
Detailed Kinetic Modeling of Gasoline Fuels

Slide show prepared by Dr. Marco Mehl, LLNL

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Tsinghua-Princeton
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Combustion
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What is the relationship between fuel quality and engine technology?

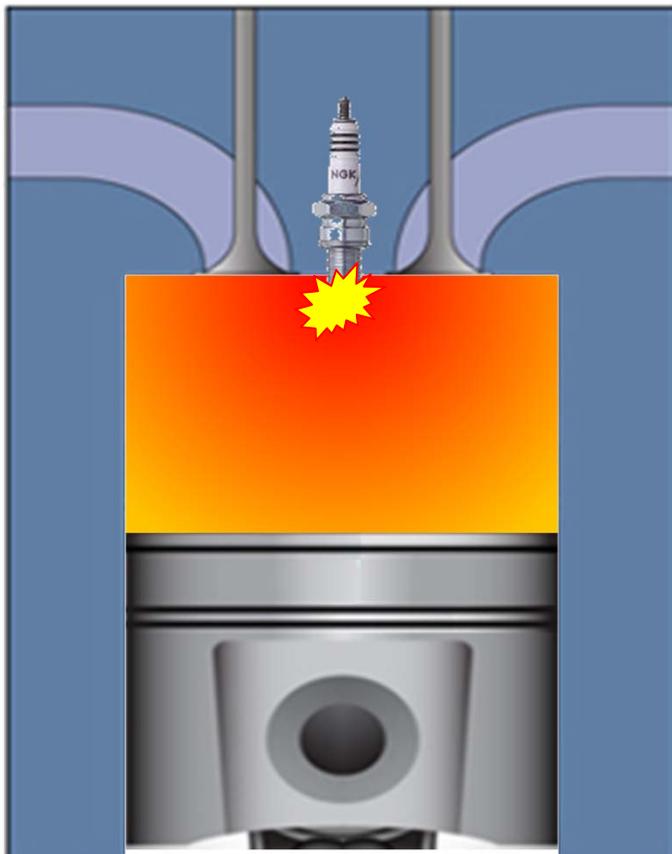


The SI Engine

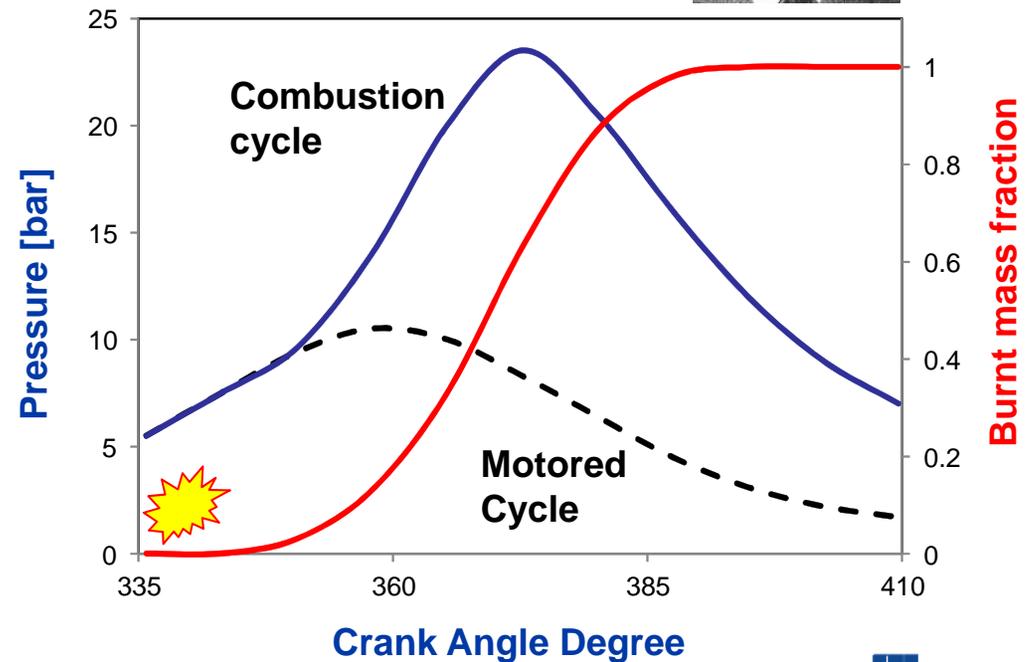
The spark starts the propagation of a turbulent flame front

Controlled Temperature and Pressure increase

Nikolaus August Otto (1832–1891)



Otto Engine (1876)



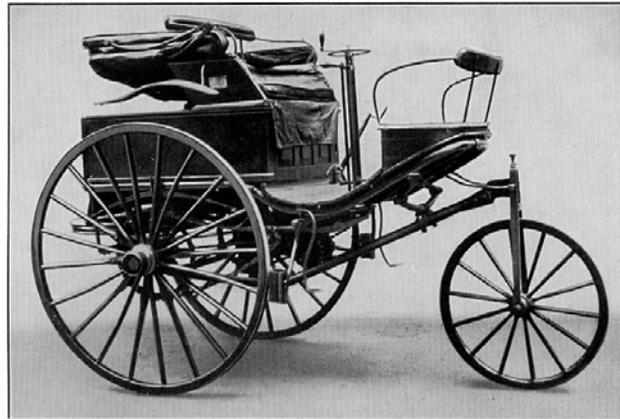
The first car road-trip in history (5th August 1888)

The Driver



Bertha Benz (1849–1944)

Her Car



Patent-Motorwagen No. 3

The Route



Mannheim to Pforzheim and back (194 km)

The First Filling Station



Willi Ockel's Pharmacy, Wiesloch

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The Fuel



Petroleum Ether



Early fuels for transportation 1885-1910



Petroleum Ether

Pioneers of the car industry used the fuels available at the time.

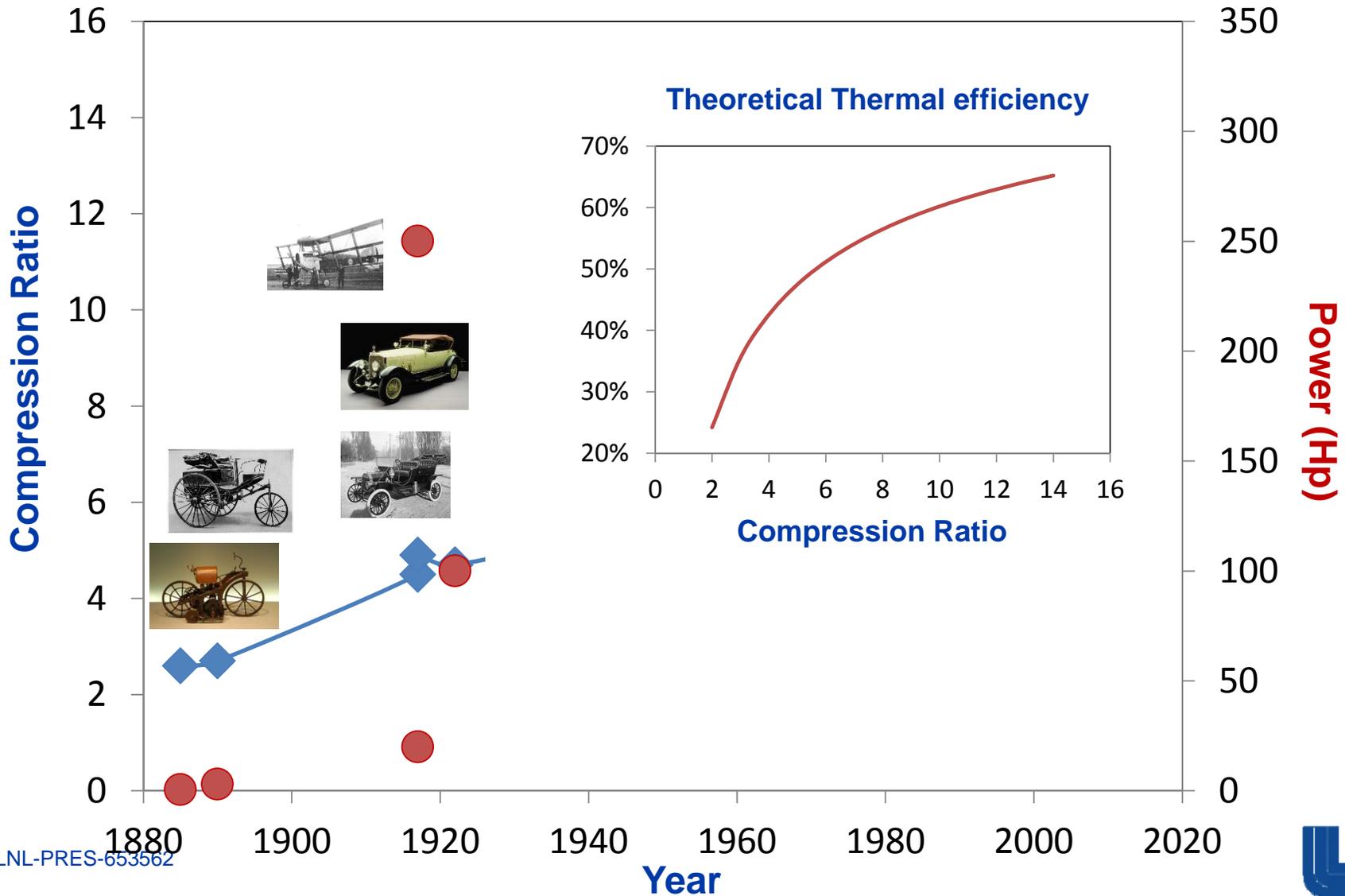
The best fit to their need was a light fraction of crude oil distillation: a byproduct of the production of lamp oil

This distillate was mainly composed of n-alkanes (C5-C7) and was sold to be used as a solvent

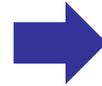
Its availability was limited (10-20% yield from crude oil fractional distillation)



Increasing power output required bigger engine and higher compression ratio...



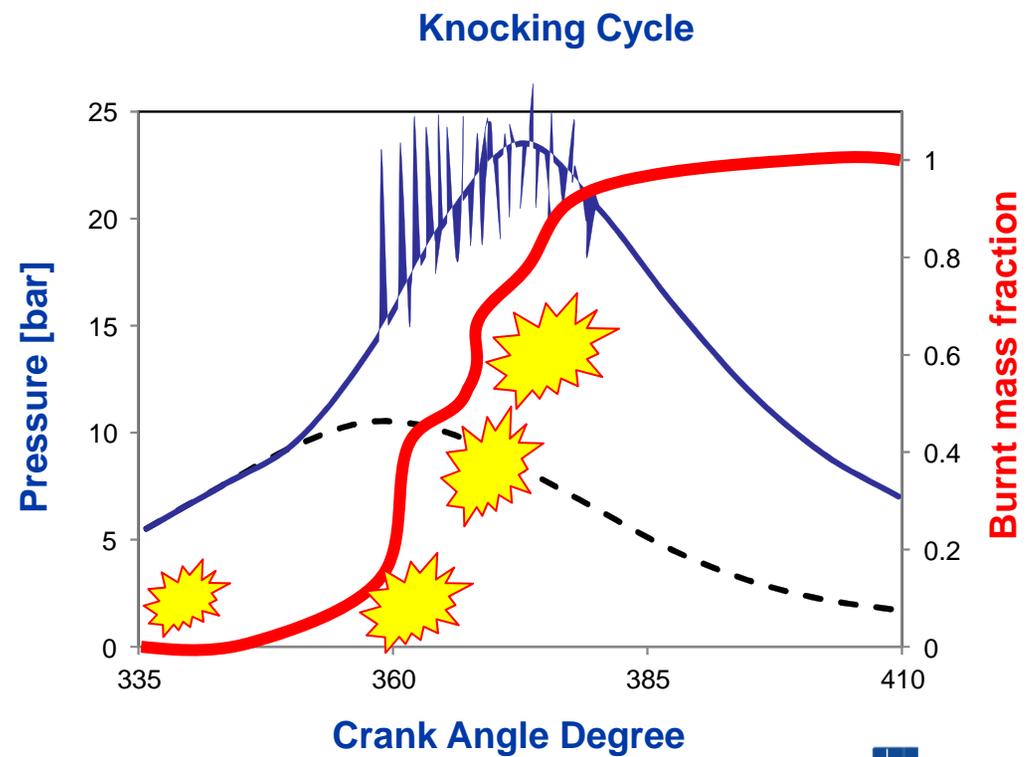
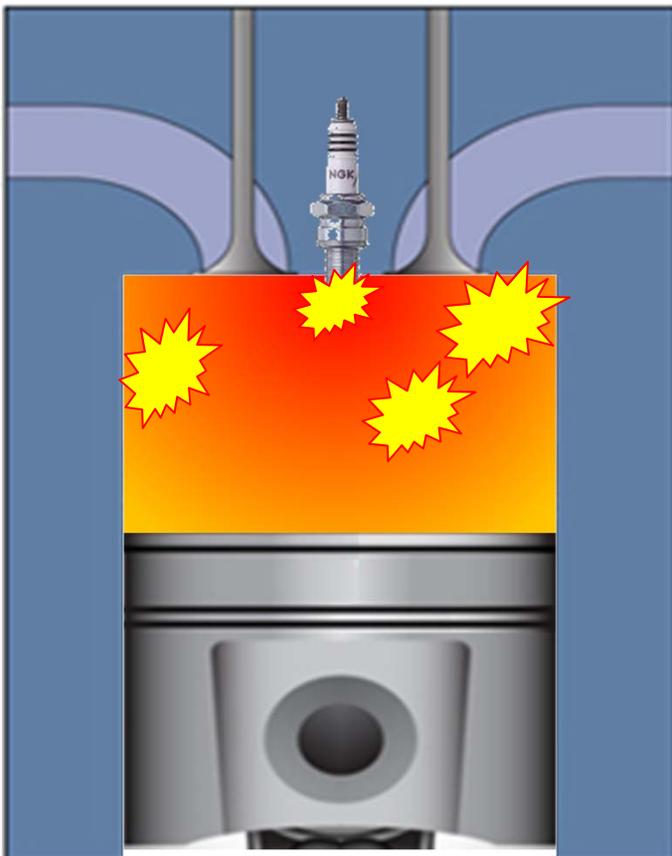
But soon engine designers (and pilots) faced catastrophic failures....



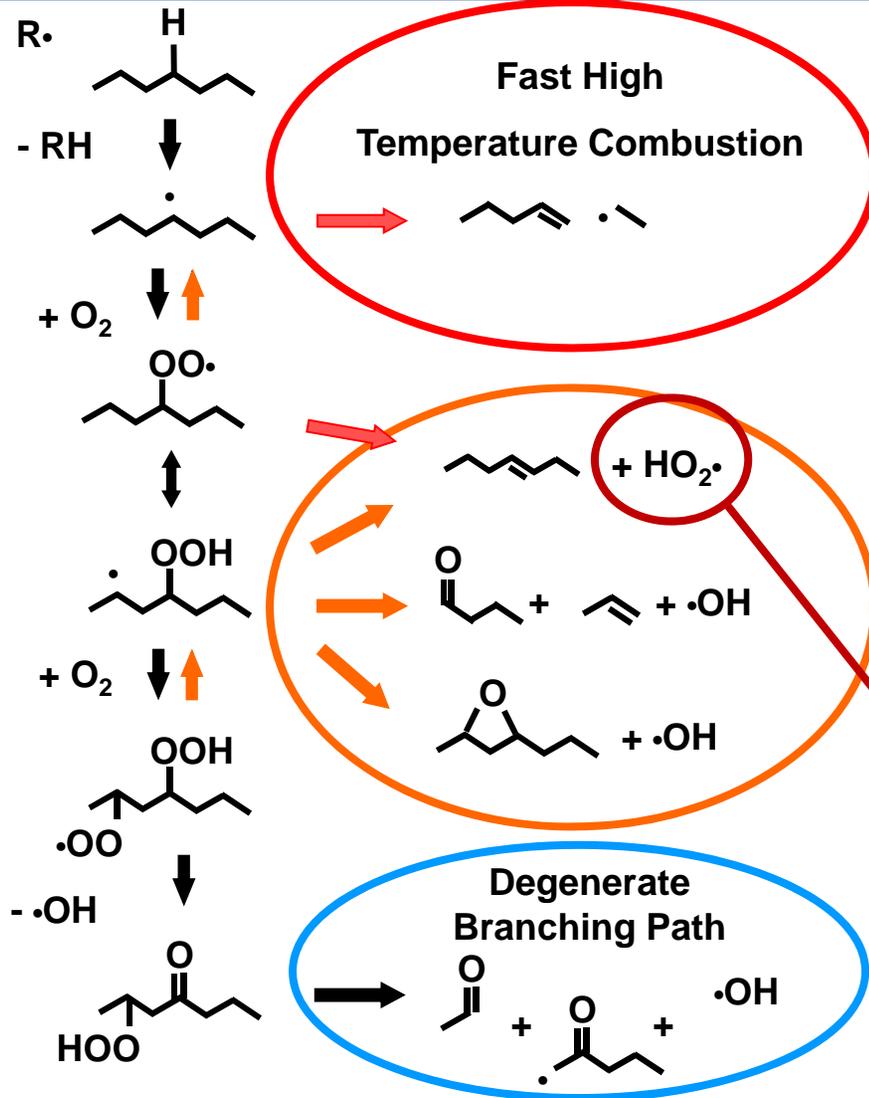
Engine became noisy and, in some cases, the cylinders it literally blew up!



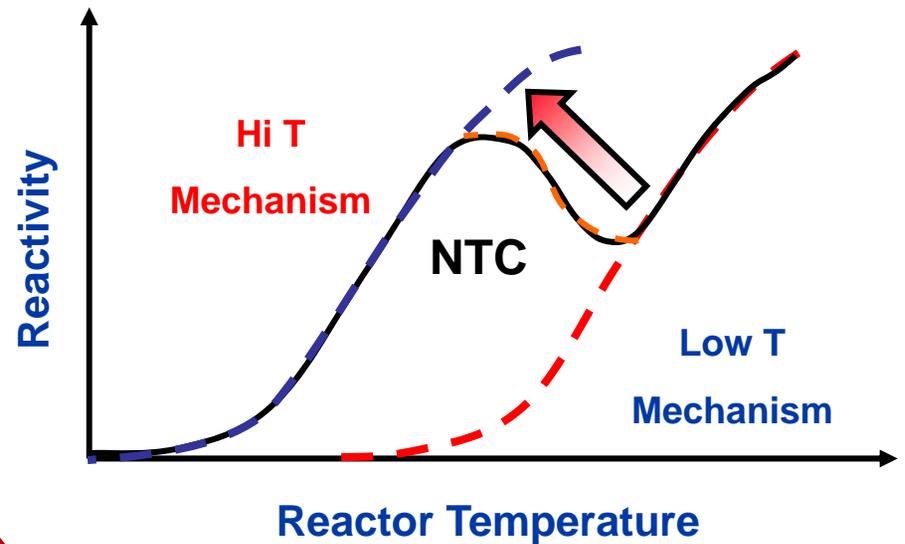
When the compression ratio was increased anomalous combustion behavior lead to engine failure



What causes knock?



Straight Chain Alkanes



HO_2 Radicals lead to the formation of H_2O_2 , when the temperature increases $H_2O_2 \rightarrow 2OH$ triggering the transition to high temperature ignition



Standard tests to measure the autoignition propensity of the fuel were introduced

The critical compression ratio (when knock reaches a prefixed intensity in a variable CR engine) was used to compare the fuel candidate to a scale of reference fuels constituted by n-heptane (PRF0) and iso-octane (PRF100)

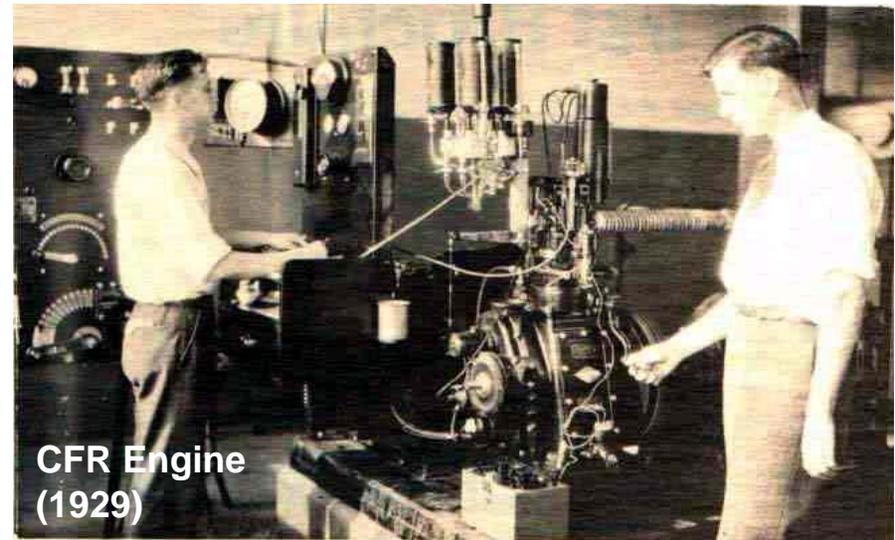
- RON:**
- Speed 600 rpm
 - Inlet Temperature 325K
 - Spark Advance 13°

Representative of idling/low load conditions

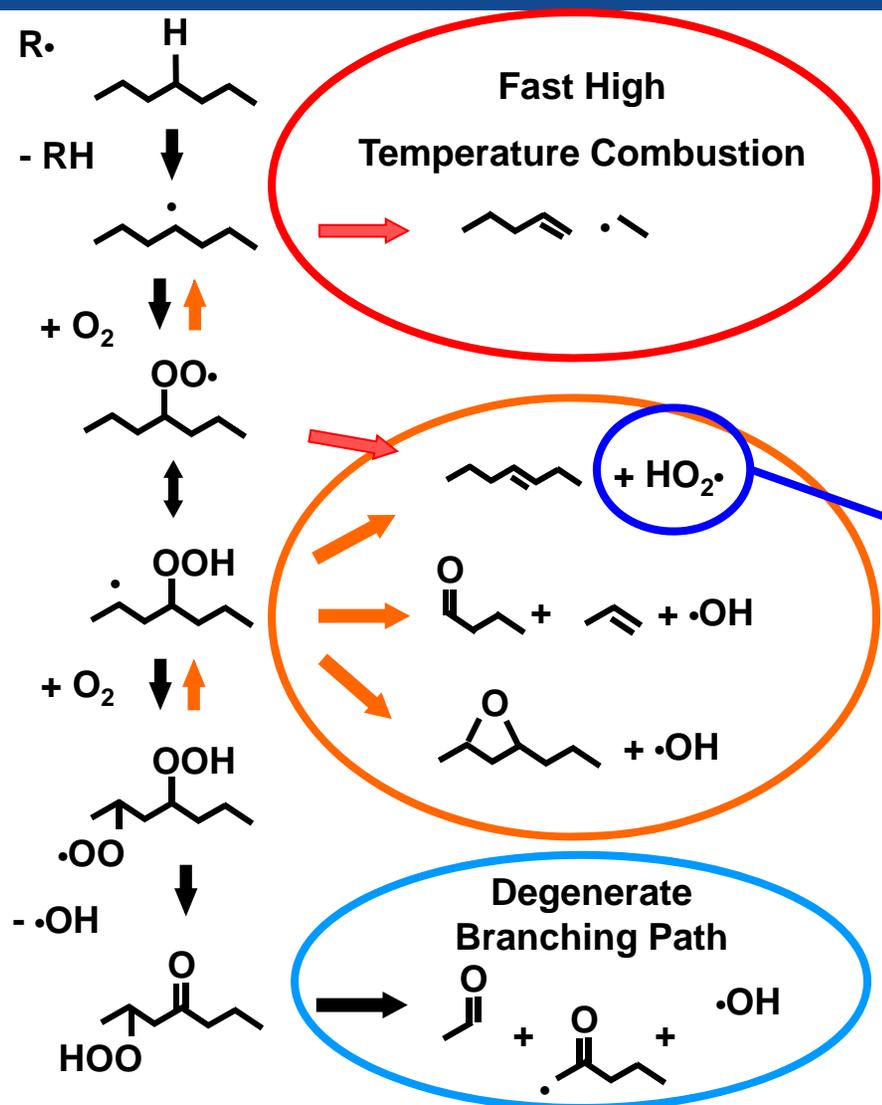
- MON:**
- Speed 900 rpm
 - Inlet Temperature 422K
 - Spark Advance 19-26°

Representative of road/high load conditions

It should be noted that today's octane rating are still based on the same type of tests

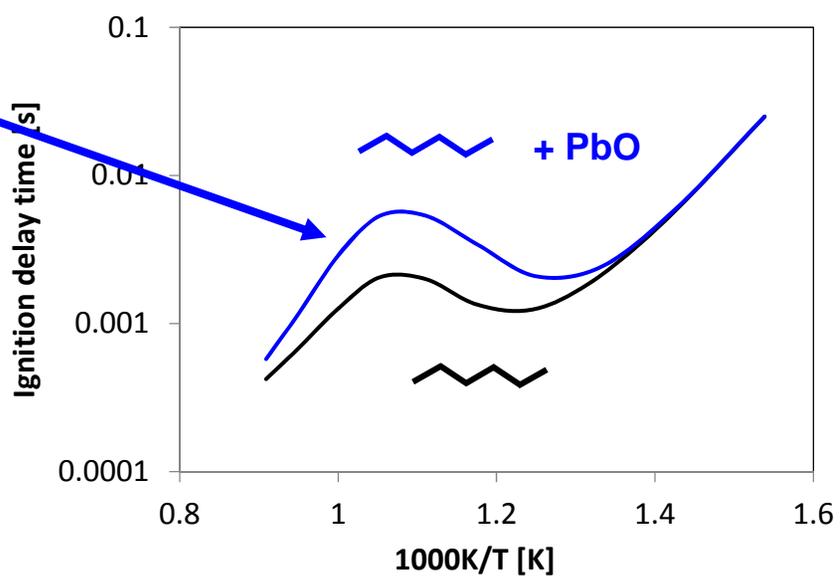


Thomas Midgley demonstrated tetraethyl lead to be an effective anti-knock agent (despite its toxicity)



It is believed that TEL forms a "fog" of PbO which scavenges HO₂ radicals and prevents the build up of H₂O₂ inhibiting the transition to high temperature ignition

Pitz & Westbrook, Combustion and Flame 63: 113-133 (1986)

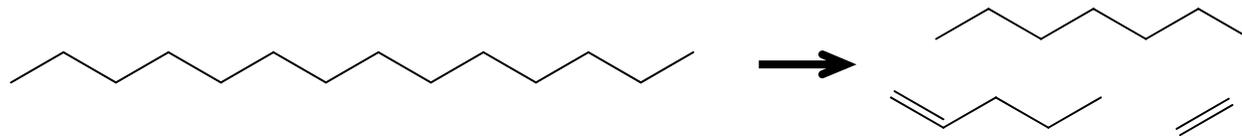


25 atm, Φ=1, constant volume



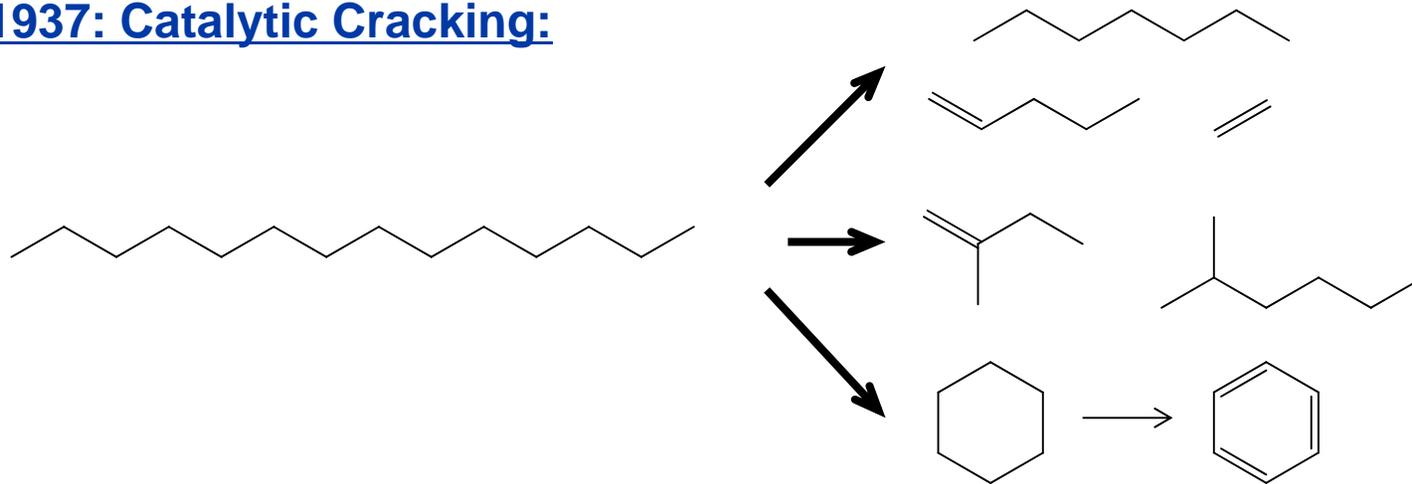
The high demand for gasoline drove the quest for new refinery technologies

1920 circa: Thermal Cracking:



- Decomposition of heavier petroleum fractions to shorter (more volatile) alkanes and olefins
- Twofold increase of the yield of gasoline from oil

1937: Catalytic Cracking:



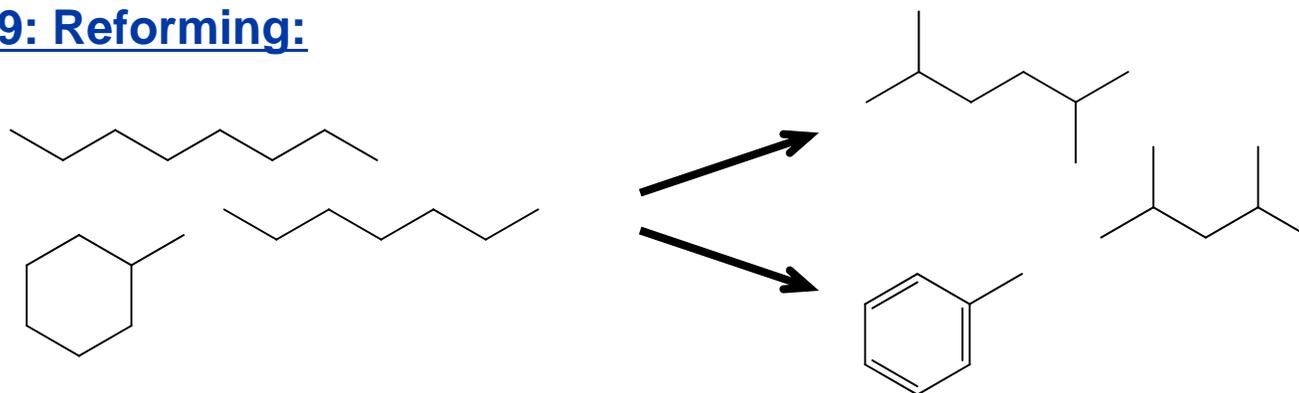
Higher yields, better fuels (higher aromatic and lightly branched paraffins)

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The high demand for gasoline drove the quest for new refinery technologies

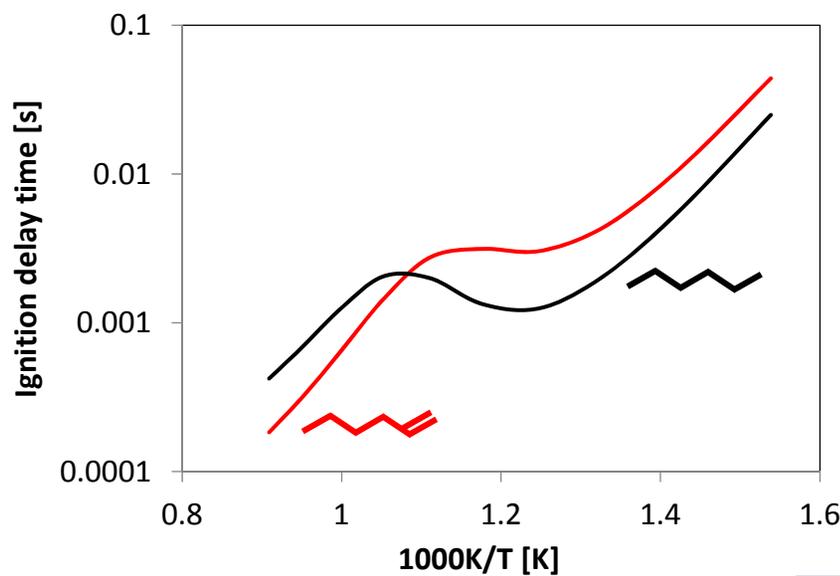
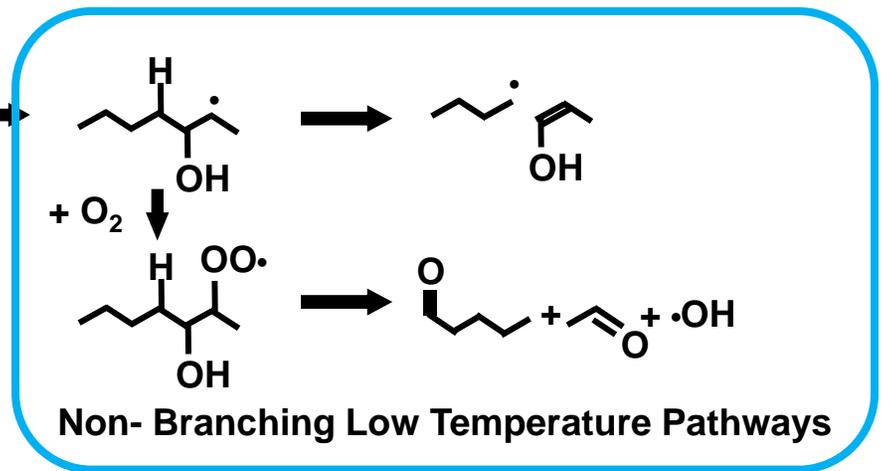
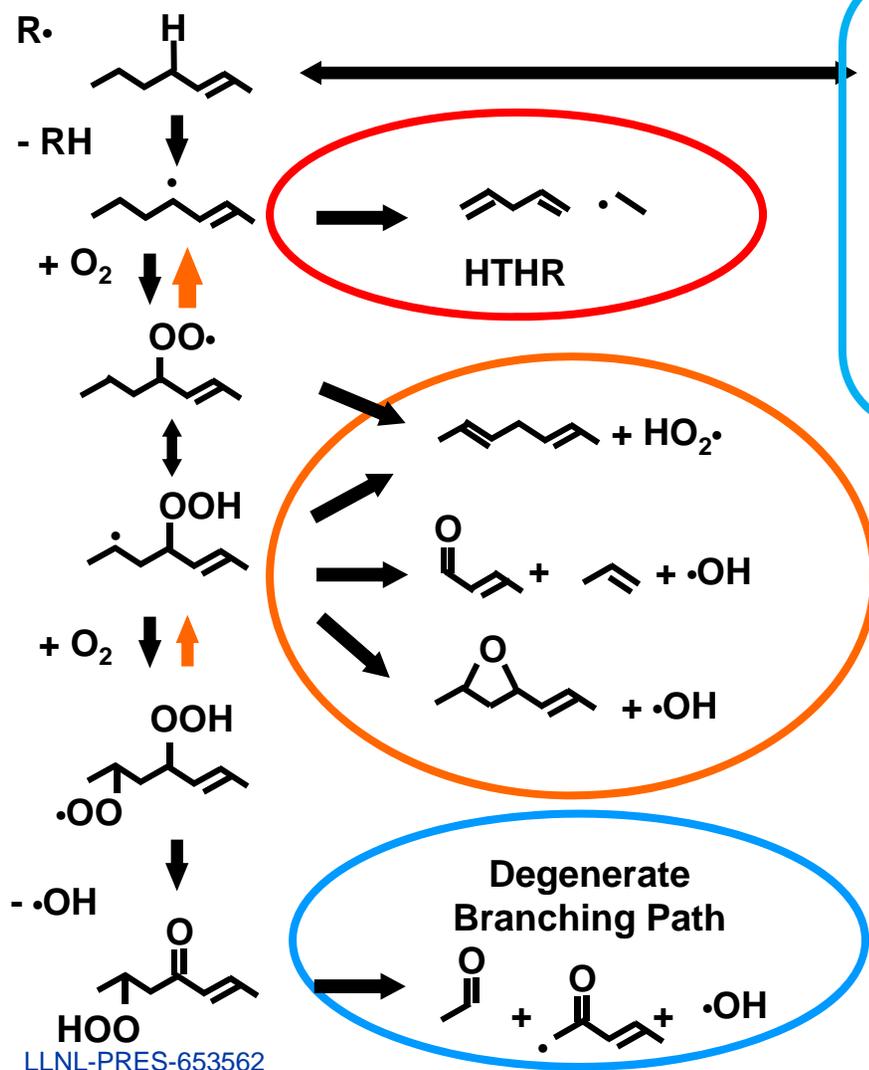
1949: Reforming:



Upgrade the fuel quality by increasing the fraction of aromatics and branched paraffins



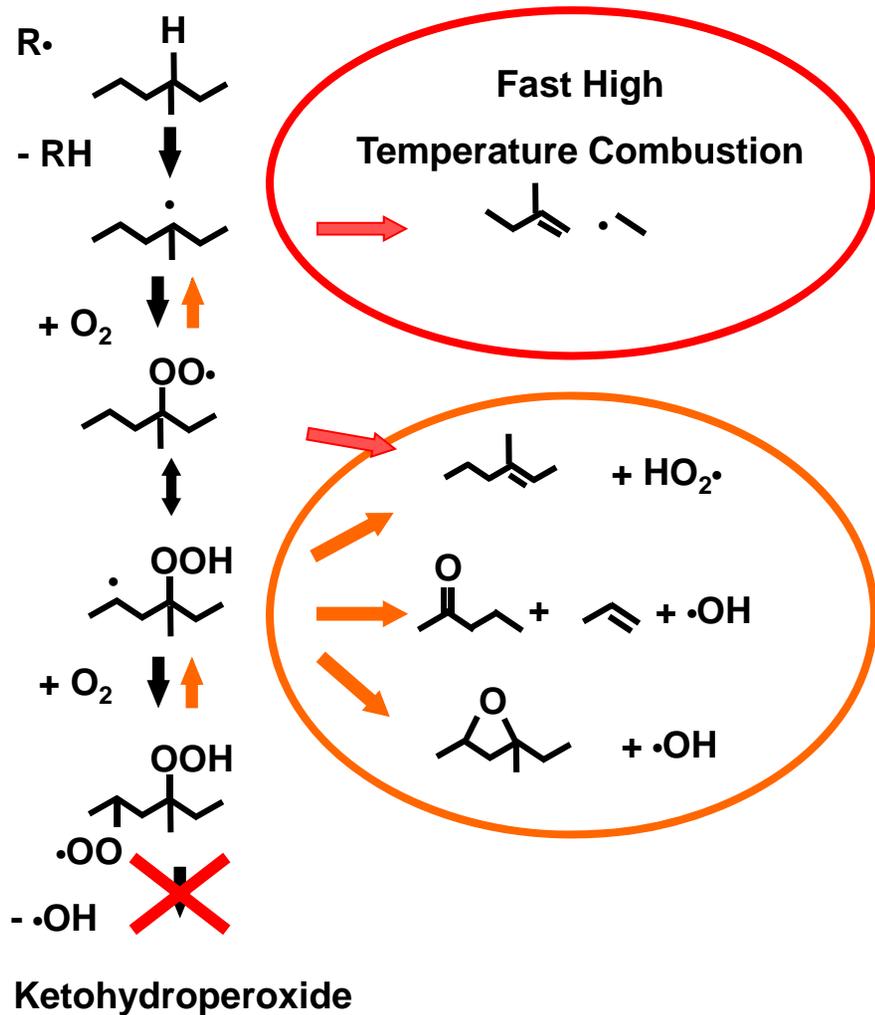
Alkenes are less reactive at LT than their saturated homologues due to alternative propagation pathways and weaker R-OO bond



