IV. Fuels and Combustion Calculations

IC Engines – 3rd Stage
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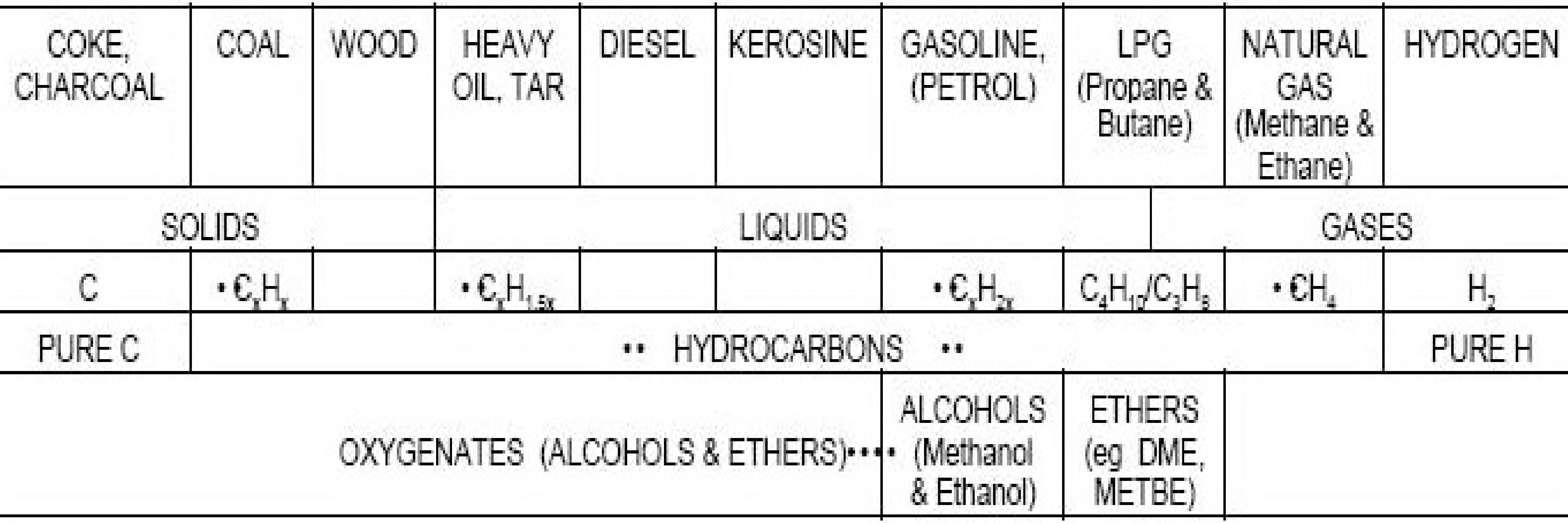
Petroleum Crude Oil

- Formed due to the fossilization of organic matter, under ground. Raw petroleum as obtained from oil wells, is a mixture of many hydrocarbons with differing molecular structure. It also contains small amounts of sulfur, oxygen, nitrogen and impurities like water and sand.
- “Sweet” and “sour” refer to the amount of sulfur.
- “Light oil” is generally composed of three hydrocarbon families:

- Saturated hydrocarbons: paraffins (or normal alkanes, C_nH_{2n+2}) with gas ($n = 1 – 4$), liquid ($n = 5 – 15$), and solids ($n > 15$).
- Unsaturated hydrocarbons, or aromatics, like benzene (C_6H_6), toluene (C_7H_8) and naphthalene ($C_{10}H_8$)
- Resin and asphaltenes, heavier hydrocarbons rich in nitrogen, oxygen and vanadium.
- Refining: distillation (separation of the lighter components), catalytic cracking (heating) and reforming (with steam or hydrogen). Products are typically refinery gas, LPG, gasoline (mostly octane C_8H_{18}) , aviation fuels diesels, heating and lube oils…

