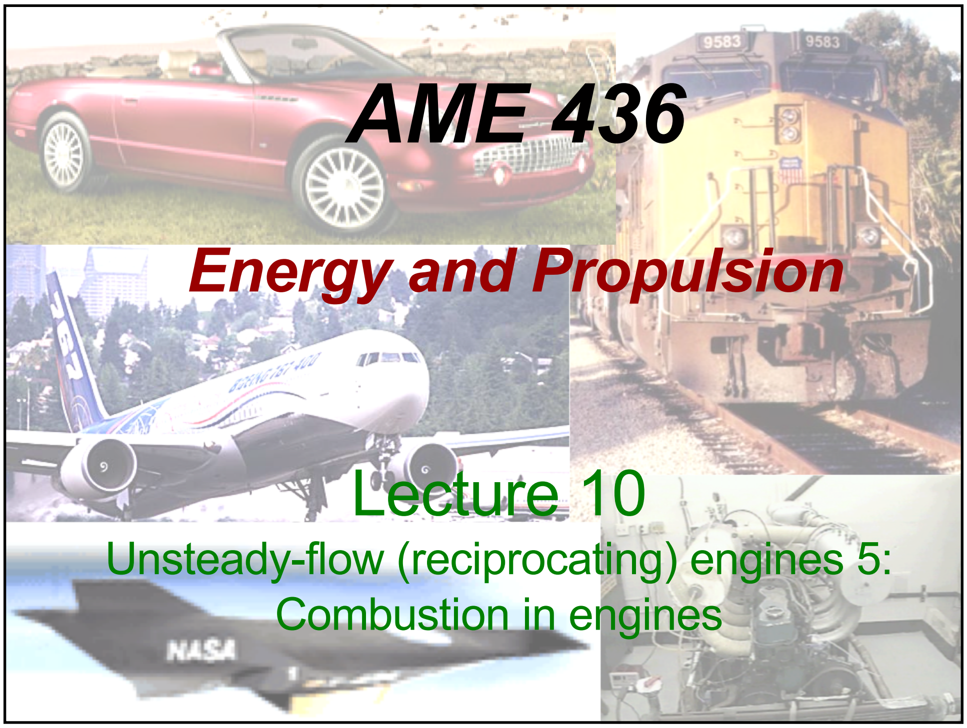

AME 436

Energy and Propulsion

Lecture 10

Unsteady-flow (reciprocating) engines 5: Combustion in engines

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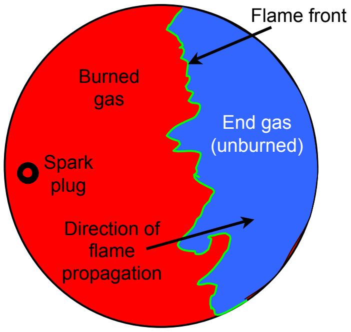
Outline

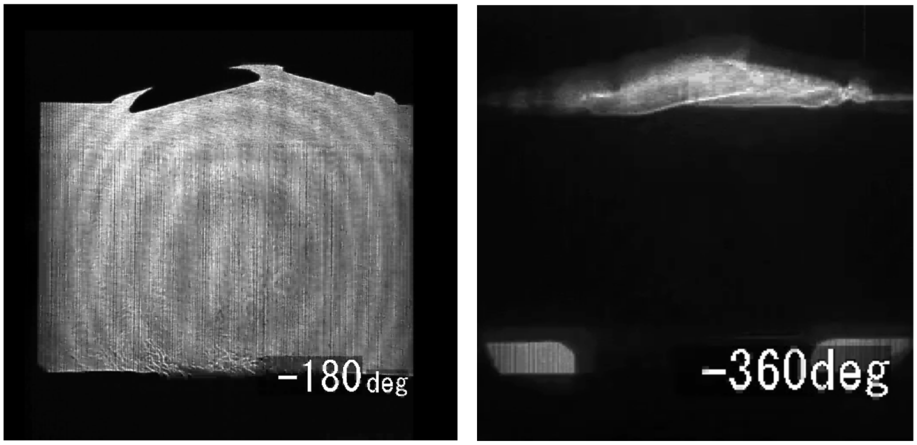
- Combustion in engines
  - Knock
  - Sidebar topic: HCCI engines
  - Misfire / flammability limits

Knock - what is it?

- Homogeneous reaction (see Lecture 4) occurring in unburned "end gas" ahead of expanding flame front
- Occurs when piston compression + "flame compression" increases T & P of end gas until homogeneous reaction rate is fast enough that a very rapid explosion occurs before turbulent flame front consumes the end gas - "horse race" between flame propagation and homogeneous reaction in end gas
- What is "rapid"? Faster than acoustic waves can relax pressure gradients
- How fast is that? Typical engine: Bore = 10 cm = 0.1 m, sound speed = 500 m/s, time scale ≈ 0.1m / 500 m/s = 2×10^{-4} s = 200 µs at most
- Why will we spend so much time on knock? It's the main limitation on compression ratio and thus power & efficiency in premixed-charge engines



Knock - movies

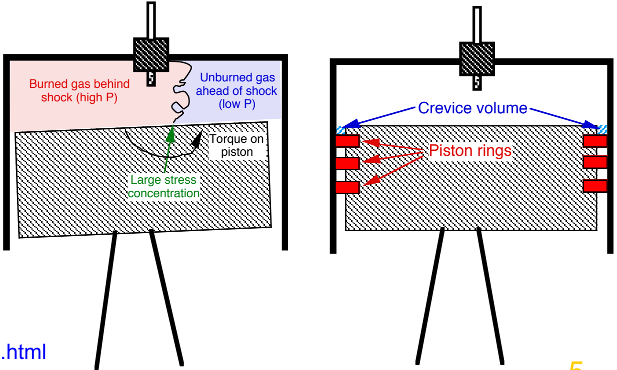


No knock Knock

Videos courtesy Prof. Yuji Ikeda, Kobe University

Knock - why is it bad?