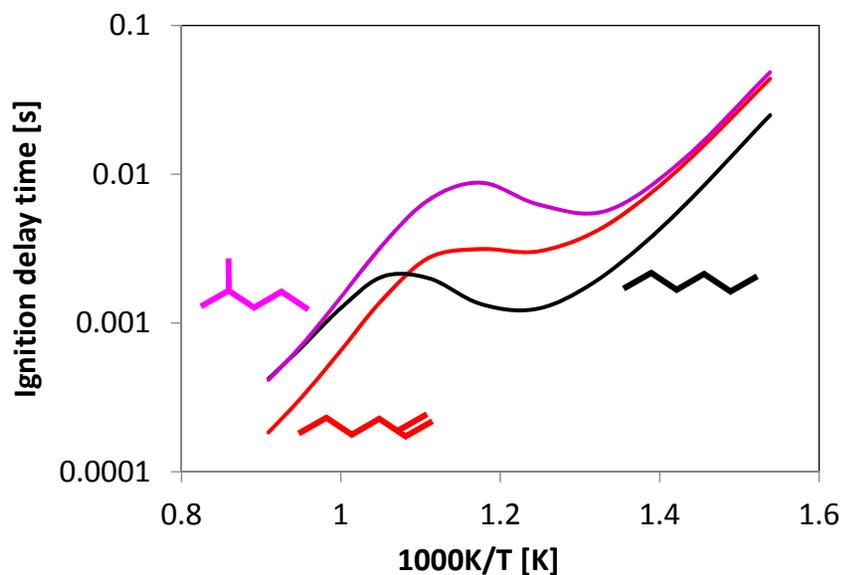
25 atm, Φ=1, constant volume



If the abstraction reaction involves a tertiary site of an isoalkane the formation of ketohydroperoxides is not possible



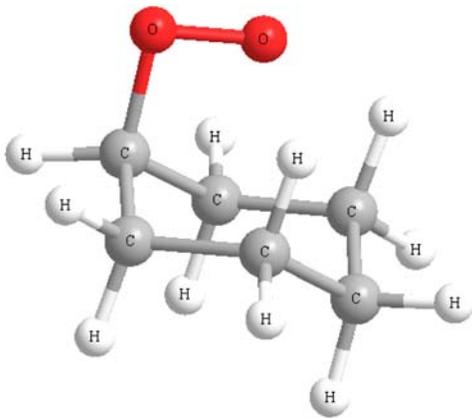
The internal isomerization steps required by the low temperature degenerate branching mechanism are slower because of the higher activation energy required for primary hydrogens



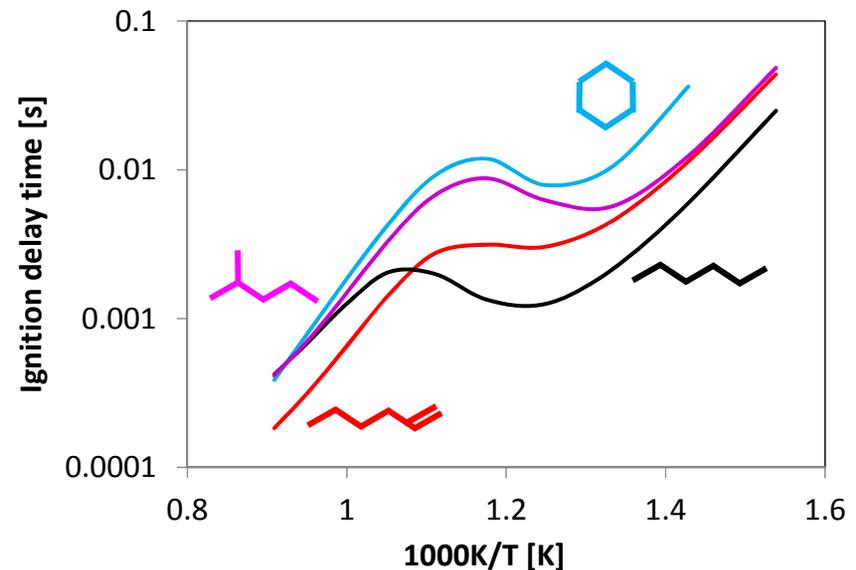
25 atm, $\Phi=1$, constant volume



The 3D structure of cycloalkane makes H atom unavailable for the internal abstraction reactions reducing the reactivity of the fuel at low temperature



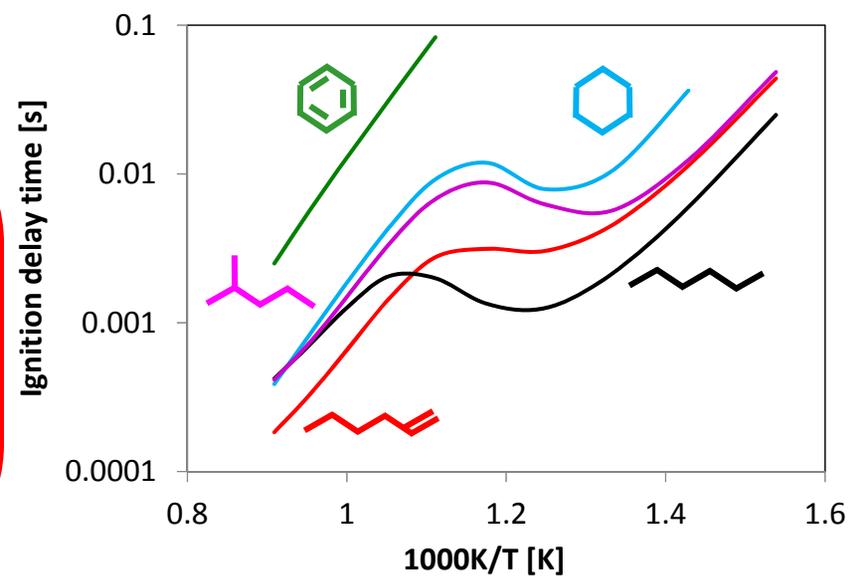
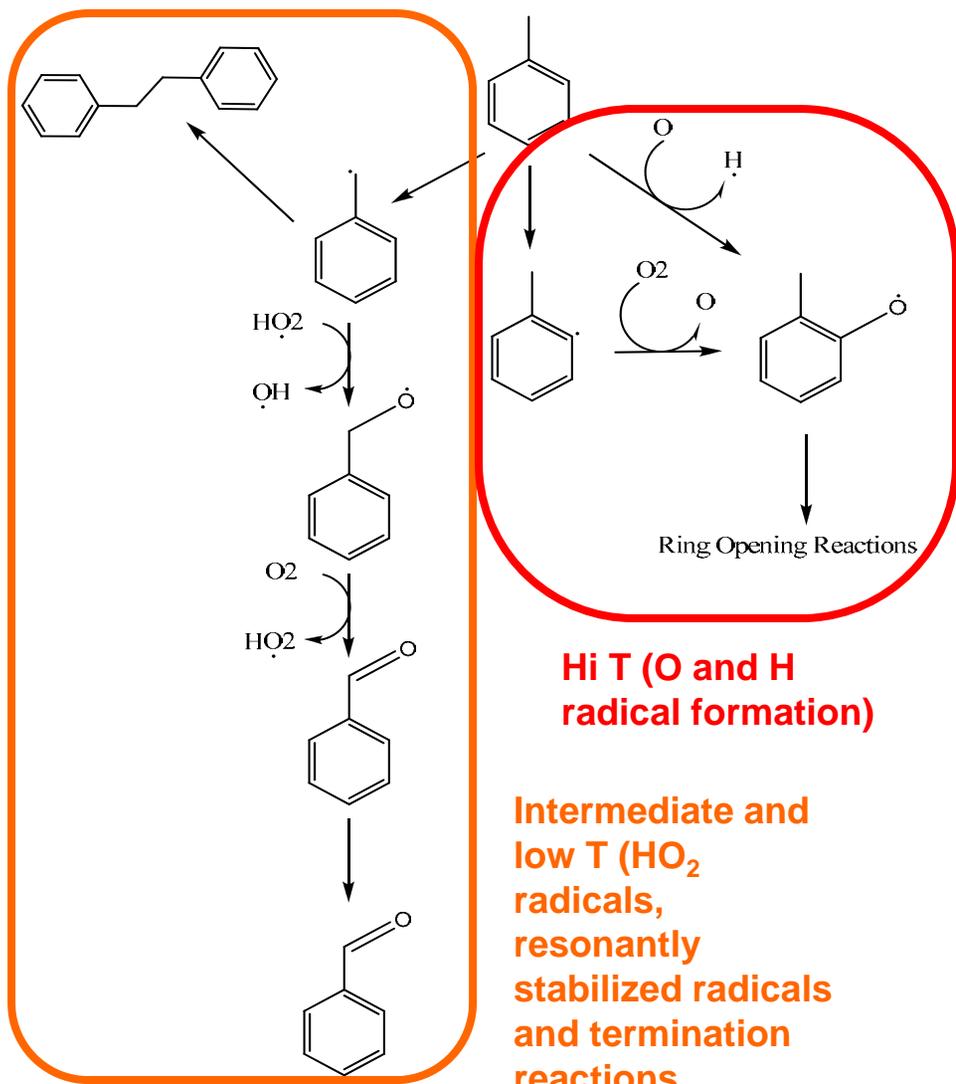
The presence of side chains, on the other hand, can provide alternative abstraction sites that increase significantly the reactivity of the cycloalkane molecule



25 atm, $\Phi=1$, constant volume



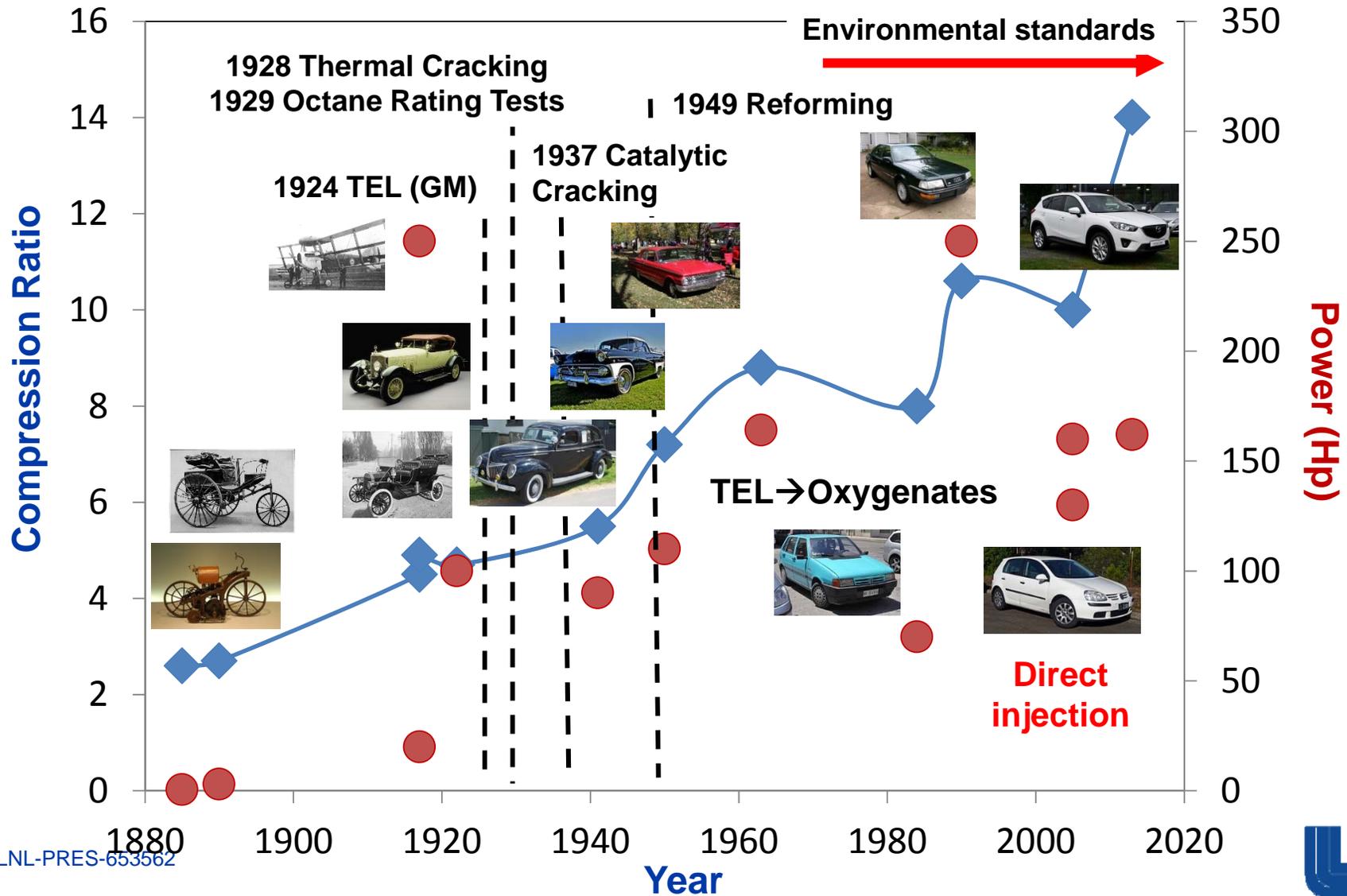
Aromatics don't have LT degenerate branching path and act as radical scavengers in mixtures (stable resonantly stabilized benzyl radicals)



25 atm, $\Phi=1$, constant volume



The introduction of additives, new refining technologies and fuel standards improved fuel quality, thus enabling the development of modern engines



How does gasoline look like today?

Today gasolines are complex mixtures of hundreds of components

Qualitative composition is known

Their composition is intrinsically variable (seasonally, depending on the feedstock,)

The introduction of alternative fuels is making things even more complicated

A detailed kinetic combustion model can include hundreds of species to describe a single component

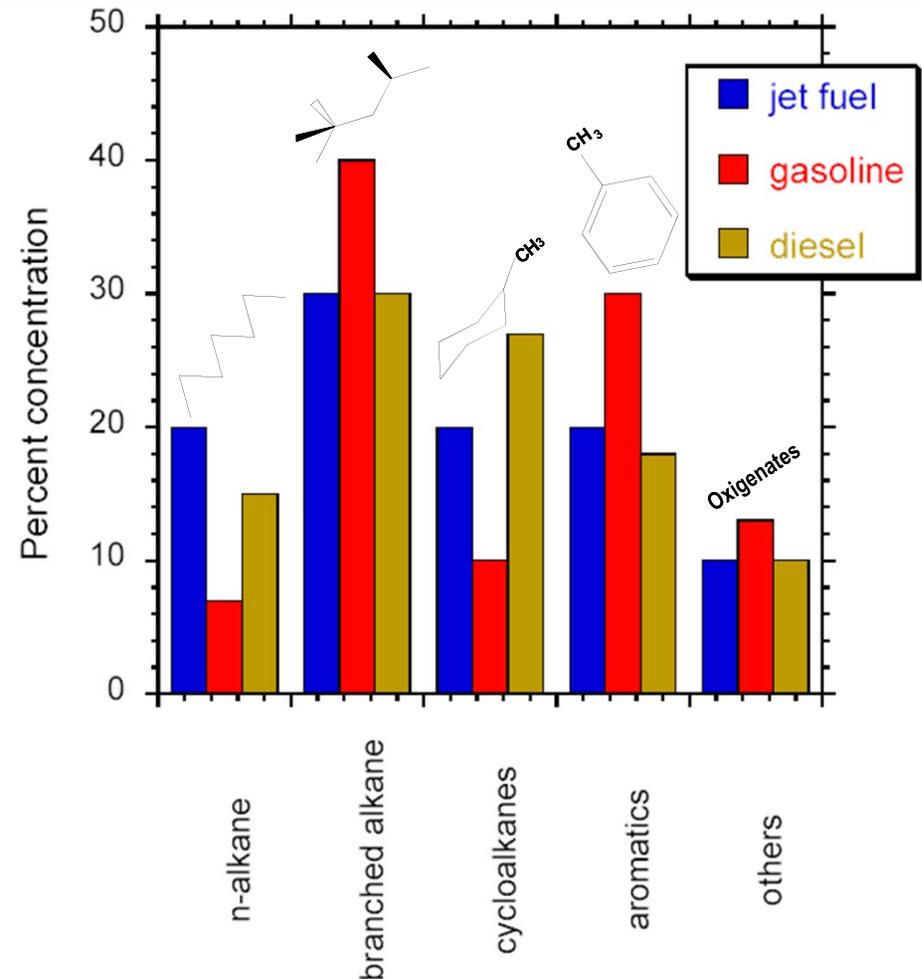
Simpler mixtures have to be defined for modeling and more reproducible experiments

Gasoline $6 < C < 10$

Jet fuel $9 < C < 13$

Diesel $13 < C < 22$

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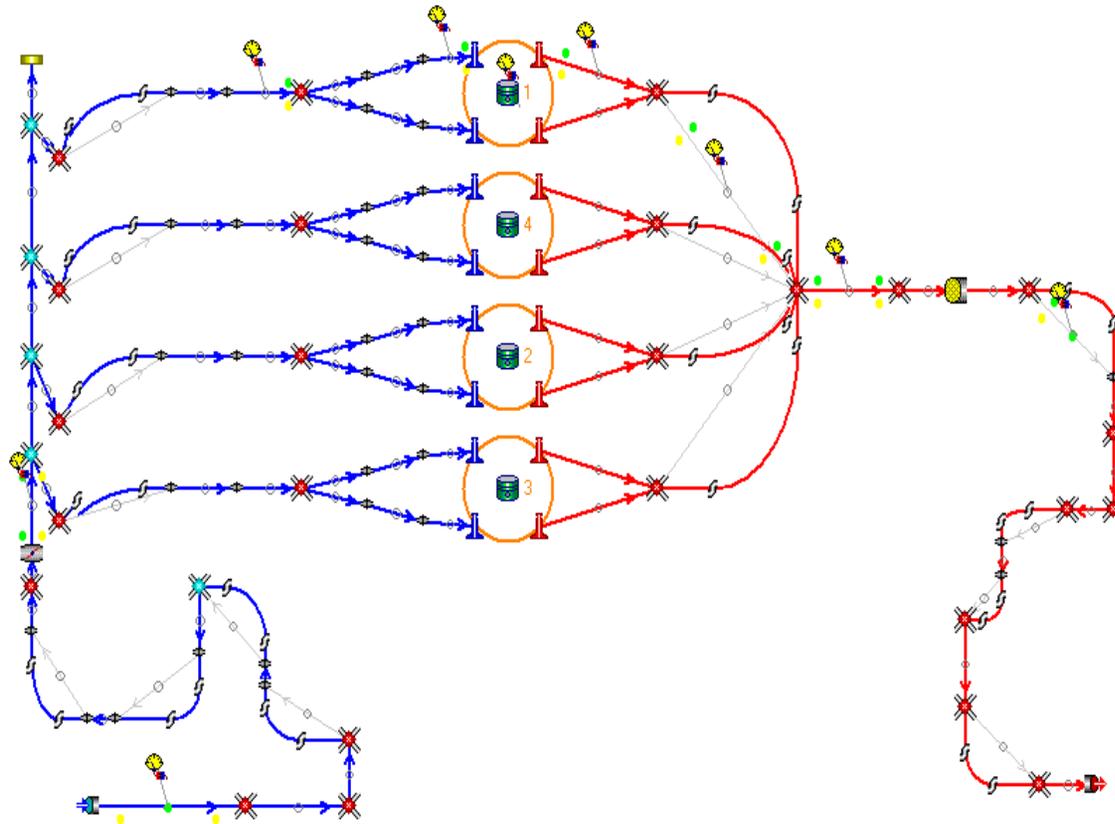


Surrogate fuels allow to cope with the compositional complexity of real fuels

- **Mixtures with a limited number of components (Surrogates) are generally used to model the physical and chemical properties of real fuels both in modeling and experimental studies (simplicity & consistency)**
- **The simplest surrogate for gasoline is considered to be iso-octane**
- **Primary reference fuels allow to characterize better the auto-ignition propensity allowing a finer tuning of the reactivity. The notion of AKI = $(RON+MON)/2$ (currently used in the US as a “road octane number”) was introduced and PRFs with that rating were used to simulate gasoline**
- **The shortcomings of these surrogates become evident when we are moving away from the operating conditions of old carbureted engines (DISI, Downsized, HCCI, ...)**



A numerical study on the engine combustion behavior of an olefinic gasoline



FIAT-Lancia 1200 16v

An “Old School” engine

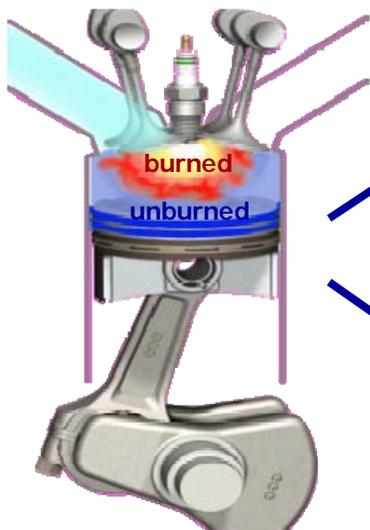
Engine schematization in
GASDYN (Politecnico di
Milano) a 1-D/quasi-D
model

Type	Spark Ignition
Valves/cylinder	4
Stroke	78.9 mm
Bore	70.8 mm
Compression Ratio	10.6
Maximum Power	51.5 kW @ 5000 rpm
Maximum Torque	104.5 Nm @ 4000 rpm



Engine Thermo Fluid Dynamic Modeling

All the typical boundaries encountered in i.c. engine duct systems (valves, abrupt area changes, throttle valves, turbines, compressors ...) are modeled adopting the classical assumption of quasi-steady flow.



Burned Zone
Equilibrium
Conditions

Unburned Zone
Detailed
Chemistry

Burning Rate estimated with
Fractal Approach

(minimum flame wrinkling is
proportional to the Kolmogorov
scale, the maximum one to the
integral length)

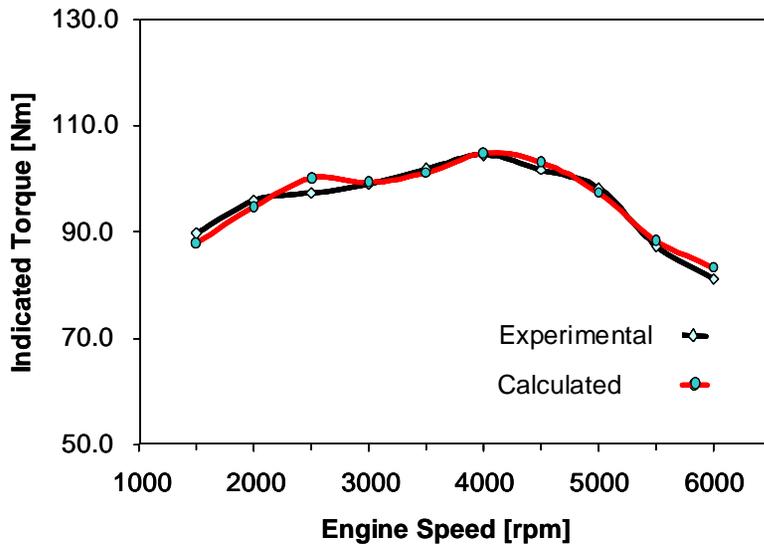
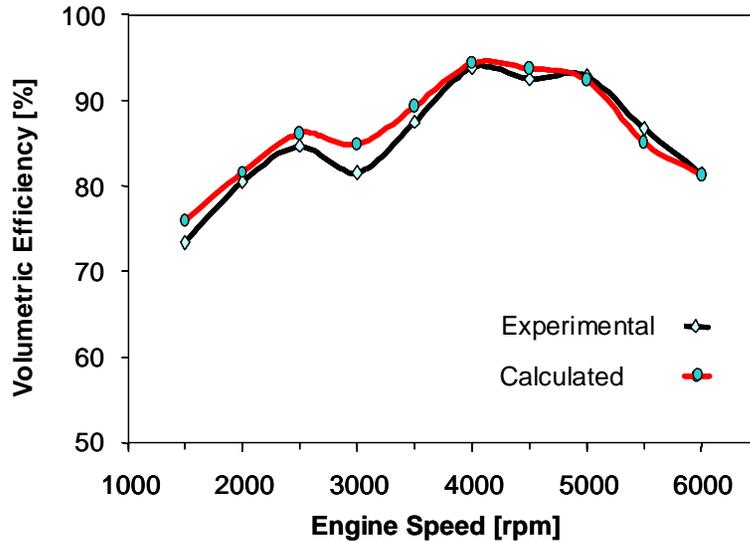
$$u_t = u_l \frac{A_t}{A_l}$$

A. Onorati, G. Ferrari, G. Montenegro, A. Caraceni, P. Pallotti, *Prediction of S.I. Engine Emissions during an ECE Driving Cycle via Integrated Thermo-Fluid Dynamic Simulation*, SAE Int. Congress & Exp. (Detroit) 2004, paper n. 2004-01-1001

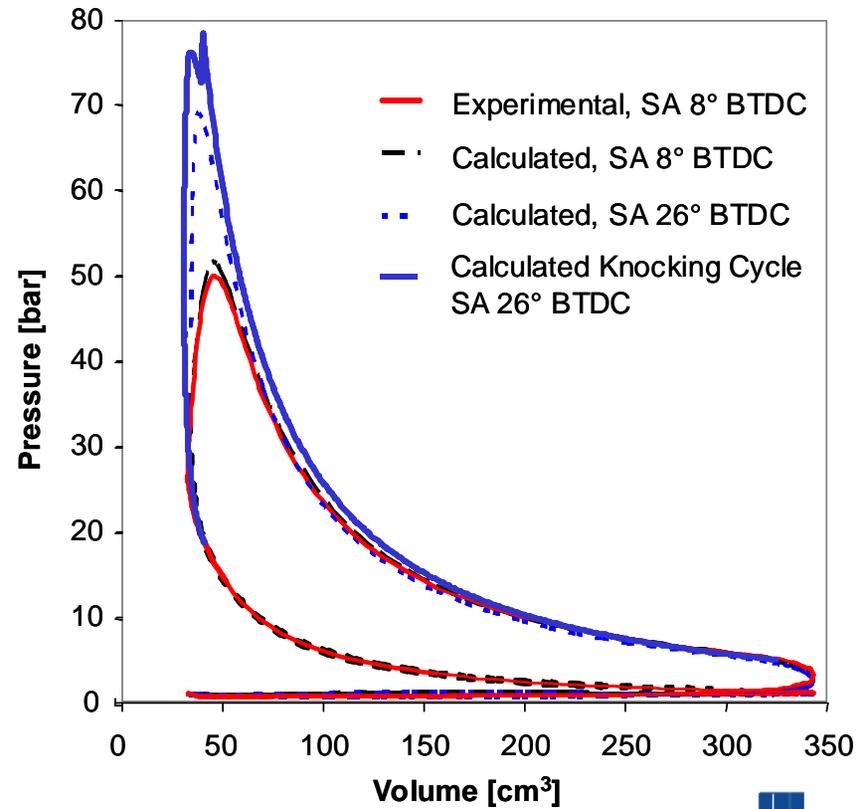
www.engines.polimi.it



Engine Model Validation



Calculated vs Experimental Volumetric Efficiency, Torque and Pressure cycle

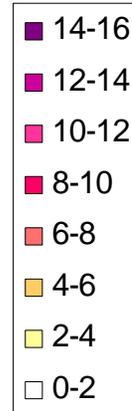
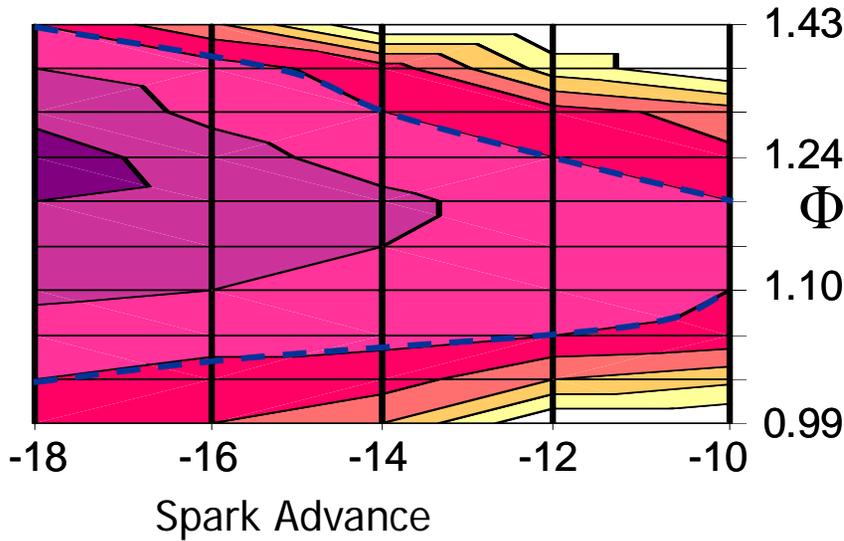


Gasoline Surrogates

		Surrogate 1	Surrogate 2
Density (15° C)	Kg/m ³	0.757	0.750
Reid Vapour Pressure	kPa	21.0	19.5
RON	-	97.3	97.3
MON	-	89.2	86.6
IBP	° C	66	76
10%	° C	89	89
50%	° C	99	99
90%	° C	102	102
FBP	° C	108	109
n-heptane	vol %	13	19
iso-octane	vol %	42	24
Toluene	vol %	32	26
MTBE	vol %	13	13
di-isobutylene	vol %	-	18



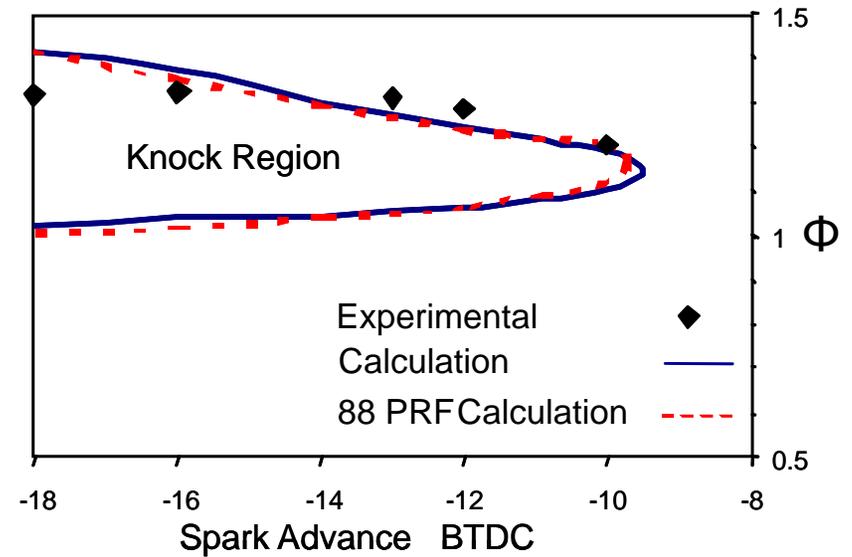
Knock Limits



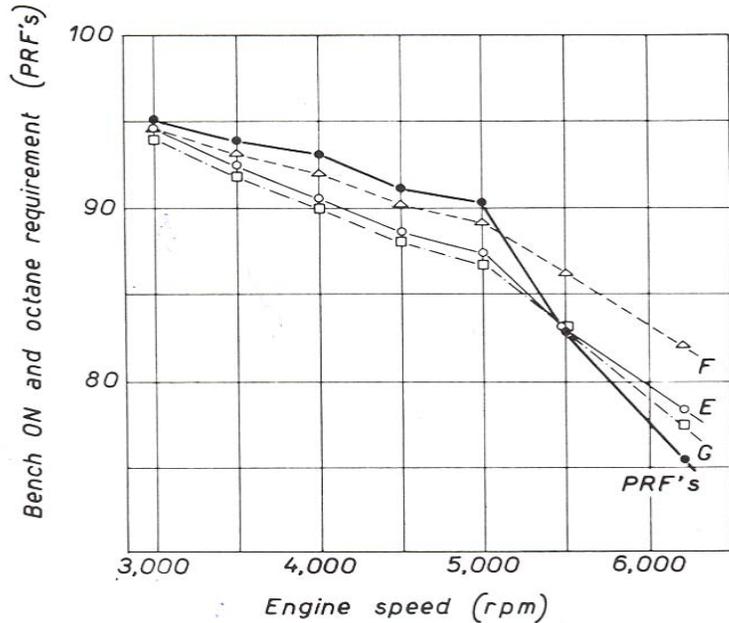
Unburnt Fraction at Knock vs Engine Operating Conditions
(4000 rpm, full load)

Knock Critical Conditions assuming 10% of unburned gases as "light knock" threshold

We define the octane performance based on the PRF showing the same knock propensity



FIAT-Lancia Comparisons



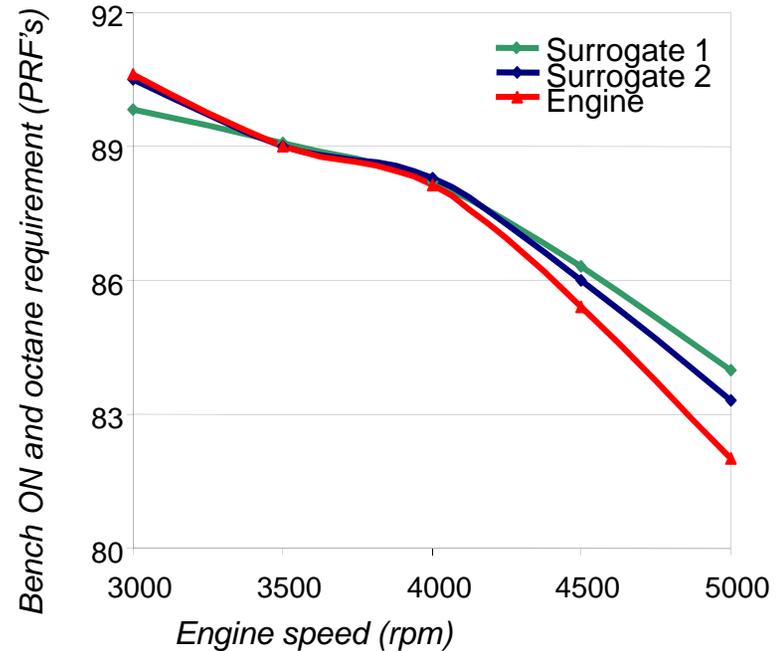
Experimental and Calculated Octane Performances of different fuels in on-road conditions...

Effect of alkenes:

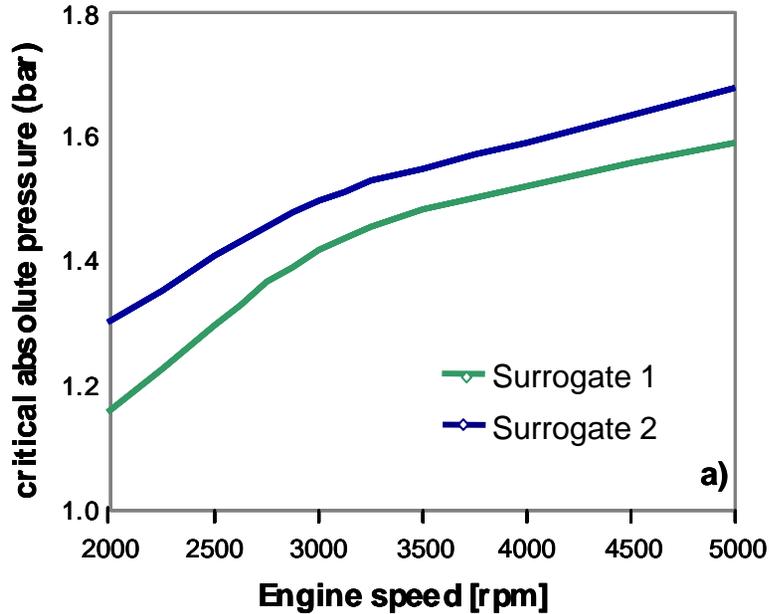
Engine Octane Requirement

Gasoline without Alkenes

Gasoline containing Alkenes



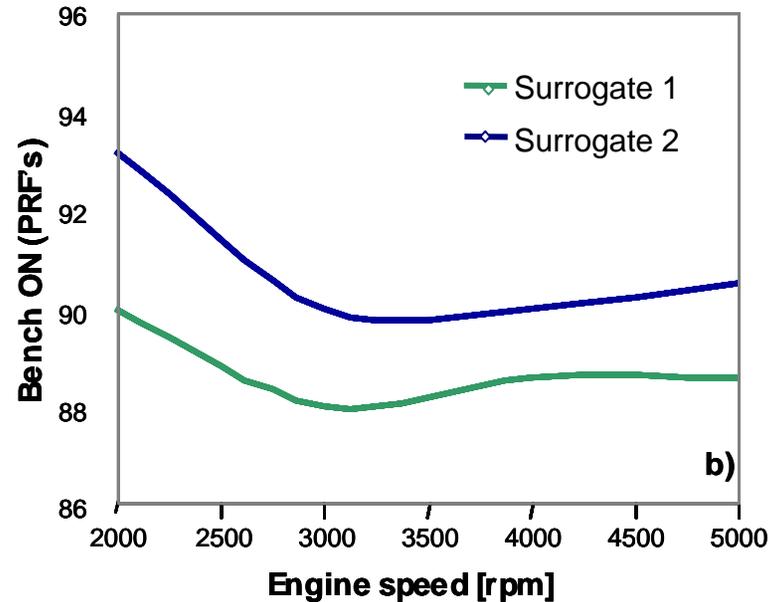
Effect of Turbocharging



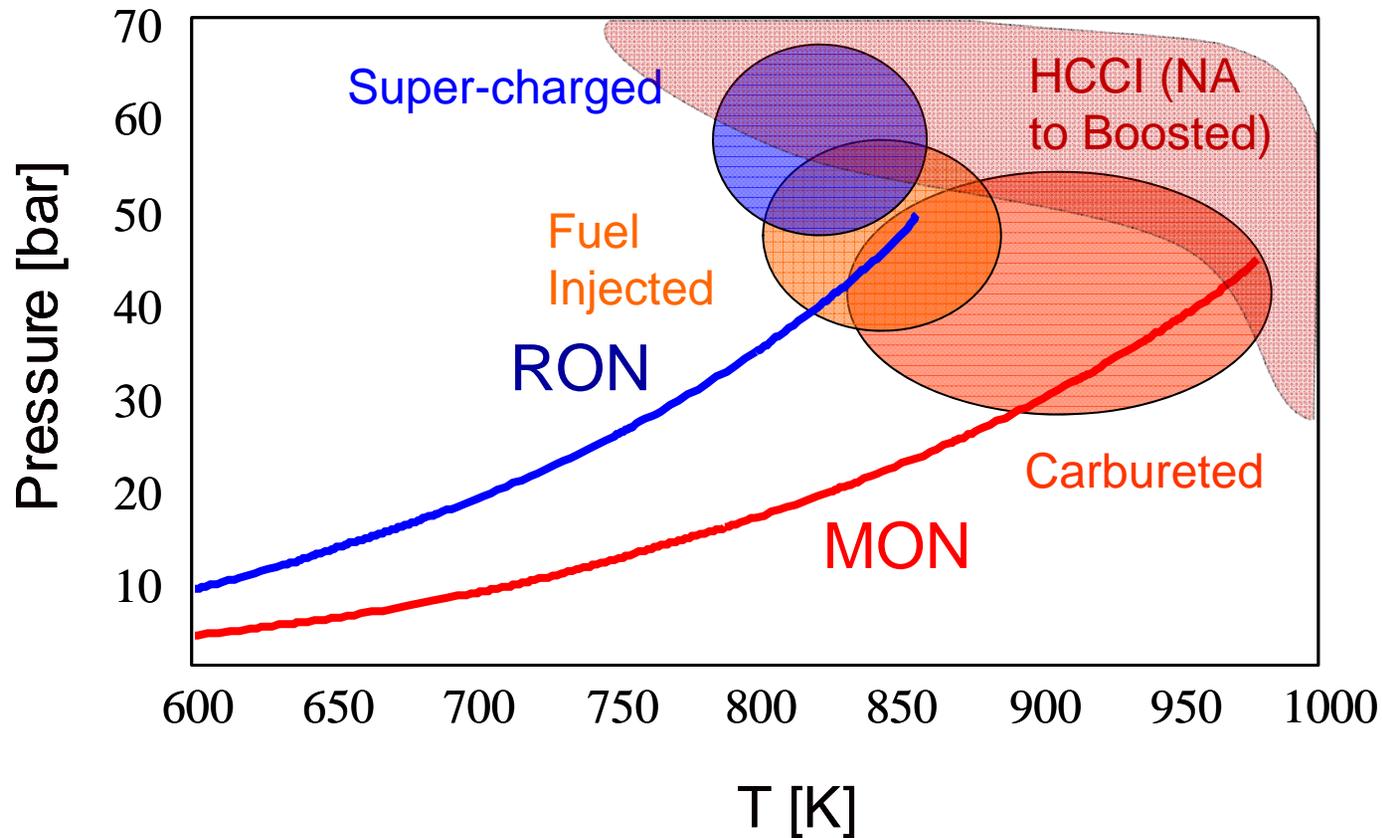
TurboCharged Engine

The lower reactivity of alkenes at low T and high P allows higher pressure boost.

