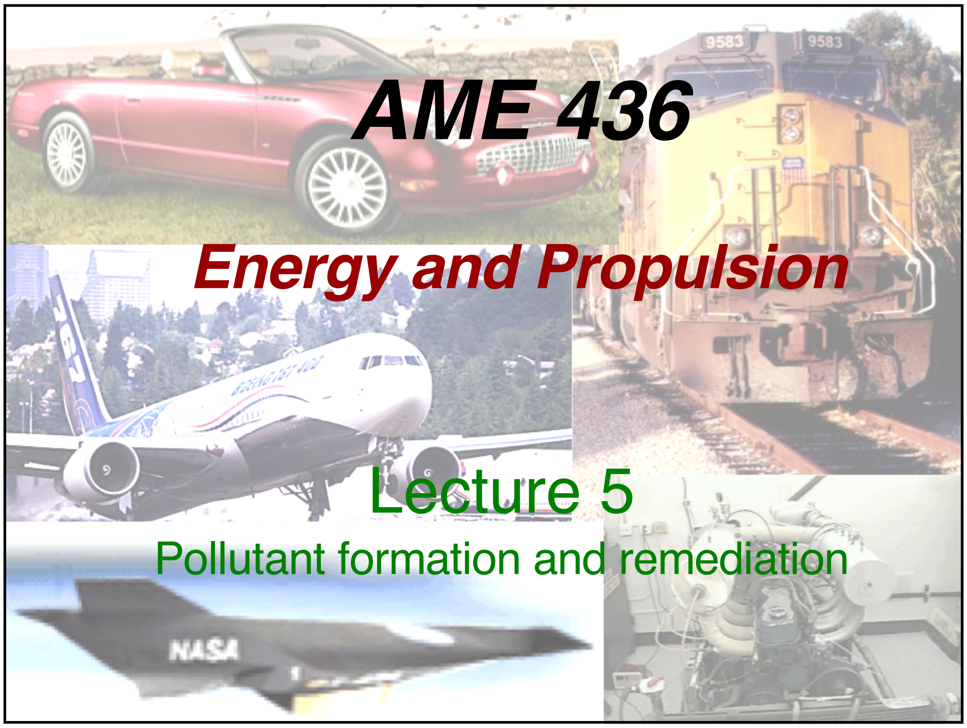


AME 436

Energy and Propulsion

Lecture 5

Pollutant formation and remediation

Outline

USC Viterbi School of Engineering

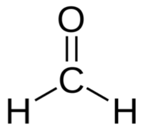
- Description of pollutants
- Emissions standards
- CO
- Hydrocarbons
- Nitrogen oxides
- Soot
- Remediation (cleanup) of emissions

Description of pollutants

- "Photochemical smog" producing compounds
  - Nitrogen oxides - collectively NO_x (pronounced "knocks")
    - NO (nitric oxide): poisonous, but concentrations are low - main problem is that it is the main NO_x emission from most combustion processes - "feedstock" for atmospheric NO_x
    - NO_2 (nitrogen dioxide): some produced during combustion, most in atmosphere; powerful oxidant; main problem it that it's BROWN - who wants to look at a brown sky???
    - N_2O (nitrous oxide): not poisonous, but a "greenhouse gas"
  - UHC (unburned hydrocarbons): participates in photocatalytic cycles of the form

    $$NO + 2O_2 + UHC + h\nu \rightarrow NO_2 + O_3 + UHC$$

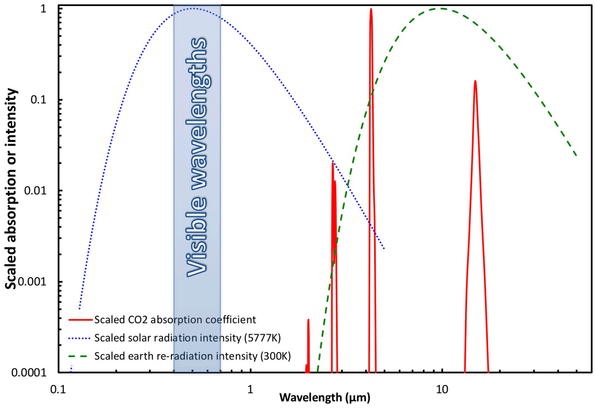
    (Methane does not participate, hence only Non-Methane Organic Gases (NMOG) are regulated)
  - Formaldehyde (HCHO): irritates eyes, mucous membranes, lungs



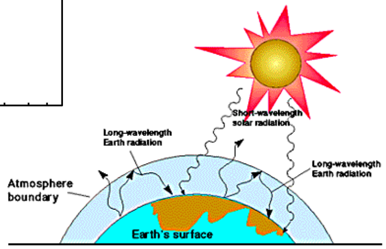
Description of pollutants

- CO (carbon monoxide): poisonous in "large" concentrations, otherwise not much of a problem (for photochemical smog or greenhouse warming)
- Soot (mostly carbon, fine particles): causes respiratory problems, obscures sky, excellent substrate for all kinds of atmospheric chemical reactions
- O_3 (ozone) - not produced by combustion (produced by photochemical reactions); powerful oxidant, highly irritating to lungs; excellent disinfectant (i.e. it kills everything in its path)
- CO_2 - the carbon has to go somewhere, CO_2 is better than CO or UHC, but still a greenhouse gas!