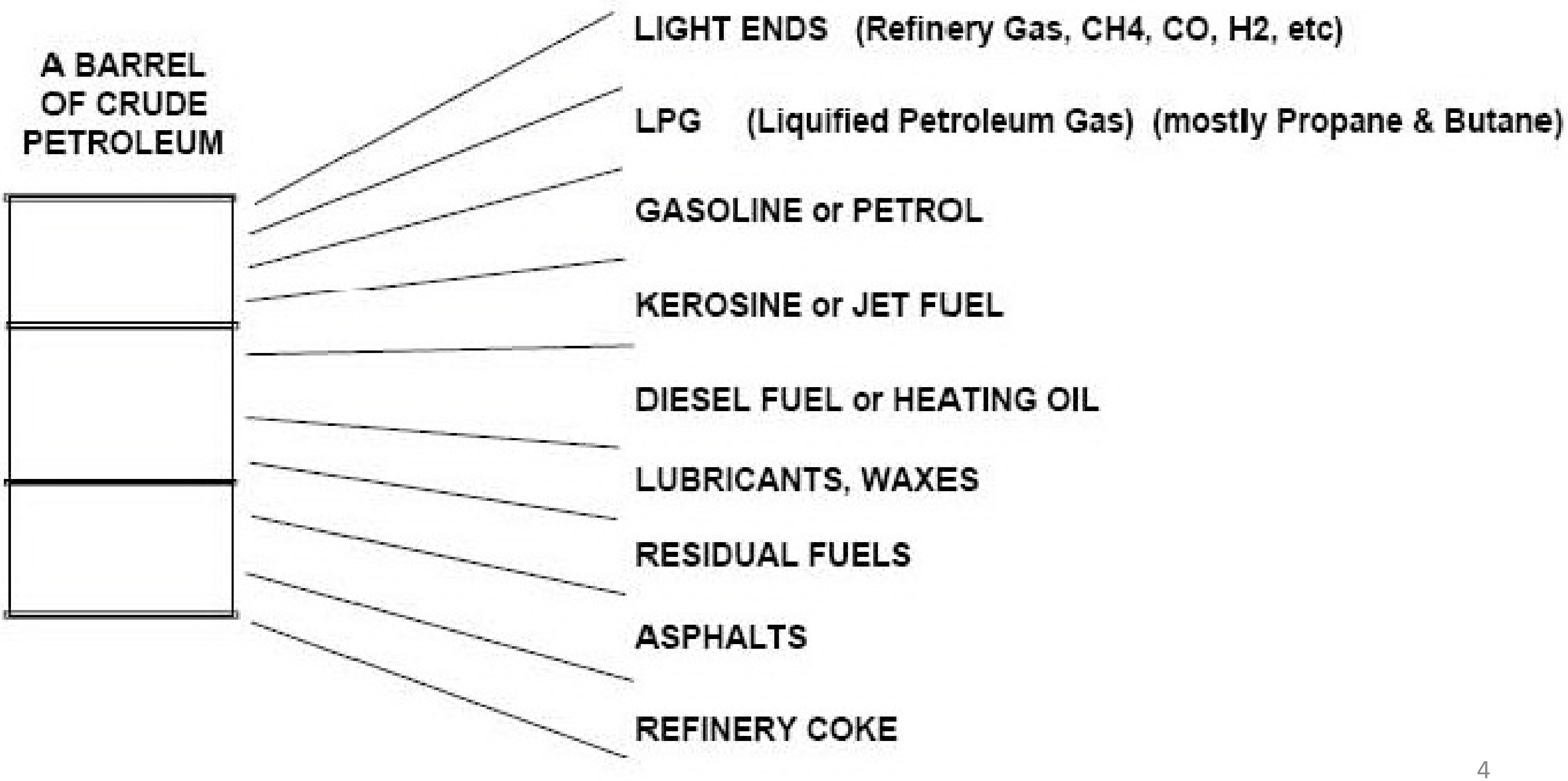
The Range of Common Carbon/Hydrogen Fuels



COKE, CHARCOAL	COAL	WOOD	HEAVY OIL, TAR	DIESEL	KEROSINE	GASOLINE, (PETROL)	LPG (Propane & Butane)	NATURAL GAS (Methane & Ethane)	HYDROGEN
SOLIDS			LIQUIDS				GASES		
C	• C_xH_x		• $C_xH_{1.5x}$			• C_xH_{2x}	C_4H_{10}/C_3H_8	• CH_4	H_2
PURE C	•• HYDROCARBONS ••								PURE H
OXYGENATES (ALCOHOLS & ETHERS)•••						ALCOHOLS (Methanol & Ethanol)	ETHERS (eg DME, METBE)		

•Schematic of the Fractionation of Crude Oil into Products of Varying Volatility .

