# APPLIED THERMODYNAMICS

## Internal Combustion Engines (Module III)

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## List of Topics



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## Lecture 6

Thermochemistry and Fuel Characteristics

- Fuels for IC Engines
- Thermochemistry of Fuels
- Self Ignition and Ignition Delay
- Knock Phenomena in SI Engines
- Octane Number of SI Engine Fuels
- Cetane Rating of CI Engine Fuels

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## Fuels for IC Engine

- Most IC engines obtain their energy from combustion of a hydrocarbon fuel with air. The engine converts heat energy of chemical combination into the mechanical energy and then to shaft power.
- Heat energy is derived from the fuel, thus, a fundamental knowledge of types of fuel and their characteristics is essential for combustion phenomena.
- The characteristics of the fuel have considerable influence on design, efficiency, output , reliability and durability of engine.
- The choice of automobile fuel plays a pivot role in atmospheric pollution.
- Fuels in general are available in solid, liquid and gaseous form. IC engines are typically habituated with petroleum fuels (petrol and diesel) commonly known as fossil fuels.
- Gaseous fuels (compressed natural gas – CNG, liquefied petroleum gas – LPG, hydrogen, biogas) are considered as alternative fuels for IC engine.
- Alternative liquid fuel – methanol, ethanol, blended alcohol, bio-diesel.

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## Fuels for IC Engine

**Hydrocarbon fuels (gasoline)**

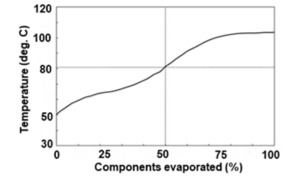
- The hydrocarbon family form 4-bonds in molecular structure while hydrogen has one bond. A 'saturated' hydrocarbon has no double/triple carbon-carbon bond and will have maximum hydrogen atom. An 'unsaturated' molecule will have double/triple carbon-carbon bonds.
- ➢ Paraffins ($C_nH_{2n+2}$): methane ($CH_4$), butane ($C_4H_{10}$), iso-octane ($C_8H_{18}$) etc
- ➢ Olefins ($C_nH_{2n}$): ethane ($C_2H_4$)
- ➢ Alcohols: methanol ($CH_3OH$), ethanol ($C_2H_5OH$), propanol ($C_3H_7OH$) etc
- Gasoline is the main fuel for SI engines which is a mixture of hydrocarbon components manufactured from crude petroleum.
- "Vapour lock" is serious phenomena that occurs in SI engine for which the fuel vaporizes in the supply line/carburetor of hot engine compartment. When it happens, the fuel is cut-off and the engine stops. So, the "temperature-vaporization curve" is considered for gasoline where the fuel components vaporize at different temperatures.



## Fuels for IC Engine

**Hydrocarbon fuels (gasoline)**

- The "temperature-vaporization" for gasoline mixture shows the fuel components getting vaporized in phased manner. Typically, gasoline is classified as, 57-81-103°C for which 50% of fuel vaporizes at 81°C.
- At low temperatures, the small molecular weight components boil and known as "front-end volatility" components (useful for cold-starting of engine).
- The volumetric efficiency of the engine reduces when the fuel vapour replaces too early in intake system. So, the larger molecular weight components are allowed to vaporize at highest temperature, known as "high-end volatility".






## Fuels for IC Engine

**Hydrocarbon fuels (diesel)**

- Diesel fuel (diesel oil/fuel oil) can be obtained from crude oils over large range of molecular weights and physical properties. In general, greater is the refining done on fuel sample, lower is the molecular weight, viscosity and higher cost.
- The diesel fuels in IC engines can be divided in two extreme categories based on their intended use in light and heavy vehicles: light diesel ($C_{12.3}H_{22.2}$; molecular weight 170) and heavy diesel ($C_{14.6}H_{24.8}$; molecular weight 200).
- Light diesel fuel is less viscous, easier to pump, injects small droplets but costly while heavy diesel fuels are highly viscous and have higher injection pressures with less cost.
- Heavy diesel fuels are used in bus/truck, marine engines, stationary engine often integrated with intake heating system so as to reduce the viscosity of the fuel.



