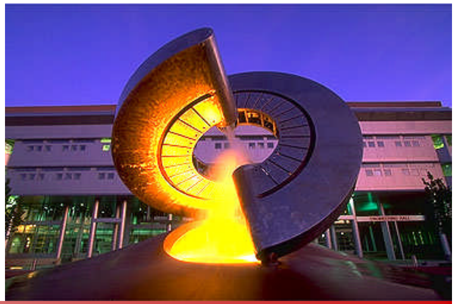
Reciprocating Internal Combustion Engines

Prof. Rolf D. Reitz,
Engine Research Center,
University of Wisconsin-Madison

2012 Princeton-CEFRC
Summer Program on Combustion
Course Length: 9 hrs

(Wed., Thur., Fri., June 27-29)

Hour 6



Hour 6: Heat transfer, NOx and Soot Emissions

Short course outine:

Engine fundamentals and performance metrics, computer modeling supported by in-depth understanding of fundamental engine processes and detailed experiments in engine design optimization.

Day 1 (Engine fundamentals)
Hour 1: IC Engine Review, 0, 1 and 3-D modeling
Hour 2: Turbochargers, Engine Performance Metrics
Hour 3: Chemical Kinetics, HCCI & SI Combustion

Day 2 (Spray combustion modeling)
Hour 4: Atomization, Drop Breakup/Coalescence
Hour 5: Drop Drag/Wall Impinge/Vaporization
Hour 6: Heat transfer, NOx and Soot Emissions

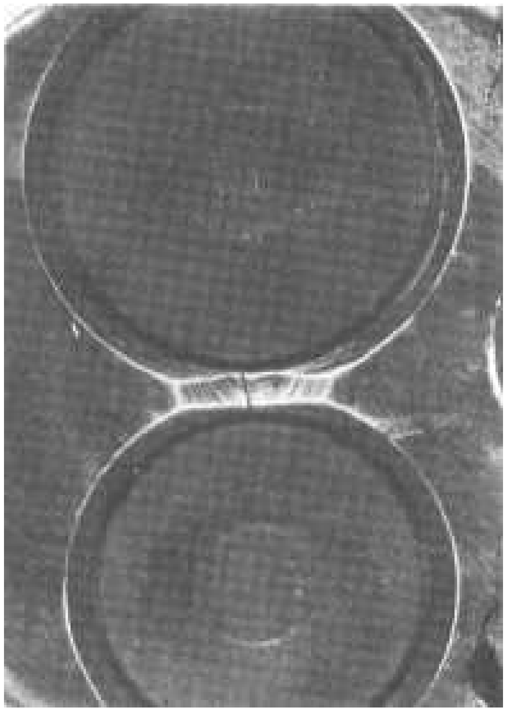
Day 3 (Applications)
Hour 7: Diesel combustion and SI knock modeling
Hour 8: Optimization and Low Temperature Combustion
Hour 9: Automotive applications and the Future

Engine Heat transfer

Up to 30% of the fuel energy is lost to wall heat transfer
Can influence engine ignition/knock
Engine durability – catastrophic engine failure


Scorching


Detonation


Cracking

Challen & Baranescu, 1998.

Heat Transfer

Gas phase energy equation

$$\frac{\partial(\rho I)}{\partial t} + \nabla \bullet (\rho \mathbf{u} I) = -p \nabla \bullet \mathbf{u} - \nabla \bullet \mathbf{J} + \rho \varepsilon + \dot{Q}^c + \dot{Q}^s + \dot{Q}^r$$

Radiation source term

$$\dot{Q}^r(\mathbf{r}) = \kappa \left[\int_{\boldsymbol{\Omega}=4\pi} I(\mathbf{r}, \boldsymbol{\Omega})\, d\boldsymbol{\Omega} - 4\pi I_b(\mathbf{r}) \right]$$

Wall heat flux (account for compressibility)

Han & Reitz, 1995

With radiation	Without radiation
$q_w = \dfrac{\rho_g C_p u^* T_g \ln(T_g/T_w) - (2.1y^+ + 33.34) G\, \upsilon / u^*}{2.1 \ln(y^+) + 2.5}$	$q_w = \dfrac{\rho C_p u^* T_g \ln(T_g/T_w)}{2.1 \ln(y^+) + 2.5}$
$\dfrac{dT}{dy} = \dfrac{q_w}{\rho_g C_p \nu} \left(\dfrac{2.1}{y^+} + 2.1 G^+ \right)$	$\dfrac{dT}{dy} = \dfrac{2.1 u^* T_g \ln\left(T_g / T_w \right)}{\upsilon y^+ \left[2.1 \ln(y^+) + 2.5 \right]}$

G radiative heat flux = $q_w{}^r$

Radiation modeling

Wiedenhoefer, SAE 2003-01-0560

Radiation Transfer Equation:

$$(\boldsymbol{\Omega}\cdot\nabla) I(\mathbf{r},\boldsymbol{\Omega}) = -(a_{net}+\sigma_s) I(\mathbf{r},\boldsymbol{\Omega}) + \kappa I_b(\mathbf{r}) + \frac{\sigma_s}{4\pi} S(\mathbf{r},\boldsymbol{\Omega})$$

a_{net} net absorption coefficient, σ_s scattering coefficient

$\kappa = a_{net} + \sigma_s$ extinction coefficient

Back body radiative flux (independent of angle) $I_b(\mathbf{r}) = \dfrac{\sigma T_w^4}{\pi}$

Scattering terms, σ_s , S ~ usually neglected compared to absorption

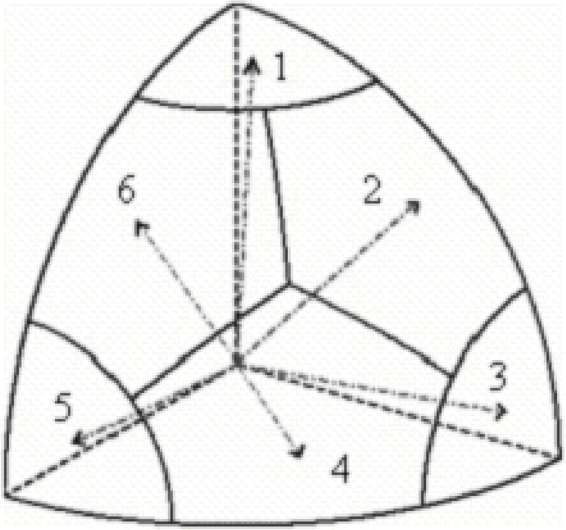
Radiation intensity at wall

$$G = q_w^r = \varepsilon \int_{\mathbf{n}\bullet\boldsymbol{\Omega}'<0} \left|\mathbf{n}\bullet\boldsymbol{\Omega}'\right| I(\mathbf{r},\boldsymbol{\Omega}')\, d\boldsymbol{\Omega}' - \varepsilon\sigma T_w^4$$

ε surface emissivity

Discrete ordinates model

$$\dot{Q}^r(\mathbf{r}) = \kappa\left[\sum_{m=1}^{nDir} \varpi^m I^m(\mathbf{r}) - 4\pi I_b(\mathbf{r})\right]$$



(e) Spherical surface division for S6

Soot and Gas Absorption

Wiedenhoefer, SAE 2003-01-0560

$$a_g\left(T,P,L_e\right)=\frac{1}{L_e}\ln\left[1-\varepsilon_g\left(T,P,L_e\right)\right]$$

$$\varepsilon=1-\left(1-\varepsilon_{fuel}\right)\left(1-\varepsilon_{CO}\right)\left(1-\varepsilon_{CO_2}\right)\left(1-\varepsilon_{H_2O}\right)$$

Total absorption coefficient

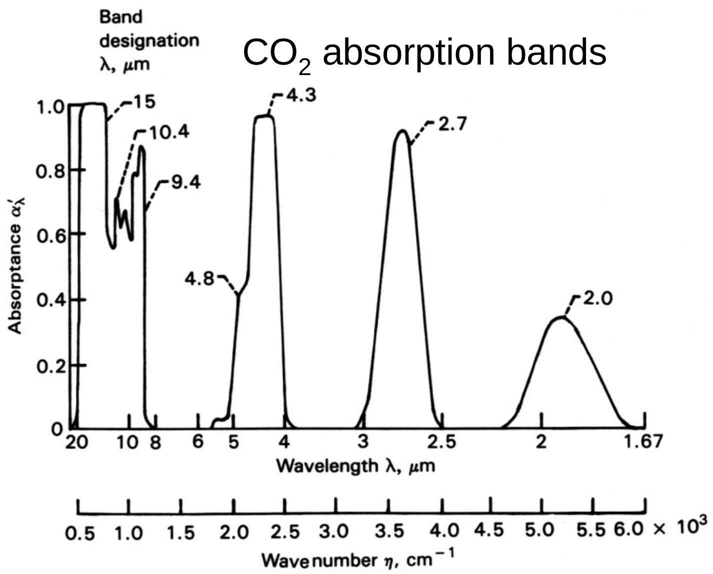
$$a_{net}=a_{soot}+a_{CO_2+H_2O}$$

Soot absorption

$$a_{soot}=1260C_{soot}T\ \mathrm{m}^{-1}$$

Wide band model for CO_2 and H_2O

$$\varepsilon_{b\eta}\left(\eta_{band\ center},T\right)=\left(\frac{2C_1\eta^3}{e^{C_2\eta/T}-1}\right)_{band\ center}$$



CO_2 absorption bands

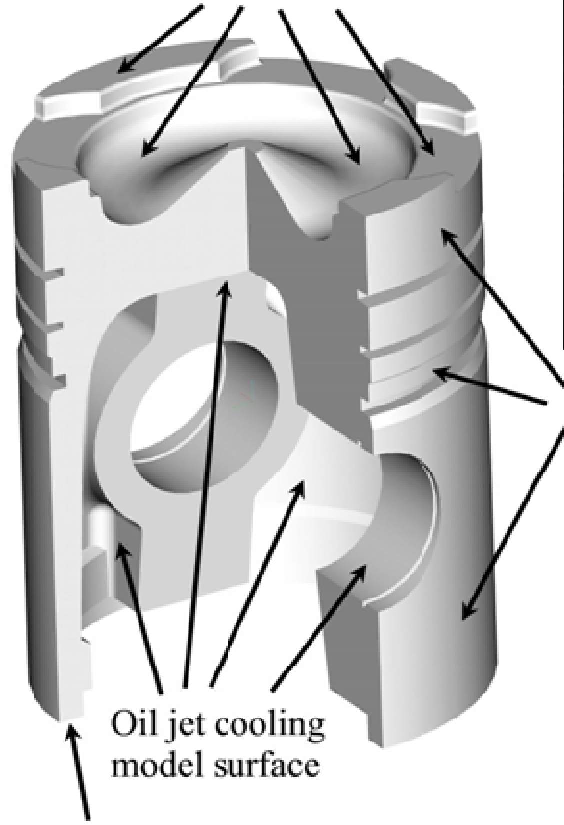
Importance of soot:

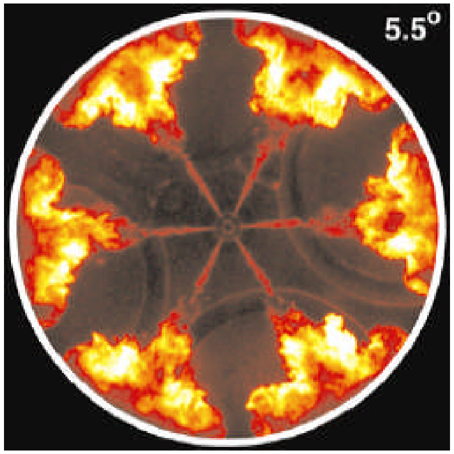
$$a_{gas}\propto\frac{1}{T}\qquad\qquad a_{soot}\propto T$$

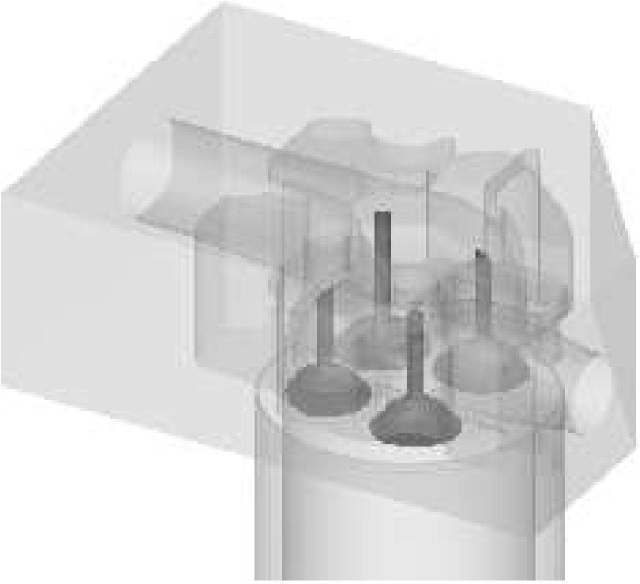
$$\dot{Q}^r\left(\mathbf{r}\right)=a\left[\int_{\boldsymbol{\Omega}=4\pi}I\left(\mathbf{r},\boldsymbol{\Omega}\right)d\boldsymbol{\Omega}-4\pi I_b\left(\mathbf{r}\right)\right]\propto\left[a_{gas}+a_{soot}\right]\sigma T^4\ \propto\sigma\left[T_{gas}^3+T_{soot}^5\right]$$