Turbocharged conditions highlight the better octane performances of surrogate 2 (containing alkenes)



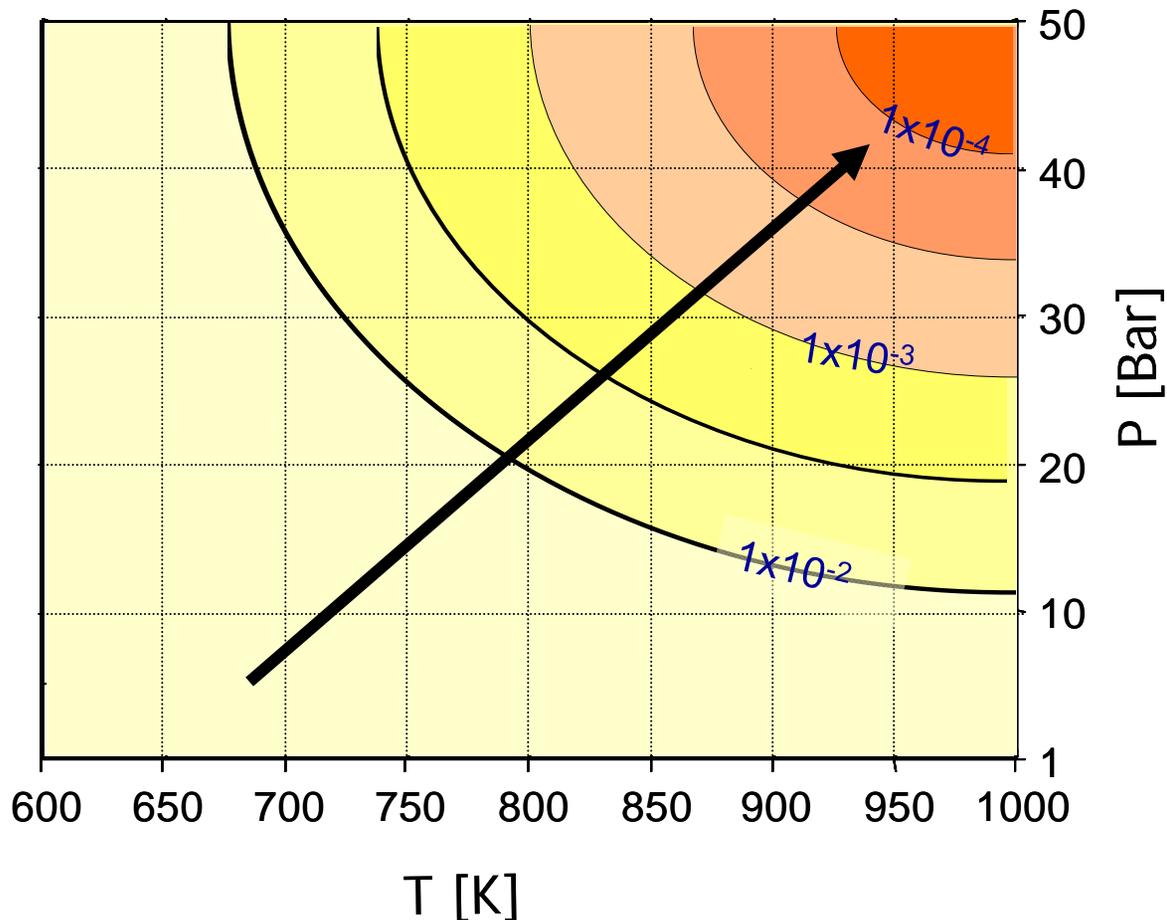
New engine technologies shift the operating region of the engine toward lower temperature and higher pressures



Modified from Andy D. B. Yates, André Swarts and Carl L. Viljoen, Correlating Auto-Ignition Delays And Knock-Limited Spark-Advance Data For Different Types Of Fuel, SAE 2005-01-2083



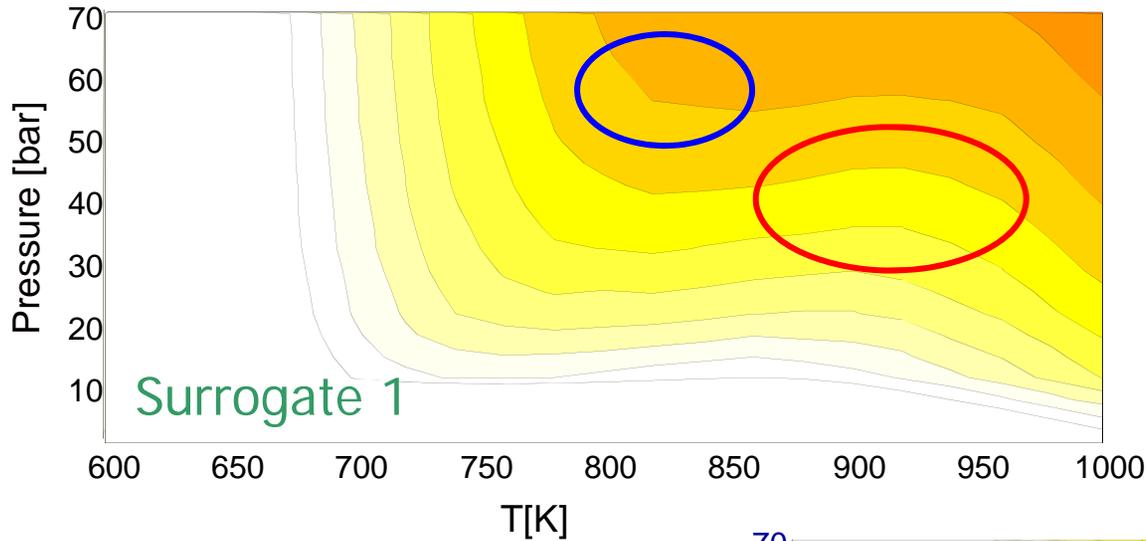
Induction times in constant volume systems and reactivity maps



Reactivity of the system is expected to increase with **pressure** and **temperature**

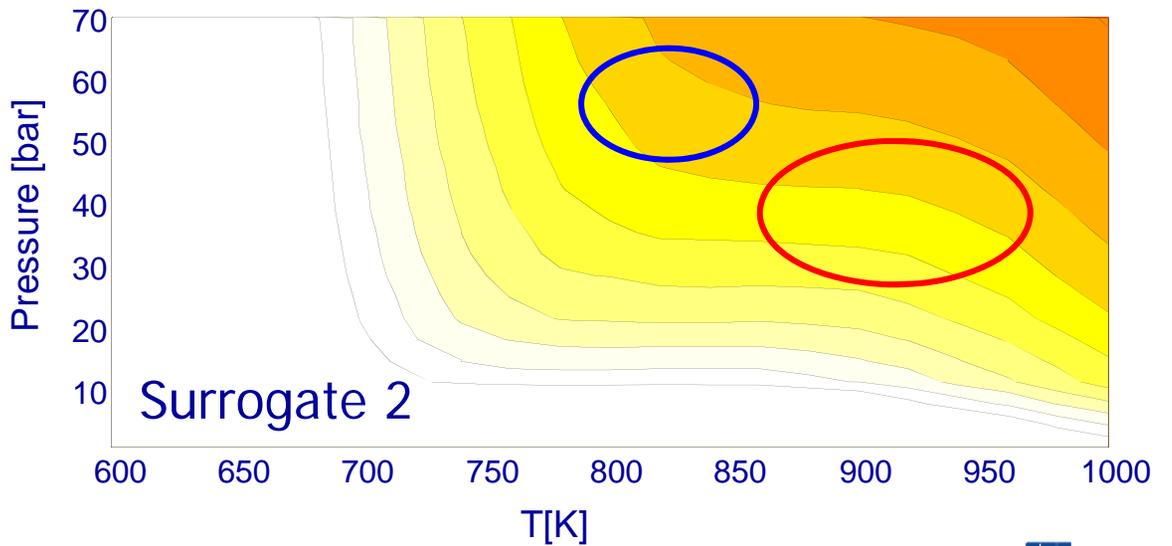


Surrogates Reactivity



Critical Operating
Conditions
Carbureted
Turbo

The different shape of
the NTC region
explains the different
performances of the
two surrogates



More complex surrogates are needed for today's engines – Can we use a kinetic model to assist the development of better surrogates???

- **As we have seen, engine technology and fuel quality has changed substantially from the '20s**

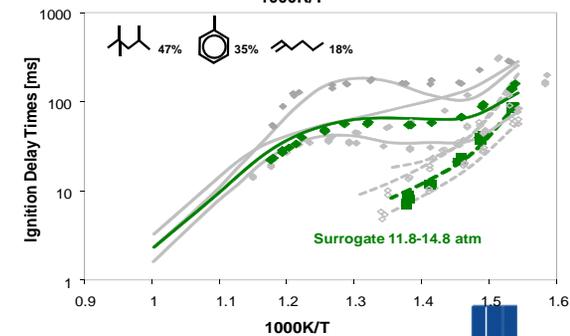
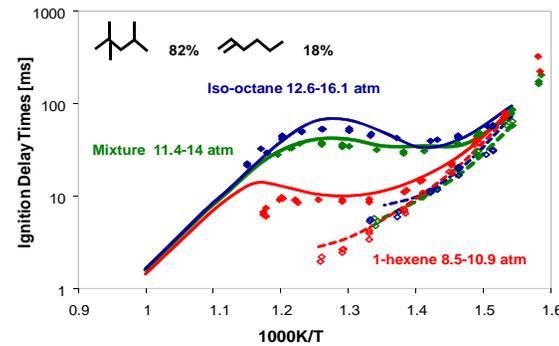
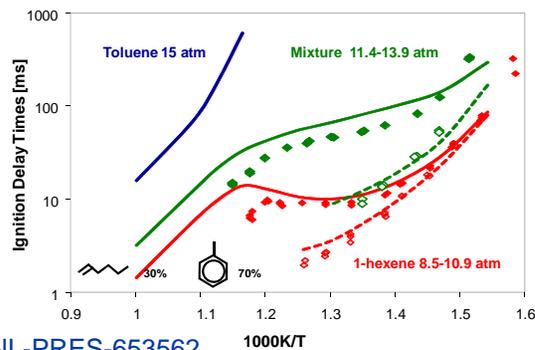
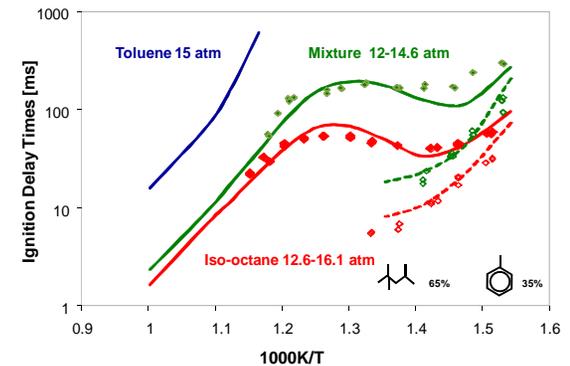
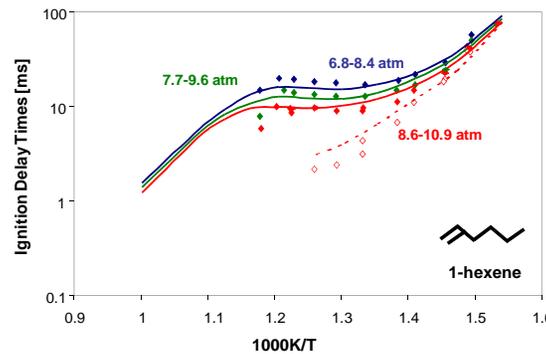
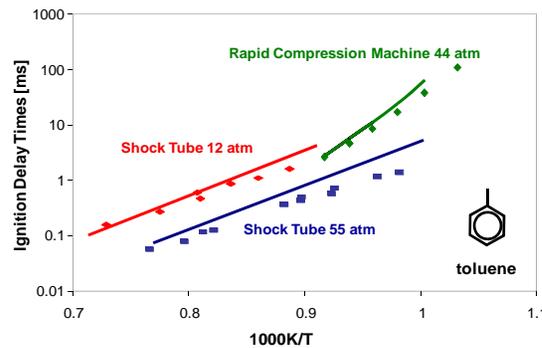
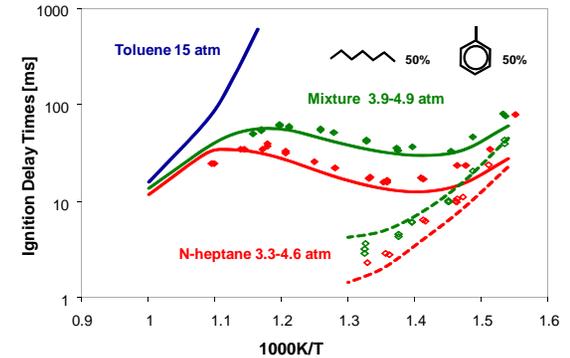
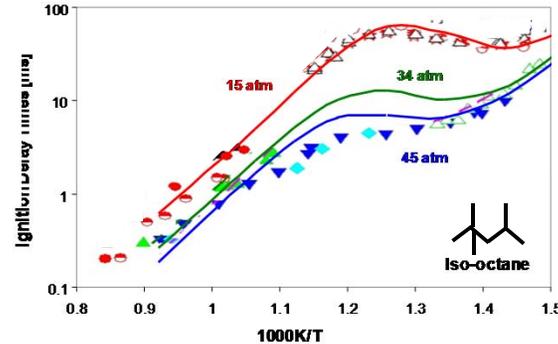
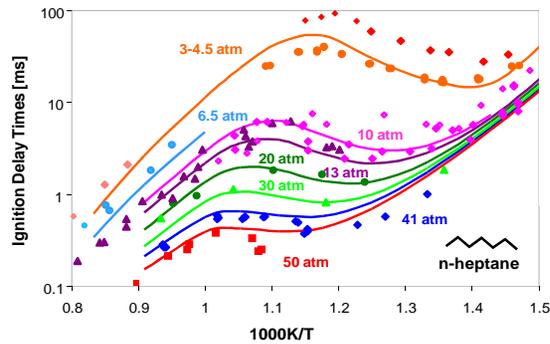
Are the standards defined back then, based on the ignition behavior of PRFs, still relevant to the combustion behavior of gasoline in modern engines?



- **Mixtures of saturated, unsaturated, oxygenated, aromatic compounds are needed to reproduce correctly the reactivity of the fuel**
- **A predictive model should take into account fuel effects on combustion and emissions**

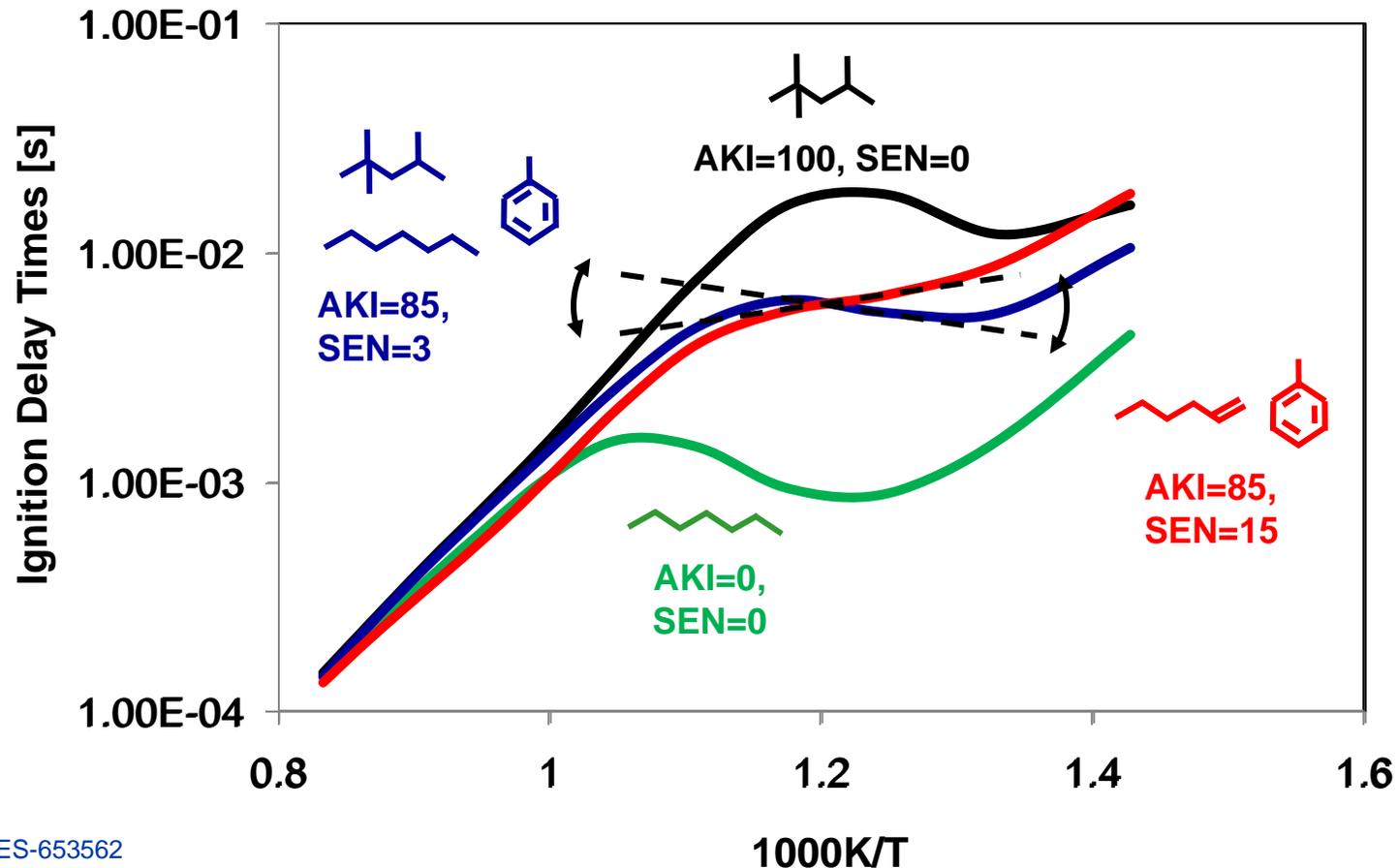


We can use a broadly validated kinetic mechanism to analyze the combustion behavior of gasoline surrogates



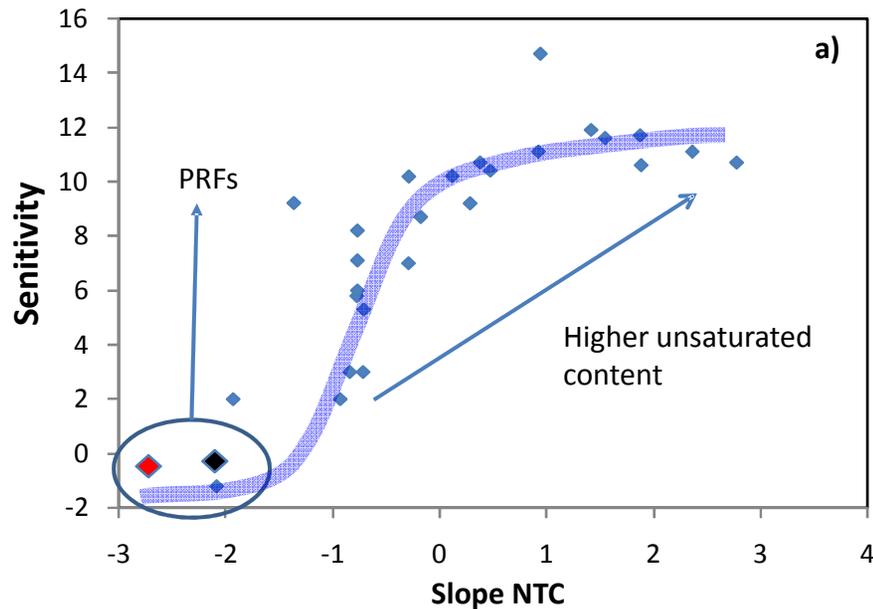
How does the presence of aromatics, olefins and oxygenates influence the reactivity of a fuel?

The two octane numbers (RON and MON) are used to determine the $AKI = (RON + MON) / 2$ and the sensitivity $(RON - MON)$ of the fuel to the operating conditions

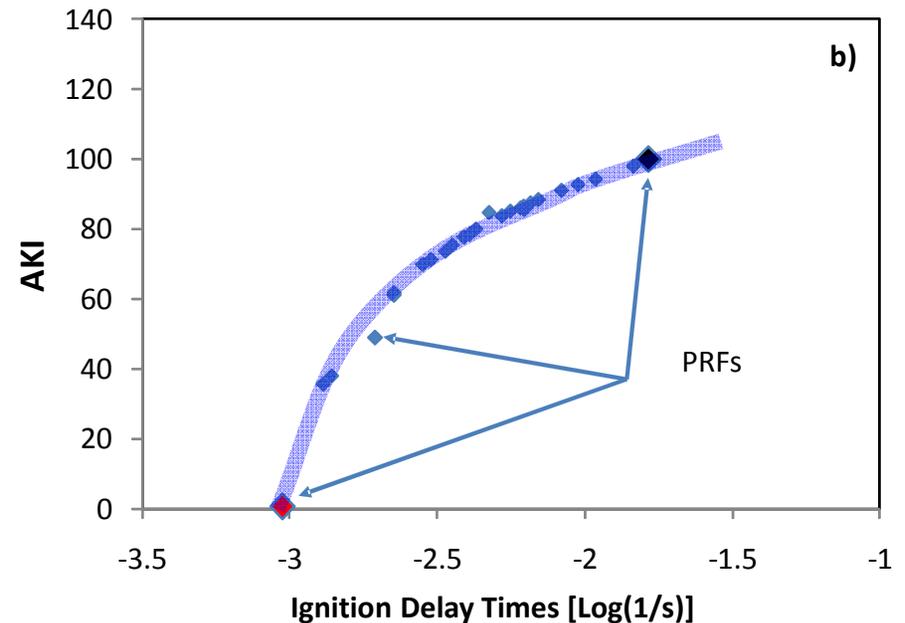


40 different surrogates were simulated using the detailed kinetic mechanism and their octane performances analyzed

Sensitivity vs. Slope



AKI vs. Ignition Delay time @ 825K



Two correlations between the octane numbers and the autoignition behavior in a kinetically controlled system were developed

Data: Personal communication, N.Morgan et al. Comb. & Flame



Boosted HCCI for High Power without Engine Knock and with Ultra-Low NOx Emissions – using Conventional Gasoline (Dec and Yang)

Approach:

Conventional Gasoline: $(R+M)/2 = 87$, RON = 90.8, MON = 83.2. Aromatics 23%, Olefins 4.2%, Alkanes 73%

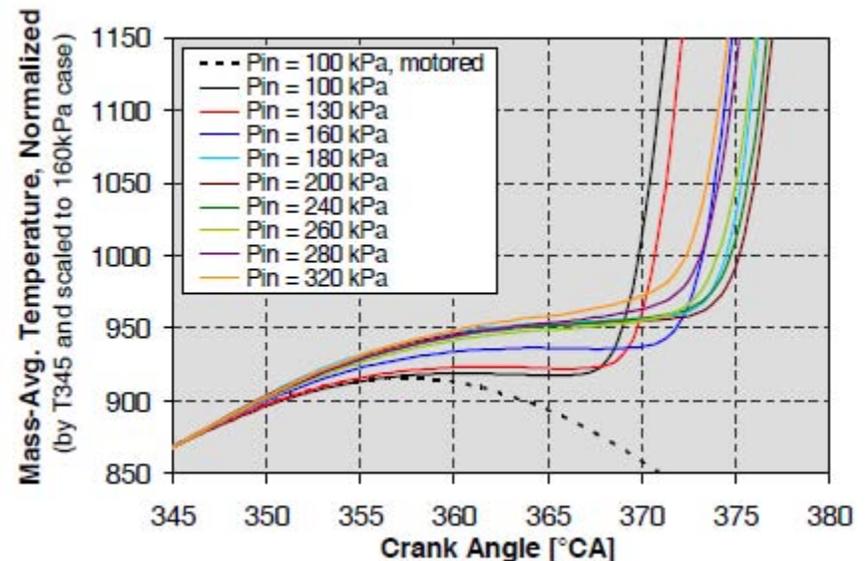
Piston: CR =14, open combustion chamber.

Current data at 1200 rpm.

Control pressure-induced enhancement of autoignition with a combination of:

- Intake temperature control
- Cooled EGR

→ Late combustion phasing thanks to intermediate temperature heat release



To understand the chemistry underlying this behavior we need a surrogate for the RD387 full blend research gasoline.

We start determining the fuel component palette

Limited information on the composition of the gasoline is typically available

4 Component surrogate:

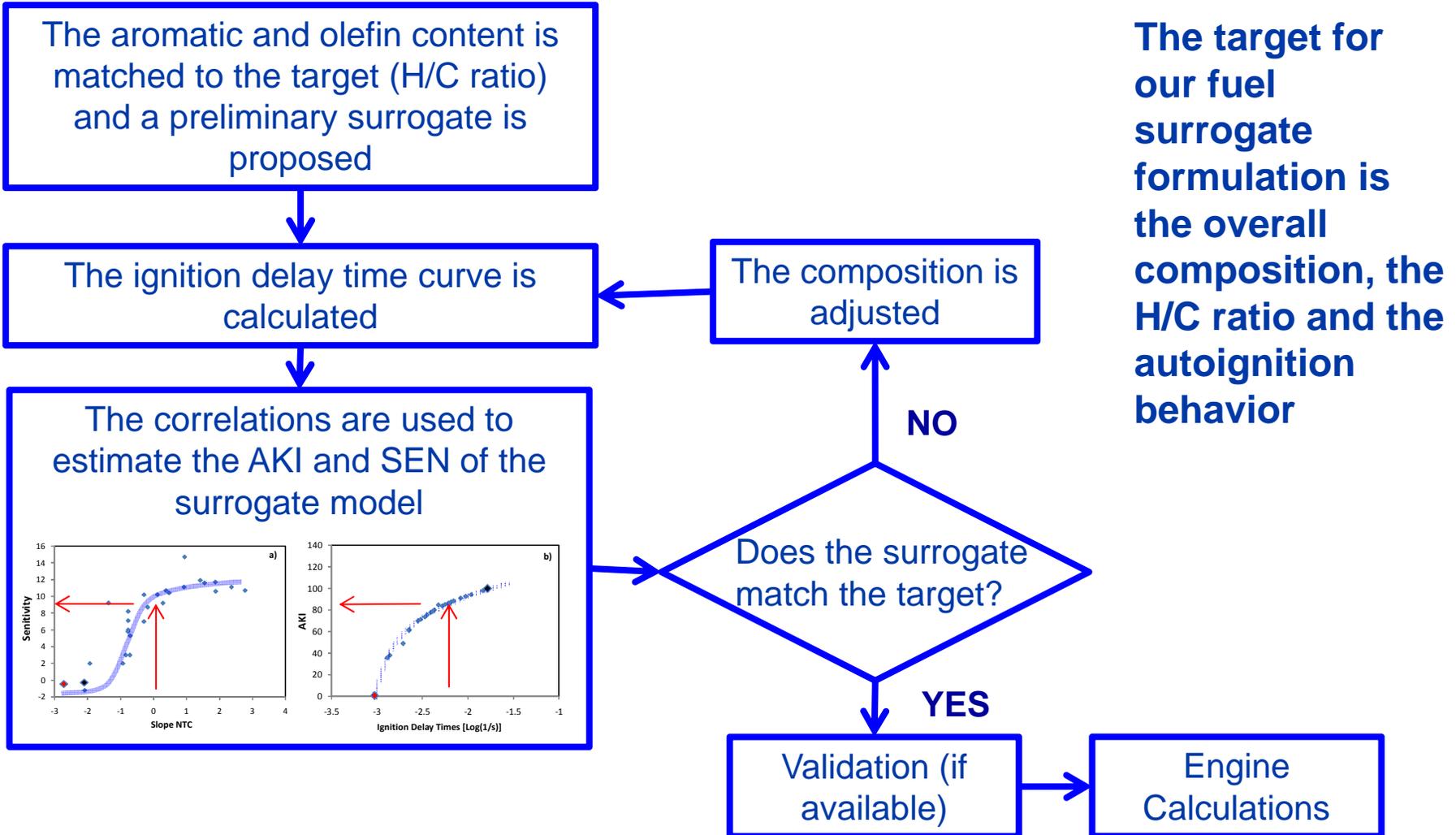
	Gasoline
Alkanes	73.1 %Vol
Aromatics	22.7 %Vol
Olefins	4.2 %Vol
H/C	1.946022
RON	83.2
MON	90.8

iso-octane } Base components of PRFs
n-heptane }
toluene High Sensitivity, best validation
2-pentene High Sensitivity, molecular weight
in the gasoline range

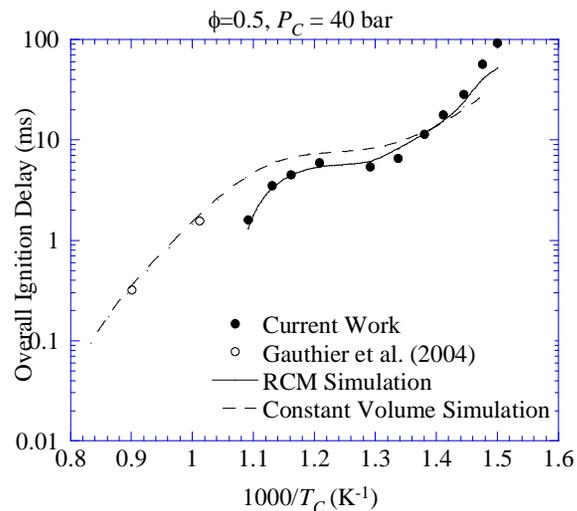
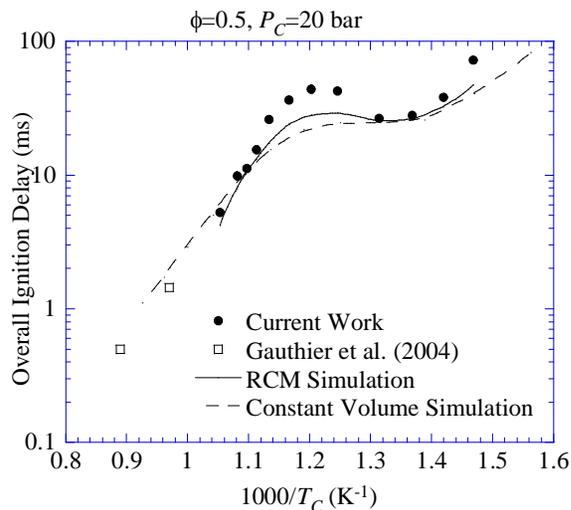
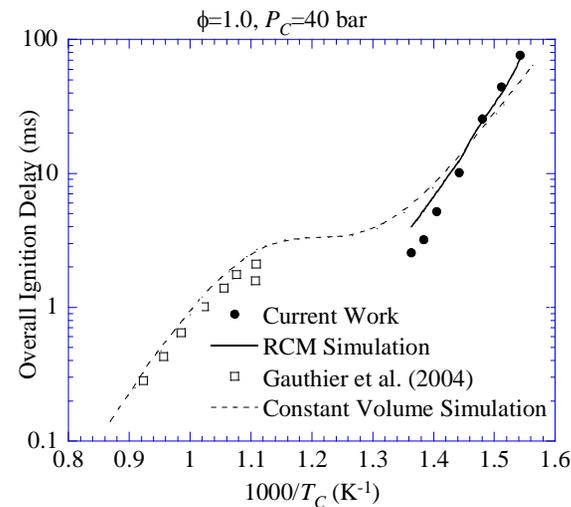
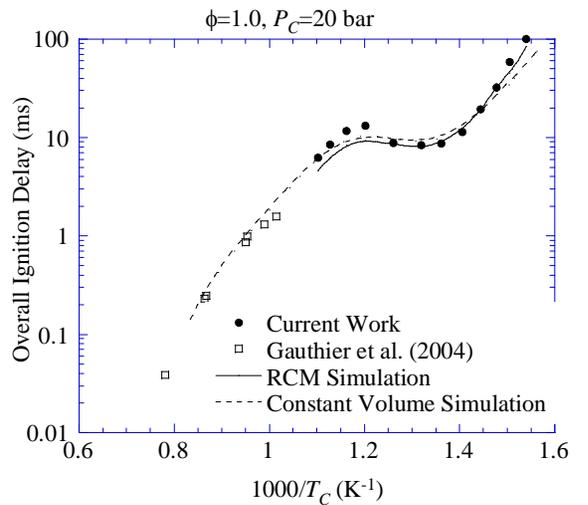
We have a well validated model for these 4 components



A numerical approach to the formulation of gasoline surrogates



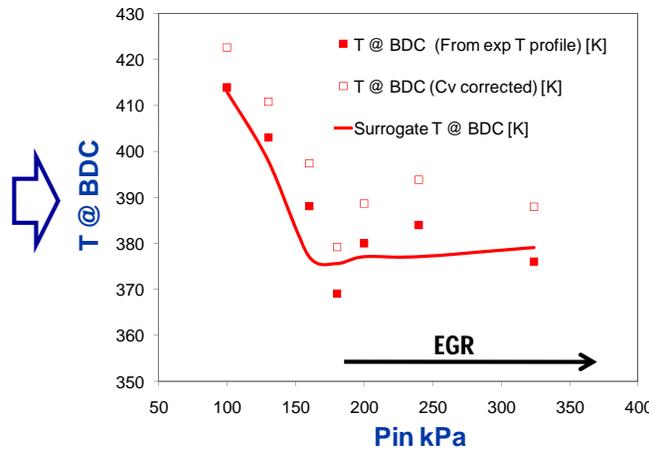
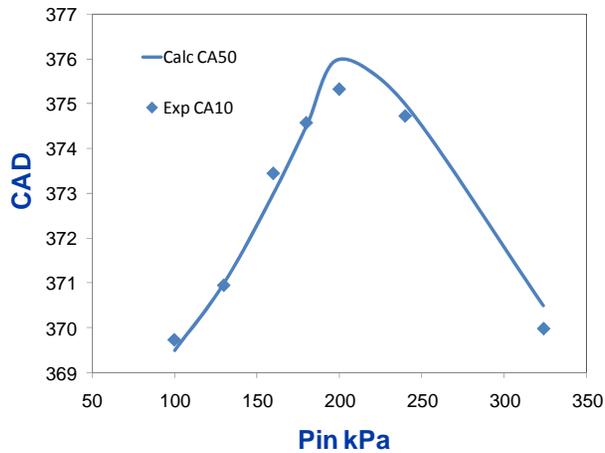
The calculated ignition delay curve of the surrogate is compared with ignition delay data of RD387



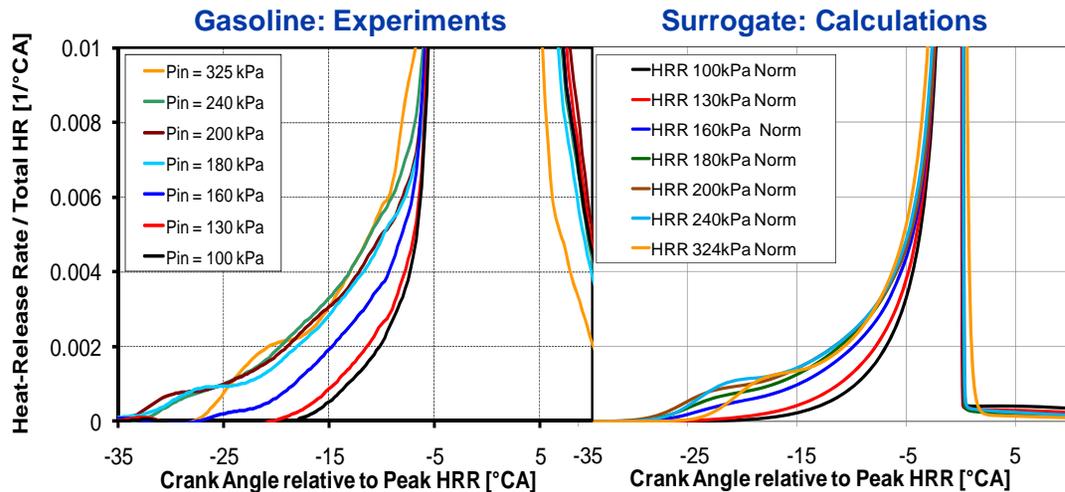
The fuel surrogate formulated based on the theoretical assumptions showed a very good agreement with gasoline data acquired in Rapid Compression Machine and Shock Tube experiments



HCCI simulations have been performed to investigate the chemistry responsible for the ITHR (SAE 2010-01-1086)



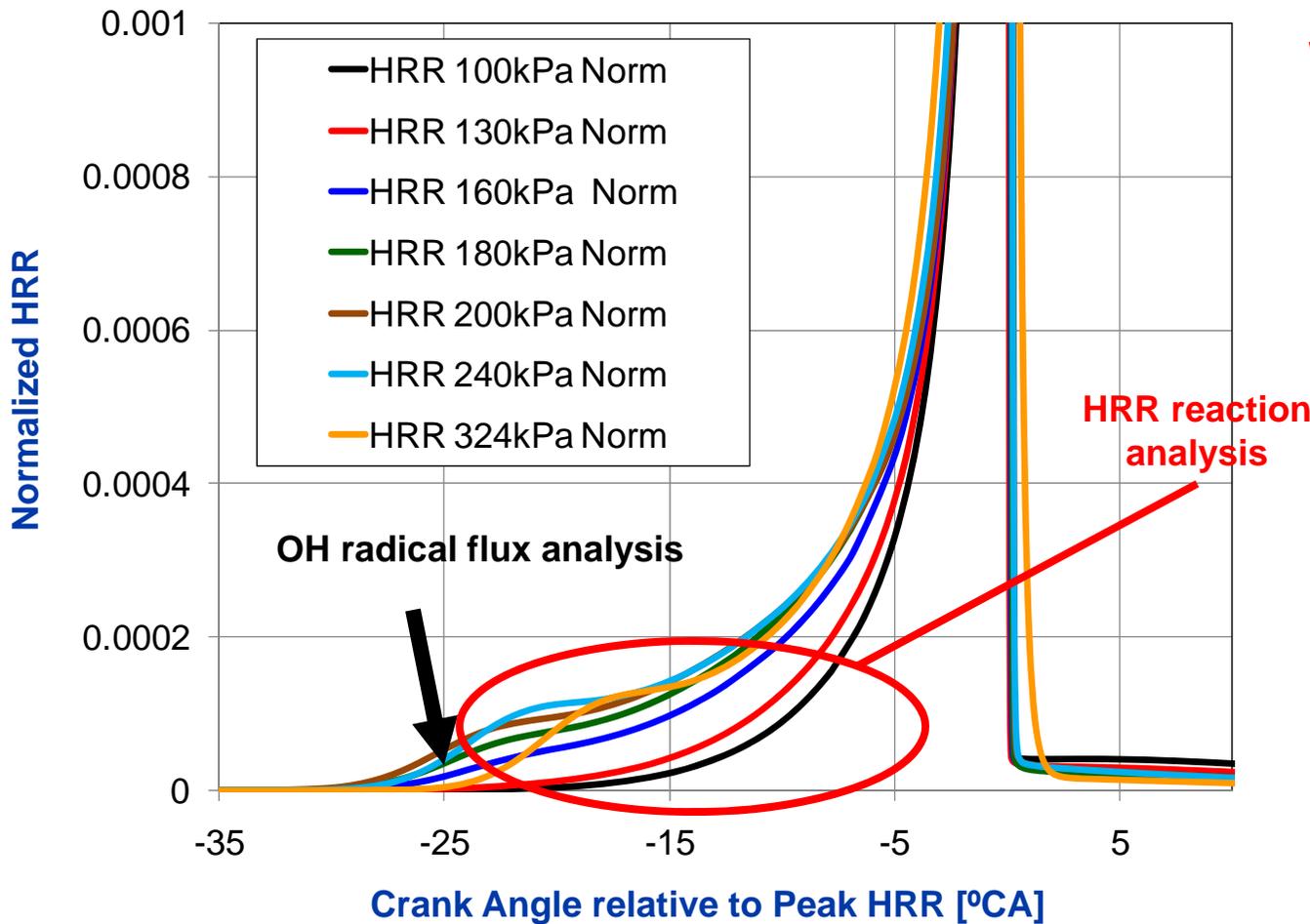
The intake temperature necessary to achieve the desired combustion timing is successfully reproduced



Heat release profiles are well reproduced too



Kinetic Analysis



What is contributing to the ITHR?