## Thermochemistry of Fuels

**Combustion reaction**

- Most of the fuels constitute mainly hydrocarbons with traces of oxygen, nitrogen and sulphur etc.
- Maximum energy is released from the fuel in the form of 'heat' when the fuel reacts with adequate amount of oxygen. Such condition is known as stoichiometric combination of fuel and oxygen in terms of its molecular mass. This ratio is just enough to convert all carbon in the fuel to carbon dioxide and all hydrogen to water with no left over oxygen. The stoichiometric reaction of methane and iso-octane fuels with oxygen are given below: $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$; $C_8H_{18} + 12.5 O_2 \rightarrow 8CO_2 + 9H_2O$
- Pure oxygen for engines are hardly used rather air (78% $N_2$ and 21% $O_2$) is considered as source of oxygen for reaction with fuel. Then, the above stoichiometric reaction with air can be given below:

$$CH_4 + 2O_2 + 2(3.76)\ N_2 \rightarrow CO_2 + 2H_2O + 2(3.76)\ N_2$$

$$C_8H_{18} + 12.5O_2 + 12.5(3.76)\ N_2 \rightarrow 8CO_2 + 9H_2O + 12.5(3.76)\ N_2$$

## Thermochemistry of Fuels

**Combustion reaction**

- **If methane is burnt with 150% stoichiometric air (lean fuel), then excess oxygen is liberated as products.**

$$CH_4 + 3O_2 + 3(3.76)\ N_2 \rightarrow CO_2 + 2H_2O + 3(3.76)\ N_2 + O_2$$

- **When, iso-octane combustion takes place with 80% stoichiometric air (rich fuel), carbon monoxide (CO) becomes residual product since there is not enough oxygen. CO is a odorless, colorless and poisonous gas that can be further burnt to form $CO_2$. This combustion process happens with deficiency in air/oxygen.**

$$C_8H_{18} + 10O_2 + 10(3.76)\ N_2 \rightarrow 8CO_2 + 9H_2O + 5CO + 12.5(3.76)\ N_2$$

- **Hence, for actual combustion in engine, "equivalence ratio" is defined as measure of relative fuel-air ratio with respect to stoichiometric fuel-air ratio.**

$$\phi = \frac{(FA)_{act}}{(FA)_{stoich}} = \frac{(AF)_{stoich}}{(AF)_{act}};\ FA = \frac{m_f}{m_a};\ AF = \frac{m_a}{m_f}$$

$\phi < 1 \Rightarrow$ Lean fuel, oxygen in exhaust; $\phi > 1 \Rightarrow$ Rich fuel, CO & fuel in exhaust

$\phi = 1 \Rightarrow$ Stoichiometric fuel, maximum energy release from fuel



## Thermochemistry of Fuels

**Chemical equilibrium**

- **Consider a general chemical reaction for which the equilibrium compositions can be found through chemical equilibrium constant.**

$\nu_A A + \nu_B B \rightarrow \nu_C C + \nu_D D$; $A$ & $B$ are reactant species while $C$ & $D$ are product species

$\nu_A, \nu_B, \nu_C$ & $\nu_D$ are stoichiometric coefficients of $A, B, C$ & $D$

Equilibrium constant, $K_e = \left(\frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}}\right)\left(\frac{p}{N_t}\right)^{\Delta\nu}$; $\Delta\nu = \nu_C + \nu_D - \nu_A - \nu_B$; $p$: Total absolute pressure (atm);

$N_i$: Number of moles of component $i$ at equilibrium; $N_t$: Number of moles at equilibrium

- **The equilibrium constant is strongly dependent on temperature and shifts to right for higher temperature for maximizing entropy.**
- **For hydrocarbon fuels in IC engines, its value is large enough so that very little reactants are left at equilibrium.**
- **At high temperatures, dissociation can happen for $CO_2 \rightarrow CO + O$; $O_2 \rightarrow O + O$; $N_2 \rightarrow N + N$ and at the same time atoms of nitrogen and carbon can readily combine to form oxides of nitrogen (NO & $NO_2$) and carbon (CO & $CO_2$) that are source of pollution. Thus, thermal efficiency of engine is lowered.**