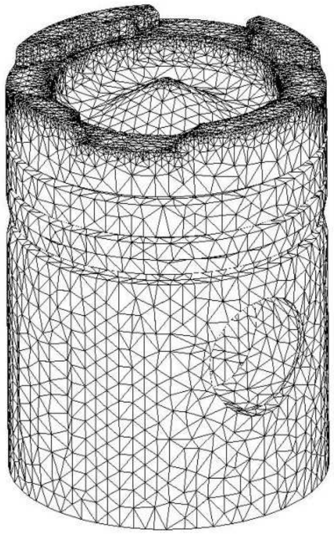
Wall heat transfer

Conjugate heat transfer modeling
ERC - Heat Conduction in Components code (HCC)









Unstructured
HCC Mesh

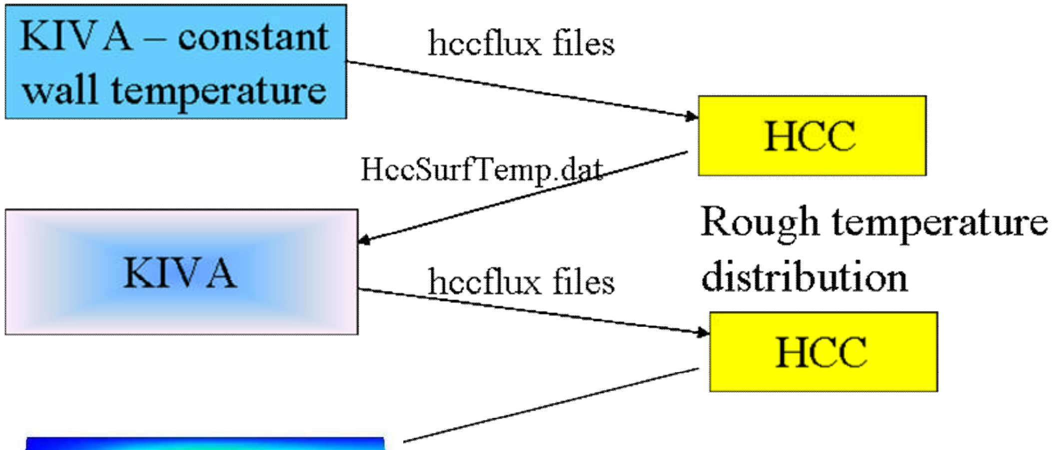
Iterative coupling
between HCC
and CFD code

Wiedenhoefer & Reitz, 2000

Hour 6: Heat transfer, NOx and Soot Emissions

Wall heat transfer

Wiedenhoefer & Reitz, 2000



KIVA – constant wall temperature

hccflux files

HCC

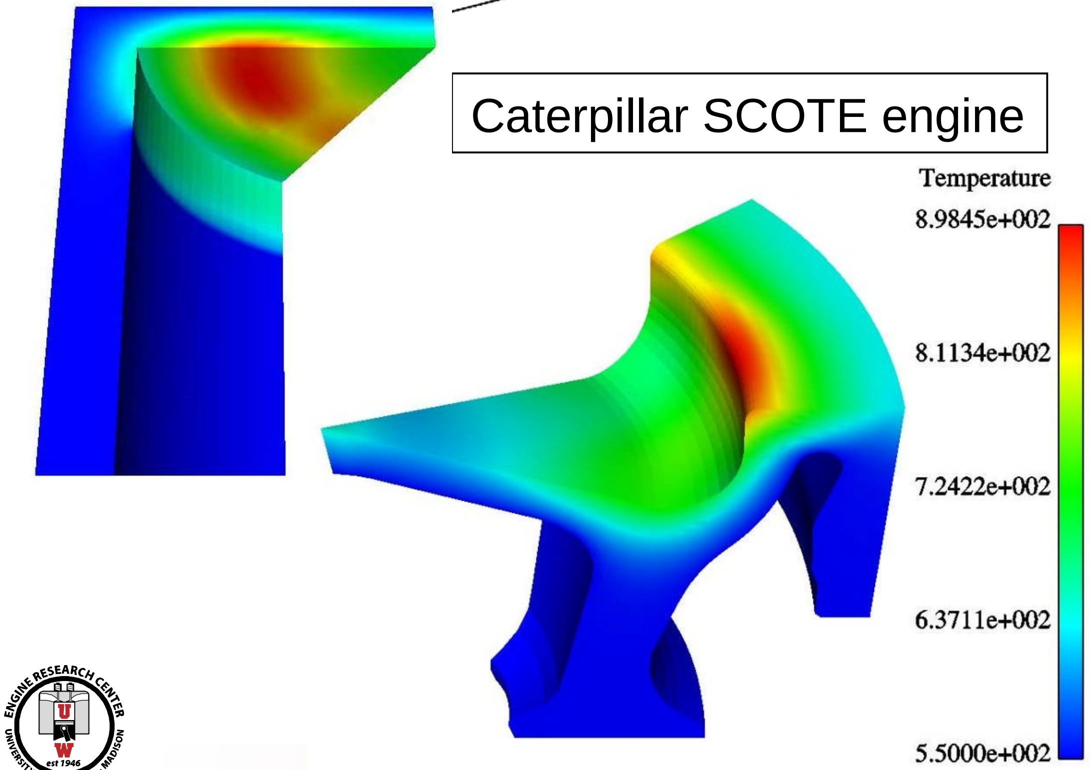
HccSurfTemp.dat

KIVA

hccflux files

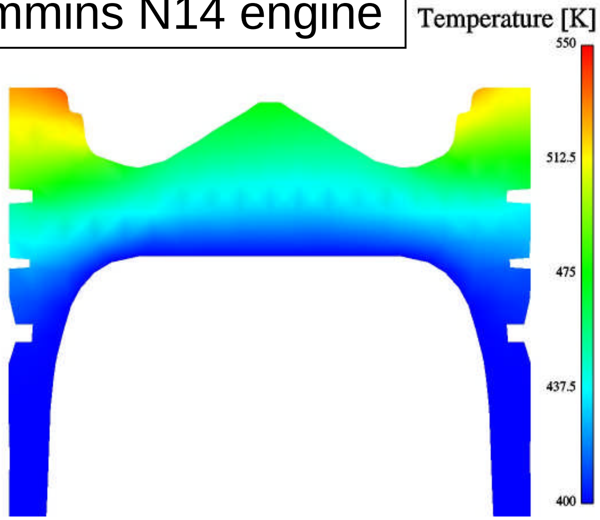
HCC

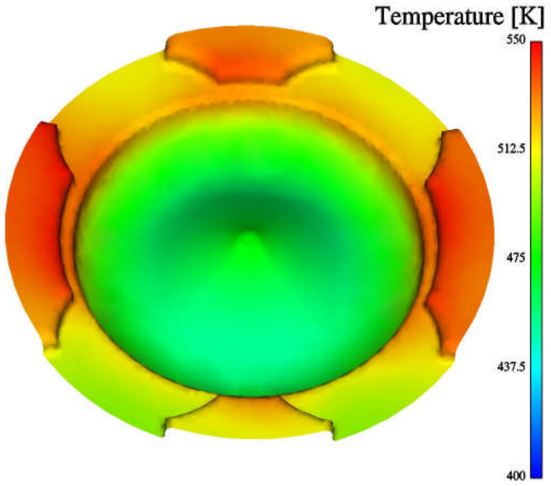
Rough temperature distribution



Caterpillar SCOTE engine

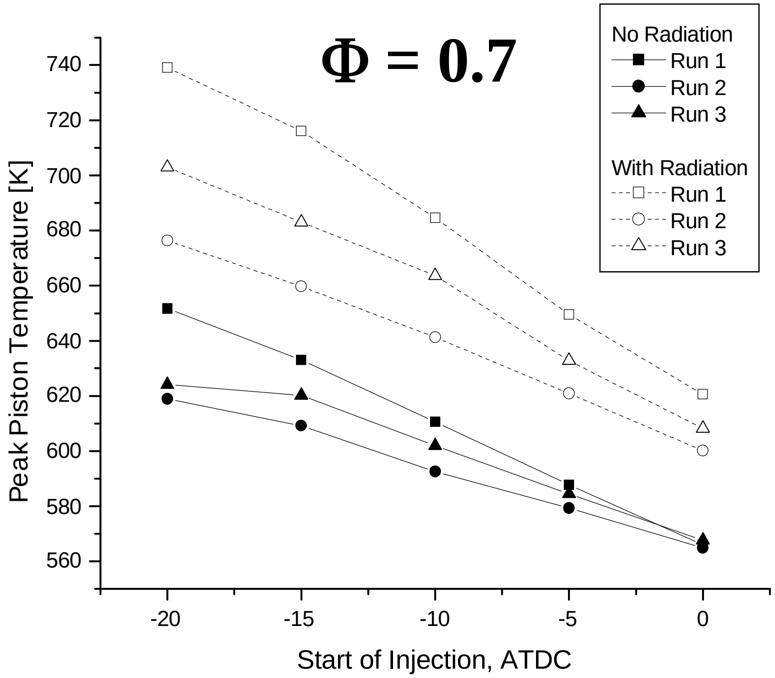
Cummins N14 engine

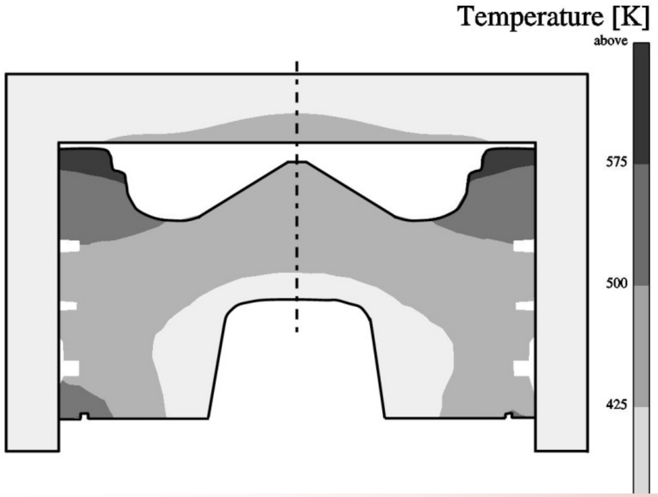




Predicted piston temperature - CDC

Wiedenhoefer & Reitz,
SAE 2003-01-0560





Effect of radiation on wall heat loss

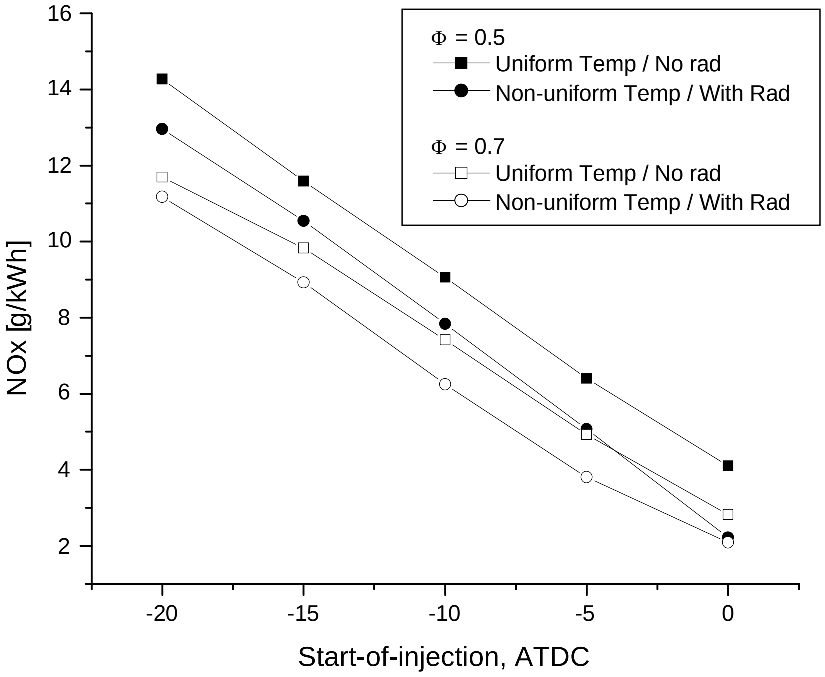
Total heat loss increased by 30% due to radiation.

34% - head, 19% - liner, 47% - piston.

Lowers bulk gas temperatures

Results in lower NOx and higher soot

NOx reduced by as much as 30% (ave)



Engine emissions - Transportation & Toxic Air Pollutants

Criteria air contaminants (CAC), or criteria pollutants

- air pollutants that cause smog, acid rain and other health hazards.

EPA sets standards on:

1.) Ozone (O3),
2.) Particulate Matter (soot):
    PM10, coarse particles: 2.5 micrometers (μm) to 10 μm in size
    PM2.5, fine particles: 2.5 μm in size or less
3.) Carbon monoxide (CO), 4.) Sulfur dioxide (SO2),
5.) Nitrogen oxides (NOx), 6.) Lead (Pb)

Toxic air pollutants - Hazardous Air Pollutants or HAPs known to cause or suspected of causing cancer or other serious health ailments.

- Clean Air Act Amendments of 1990 lists 188 HAPs from transportation.

In 2001, EPA issued Mobile Source Air Toxics Rule:

- identified 21 MSAT compounds.
- a subset of six identified having the greatest influence on health:
  benzene, 1,3-butadiene, formaldehyde, acrolein, acetaldehyde,
  and diesel particulate matter (DPM).