Reaction contribution to the HRR

What is triggering the ITHR?



OH radical flux analysis

(13 CAD BTDC 328kPa)



OH radical fluxes @ 13CAD BTDC

Absolute Rate of Production OH

$\text{IC8H18} + \text{OH} \rightleftharpoons \text{AC8H17} + \text{H}_2\text{O}$
 $\text{C6H5CH}_3 + \text{OH} \rightleftharpoons \text{C6H5CH}_2\text{J} + \text{H}_2\text{O}$
 $\text{NC7H16} + \text{OH} \rightleftharpoons \text{C7H15-2} + \text{H}_2\text{O}$
 $\text{NC7H16} + \text{OH} \rightleftharpoons \text{C7H15-3} + \text{H}_2\text{O}$
 $\text{IC8H18} + \text{OH} \rightleftharpoons \text{CC8H17} + \text{H}_2\text{O}$
 $\text{IC8H18} + \text{OH} \rightleftharpoons \text{DC8H17} + \text{H}_2\text{O}$
 $\text{IC8H18} + \text{OH} \rightleftharpoons \text{BC8H17} + \text{H}_2\text{O}$
 $\text{C5H10-2} + \text{OH} \rightleftharpoons \text{C5H10OH-2}$
 $\text{O2C5H10OH-2} \rightleftharpoons \text{C2H5CHO} + \text{CH}_3\text{CHO} + \text{OH}$
 $\text{NC7H16} + \text{OH} \rightleftharpoons \text{C7H15-1} + \text{H}_2\text{O}$
 $\text{NC7H16} + \text{OH} \rightleftharpoons \text{C7H15-4} + \text{H}_2\text{O}$
 $\text{C7H1400H2-402} \rightleftharpoons \text{NC7KET24} + \text{OH}$
 $\text{NC7KET24} \rightleftharpoons \text{NC3H7CHO} + \text{CH}_3\text{COCH}_2 + \text{OH}$
 $\text{C6H5CH}_2\text{J} + \text{H}_2\text{O} \rightleftharpoons \text{C6H5CH}_2\text{OJ} + \text{OH}$
 $\text{C6H5CH}_3 + \text{OH} \rightleftharpoons \text{C6H4CH}_3 + \text{H}_2\text{O}$
 $\text{C7H1400H3-502} \rightleftharpoons \text{NC7KET35} + \text{OH}$
 $\text{AC8H1600H-B} \rightleftharpoons \text{IC8ETERAR} + \text{OH}$
 $\text{NC7KET35} \rightleftharpoons \text{C2H5CHO} + \text{C2H5COCH}_2 + \text{OH}$
 $\text{AC8H1600H-C} \rightleftharpoons \text{IC8ETERAC} + \text{OH}$
 $\text{C7H1400H4-202} \rightleftharpoons \text{NC7KET42} + \text{OH}$
 $\text{NC7KET42} \rightleftharpoons \text{CH}_3\text{CHO} + \text{NC3H7COCH}_2 + \text{OH}$
 $\text{C5H10-2} + \text{OH} \rightleftharpoons \text{C5H91-3} + \text{H}_2\text{O}$
 $\text{C5H10-2} + \text{OH} \rightleftharpoons \text{C5H92-4} + \text{H}_2\text{O}$
 $\text{CH}_2\text{CHO} + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CO} + \text{OH}$
 $\text{DC8H1600H-B} \rightleftharpoons \text{IC8ETERBD} + \text{OH}$
 $\text{CH}_3\text{O}_2\text{H} \rightleftharpoons \text{CH}_3\text{O} + \text{OH}$
 $\text{C7H1400H1-302} \rightleftharpoons \text{NC7KET13} + \text{OH}$
 $\text{NC7KET13} \rightleftharpoons \text{NC4H9CHO} + \text{CH}_2\text{CHO} + \text{OH}$
 $\text{AC8H1600H-B02} \rightleftharpoons \text{IC8KETAB} + \text{OH}$
 $\text{IC8KETAB} \rightleftharpoons \text{IC3H7CHO} + \text{TC3H6CHO} + \text{OH}$

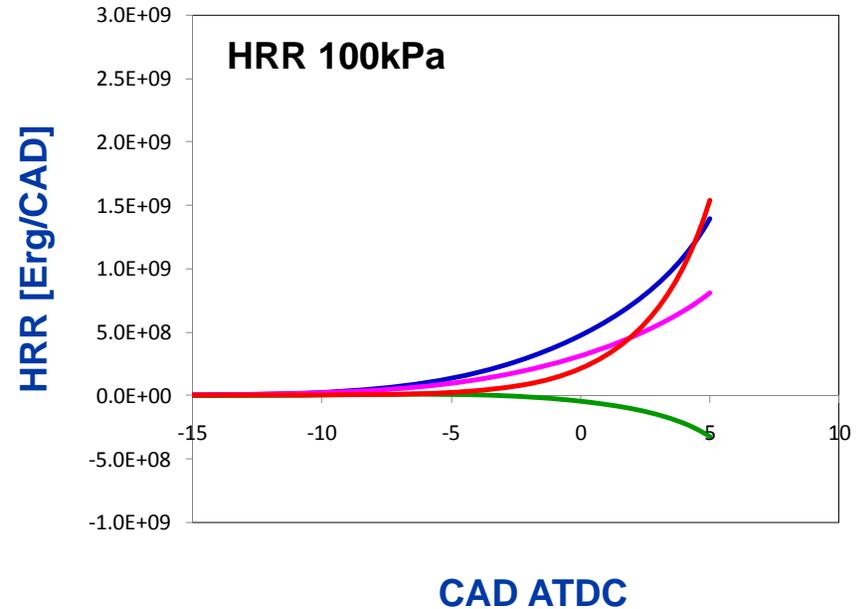
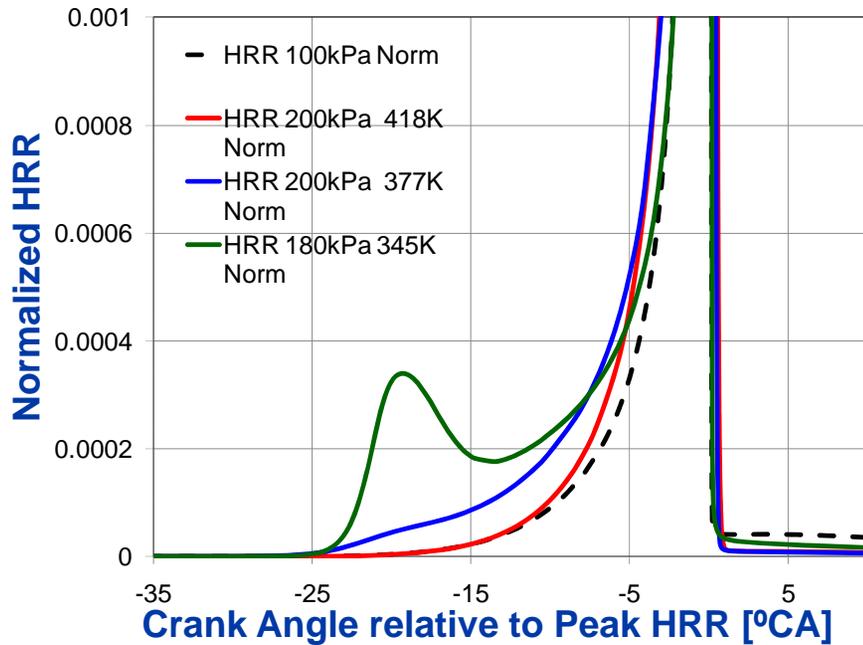
LLNL-PRES-653562

Non branching low temperature oxidation of the olefins (net flux nearly = 0)

Low temperature branching from linear alkanes



Reaction Contribution to HRR



— $\text{H} + \text{O}_2(+\text{M}) \rightleftharpoons \text{HO}_2(+\text{M})$

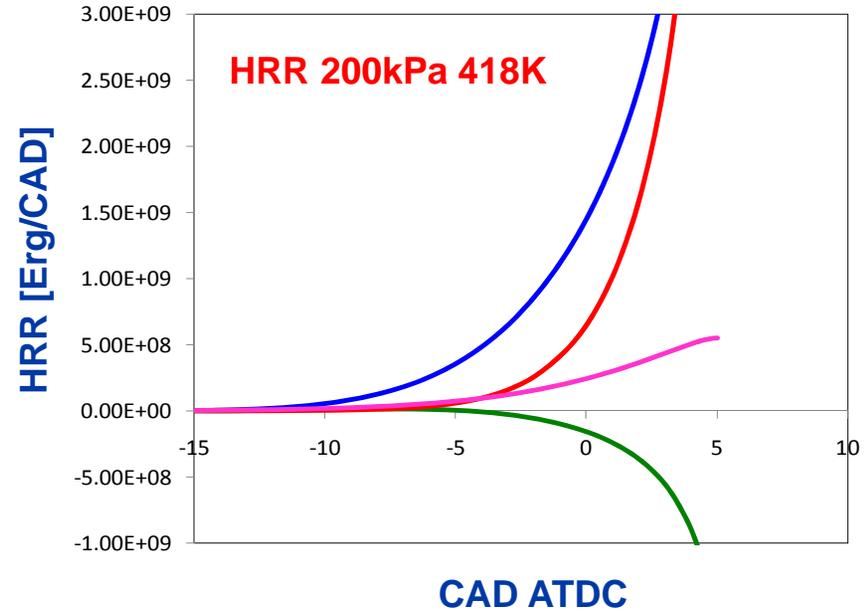
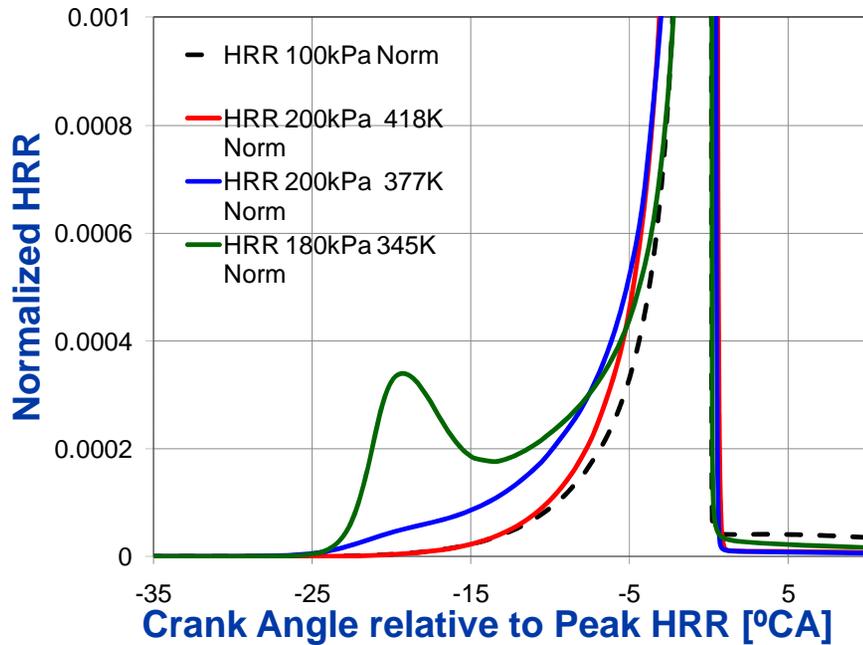
— $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{OH}$

— Methyl Oxidation to Formaldehyde via $\text{CH}_3\text{O}_2\text{H}$

— Formaldehyde Oxidation (CH_2O abstraction and HCO stabilization to $\text{CO} + \text{HO}_2$)



Reaction Contribution to HRR



— $\text{H} + \text{O}_2(+\text{M}) \rightleftharpoons \text{HO}_2(+\text{M})$

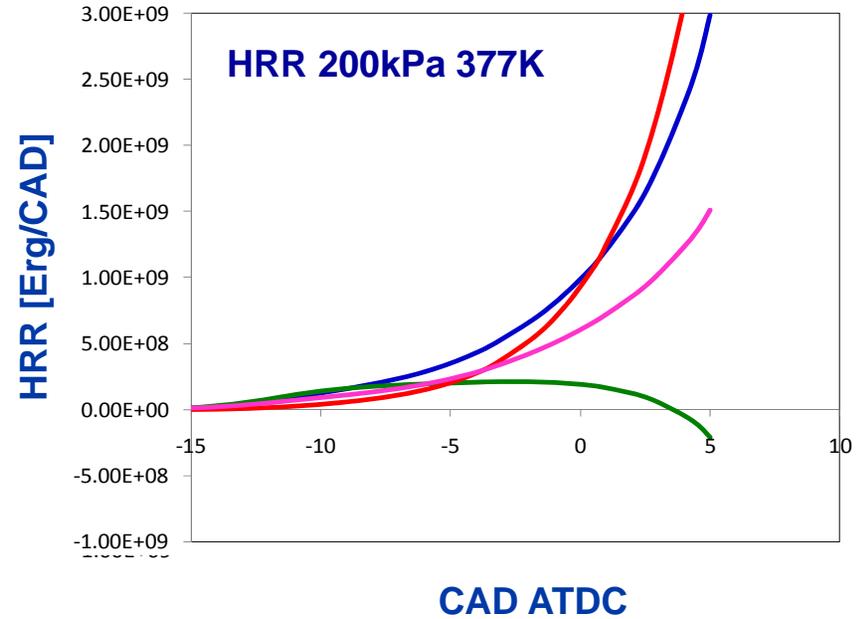
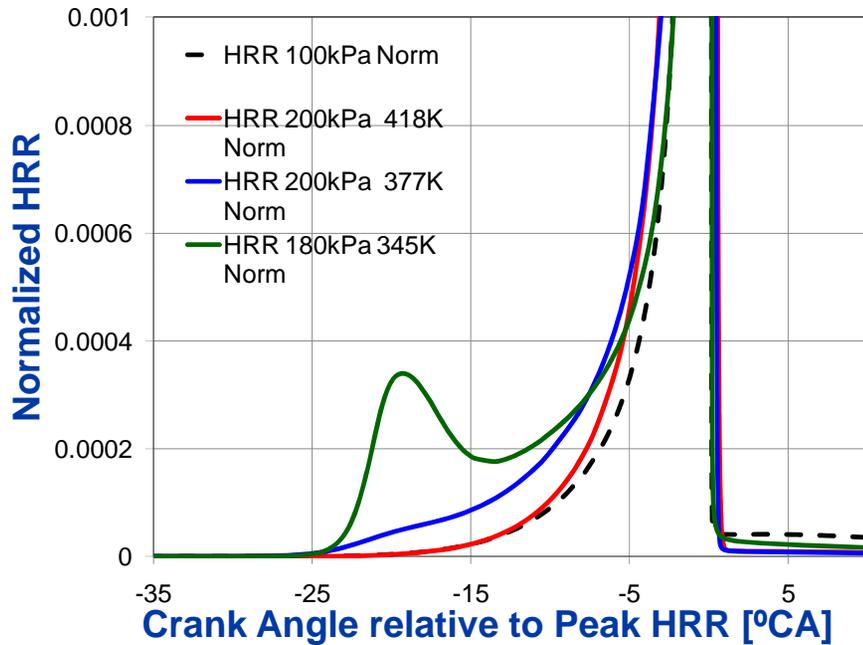
— $2\text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{OH}$

— Methyl Oxidation to Formaldehyde via $\text{CH}_3\text{O}_2\text{H}$

— Formaldehyde Oxidation (CH_2O abstraction and HCO stabilization to $\text{CO} + \text{HO}_2$)



Reaction Contribution to HRR



— $H+O_2(+M) \rightleftharpoons HO_2(+M)$

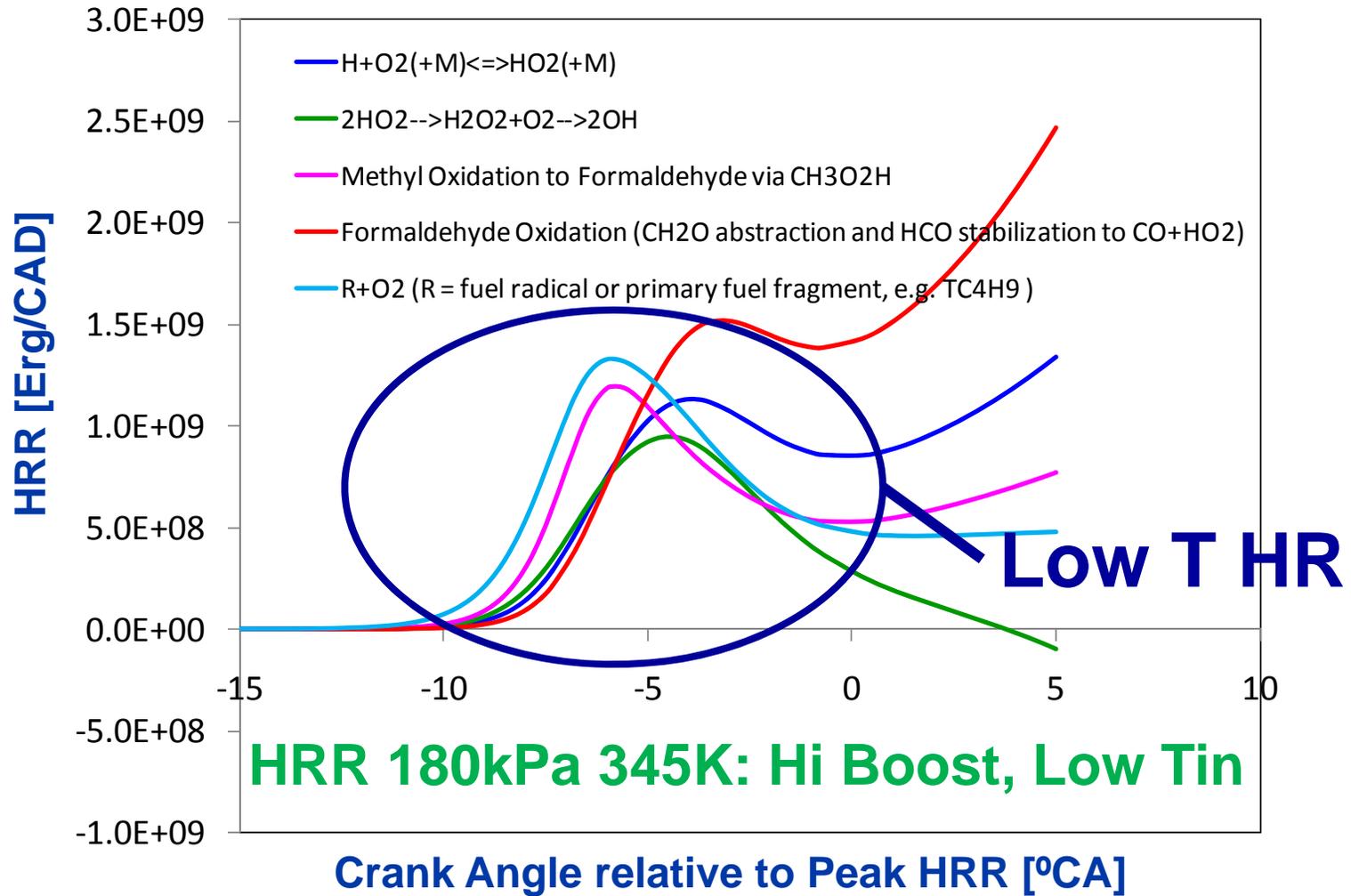
— $2HO_2 \rightarrow H_2O_2 + O_2 \rightarrow 2OH$

— Methyl Oxidation to Formaldehyde via CH_3O_2H

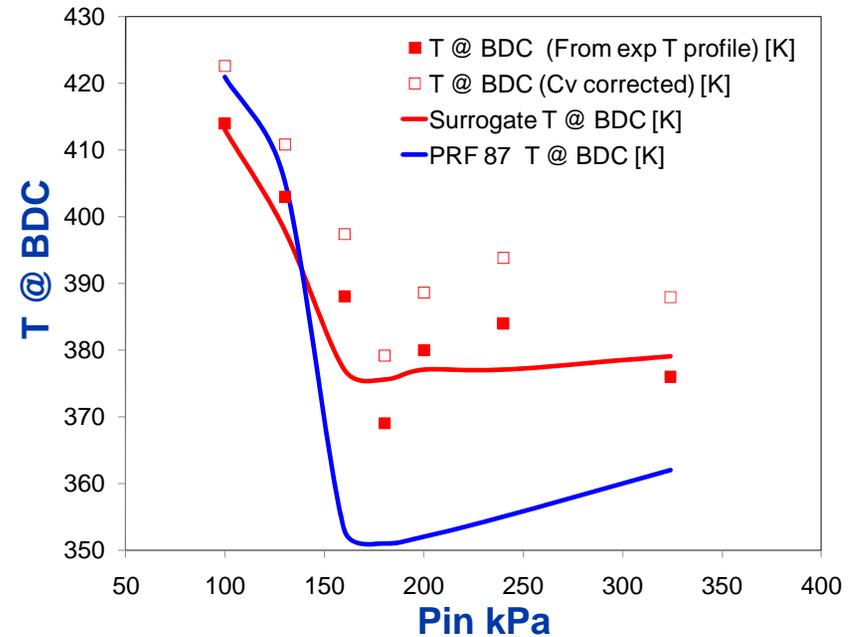
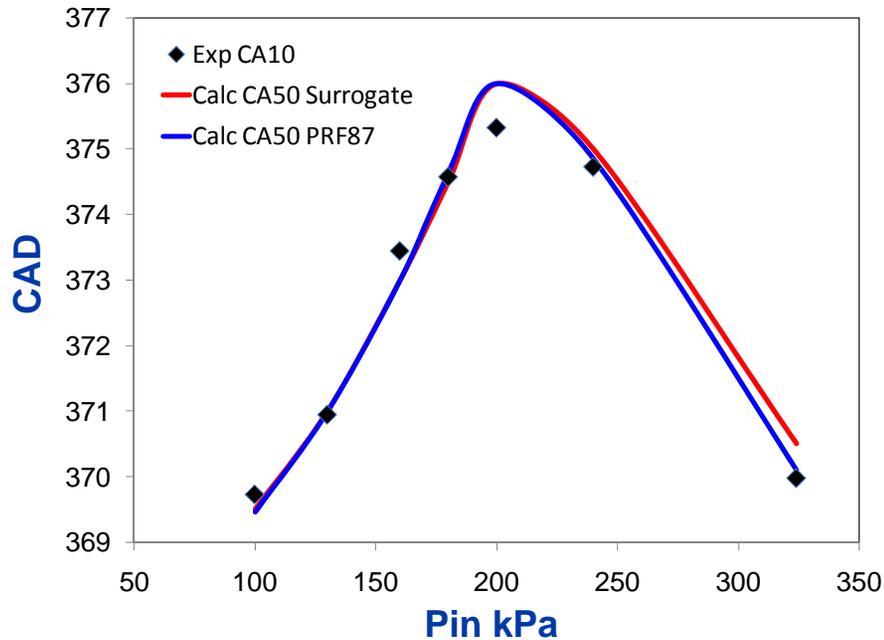
— Formaldehyde Oxidation (CH_2O abstraction and HCO stabilization to $CO+HO_2$)



Reaction Contribution to HRR



PRF87 Calculations vs. Surrogate Calculations



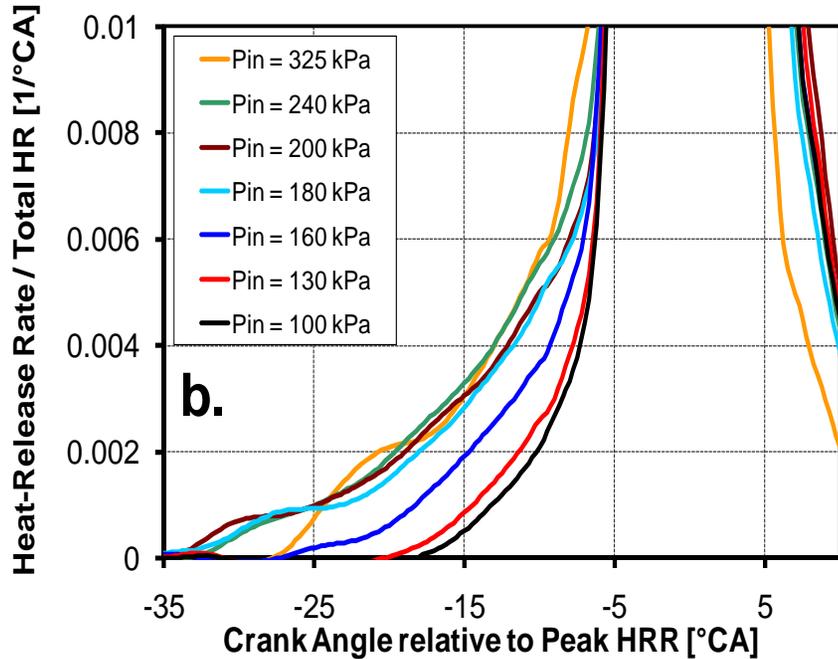
Using a PRF87 a much lower T @ BDC is required to match the same combustion phasing

A correct surrogate formulation is mandatory to model these data!

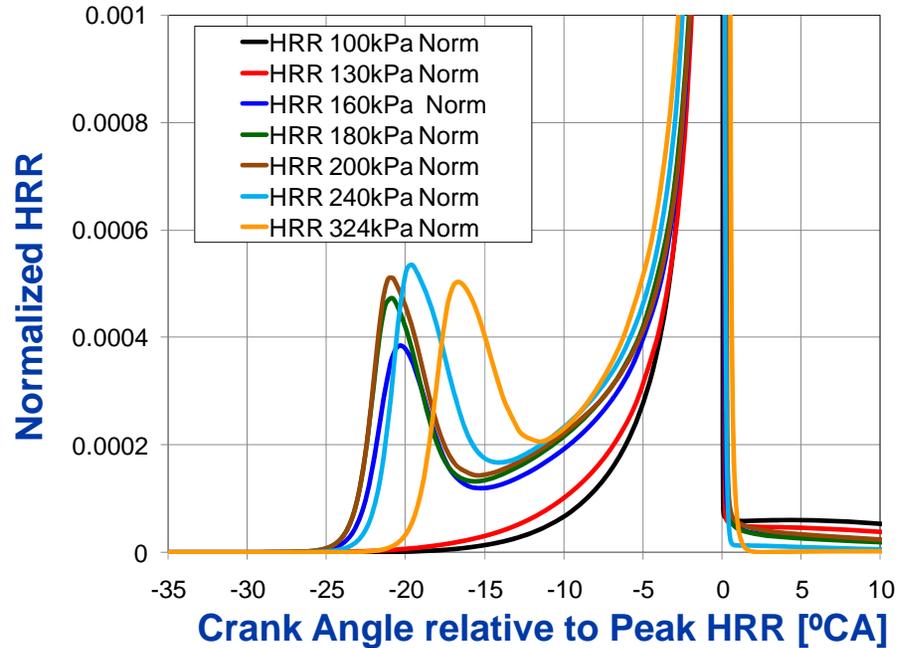


Normalized HRR (PRF87)

Gasoline: Experiments



PRF87: Calculations



PRF87 shows a much more intense early LTHR

Despite the very close ignition delay time profiles, the two fuels behave quite differently (Sensitivity ⇔ Lack of NTC)

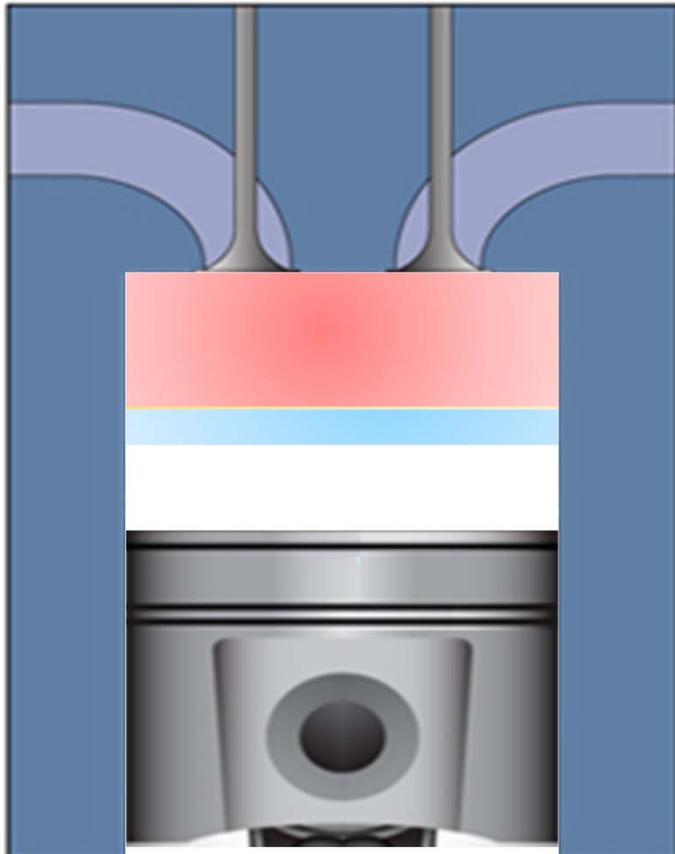


Final Remarks

- **The evolution of engines and fuels proceeded in tandem since the dawn of the automotive industry with fuel quality being the limiting factor in engine development**
- **In the last 90 years both engines and fuels have dramatically changed, but, for fuel properties specifications, we are still using fuel quality standards defined back then**
- **Fuel surrogates allow us to run more reproducible experiments and sophisticated engine numerical analysis, though there are still many open questions on how a good surrogate should be formulated**
- **Detailed kinetic models can be used to guide the formulation of surrogates and are effective tools to interpret fuel behavior in the combustion chamber**



Engine Combustion: Homogeneous Charge Compression Ignition (HCCI): two Stage Fuels

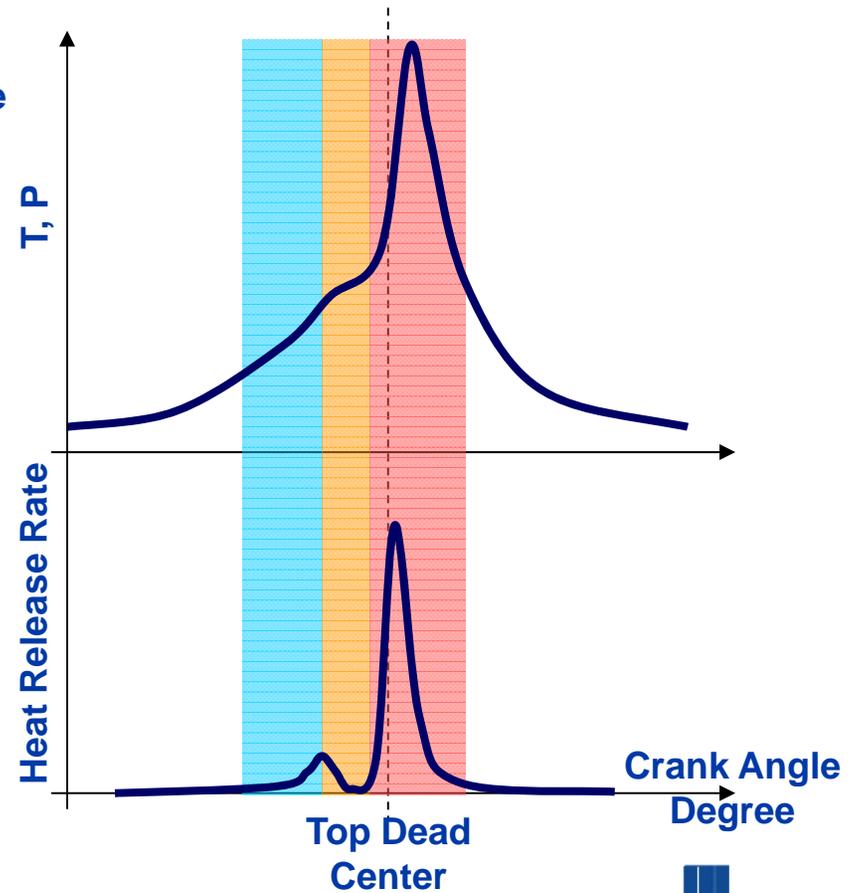


Typical HCCI Combustion Temperature and Heat Release Rate profiles

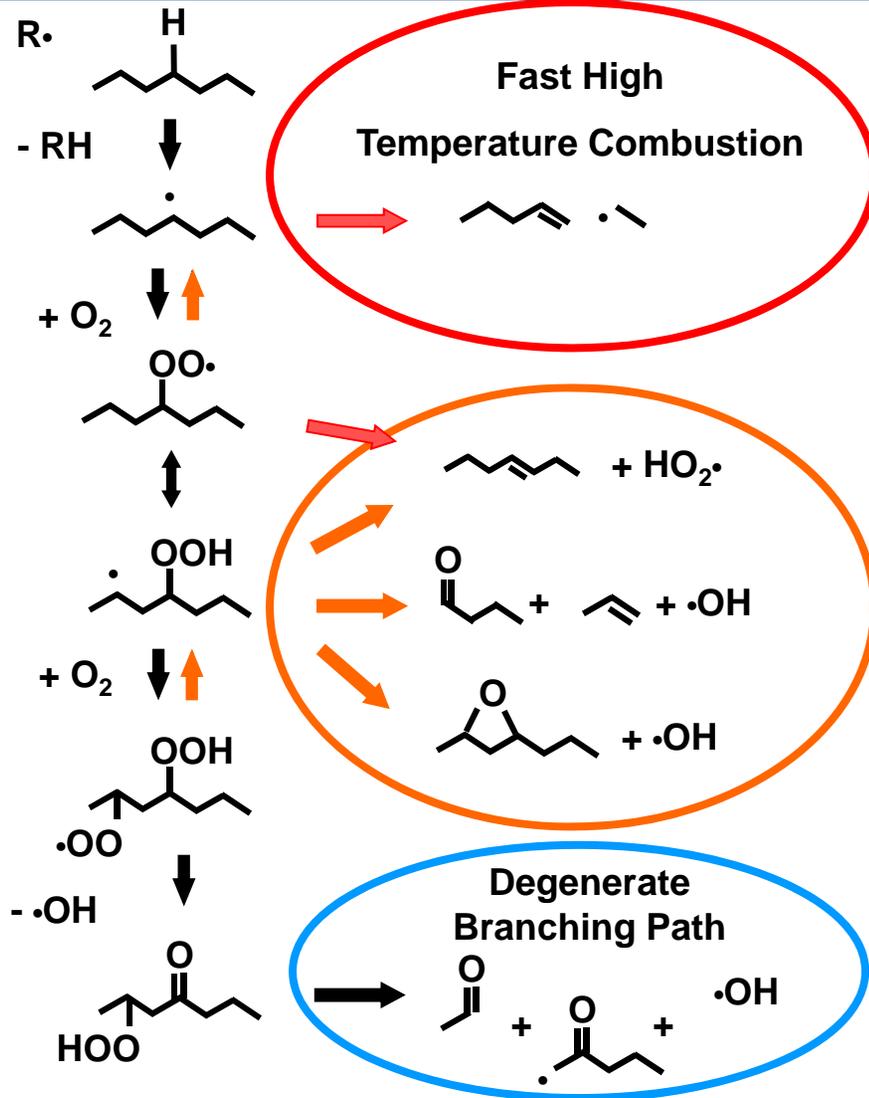
1st Heat release stage

The HRR slows down
(Negative Temperature Coefficient)