## Thermochemistry of Fuels

**Heating value of fuel**

- **The heat liberated by combustion reaction between hydrocarbon fuel and air is the difference between the total enthalpy of products and reactants. It is commonly known as "heat of reaction/heat of combustion/enthalpy of reaction" and is a negative quantity. The heating value of the fuel ($Q_{HV}$) is taken as negative of heat of reaction for one unit of fuel.**
- **When the exhaust gases of IC engine are cooled below their dew point temperature, the water vapour at the exhaust starts to condense to liquid. It is known as exhaust dew point temperature. This is a very common phenomena to see water droplets coming out of automobile exhaust pipes when the engine is started and the pipe is cold.**

$Q = \sum_{prod} N_i h_i - \sum_{react} N_i h_i$; $h_i = \left(h_f^o\right)_i + \Delta h_i$; $N_i$ : Number of moles of component $i$;

$\Delta h_i$ : change of enthalpy from standard temperature for component $i$;

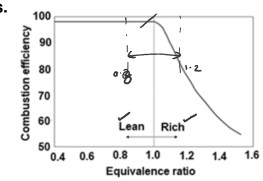
$h_f^o$ : enthalpy of formation for the species at standard pressure and temperature

$Q_{HV} = -Q$; $Q_{HHV} = Q_{LHV} + \Delta h_{vap}$; $Q_{in} = \eta_c\, m_f\, Q_{LHV}$ comb. eff.



## Thermochemistry of Fuels

- **There are two heating value of fuel – higher heating value ($Q_{HHV}$) is considered when the water in the exhaust product is in liquid state. The lower heating value ($Q_{LHV}$) is used when the water in the product is mainly vapour. The difference between these values is the heat of vaporaization of water. It is logical to use lower heating value of fuel while considering heat input (Qin) for conversion of work output through combustion efficiency.**
- **The combustion efficiency is a function of fuel equivalence ratio and its value is about 98% when engines (mostly CI) operate with lean mixture.**
- **When engine operate with fuel-rich, there is not enough oxygen to react with the fuel and combustion efficiency decreases.**



## Thermochemistry of Fuels

**Adiabatic flame temperature**

- The maximum combustion temperature through fuel and oxygen in IC engine can be considered as theoretical estimate. It is known as "adiabatic flame temperature" of input air-fuel mixture. Mathematically, it is represented as by considering the heat of reaction as zero.
- Assuming the inlet conditions of reactants are known, it is necessary to find the temperature of product such that the equation is satisfied.
- The adiabatic flame temperature is the ideal theoretical maximum temperature that can be obtained for a given fuel and air mixture. The actual peak temperature may be several hundred degree less than this value due to heat loss and combustion efficiency.

$$Q = \sum_{prod} N_i h_i - \sum_{react} N_i h_i = 0 \quad \Rightarrow \sum_{prod} N_i h_i = \sum_{react} N_i h_i$$

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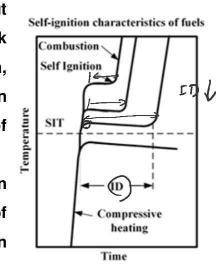
## Self Ignition and Ignition Delay

- When the temperature air-fuel mixture is raised high enough, the mixture will self ignite without involvement of any external device (such as spark plug or fuel igniter). The temperature above which, this phenomena occurs, is known as "self ignition temperature (SIT)". This is the basic principle of ignition in CI engines.
- The temperature rise at the end of compression stroke is higher than SIT of fuel so that self ignition of fuel occurs when it is injected into the combustion chamber. If a fuel-air mixture is heated to a temperature above SIT, the self-ignition will occur after a short time, known as "ignition delay (ID)". Typically, ID is of the order of thousandths of a second.

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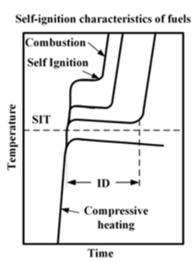
## Self Ignition and Ignition Delay

- ID is generally a very small fraction of a second, during which pre-ignition reaction occurs.
- It includes oxidation of small fuel components an cracking of larger HC molecules into smaller one. This pre-ignition rises temperature of local spots and promotes actual combustion.
- If the temperature of the fuel is raised above SIT, the fuel will spontaneously ignite after a short ID.
- For CI engines, higher is the initial temperature rise above SIT, the shorter will be the ID and vice-versa.
- The values of SIT and ID for a given air-fuel mixture, depends on many factors such as temperature, pressure, density, turbulence, air-fuel ratio, swirl, turbulence and presence of inert gases.