Greenhouse effect



Peak of Planck function shifts from visible (≈ 0.5 µm) at solar T (where gases don't absorb) to ≈ 10 µm where CO_2 & other gases absorb strongly – more CO_2 in atmosphere doesn't change incoming radiation but reduces outgoing radiation



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Tier III emissions standards

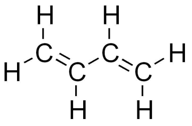
- Emissions (in g or mg per mile) measured using a particular EPA-standard driving cycle
- U.S. "Tier III" emissions standards (started 2017) require a certain fleet average for each manufacturer – can sell "dirty" Bin 160 vehicles if offset by cleaner lower-number Bin vehicles
- See for example https://www.dieselnet.com/standards/us/ld_t3.php
- "Bin 0" vehicles (e.g. electric) not charged for emissions resulting from making the electricity!

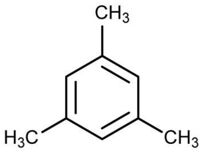
Bin	NMOG+NOx	PM	CO	HCHO
	mg/mi	*mg/mi*	*g/mi*	*mg/mi*
Bin 160	160	3	4.2	4
Bin 125	125	3	2.1	4
Bin 70	70	3	1.7	4
Bin 50	50	3	1.7	4
Bin 30	30	3	1.0	4
Bin 20	20	3	1.0	4
Bin 0	0	0	0	0

Unburned hydrocarbon reactivity

- UHCs weighted by reactivity to produce O_3 in a standardized test
  - CH_4 almost inert
  - Other paraffins (C_2H_6, etc.) weakly active
  - 2, 3 butadiene - mother of all photochemical agents - not a component of fuels, but produced in flames, also important soot precursor
  - Some aromatics bad also (e.g. 1,3,5 trimethylbenzene)

Volatile Organic Compound (VOC)	Reactivity (mg Ozone produced per mg VOC)
carbon monoxide	0.054
alkanes	
methane	0.0148
ethane	0.25
propane	0.48
n-butane	1.02
olefins	
ethylene	7.29
propylene	9.40
1,3 butadiene	10.89
aromatics	
benzene	0.42
toluene	2.73
meta-xylene	8.15
1,3,5-trimethylbenzene	10.12
oxygenates	
methanol	0.56
ethanol	1.34
MTBE	0.62
ETBE	1.98


1, 3 butadiene


1,3,5 trimethyl benzene

Description of pollutants

- Emissions are trace amounts in the combustion products
  - Example: octane-air combustion

$$C_8H_{18} + 12.5(O_2 + 3.77N_2) \rightarrow 8\ CO_2 + 9\ H_2O + 12.5*3.77\ N_2$$

  - Allowable CO emission = 1 g/mi for Bin 30 vehicle; assume 30 mi/gal:

$$\frac{1\ g\_CO}{mi}\frac{12\ \ g\_C_{in\ CO}}{28\ \ g\_CO}\frac{30\ \ mi}{gal\_fuel}\frac{gal\_fuel}{6.0\ \ lb\_fuel}\frac{2.205\ \ lb\_fuel}{1000\ \ g\_fuel}\frac{[8(12)+18]\ \ g\_fuel}{8(12)\ \ g\_C_{in\ \mathrm{fuel}}}=0.0056\frac{g\_C_{in\ CO}}{g\_C_{in\ \mathrm{fuel}}}$$

  - Only 1 C atom in 1/0.0056 = 178 can be emitted as CO not CO_2
  - Other emissions (NO, CH_2O, etc.) much lower fractions, e.g. 10^{-4}
- Recall our mantra (Lecture 1) - “emissions are a NON-EQUILIBRIUM PROCESS”
- If we follow two simple rules:
  - Use lean or stoichiometric mixtures
  - Allow enough time for chemical equilibrium as products cool down

  … then NO, CO, UHCs and C(s) (soot) are practically zero
- … but we are not patient enough (or unable to cool down slowly enough)!

Methane-air equilibrium products (1 atm)

- Check this out via chemical equilibrium, e.g. with GASEQ
- Relatively high NO & CO at adiabatic flame temperature, practically none if we cool this mixture down to equilibrium at 700K

Mole fractions (X_i) at equilibrium

Species	At AFT (2226K)	At 1500K	At 700K
N2	0.70864	0.71488	0.71493
H2O	0.18336	0.18997	0.19005
CO2	0.08536	0.09495	0.09502
CO	0.00896	6.698e-05	9.168e-13
O2	4.561e-03	4.675e-05	8.094e-12
OH	2.922e-03	1.350e-05	9.757e-14
H	3.898e-04	1.264e-07	1.049e-19
O	2.130e-04	2.745e-08	1.008e-21
H2	3.621e-03	5.208e-05	1.736e-11
NO	1.975e-03	1.883e-05	1.971e-12
HCO	7.688e-10	1.292e-14	9.577e-32
CH2O	2.002e-11	2.853e-15	4.096e-29
CH4	2.712e-17	2.170e-22	9.773e-41
CH3	7.107e-17	1.275e-23	0.00000
HO2	5.585e-07	5.826e-10	3.034e-20
NO2	3.306e-07	1.439e-09	1.320e-17
NH3	2.740e-09	2.017e-11	5.795e-19
NH2	9.167e-10	1.079e-13	1.474e-27
N	1.416e-08	5.112e-14	5.604e-33
HCN	1.547e-11	2.045e-16	6.612e-34
CN	8.234e-14	3.688e-21	0.00000
N2O	9.383e-08	9.708e-10	1.934e-16
C2	2.205e-26	9.109e-41	0.00000
CH	4.128e-18	3.336e-28	0.00000

CO, UHCs, formaldehyde

- Won't discuss hydrocarbon oxidation chemistry at length here - covered in AME 513 (Fundamentals of Combustion); also a bit in AME 436 Lecture 10 (in context of engine knock)
- Key steps in oxidation (see next page)

  Fuel + $O_2 \rightarrow CO + H_2$ (fuel breakdown in flames is relatively fast)

  $2H_2 + O_2 \rightarrow 2H_2O$

  $2CO + O_2 \rightarrow 2CO_2$ (last and slowest step)
- If insufficient time for combustion, CO is emitted from flame
- Need OH radicals to obtain $CO + OH \rightarrow CO_2 + H$, so need high enough temperatures for $H + O_2 \rightarrow OH + O$ chain branching
- Formaldehyde (HCHO) an important step to CO formation, e.g.

