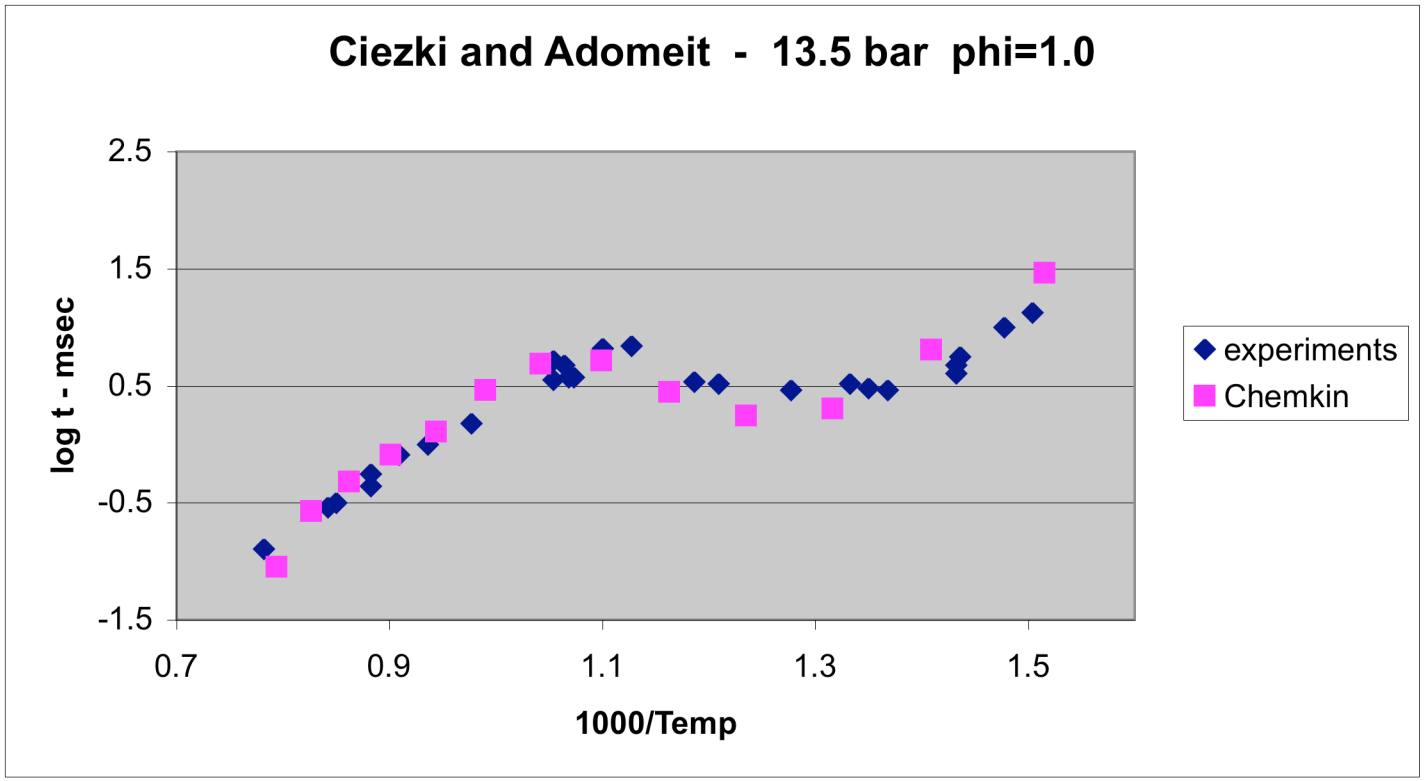
Used semi-detailed mechanisms from Ranzi et al.

Included boiling point and other physical properties

n-Heptane mechanism validation

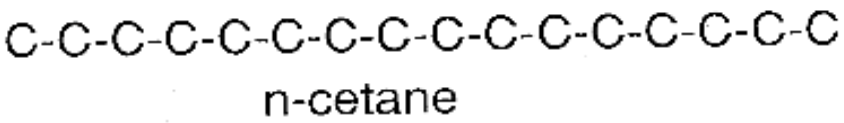
- Shock tube ignition
- Stirred reactor
- Flow reactor
- Rapid compression machine
- Laminar flame

Shock tube ignition, higher pressure, lower temperatures

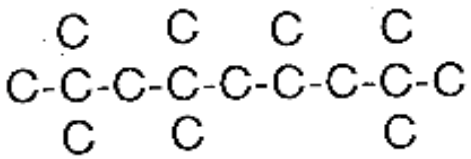


660K - 1300K, Φ = 0.5, 1.0, 2.0 P = 6, 13.5, 40 bar

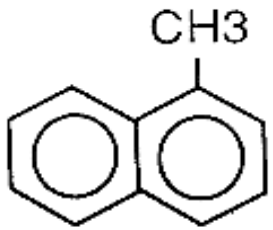
Reference fuels for cetane number in Diesel combustion



n-cetane



heptamethylnonane



α-methyl naphthalene

We are ready to provide additional complexity to our simplified diesel fuel

- We have used n-heptane due to its ignition properties and cetane number
- n-heptane has no aromatic characteristics
- Aromatics ignite more slowly than n-heptane
- To simulate ignition timing of diesel fuel with aromatic components, we will have to include a component more reactive than n-heptane
- Solution is to combine aromatics and dodecane or hexadecane

Diesel surrogate fuel in the future

- Made up of straight-chain alkanes, branched-chain alkanes,

  cyclic alkanes, simple aromatics, alkylated aromatics,

  polycyclic aromatics and others

- Example test: Surrogate diesel:

  n-alkane: n-hexadecane, n-dodecane or n-decane

  branched chain component: iso-octane or branched heptane

  cyclic alkane component: cyclohexane or methyl cyclohexane

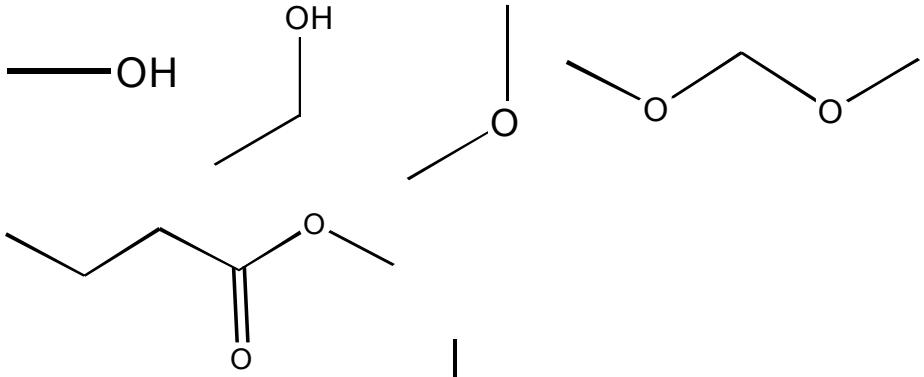
  aromatic component: toluene or mixture of xylenes