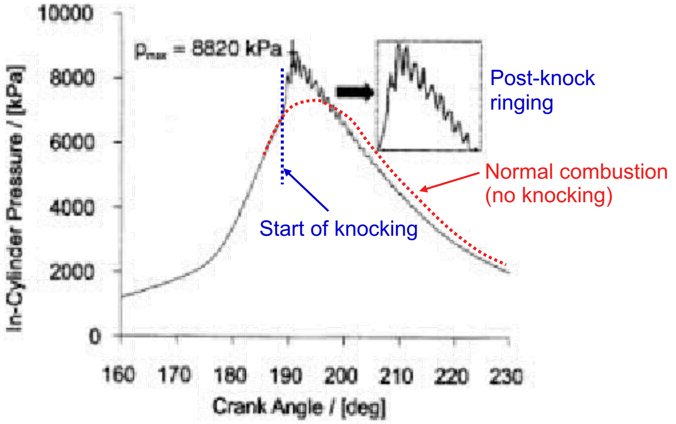
- Pressures generated by knock are not substantially higher than ordinary (deflagration) combustion but pressure gradients are huge, causing enormous stresses on piston; also causes large torque on piston, thus tilting & rubbing against cylinder wall
- Shock propagation into crevice volume causes shock strength to increase, causing locally severe damage – often crevice volume is where maximum knocking damage occurs



http://www.llnl.gov/str/Westbrook.html

Knock

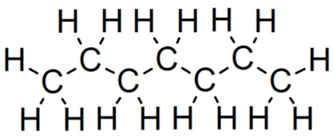
- Shock formation causes “ringing” of pressure waves back & forth across cylinder - sounds like you're hitting the piston with a hammer, not too far from the truth – oscillation period ≈ 200 μs

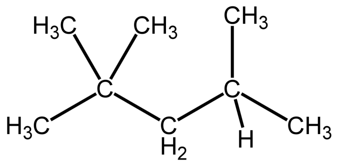


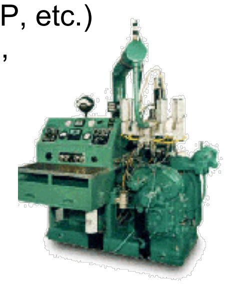
Töpfer et al., SAE Paper 2000-01-0252 (2000)

Knock - how do different fuels compare?

- Fuels are compared by octane number
- Determine knock-limited compression ratio (CR) for test fuel using adjustable CR engine (CFR engine, used only for research) at specific conditions (RPM, spark timing, intake T & P, etc.)
- Define n-heptane as having octane number = zero, 2-2-4 trimethylpentane = 100


n-heptane

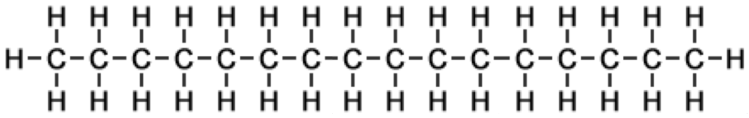

2,2,4 trimethylpentane

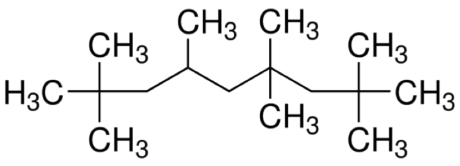

CFR engine

- Blend two reference fuels to get same knock limited compression ratio as test fuel; the percent 2,2,4 trimethylpentane in this blend is the octane number
- Two different test conditions used, called “Research” and “Motor” methods; what's displayed at gas pump is the average (R+M)/2

Diesel fuel characterization

- For non-premixed-charge engines (i.e. Diesels), you want rapid ignition once the fuel is injected, so fuel requirements are opposite premixed-charge engines
- Relevant property is cetane scale, with n-cetane = 100 and a cetane isomer, heptamethylnonane = 15 (not zero!)


n-cetane


2, 2, 4, 4, 6, 8, 8 heptamethyl nonane (iso-cetane)

What does octane number measure?