  $CH_4 + OH \rightarrow CH_3 + H_2O$ (formation of methyl radical)

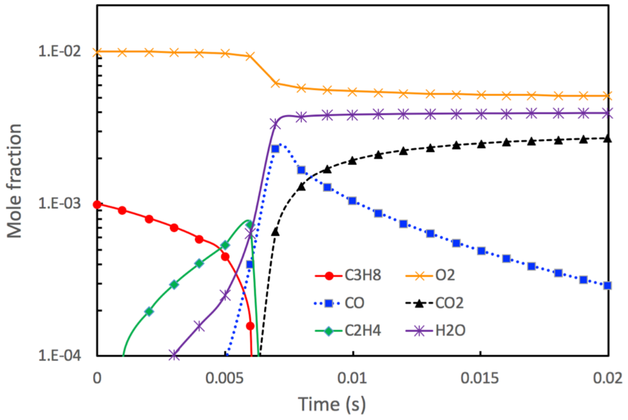
  $CH_3 + O \rightarrow HCHO + H$ (formation of formaldehyde)

  $HCHO + H \rightarrow HCO + H_2$ (formation of formyl radical)

  $HCO + H \rightarrow CO + H_2$ (formation of CO)

CO, UHCs, formaldehyde

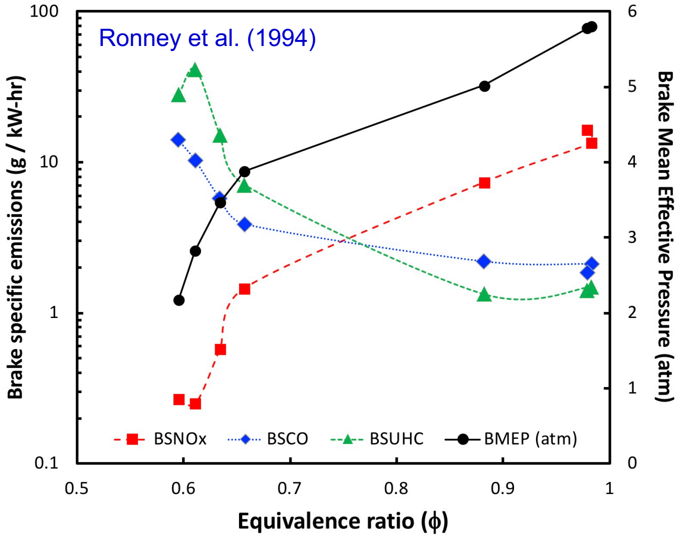
- 0.1% C_3H_8 – 1% O_2 – 98.9% N_2 (lean [$\phi = 0.5$] dilute mixture)
- Constant 1273K, 1 atm
- Fuel decomposes, intermediate hydrocarbon (C_2H_4) formed
- Very little CO or H_2O formed until all fuel gone
- H_2O forms quickly afterwards, $CO \rightarrow CO_2$ much slower



CO and UHCs

- CO
    - Usually expressed as Brake Specific CO (grams of CO emitted per kW-hr of shaft work produced)
    - Rich mixtures: CO is unavoidable - not enough O_2 to burn all C to CO_2 (but we don't want to burn rich anyway, efficiency will be low)
    - Lean mixtures: CO still formed, actually gets worse as ϕ decreases (decreases T_{ad}, slower reaction, less time for CO to CO_2 conversion)
    - Net result: CO is minimum at ϕ slightly lean - high T_{ad}, excess O_2 available
- UHCs
    - Similar to CO: higher for leaner mixtures - decreases T_{ad}, slower reaction, more unburned fuel

CO and UHCs



Engine: 2.5 liter, 4 cylinder, 1200 RPM, natural gas fuel, wide-open throttle

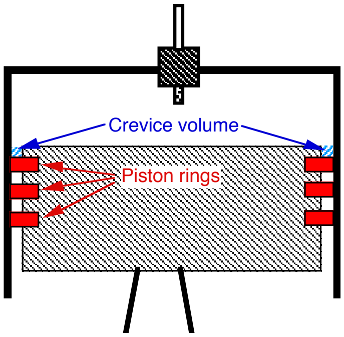
Brake Mean Effective Pressure = measure of work output

Unburned hydrocarbons (UHCs)

- If fuel decomposes quickly, why are UHCs still emitted?
- In the engine, emissions of UHCs come from
    - Raw unburned fuel (next slide)
    - Fuel that didn't burn all the way to CO_2 and H_2O
    - Lubricating oil (especially in 2-stroke engines using fuel + oil mixtures)
- Other than tailpipe, UHCs may come from
    - Fuel tank (older cars without evaporative emission controls)
    - Gasoline filling station (in regions without vapor recovery system)
    - Tires (!!!) – several mg/mile

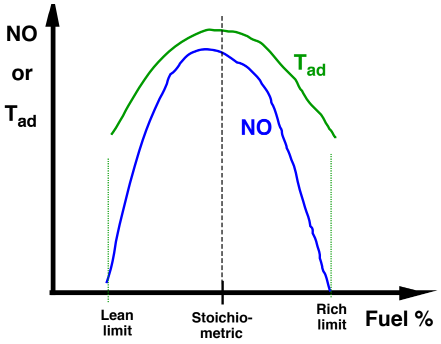
Unburned hydrocarbons (UHC)