- economic pressure is to increase gasoline/petrol fraction.



A BARREL OF CRUDE PETROLEUM

LIGHT ENDS (Refinery Gas, CH4, CO, H2, etc)

LPG (Liquified Petroleum Gas) (mostly Propane & Butane)

GASOLINE or PETROL

KEROSINE or JET FUEL

DIESEL FUEL or HEATING OIL

LUBRICANTS, WAXES

RESIDUAL FUELS

ASPHALTS

REFINERY COKE

Fuel Types

- Gasoline and diesel fuel are both produced from crude oil. Together, gasoline and diesel fuel power approximately 99% of the motor vehicle fleet.
- However, alternative fuels are being used more and more to reduce vehicle emissions.
- This section briefly explains various fuel types

1 Fuel Types

1.1 Indolene - Indolene is used as the standard gasoline emission test fuel for spark ignition engines.

Indolene is a well refined gasoline with low levels of sulfur, phosphorus, and vapor pressure.

1.2 Diesel Fuel - The diesel fuel is commonly used in relatively large displacement compression ignition engines.

Diesel fuel is used in a broader range of engine sizes in Europe and other areas of the world.

The average molecular weight and boiling point of diesel fuel is greater than that for gasoline, which makes it suitable for use in compression ignition engines, characterized by higher in-cylinder temperatures and pressures.

1 Fuel Types

1.4 Reformulated Gasoline - Reformulated gasoline is similar to CF2 gasoline.

The reformulated blends usually contain an oxygenate additive such as MTBE, EtOH, or ETBE.

1.5 Compressed Natural Gas - Compressed natural gas (CNG) is comprised primarily of methane (CH4). CNG vehicles generally produce lower emissions than their gasoline counterparts.

However, there are tradeoffs in engine power and efficiency.

1 Fuel Types

1.6 Methanol (CH3OH) - Methanol is a promising alternative fuel because it generally produces lower tailpipe emissions than gasoline and can be manufactured at prices comparable to gasoline.

A blend of 85% methanol and 15% unleaded gasoline (M85) is typically used. However, M85 vehicles are virtually phased out of new vehicle manufacture in Brazil.

Vehicles that operate on methanol consume more fuel than if they were operating on 100% gasoline because its energy content (calorific value) is less.

1 Fuel Types

1.7 Ethanol (C2H5OH) - Ethanol is an important component of automotive fuel used in Brazil.

A mixture of 22% ethanol with gasoline (E22) is commonly used.

Ethanol is also used in the USA as an octane enhancer for gasoline (up to 10%).

It is also used for flexible fuel vehicles as a blend of 85% ethanol and 15% unleaded gasoline.

Ethanol is produced from corn, sugar cane or other crops but is currently more expensive than gasoline.

2 Fuel Properties

- Fuel properties and compositions are regulated by most governments.
- U.S. Federal requirements for test fuels are specified in the Code of Federal Regulations (CFR).
- The following subsections briefly describe some important fuel characteristics and their influence on engine performance.
- Subsequent to these sections, Tables 1 and 2 provide some fuel properties for liquid and gaseous fuels.

2 Fuel Properties

2.1 Fuel Volatility - Volatility is loosely defined as the tendency of a liquid to evaporate.

Fuel for engines must conform to strict specifications regarding their volatility characteristics to ensure satisfactory operation.

The fuel must contain a large enough proportion of highly volatile components to ensure good cold starts, but the volatility must not be so high as to impair operation (vapor lock) and starting when the engine is hot.

2 Fuel Properties

2.2 Distillation Curve - Three areas on the distillation or boiling curve have a pronounced effect on an engine's operating behavior. They can be defined according to the percent of fuel evaporated at three temperatures during a standard ASTM distillation test.

a] The volume of fuel that evaporates up to 70° C must be adequate to ensure good cold starting, but not so large as to cause vapor lock when the engine is hot.