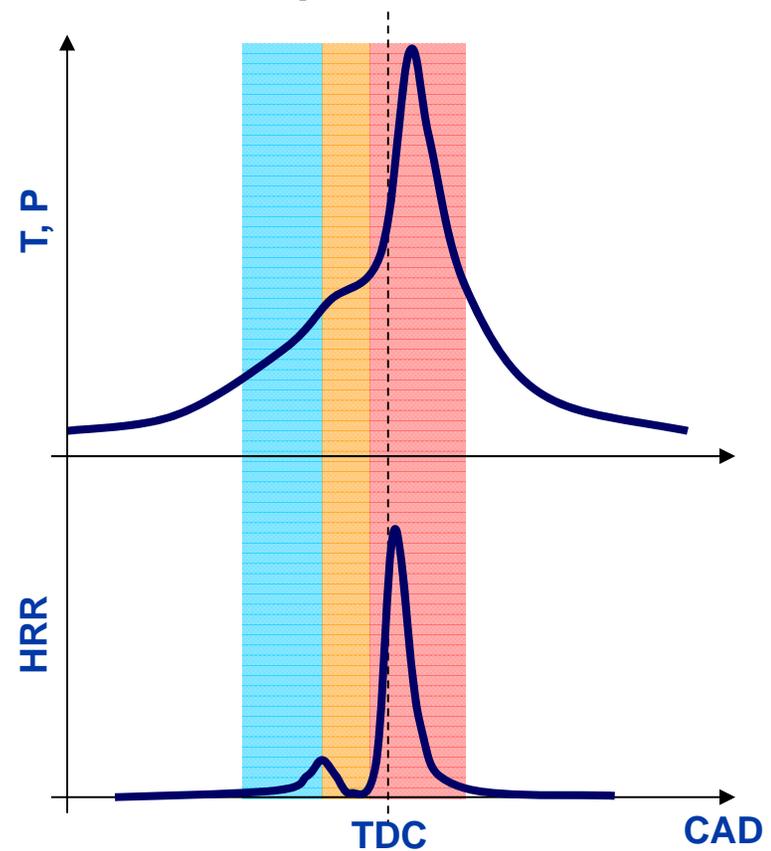
Main Heat Release

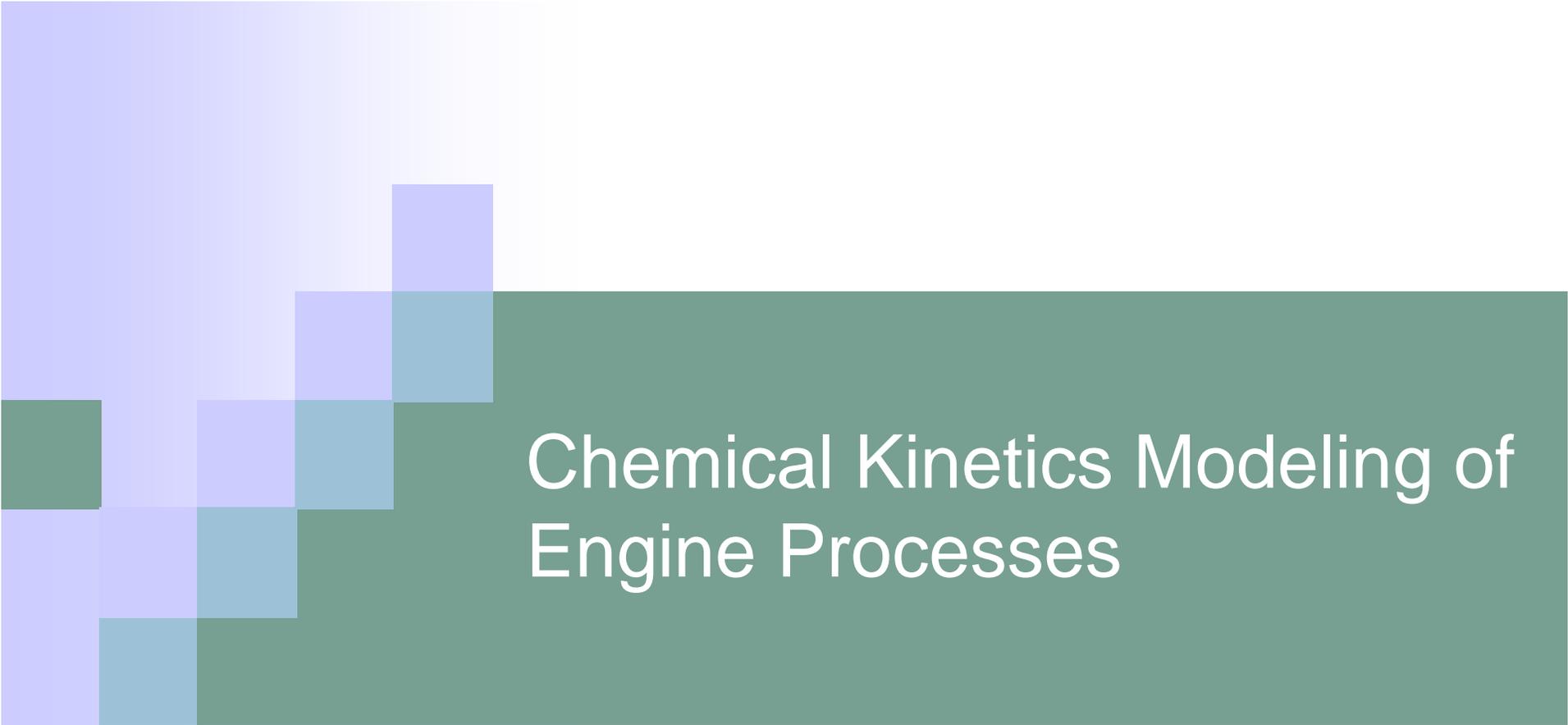


HCCI combustion kinetics: two Stage Fuels



Typical HCCI Combustion Temperature and Heat Release Rate profiles





Chemical Kinetics Modeling of Engine Processes

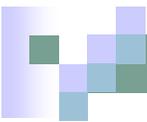
Charles Westbrook

Tsinghua-Princeton
2014 Summer School on Combustion
July 20-25, 2014



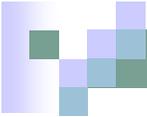
Kinetic analyses of engine processes

- Stratified charge engine details
- Flame quench in lean-burn engines
- Flame quench on engine chamber walls
- Heat transfer to engine walls during flame quenching
- Flame quench in expanding engine chamber
- Fuel additive studies
- Detonation parameters
- Engine knock and octane numbers, proknocks and antiknocks
- Diesel ignition and cetane numbers
- Biodiesel fuel combustion
- Soot production
- Reduction of soot in diesel engines with oxygen added
- Pulse combustor optimization
- HCCI combustion mechanisms
- Surrogate fuel formulations
- Reduced mechanisms for ignition and combustion
- Ignition models



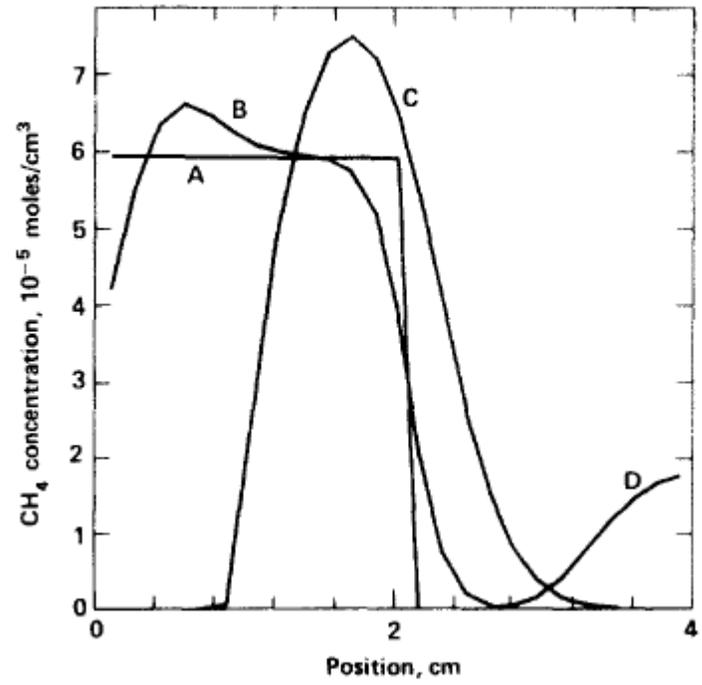
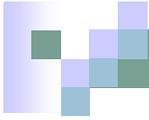
Laminar flames in quenching problems

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



Emissions from DISC engine

- Interest in mid 1970's by engine designers in stratified charge engine. Honda CVCC, Ford PROCOC, GM DISC
- Principle was spatial charge stratification, achieved by spray injection.
- Flame should burn fuel, halt abruptly when it reached the discontinuity in fuel concentration.
- Experimental observations of Lancaster (GMR) of excessive UHC emissions.





Flame quenching by volume expansion

- **Concept of “lean burn” engine in mid-1970’s**
- **Experimental studies in real engines by Quader demonstrated large UHC emissions and flame failure for late-ignition, extremely lean fuel/air mixtures.**
- **“What limits lean operation in spark ignition engines - Flame initiation or propagation?”
A.A. Quader, 1976.**
- **Laboratory experiments by Smith and Sawyer, with supporting laminar flame modeling, answered Quader’s questions.**

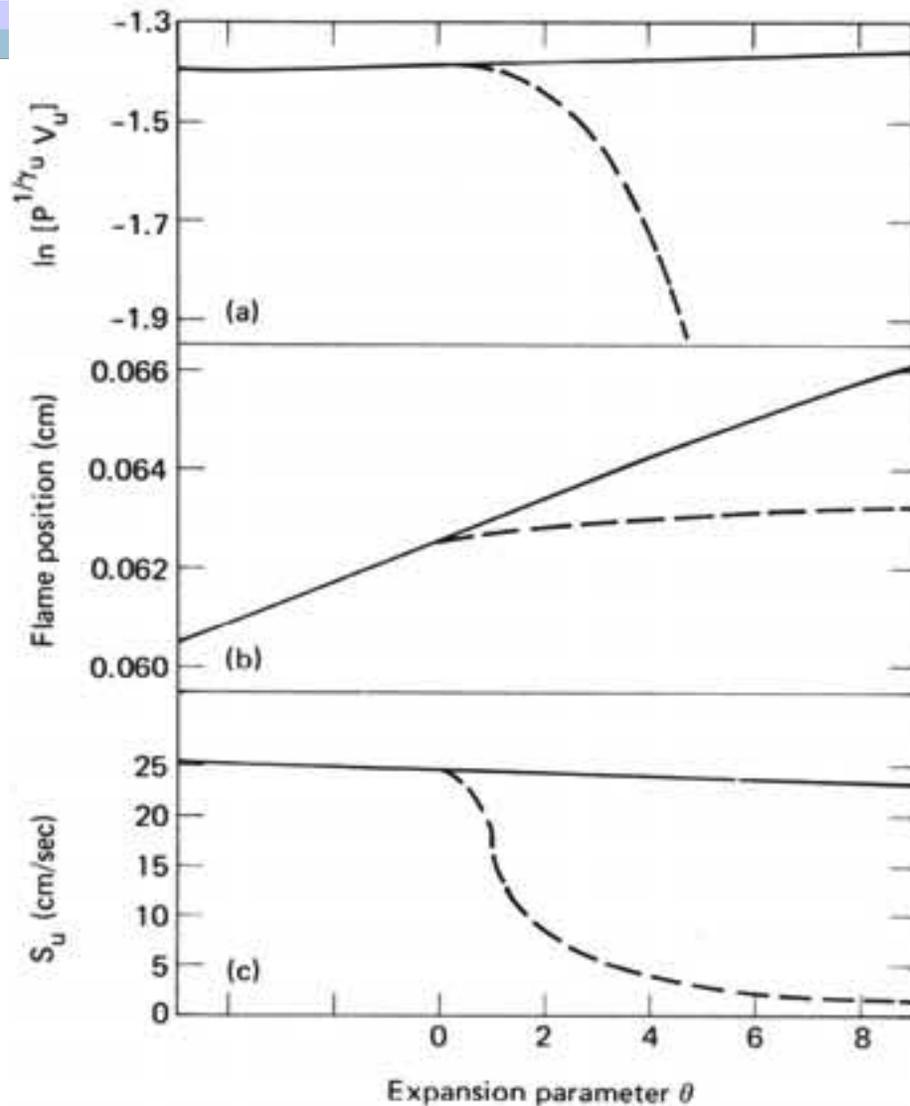
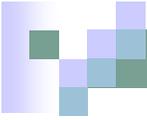


FIG. 6. Comparison between expanded (broken curves) and unexpanded (solid curves) model calculations showing the quenching function, flame position, and flame speed as functions of time, expressed in units of the expansion ratio, θ .

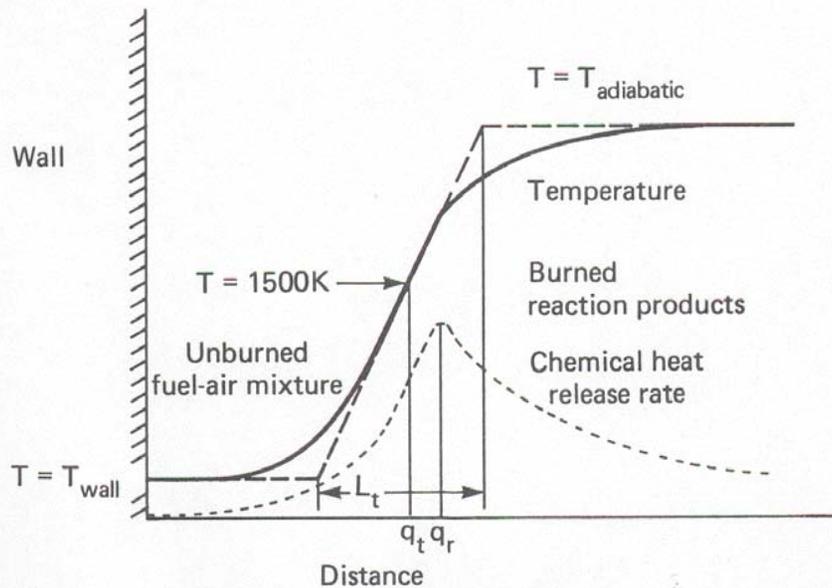
Expansion of the combustion chamber reduces radical levels below a critical value



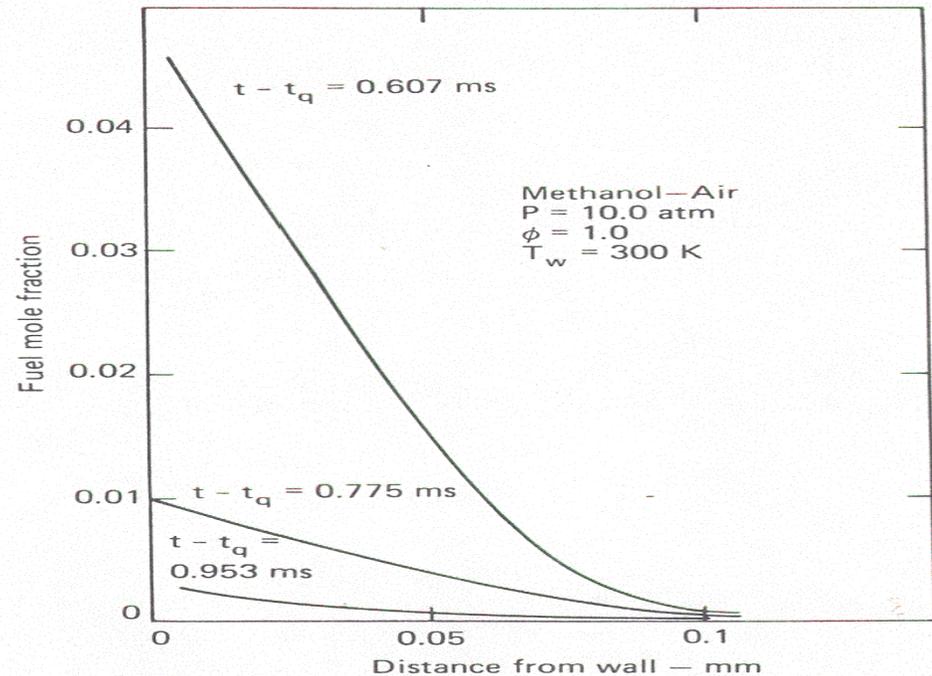
Flame quenching on engine walls

- **Previous concept of UHC emissions**
- **Idea of making wall layers thinner**
- **Simple flame model results at Ford weren't believed**
- **Detailed modeling results**
- **Evidence had been there, Wentworth**

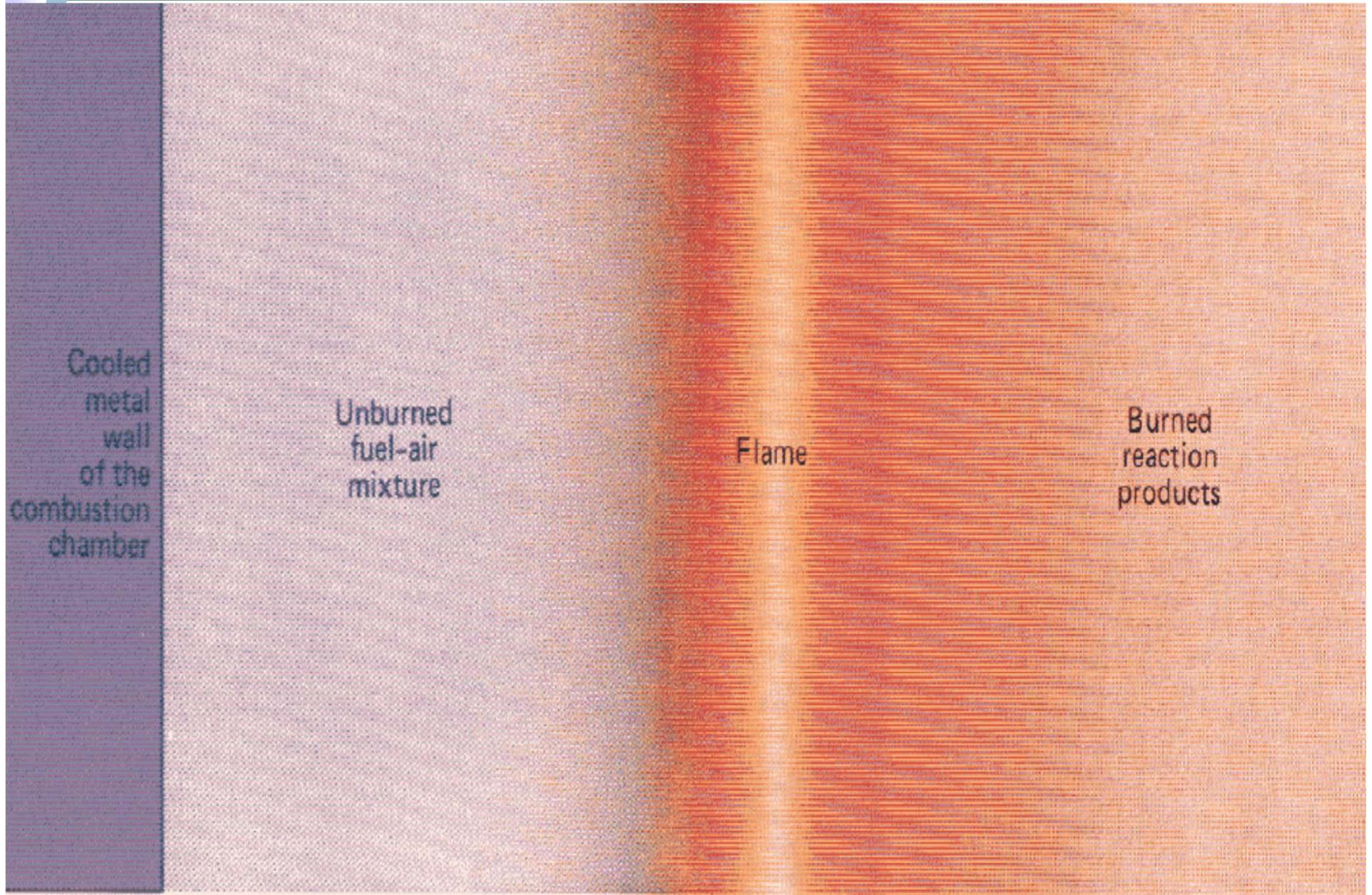
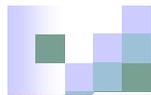
Pictures of wall quenching



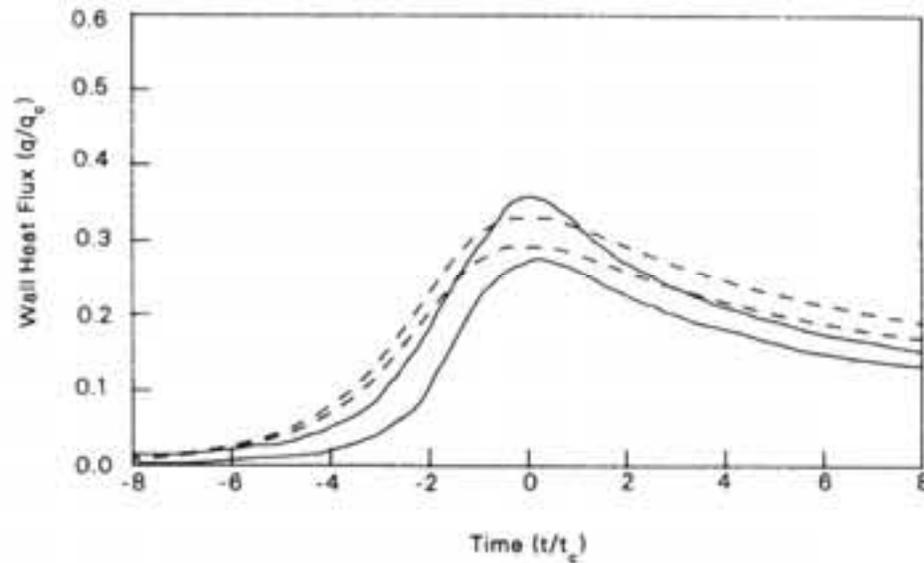
Flame approaching wall



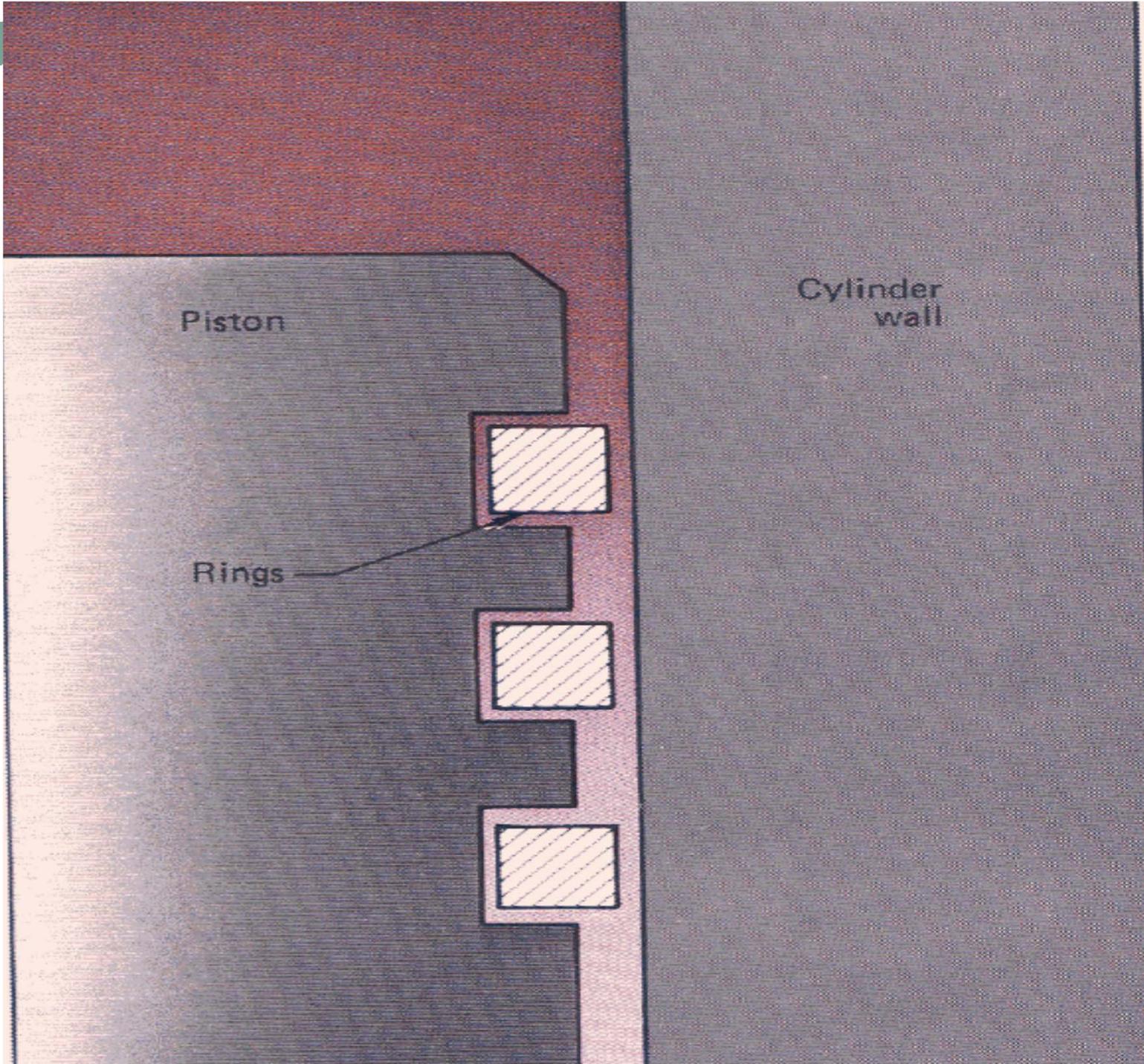
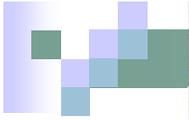
Fuel diffuses away from wall and is rapidly consumed

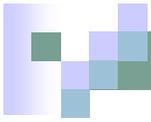


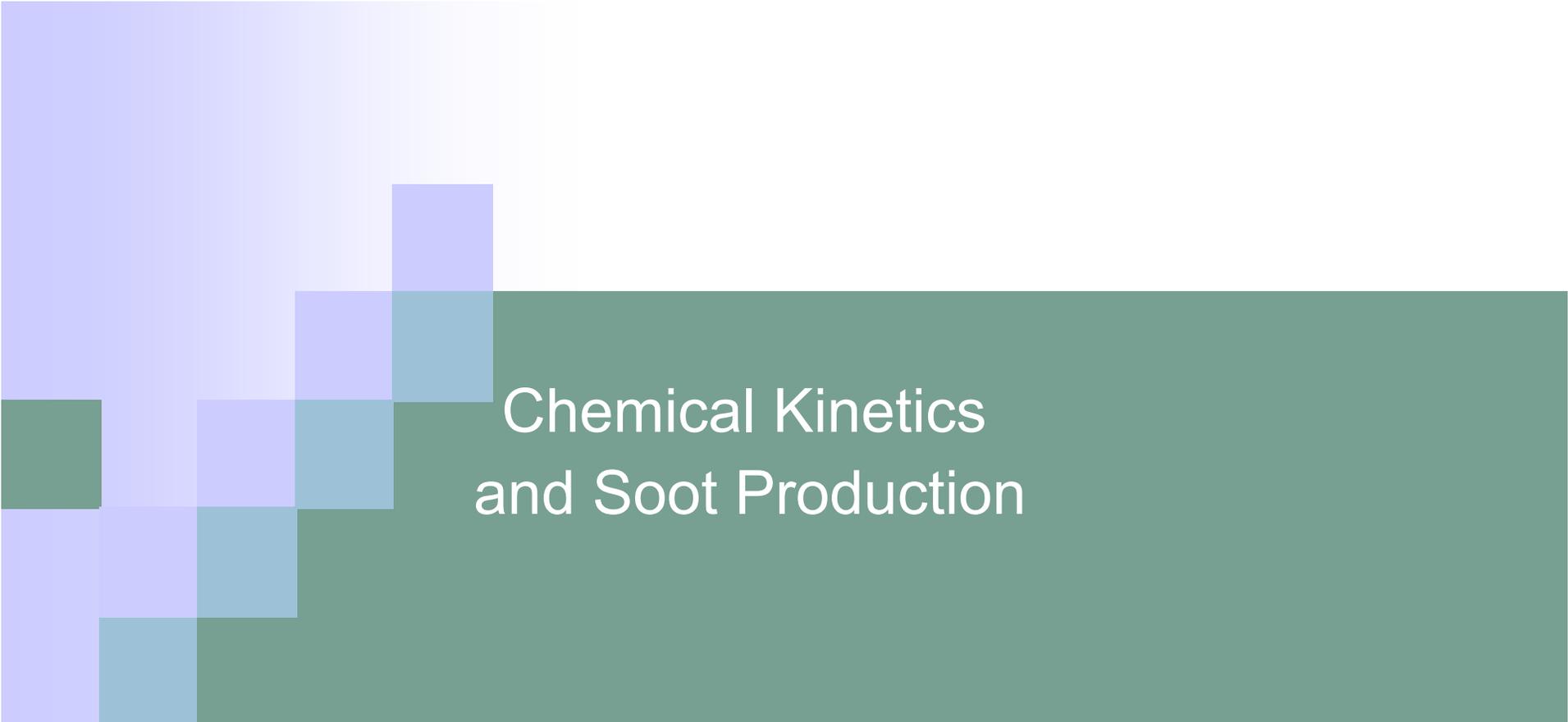
Heat transfer to walls during flame quench compares well with experimental results



Experiments (solid curves) from thin film resistance thermometer (Vosen, Greif and Westbrook, 1984)
Calculations (dashed curves) using laminar flame with detailed chemical kinetics





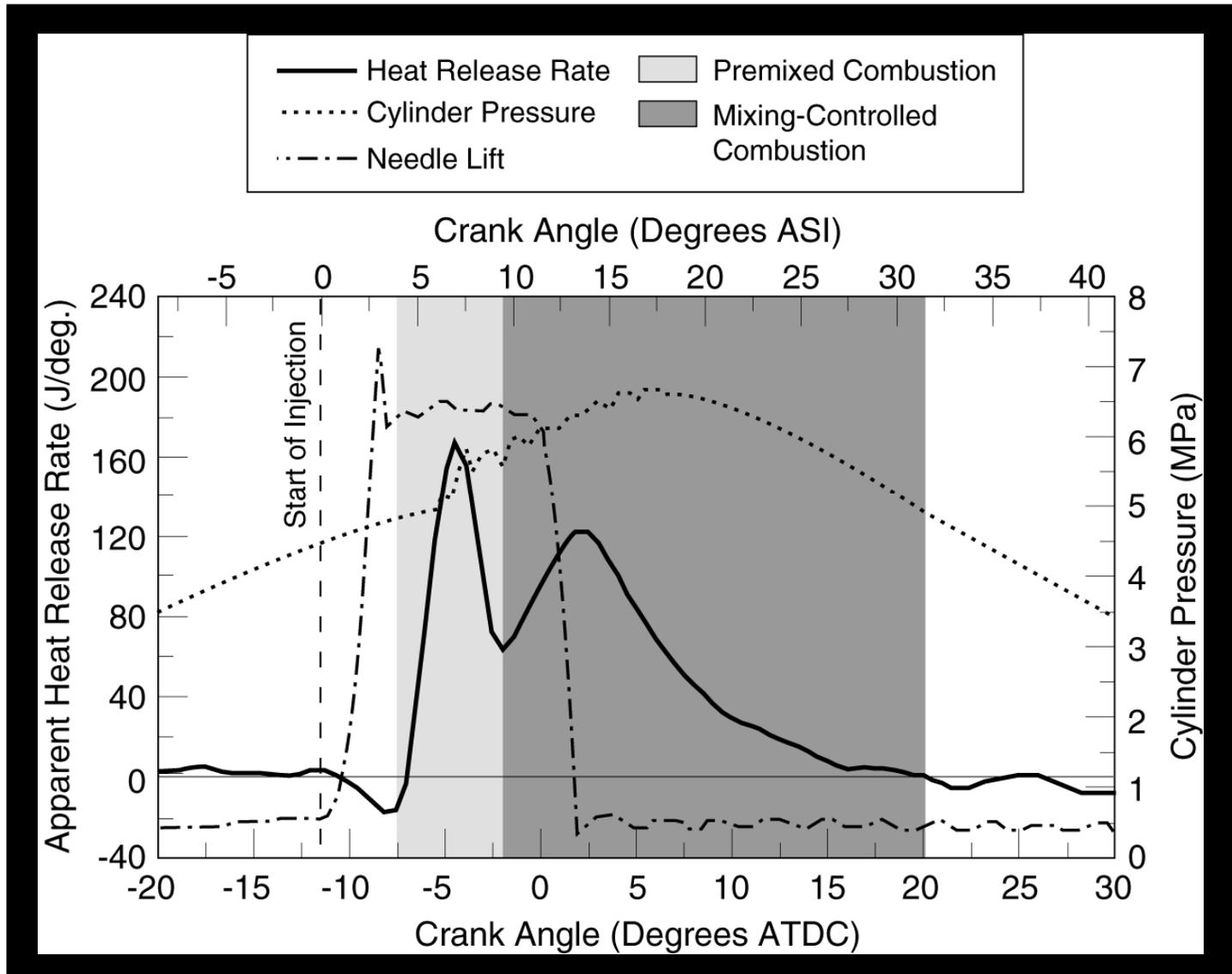


Chemical Kinetics and Soot Production

Charles Westbrook

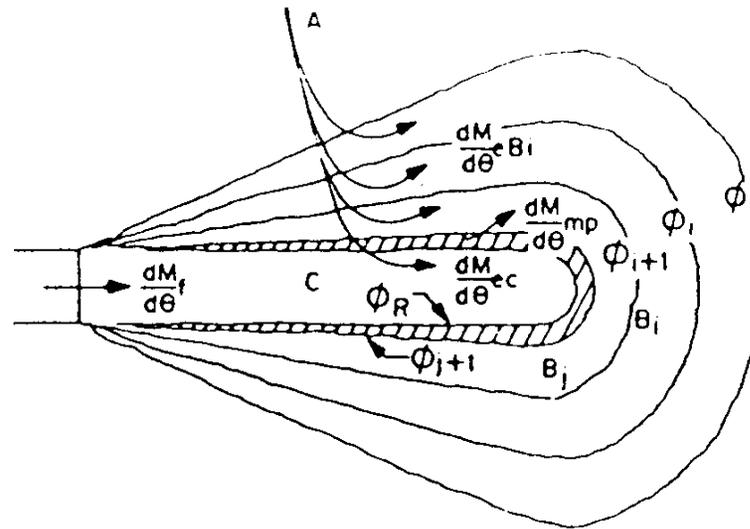
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July 20-25, 2014

Diesel engine combustion: A revolution



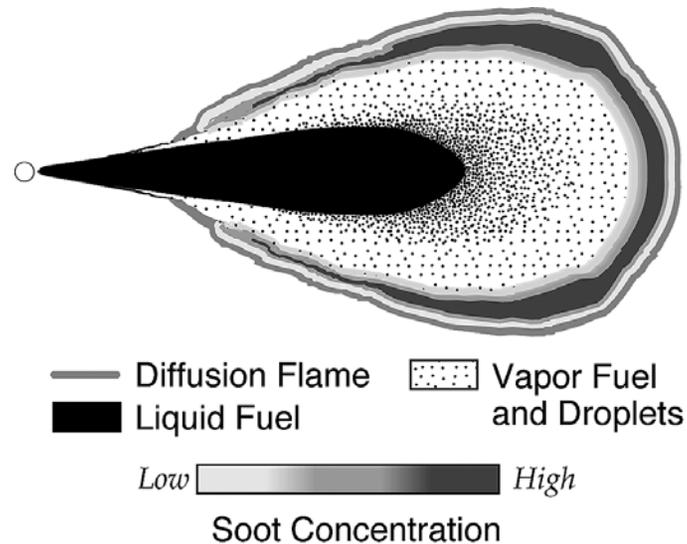
Early models of Diesel combustion

Liquid core with continuous evaporation
(1976)



Early models of Diesel combustion

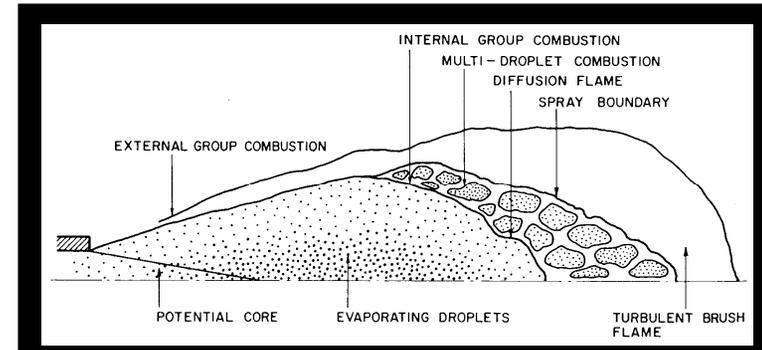
Liquid fuel jet shedding droplets, with combustion at the edge of a stoichiometric shell (diffusion flame)



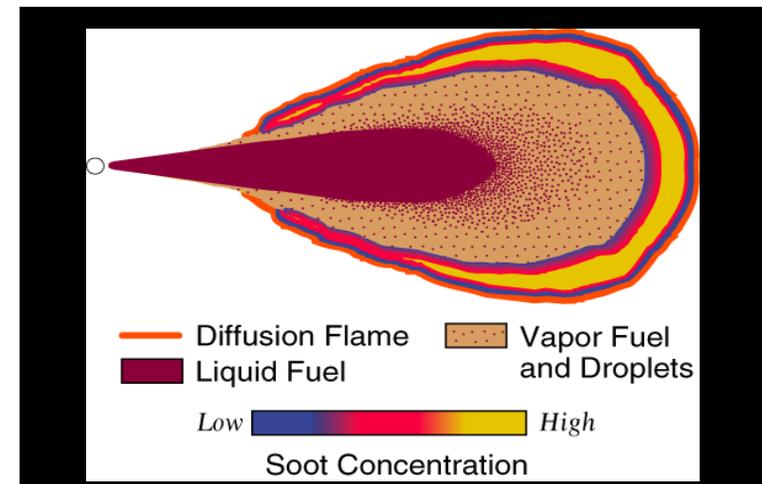
Prior to Laser-Sheet Imaging



- Autoignition and premixed burn were thought to occur in near-stoichiometric regions.
- The "quasi-steady" portion of Diesel combustion was thought to be adequately described by steady spray combustion theory.
- Appeared to fit most available data.
- This "old" description was never fully developed into a conceptual model.
A "representative" schematic is given.