- Why didn't fuel burn in engine?
  - Bad mixing (especially Diesels at high load, near $\phi = 1$); last molecule of fuel can't find last molecule of air with available time
  - Misfire - too small S_T (low ϕ, low u', high EGR, etc.), bad spark, etc.
  - Solution / dissolution of fuel into oil or engine deposits
  - Quenching near walls and in crevice volumes - if ratio of crevice thickness to flame thickness $\delta \approx \alpha/S_L < 40$, flame will not be able to propagate into crevice, mixture will not be burned, UHCs will be formed
  - Some UHCs formed in these ways will burn before leaving engine



Nitrogen oxides

- Typical experimental result
  - Peak NO slightly lean ($\phi \approx 0.9$) since N_2 is plentiful at all ϕ, but surplus O_2 present only for lean mixtures
  - Very sensitive to temperature (high activation energy E) so peak still close to $\phi = 1$ where T is highest (thermal NO)
  - Slower decrease on rich side than lean side (prompt NO)
- Two flavors of NO
  - "Thermal" or "Zeldovich"
  - "Prompt" or "Fenimore"



Thermal or Zeldovich NO

- Extremely high activation energy due to enormous strength of N≡N bond (≈ 220 kcal/mole)

(1) $O + N_2 \rightarrow NO + N$ (E_1 = 76,500 cal/mole; $Z_1 = 2 \times 10^{14}$, $n_1 = 0$)
(2) $N + O_2 \rightarrow NO + O$ (E_2 = 6,300 cal/mole; $Z_2 = 6 \times 10^{9}$, $n_2 = 0$)

$N_2 + O_2 \rightarrow 2\ NO$

- Recall reaction rate expressions (lecture 4)

$$\text{Generic: } \frac{d}{dt}\{\nu_A[A]\} = \frac{d}{dt}\{\nu_B[B]\} = -Z[A]^{\nu_A}[B]^{\nu_B}T^n \exp\left(-E/\Re T\right)$$

$$\Rightarrow \frac{d[N_2]}{dt} = \frac{d[O]}{dt} = -Z_1[N_2]^1[O]^1 T^{n_1} \exp\left(-E_1/\Re T\right)$$

$$\Rightarrow \frac{d[N]}{dt} = \frac{d[O_2]}{dt} = -Z_2[N]^1[O_2]^1 T^{n_2} \exp\left(-E_2/\Re T\right)$$

- Reaction (1) usually slower; $Z_1\exp(-E_1/\Re T) < Z_2\exp(-E_2/\Re T)$ for $T < 3394$K
- 1 NO molecule from reaction (1) quickly yields 2 NO molecules if (2) is fast

Zeldovich mechanism

- Where do O atoms come from? From inside the flame (often super-equilibrium O concentration) or equilibrium dissociation of O_2 in products

$$\frac{d[NO]}{dt} = 2k_{O+N_2}[N_2][O] = 2k_{O+N_2}[N_2]K_{eq\ (O \Leftrightarrow 0.5O_2)}[O_2]^{1/2}$$

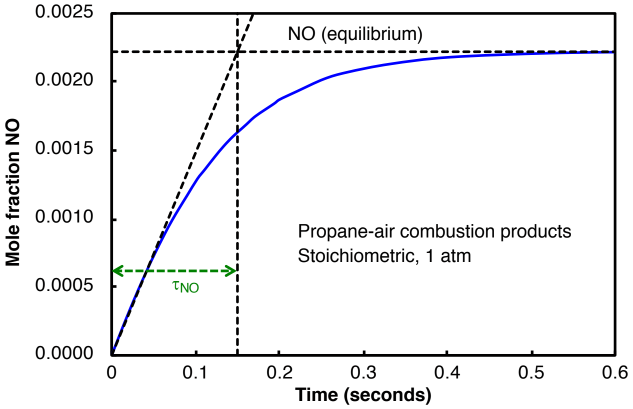
- E_{O+N2} = 76.5 kcal/mole, $K_{eq(O \Leftrightarrow .5O2)}$ ≈ 60 kcal/mole, overall > 135 kcal/mole
- Heywood (1988): characteristic time t = $[NO]_{equil}/(d[NO]/dt)_{[NO]=0}$ for initial formation rate of NO in lean combustion products, assuming equilibrium [O]

$$\tau_{NO} = 8\text{x}10^{-16} T \exp\left(\frac{116{,}000 \text{ cal/mole}}{\Re T}\right) P^{-1/2} \text{ (T in K, P in atm, } \tau \text{ in sec)}$$

  - T = 2200K, P = 1 atm: τ_{NO} = 0.59 second
  - By comparison, time scale for chemical reactions in flame front (Lecture 4) $\tau_{flame} \sim \alpha/S_L^2 \approx 0.0006$ second for stoichiometric hydrocarbon-air - WAY shorter
- Thus, Zeldovich NO occurs in the burned gases downstream of the flame front, not in the flame front itself