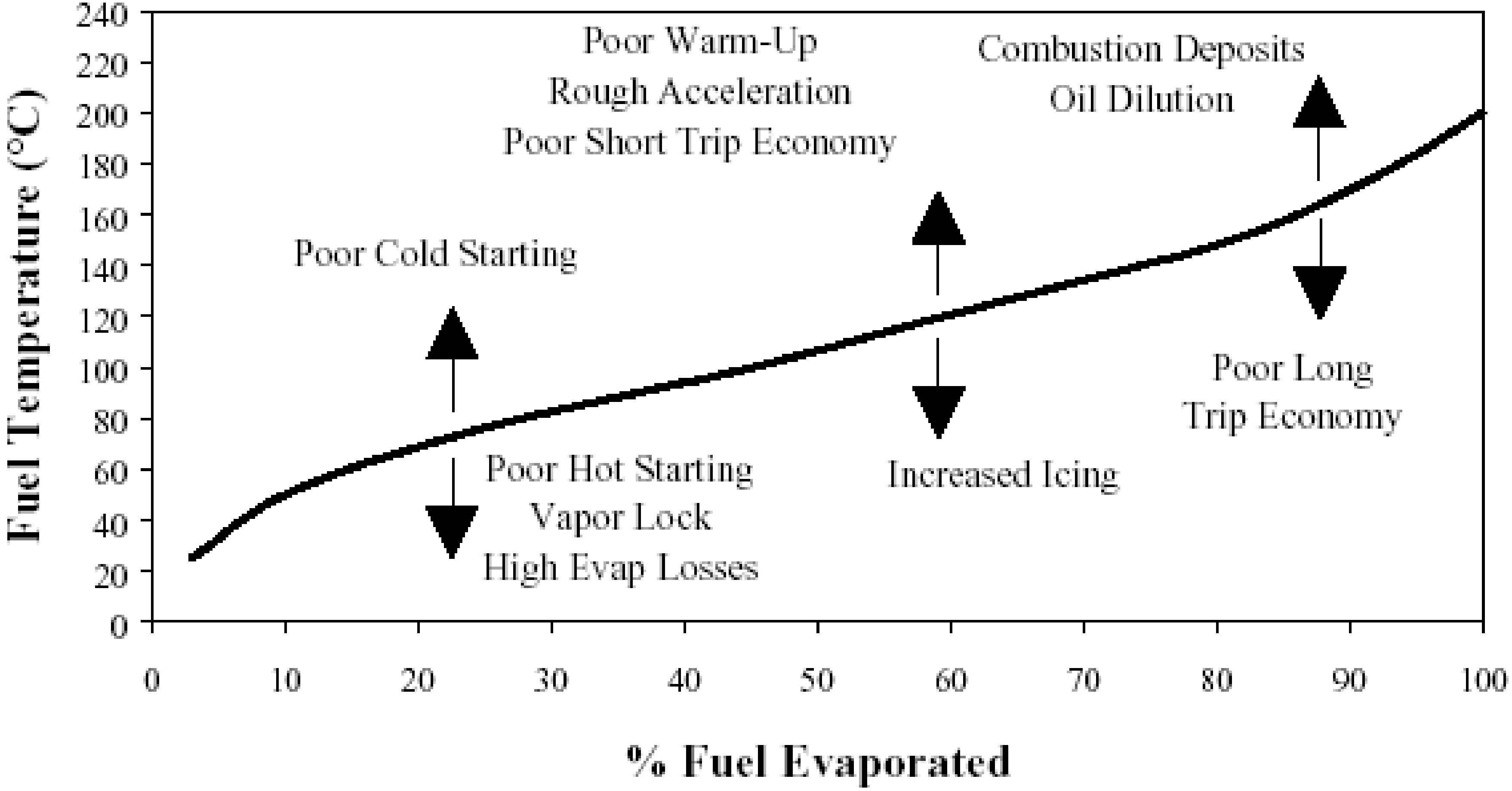
b] The vaporized volume at 100° C should be high enough to minimize dilution of the engine's lubricating oil.

c] The percentage of fuel which evaporates at 180° C determines the engine's warm up qualities, as well as it's acceleration and response characteristics once it has reached normal operating temperature.

2 Fuel Properties

2.2 Distillation Curve-

Figure 1 illustrates the effect of changing the shape of the distillation curve.



2 Fuel Properties

2.2 Distillation Curve - From Figure 1,

- Raising the left end, by reducing the amount of highly volatile (low boiling point) compounds in the blend, degrades cold starting.
- Lowering the left end can cause vapor lock, poor hot starts, and high evaporative losses.
- Raising the right end, by adding compounds with higher molecular weights, leads to increased oil dilution and deposit formation.
- Lowering the right end increases fuel consumption during warm engine operation.
- Raising the middle degrades warm-up driveability, causes rough accelerations, and degrades fuel economy during short trips.