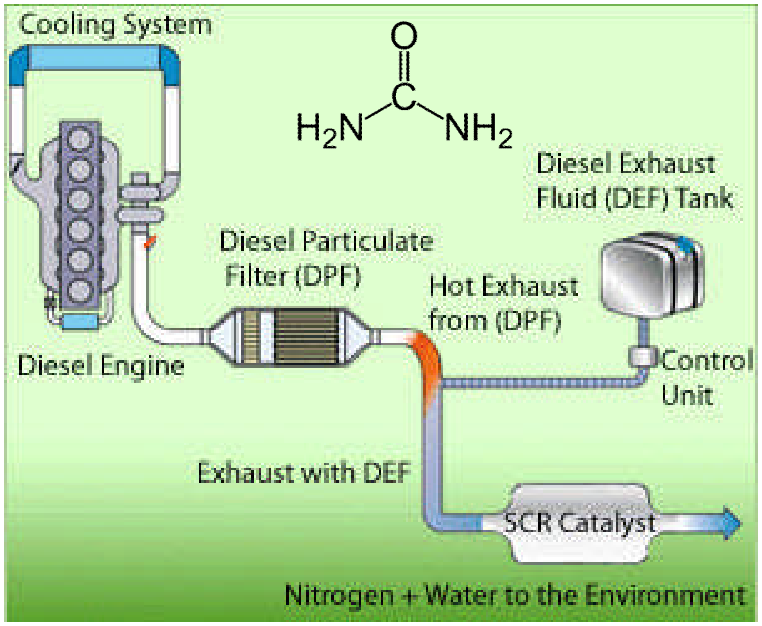
Harmful effects on the central nervous system:

BTEX/N/S - benzene, toluene, ethylbenzene, xylenes, Naphthalene, Styrene

Diesel emission solutions

– Selective Catalytic Reduction (SCR) and Diesel Particulate Filter (DPF)

US EPA 2010 HD soot: 0.0134 g/kW-hr
NOx: 0.2682 g/kW-hr.



1.) EGR?

Navistar – no SCR

Enabling technologies (Cost?):

Improved combustion bowl design - PCCI

Improved EGR valves, air-handling, VVA

Twin-series turbochargers, inter-stage cooling

High-pressure CR fuel injection (31,800 psi)

2.) SCR?

Cummins Cu-Zeolite with DEF for 2010

Claim 3-5% fuel economy gain (Class 8 truck 1% ≈$1,000 per year)

“StableGuard Premix” dose rate ~2% of fuel consumption rate

Cost? $3/gal? AdBlue at pump in Germany $12/gal

Volvo announced surcharge of $9,600 for 2010 compliance

(complex – dosing rate, DEF freezes at 12F, gasifies at 130F)

Plus $7,500 for 2007 compliance → AT system cost equals cost of engine!

NOx modeling

Yoshikawa SAE 2008-01-2413

Zeldo'vich thermal NOx mechanism

$O + N_2 <=> NO + N$ ← Rate controlling step due to high N_2 bond strength

$N + O_2 <=> NO + O$

$N + OH <=> NO + H$

ERC 12-step NOx model is based on GRI-Mech v3.11 and includes:

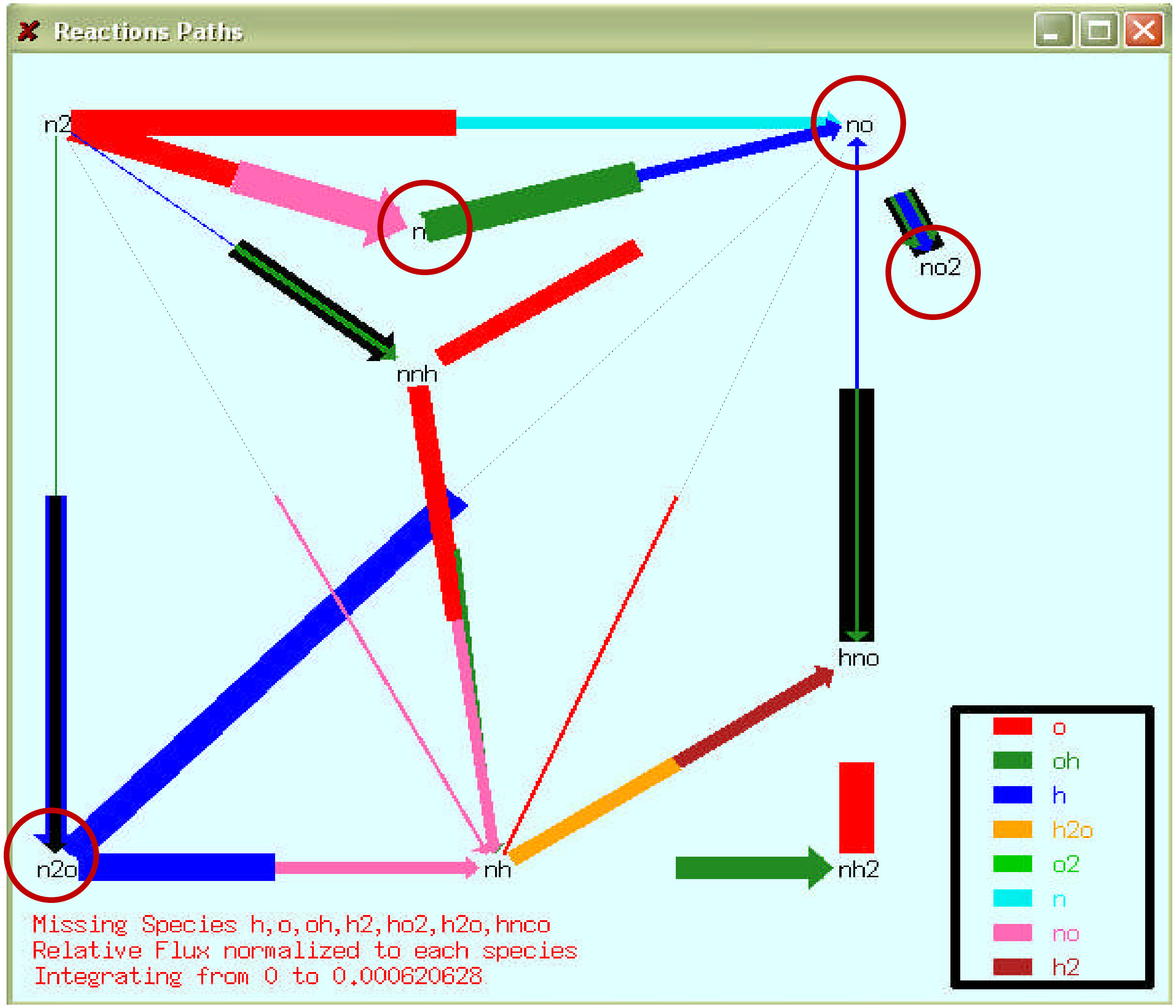
- Thermal NOx Zeldovich, 1946
- Prompt NOx around 1000 K. Fenimore, 1979

Extensions

- NO can convert HCN and NH_3 Eberius, 1987
- Interaction between NO and Soot Guo, 2007

ERC 12 step NOx Mechanism

Kong, ASME 2007



Missing Species h,o,oh,h2,ho2,h2o,hnco
Relative Flux normalized to each species
Integrating from 0 to 0.000620628

- SENKIN2 used to predict species histories.
- XSENKPLOT used to visualize reaction pathways and identify important reactions and species.
- Reduced mechanism validated for test temperatures from 700K to 1100 K and equivalence ratios from 0.3 to 3.0.
- Four additional species (N, NO, N_2O, NO_2) and 12 reactions added to ERC PRF mechanism

Detailed mechanism: Smith, GRI-mech, 2005

ERC 12 step NOx Mechanism

Kong, ASME 2007

Diesel spray computation

$N + NO <=> N_2 + O$

$N + O_2 <=> NO + O$

$N + OH <=> NO + H$

$N_2O + O <=> N_2 + O_2$

$N_2O + O <=> 2NO$

$N_2O + H <=> N_2 + OH$

$N_2O + OH <=> N_2 + HO_2$

$N_2O + M <=> N_2 + O + M$

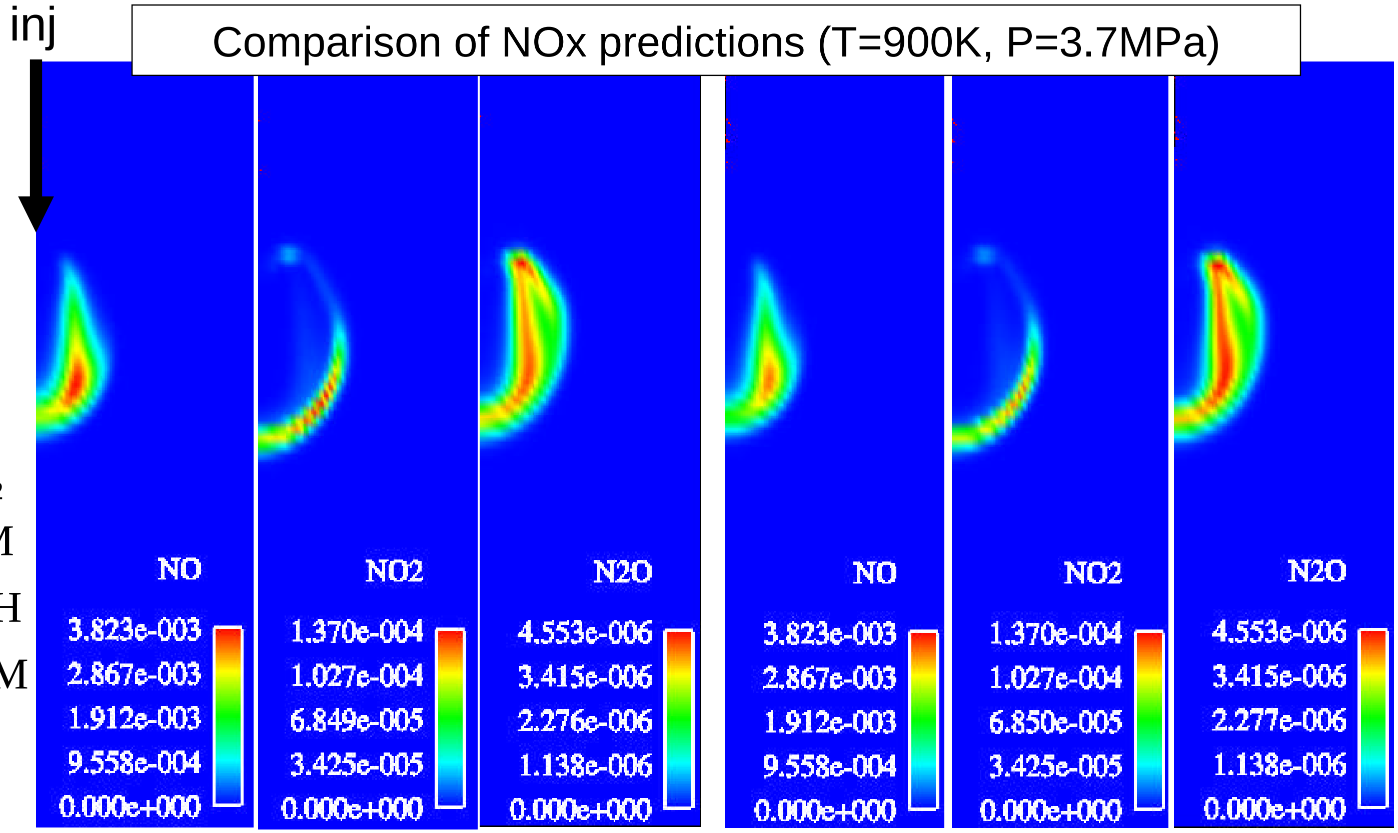
$HO_2 + NO <=> NO_2 + OH$

$NO + O + M <=> NO_2 + M$

$NO_2 + O <=> NO + O_2$

$NO_2 + H <=> NO + OH$

Comparison of NOx predictions (T=900K, P=3.7MPa)