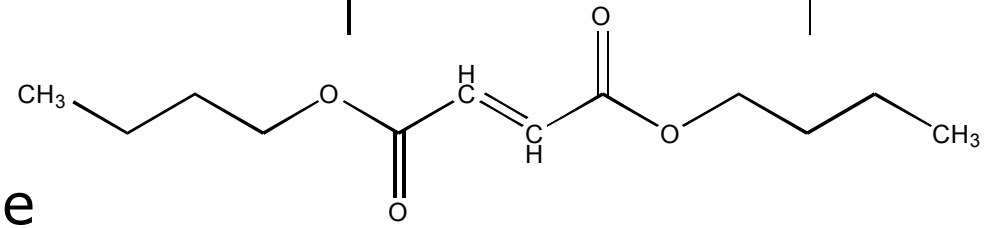
In some classes, we have many examples of fuels with reaction mechanisms

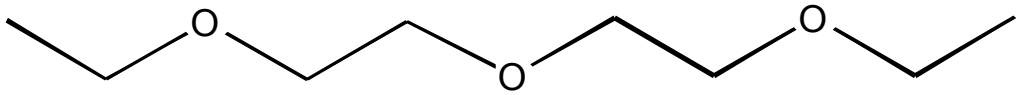
- n-paraffins
  - CH_4 (methane) through $nC_{16}H_{34}$ (n-hexadecane)
- iso-paraffins
  - all isomers through octanes, selected larger iso-paraffins
- Large variety of olefins through C8 and selected larger species

We can have mechanisms for many oxygenated components

- Methanol, ethanol
- dimethyl ether, dimethoxymethane
- Methyl butanoate (surrogate for biodiesel)
- TPGME (tripropylene glycol monomethyl ether)
- DBM (di-butyl maleate)
- DGE (diethylene glycol diethyl ether)
  - Under development

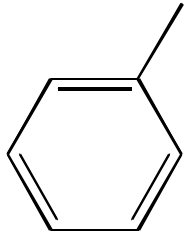




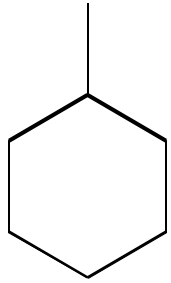


We now have more components to represent classes of hydrocarbons

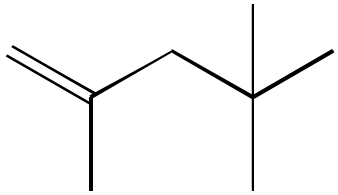
- toluene (aromatics)



- methylcyclohexane (cycloalkanes)

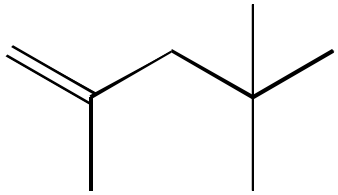


- diisobutylene (alkenes)

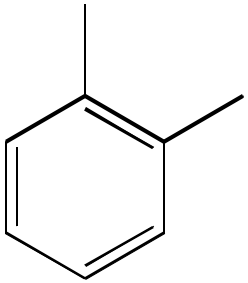


New components

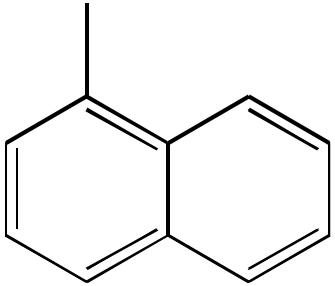
- diisobutylene
  - low temperature chemistry