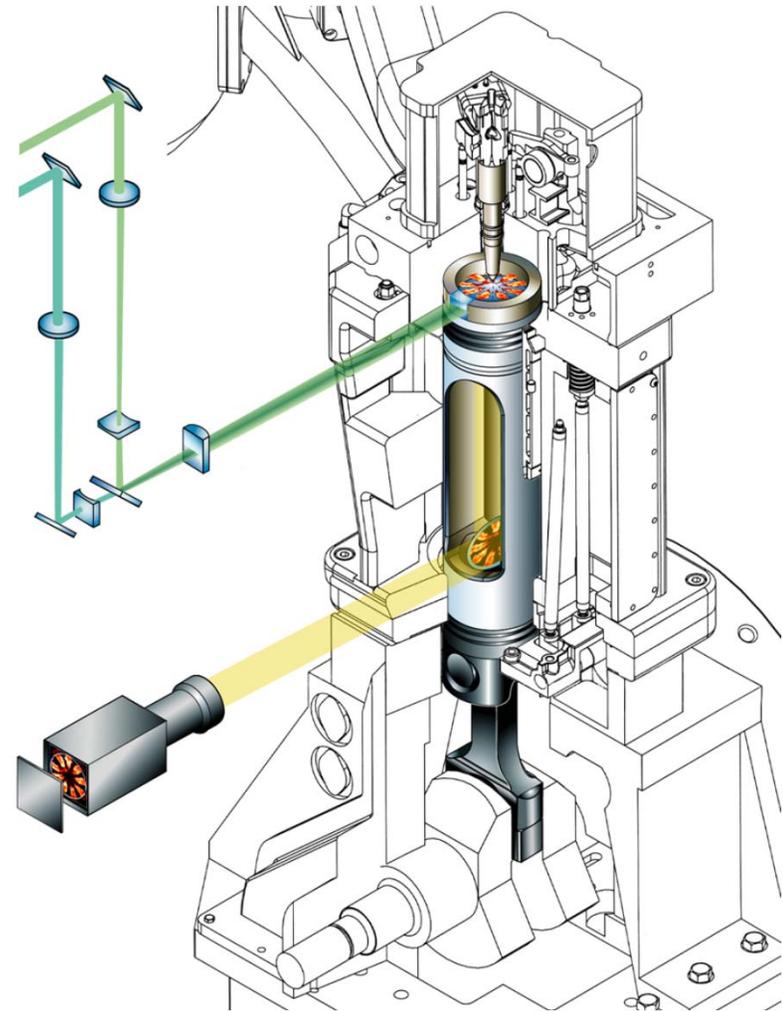
Schematic of group combustion for a fuel spray.
From Kuo, as adapted from H. Chiu and Croke



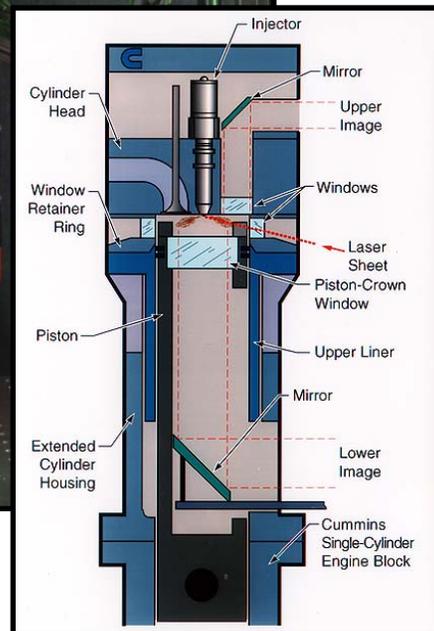
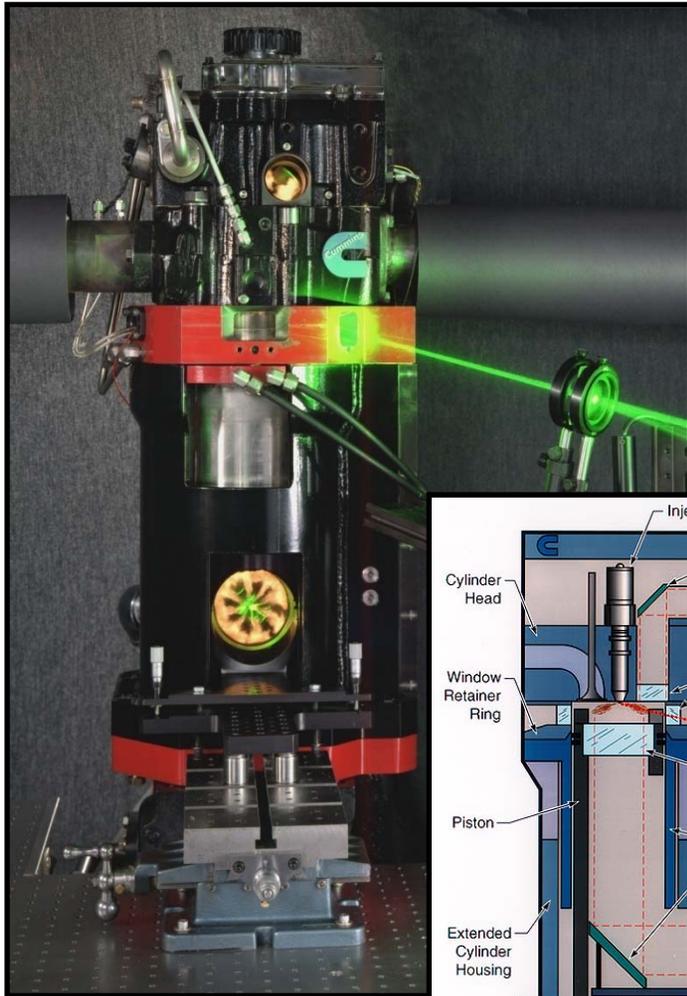
Old description of DI Diesel combustion.

The DOE Engine Combustion Research Program at Sandia's CRF played a major role in solving the diesel "mystery".

- **Mission** - Develop the science-base for in-cylinder combustion and emissions processes.
 - Help U.S. manufacturers reduce emissions & improve performance.
- **Approach** –
 - Strong interaction and collaboration with industry.
 - Optical diagnostics.
 - Realistic engine geometries with optical access through:
 - > *pistons*
 - > *cylinder liner*
 - > *spacer plates*
 - > *exhaust ports*



Heavy-Duty Diesel Engine Research

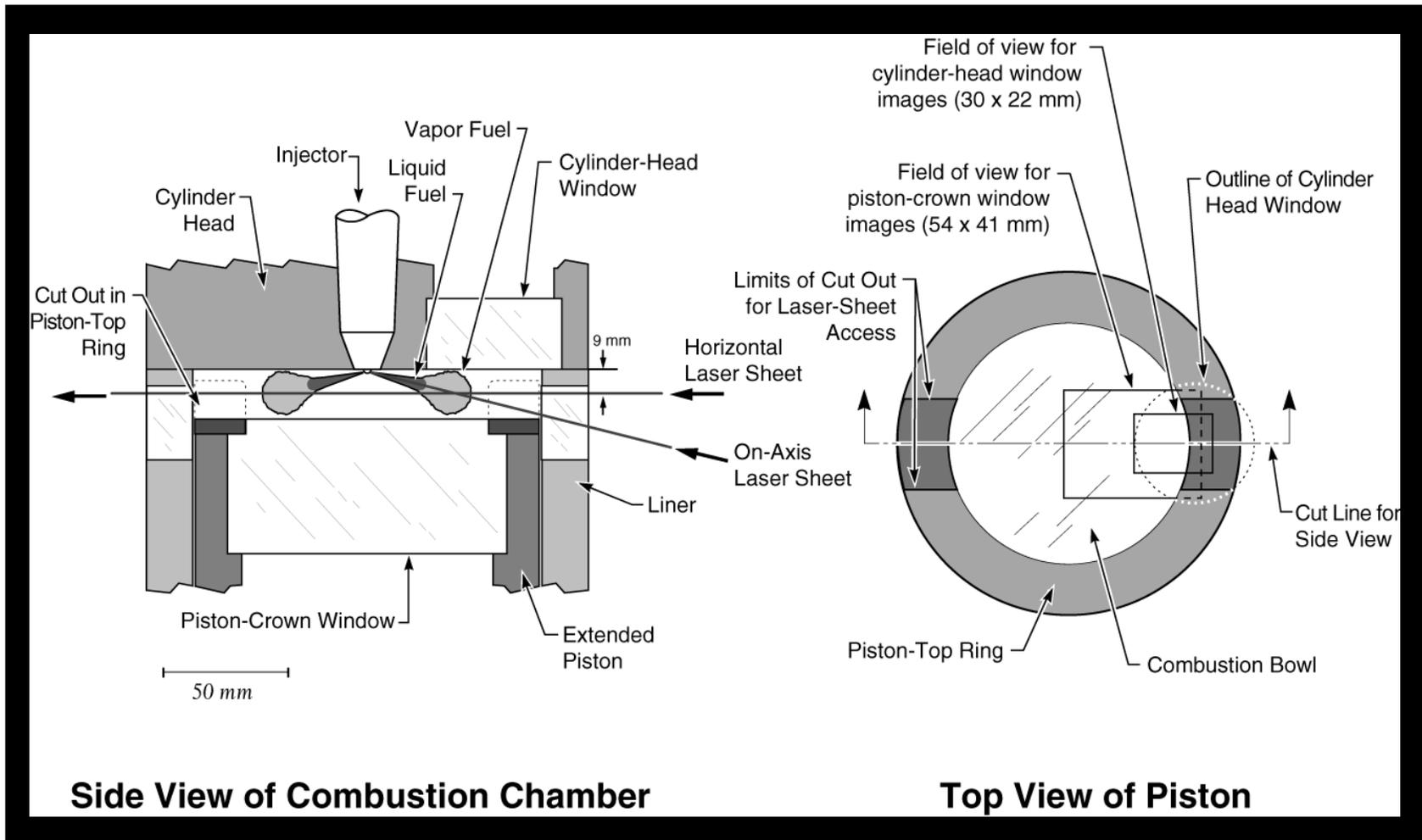


Approach: Investigate the processes in the cylinder of an operating diesel engine using advanced optical diagnostics

Modified heavy-duty truck engine provides good optical access while maintaining the basic combustion characteristics of a production engine.

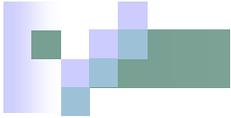
Data from multiple advanced laser diagnostics have substantially improved our understanding of diesel combustion and emissions formation.

Optical Setup



Side View of Combustion Chamber

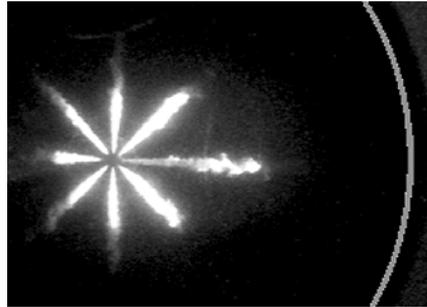
Top View of Piston



Laser-Sheet Imaging Data - 1

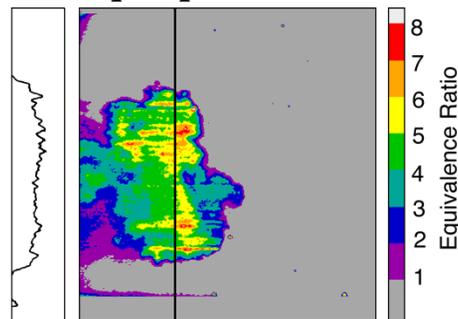


Liquid-phase Fuel



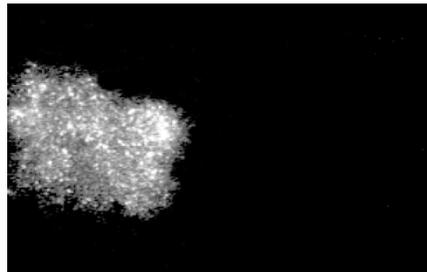
- Liquid fuel images show that all the fuel vaporizes within a characteristic length (~1 inch) from the injector.

Vapor-phase Fuel



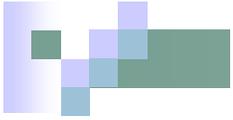
- Vapor fuel images show that downstream of the liquid region, the fuel and air are uniformly mixed to an equivalence ratio of 3-4.

Chemiluminescence



- Chemiluminescence images show autoignition occurring across the downstream portion of the fuel jet.

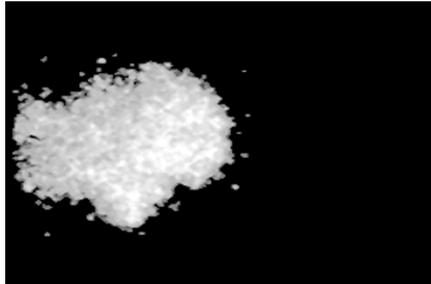
Quiescent Chamber, 1200 rpm, $T_{TDC} = 1000$ K, $\rho_{TDC} = 16.6$ kg/m³



Laser-Sheet Imaging Data - 2

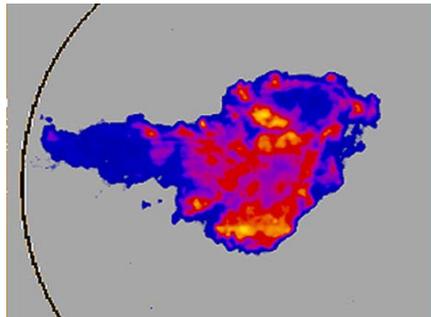


PAH Distribution



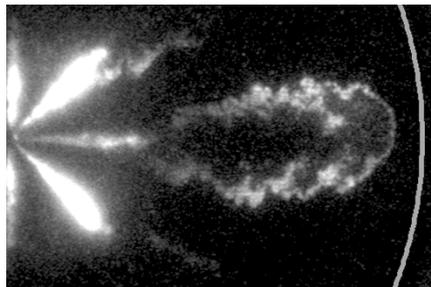
- PAHs form throughout the cross-section of the fuel jet immediately following fuel breakdown at the start of the apparent heat release.

Soot Distribution



- LII soot images show that soot forms throughout the cross-section of the fuel jet beginning just downstream of the liquid-fuel region.

OH PLIF Image



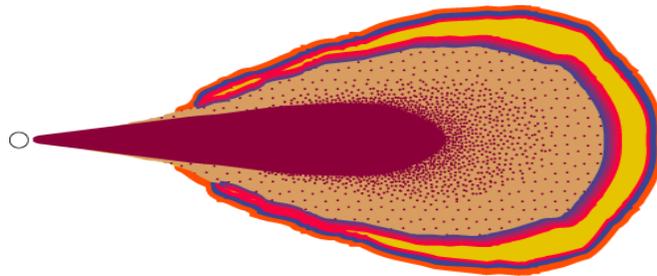
- OH radical images show that the diffusion flame forms at the jet periphery subsequent to an initial fuel-rich premixed combustion phase.

Quiescent Chamber, 1200 rpm, $T_{TDC} = 1000$ K, $\rho_{TDC} = 16.6$ kg/m³

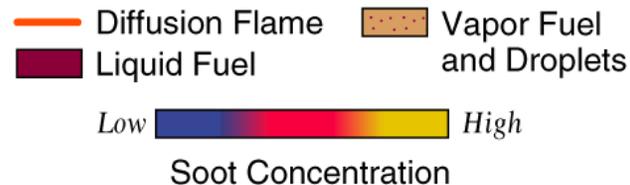
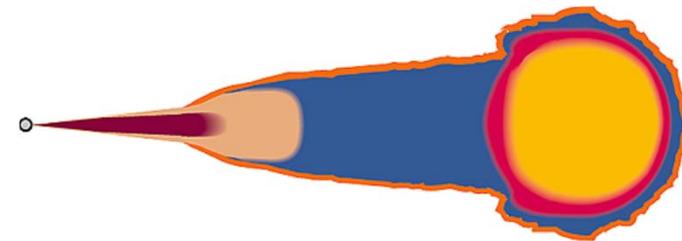
Laser Sheet Imaging is Providing a New Understanding of DI Diesel Combustion



Old Description



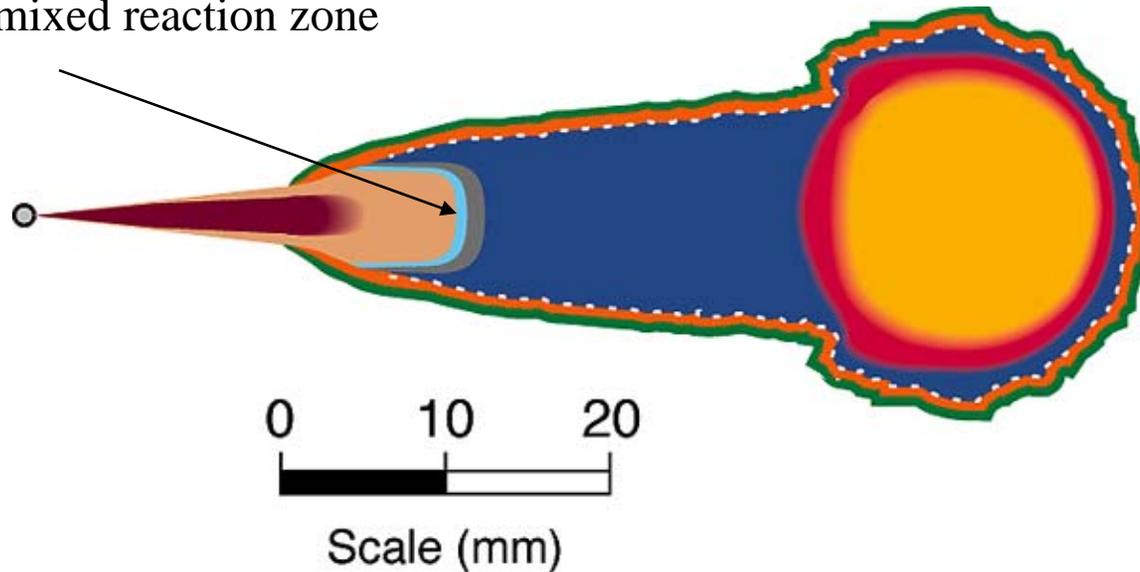
New Conceptual Model



- The appearance is significantly different.
 - Regimes of Diesel combustion are different than thought. (flame standoff, upstream mixing, instantaneous vs. averaged).

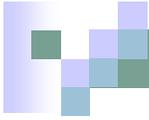
Predicting the soot precursors is one of the keys to predicting soot emissions from a Diesel engine

Fuel-rich premixed reaction zone

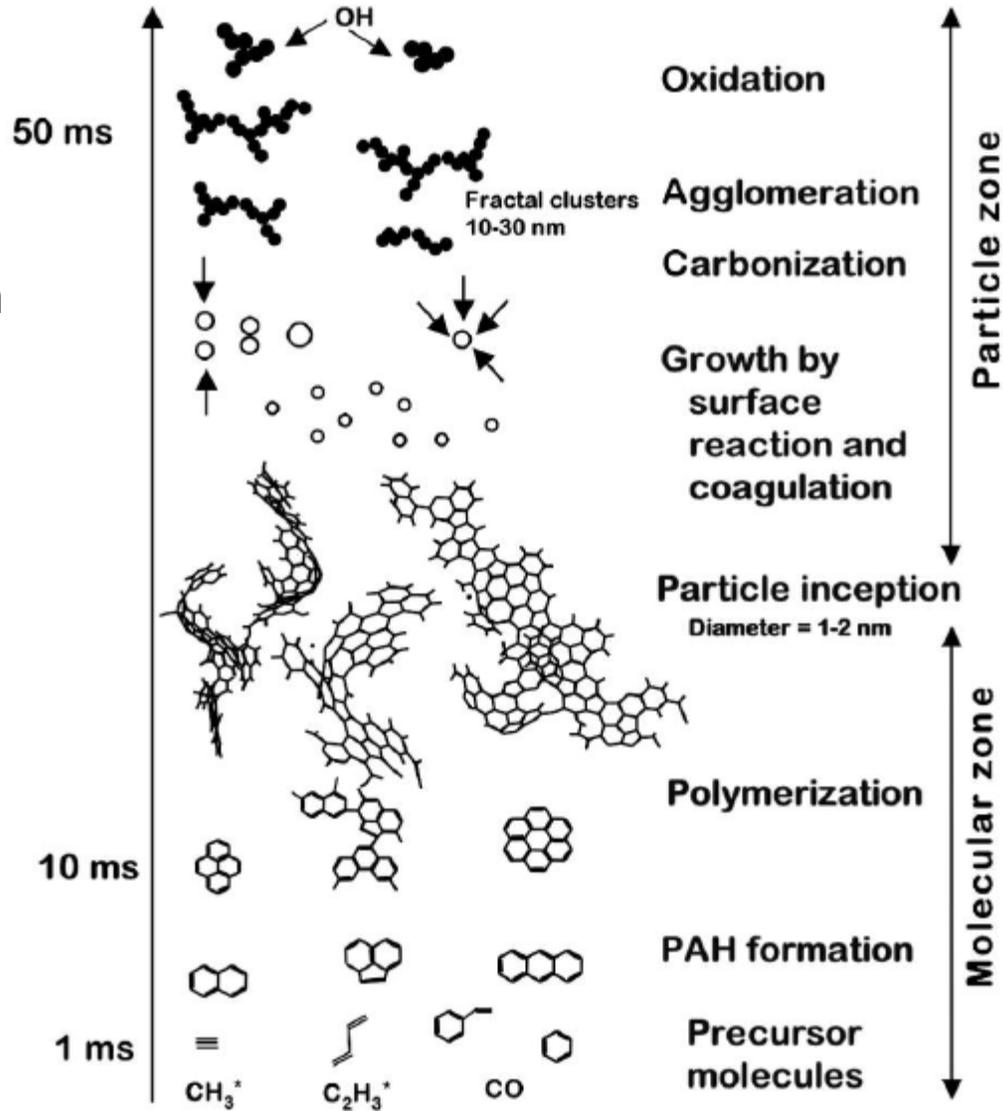


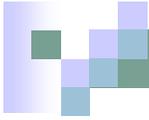
From:
John Dec,
SAE paper
970873

-  **Fuel-Rich Premixed Reaction Zone**
-  Initial Soot Formation
-  Thermal NO Production Zone
-  Soot Oxidation Zone



Steady growth
in molecular
size leads to
visible soot





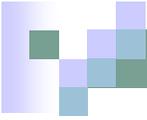
Correlations between Fuel Structural Features and Benzene Formation

Hongzhi R. Zhang, Eric G. Eddings, Adel F. Sarofim
The University of Utah

and Charles K. Westbrook
Lawrence Livermore National Lab

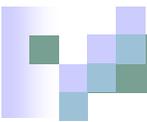
presented at

**2008 International Combustion Institute Meeting
Montreal, Canada, August 8th, 2008**



Outline

- Introduction
- Chemistry of Benzene Precursors and Comparison of Measured and Predicted Benzene Concentrations
- Benzene Formation Potential
- Benzene Formation Pathways



Introduction

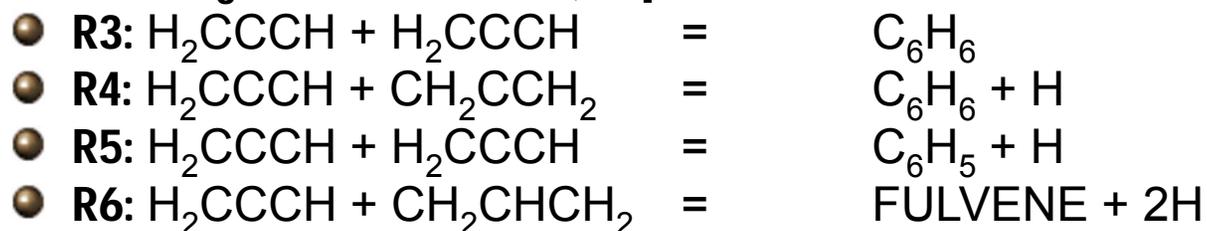
- Combustion generated benzene is a health concern
 - Benzene is a major precursor for particulate pollution
 - Benzene is a known carcinogen
 - Benzene is a major precursor of PAH, also carcinogens
- We want to identify fuel properties that are critical to major benzene formation pathways and benzene formation potentials for individual fuel components
 - Fuel structure: between normal, iso-, and cyclo paraffins
 - Fuel structure: C_3 , C_4 vs. C_{12} , C_{16} fuels
 - Other properties: Equivalence ratio, Hydrogen deficiency, Combustion temperature
- 22 premixed flames; C_1 - C_{12} fuels; $\Phi = 1.0$ - 3.06 ; $P = 20$ - 760 torr; $T_{\max} = 1600$ - 2370 K
- Benzene concentrations were predicted within 30% of the experimental data for 15 flames (total of 22 flames)

Major Benzene Formation Pathways Revisited

- **Class 1: Acetylene addition (Westmoreland et al., 1989; Frenklach et al., 1985)**



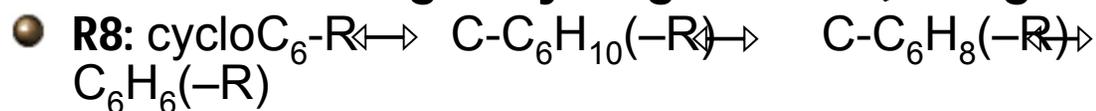
- **Class 2: C₃ combination (Hopf, 1971; Miller-Melius, 1992)**



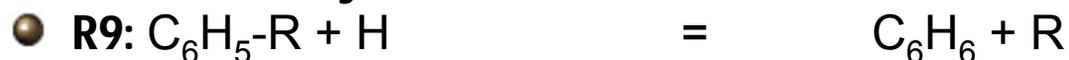
- **Class 3: Combination of CH₃ and C₅H₅**



- **Class 4: Cascading dehydrogenation (Zhang et al., 2007)**



- **Class 5: De-alkylation**



Natural Gas, Synfuel, Indicator Fuels, Biofuels

Liquid Fuels from Oil and Coal

Experimental: Benzene from Cyclo-Paraffins

Author	Fuel	ϕ	P torr	T(Max) in K	$[\text{C}_6\text{H}_6]_{\text{Max}}$
V	C_7H_{16}	1.0	760	1843	12 PPM
HSP	gasoline	1.0	760	1990	344
LWC	$\text{C-C}_6\text{H}_{12}$	1.0	30	1960	473

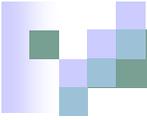
Questions:

1. Why gasoline produces more benzene than n-heptane, the indicator fuel for octane rating?
2. What are the benzene sources in gasoline?
3. How is benzene formed from various chemical classes?



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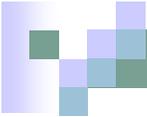
Sub-Models Compiled from Literatures

We took

- Marinov-Westbrook-Pitz's hydrogen model
- Hwang, Miller et al.'s, and Westbrook's acetylene oxid. models
- Wang and Frenklach's acetylene reaction set with vinylic and aromatic radicals
- Marinov and Malte's ethylene oxidation sub-model
- Tsang's propane and propene chemical kinetics
- Pitz and Westbrook's n-butane sub-model
- Miller and Melius benzene formation sub-model
- Emdee-Brezinsky-Glassman's toluene and benzene oxidation sub-model

We have added

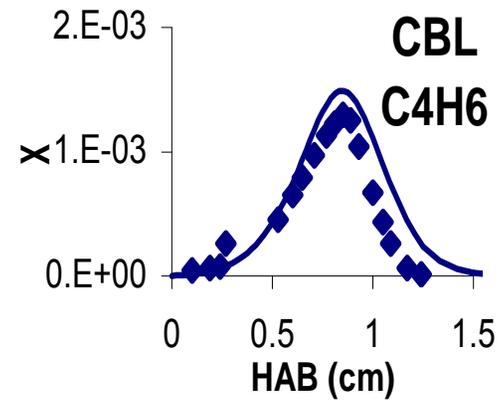
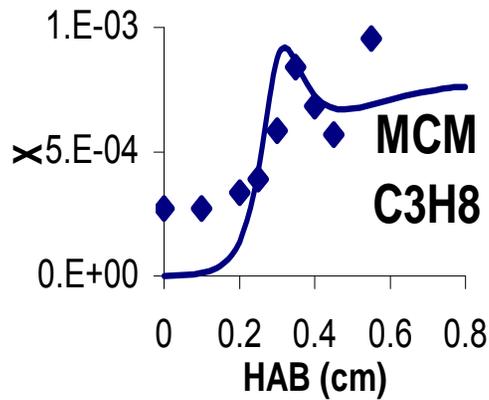
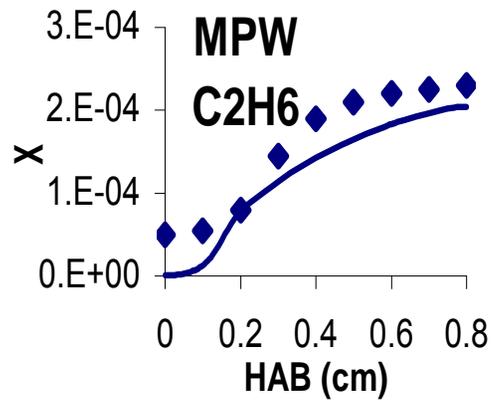
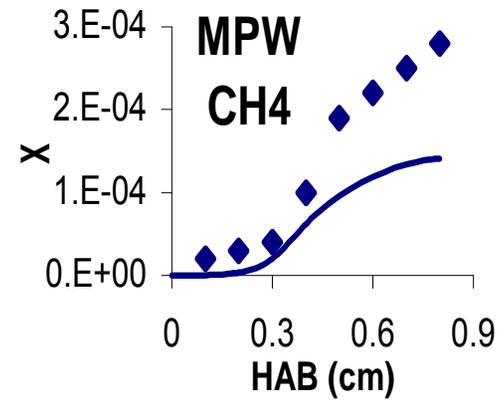
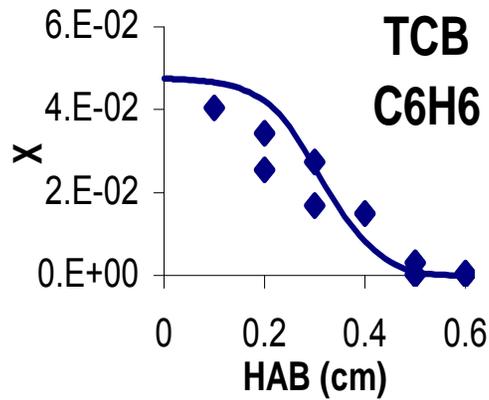
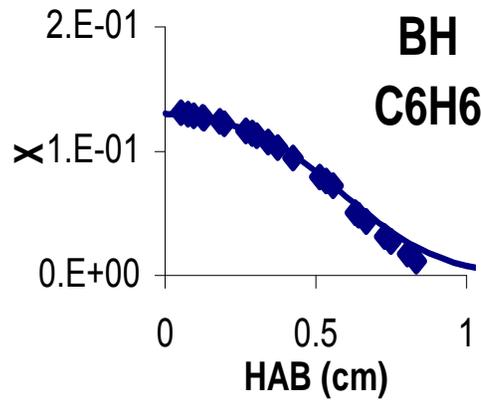
- 100 modification steps to the base gas core concerning benzene chemistry
- Fuel Component Sub-Mechanisms



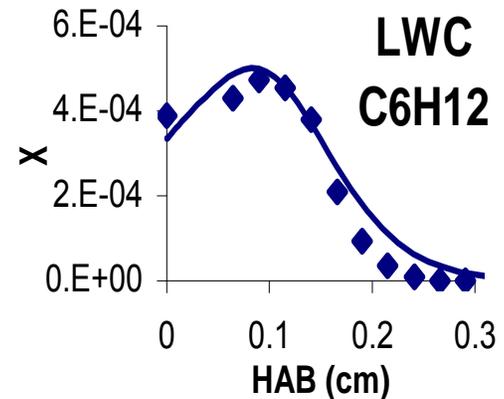
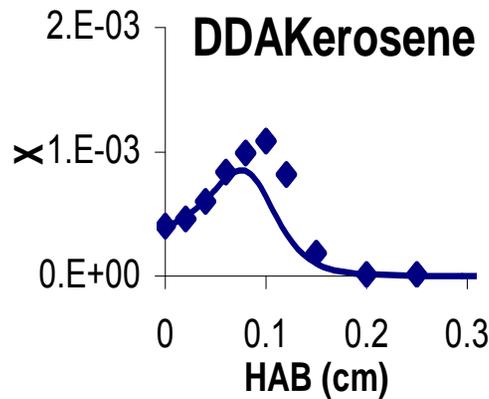
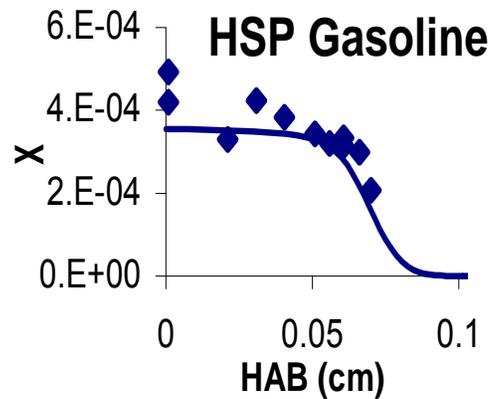
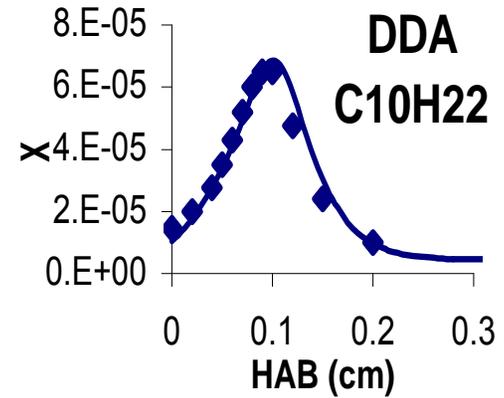
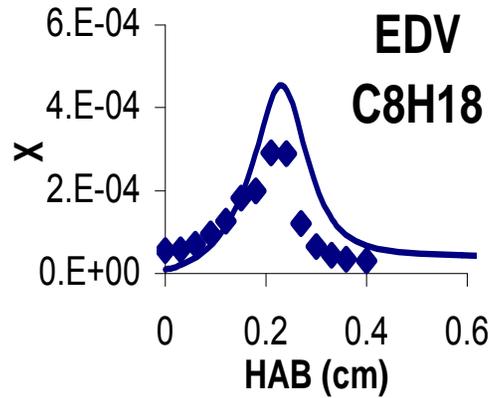
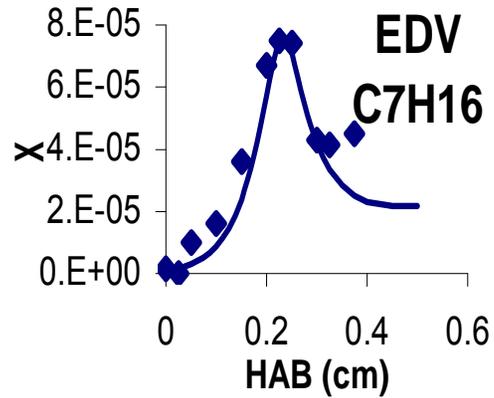
Precursor Chemistry

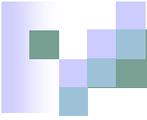
- A list of benzene precursors includes
 - Major precursors: C_3H_3 , C_2H_2 , $n-C_4H_3$, $n-C_4H_5$
 - Minor precursors: $C-C_5H_5$, $C-C_6H_x$, Ph-R
 - Bridging Species: $a-C_3H_5$, C_2H_3
 - Other Related Species: $a-C_3H_4$, $p-C_3H_4$, C_4H_6 isomers, C_3H_5 isomers, $C-C_5H_6$, C_4H_4 , C_4H_2 , C_2-C_4 olefins
- New Reactions in the mechanism
 - Large olefin decomposition: $1-C_7H_{14} = a-C_3H_5 + C_4H_9-1$
 - New addition of chemistry of $p-C_3H_4$
 - $p-C_3H_4$ has comparable, if not higher, concentrations in flames, in comparison with those of $a-C_3H_4$
 - It is easier to form C_3H_3 radicals from $p-C_3H_4$ than from $a-C_3H_4$
 - Reactions involving C_4 species
- Reaction of $C_2H_3=C_2H_2+H$ critically examined

Modeled Benzene Concentrations



Modeled Benzene Concentrations





Outline

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Benzene Formation Potential

#	Fuel	Inert Ar, %	C/O	Eq. Ratio	P torr	T(Max) K at cm	Exp. Max. [C ₆ H ₆] ^b at cm	Cal. Max. [C ₆ H ₆] ^b at cm	Deviation
F1	CH ₄	0.453	0.626	2.50	760	1605 at 0.4	280 at 0.8	141 at 0.8	-49.6
F2	C ₂ H ₆	0.453	0.715	2.50	760	1600 at 0.24	230 at 0.8	205 at 0.8	-10.9
F3	C ₃ H ₈	0.44	0.833	2.78	760	1640 at 0.4	840 at 0.35	922 at 0.32	+9.8
F4	C ₃ H ₈	0.424	0.54	1.80	30	2190 at 0.95	17.5 at 0.75	72.9 at 0.77	+×4.2 ^e
F5	C ₂ H ₂	0.05	0.959	2.40	20	1901 at 1.0	40 at 0.37	82.7 at 0.37	+×2.1 ^e
F6	C ₂ H ₂	0.45	1.00	2.50	19.5	1850 at 1.0	58.9 at 0.6	39.1 at 0.64	-33.6
F7	C ₂ H ₂	0.55	1.103	2.76	90	1988 at 0.73	140 at 0.6	96.7 at 0.55	-30.9
F8	C ₂ H ₄	0.5	0.634	1.90	20	2192 at 1.7	33.1 at 0.9	11.4 at 0.77	-×2.9 ^e
F9	C ₂ H ₄	0	0.80	2.40	760	1815 at 0.1	936 at 0.15	136 at 0.14	-×6.9 ^e
F10	C ₂ H ₄	0.656	0.92	2.76	760	1600 at 0.3	250 at 0.35	212 at 0.35	-15.2
F11	C ₂ H ₄	0.578	1.02	3.06	760	1420 at 0.3	575 at 1.0	553 at 1.0	-3.8
F12	C ₃ H ₆	0.25	0.773	2.32	37.5	2371 at 0.71	1220 at 0.39	927 at 0.39	-24.0
F13	C ₄ H ₆	0.03	0.874	2.40	20	2310 at 1.65	1300 at 0.85	1490 at 0.85	+14.6
F14	C ₆ H ₆	0.3	0.717	1.79	20	1905 at 0.2	N/A	N/A	Good
F15	C ₆ H ₆	0.752 ^c	0.72	1.80	760	1850 at 0.45	N/A	N/A	Good
F16	C ₇ H ₁₆	0.841 ^c	0.318	1.00	760	1843 at 0.25	12 at 0.08	1.77 at 0.09	-×6.8 ^e
F17	C ₇ H ₁₆	0.73 ^c	0.605	1.90	760	1640 at 0.30	75 at 0.225	75.8 at 0.23	+1.1
F18	i-C ₈ H ₁₈	0.682 ^c	0.608	1.90	760	1670 at 0.30	292 at 0.21	455 at 0.23	+55.8
F19	C ₁₀ H ₂₂	0.682 ^c	0.558	1.73	760	1688 at 0.20	65 at 0.10	68.5 at 0.10	+5.4
F20	gasoline	0.768 ^c , 0.01 ^d		0.9-1	760	1990 at 0.046	344 at 0.05	330 at 0.05	-4.1
F21	kerosene	0.684 ^c		≈1.7	760	1775 at 0.20	1090 at 0.1	850 at 0.75	-22.0
F22	C-C ₆ H ₁₂	0.325	0.333	1.00	30	1960 at 0.6	473 at 0.09	498 at 0.09	+5.3