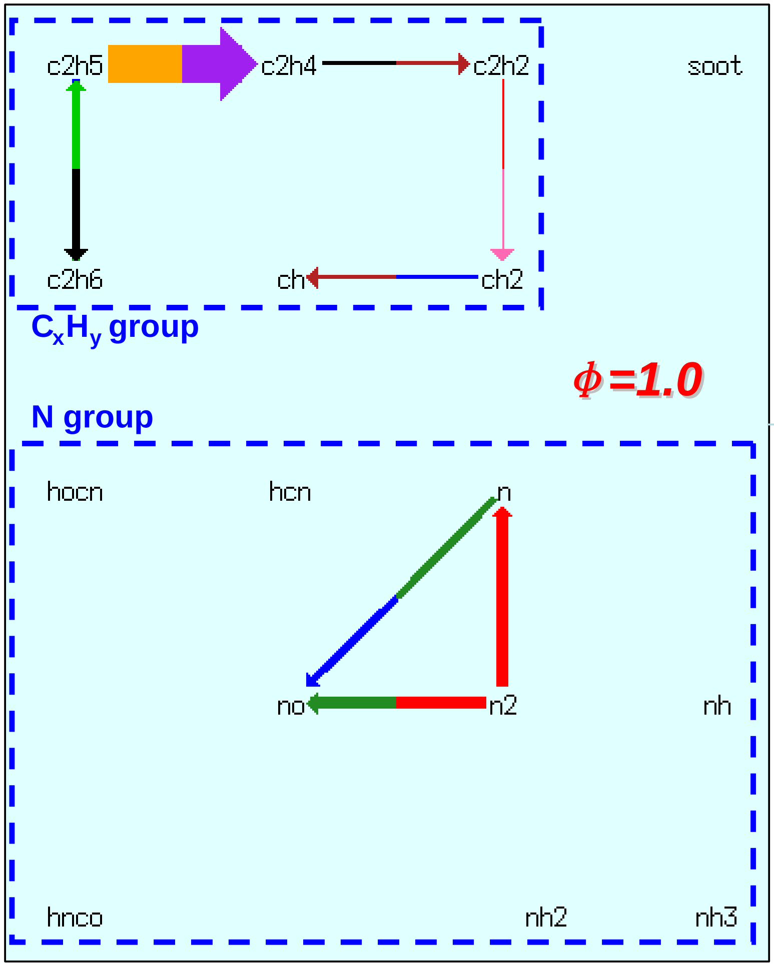


GRI mechanism results

Reduced mechanism results

Detailed mechanism: Smith, GRI-mech, 2005

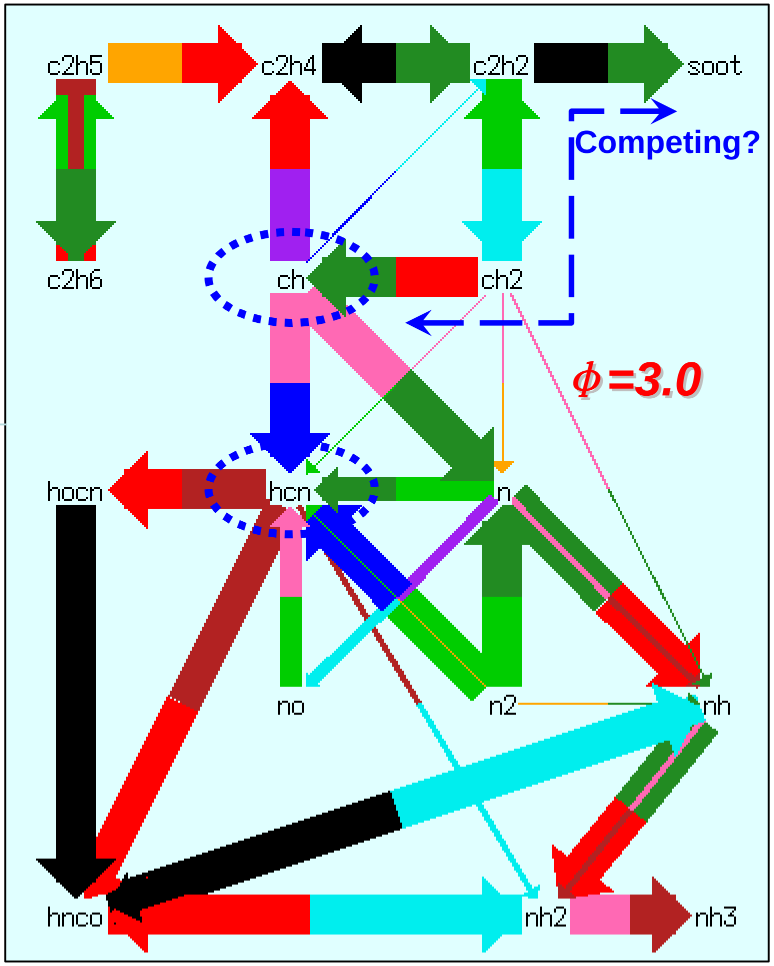
CH radical and HCN bridge in fuel-rich regions



Constant volume SENKIN analysis with ERC n-heptane mechanism & GRI ver.3 NOx mechanism

Absolute Flux normalized to NO by XSENKPLOT

T_{ini}=769K
P_{ini}=40bar
Time=100ms



Yoshikawa & Reitz, SAE 2008-01-2413

Expanded ERC NOx reaction mechanism

12-step NOx reactions
[Sun, 2007]

Main species

N, NO, N_2O, NO_2

```
n+no    <=> n2+o             3.500e+13   .00    330.0
n+o2    <=> no+o             2.650e+12   .00   6400.0
n+oh    <=> no+h             7.333e+13   .00   1120.0
n2o+o   <=> n2+o2            1.400e+12   .00  10810.0
n2o+o   <=> 2no              2.900e+13   .00  23150.0
n2o+h   <=> n2+oh            4.400e+14   .00  18880.0
n2o+oh  <=> n2+ho2           2.000e+12   .00  21060.0
n2o(+m)<=> n2+o(+m)          1.300e+11   .00  59620.0
   low  /  6.200e+14   .000  56100.00/
   h2/2.00/ h2o/6.00/ ch4/2.00/ co/1.50/ co2/2.00/
ho2+no  <=> no2+oh           2.110e+12   .00   -480.0
no+o+m <=> no2+m             1.060e+20 -1.410      .0
   h2/2.00/ h2o/6.00/ ch4/2.00/ co/1.50/ co2/2.00/
no2+o   <=> no+o2            3.900e+12   .00   -240.0
no2+h   <=> no+oh            1.320e+14   .00    360.0
```

Additional 15 reactions

with CH and HCN

```
ch+n2   <=> hcn+n            2.857e+08  1.10  20400.0
ch+no   <=> hcn+o            5.000e+13   .00       .0
ch+no   <=> n+hco            3.000e+13   .00       .0
ch2+no  <=> oh+hcn           2.900e+14  -.69    760.0
ch3+no  <=> hcn+h2o          9.600e+13   .00  28800.0
ch3+n   <=> hcn+h2           3.700e+12   .15    -90.0
oh+ch   <=> h+hco            3.000E+13   .00       .0
oh+ch2  <=>ch+h2o            1.130E+07  2.00   3000.0
ch+o2   <=> o+hco            3.300E+13   .00       .0
ch+h2   <=> h+ch2            1.107E+08  1.79   1670.0
ch+h2o  <=> h+ch2o           1.713E+13   .00   -755.0
ch+ch2  <=> h+c2h2           4.000E+13   .00       .0
ch+ch3  <=> h+c2h3           3.000E+13   .00       .0
ch+ch4  <=> h+c2h4           6.000E+13   .00       .0
ch+co2  <=> hco+co           3.400E+12   .00    690.0
```

Yoshikawa & Reitz,
SAE 2008-01-2413

Expanded ERC NOx reaction mechanism

Additional 22 reactions

with NH_3, HNCO, NH_2, and NH

```
nh3+h    <=> nh2+h2        5.400e+05   2.400    9915.0
nh3+oh   <=> nh2+h2o       5.000e+07   1.600     955.0
nh3+o    <=> nh2+oh        9.400e+06   1.940    6460.0
hcn+oh    <=> hnco+h*      39.60e+00   3.217    8210.7
ch2+no    <=> h+hnco       3.100e+17  -1.380    1270.0
hnco+o    <=> nh+co2       9.800e+07   1.410    8500.0
hnco+h    <=> nh2+co       2.250e+07   1.700    3800.0
hnco+oh <=> nh2+co2        1.550e+12    .000    6850.0
hnco+m  <=> nh+co+m        1.180e+16    .000   84720.0
   h2/2.00/ h2o/6.00/ ch4/2.00/ co/1.50/ co2/2.00/
nh2+o    <=> oh+nh         7.000e+12    .000        .0
nh2+h    <=> nh+h2         4.000e+13    .000    3650.0
nh2+oh   <=> nh+h2o        9.000e+07   1.500    -460.0
hcn+oh  <=> nh2+co         1.600e+02   2.560    9000.0
nh+o     <=> no+h          5.000e+13    .000        .0
nh+h     <=> n+h2          3.200e+13    .000     330.0
nh+oh    <=> n+h2o         2.000e+09   1.200        .0
nh+o2    <=> no+oh         1.280e+06   1.500     100.0
nh+n     <=> n2+h          1.500e+13    .000        .0
nh+no    <=> n2+oh         2.160e+13   -.230        .0
nh+no    <=> n2o+h         4.160e+14   -.450        .0
hcn+o   <=> nh+co          2.767e+03   2.640    4980.0
ch2+n2  <=> hcn+nh         1.000e+13    .000   74000.0
```