- o-xylene,
  m-xylene,
  p-xylene

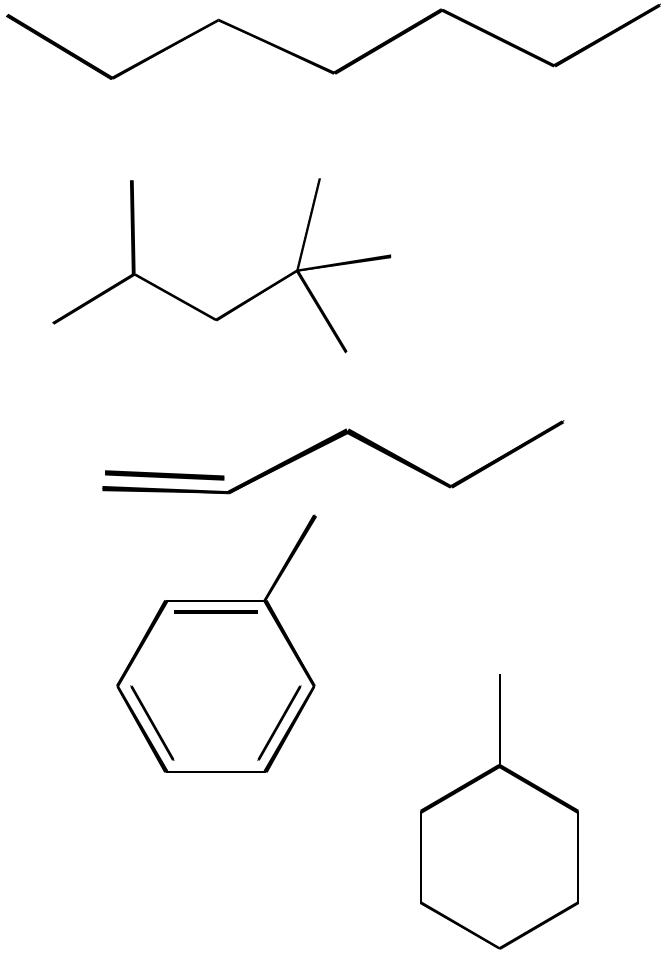


- α-methyl naphthalene



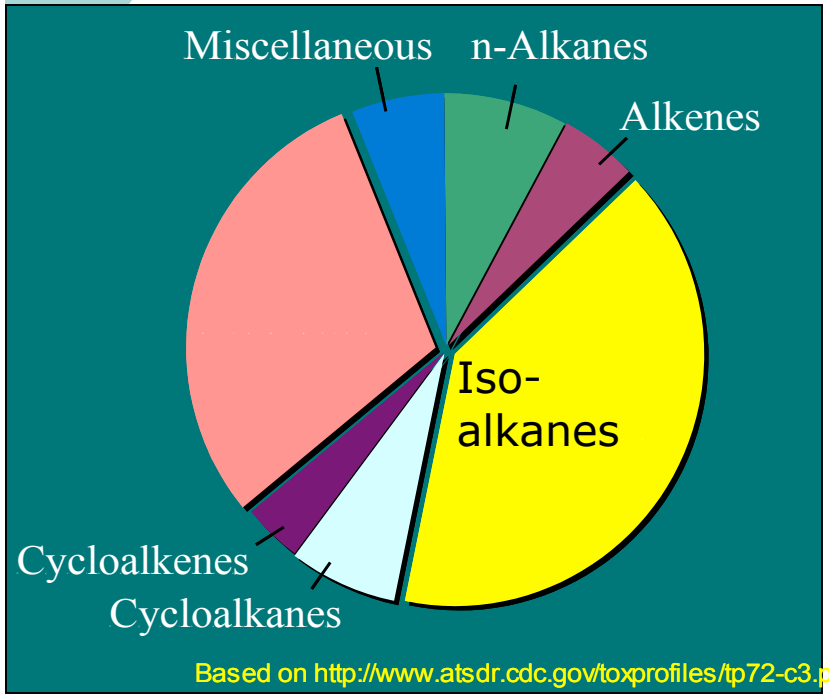
A five component surrogate to represent gasoline

- n-heptane (straight chain alkanes)
- iso-octane (branched alkanes)
- 1-pentene (alkenes)
- toluene (aromatics)
- methylcyclohexane (cycloalkanes)



Surrogate mixtures for gasoline based on composition and octane number

- Typical gasoline: RON = 90.8, MON = 83.4



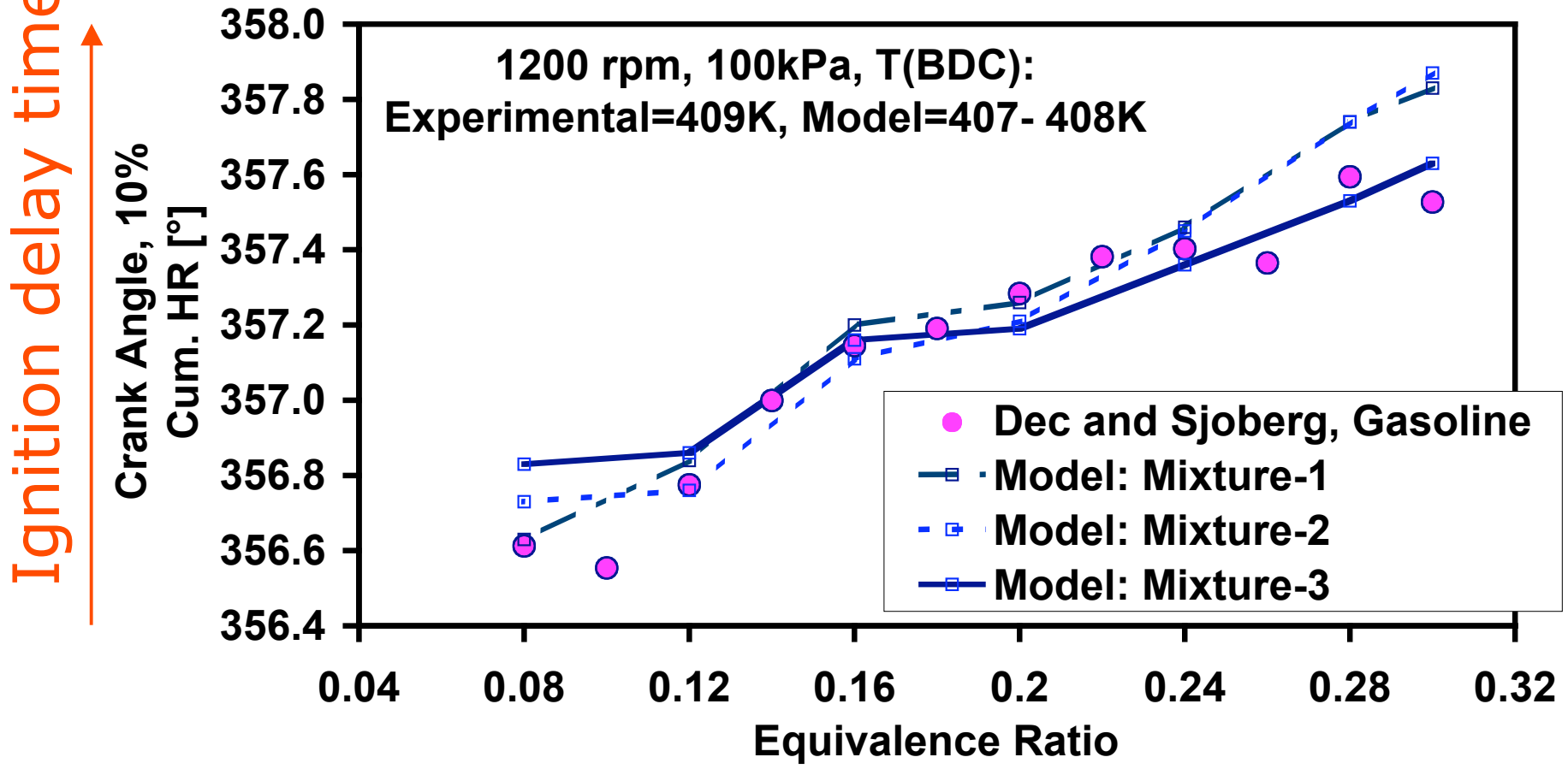
% Composition	Mixture 1
iso-Octane	60
n-Heptane	8
Toluene	20
Methyl cyclohexane	8
1-Pentene	4
RON (linear mixing)	93.7
MON (linear mixing)	90.6
RON (blend*)	99.2
MON (blend*)	94.5