- Heating value? Nope - all hydrocarbon fuels have very similar heating values (see Lecture 2)
- Laminar burning velocity (S_L)? Nope - S_L is practically the same for all stoichiometric hydrocarbon-air mixtures (≈ 40 cm/s) since
    - As discussed in Lecture 4, $S_L \sim (\alpha\omega)^{1/2}$
    - All such mixtures mostly air, so thermal diffusivity (α) ≈ same for all
    - Overall reaction rate (ω) is controlled by its value at adiabatic flame temperatures (T_{ad}); all such mixtures have nearly equal T_{ad}
    - At these temperatures, controlling reactions are

        $H + O_2 \rightarrow OH + O$ (breaking of O=O double bond, accelerates reaction)

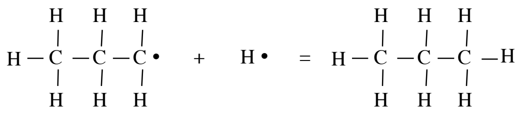
        $H + O_2 + M \rightarrow HO_2 + M$ (competing for H atoms, decelerates reaction)

        $CO + OH \rightarrow CO_2 + H$ (only way to oxidize CO; regenerates H)

      None of these reactions depend on the fuel molecule; fuel decomposition is very fast by comparison at these temperatures
- Tendency for mixture to exhibit homogeneous reaction at the typical T & P of end gases (≈ 30 atm, 900K)? YES!!
- To understand this, look at what reactions occur at these T's & P's

What reactions occur during knock?

- Start with fuel molecule RH, where R is an "organic radical", e.g. propane without an H



propyl radical

propane

- Remove an H atom from RH

    $RH + O_2 \rightarrow R\bullet + HOO\bullet$
- Add an O_2 to R•

    $R\bullet + O_2 \rightarrow ROO\bullet$
- Produce peroxides with O-O single bond (half as strong as O=O double bond (120 kcal/mole vs. 60 kcal/mole), much easier to break)

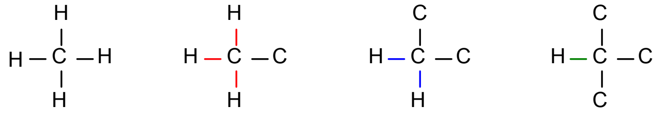
    $ROO\bullet + RH \rightarrow R\bullet + ROOH$ or $HOO\bullet + RH \rightarrow R\bullet + HOOH$
- Break O-O single bond, create "chain branching" process

    $ROOH + M \rightarrow RO\bullet + \bullet OH$ or $HOOH + M \rightarrow HO\bullet + \bullet OH$
- Newly created radicals generate more organic radicals

    $RH + \bullet OH \rightarrow R\bullet + HOH$ or $RH + RO\bullet \rightarrow R\bullet + ROH$
- Note that rate of knocking reactions will be sensitive to rates of H atom removal from fuel molecule RH

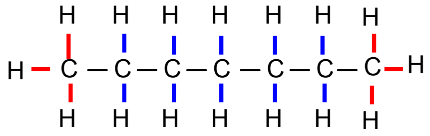
How does fuel structure affect knock?

- Rate of H atom removal depends on strength of C-H bond, which in turn depends on how many other carbons are bonded to that C - stronger bond, slower reaction, less knock

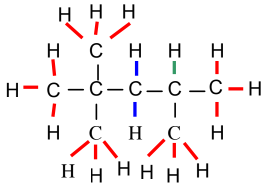


methane 105 kcal/mole | primary C-H bond 98 kcal/mole | secondary C-H bond 95 kcal/mole | tertiary C-H bond 93 kcal/mole

- Examples: n-heptane: 6 primary, 12 secondary C-H bonds
  2, 2, 4 trimethypentane: 15 primary, 2 secondary, 1 tertiary



n-heptane



2, 2, 4 trimethylpentane
(iso-octane)

▌ primary ▌ secondary ▌ tertiary

How does fuel structure affect knock?

- Does this small difference in bond strength matter? YES because activation energy (E) is high
- Using bond strength ≈ E (dangerous in general) at typical 900K

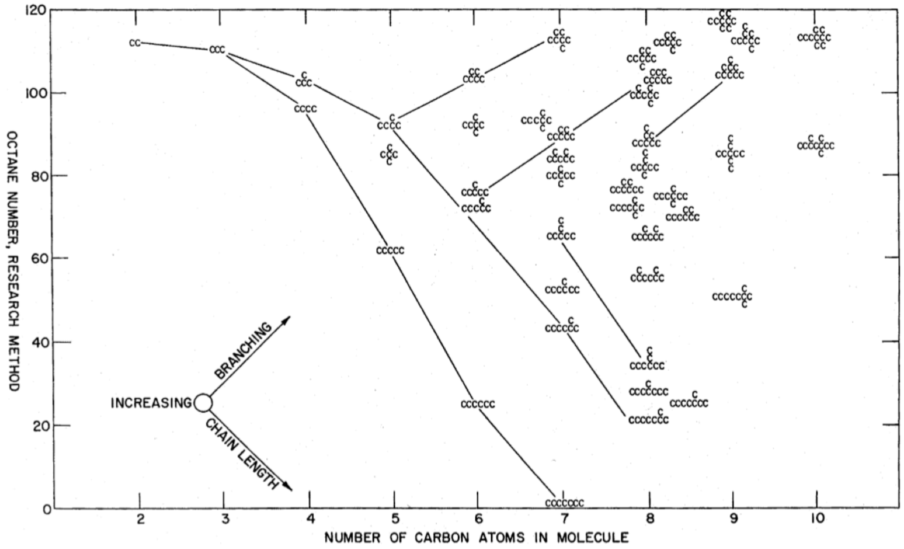
$$\omega_{CH_4} : \omega_{primary} : \omega_{secondary} : \omega_{tertiary} = \exp\left(\frac{-E_{CH_4}}{\Re T}\right) : \exp\left(\frac{-E_{primary}}{\Re T}\right) : \exp\left(\frac{-E_{secondary}}{\Re T}\right) : \exp\left(\frac{-E_{tertiary}}{\Re T}\right)$$