2 Fuel Properties

2.3 Vapor Pressure - Fuel vapor pressure curves are strongly influenced by fuel composition.

The curves for fuels containing alcohol, for instance, are much steeper than those for pure hydrocarbon mixtures.

The result is that fuels with alcohol display a greater tendency to vaporize and form vapor lock, thus impairing operation at higher temperatures.

Since 1992, federal emission laws have regulated maximum RVP to reduce evaporative and exhaust emissions, particularly in California.

2 Fuel Properties

2.4 Vapor/Liquid Ratio - This specification provides an index of a fuel's tendency to form vapor bubbles (vapor locks).

It is based on the volume of vapor generated by a specific quantity of fuel at a set temperature.

Assuming a constant temperature, a larger volume of vapor will form at low pressures (i.e., at high altitudes) than at higher pressures (i.e., at sea level).

This phenomenon can lead to vapor-lock problems when driving in mountainous areas.

The addition of alcohols, methanol in particular, raises the vapor/liquid ratio.

2 Fuel Properties

2.5 Driveability Index - The driveability index (DI) is used often by engineers to predict engine performance based on three points from a fuel's distillation curve.

These points are referred to as the T10, T50 and T90 temperatures, and correspond to temperatures in °F at which 10%, 50%, and 90% of the volume of a fuel has evaporated.

The index is calculated using Equation 1:

$$DI = 1.5\,T10 + 3.0\,T50 + T90. \qquad (1)$$

2 Fuel Properties

2.5 Driveability Index –

- Note that more emphasis is placed on the T50 temperature since this is the approximate temperature at which the fuel enters the combustion chamber.
- A larger DI results from a less volatile fuel and vice versa.
- Typical DI’s for gasoline range from 1,000 to 1,200.
- Fuels with a DI greater than 1200 may cause hesitation, stumbles and misfires, contributing to higher emissions.

2 Fuel Properties

2.6 Octane/Cetane Rating –

The octane rating defines a gasoline's ignition quality (engine "knock resistance") for gasoline engines.

The cetane number carries similar meaning but for diesel engines.

However, the two numbers have inverse relationships with respect to knock resistance; the resistance to engine knock increases with increasing octane number and decreasing cetane number.

2 Fuel Properties

2.7 Knock Inhibitors - The most effective knock inhibitors are organic lead compounds. These can raise the octane number by several points.

Environmental concerns have lead to a steady reduction in the amount of lead in fuels.

A compound developed to replace lead compounds methylcyclopentadienyl manganese tricarbonyl (MMT) is currently used in Canada and adversely affects emissions.

In U.S. gasoline, refiners have not currently used MMT. Data is being generated to effect a ban of MMT by the U.S. EPA.

2 Fuel Properties

2.8 Calorific Value - The specific values for the net (lower) and gross (higher) calorific values, provide an index for the energy content of fuels.

When fuels (such as methanol), with a lower calorific value are used, greater quantities will be required to achieve comparable engine output.

3 Fuel Composition

Fuels vary widely in chemical composition, depending on the source of crude and on the methods used in refining.

In every case, however, the fuel consists almost entirely of a mixture of hydrocarbon compounds having different molecular weights and different types of structure

3 Fuel Composition

Most common hydrocarbon fuels are **Alkyl Compounds** and are grouped as:

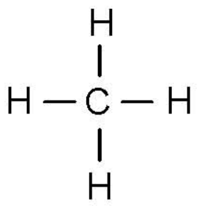
3.1 Paraffins - Paraffins are straight chained hydrocarbons, also called alkanes. Some examples are propane and butane. Isoparaffins have a branched chain structure.