Surrogate fuel compositions examined:

- Mixture 1: Five components to represent the different classes of compound in gasoline at the typical level.
- Mixture 2: Match the octane number of gasoline based on *blended* octane numbers.
- Mixture 3: Increase the low temperature chemistry by adding more n-heptane

% molar composition	Mixture 1	Mixture 2	Mixture 3
iso-Octane	60	40	40
n-Heptane	8	10	20
Toluene	20	10	10
Methyl cyclohexane	8	40	30
1-Pentene	4	0	0
RON (linear)	93.7	81.7	83.7
MON (linear)	90.6	79.3	79.8
RON (blend)	99.2	94	87.6
MON (blend)	94.5	84.8	82

Effect of equivalence ratio on timing for start of combustion

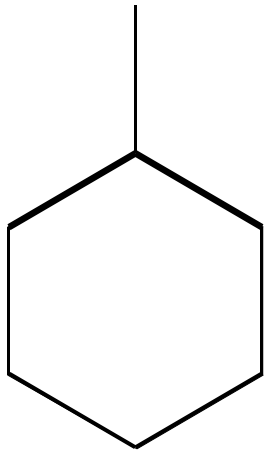


Add new fuel components as needed to model important features of the overall fuel

- New sources of diesel fuels has led to much greater levels of cycloalkanes, for which detailed mechanisms did not exist
- Methyl cyclohexane chosen as representative sample for this class
- Additional experiments needed for validation of this new component

Cycloalkanes: methyl cyclohexane

- Cycloalkanes are becoming of much interest due to oil sands



methylcyclohexane

Canada's oil sands

JOE SHOULAK / *The Chronicle*

Canadian oil sands

- Second only to Saudi Arabia in proven oil reserves
  - Saudi Arabia 262 billion barrels
  - Canada oil sands 175 billion barrels
  - Arctic National Wildlife Refuge 10 billion barrels (est)
- Currently largely strip mined
- Production is a serious source of greenhouse gases
  - 2 tons of sand produce one barrel of oil
  - production of one barrel of oil =
    daily emissions from 4 cars
  - huge usage of natural gas for extraction

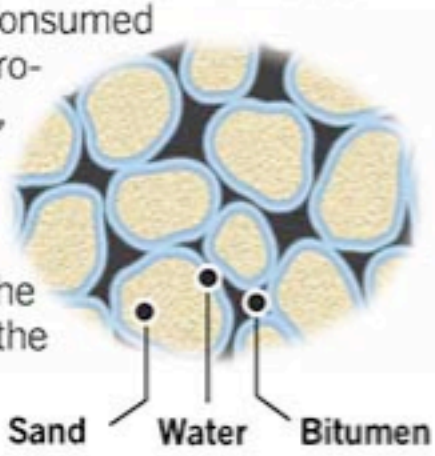
Athabasca oil sands

Chronicle / Brant Ward

Strip mining oil sands, using 400 ton capacity trucks

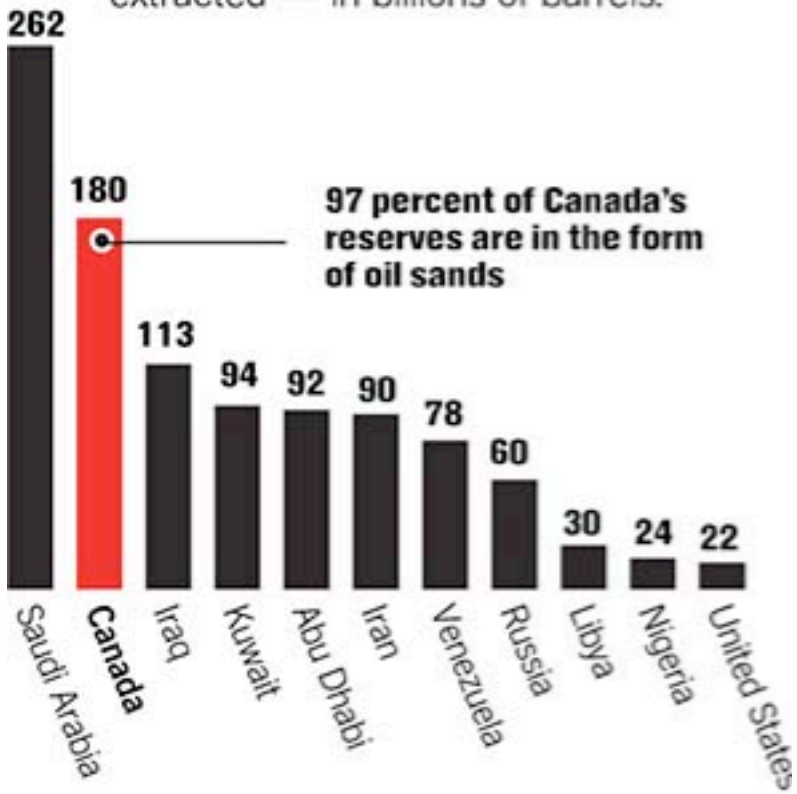
WHAT ARE OIL SANDS?

Fifty-million years ago, huge deposits of oil were pushed up through the Earth in what is now Canada. Bacteria consumed much of the lighter hydrocarbons, leaving a thick, sticky mixture of heavy petroleum called bitumen mixed with water and sandstone. The deposits cover an area the size of Florida.



GLOBAL CRUDE OIL RESERVES

Estimates of "proven" oil reserves — known existing deposits that can be profitably extracted — in billions of barrels.