$$\approx \exp\left(\frac{-105000 cal/mole}{\frac{1.987 cal}{moleK} 900K}\right) : \exp\left(\frac{-98000}{1.987 \times 900}\right) : \exp\left(\frac{-95000}{1.987 \times 900}\right) : \exp\left(\frac{-93000}{1.987 \times 900}\right)$$

$$= 1 : 50 : 268 : 820$$

- Comparison of fuels
  - Methane (RON=120, MON=120) - highest of any common fuel
  - Larger n-alkanes lower, e.g. propane RON=112, MON=97
  - Alkenes (C=C double bonds, e.g. ethylene, C_2H_4) lower
  - Benzene - 113 kcal/mole C-H bond strength - MON=115
  - Alcohols good too - methanol: RON=106, MON=92; ethanol RON=106, MON=89

How does fuel structure affect knock?



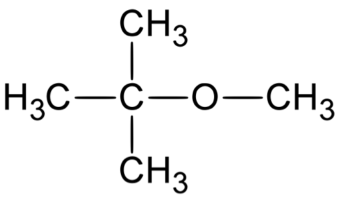
Ghosh et al., *Ind. Eng. Chem. Res.*, Vol. 45, p. 337 (2006)

Anti-knock additives

- Any successful additive must inhibit knock reactions without inhibiting flame propagation reactions!
- Midgley, Boyd, Kettering (GM laboratories, Dec. 9, 1921) after trying 1000's of compounds found tetraethyl lead - $(C_2H_5)_4Pb$
- Introduced into gasoline in 1923 - immediately doubled knock-limited compression ratio from 4 to 8, power & efficiency increased (from 20.8% to 29.2% according to AirCycles4recips.xls)
- Last nail in the coffin for steam & electric vehicles in early 1900's
- Mechanism not understood until 1970's - production of fine PbO particle “fog” that acts as a “scavenger” of HOO• and HOOH - takes them out of system before they lead to chain branching
- … but PbO poisons catalytic converters (lecture 5) introduced in 1975 - needed to switch to unleaded gasoline (Pb not environmentally friendly anyway)

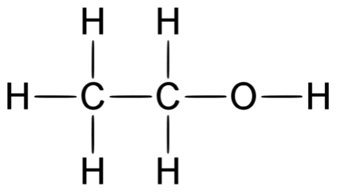
Other anti-knock additives

- Methylcyclopentadienyl manganese tricarbonyl ($C_9H_7MnO_3$, MMT)
- Methyl tert-butyl ether (MTBE) - looked good for a while, but now prohibited - water soluble, can be smelled and tasted in water at the parts per billion level
- Now: ethanol from corn - very desirable to powerful senators from farm states



$H_3C-C(CH_3)_2-O-CH_3$

MTBE



$H-CH_2-CH_2-O-H$

Ethanol

How do operating conditions affect knock?

- Key points
  - Whether knock occurs is a horse race between flame propagation and homogeneous reaction of end gas
  - Chemical reactions that affect flame propagation are different from those that affect knock
  - Homogeneous reaction rates depend primarily on the initial T & P, whereas flame propagation depends primarily on the final T & P (see lecture 4)
  - As a result, operating conditions that affect knock and flame propagation are very different!!!
- Since knock occurs in end gas, need to see how operating conditions affect end gas T & P

How do operating conditions affect knock?

- Simple estimate of maximum T & P of end gas in terms of intake conditions T_2, P_2 and compression ratio r - assume adiabatic compression, constant-v combustion, reversible adiabatic compression of end gas to (maximum) pressure P_4

Isentropic compression: $P_3 = P_2 r^{\gamma}; T_3 = T_2 r^{\gamma-1}$

Constant-volume combustion: $T_4 = T_3 + fQ_R / C_v = T_2 r^{\gamma-1} + fQ_R / C_v$

Ideal gas: $P_4 v_4 = RT_4, P_3 v_3 = RT_3, v_4 = v_3 \Rightarrow P_4 = P_3 \left(T_4 / T_3\right) = P_{\text{end gas (max)}}$

$$P_{\text{end gas (max)}} = P_3 \left(T_4 / T_3\right) = P_2 r^{\gamma} \left[(T_3 + fQ_R / C_v)/T_3\right] = P_2 r^{\gamma} \left[1 + fQ_R / C_v T_2 r^{\gamma-1}\right]$$

$$T_{\text{end gas (max)}} = T_2 \left(P_4 / P_2\right)^{\gamma-1/\gamma} = T_2 \left(r^{\gamma}\left[1 + fQ_R / C_v T_2 r^{\gamma-1}\right]\right)^{\gamma-1/\gamma}$$

$$= T_2 \left(r^{\gamma-1}\left[1 + fQ_R / C_v T_2 r^{\gamma-1}\right]^{\gamma-1/\gamma}\right)$$

