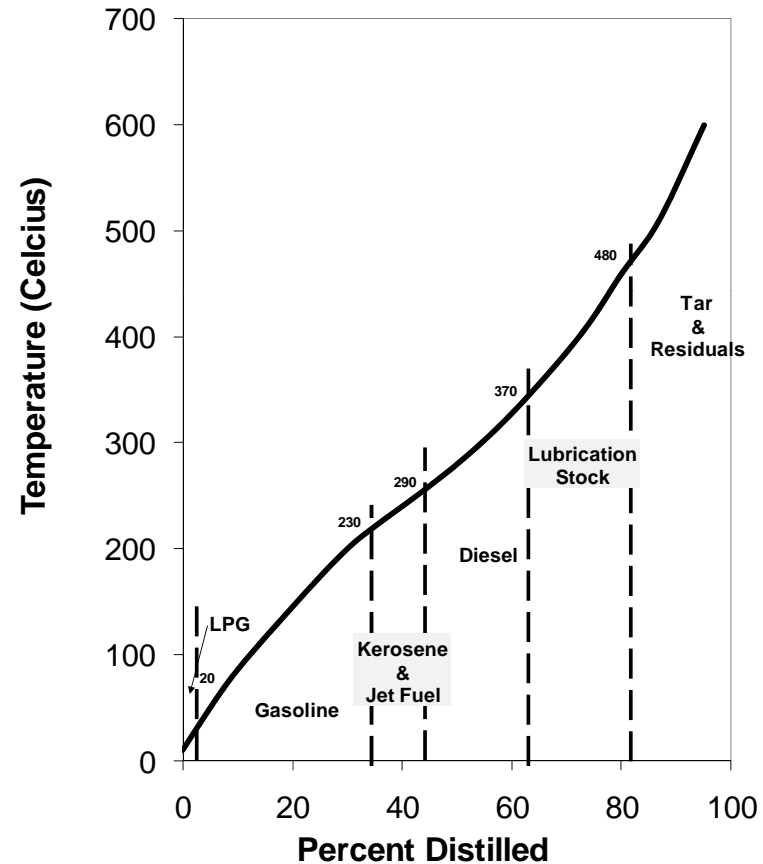




# Crude Oil and Distillation

- Fractionation tower,
  - hydrocarbons condensing and re-vaporizing
- The heaviest components (high boiling temperatures)
  - withdrawn toward the bottom of the tower
- lighter components rise through the tower
  - withdrawn higher up the tower
  - temperatures are cooler.
- For proper engine performance
  - Fuels boiling ranges:
    - Gasoline: 30-230°C
    - Diesel: 230-370°C



Typical Distillation curve of Louisiana-Mississippi (after Georing, 1986)

# Combustion and Exhaust Emissions

Complete Combustion (**Stoichiometric Combustion**) ,fuel burns completely to produce carbon dioxide and water.

Note: Atomic Mass Carbon=12, Hydrogen=1 Nitrogen=14, Oxygen=16

Molecular Mass :  $C_8H_{18} = [8(12)+18(1)]=114$  (Octane, which is used to represent gasoline)

$C_{16}H_{34} = [16(12)+34(1)]=226$  (Cetane, which is used to represent diesel)

$$CO_2 = [12+2(16)]=44$$

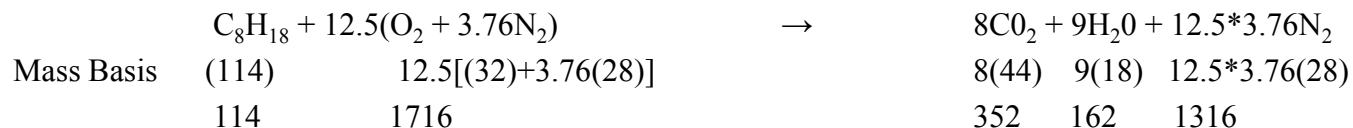
$$CO = [12+(16)]=28$$

$$H_2O = [2(1)+16]=18$$

$$N_2 = [2(14)]=28$$

$$O_2 = [2(16)]=32$$

Gasoline: ( Octane  $C_8H_{18}$  )



Therefore: For Stoichiometric (chemically correct) Air to Fuel Ratio is:

$$\begin{aligned} \text{A/F Ratio} &= \text{Mass Air} / \text{Mass Fuel} \\ &= 1716/114 \\ &= 15.05 \end{aligned}$$

When fuel burns at the Stoichiometric ratio, the maximum amount of energy is released from the fuel, i.e., Highest thermal efficiency.