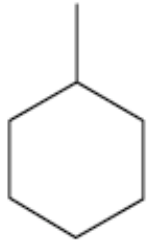


Source: Suncor Energy Inc., Petroleum Communication Foundation, Oil and Gas Journal

The Denver Post

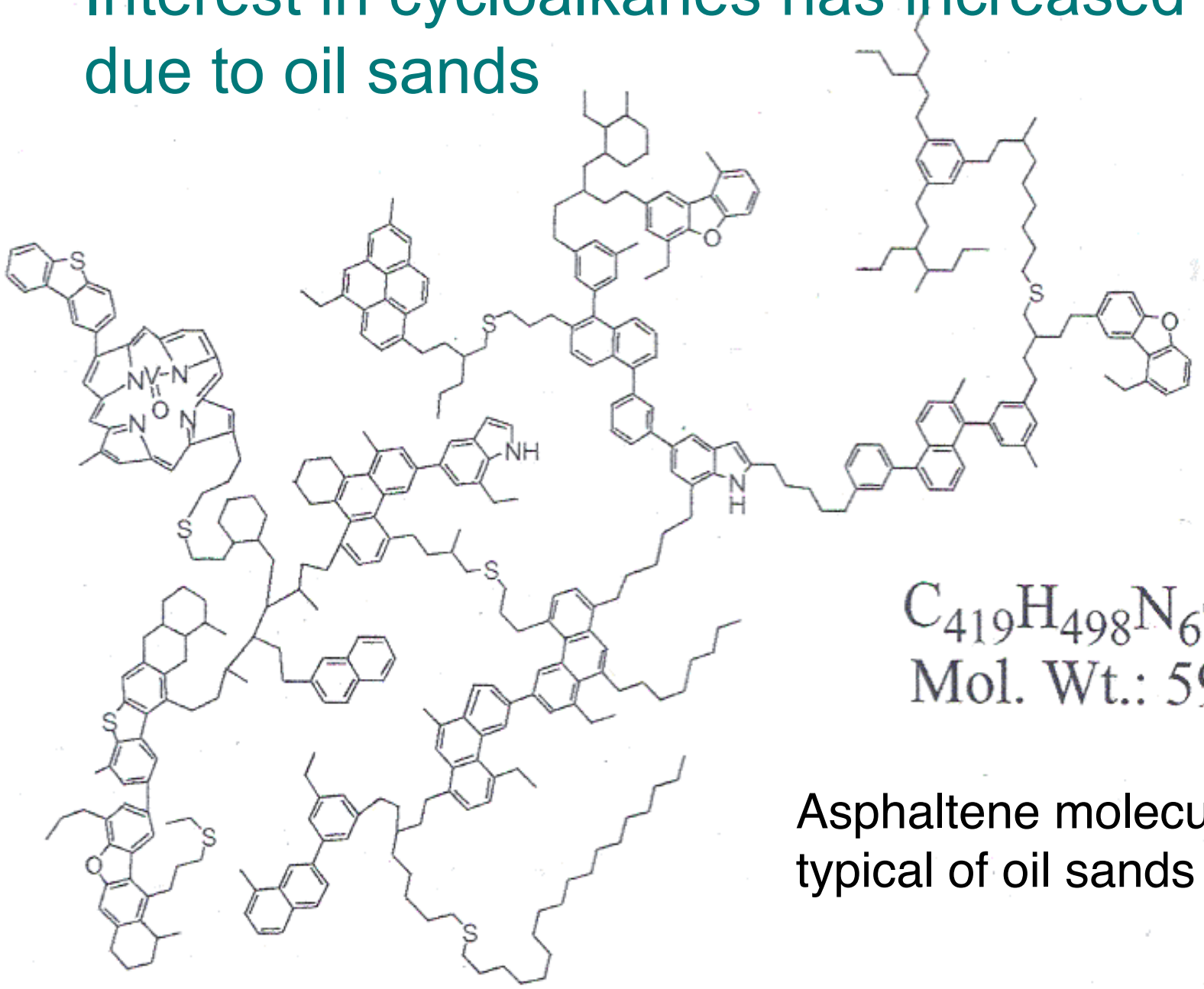
Diesel fuels derived from oil sands present combustion challenges that require research

- Derived diesel fuel is rich in cyclic alkanes
  - e.g., methyl cyclohexane



- Most of these are rather large, complex cyclic alkanes
- Very little scientific research has been done on any cyclic alkanes
- Preliminary practical experience suggests that these species are important in determining ignition and soot production in diesels

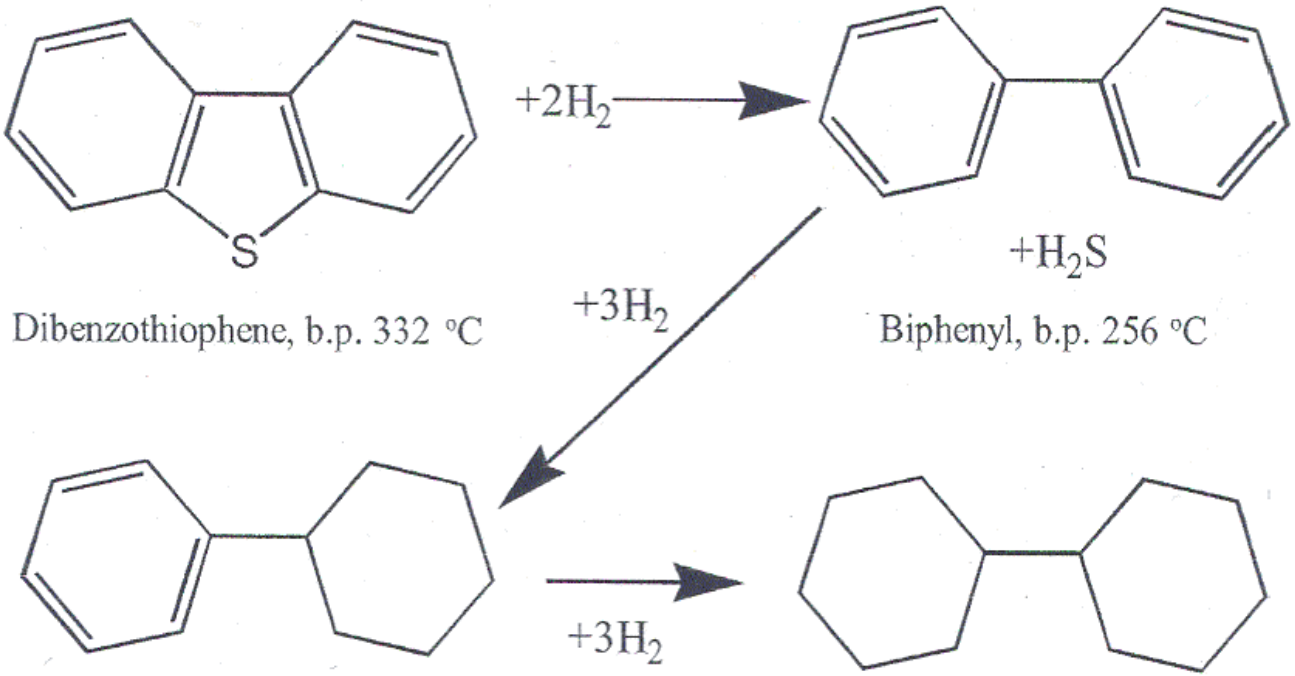
Interest in cycloalkanes has increased due to oil sands