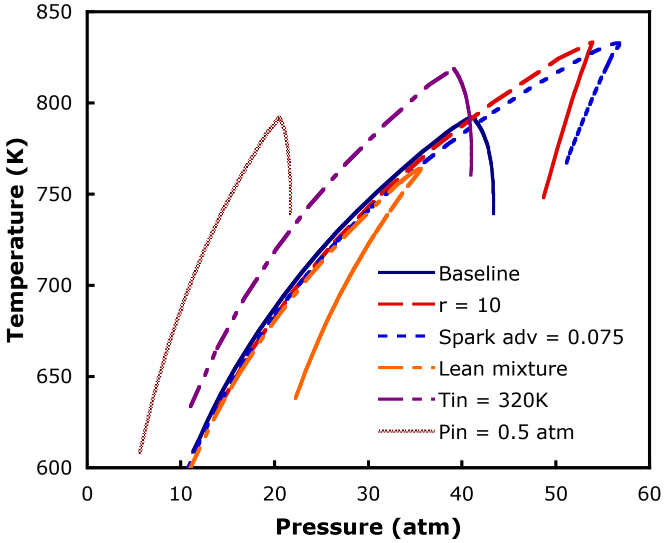
How do operating conditions affect knock?

- AirCycles4recips.xls end gas calculation
  - Assumes a tiny portion of mixture does not combust but undergoes compression/expansion according due to pressure increase /decrease of cylinder gas that DOES have heat input from combustion

$$P_{\text{end gas}} = P_{\text{rest of gas}}; T_{endgas,n+1} = T_{endgas,n} \left(P_{n+1} / P_n\right)^{\gamma-1/\gamma}$$

  - End gas undergoes heat loss according to usual formula
  - The following plot shows effects of compression ratio, spark advance, mixture strength, T_{intake} and P_{intake} on the P-T history of end gas

P-T trajectory of end gas (combustion process only)



For lean mixture case:
f = 0.051,
BurnDuration = 0.3,
BurnStart = 0.084
(best efficiency timing)

Baseline: $r = 8$, $\gamma = 1.3$, $f = 0.068$, $Q_R = 4.5 \times 10^7$ J/kg, $T_{in} = 300K$, $P_{in} = P_{exh} = 1$ atm
BurnStart = 0.045, BurnDuration= 0.15, BurnRateProfile = 0, h = 0.01, $T_{wall} = 400K$
$\eta_{comp} = \eta_{exp} = 0.9$

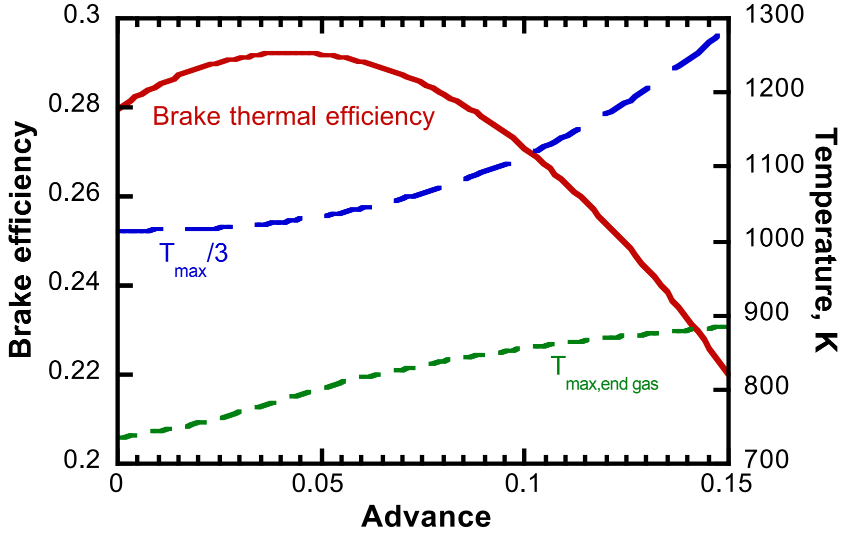
How do operating conditions affect knock?

- Compression ratio
  - As r ↑, $T_{\text{end gas}}$ ↑ and $P_{\text{end gas}}$ ↑, thus knock tendency ↑
  - Recall d[fuel]/dt ~ $P^n \exp(-E/\Re T)$, (n = order of reaction, E = activation energy) thus both P and T affect knock
  - P increases more than T, but reaction rate is more sensitive to T than P
- Intake temperature: increasing T_{intake} increases $T_{\text{end gas}}$, thus knock tendency ↑↑↑ (your car knocks more on a hot day)
- Intake pressure: increasing P_{intake} increases $P_{\text{end gas}}$, thus knock tendency ↑ (your car knocks when you put your foot to the floor)
- Engine RPM
  - Most important effect is less time available for knock to occur
  - At higher RPM, more turbulence, S_T increases, time needed for flame propagation to occur decreases
  - … but turbulence has no effect on time for homogeneous reaction of end gas
  - "Horse race" favors flame propagation horse at higher RPM

How do operating conditions affect knock?