*** 3 reactions were combined into 1 reaction:**

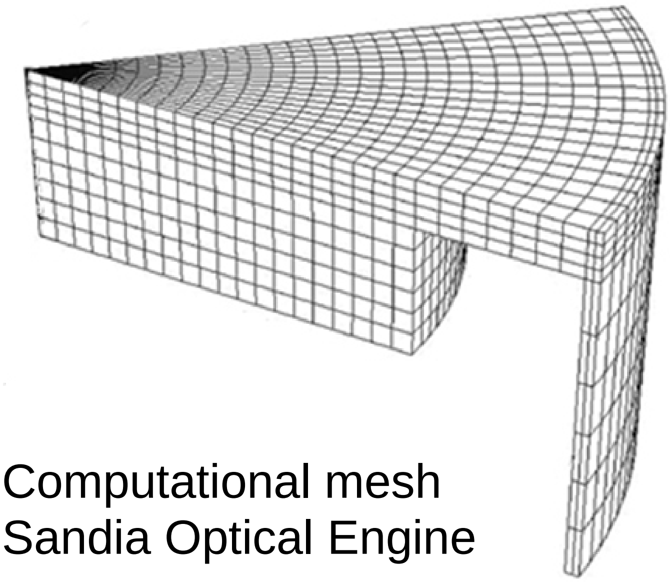
hcn+oh<=>hnco+h

hcn+oh<=>hocn+h

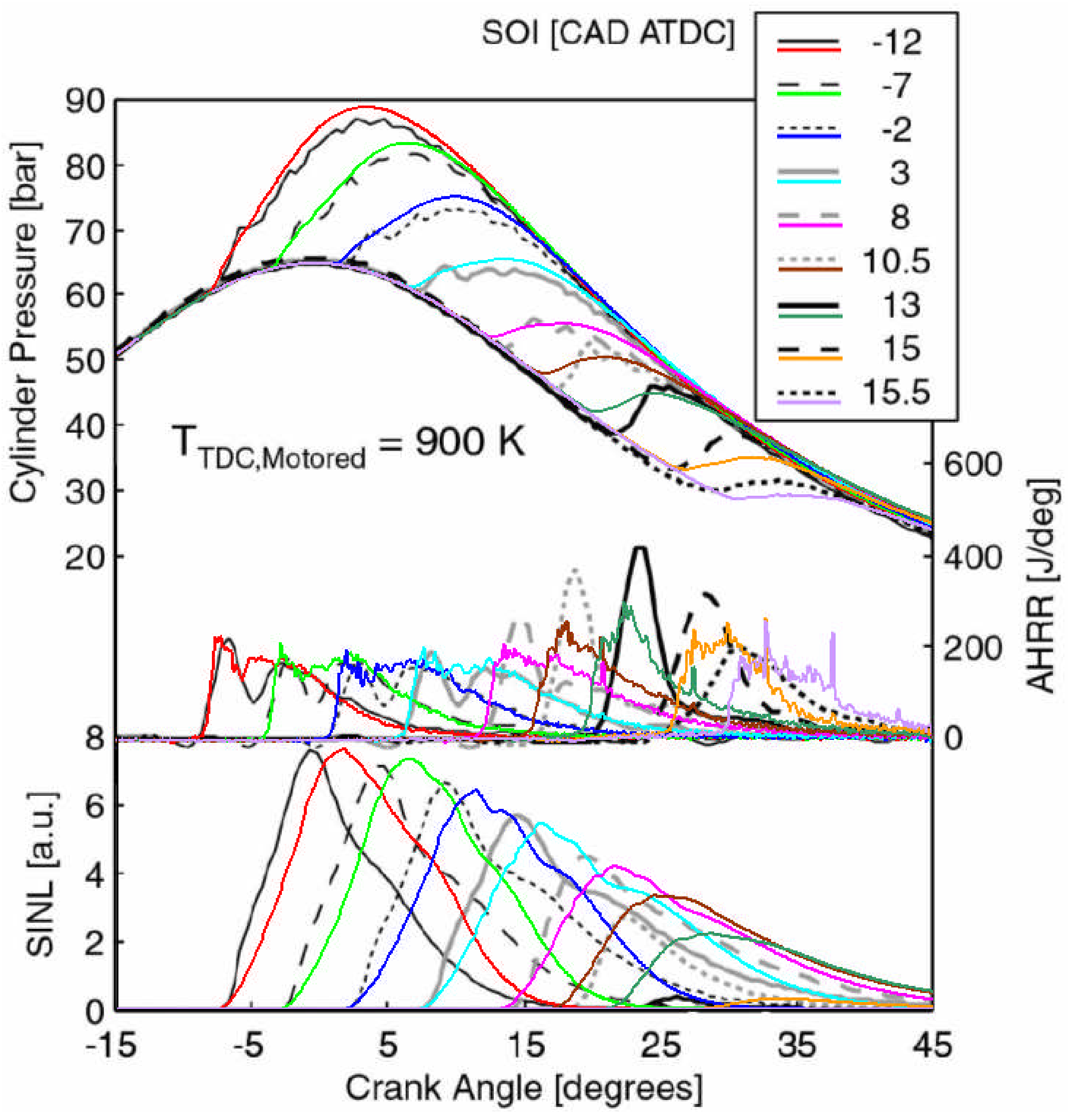
hocn+h<=>h+hnco

Yoshikawa & Reitz,
SAE 2008-01-2413

Influence of Soot Radiation on Combustion and NOx



Computational mesh
Sandia Optical Engine



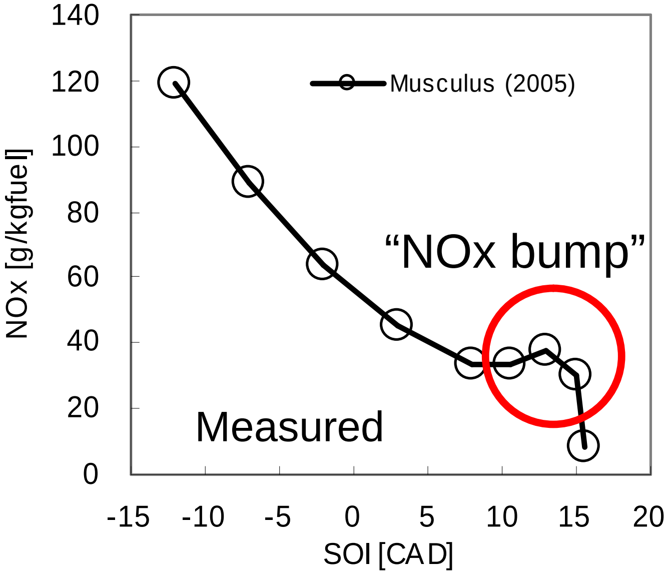
BW: measured

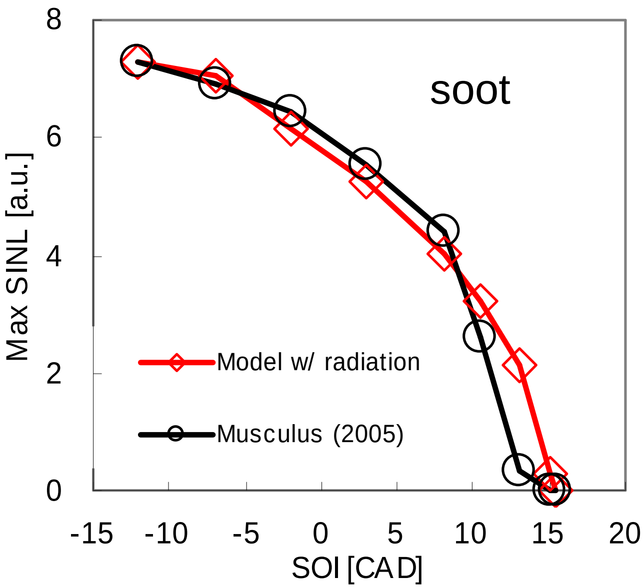
Musculus, SAE 2005-01-0925

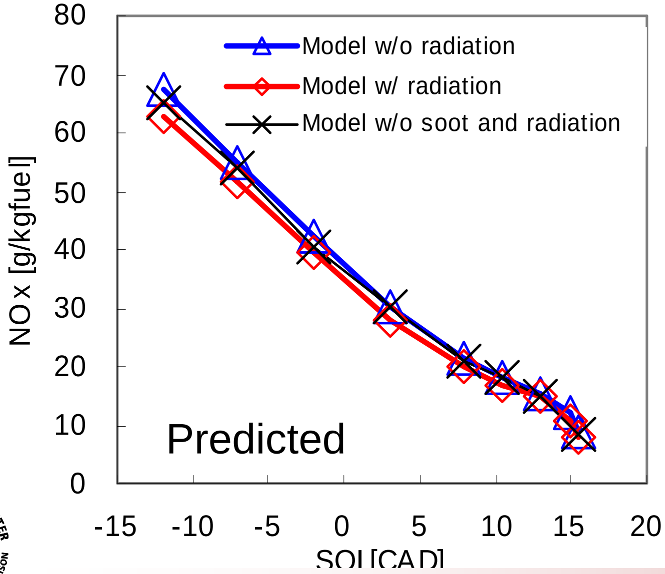
Colored: prediction

Yoshikawa & Reitz, 2009

Influence of Soot Radiation on Combustion and NOx







"NOx bump" not observed in prediction, but reduction in predicted NOx seen with retard of SOI (~ SOI=8 CAD ATDC)

Radiation lowers predicted NOx ~ 7.5 %

Absence of soot lowered predicted NOx ~ 2.5 %

NOx model underpredicts measured NOx

Magnitude sensitive to turbulent Schmidt #

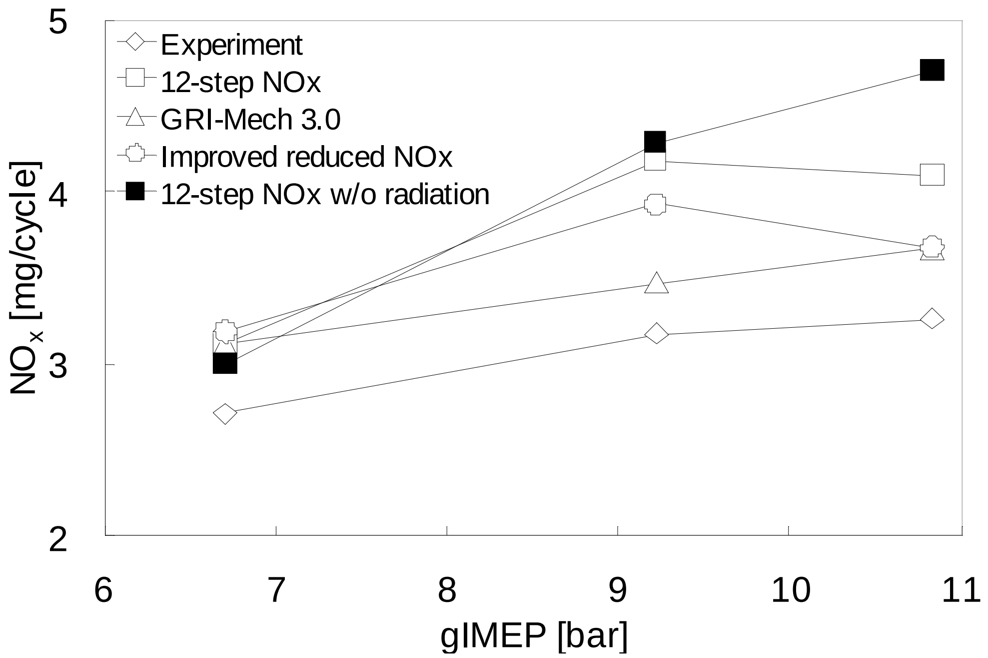
Yoshikawa & Reitz, 2009

Hour 6: Heat transfer, NOx and Soot Emissions

Yoshikawa & Reitz, SAE 2008-01-2413

Measured and predicted engine-out NOx as a function of load

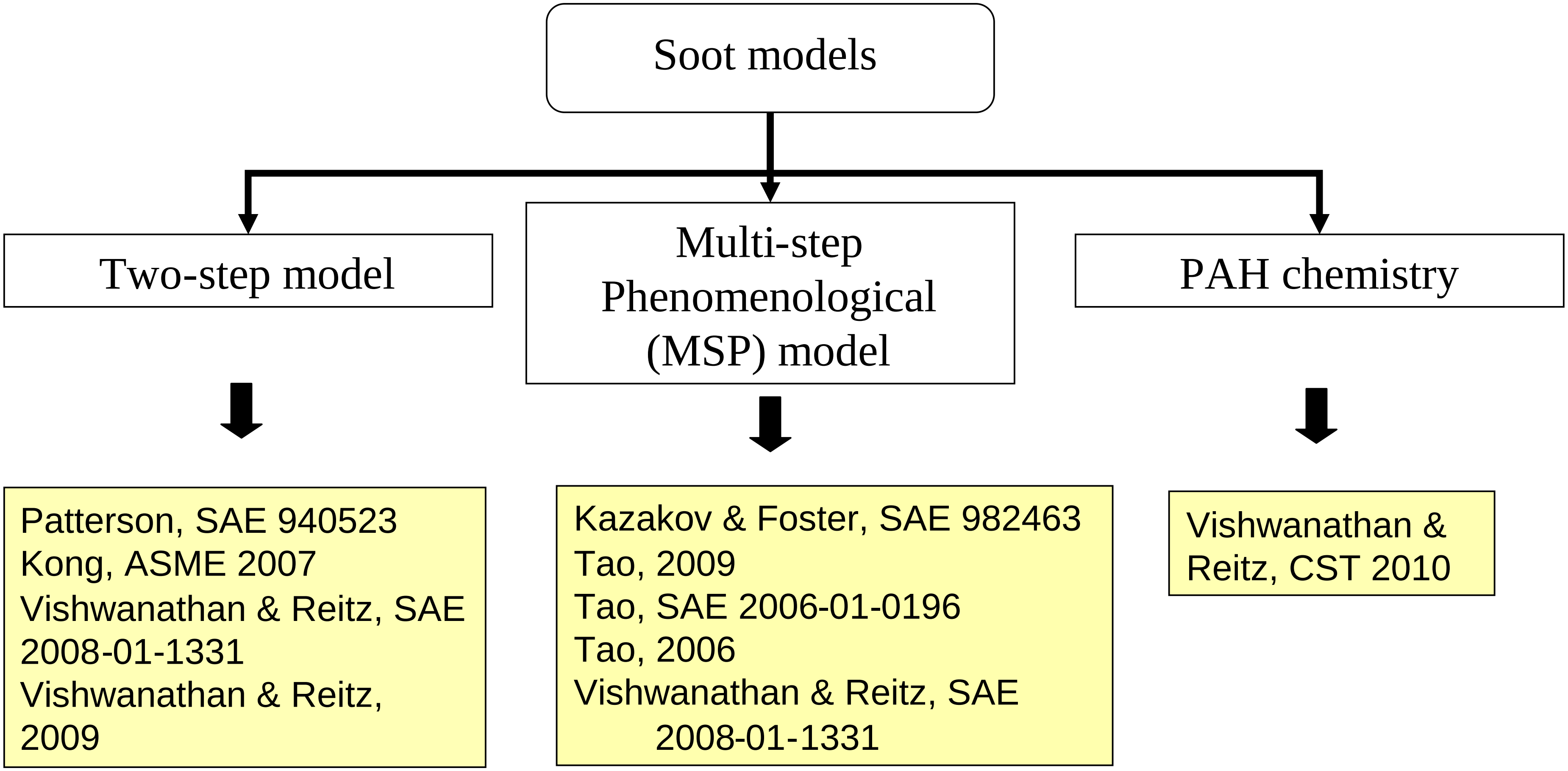
(Sandia experiments)



	ERC 12-step	Species 4 (N, NO, N_2O, NO_2)	Reactions 12
	ERC 12-step + HCN, CH	6	27
	ERC 12-step + HCN, CH, NH_3, HNCO, NH_2, NH	10	49
	GRI v2.11	29	197
	GRI v3.11	32	235

Smith, GRI-mech, 2005

Soot Modeling at ERC



Soot models

Two-step model

Multi-step Phenomenological (MSP) model

PAH chemistry

Patterson, SAE 940523
Kong, ASME 2007
Vishwanathan & Reitz, SAE 2008-01-1331
Vishwanathan & Reitz, 2009

Kazakov & Foster, SAE 982463
Tao, 2009
Tao, SAE 2006-01-0196
Tao, 2006
Vishwanathan & Reitz, SAE 2008-01-1331

Vishwanathan & Reitz, CST 2010

Models of soot formation/oxidation – Kennedy, Prog. Energy Comb. Sc., 1997
Soot processes in engines - Tree and Svenson, Prog. Energy Comb. Sc., V2007

Two-step model

“tuning” constant

Hiroyasu soot formation

$$\dot{M}_{sf} = \boxed{A_{sf}} \cdot P^{0.5} \cdot \exp(-E_{sf}/RT) \cdot M_{C2H2}$$

Nagle and Strickland-Constable (NSC) oxidation

$$\dot{M}_{so} = \frac{6}{\rho_s D_{nom}} \cdot W_{nsc} \cdot M_s$$

Net soot mass

$$\frac{d(M_s)}{dt} = \dot{M}_{sf} - \dot{M}_{so}$$

C_2H_2 soot precursor

ρ_s = Soot density = 2 g/cm^3

D_{nom} = assumed nominal soot diameter

= 25 nm

W_{nsc} = NSC oxidation rate/area

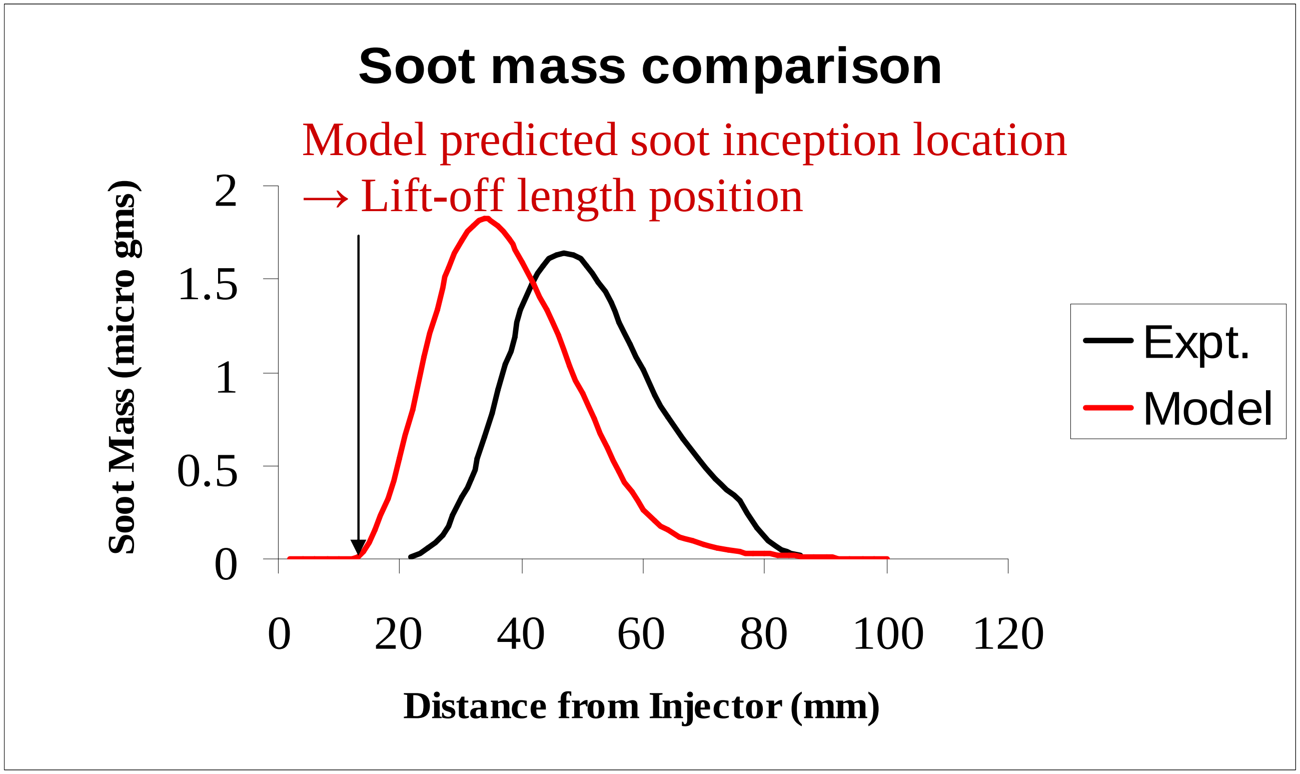
M_{c2h2} = C_2H_2 Mass, M_s = Mass of soot