$C_{419}H_{498}N_6O_4S_8V$
Mol. Wt.: 5989.94

Asphaltene molecule typical of oil sands

Benefits of Hydrotreating and Aromatic Saturation



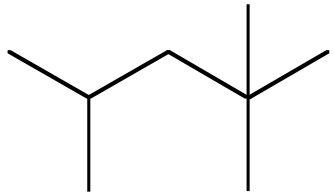
Dibenzothiophene, b.p. 332 °C

Biphenyl, b.p. 256 °C

A mechanism for diisobutylene to further represent alkenes in gasoline (17 new species, 83 new reactions)

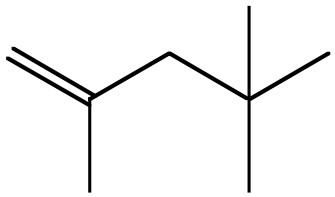
- Diisobutylene molecular structure is similar to iso-octane

Iso-octane:

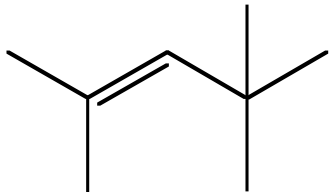


(2,2,4-trimethyl-pentane)

Diisobutylene is comprised of two isomers:



2,4,4-trimethyl-1-pentene
(jc8h16)



2,4,4-trimethyl-2-pentene
(ic8h16)

Biodiesel fuels

- Alternative fuel from vegetable oils and animal fat
- Methyl esters with ≈ 16-18 Carbon atoms
- Low sulfur allows use of catalysts for NO_x removal
- 10% oxygen content in fuel lowers soot emissions
- Liquid fuel at room temperature
- Renewable diesel fuel

Note the methyl ester group at the end of each long hydrocarbon chain

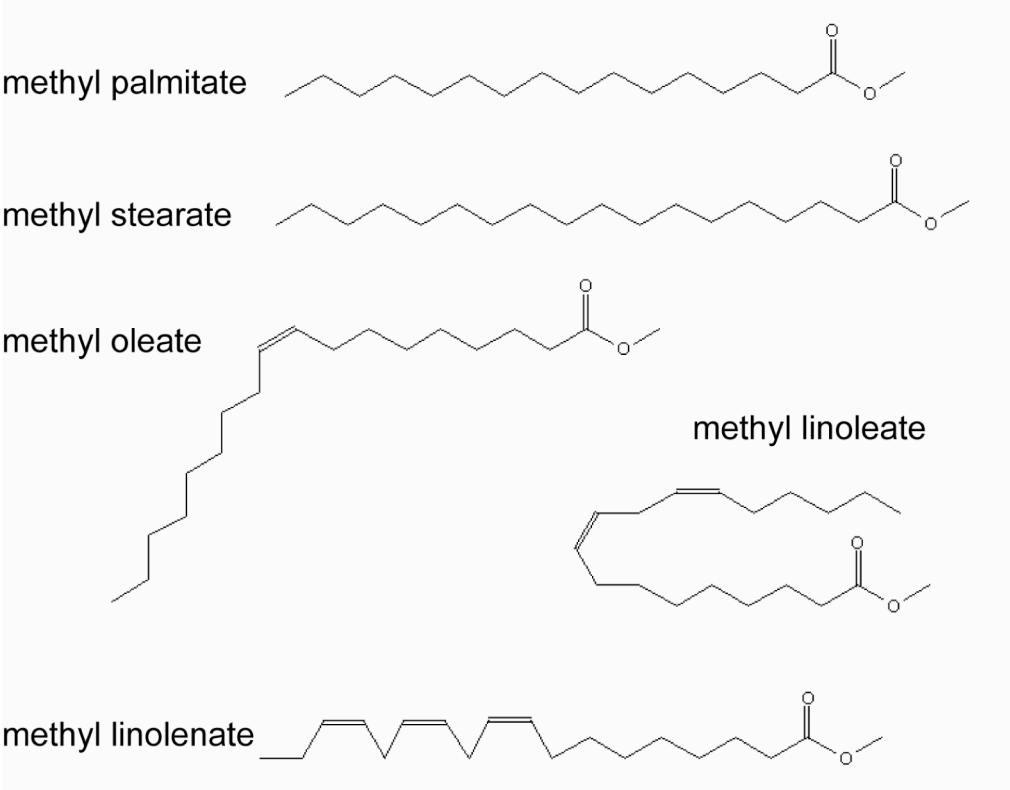
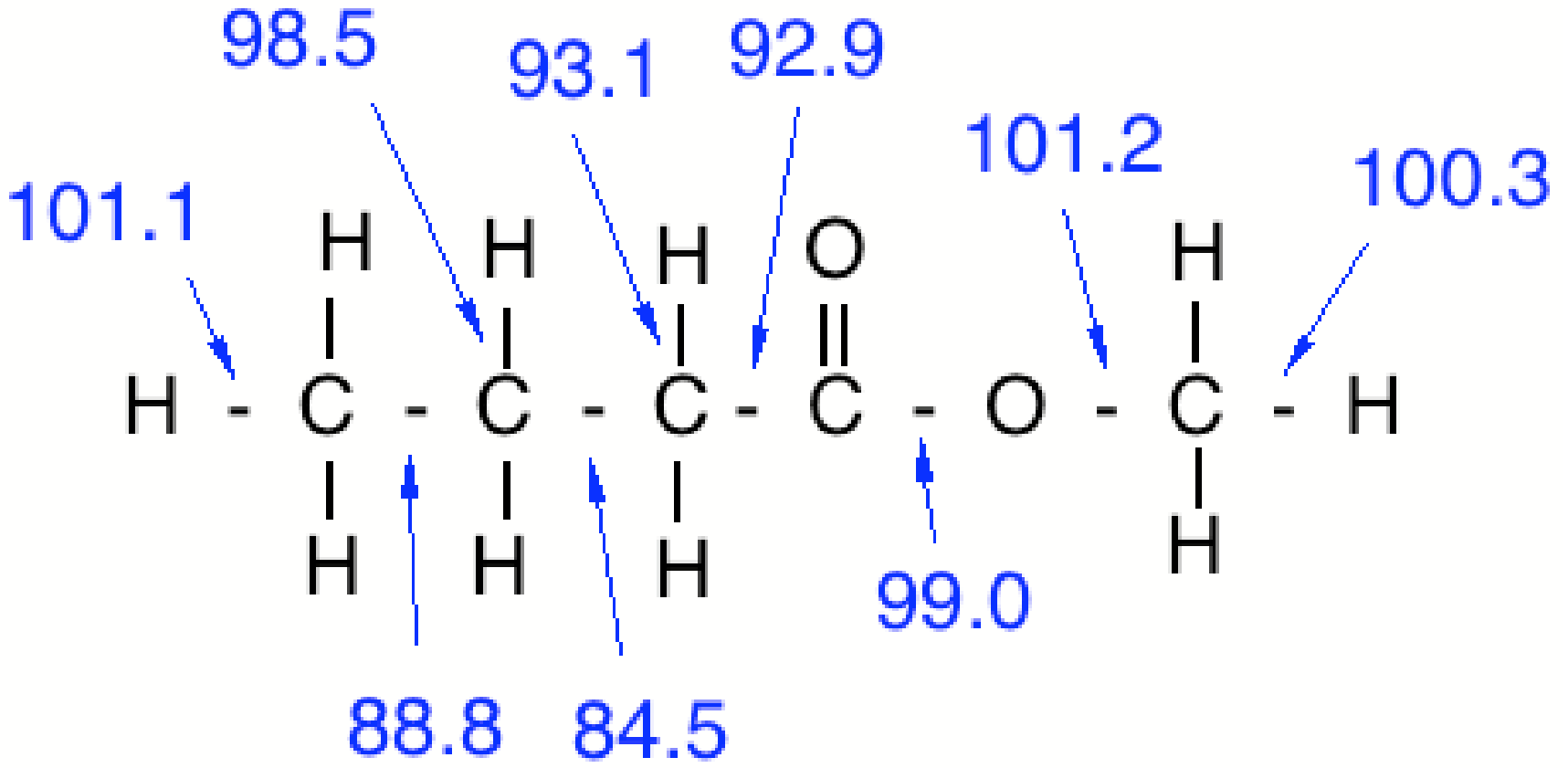