- Spark timing
  - Page 19: as ignition timing is advanced, more “burn then compress” compared to “compress then burn” thus higher $T_{\text{end gas}}$
  - Also more time for knock to occur
  - Fundamental tradeoff between increasing spark advance to obtain best thermal efficiency and decreasing spark advance to minimize knock and NO_x
  - Spark advance up to ≈ 0.05 increases thermal efficiency (see next page) but there's a penalty in terms of knock ($T_{\text{end gas}}$ increasing) and NO_x (T_{max} increasing)
  - T_{max} and $T_{\text{end gas}}$ don't increase much as advance increases, but both knock and NO_x are high activation energy processes, so a little increase in T matters
  - Recall knock and NO_x are controlled by very different reactions, but for both higher T is worse

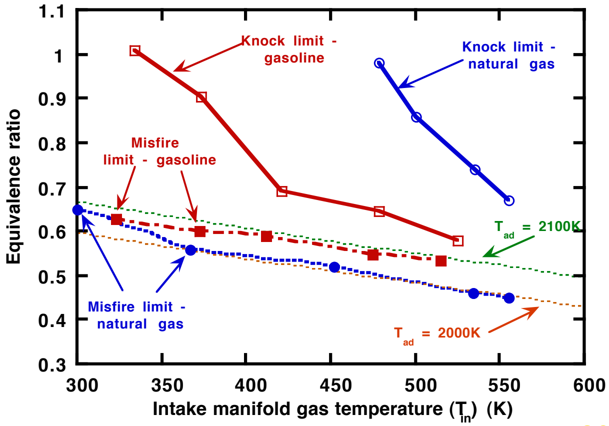
How do operating conditions affect knock?



How do operating conditions affect knock?

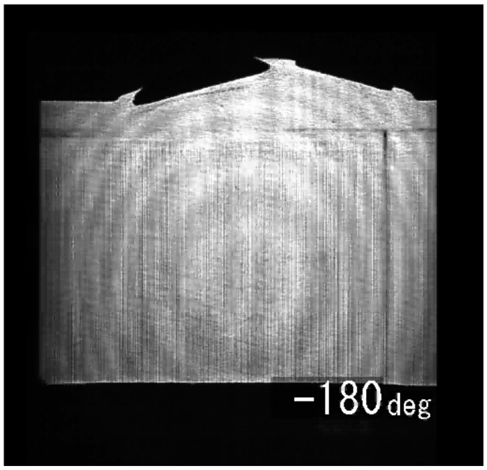
- Mixture strength
  - Leaner mixtures burn slower, so need more spark advance, but even when spark timing adjusted for best efficiency, still less knock that stoichiometric mixtures
  - Less heat release, thus lower peak P, thus lower $T_{\text{end gas}}$

Ronney, et al., J. Auto. Eng., (*Proc. Instit. Mech. Eng., Part D*), Vol. 208, pp. 13-24 (1994).



Sidebar topic: HCCI engines

- Actually, burning rapidly at minimum volume yields best possible thermal efficiency, but engine damage due to knocking
- Want to burn "fast but not too fast"
- Homogeneous Charge Compression Ignition (HCCI) engines - "controlled knocking"

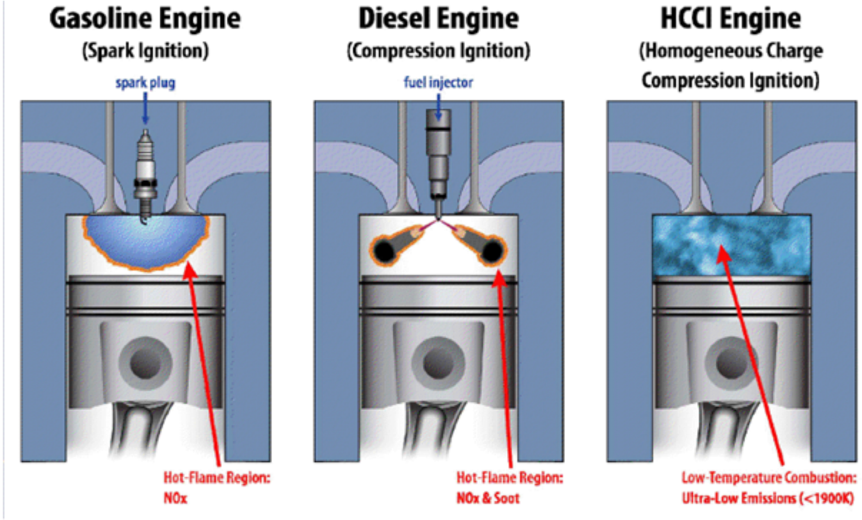


Video courtesy Prof. Yuji Ikeda, Kobe University

HCCI engines

- By using homogeneous reaction instead of flame propagation, no conventional flammability/misfire limit – recall (Lecture 4) for homogeneous reaction, burn time is nearly independent of ϕ
- With HCCI, in principle very lean mixtures with low T_{ad}, low peak temperature, low NO_x formation, etc. can be burned
- Lean mixtures - part-load operation without throttling losses
- Since we're asking for homogeneous ignition, use high compression ratios, thus high η_{th}
- Much more difficult to control <u>rate</u> and <u>timing</u> of homogeneous reaction than of spark-ignited propagating flame; various control schemes considered
  - Variable intake temperature
  - Variable exhaust gas recirculation
  - Variable compression ratio and valve timing
  - Cycle-to-cycle control probably needed
- As a result, not in commercial use yet (Mazda claimed they would in 2019 in "Skyactiv-X engine", but it's not yet available)