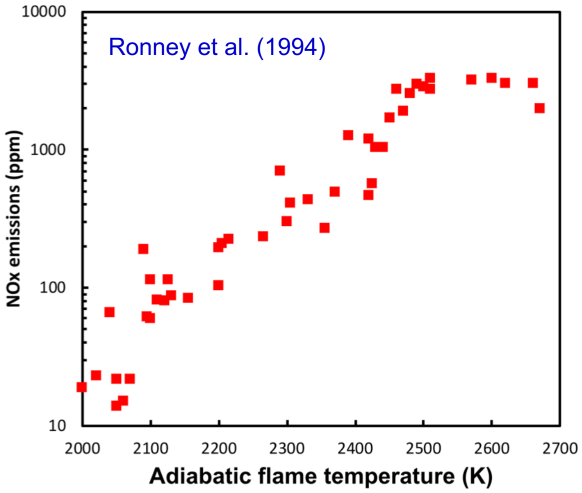
Zeldovich mechanism

- Physical interpretation of τ_{NO} - infinite time required to reach equilibrium, but τ_{NO} is the the time constant in the asymptotic approach to equilibrium, e.g. $[NO](t) = [NO]_{equil}\{1 - \exp(-t/\tau_{NO})\}$



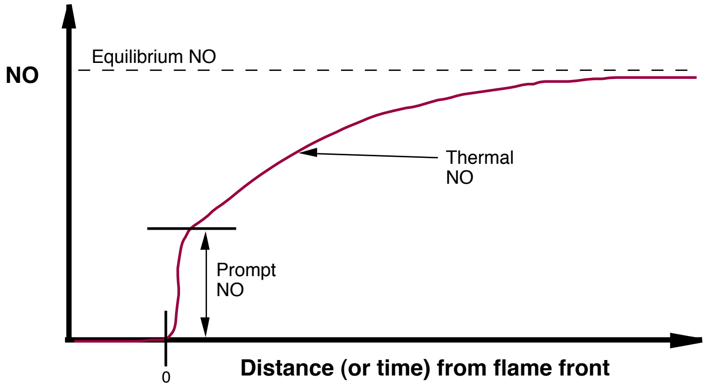
Zeldovich mechanism

- NO_x vs T_{ad} shows logarithmic trend – plot of $\ln(NO_x)$ vs. $1/T_{ad}$ shows slope corresponding to activation energy E = 93.2 kcal/mole
- (T_{ad} varied by changing both ϕ and T_∞, corrected for heat loss to cylinder walls)



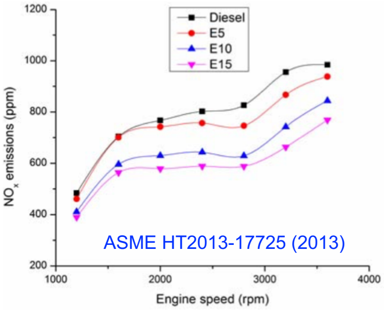
Prompt mechanism

- Experiments show that some NO forms *inside the flame* (“Prompt” NO)
- Plot [NO] vs. distance from flame, extrapolate back to flame front location, [NO] there is defined as prompt NO
- Prompt NO more prevalent in hydrocarbon flames (not CO, H_2), and fuel-rich flames (even though less O, thus Zeldovich less important)
- Still high activation energy, but not as high as “thermal” NO



Factors affecting NO formation in engines

- Equivalence ratio or FAR - already discussed
- Exhaust residual - dilutes fuel-air mixture, reduces T (assuming exhaust is cooler than adiabatic T) (diluting a cold fuel-air mixture with adiabatic exhaust has no effect on flame temperature!)
- Intake pressure - $\tau_{NO} \sim P^{-1/2}$ - weak effect
- Engine RPM (N): higher N $\Rightarrow$ less time for NO to form, but less time to shift to equilibrium, no clear winner (diesel slightly higher at higher RPM)
- Spark timing – see Lecture 10 - more advance improves η_{th} up to a point, but yields higher maximum T, more NO_x



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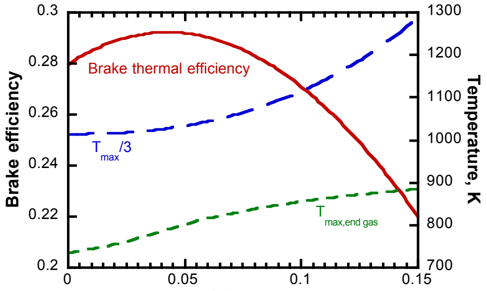


How to reduce NO during combustion?

- Premixed flames - every parcel of gas experiences same peak temperature - lean mixtures (good idea) or rich mixtures (bad idea)with lower T_{ad} will have much lower NO (but then have flammability/stability limit problems…)
- Better idea: use $\phi = 1$ mixtures and minimize temperature with Exhaust Gas Recirculation (EGR)
  - $\phi = 1$ mixtures have less available O atoms
  - $\phi \approx 1$ mixtures needed for 3-way catalyst operation (in a few slides…)
- Improve mixing - if poor mixing, get hot spots with much more NO_x
  - Example: 2 equal volumes of combustible gas with E = 100 kcal/mole, 1 volume at 1900K, another at 2100K

    $\omega(1900) \sim \exp(-100000/(1.987*1900)) = 3.14 \times 10^{-12}$

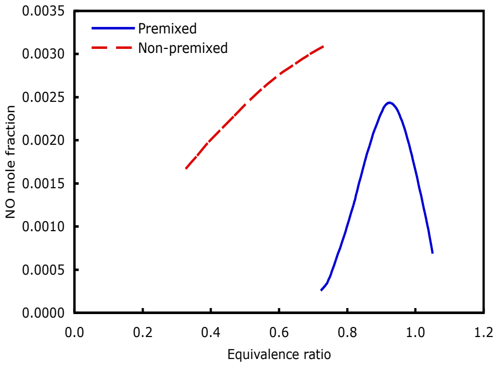
    $\omega\ (2100) \sim \exp(-100000/(1.987*2100)) = 3.91 \times 10^{-11}$

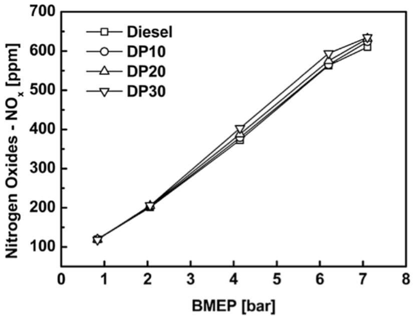
    Average $\omega = 2.11 \times 10^{-11}$

    whereas $\omega(2000) = 1.18 \times 10^{-11}$, nearly 2x smaller

How to reduce NO during combustion?