Hiroyasu & Kadota, SAE 760129
Nagle & Strickland-Constable, 1962

Performance of two-step soot model

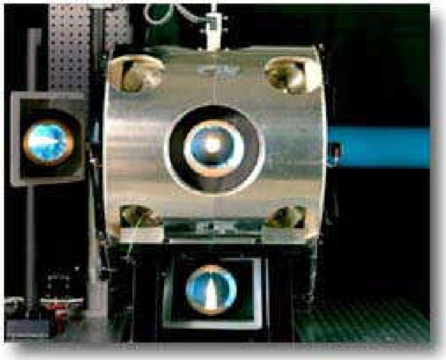
Vishwanathan & Reitz,
SAE 2008-01-1331

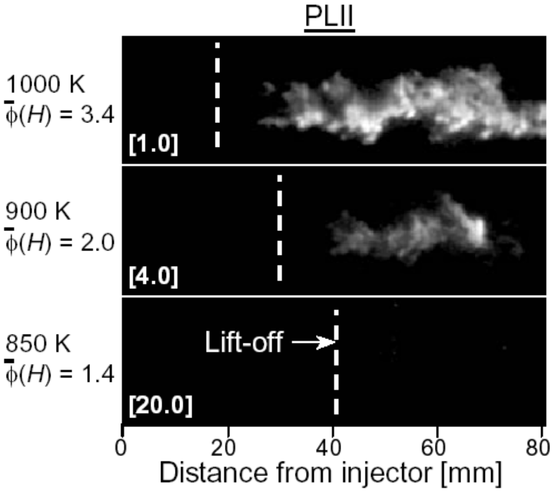
SANDIA spray chamber: Pickett & Siebers, 2004



Soot mass comparison

Model predicted soot inception location
→ Lift-off length position

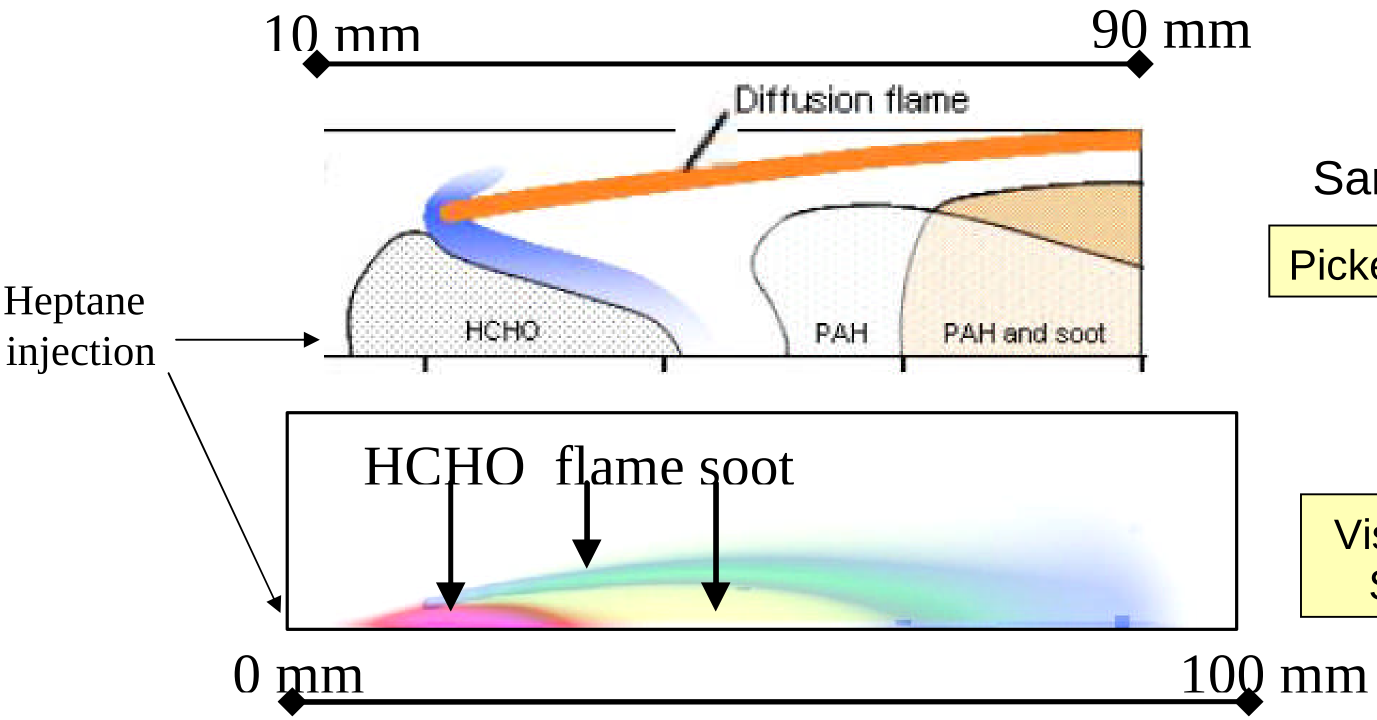




C_2H_2 inception occurs at lift-off location

Inclusion of PAH chemistry needed for accurate prediction of soot form/oxid.

Performance of two-step soot model



Sandia experiment

Pickett & Siebers, 2004

Model

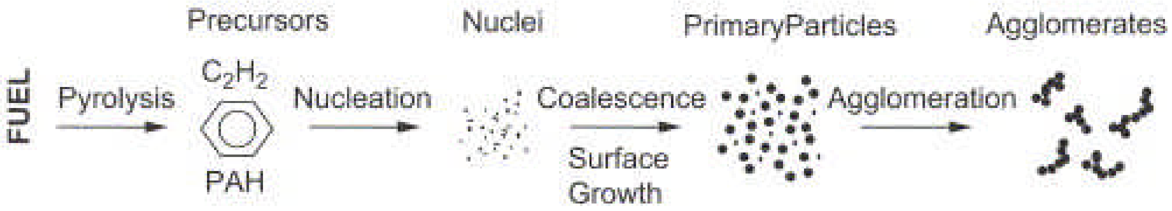
Vishwanathan & Reitz, SAE 2008-01-1331

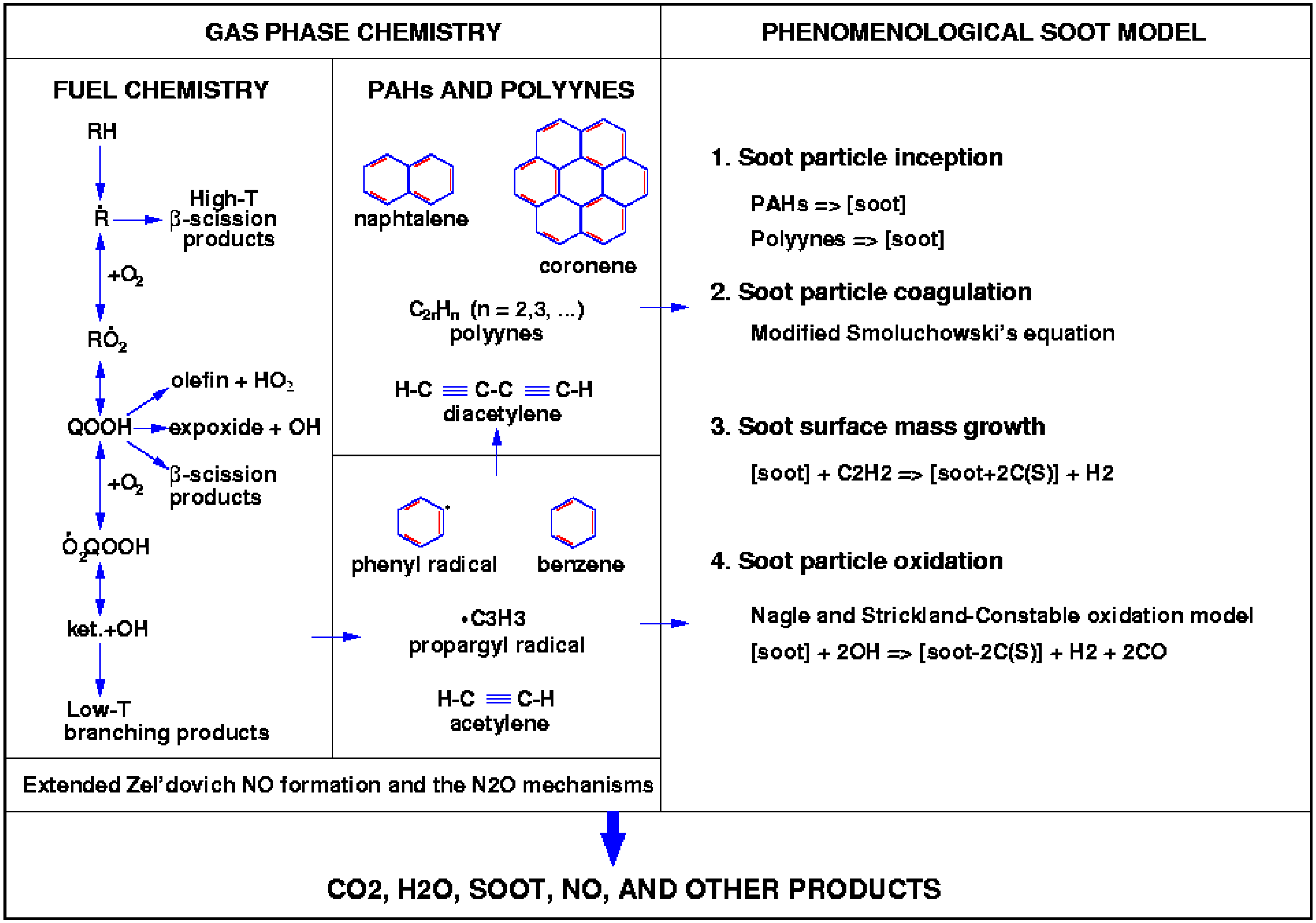
C_2H_2 inception occurs at lift-off location

Inclusion of PAH chemistry needed for accurate prediction of soot form/oxid.

Hour 6: Heat transfer, NOx and Soot Emissions

Soot Modeling





GAS PHASE CHEMISTRY

FUEL CHEMISTRY

RH

$\dot{R}$ → High-T β-scission products

$+O_2$

$R\dot{O}_2$

QOOH → olefin + HO_2

QOOH → expoxide + OH

QOOH → β-scission products

$+O_2$

$\dot{O}_2QOOH$

ket.+OH

Low-T branching products

PAHs AND POLYYNES

naphtalene

coronene

$C_{2n}H_n$ (n = 2,3, ...)
polyynes

H-C ≡ C-C ≡ C-H
diacetylene

phenyl radical

benzene

•C3H3
propargyl radical

H-C ≡ C-H
acetylene

Extended Zel'dovich NO formation and the N2O mechanisms

PHENOMENOLOGICAL SOOT MODEL

1. **Soot particle inception**

   PAHs => [soot]

   Polyynes => [soot]

2. **Soot particle coagulation**

   Modified Smoluchowski's equation

3. **Soot surface mass growth**

   [soot] + C2H2 => [soot+2C(S)] + H2

4. **Soot particle oxidation**

   Nagle and Strickland-Constable oxidation model

   [soot] + 2OH => [soot-2C(S)] + H2 + 2CO

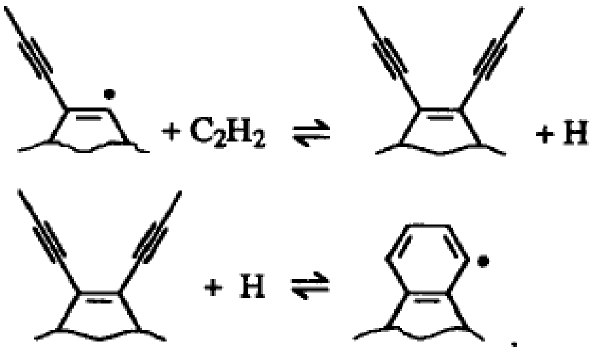
CO2, H2O, SOOT, NO, AND OTHER PRODUCTS

Reduced PAH mechanism

Reduced PAH mechanism of Xi & Zhong, 2006 based on detailed mechanism of Wang &Frenklach, 1997 was integrated (**20 species and 52 reactions**)

A_1 formation through propargyl radical (C_3H_3)

Higher aromatics formed through HACA scheme (hydrogen abstraction, carbon addition)