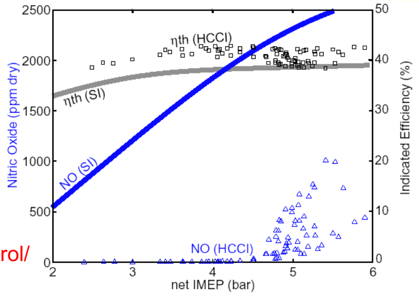
Comparison of gasoline, diesel & HCCI



HCCI experiments in a single-cylinder engine

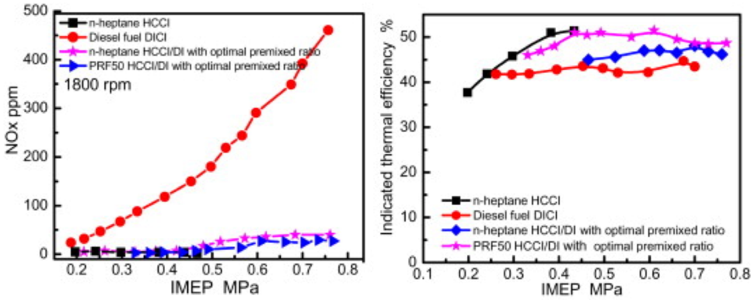
USC Viterbi School of Engineering

Throttled premixed-charge spark ignition (SI) vs. HCCI



http://www-cdr.stanford.edu/dynamic/hcci_control/MODELING_talk.pdf

Nonpremixed-charge Diesel (DICI) vs. HCCI



Prog. Energy Comb. Sci. 37, 741 (2011)

HCCI experiments in 6 cyl. engine (1 cyl. HCCI)

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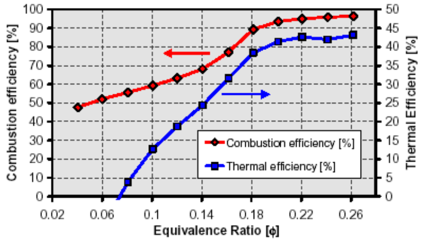
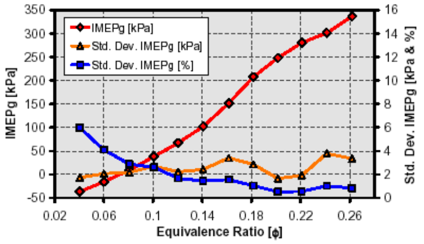
Efficiencies and Combustion Stability





CR = 18; P_{in} = 120 kPa; T_{in} = 140° C; Pre-Mixed

- Combustion efficiency drops from 95% to 60% as fuel is reduced to low-idle, ϕ = 0.1.
  - Similar drop in pressure-indicated thermal efficiency.
  - Commensurate with the rapid rise in CO.
- Std. Dev. of IMEP is 2 – 4 kPa for all fueling rates (ϕ).
  - Increase at ϕ = 0.16 due this being in the middle of the rapid rise in CO.
- Normalized σIMEP increases below ϕ = 0.1 because IMEP is near zero.
  - Std. Dev. of IMEPg ≤ 2.6% from ϕ = 0.1 to ϕ = 0.26.

http://www.orau.gov/deer/DEER2002/Session9/dec.pdf

HCCI - disadvantages (opportunities?)

- Difficult to control timing and rate of combustion
- If misfire occurs, gas mixture on next cycle will be too cold for autoignition and engine will stop
- Cold starting?
- Operating window for HCCI operation (load and engine RPM) is small - most HCCI concepts use conventional spark-ignited operation at higher loads (less-lean mixtures)
- Additional components for control system – increased cost - Mazda Skyactiv-X system has
  - Pressure transducers for every cylinder
  - Variable valve timing – switch to lower compression, spark-ignited operation when HCCI won't work
  - Supercharger
- Relatively high friction losses at low IMEP, thus FMEP is a higher % of BMEP

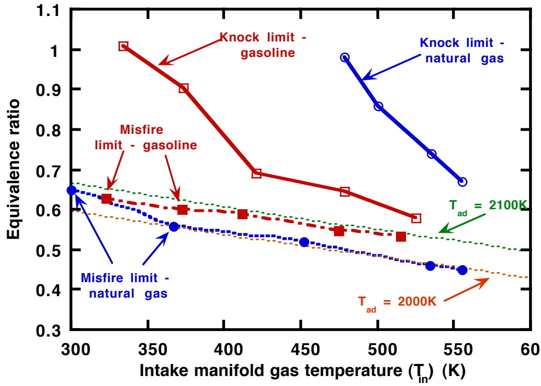
Misfire / ignition limits

- If an engine operates too lean or too rich, engine will operate roughly, misfire and may quit altogether
- The misfire limit is usually defined by a certain % standard deviation in IMEP
- With conventional spark ignition premixed-charge engines, misfire limit at $\phi \approx 0.65 - 0.75$, whereas in laboratory experiments typically $\phi \approx 0.5$
- Why the difference? In the laboratory, the mixture can take as long as it wants to burn, whereas in engine, limited time ~ 1/N available for burning - minimum turbulent burning velocity (S_T) requirement
- To avoid misfire
  - Increase burning velocity (S_T)
  - Increase time available for burning
  - Decrease time needed for burning

Misfire - effects of operating conditions

- Inlet temperature
  - As T_∞ ↑ with ϕ fixed, T_{ad} ↑, S_L ↑, thus S_T ↑ (slightly)
  - Since S_L depends more on T_{ad} than any other property, limit criterion is basically a minimum T_{ad} criterion
  - Recall $T_{ad} = T_\infty + fQ_R/C_v$ - can get a given T_{ad} with a high f (thus high ϕ) and low T_∞ or vice versa
  - "Brilliant" experiments show this - limit T_{ad} 2000K - 2100K

Ronney, et al., *J. Auto. Eng., (Proc. Instit. Mech. Eng., Part D)*, Vol. 208, pp. 13-24 (1994).