- Non-premixed flames
  - Always have hot stoichiometric surfaces with $T \approx T_{ad,stoich}$ - even when overall ϕ is very low $\Rightarrow$ thermal NO; NO ~ fuel used
  - Always have fuel-rich, "warm" regions - Fenimore NO
  - ∴ Hard to control NO in Diesel (non-premixed charge) engines!
  - Recall for premixed flames, every parcel of gas has same peak temperature - lean mixtures will have much lower NO

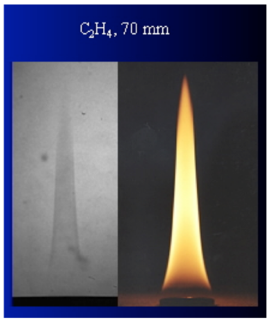




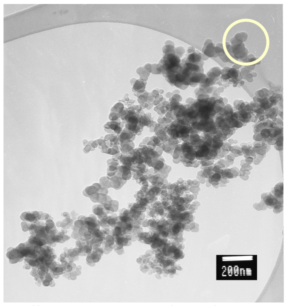
Soot formation

- Typically C_8H_1 (not a misprint - mostly C)
- Structure mostly independent of fuel & environment
  - Quasi-spherical particles, 10^5 - 10^6 atoms (100 - 500 Å), strung together like a “fractal pearl necklace”
  - Each quasi-spherical particle composed of many (~10^4) slabs of graphite (chicken wire) carbon sheets, randomly oriented
- Quantity of soot produced highly dependent on fuel & environment
  - Does not form at all in lean or stoichiometric premixed flames
  - Forms in rich premixed flames and nonpremixed flames, where high T and carbon are present
- Benzene-ring structures are the building blocks of soot because they’re very stable at high temperature - most other large molecules won’t survive, even if no O_2 present

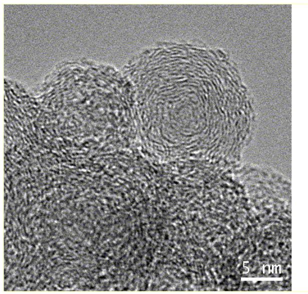
Soot photographs



L: laser soot absorption;
R: direct photo
(R. Axelbaum, Washington Univ.)

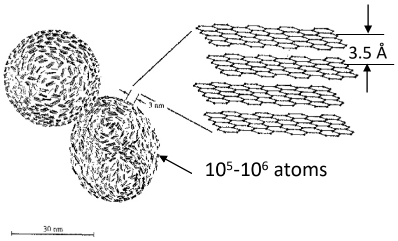


http://www.asn.u-bordeaux.fr/images/soot.jpg



A. Boehman, Penn State

Soot “particle”



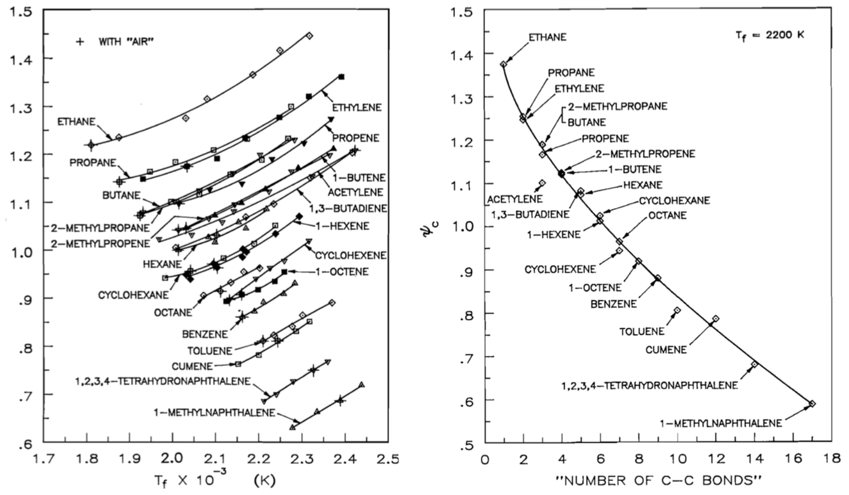
http://www.atmos.umd.edu/~pedro/soot2.jpg

Nonpremixed flames, e.g. candle: soot is formed, gives off blackbody radiation (thus light), but soot is oxidized to CO_2, so soot is not emitted from the flame

Soot formation - premixed flames

- For fixed experimental conditions, soot formation occurs for mixtures richer than a critical equivalence ratio (ϕ_c) – higher ϕ_c, less sooting tendency
- Experiments controlling ϕ and T_{ad} independently (using fuel-O_2-N_2 mixtures) (next page) show ϕ_c is related to the number of C-C bonds in the fuel molecule (makes sense - more C-C bonds already made, fewer C-H bonds)
- Fuel structure doesn't matter except in terms of number of C-C bonds (next page) – shows that all C passes through the same set of intermediate chemical steps
- In premixed flames, less sooting tendency (higher ϕ_c) at higher T_{ad} because soot formation has high activation energy, but oxidation has higher activation energy; since fuel and air are premixed, both soot formation and oxidation occur simultaneously (a horse race; formation wins at low T, oxidation at high T)