# Combustion and Exhaust Emissions

Diesel: ( Cetane C<sub>16</sub>H<sub>34</sub>)



Therefore: For Stoichiometric (chemically correct) Air to Fuel Ratio is:

$$\begin{aligned}
 \text{A/F Ratio} &= \text{Mass Air} / \text{Mass Fuel} \\
 &= 3363.36/226 \\
 &= 14.88
 \end{aligned}$$

When fuel burns at the Stoichiometric ratio, the maximum amount of energy is released from the fuel, i.e., Highest thermal efficiency.

For Rich Mixture: More Fuel available than air, that is the air fuel ratio less than 15 for gasoline and A/F ratio > 14.88 for diesel. For instance if A/F ratio=10

**What will be the products of combustion for rich mixture?: Water, Carbon Dioxide, Carbon Monoxide, (and even in some unburnt fuel).** This will produce less heat energy per mass of fuel, that is reduce the thermal efficiency.

For Lean Mixture: More Air available than that required for complete combustion of the fuel, that is the air fuel ratio greater than 15. For instance if A/F ratio > 15.05 for gasoline and A/F ratio > 14.88 for diesel

**What will be the products of combustion for lean mixture: Water, Carbon Dioxide, and excess oxygen.**

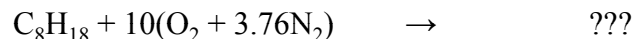
# Combustion and Exhaust Emissions

Example Rich Mixture, A/F ratio of 12.04 (Gasoline): That is for every 114 kg of fuel 1372.8 kg of air is available.

( For this example assume no unburnt fuel remains.)

For 114kg of fuel,  $\rightarrow 114/\text{molecular Mass fuel} = 114/(114)$  kmoles of fuel available  
 $= 1$  kmoles fuel.

For 1372.8 kg of air,  $\rightarrow 1372.8/(\text{'molecular mass' of air mixture}) = 1372.8/[(32)+3.76(28)]$  kmoles of air  
 $= 10$  kmoles air



All Hydrogen will become water, and nitrogen molecule will be unchanged.



Therefore 4.5(O<sub>2</sub>) molecules will be left to burn with the 8 carbon atoms remaining



For mass balance: Carbon;  $8 = x + y$   
 Oxygen;  $5.5(2) = x(2)+y(1)$   
 Solving for x & y,  $x=3, y=5$



Check Mass

Mass Basis	(114)		10[(32)+3.76(28)]	$\rightarrow$	3(44)	5(28)	9(18)	10*3.76(28)
	114	+	1372.8		132	+ 140	+ 162	+ 1052.8
			1486.8				1486.8	T

Check A/F Ratio

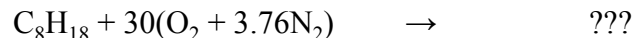
A/F Ratio =  $1372.8/114 = 12.04$  T

# Combustion and Exhaust Emissions

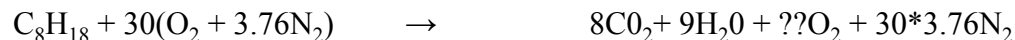
Example Lean Mixture, A/F ratio of 36.13 (Gasoline): That is for every 114 kg of fuel 4118.4 kg of air is available.

For 114kg of fuel,  $\rightarrow 114/\text{molecular Mass fuel} = 114/(114)$  kmoles of fuel available  
 $= 1$  kmoles fuel.

For 4118.4 kg of air,  $\rightarrow 4118.4/(\text{'molecular mass' of air mixture}) = 4118.4/[(32)+3.76(28)]$  kmoles of air  
 $= 30$  kmoles air



Excess air, therefore all Hydrogen and carbon atoms in fuel will become water, and carbon dioxide.