3 Fuel Composition

Paraffins (alkanes): single-bonded, open-chain, saturated (no more hydrogen can be added)

C_nH_{2n+2}

n= 1 CH_4 methane
n= 2 C_2H_6 ethane
n= 3 C_3H_8 propane
n= 4 C_4H_{10} butane
n= 8 C_8H_{18} n-octane and isooctane



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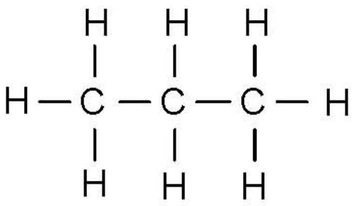
methane



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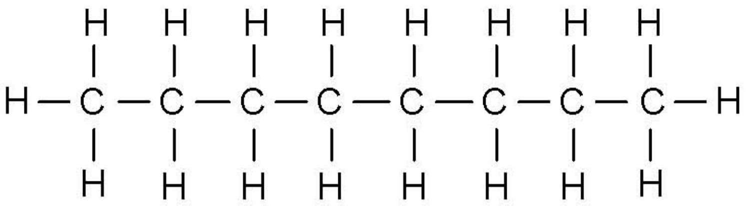
propane



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n-octane

There are several isooctanes, depending on position of methyl (CH_3) branches which replace hydrogen atoms (eg. 3 H are replaced with 3 CH_3)

3 Fuel Composition

3.2 Aromatics - Aromatics are high octane blending hydrocarbons that have a benzene ring in their molecular structure. Examples are benzene, toluene, xylene.

3.3 Olefins - Olefins are gasoline hydrocarbons resulting from several refining processes. Examples are ethylene, propylene, butylene. Olefins often contribute to the formation of gum and deposits in engines and the induction system. Olefins are also called alkenes.

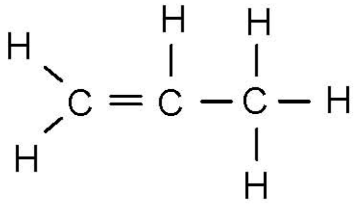
3 Fuel Composition

Olefins (alkenes): open-chain containing one double-bond, unsaturated (break bond more hydrogen can be added)

C_nH_{2n}

n=2 C_2H_4 ethene
n=3 C_3H_6 propene

Note: n=1 yields CH_2 is an unstable molecule



propene

Acetylenes (alkynes): open-chain containing one C-C triple-bond unsaturated

C_nH_{2n-2}

n=2 C_2H_2 acetylene
n=3 C_3H_4 propyne

$H-C\equiv C-H$

acetylene

For **alcohols** one hydroxyl (OH) group is substituted for one hydrogen
e.g. methane becomes methyl alcohol (CH_3OH) also known as methanol
ethane becomes ethyl alcohol (C_2H_5OH) also known as ethanol