Soot formation – premixed flames



Critical ϕ vs. T_{ad}

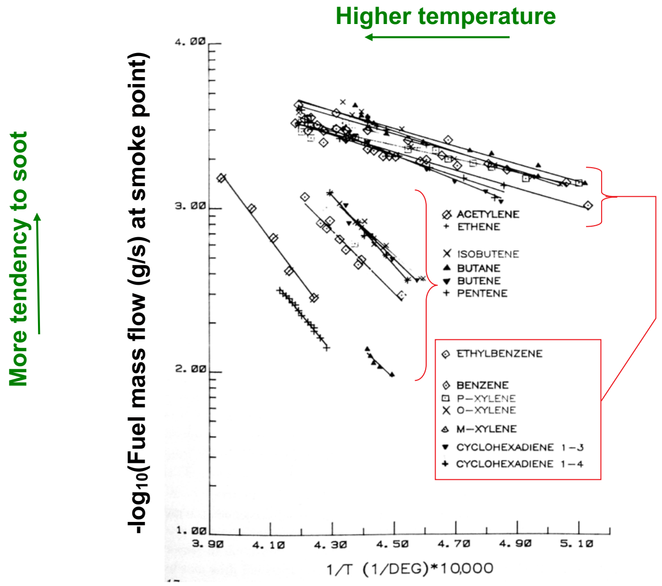
Critical ϕ at T_{ad} = 2200K

Note: ϕ (called ψ in these plots) is referenced to $CO + H_2O$, not $CO_2 + H_2O$, as products

Soot - nonpremixed flames

- ϕ_c irrelevant parameter - always have full range of ϕ from 0 to ∞
- Smoke height criterion - soot emission from flame (black smoke) occurs at a flow rate higher than a critical value, corresponding to critical residence time - refers to soot emission (black smoke), whereas criterion used for premixed flames (ϕ_c) refers just to formation (yellow flame color)
- Experiments with fuel dilution to control T_{ad} show less soot tendency (higher flow rate at onset of soot) at lower T_{ad} (different from premixed flames!) because soot forms on rich side of stoichiometric where no O_2 is present - no competition between soot oxidation & growth
- As a result, fuel structure matters (unlike premixed flames)

Soot formation – nonpremixed flames

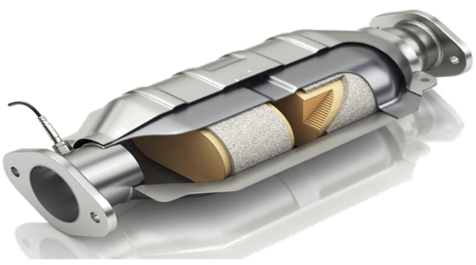


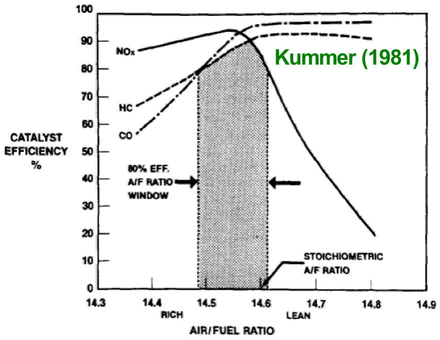
Emissions cleanup – premixed engines

- Conflicting needs
  - For NO_x control, need to burn rich and cool
  - For CO & UHC, need to burn lean (but still near $\phi = 1$ to stay hot) to provide good oxidizing environment
  - Soot formation is not an issue for premixed-charge engines (since lean or stoichiometric)
- Since 1975: use $\phi = 1$ mixtures and minimize T_{ad} with Exhaust Gas Recirculation (EGR) rather than lean mixtures
  - $\phi = 1$ mixtures have less available O atoms
  - $\phi \approx 1$ mixtures needed for 3-way catalyst operation - simultaneous reduction of NO to N_2 & O_2, oxidation of CO and UHCs to CO_2 & H_2O
  - Can't use $\phi = 1$ in diesels - massive sooting would result!

Catalytic converters for premixed-charge engines

- 3-way catalyst - since 1975
  - Reduce NO to N_2 & O_2, oxidize CO & UHC to CO_2 & H_2O
  - Can only get simultaneous reduction & oxidation very close to $\phi = 1$ - need good fuel control system with sensor to monitor O_2 level in exhaust, adjust fuel to maintain $\phi = 1$
  - Use EGR with $\phi = 1$ to lower T_{ad}, thus lower in-cylinder NO
  - Catalyst poisoned by lead oxide - need to remove antiknock agent $Pb(C_2H_5)_4$ from gasoline



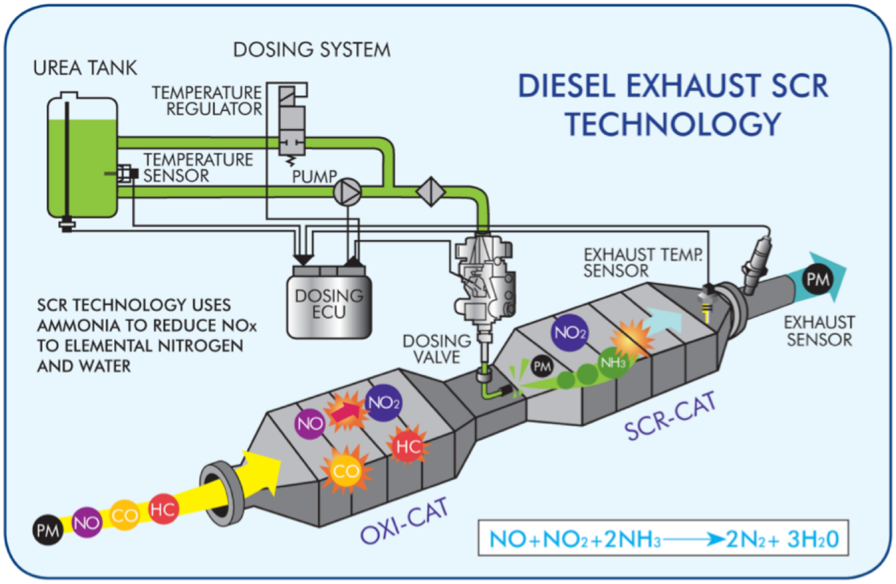


Kummer (1981)