Therefore  $30(\text{O}_2) - 8(\text{O}_2) - 9/2(\text{O}_2) = 17.5$  molecules of oxygen will be left after carbon dioxide and water produced



Check Mass

	$\text{C}_8\text{H}_{18} + 30(\text{O}_2 + 3.76\text{N}_2)$	$\rightarrow$	$8\text{CO}_2 + 9\text{H}_2\text{O} + 17.5\text{O}_2 + 30*3.76\text{N}_2$	
Mass Basis	(114)    30[(32)+3.76(28)]		8(44)    9(18)    17.5(32)    30*3.76(28)	
	114    +    4118.4		352    162    560    3158.4	
			4232.4	

Check A/F Ratio

$$\text{A/F Ratio} = 4118.4/114 = 36.13$$

# Blended Fuels

$C_{xc}H_{yc}O_{zc}$  represents a blended fuel with  
primary fuel  $C_{xp}H_{yp}O_{zp}$  and  
secondary fuel  $C_{xs}H_{ys}O_{zs}$

$$R_s = (\rho_s/\rho_p) * (f_s/f_p) * (m_p/m_s)$$

Where:

$R_s$	number of moles of secondary fuel per mole of primary fuel
$\rho_p, \rho_s$	density of primary and secondary fuel, respectively
$m_p, m_s$	molecular mass of primary and secondary, fuel respectively
$f_p$	fraction of blended fuel volume occupied by primary fuel
$f_s$	fraction of blended fuel volume occupied by secondary fuel

$$xc = xp + R_s * xs$$

$$yc = yp + R_s * ys$$

$$zc = zp + R_s * zs$$

# Exhaust Emissions

Assumed that all the air/fuel mixture is homogenous. However, in a real engine areas

- Rich mixture
- lean mixture.
- Therefore, even with rich mixtures
  - some oxygen present in the emissions
  - most the oxygen will be in the form of carbon dioxide and carbon monoxide.
- Likewise in lean mixtures,
  - some carbon monoxide will be produced, and engines ventilated area to prevent carbon monoxide poisoning.
- Gasoline engines
  - operate near the Stoichiometric ratio, 8-20:1
  - Fuel & air is mixed with the air in the intake manifold , homogenous mixture.
- Diesel engines
  - much leaner than the Stoichiometric ratio to achieve complete combustion of the fuel.
  - fuel is injected into the cylinder immediately prior
  - little time for mixing,
  - excess air must be present for complete combustion and prevent excess smoke.
  - significant amount of oxygen is present in the exhaust.
- Exhaust emissions will contain other combustion products, in addition to carbon dioxide, carbon monoxide, oxygen and water.
  - Unburnt hydrocarbons and soot will be found in the exhaust.
  - At high temperatures the nitrogen molecule will be broken down
  - nitrogen oxide (NO) and nitrogen dioxide (NO<sub>2</sub>) nitrous oxides (NO<sub>x</sub>).
  - This is a particular problem with diesel engines.

# Fuel Property Measurements

Many different standards have been developed to measure fuel properties. Most of the standards have been developed through the efforts of American Society of Testing Materials (ASTM), Society of Automotive Engineers (SAE) and American Petroleum Institute (API)

**Specific Gravity** is defined as the ratio of the density of fuel at 15.6°C (60°F) to the density of water at the same temperature.

The specific gravity is measured with a **hydrometer**. Some hydrometer include a thermometer and correction scale so the SG can be measured at any temperature and then calibrated to the standard temperature.

The American Petroleum Institute (API) has devised a special scale for gravities. This scale can be used to estimate the heating value of fuels. It is expressed in API degrees and is calculated as follows:

$$\text{API}^\circ = 141.5/\text{SG} - 131.5$$

# Fuel Property Measurements

**Heating Values** is a measure of the amount of energy stored in the fuel and released on combustion.

The heating value is measured by burning the fuel in a bomb calorimeter. Some of the energy released from the fuel will be used to convert the water produced during combustion to vapor. The net heating value measured by the calorimeter is called the **net or lower heating value (LHV)**. The **gross or higher heating value (HHV)** is determined by adding the latent heat of vaporization of the water created during combustion to the lower heating value.

The following equations can be used to estimate the heating values from the API gravity:

$$\text{HHV (kJ/kg)} = 42,860 + 93(\text{API}-10)$$

$$\text{LHV (kJ/kg)} = 0.7190\text{HHV} + 10,000$$

# Fuel Property Measurements

**Fuel Volatility and Flash Point** : Fuels must vaporize before combustion, and fuel volatility refers to the ability of the fuel to vaporize.