Reaction	Arrhenius parameters-A, n, E. (Units of A in mole-cm-sec-K and units of E in cal/mole)
$C_3H_3 + C_3H_3 \rightarrow A_1$	2.0E+12, 0.0, 0.0
$A_1\text{-} + C_4H_4 \leftrightarrow A_2 + H$	2.50E+29, -4.4, 26400.0
$A_1 + A_1\text{-} \leftrightarrow P_2 + H$	1.10E+23, -2.9, 15890.0
$A_2\text{-}1 + C_4H_4 \leftrightarrow A_3 + H$	2.50E+29, -4.4, 26400.0
$A_1C_2H^* + A_1 \leftrightarrow A_3 + H$	1.10E+23, -2.9, 15890.0
$A_3\text{-}4 + C_2H_2 \leftrightarrow A_4 + H$	3.00E+26, -3.6, 22700.0

A_1 = benzene, A_2 = naphthalene, P_2 = biphenyl, A_3 = phenanthrene, A_4= pyrene, A_1- = phenyl, A_2-1 = 1-naphthyl, A_3-4 = 4-phenanthryl, $A_1C_2H^*$ = phenylacetylene radical

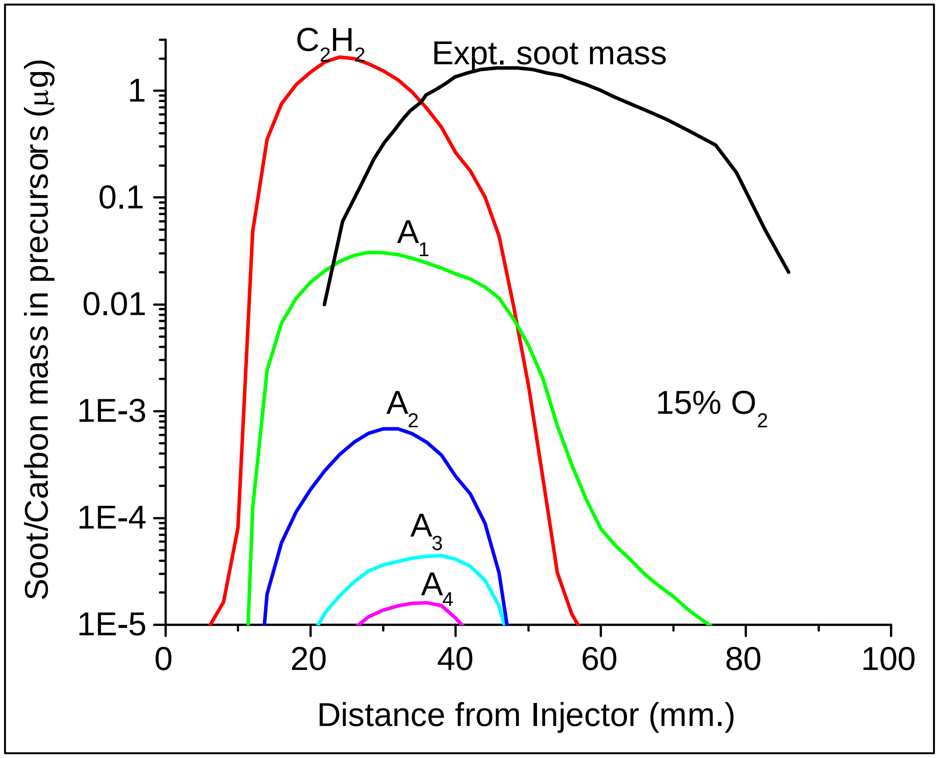
Vishwanathan & Reitz, ASME 2009

PAH species

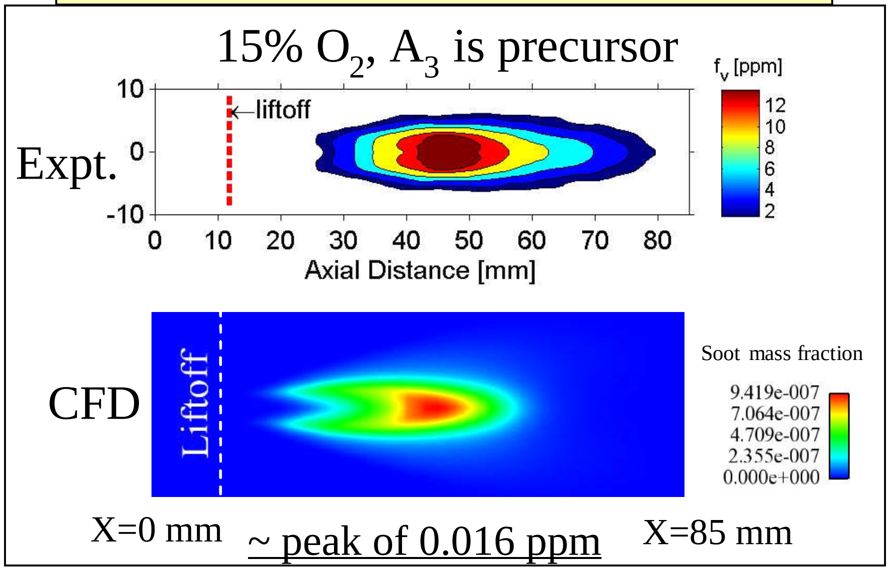
Vishwanathan & Reitz, ASME 2009

Reduced PAH mechanism implemented considering up to 4 aromatic rings (pyrene)

- A_3 (Phenanthrene) as precursor for formation



Sandia expts: Pickett & Idicheria, 2006



Improvement in soot location

Amount of dry-carbon mass locked-up in aromatic precursors small compared to measured soot

Soot model implementation in KIVA

Vishwanathan & Reitz, CST 2010

1. Soot inception through A_4: $C_{16}H_{10}\ (A_4) \xrightarrow{\dot{\omega}_1} 16C(s) + 5H_2$ → Graphitization

$$\dot{\omega}_1 = k_1 \cdot [A_4],\ k_1 = 2000\ \{s^{-1}\}$$

2. C_2H_2 assisted surface growth: Leung CNF 1991 $C(s) + C_2H_2 \xrightarrow{\dot{\omega}_2} 3C(s) + H_2$

$$\dot{\omega}_2 = k_2 \cdot [C_2H_2],\ k_2 = 9.0 \cdot 10^4 \exp(-12100/T) \cdot \sqrt{S}\ \ \{s^{-1}\}$$

$$S = \pi d_p^2 N\ \ \{cm^{-1}\}$$ → Surface area per unit volume

$$d_p = \left(\frac{6\boxed{Y_{c(s)}\rho}}{\pi\rho_{c(s)}\boxed{N}}\right)^{1/3}\ \ \{cm\}$$ → Particle size

$Y_{C(S)}$ = soot mass fraction

N = soot number density (per cc)

$\rho_{C(S)} = 2.0\ gm/cm^3$

$M_{C(S)}$ = MW of carbon

K_{bc} = Boltzmann's constant

C_a = agglomeration constant = 9

Mono –disperse locally: All soot in a comp. cell have same diameter

3. Soot coagulation: Leung CNF 1991 $nC(s) \xrightarrow{\dot{\omega}_3} C(s)_n$

$$\dot{\omega}_3 = 2C_a \left(\frac{6M_{c(s)}}{\pi\rho_{c(s)}}\right)^{1/6} \cdot \left(\frac{6K_{bc}T}{\rho_{c(s)}}\right)^{1/2} \cdot \left[\frac{\rho Y_{c(s)}}{M_{c(s)}}\right]^{1/6} \cdot [N]^{11/6}\ \ \{particles\ cm^{-3} s^{-1}\}$$

Soot model implementation in KIVA

Vishwanathan & Reitz, CST 2010

4. O$_2$ assisted soot oxidation (NSC model):

$$C(s) + \frac{1}{2} O_2 \xrightarrow{\dot{\omega}_4} CO$$

$$\dot{\omega}_4 = \frac{12}{M_{c(s)}} \cdot \left(\left(\frac{K_A P_{O_2}}{1+K_Z P_{O_2}} \right) \cdot x + K_B P_{O_2} \cdot (1-x) \right) \cdot S \ \{\mathrm{mol\ cm^{-3}\ s^{-1}}\}$$

$$x = P_{O_2} \Big/ (P_{O_2} + (K_T/K_B))$$

$$K_A = 30.0 \cdot \exp(-15800/T) \ \{\mathrm{g\ cm^{-2}\ s^{-1}\ atm^{-1}}\}$$

$$K_B = 8.0 \cdot 10^{-3} \cdot \exp(-7640/T) \ \{\mathrm{g\ cm^{-2}\ s^{-1}\ atm^{-1}}\}$$

$$K_T = 1.51 \cdot 10^{5} \cdot \exp(-49800/T) \ \{\mathrm{g\ cm^{-2}\ s^{-1}}\}$$

$$K_Z = 27.0 \cdot \exp(3000/T) \ \{\mathrm{atm^{-1}}\}$$

x = fraction of A sites

$(1-x)$ = fraction of B sites

P_{O2} = partial pressure of O$_2$

$K_{A,B,T,Z}$ = rate constants

X_{OH} = mole fraction of OH

γ_{OH} = OH collision efficiency = 0.13

Fenimore & Jones, 1967

5. OH assisted oxidation (Modified Fenimore and Jones model):

$$C(s) + OH \xrightarrow{\dot{\omega}_5} CO + \frac{1}{2} H_2 \qquad \dot{\omega}_5 = (12) \cdot 10.58 \cdot \gamma_{OH} \cdot X_{OH} \cdot T^{-1/2} \cdot S \ \{\mathrm{mol\ cm^{-3}\ s^{-1}}\}$$

Soot model implementation in KIVA

Vishwanathan & Reitz, CST 2010

6. PAH-assisted surface-growth

$$C(s) + PAH_{k,j} \xrightarrow{\dot{\omega}_6} C(s{+}k) + \frac{j}{2}H_2,\ \dot{\omega}_6 = \gamma_{ks}\cdot\beta_{ks}\cdot\left[PAH_{k,j}\right]\cdot N$$

$$\beta_{ks} = 2.2\cdot\sqrt{\frac{\pi\cdot K_{bc}\cdot T}{2\cdot\mu_{i,j}}}\cdot(d_p + d_{PAH})^2\ \left\{cm^3 s^{-1}\right\}$$

$$d_{PAH} = d_A\cdot\sqrt{\frac{2m_i}{3}}$$

k = number of carbon atoms and j = number of hydrogen atoms,

γ_{ks} = 0.3 is the collision efficiency between soot and PAH, β_{ks} = collision frequency,

d_i = collisional diameter of PAH, d_A = size of single aromatic ring = 1.393√3 Ǻ,

$\mu_{i,j}$ = Reduced mass of colliding species = Mass of PAH,

m_i = mass of PAH expressed in terms of number of carbon atoms - k

Most models consider only mono-aromatic benzene as growth species.

Soot model implementation in KIVA

Vishwanathan & Reitz, CST 2010

7. Transport equations:

$$\frac{\partial M}{\partial t} = \underbrace{-\nabla\cdot\left(M\cdot v\right)}_{\text{convection}} + \nabla\cdot\left(\underbrace{\frac{\mu}{SC}\nabla\left(\frac{M}{\rho}\right)}_{\text{diffusion}} + \underbrace{\xi\cdot M\cdot\frac{\mu}{\rho}\frac{\nabla T}{T}}_{\text{Thermophoresis}}\right) + \underbrace{\dot{S}_M}_{\text{Source terms}} \qquad \xi = 0.75\Big/\left(1+\frac{\pi\eta}{8}\right),\ \eta = 0.9$$

$M = \rho Y_{c(s)}$ (soot species density) and N (number density) with N being treated as **passive species**

Thermophoresis term implemented as a source term

$$\dot{S}_M = \left(16\dot{\omega}_1 + 2\dot{\omega}_2 + 6\dot{\omega}_6 - \dot{\omega}_4 - \dot{\omega}_5\right)\cdot M_{c(s)} \quad \{\text{g cm}^{-3}\ \text{s}^{-1}\}\ \text{for}\ \rho Y_{c(s)}$$

$$\dot{S}_M = \left(16\dot{\omega}_1\cdot\frac{M_{c(s)}}{M_{nuci}} - \dot{\omega}_3\right) \quad \{\text{particles cm}^{-3}\ \text{s}^{-1}\}\ \text{for N}$$

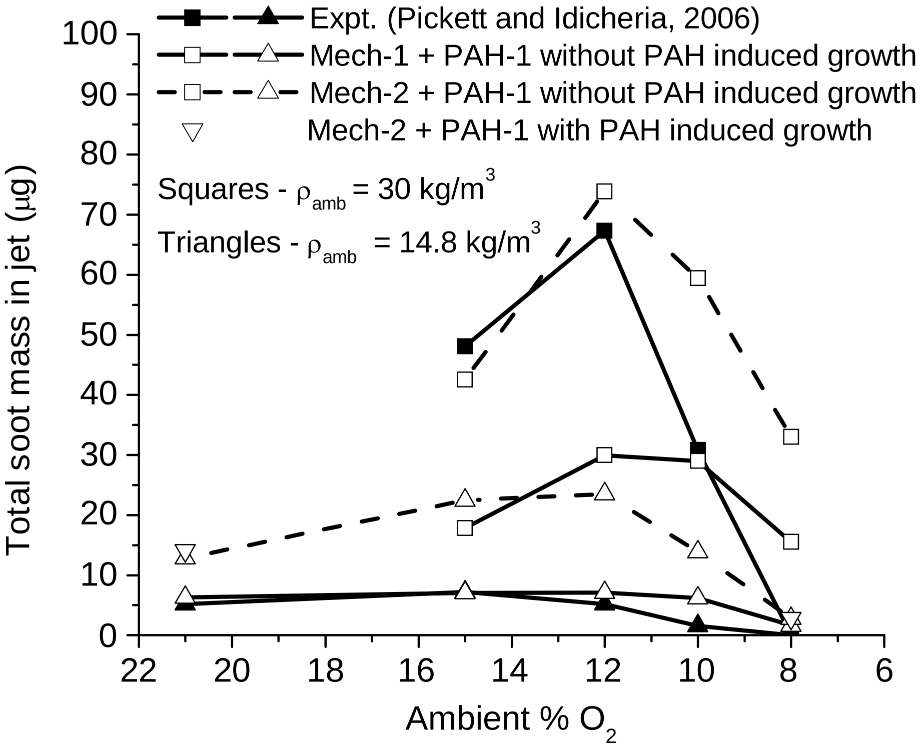
$$M_{nuci} = \frac{\pi}{6}\cdot d_{nuci}^3\cdot\rho_{c(s)}$$

d_{nuci} = 1.25 nm (~100 carbon atoms)