X means "a Factor of X"

Benzene Formation Potential

The Highest and Lowest Benzene Producer

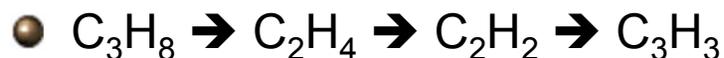
Fuel	Inert Ar, %	C/O	P torr	Exp. Max. Y(C ₆ H ₆) ^b	Cal. Max. Y(C ₆ H ₆) ^b	Deviation, %
C ₄ H ₆	0.03	0.874	20	1300 at 0.85	1490 at 0.85	+14.6
C ₃ H ₆	0.25	0.773	37.5	1220 at 0.39	927 at 0.39	-24.0
kerosene	0.684 ^c	φ=1.7	760	1090 at 0.1	850 at 0.75	-22.0
C ₂ H ₄	0	0.80	760	936 at 0.15	136 at 0.14	-X6.9 ^e
C ₃ H ₈	0.44	0.833	760	840 at 0.35	922 at 0.32	+9.8
C ₇ H ₁₆	0.73 ^c	0.605	760	75 at 0.225	75.8 at 0.23	+1.1
C ₁₀ H ₂₂	0.682 ^c	0.558	760	65 at 0.10	68.5 at 0.10	+5.4
C ₂ H ₂	0.45	1.00	19.5	58.9 at 0.6	39.1 at 0.64	-33.6
C ₂ H ₂	0.05	0.959	20	40 at 0.37	82.7 at 0.37	+X2.1 ^e
C ₂ H ₄	0.5	0.634	20	33.1 at 0.9	11.4 at 0.77	-X2.9 ^e
C ₃ H ₈	0.424	0.54	30	17.5 at 0.75	72.9 at 0.77	+X4.2 ^e
C ₇ H ₁₆	0.841 ^c	0.318	760	12 at 0.08	1.77 at 0.09	-X6.8 ^e

Benzene Formation Potential

Effects of Carbon Backbone: C₃ Species

Fuel	C/O	P torr	T(Max) K at cm	T(Max), K at cm, Fitted	Exp. Max. Y(C ₆ H ₆) ^b	Cal. Max. Y(C ₆ H ₆) ^b	Deviati on, %
C ₃ H ₆	0.773	37.5	2371 at 0.71		1220 at 0.39	927 at 0.39	-24.0
C ₂ H ₄	0.92	760	1600 at 0.3		250 at 0.35	212 at 0.35	-15.2
C ₂ H ₄	1.02	760	1420 at 0.3		575 at 1.0	553 at 1.0	-3.8
C ₃ H ₈	0.833	760	1640 at 0.4		840 at 0.35	922 at 0.32	+9.8
CH ₄	0.626	760	1605 at 0.4		280 at 0.8	141 at 0.8	-49.6
C ₂ H ₆	0.715	760	1600 at 0.24		230 at 0.8	205 at 0.8	-10.9

- Fuel decomposition



- Benzene formation

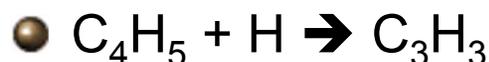
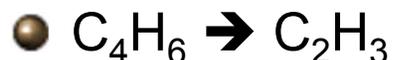


Benzene Formation Potential

Effects of Carbon Backbone: C₄ Species

Fuel	C/O	P torr	T(Max) K at cm	T(Max), K at cm, Fitted	Exp. Max. Y(C ₆ H ₆) ^b	Cal. Max. Y(C ₆ H ₆) ^b	Deviati on, %
C ₄ H ₆	0.874	20	2310 at 1.65	2050 at 1.75	1300 at 0.85	1490 at 0.85	+14.6
C ₂ H ₂	0.959	20	1901 at 1.0		40 at 0.37	82.7 at 0.37	+X2.1 ^e
C ₂ H ₂	1.00	19.5	1850 at 1.0		58.9 at 0.6	39.1 at 0.64	-33.6

- Fuel decomposition



- Benzene formation



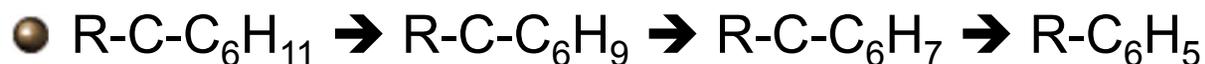
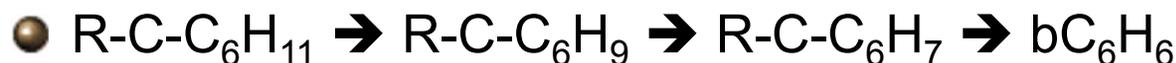
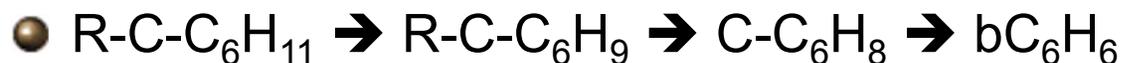
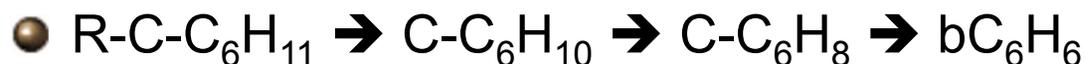
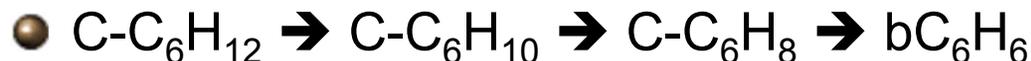
Benzene Formation Potential

Effects of Carbon Backbone: Cyclohexanes

Fuel	C/O	P torr	T(Max) K at cm	T(Max), K at cm, Fitted	Exp. Max. Y(C ₆ H ₆) ^b	Cal. Max. Y(C ₆ H ₆) ^b	Deviati on, %
<i>kerosene</i>	$\phi=1.7$	760	1775 at 0.20	1775 at 0.25	1090 at 0.1	850 at 0.75	-22.0
C ₁₀ H ₂₂	0.558	760	1688 at 0.20	1688 at 0.22	65 at 0.10	68.5 at 0.10	+5.4
<i>C-C₆H₁₂</i>	0.333	30	1960 at 0.6	1960 at 0.55	473 at 0.09	498 at 0.09	+5.3
C ₇ H ₁₆	0.318	760	1843 at 0.25		12 at 0.08	1.77 at 0.09	-X6.8 ^e
<i>gasoline</i>	$\phi=1$	760	1990 at 0.046	1990 at 0.106	344 at 0.05	330 at 0.05	-4.1

- Benzene formation

- Cascading dehydrogenation & Interweaving dehydrogenation

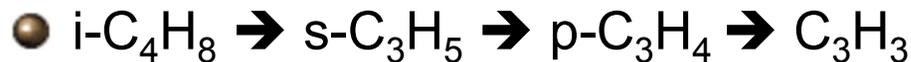
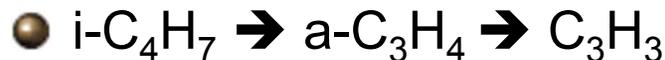


Benzene Formation Potential

Effects of Branching: cyclo > iso > normal
paraffins

Fuel	C/O	P torr	T(Max) K at cm	T(Max), K at cm, Fitted	Exp. Max. Y(C ₆ H ₆) ^b	Cal. Max. Y(C ₆ H ₆) ^b	Deviation, %
<i>i</i> -C ₈ H ₁₈	0.608	760	1670 at 0.30	1670 at 0.36	292 at 0.21	455 at 0.23	+55.3
C ₇ H ₁₆	0.605	760	1640 at 0.30	1640 at 0.40	75 at 0.225	75.8 at 0.23	+1.1
C ₁₀ H ₂₂	0.558	760	1688 at 0.20	1688 at 0.22	65 at 0.10	68.5 at 0.10	+5.4
<i>n</i> -C ₆ H ₁₂	0.333	30	1960 at 0.6	1960 at 0.55	473 at 0.09	498 at 0.09	+5.3
C ₇ H ₁₆	0.318	760	1843 at 0.25		12 at 0.08	1.77 at 0.09	-X6.9

- Fuel decomposition



- Benzene formation

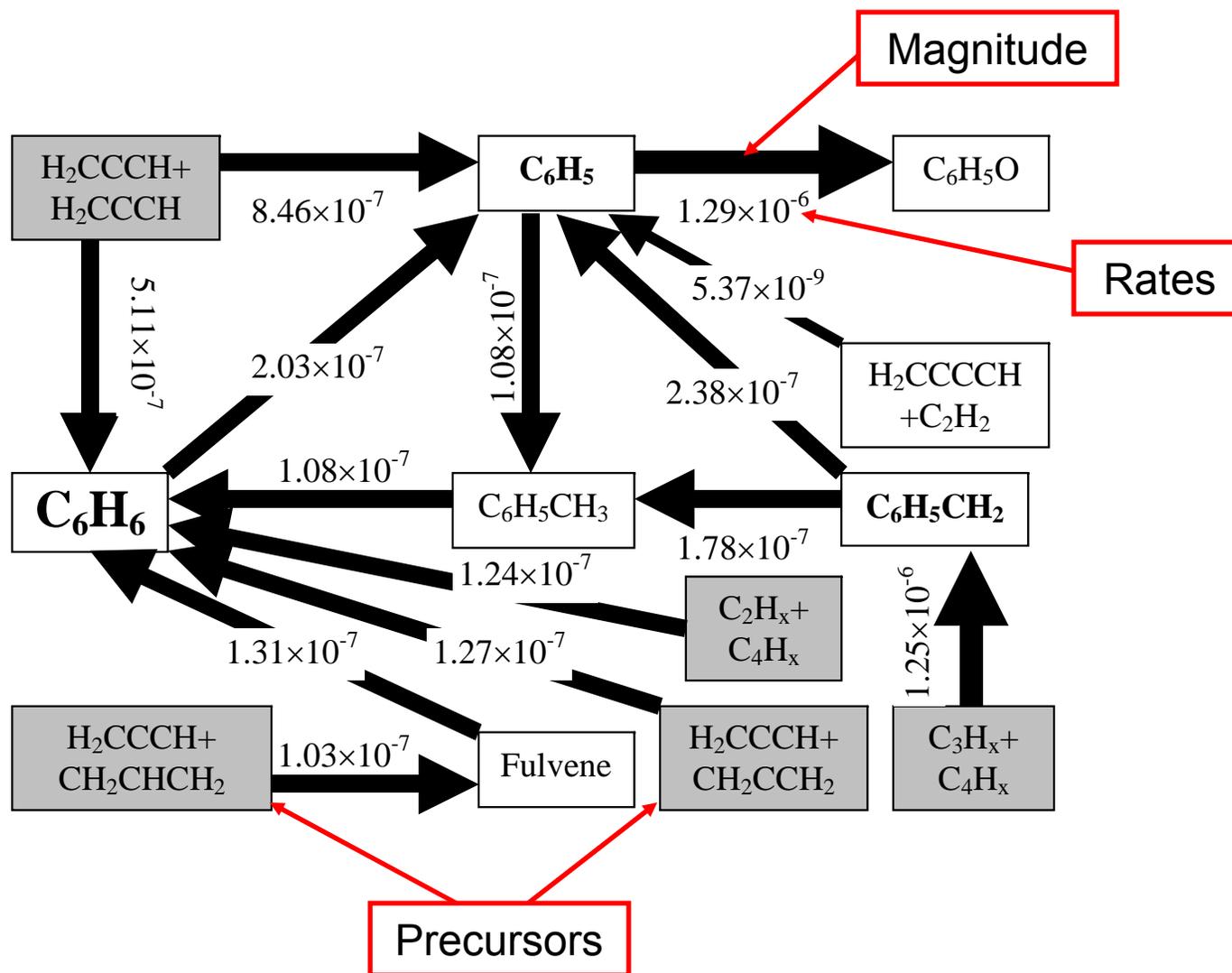




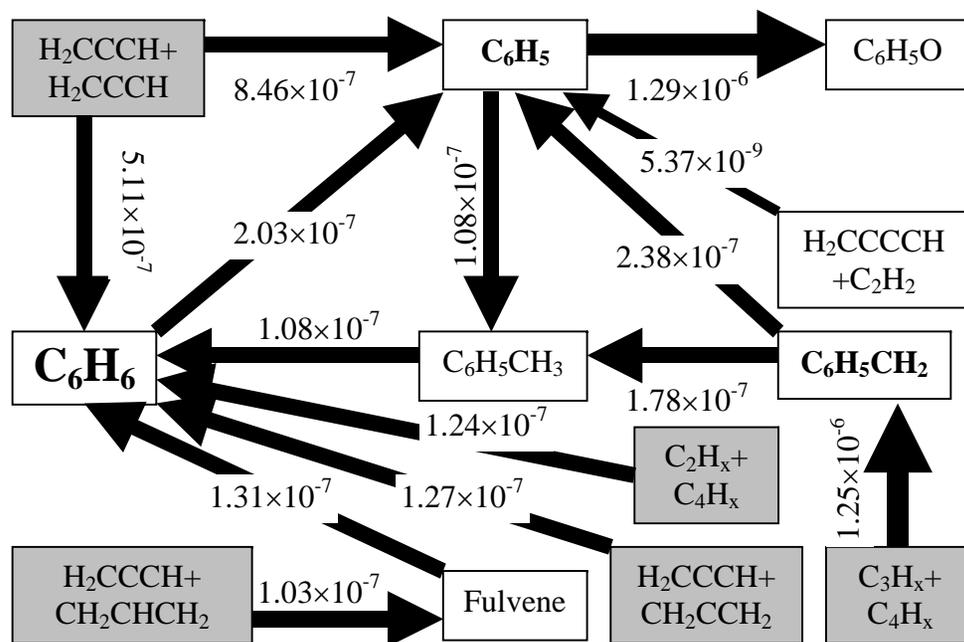
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Benzene Formation Pathways



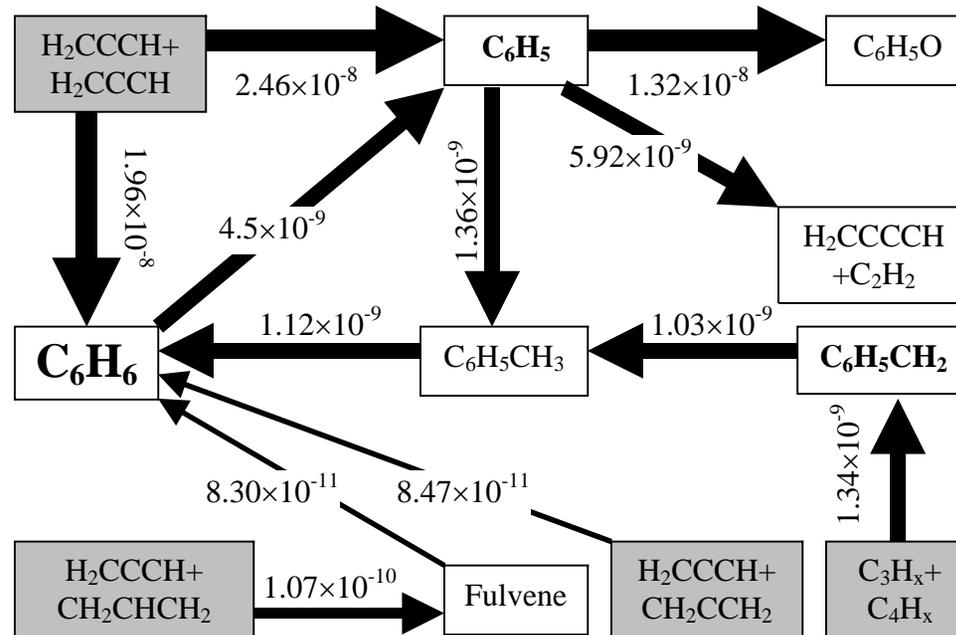
In a Normal Decane Flame



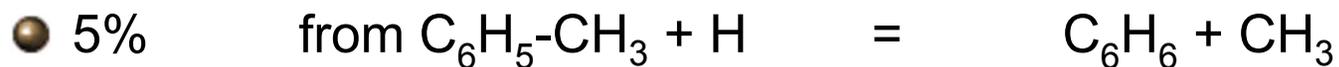
● Contribution of Major Benzene Formation Pathways

- 51% from $C_3H_3 + C_3H_3 = bC_6H_6$
- 13% from $C_3H_3 + a-C_3H_5 = fC_6H_6 + 2H$
- 13% from $C_3H_3 + a-C_3H_4 = bC_6H_6 + H$
- 12% from $C_2H_3 + C_4H_3 (C_4H_5) = C_6H_5$
($bC_6H_6 + H$)
- 11% from $C_6H_5-CH_3 + H = C_6H_6 + CH_3$

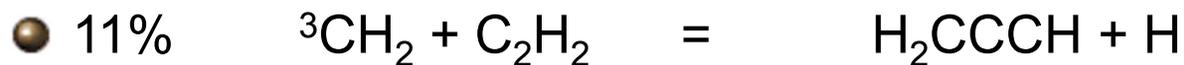
In an Acetylene Flame



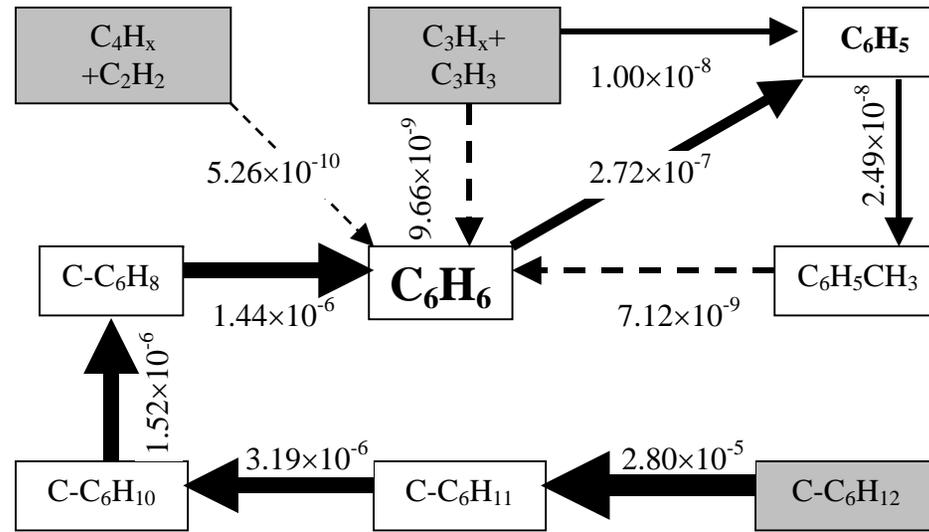
- Contribution of Major Benzene Formation Pathways



- Propargyl Radical Formation Pathways



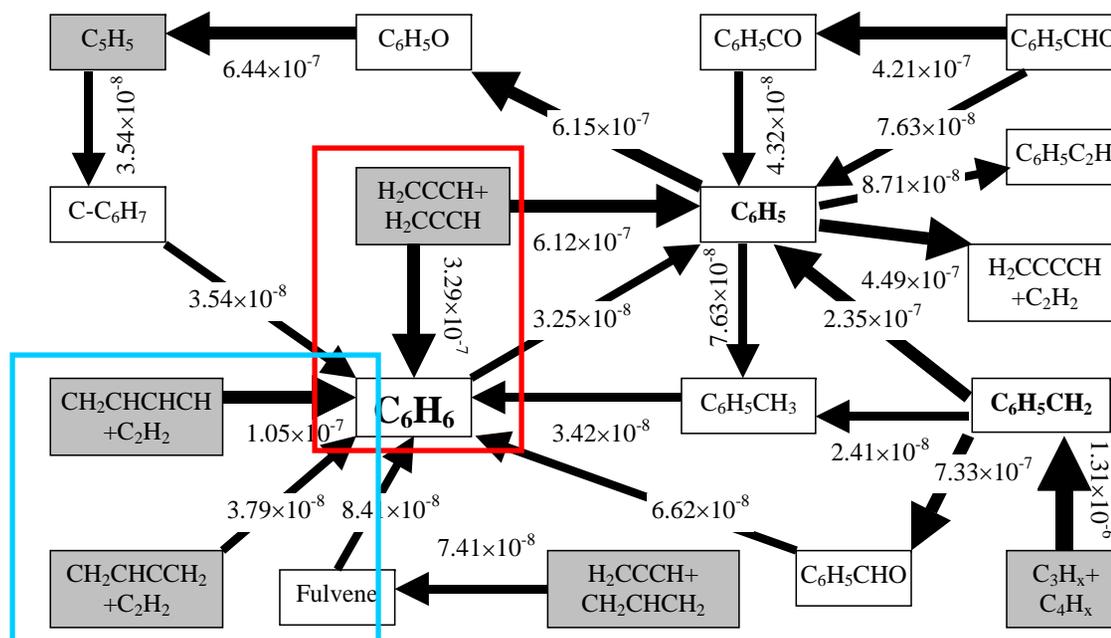
In a Cyclohexane Flame



- Contribution of Major Benzene Formation Pathways

- 100% from $cycloC_6-R \rightarrow C-C_6H_{10} \rightarrow C-C_6H_8 \rightarrow bC_6H_6$

Benzene Formation Pathways: in Butadiene Flames



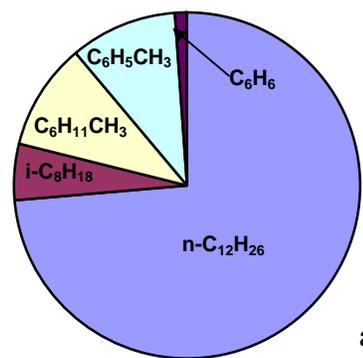
● Contribution of Major Benzene Formation Pathways

- 48% from $C_3H_3 + C_3H_3 = bC_6H_6$
- 20% from $C_2H_2 + C_4H_3 (C_4H_5) = C_6H_5 (bC_6H_6 + H)$
- 12% from $C_3H_3 + a-C_3H_5 = fC_6H_6 + 2H$
- 10% from $C_6H_5-CHO + H = C_6H_6 + CHO$
- 5% from $C_6H_5-CH_3 + H = C_6H_6 + CH_3$
- 5% from $C_5H_5 + CH_3 = C-C_6H_8 = C_6H_6 + 2H$

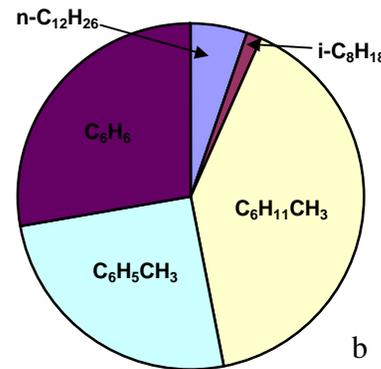
Soot Precursor Production Potential

Contribution from Individual Surrogate Components to the Formation of Benzene (a kerosene fuel)

- **Benzene Contributors:** Benzene (28%), Toluene (26%) and Methyl Cyclohexane (40%)
- **Component Fractions:** Benzene (1%), Toluene (10%), Methyl Cyclohexane (10%), and paraffins (79%)



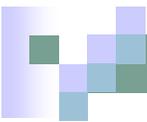
Surrogate Distribution



Benzene Formation

* Experimental: Doute et al., *Combustion Science Technology*, 106 (4-6) (1995) 327–344.

* Modeling: Zhang et al., *Proceedings of Combustion Institute*, (2007) 31, 401–409.



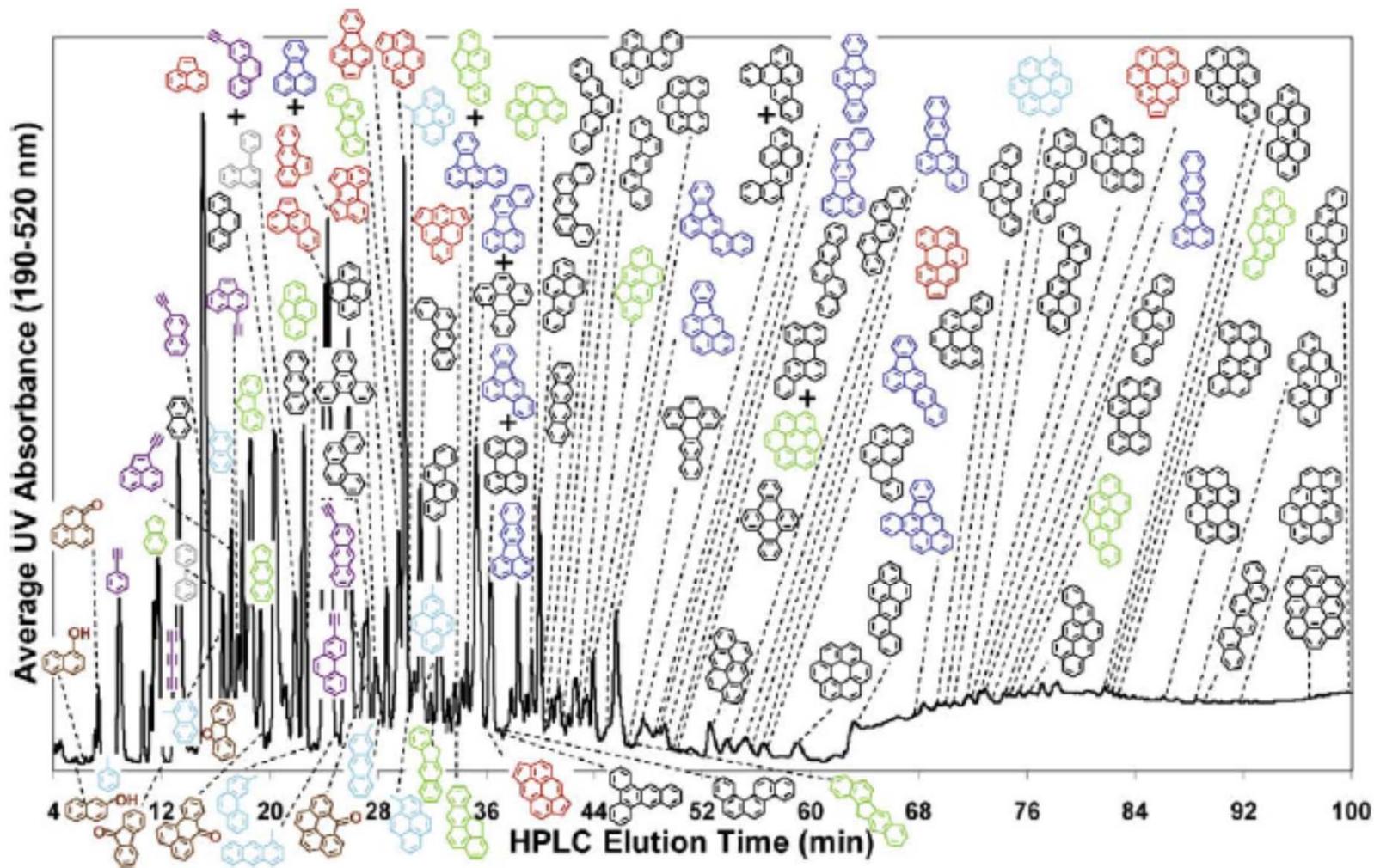
Concluding Comments

- The Utah Surrogate Model Was Validated for 22 Premixed Flames of Various Fuels (C_1 - C_{12} fuels; $\Phi = 1.0$ - 3.06 ; $P = 20$ - 760 torr; $T = 1600$ - 2370 K).
- Benzene Concentrations Were Predicted within 30% of the Experimental Data for 15 (out of 22) Flames.
- Both Formation Pathways and Formation Potential of Benzene Were Found to Be Dependent on the Fuel Structure, and C_3 , C_4 and $C-C_6$ Were among the Most Productive Fuels.
- C_3 Combination Was Identified to be the Major Benzene Formation Pathway for Most Fuels; That Is Replaced with Dehydrogenation Only for Cyclohexanes.
- Acetylene Addition Was Found to Be Important in C_4 Flames and Those with Large Paraffinic Fuels.



Flame experiments on formation of the first aromatics, usually benzene or toluene

- McNesby et al., Combust. Flame 142, 413-427 (2005)
 - Opposed flow diffusion flames
- McEnally et al., Prog. En. Comb. Sci. 32, 247-294 (2006)
 - Co-flow non-premixed flames
- Violi and Izvekov, PROCI 31, 529-537 (2007).
 - Molecular dynamics
- Desgroux et al., PROCI 34, 1713-1738 (2013)
 - Review of use of optical diagnostics



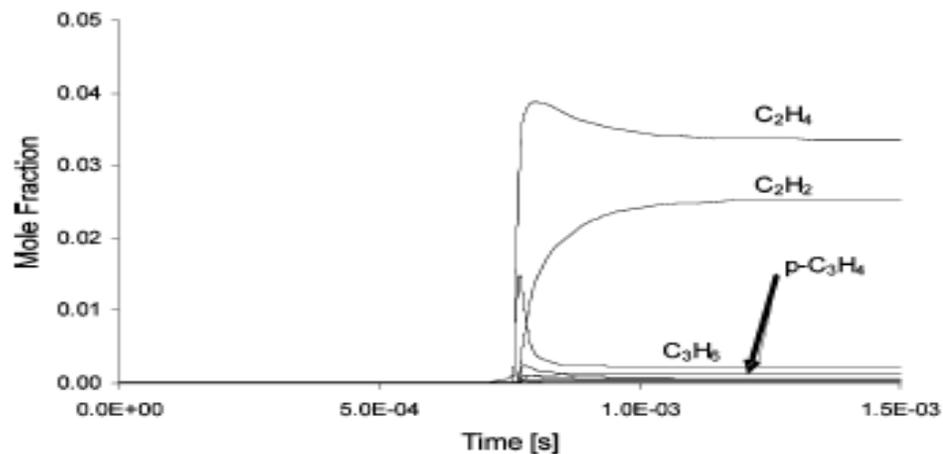
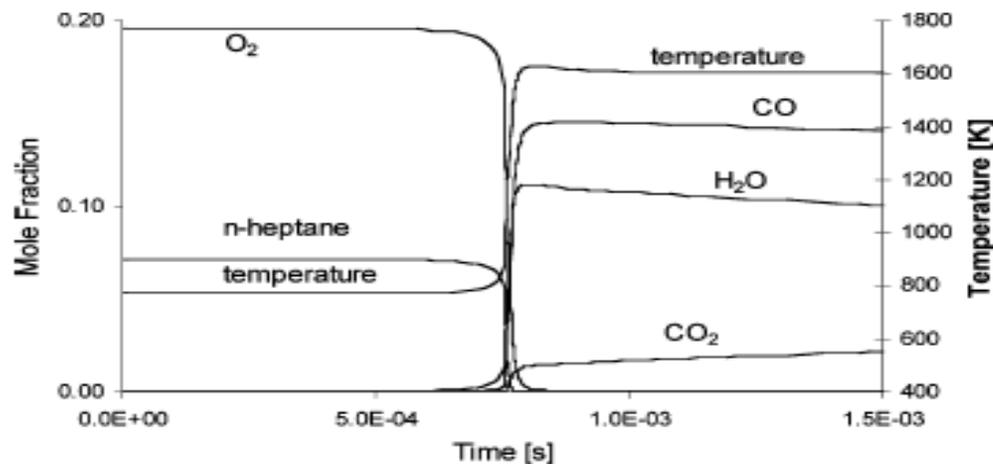
Thomas and Wornat, PROCI 32, 2009. Pyrolysis of catechol and butadiene at 1000 C, residence time of 0.3 seconds

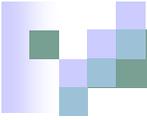


Premixed ignition in Diesel combustion

- Fuel-rich conditions ($\Phi \approx 4$)
- Relatively low temperature ($T \approx 850$ K)
 - Source of cetane ratings in Diesel engines
 - Very similar to conditions of engine knock
 - Very complex chemical kinetic pathways
- Products are good producers of soot precursor species
- Ignition kinetics are the same as in engine knock in SI engines, driven by H_2O_2 decomposition

Products of rich premixed ignition are mostly small unsaturated hydrocarbons, especially acetylene and ethene, which are known precursors to soot

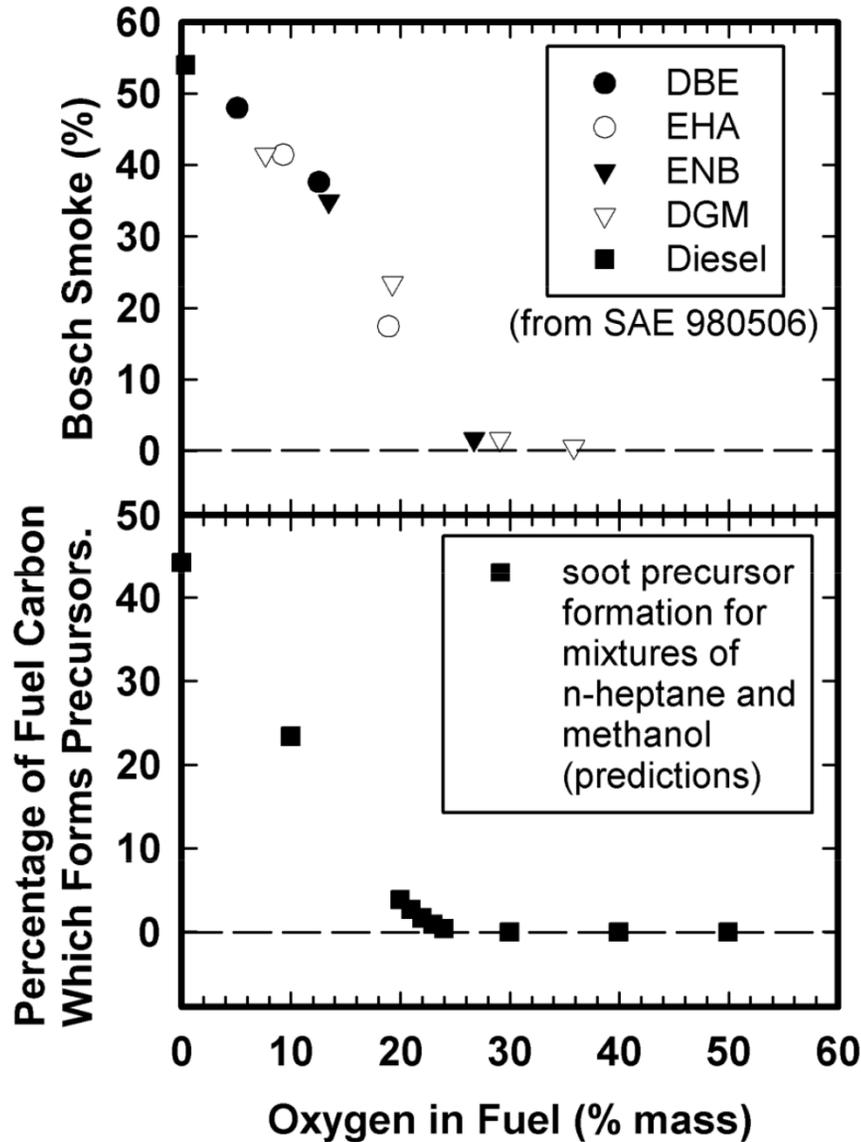




Experimental background

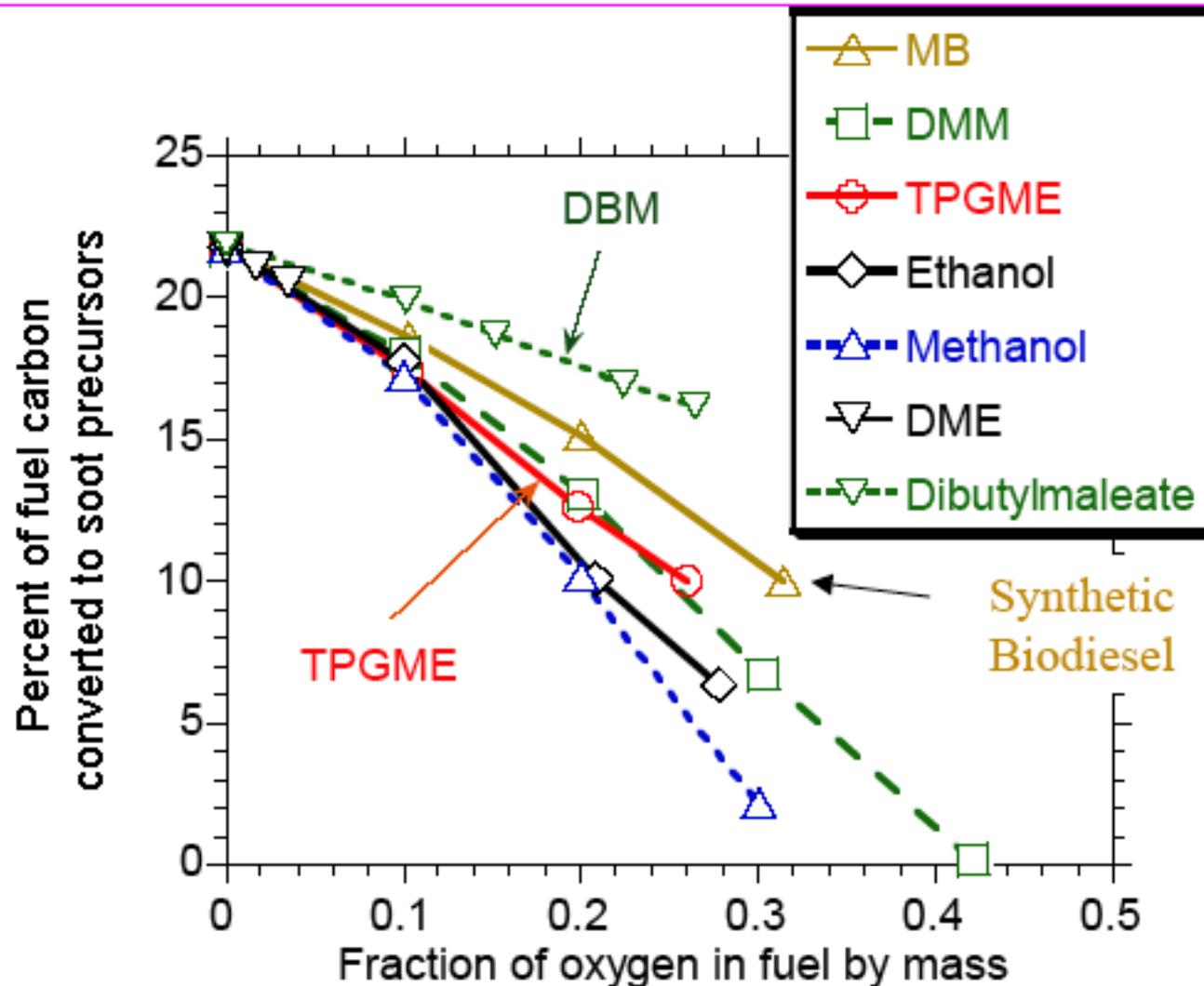
- Addition of oxygenated species reduces soot
 - Important possible oxygenates include biodiesel fuels
- Soot production correlates with post-ignition levels of selected chemical species
- Suggestions that this is due to presence of C - C bonds or total O concentrations
- Use kinetic model to examine these possibilities