Misfire - effects of operating conditions

- Intake pressure
  - Recall $S_L \sim P^{(n-2)/2}$, with n ≈ 1.2, not much effect
  - … but as P_{intake} decreases, more exhaust gas (at 1 atm) relative to fresh mixture (at P < 1 atm), so more dilution of fresh mixture, thus lower T_{ad}, lower S_L, thus, more misfire at throttled conditions
- Turbulence: more turbulence, higher S_T - helps limit problem, but recall too much turbulence may extinguish flame!
- Engine RPM (N)
  - Time available for burning ~ 1/N
  - But $u' \sim u_{piston} \sim N$ and $S_T \sim u'$
  - So (time available for burning)/(time needed) ≈ constant
  - But actually $S_T \sim u'^{(1-\varepsilon)}$, so more misfire at higher N
- Multiple spark plugs: reduces distance each evolving flame kernel must propagate, less chance of misfire
- Knock additives, e.g. $(C_2H_5)_4Pb$: no effect (affects knock reactions, not flame propagation reactions)

Example #1

For the Otto cycle example in Lecture 9 with $r = 9$, $\gamma = 1.3$, $M = 0.029$ kg/mole, $f = 0.062$, $Q_R = 4.3 \times 10^7$ J/kg, $T_2 = 300$K, $P_2 = P_{in} = 0.5$ atm, $P_6 = P_{ex} = 1$ atm, $h = 0$, $\eta_{comp} = \eta_{exp} = 0.9$, determine the end gas temperature and pressure

If this were an ideal cycle we could use the formula on page 16, i.e.

$$P_{\text{end gas (max)}} = P_2 r^{\gamma}\left[1 + fQ_R / C_v T_2 r^{\gamma-1}\right]$$

$$= (0.5atm)\left(9^{1.3}\right)\left[1 + \frac{(0.062)\left(4.3\times10^7 J/kg\right)}{(955.6 J/kgK)(300K)\left(9^{1.3-1}\right)}\right] = 50.5atm$$

$$T_{\text{end gas (max)}} = T_2\left(P_4/P_2\right)^{\gamma-1/\gamma} = (300K)(50.5atm/0.5atm)^{1.3-1/1.3} = 870.5K$$

But since this is not an ideal cycle we compress the end gas isentropically from its pressure (9.165 atm) and temperature (611K) after compression to the pressure after combustion (51.02 atm) , i.e.

$$T_{\text{end gas (max)}} = T_3\left(P_4/P_3\right)^{\gamma-1/\gamma} = (611K)(51.02atm/9.165atm)^{1.3-1/1.3} = 908K$$

which is not much different.

Example #2

During WWII, fighter aircraft engines were equipped with systems to inject water into the cylinders during compression. How would water injection affect

(a) **Knock tendency**: The water would cool the intake charge and decrease its γ (since $\gamma_{H2O} < \gamma_{air}$) thus reducing the end-gas temperature substantially. Also, while the compression ratio could not be changed, the intake pressure could be increased (these were turbocharged engines) without knocking, thus allowing more air to be ingested

(b) **Misfire tendency:** The greater mass of un-burnable water vapor and its higher C_p (compared to air) led to lower T_{ad}, thus more tendency to misfire. This limited the amount of water that could be injected.

(c) **Power:** This was the main reason for water injection. The liquid water requires much less Work/mass to compress than air (Work = $\int PdV$ thus Work/m = $\int Pd(V/m) = \int Pd(1/\rho)$, and $\rho_{water} >> \rho_{air}$), yet when the liquid water vaporizes, its volume increases tremendously, generating more expansion work / compression work (this is why steam cycles are more efficient that gas cycles!) Also as mentioned above, the intake air pressure could be increased, thus allowing more fuel to be added and burned

(d) **Brake thermal efficiency:** The slower burning would decrease efficiency, but the steam cycle has inherently higher efficiency, so it could go either way.

(e) **Work per unit mass of (fuel + water):** This would definitely decrease, since the water provided no additional heat release but much additional mass. In actuality, these aircraft used a methanol/water mixture, not just water, to recover some energy release from the injected liquid (though note methanol has only 40% of Q_R of gasoline)

Summary

- Knock
    - Rapid homogeneous reaction in “end gas” ahead of flame front
    - “Horse race” between knock (bad) and flame propagation (good)
    - Knock tendency depends on reaction rates at initial T, P & composition of reactants (end gas), flame propagation depends on final (burned gas) temperature, so factors affecting knock & flame propagation are very different
    - Knock tendency characterized by octane number - higher ON, more resistant to homogeneous reaction
    - Diesel fuels - opposite characteristics desired
- Misfire / flammability limits
    - Due to insufficient time to burn - roughly corresponds to fixed T_{ad}
    - Depends on required propagation time (~ d/S_T) vs. available time (~1/N)