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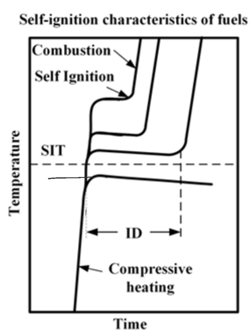
## Self Ignition and Ignition Delay

- If a combustible mixture is heated to a temperature below SIT, no ignition occurs. It is an ideal scenario for SI engines.
- The self-ignition (or pre-ignition or auto-ignition) is not desirable for SI engine.
- Here, a spark plug is used to ignite the mixture at proper time in the cycle. Hence, the CR in SI engines is limited within 11 to avoid self-ignition.

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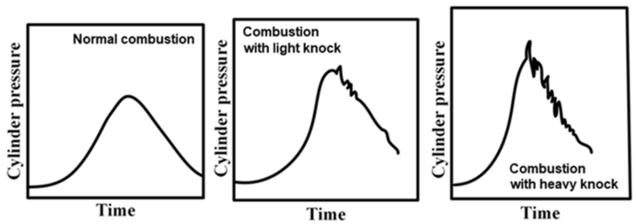
## Knock Phenomena in SI Engines

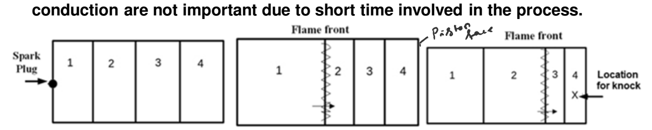
- When self-ignition occurs in SI engines, the pressure pulses are generated higher than the desirable value. These pulses can damage the engine and often fall under audible frequency range. This phenomena is known as "knock/ping".
- From the *pressure-time* history, the pressure force on piston follows a smooth pattern with no self-ignition while the curve becomes oscillatory indicating undesirable force patterns with self-ignition.






## Knock Phenomena in SI Engines

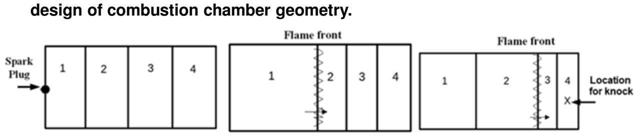
- A simple approach to explain the knock in SI engines is followed by visualizing the combustion chamber as a long hollow tube divided into equal mass units with equal volume with spark plug located at left end.
- Combustion starts with spark plug on the left side and flame front travels from left to right. Then, the temperature of the burnt gases is increased to a high value. As a result the pressure of burnt gases also increases and they expand the volume of that mass.
- The unburnt gases in front of the flame-front is compressed by this high pressure and the compression heating results in higher temperature of the gas. The temperature of unburnt gases is further raised by radiation heating from the flame even with higher pressure. At this juncture, the convection and conduction are not important due to short time involved in the process.

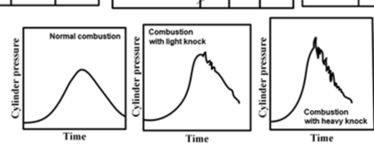





## Knock Phenomena in SI Engines

- The flame front continues to compress unburnt mixture into smaller volume in subsequent units, which increases pressure as well as temperature.
- If compression stroke raises temperature of end gas above SIT, self-ignition and knock can occur. In order to avoid knock, it is necessary for the flame to pass through and consume all unburnt gases which have risen above SIT before the ID lapses. This can be done by combination of fuel property and design of combustion chamber geometry.