Predicted level of soot precursors correlates well with soot emissions from a Diesel engine

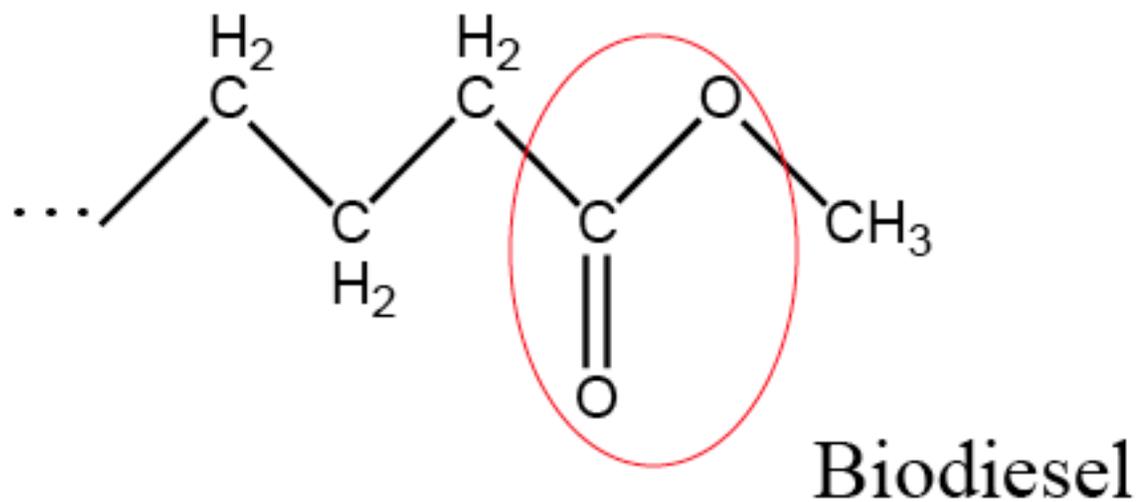
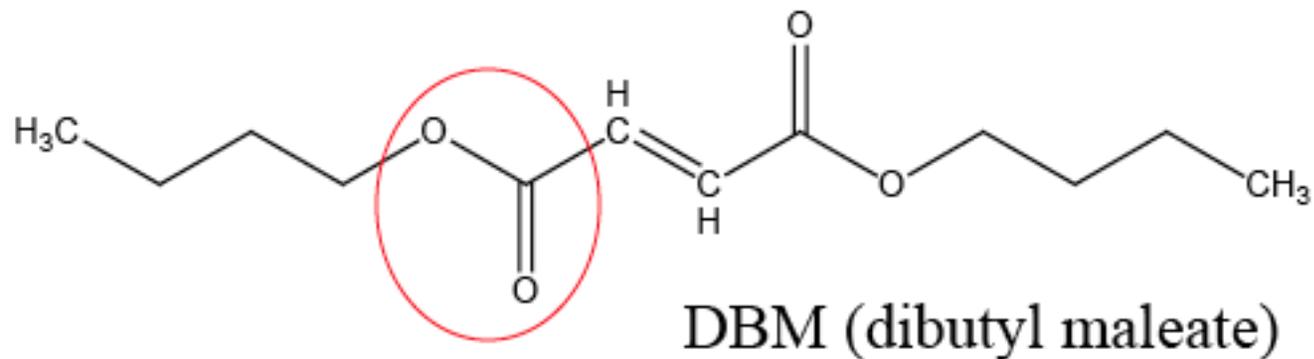


From:
Flynn, Durrett,
Dec, Westbrook, et
al., SAE paper
1999-01-0509

How well an oxygenated fuel works depends on its molecular structure

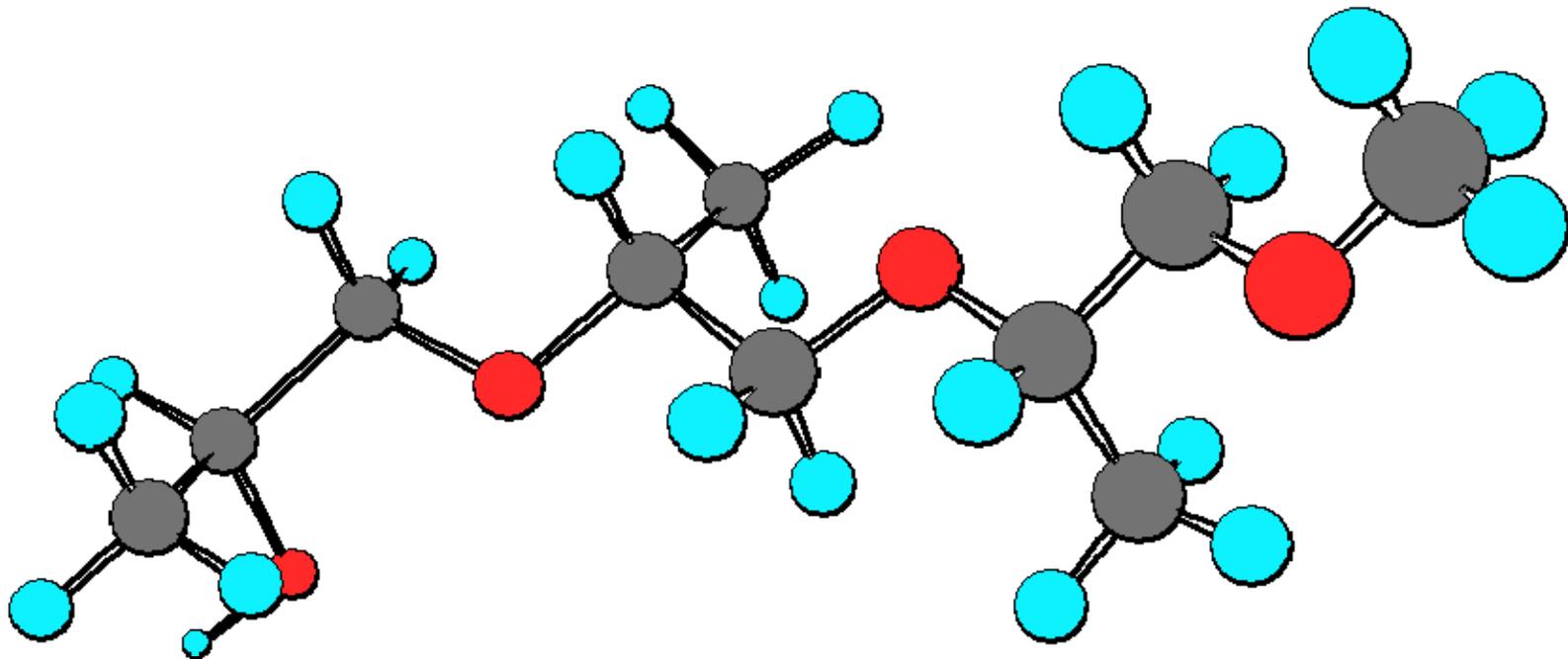


One large group of oxygenates have ester structures where one carbon atom is attached to two oxygen atoms

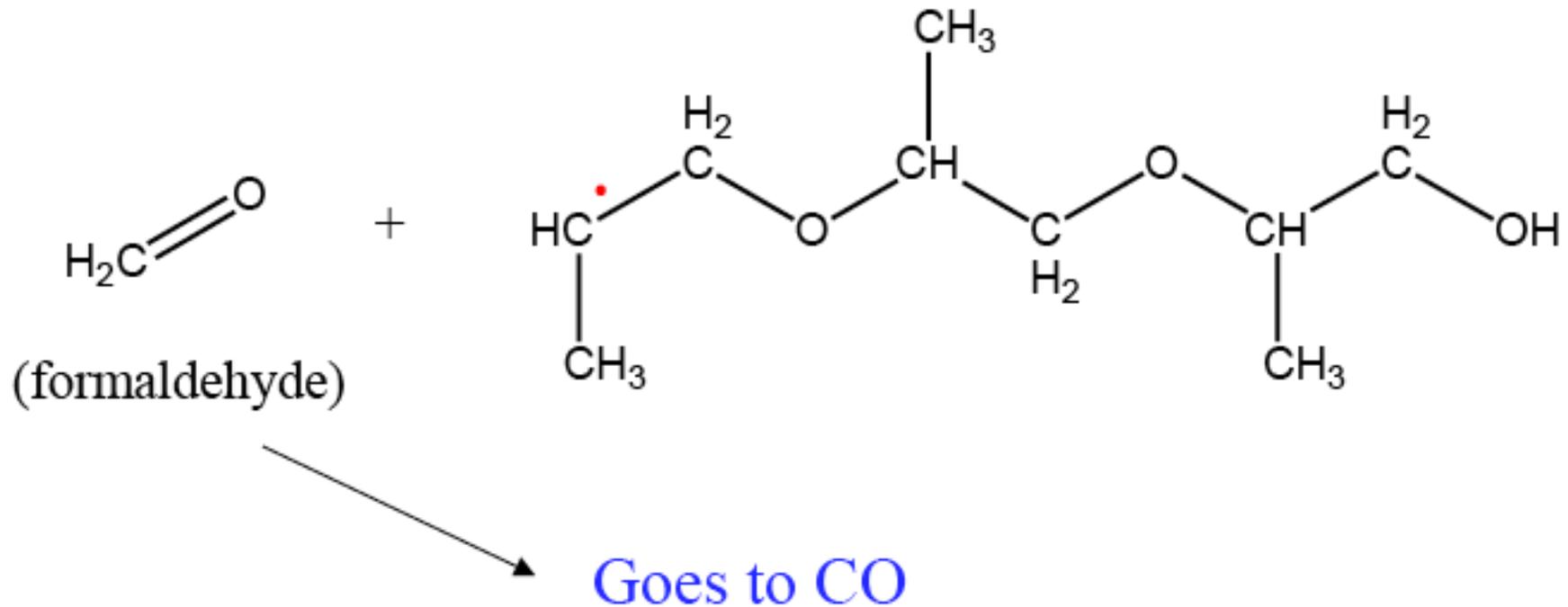


One oxygen atom could be wasted

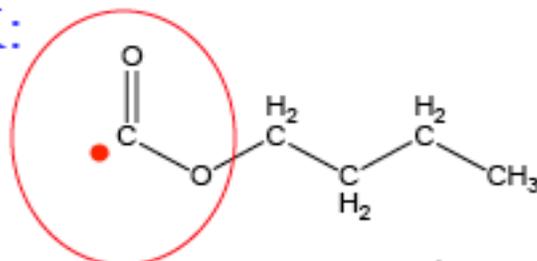
Structure of Tripropylene Glycol Monomethyl Ether (TPGME)



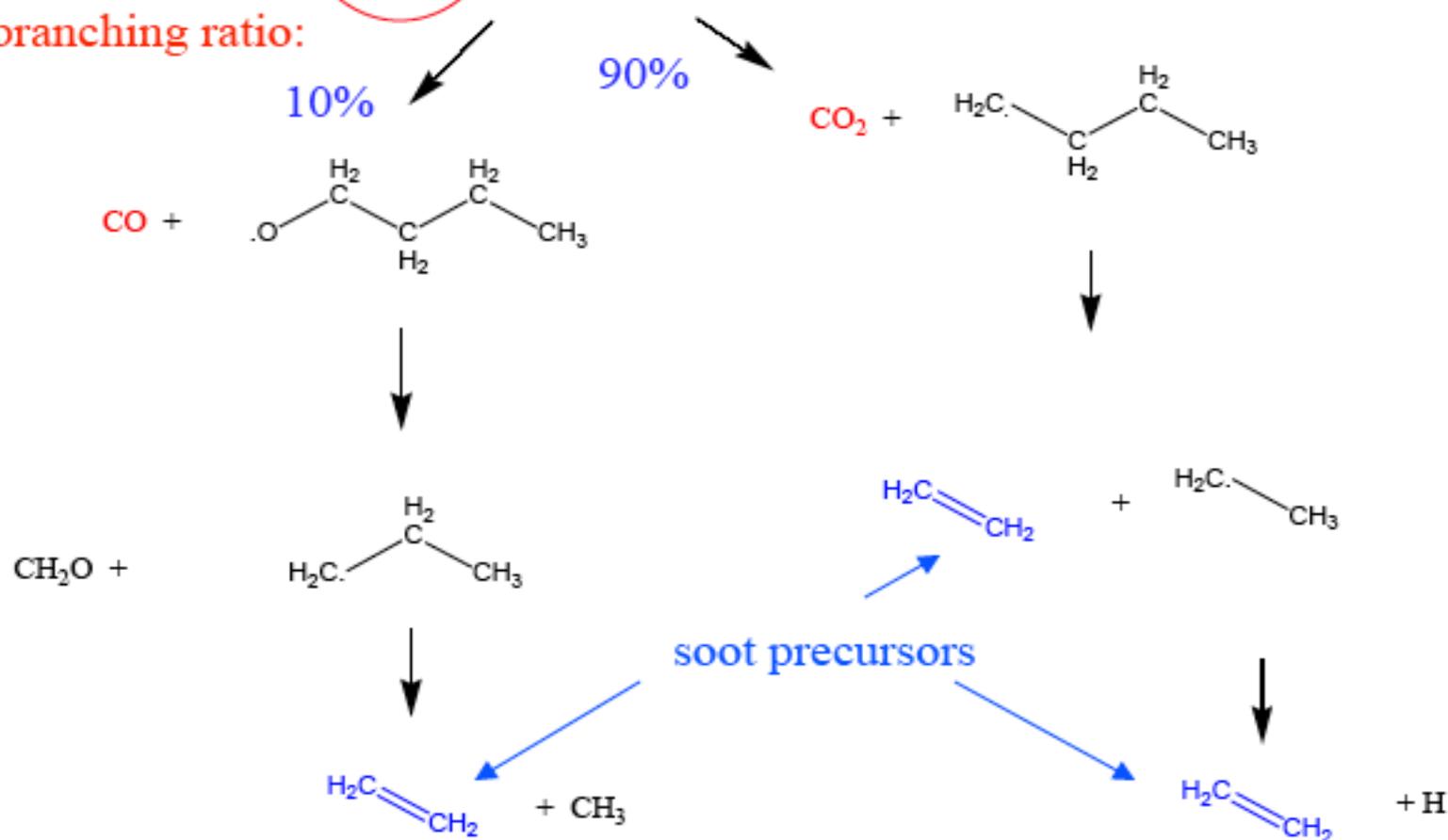
As the oxygenate is consumed, ideally each O atom should stay attached to one C atom to make CO



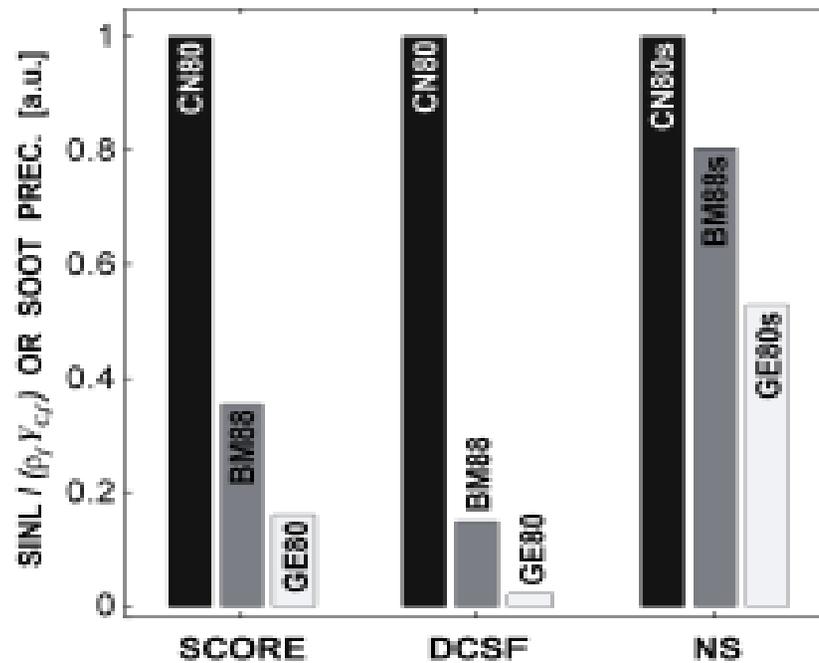
Based on new rates, 90% of key ester structure in DBM goes to CO_2 at 1000K:



Key branching ratio:

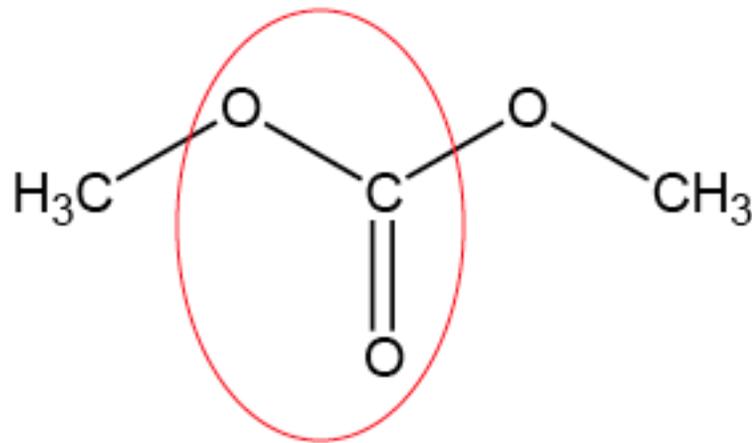


Experiments at Sandia show same trends as LLNL kinetic models



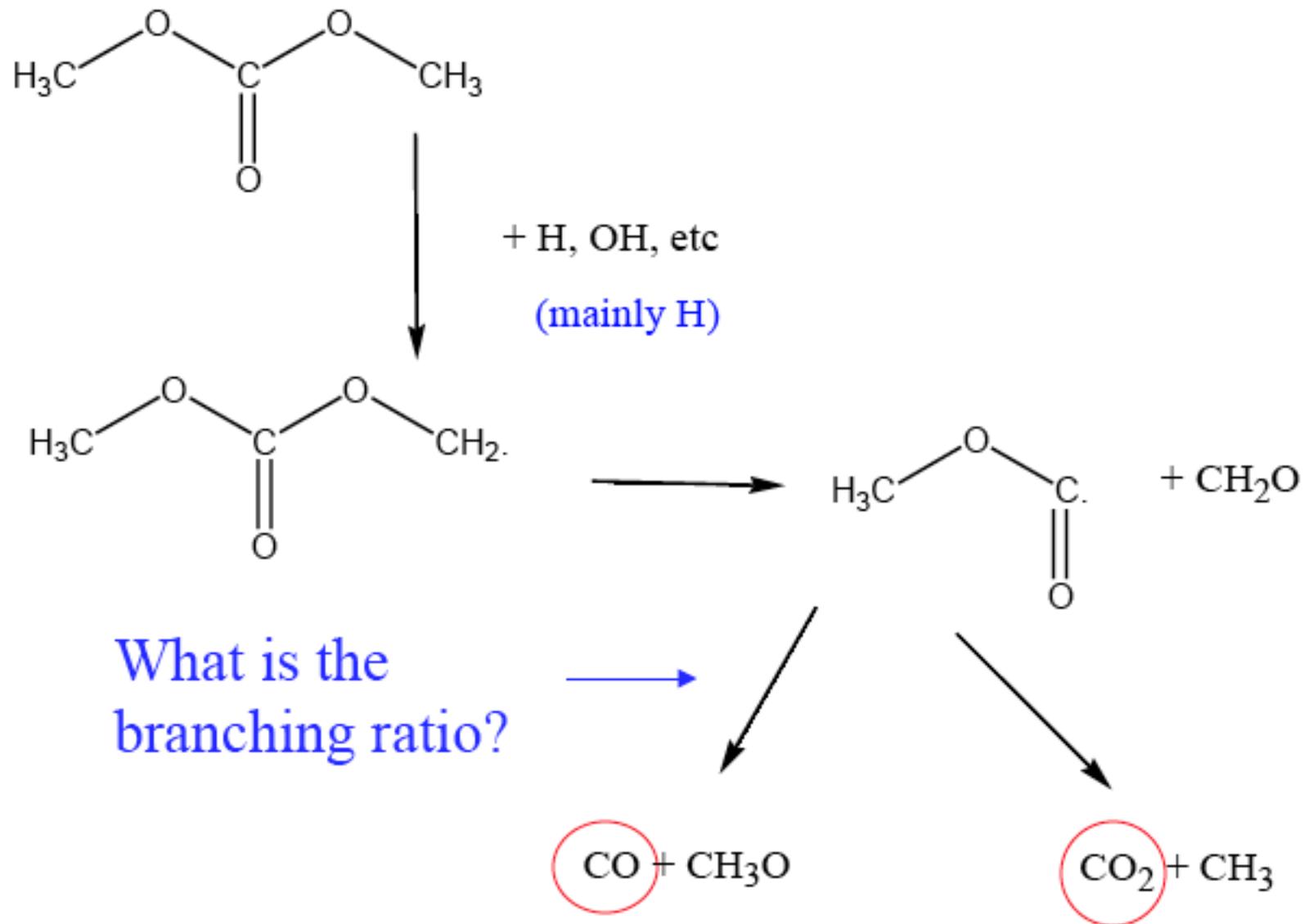
DBM and TPGME reduce sooting, but DBM is less effective than TPGME

DMC (dimethylcarbonate) has ester structure

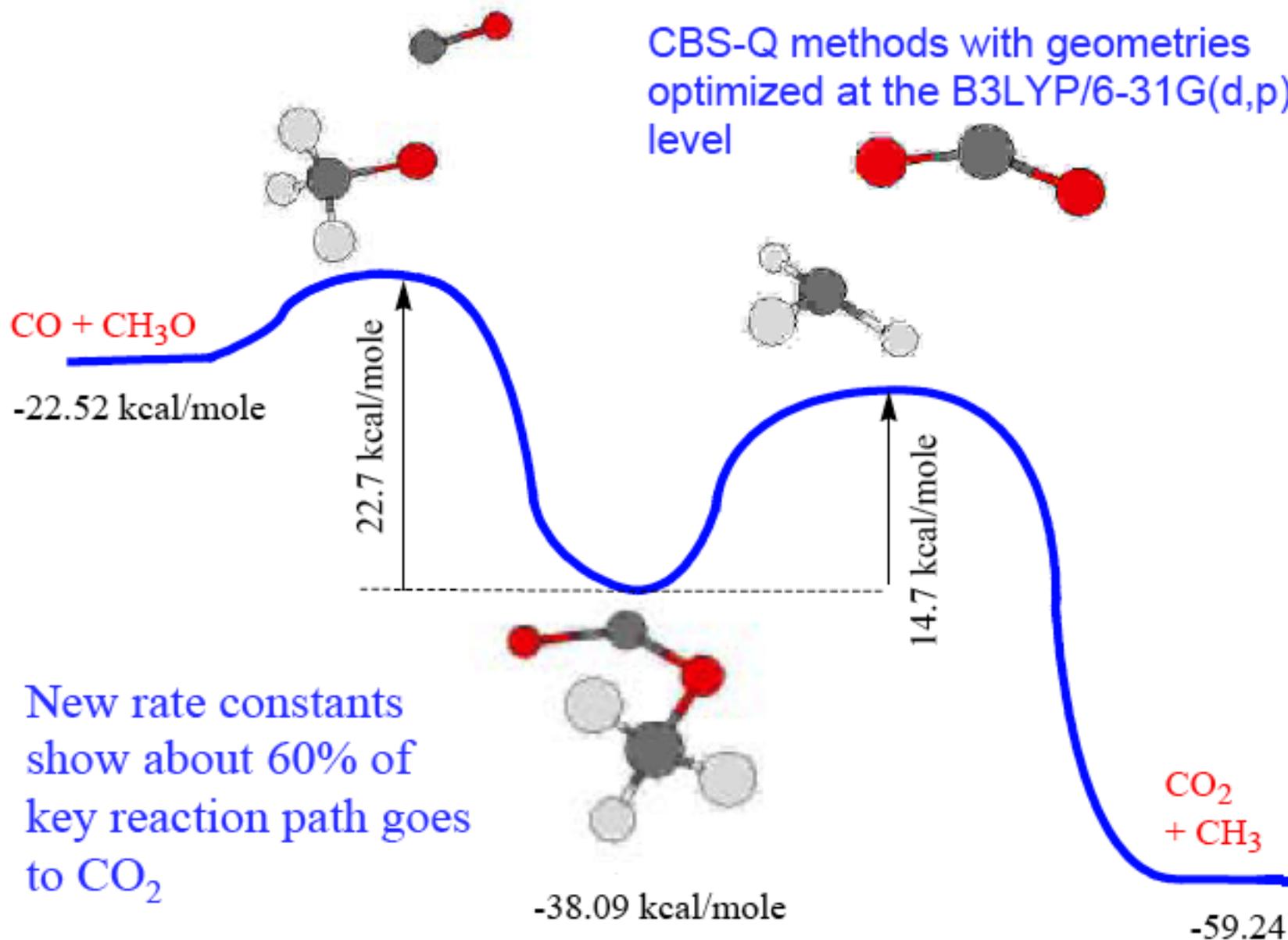


⇒ study it, because it is a small, simpler molecule than the large DBM or biodiesel fuels and some experimental data was available

DMC leads to choice of CO or CO₂ too

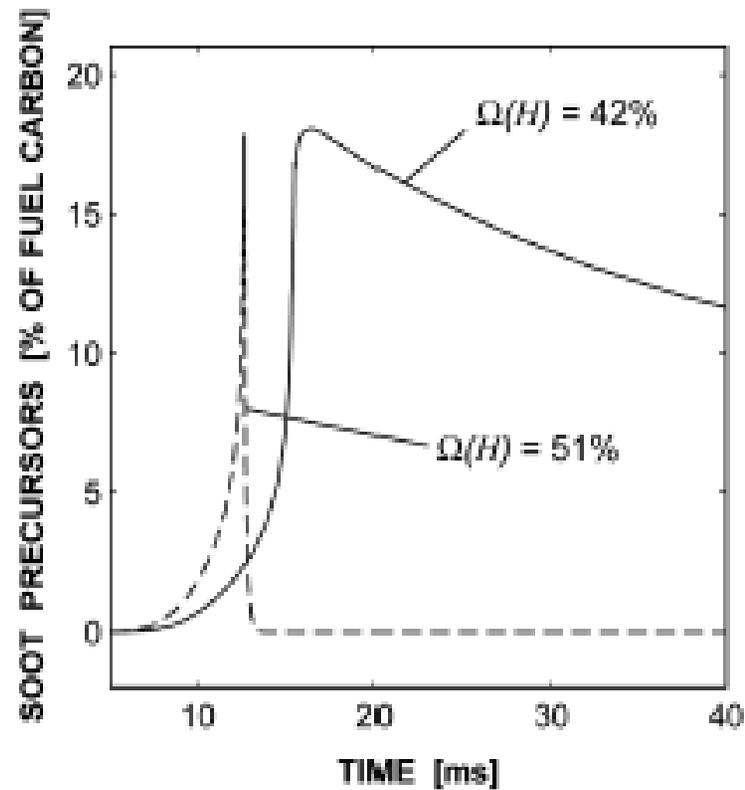


CBS-Q methods with geometries optimized at the B3LYP/6-31G(d,p) level



New rate constants show about 60% of key reaction path goes to CO₂

Models show same soot precursor formation, but oxygen enhances precursor consumption



Example of $C_2H_3 + O_2$ breaking C - C bond

Understand and predict emissions from open burning or detonation of explosives



Figure 5. Projectile placement for FY99 Tests 1 and 2.



Figure 6. Projectile placement for FY99 Test 3.

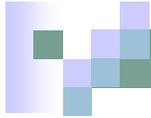
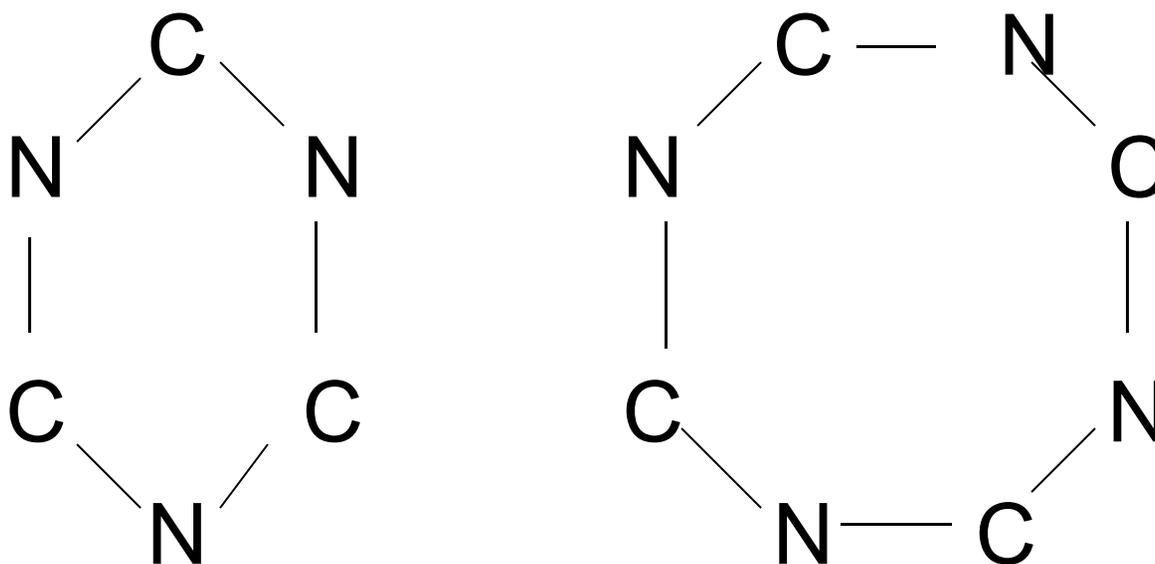


Fig. 3. Open detonation of TNT. Upper figure shows ignition and early burn, lower figure shows entrained cloud of dirt and soot.



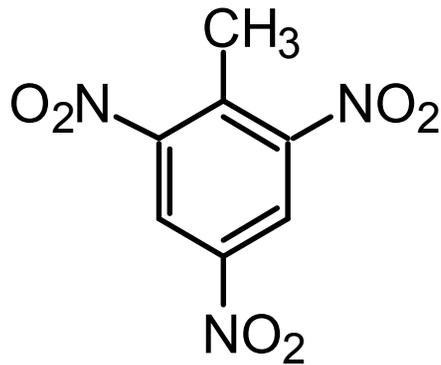
RDX and HMX are based on non-aromatic rings



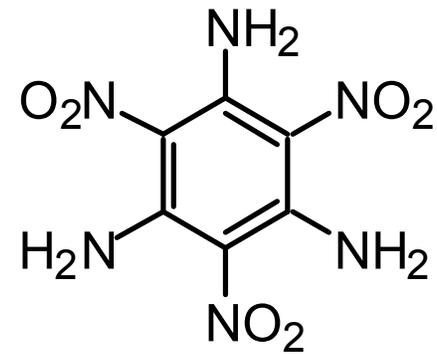
Note the absence of C - C bonds or aromatic rings

Presence of aromatic rings indicates explosive will lead to soot.

TNT

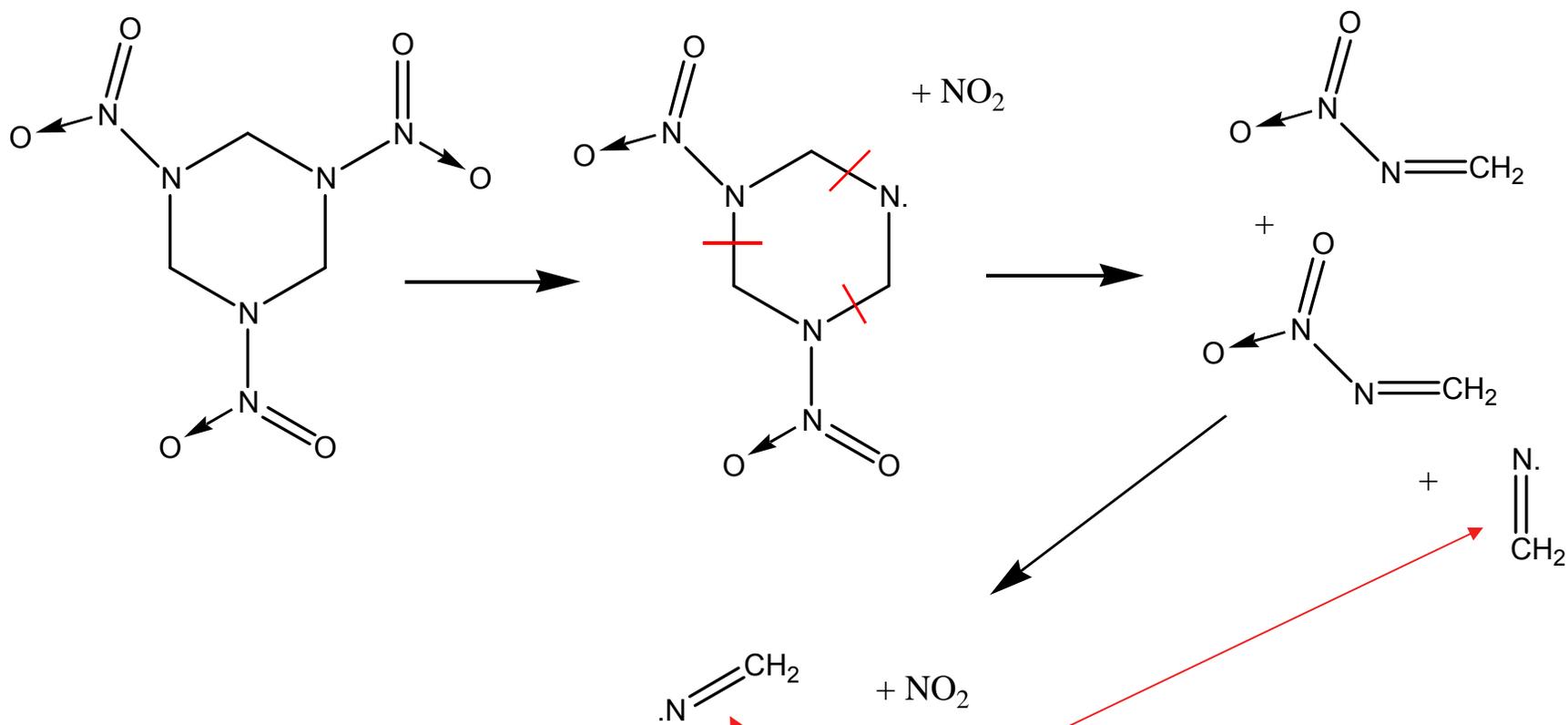


TATB



Aromatic rings and lots of C - C bonds

RDX does not produce soot precursors



No carbon – carbon bonds!

Soot tendencies depend on molecular structure

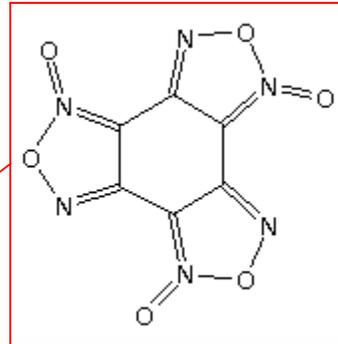
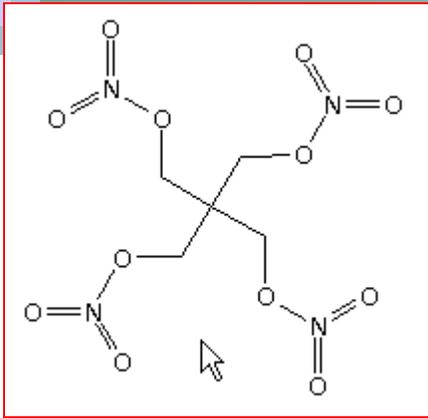
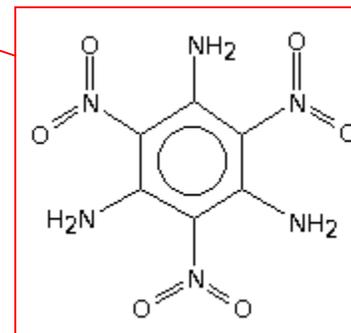


TABLE 1: Detonation Products (in mol) of PETN, BTF, and TATB from Calorimetry Data vs Two Equilibrium Predictions Taken along the CJ Adiabats^a

	condition		CO	CO ₂	graphite	CH ₄	H ₂ O	N ₂
PETN 1.74 g/cm ³	confined	experiment	1.6	3.4	0.0	0.0	3.5	2.0
	frozen 1800 K	CHEQ	1.6	3.4	0.0	0.0	3.6	2.0
	equilibrium	CHEQ	0.0	3.8	0.0	0.2	3.1	2.0
BTF 1.86 g/cm ³	confined	experiment	2.9	1.6	1.6	0.0	0.1	2.9
	frozen 1800 K	CHEQ	3.9	1.1	1.1	0.0	0.0	3.0
	equilibrium	CHEQ	0.6	1.7	2.7	0.0	0.0	3.0
TATB 1.87 g/cm ³	confined	experiment	0.4	2.0	3.6	0.0	2.1	2.3
	frozen 1800 K	CHEQ	0.8	1.5	3.6	0.2	2.3	2.9
	equilibrium	CHEQ	0.0	1.7	4.1	0.2	2.6	3.0

^a “Frozen” data are taken at 1800 K, and “equilibrium” data at 1 atm. These data are computed by the CHEQ code. Results are based on 1 mol of explosives.

From Ree et al, J. Phys. Chem. A, 1996





Oxygen is the main obstacle to soot production

- Goal is to produce C - O bonds
- There are many possible sources of oxygen
 - Simplest alternative is air
 - Oxygenated hydrocarbon or other molecules
- This is the principle used in diesel engines to reduce soot production
- This is the explanation for some munitions combustion observations



Molecular structure of oxygenated fuel additive determines its soot reduction properties

- Variability in soot precursor production observed computationally
- Before modeling approach was used, all oxygenates were believed to be equally effective at soot reduction
- Subsequent engine experiments consistent with model results
- Reaction pathways that lead to early CO₂ production “waste” available oxygen atoms in the oxygenate
- Same approach provided sooting estimates for oil sands fuel
- All analysis based on single-component “diesel fuel” surrogate
- Need for more thorough, multicomponent diesel simulations
- Opportunities for designing optimal oxygenated additives

Kitamura, et al. 2002