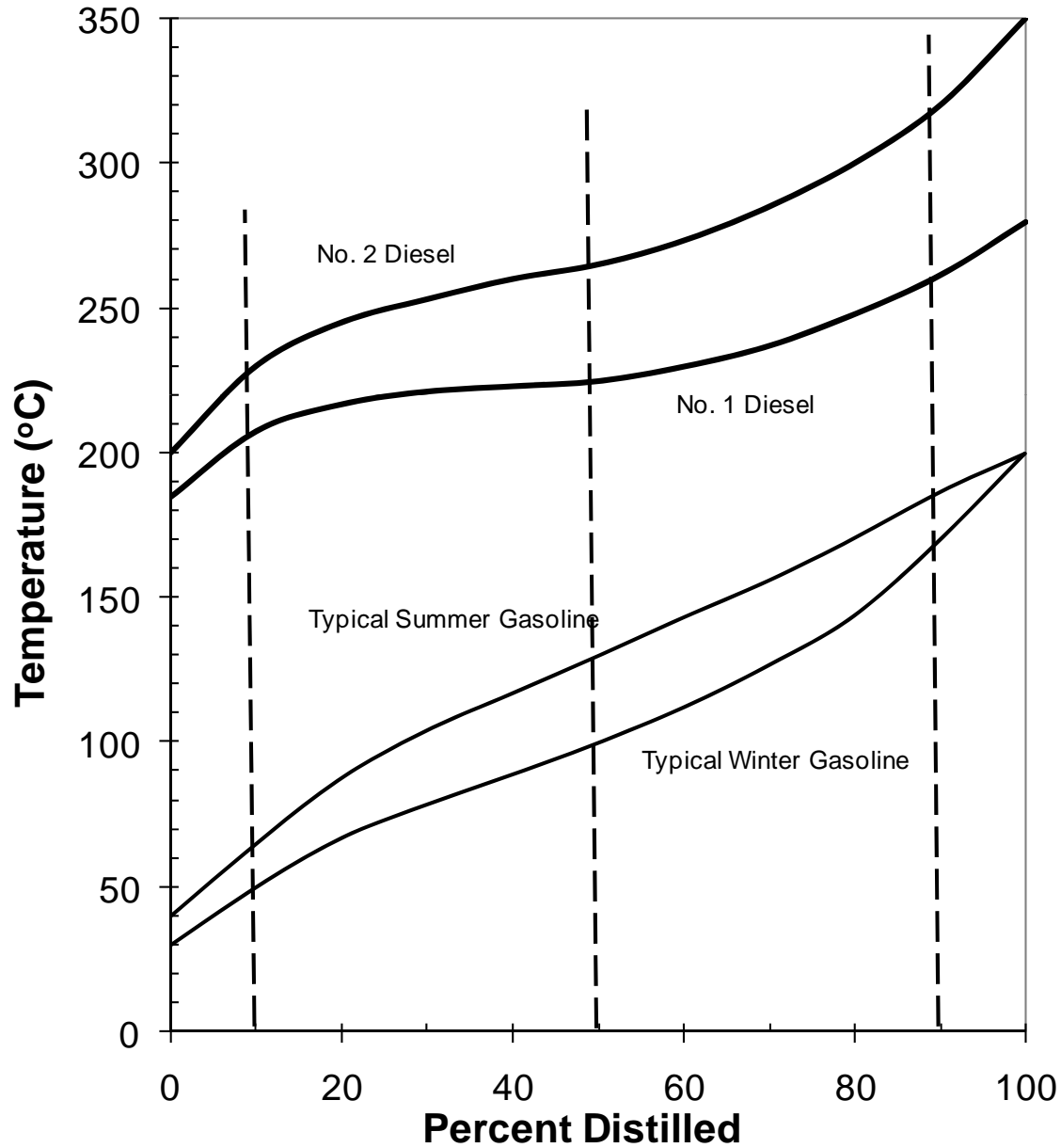
**Reid Vapor Pressure:** The Reid vapor pressure is measured with special pressure gauge apparatus, with the fuel immersed in a water bath to maintain the temperature at 37.8°C (100°F).

Typical Pressures: Winter Gasoline 60-80kPa

Vapor pressure of summer gasoline are approximately 15-20 kPa lower than winter pressures, to reduce potential for vapor lock.