figure from C. Mueller, Sandia

Methyl Butanoate
Bond Strengths (kcal/mole)



Methyl butanoate, a biodiesel surrogate fuel

- MB has the essential structure characteristic of biodiesel fuels
- MB has basic chemical features of larger methyl esters
- Does not have the higher molecular weight of biodiesel fuels
- Molecule is long enough to display alkylperoxy isomerization kinetics characteristic of biodiesel fuels
- Computationally much easier to model than true biodiesel fuels
- Optimal vehicle to learn about modeling methyl ester kinetics
- Paper in current symposium examines the strengths and limits of methyl butanoate as a biodiesel surrogate

Fischer-Tropsch fuel can be treated as a mixture of n-paraffin and iso-paraffin components

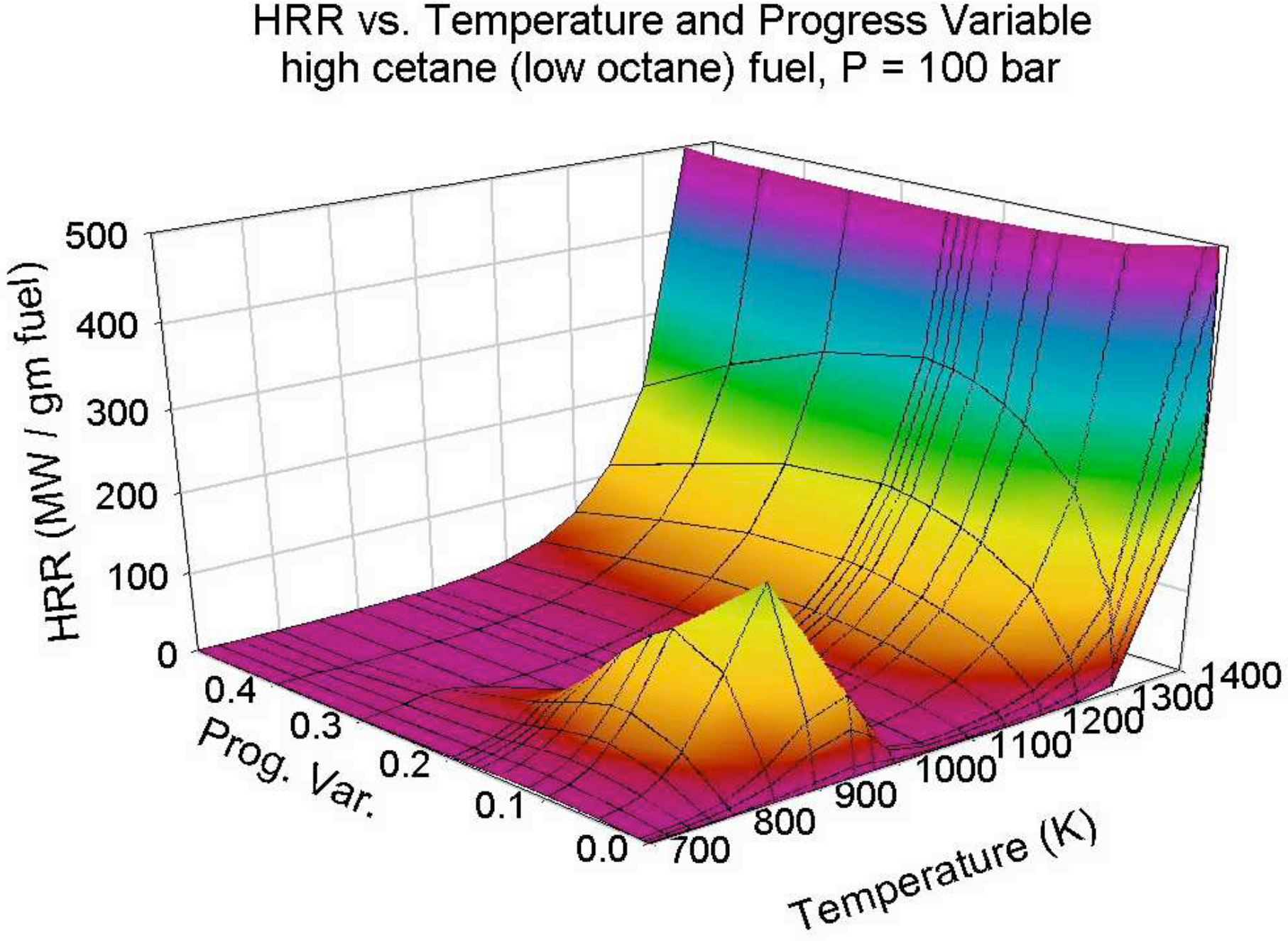
- Recent advances in catalysts for Fischer-Tropsch production from CO and H_2 help economics
- Extremely clean fuel, with virtually no sulfur or other atoms
- We have kinetic models for many n-paraffin and iso-paraffin molecules
  - isomers of heptane on LLNL webpage