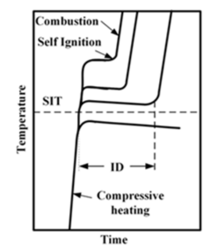


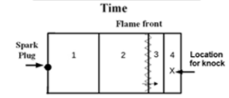






## Knock Phenomena in SI Engines

- The hottest part in the cylinder is near the spark plug at the end of combustion. This part remains hot through out the combustion process due to compression heating and radiation of the flame front.
- Hence, by limiting CR in SI engines, the temperature at the end of compression stroke can be limited. This will subsequently reduce the temperature throughout the process and knock can be avoided.
- On the other hand, a high CR will result high temperature at the start of the combustion. This will cause all temperatures in the rest of the cycle in higher limit. The higher temperature will create short ID time and knock is likely to occur.



## Octane Number of SI Engine Fuels

Octane number *vs* engine knock

- Octane number (ON)/octane is the property that describes effectiveness of self-ignition of a SI engine fuel. A numerical value (0 to 100) is generated by comparing the self-ignition characteristics of the fuel to that of standard fuels in a specific test engine at specific operating conditions.
- There are two standard reference fuels i.e. iso-octane (2,2,4 trimehylpentane, $C_8H_{18}$; ON = 100) and n-heptene ($C_7H_{16}$; ON = 0) are considered. All available SI engine fuels are assigned an octane number based on reference fuels.
- Higher is the ON of a fuel, it is less likely to self-ignite. In order to avoid self-ignition and knock, high CR engines must use high ON fuels and vice versa.
- The ON value to a fuel is assigned by three standard methods:
  - Motor octane number (MON): automobile fuels for SI engines
  - Research octane number (RON): supplied by fuel manufacture
  - Aviation octane number (AON): used for aircraft (aviation fuels)

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## Octane Number of SI Engine Fuels

Octane number *vs* engine knock

- When several fuels with known ON are mixed, a good approximation is to obtain the ON of blended fuels with their mass percentage.

  $ON_{blend}$ = (% of A) ($ON_A$) + (% of B) ($ON_B$) + (% of C) ($ON_C$)
- "Anti-knock index (AKI)" is normally assigned to all fuels available at filling station and standardized as octane rating of any given fuel. [AKI = (MON + RON)/2]
- Operating conditions used to measure MON is more severe than those used as RON. Hence, "fuel sensitivity (FS)" is defined for most of the fuels with acceptable range between 0 to 10. (FS = RON – MON)
- The common values of ON (or AKI) for gasolines used in automobiles fall in the range of 87 to 95.
- Apart from ON, the deposits build up in the combustion chamber with aging, lowering of clearance volume, surface ignition due to local hot-spots on the combustion chamber wall are some of the other causes of knocking in engines.

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## Cetane Rating of CI Engine Fuels

Cetane number

- In a CI engine, self-ignition of air-fuel mixture is a necessity. The correct fuel must be chosen which will self-ignite at precise time in the engine cycle. So, the knowledge of and control of ID is a vital requirement.
- The property that quantifies self-ignition characteristics of diesel fuel is known as "cetane rating or cetane number (CN)".
- The larger CN fuels will have shorter ID and quicker self-ignition. Low CN fuels will have longer ID.
- There are two standard reference fuels for CN calculation i.e. n-cetane (hexadecane; $C_{16}H_{34}$; CN = 100 & heptamethylnonane (HMN; $C_{12}H_{34}$; CN = 15).

  CN of fuel = (% of n-cetane) + (0.15) (% of HMN)
- The normal CN values for vehicle fuels is about 40 to 60.
- There is a strong inverse correlation between CN of a fuel and its ON.
- The CN of a fuel can be raised by certain additives mainly nitrates and nitrides, organic peroxide, Sulphur compounds.

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## Cetane Rating of CI Engine Fuels

Cetane number

- CN is a measure of ID and is matched to a given engine cycle and injection process. Generally, ID $\alpha$ (1/CN) and CN $\alpha$ (1/ON)
- For a given injection timing and rate, if the CN is very low, it will have following consequences:
  - Longer ID and low thermal efficiency (because more than desirable fuel quantity enters the cylinder before the combustion starts)
  - More fuel (than desirable – very rich air-fuel mixture) will be injected before 1st fuel particle ignites and unacceptable levels of exhaust emission
  - Fast pressure rise at the start of combustion i.e. larger initial force on piston face, thus rough engine cycle
- For a given injection timing and rate if the CN is very high, it will have following consequences:
  - Combustion starts early in the cycle (before TDC)
  - Pressure rises before TDC
  - More work is required for compression stroke and thus loss in engine power