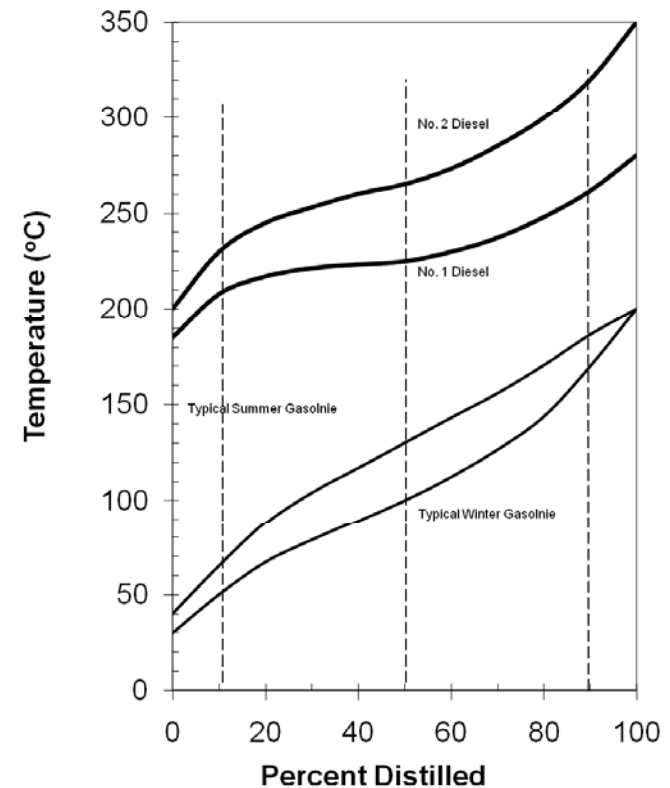
**Distillation Curves** The vapor pressures are a single value and the distillation curve provides better indication of fuel volatility

# Fuel Property Measurements



# Fuel Property Measurements

- $T_{10}$  temperature must be low enough to make sure enough fuel evaporate for engine to start
- $T_{50}$  temperature is associated with engine warmup. Lower  $T_{50}$  will allow faster engine warmup.
- $T_{90}$  temperature is associated with crankcase dilution and fuel economy. If  $T_{90}$  is too high fuel will condense on cylinder walls and leak into the crankcase, diluting the oil.
- Summer Gasoline Fuel (and at higher elevations). The fuel will be vaporize quicker and therefore summer fuels are made less volatile. Vapor lock is also a potential problem.
- Volatility of diesel fuels not as critical as gasoline
  - Vaporization in the combustion chamber.
  - If too low, droplets will evaporate too quickly
  - Reduce spray penetration into the chamber
  - reduce mixing of diesel and air.
- Low  $T_{10}$  temperature for easy engine starting
- Low  $T_{50}$  temperature will minimize smoke and soot.
- $T_{90}$  temperature is associated with crankcase dilution and fuel economy.



Distillation curves for several fuels (after Georing, 1986)

# Octane Rating & Engine Knock

Octane Rating: Measure of the knock (auto-ignition) resistance of gasoline.

Knock depends on the self-ignition temperature of the fuel, ignition delay and time allowable.

Measured in engine with adjustable compression ratio.

Fuel performance determined by comparison of fuel performance to blends iso-octane and normal heptane.

Octane Number = 1\*(Percentage of iso-octane) + 0\*(Percentage of n-heptane)

Motor Octane Number:	More severe test, lower octane number (-8). Similar to knock at high speed and part load conditions.
Research Octane Number:	Less severe. Similar to knock at low speed conditions.

Octane Index: Average of two number

Fuel Sensitivity = RON - MON

# Octane Rating & Engine Knock

- Autoignition in a SI engine depend on the following factors:
  - A. Temperature
  - B. Pressure (Density)
  - C. Time (Ignition Delay)
  - D. Composition
    - 1. Fuel
    - 2. A/F Ratio
    - 3. Turbulence (mixing)
    - 4. Catalyst, inert gases, wall temp etc
- Factors affecting Temperature
  - Compression Ratio, Inlet Air Temp, Coolant Temp, Increasing Throttle, advance spark
- Factors affecting Density
  - Open Throttle, Turbocharging, Advance Timing
- Factors affecting Time
  - Travel Distance, Decrease Turbulence (Slower Flame Speed), Lower Engine Speed (decrease Turbulence, Increase time).
- Composition Effects
  - Lower Octane number, Stiochiometric A/F Ration, Stratification of charge, increasing Humidity reduces knock.
- 
- Consequences of Autoignition
  - 1. Impact on engine components and noise
  - 2. Erratic Pressure Rise
  - 3. Shrubbing of cylinder walls, reducing boundary layer and increase loss of heat to coolant
  - 4. Pre-Ignition and local overheating

# Cetane Rating & Engine Knock

Cetane Rating: Measure of the ignition delay of the fuel and ability to self-ignite.