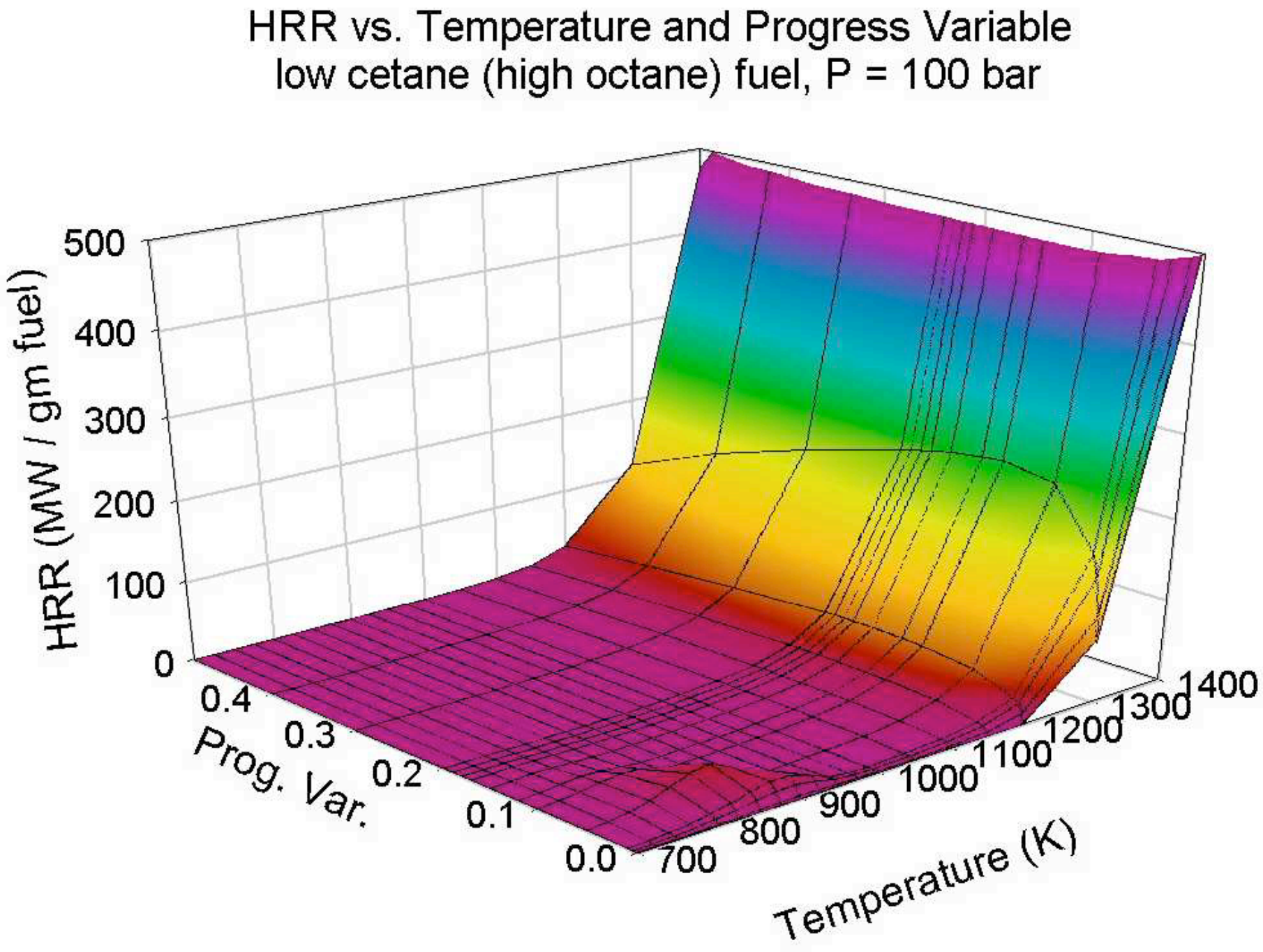
Next steps in model development

- Choose model components for specific applications from library of fuel components
- Demonstrate simulation properties of the substute fuel under relevant conditions
  - idealized conditions (e.g., shock ignition, flames)
  - application-specific conditions
- Many essential tasks are becoming automated, incl. mechanism generation and reduction, with enormous savings in development time

Next steps - 2

- Mechanism reduction to intermediate levels useful for efficient modeling calculations
- Mechanism reduction to very small models useful for CFD applications
- CARM or other techniques, automatic operation is highly desirable
- Note that reduction can be application-dependent and environment-dependent


HRR vs. Temperature and Progress Variable
high cetane (low octane) fuel, P = 100 bar
HRR (MW / gm fuel)
500
400
300
200
100
0
0.4
0.3
0.2
0.1
0.0
Prog. Var.
700
800
900
1000
1100
1200
1300
1400
Temperature (K)


HRR vs. Temperature and Progress Variable
low cetane (high octane) fuel, P = 100 bar
HRR (MW / gm fuel)
500
400
300
200
100
0
0.4
0.3
0.2
0.1
0.0
Prog. Var.
700
800
900
1000
1100
1200
1300
1400
Temperature (K)

The End
御静聴有難うございました。