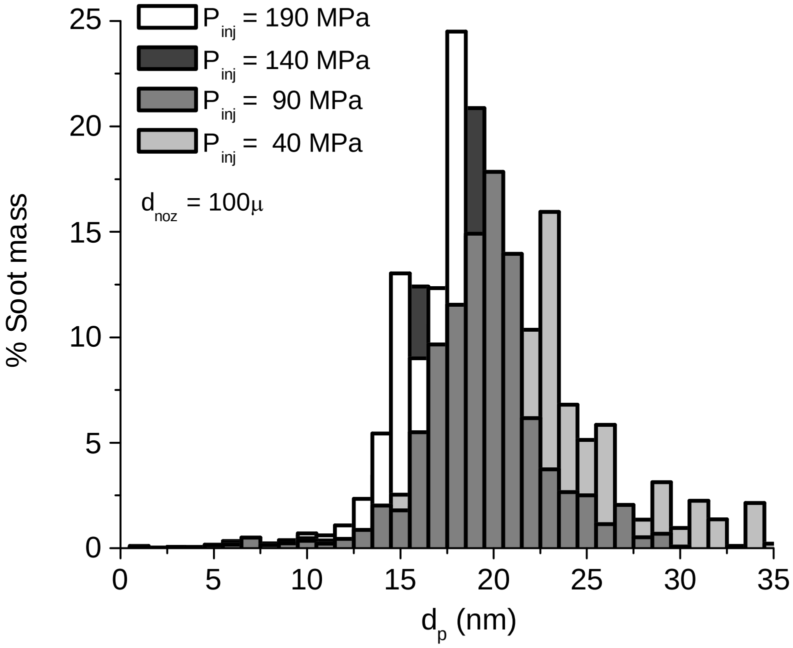
Soot mass and particle diameter predictions

PAH-1 (21 species and 52 reactions)
PAH-2 (21 species and 208 reactions)

Vishwanathan & Reitz, CST 2010



Effect of injection pressure



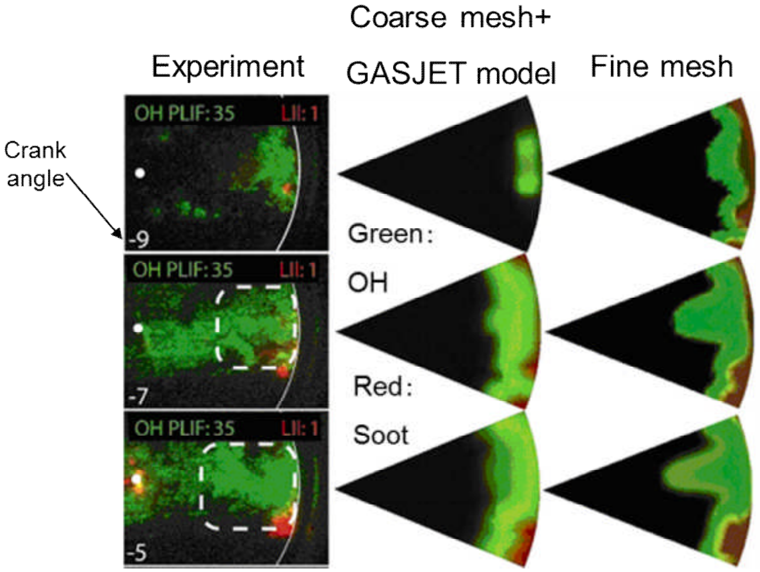
SANDIA optical engine – HTC/LTC

Engine	Parameter
Bore x stroke (cm)	13.97 x 15.24
Speed (rpm)	1200
Compression ratio (CR)	11.2:1
Swirl ratio	0.5
Number of nozzle holes	8
Orifice diameter (mm)	0.196
Included angle	152°
Fuel	Diesel #2
Sector angle	45

Expt. Data: Singh, IJER 2007

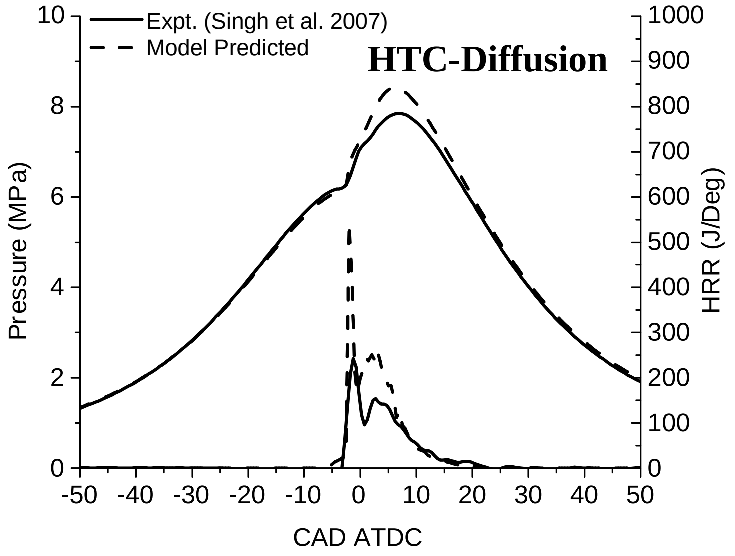
Vishwanathan & Reitz, CST 2010

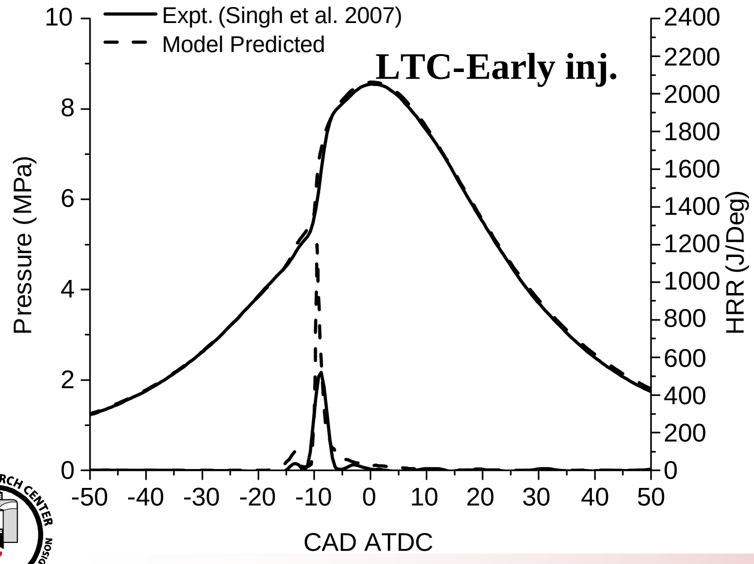
	HTC-diff./ premixed	LTC Early/late
Amb. O_2 %	21	12.7
SOI	-7/-5	-22/0
P_{in} (bar)	2.33/1.92	2.14/2.02
T_{in} (C)	111/47	90/70
Fuel (mg)	61	56
P_{inj} (bar)	1200	1600



SANDIA optical engine – HTC/LTC

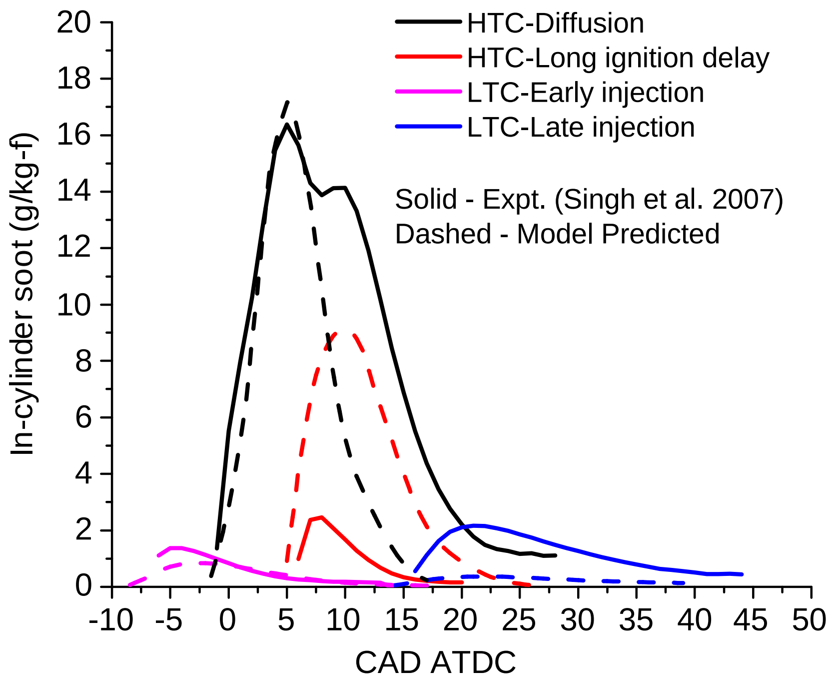
Vishwanathan & Reitz, CST 2010





In-cylinder soot formation/oxidation

Difference in HTC and LTC soot amounts well captured

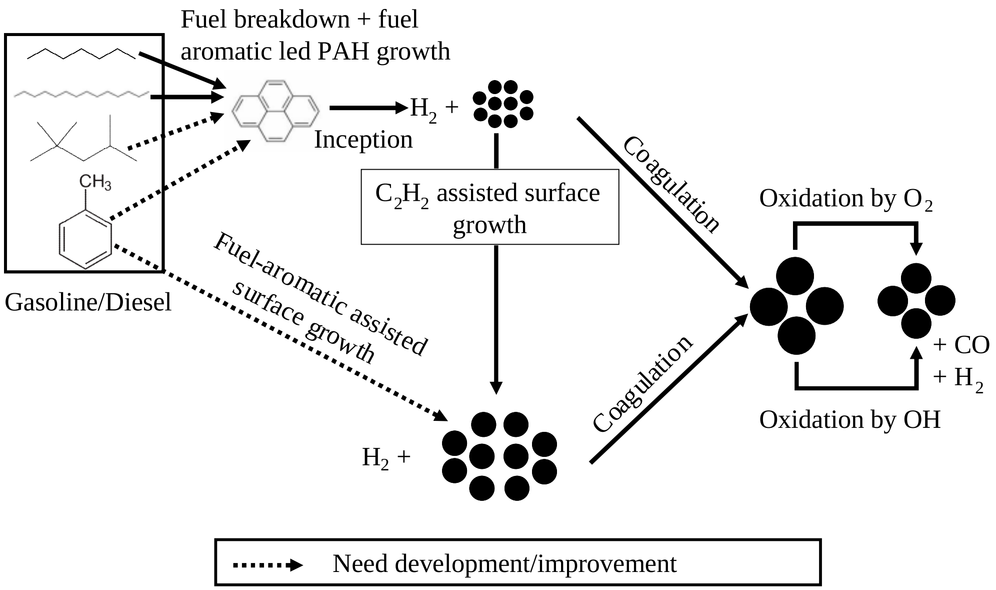


Diffusion to premixed combustion, soot ↓

HTC to LTC, soot ↓

Summary and Future directions

Integration of soot model with multi-component vaporization and chemistry models


Fuel breakdown + fuel aromatic led PAH growth

$\rightarrow H_2$ +

Inception

C_2H_2 assisted surface growth

Fuel-aromatic assisted surface growth

Coagulation

Coagulation

Oxidation by O_2

+ CO
+ H_2

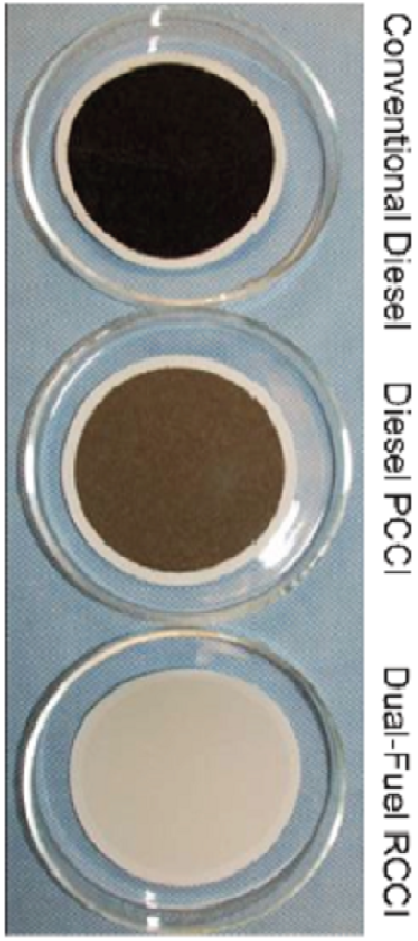
Oxidation by OH

H_2 +

CH_3

Gasoline/Diesel

Need development/improvement



Extension to GDI and H/P/RCCI

Organic fraction modeling:
OF correlates with premixedness

Soot diameter comparisons with TEM measurements obtained from various combustion modes