NOx cleanup - non-premixed-charge engines

- NO_x a major issue for non-premixed charge engines
- Can use EGR to reduce T_{ad}, thus reduce NO_x, but can't use catalytic converter to reduce NO_x further, since mixtures are always lean
- Thus, diesels produce less CO & UHC (lean & hot) than gasoline engines, but more NO
  - With Tier III system, clean small gasoline vehicles can offset dirty large diesels
  - Larger vehicles and stationary engines, standards based on g/bhp-hr (grams of emission per brake horsepower hour), i.e. emission per unit of work generated, not g/mi (engine-based, not vehicle-based)
- "Selective Catalytic Reduction" used to reduce NO (but need urea $\{(NH_2)_2CO\}$ supply!) (now called "Diesel Exhaust Fluid" (DEF) because "urea" has a bad connotation!)

Emissions cleanup - non-premixed-charge engines



Soot cleanup - non-premixed-charge engines

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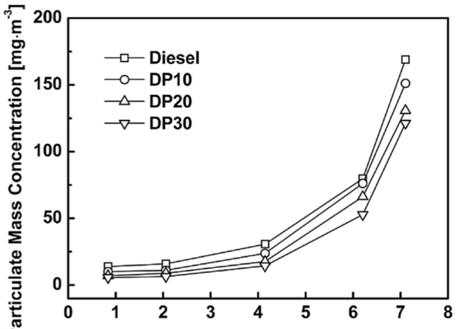
- More soot formed at high fuel loads (closer to but still less than stoichiometric), due to insufficient mixing time – harder to find all the available O_2
- Very difficult to eliminate soot formation in the engine - instead use traps to capture emitted soot
- Regulations for passenger vehicles: emissions system must be zero maintenance - can't require driver to remove accumulated soot (e.g. like a vacuum cleaner bag)
- Zero-maintenance designs use extra fuel periodically to burn off particles accumulated in traps



Example

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Planet X is exactly the same as earth except that, due to a disturbance in The Force, **all chemical reaction rates are a factor of 2 lower than on earth.** How would each of the following be affected, i.e., state whether the property would increase, decrease or remain the same?

(a) **Amount of NO in the combustion products of a premixed-gas flame, far downstream of the flame front.** Would not change since this corresponds to equilibrium, and in equilibrium, the forward and reverse rates are equal, thus decreasing both rates by a factor of 2 would have **no effect** on the balance between N_2, O_2 and NO at equilibrium.

(b) **Time constant for thermal NO formation (τ_{NO}).** If the reaction rate decreased by a factor of 2, the time constant for reaction (inverse of a rate) would **increase by a factor of 2.** Unlike part (a), the reverse rate would not matter because τ_{NO} is based on the initial rate of NO formation, before any NO is present and the reverse reaction can occur.

(c) **Amount of CO emission from a premixed-charge engine**. Since combustion would be slower, more CO would be emitted (i.e. less of the CO to CO_2 conversion would occur), probably by a factor of 2.

(d) **Amount of unburned hydrocarbon emission from a premixed-charge engine.** Similar to CO, since combustion would be slower, more unburned hydrocarbons would be emitted would be emitted (i.e. less of the hydrocarbon conversion to CO_2 and H_2O would occur).

(e) **Amount of soot emission from a premixed flame**. Both soot formation and oxidations rates would decrease by the same factor, so there would not be much change in the amount of soot emitted.

(f) **Amount of soot emission from a non-premixed flame.** Would decrease by a factor of 2 since in this case there is no competition between formation and oxidation.

Summary - most important points

- Emissions are non-equilibrium effects - depend on reaction rates
- CO & UHC - form due to flame quenching or incomplete combustion - go lean (extra O_2) and hot (high reaction rate) to oxidize to CO_2 & H_2O
- NO_x formation has very high activation energy - temperature dependent - small decrease in T causes large decrease in NO_x; also need O - go rich and cool
- Soot
  - Premixed - lower T leads to more soot since formation is always competing with oxidation (O_2 always present), and oxidation rates increase faster with T than formation rates; fuel structure unimportant
  - Nonpremixed - higher T leads to more soot since formation on rich side of flame front (no O_2 present, no oxidation); fuel structure important
  - Either way, lean and hot means less soot

Summary - most important points

- Emissions cleanup
  - Conflicting requirements - rich & cool for NO_x, lean & hot for CO & UHC
  - Premixed-charge (gasoline-type) engines
    - Catalytic converter can do both jobs only very close to stoichiometric
    - Use EGR (no excess O_2) rather than lean mixture to reduce T_f for NO_x reduction
  - Nonpremixed-charge (Diesel-type) engines
    - Can't burn near-stoichiometric because of sooting – must stay lean
    - CO and UHC low due to lean mixtures
    - Need particulate traps for soot
    - Need SCR for NO_x – works even in lean mixtures