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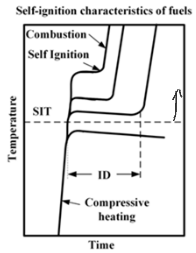
## Cetane Rating of CI Engine Fuels

**Ignition delay vs Cetane number**

- Typically, ID falls in the range of 0.4 to 3 ms for a combustible air-fuel mixture.
- Increase in temperature, pressure, engine speed and CR leads to decrease in ID.
- Fuel droplet size, injection velocity, injection rate, and physical characteristics of fuel have no impact on ID.
- ID is almost constant in cycle time that results fairly constant crank-shaft angle position for combustion process at all speeds.
- If the injection process occurs too early, ID will increase because the temperature and pressure in the cylinder is lower.
- If injection occurs late, the piston will move past TDC so that the temperature and pressure will decrease. Hence, ID will increase.






## Numerical Problems

**Q1. In a SI engine, the isooctane is burnt with 115% theoretical air. Calculate the air-fuel ratio, fuel-air ratio and equivalence ratio.**

**Stoichiometric reaction for Isooctane: $C_8H_{18} + 12.5O_2 + 12.5(3.76)\,N_2 \rightarrow 8CO_2 + 9H_2O + 12.5(3.76)\,N_2$**

Actual $C_{18}H_{18} + 14.375\,O_2 + 14.375(3.76)N_2 \longrightarrow 8CO_2 + 9H_2O + 14.375(3.76)\,N_2 + 1.875\,O_2$

(i) $AF = \frac{m_a}{m_f} = \frac{N_a M_a}{N_f M_f}$

$M_f = 114$. $M_a = 29$

$N_a = 14.375$ $N_f = 1$

$AF = 17.4$

(ii) $FA = \frac{1}{AF} = \frac{m_f}{m_a} = 0.057$

$(FA)_{stoi} = \frac{m_f}{m_a} = \frac{N_f M_f}{N_a M_a}$

$N_f = 1$ $M_f = 114$

$N_a = 12$ $M_a = 29$

$(FA)_{stoi} = 0.066$

(iii) $\phi = \frac{(FA)_{act}}{(FA)_{stoi}} = \frac{0.057}{0.066}$

$\phi = 0.87$ Lean



## Numerical Problems

**Q2. A fuel is designed through blending by weight with 10% butane, 70% triptane and 15% isodecane. Determine the anti-knock index and sensitivity of blended fuel with respect to combustion chamber geometry.**

**Octane rating of blended fuel, $ON_{blend}$ = (% of A) ($ON_A$) + (% of B) ($ON_B$) + (% of C) ($ON_C$)**

| Fuel | RON | MON | % |
|---|---|---|---|
| A : Butane | 99 | 80 | 10 |
| B : Triptane | 112 | 101 | 70 |
| C : Isodecane | 113 | 92 | 15 |

$\rightarrow (ON)_{blend}$

$(RON)_b = 103$

$(MON)_b = 92.5$

$AKI = \frac{RON + MON}{2} = 97.5$

$FS = RON - MON = 10.5 > 10$

$\downarrow$

Slight tendency to knock.



## Numerical Problems

**Q3. It is desired for a combustion to start at 15°bTDC in a CI engine running at 1600 rpm with diesel having cetane number of 45 for which the ignition delay is 5.2°CA. Calculate the ignition delay in time scale and start of fuel injection in terms of °CA.**

Soln

$ID\,(time) = \frac{\text{Crank angle}}{\text{Crank speed}} = \frac{\left(\frac{5.2}{360}\right)\text{rev}}{\left(\frac{1600}{60}\right)\text{rev/s}}$

$ID = 0.54\ ms$ (45 CN)

[Range 0.5 ms to 3 ms.]

Fuel injection = ID + Start of combustion

$= 5.2 + 15 = 20.2\ bTDC$

$\downarrow$

bTDC

# THANK YOU

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