Knock depends on the ignition delay of the fuel.

Measured in engine with adjustable compression ratio.

Fuel performance determined by comparison of fuel performance to blends iso-octane and normal heptane.

$$\text{Cetane Number} = 1 * (\text{Percentage of Cetane}) + 0.15 * (\text{Percentage of heptmethynonae})$$

Ignition Delay = Physical Delay + Chemical Delay

Premix Combustion. Combustion of all fuel that is already mixed when combustion starts. Very high rate of pressure rise.

Diffusion Combustion. Combustion as rich fuel core mixes with air

Late Burning. Evaporation of cylinder walls etc.

Low Cetane Number:

Late Burning during expansion stroke, difficult starting, white smoke

High Cetane:

Ignition delay too short, more diffusion combustion with lower cycle efficiency, incomplete combustion, black smoke

# Cetane Rating & Engine Knock

- Physical Delay
  - Temperature and density of air in cylinder
  - Atomization, penetration and shape of injection spray
  - Fuel properties such as volatility and viscosity which affect spray characteristics.
  - Turbulence which increases mixing

## Ignition Delay decreases with:

- Increase in Temperature
  - Compression ratio, inlet air temp, coolant temp, load, incorrect injection timing
- Increase in Pressure
  - Inlet Pressure, compression ratio
- Increase in speed
  - Turbulence, decreases physical delay
  - Compression Temp Increases, decreases physical and chemical delay
- Increase in Cetane
  - Reduce Chemical delay
- Decrease A/F Ratio
  - Decrease chemical delay
- Optimum Injection Timing

# Energy Release

## Pre-Mix Combustion

- Ignition Delay
  - Physical Delay
  - Chemical Delay
- High Rate Pressure Rise
- High Efficiency

## Diffusion Combustion

- Low Rate Pressure Rise
- Lower Cycle Efficiency

## Late Burning

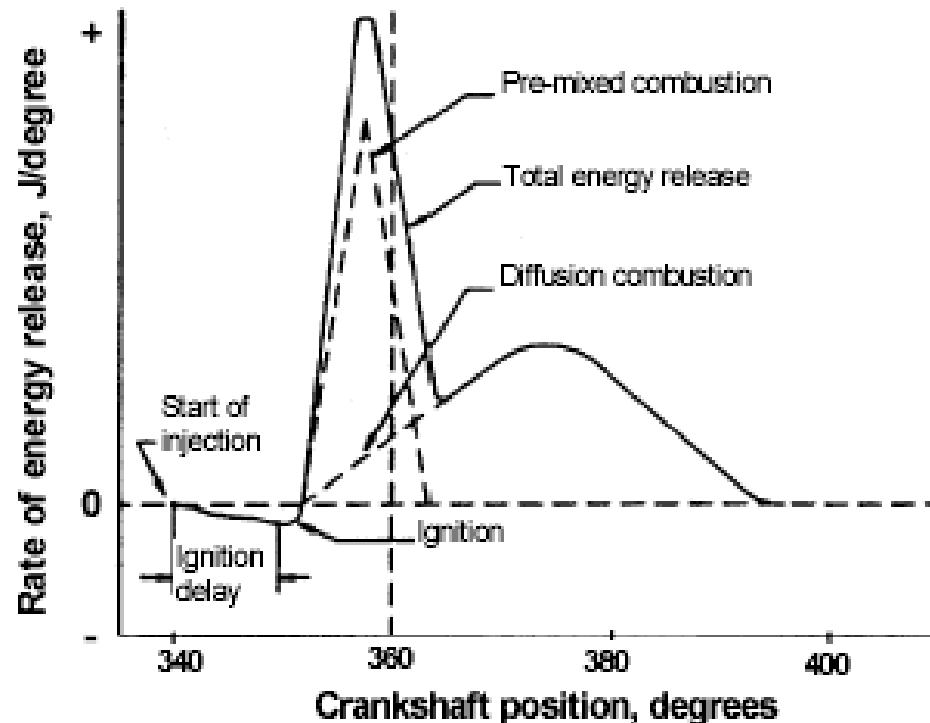


Figure 5.8. Energy release from compression-ignition fuels.