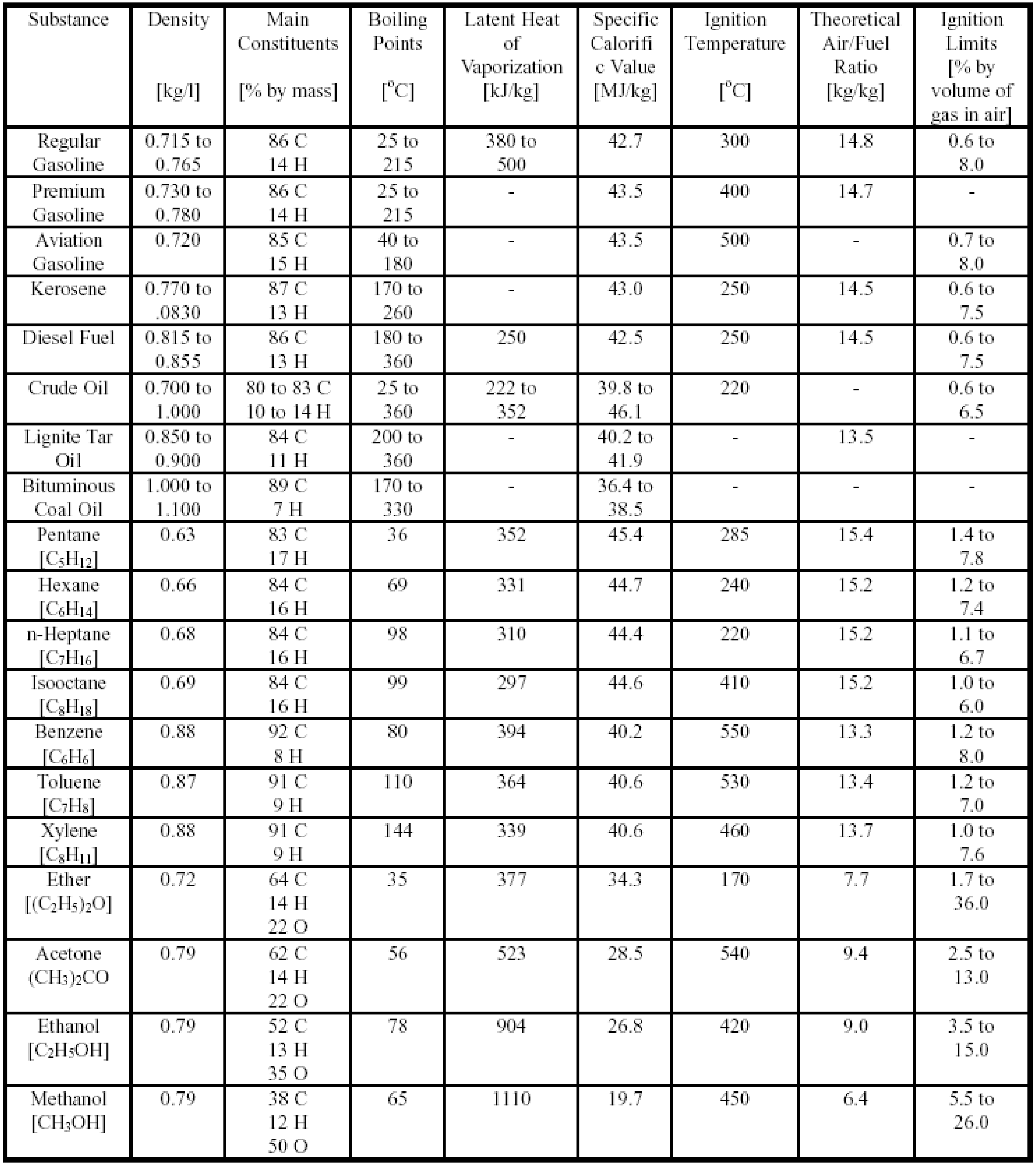
3 Fuel Composition

3.4 Oxygenates - Oxygenates are an octane component containing hydrogen, carbon, and oxygen in their molecular structure.

Includes ethers such as MTBE and alcohols such as ethanol and methanol.

Adding an oxygenate to gasoline results in enleanment thereby improving combustion and reducing tailpipe emissions.

3. Typical Properties of Liquid Fuels and Hydrocarbons



Substance	Density [kg/l]	Main Constituents [% by mass]	Boiling Points [^oC]	Latent Heat of Vaporization [kJ/kg]	Specific Calorific Value [MJ/kg]	Ignition Temperature [^oC]	Theoretical Air/Fuel Ratio [kg/kg]	Ignition Limits [% by volume of gas in air]
Regular Gasoline	0.715 to 0.765	86 C 14 H	25 to 215	380 to 500	42.7	300	14.8	0.6 to 8.0
Premium Gasoline	0.730 to 0.780	86 C 14 H	25 to 215	-	43.5	400	14.7	-
Aviation Gasoline	0.720	85 C 15 H	40 to 180	-	43.5	500	-	0.7 to 8.0
Kerosene	0.770 to .0830	87 C 13 H	170 to 260	-	43.0	250	14.5	0.6 to 7.5
Diesel Fuel	0.815 to 0.855	86 C 13 H	180 to 360	250	42.5	250	14.5	0.6 to 7.5
Crude Oil	0.700 to 1.000	80 to 83 C 10 to 14 H	25 to 360	222 to 352	39.8 to 46.1	220	-	0.6 to 6.5
Lignite Tar Oil	0.850 to 0.900	84 C 11 H	200 to 360	-	40.2 to 41.9	-	13.5	-
Bituminous Coal Oil	1.000 to 1.100	89 C 7 H	170 to 330	-	36.4 to 38.5	-	-	-
Pentane [C_5H_{12}]	0.63	83 C 17 H	36	352	45.4	285	15.4	1.4 to 7.8
Hexane [C_6H_{14}]	0.66	84 C 16 H	69	331	44.7	240	15.2	1.2 to 7.4
n-Heptane [C_7H_{16}]	0.68	84 C 16 H	98	310	44.4	220	15.2	1.1 to 6.7
Isooctane [C_8H_{18}]	0.69	84 C 16 H	99	297	44.6	410	15.2	1.0 to 6.0
Benzene [C_6H_6]	0.88	92 C 8 H	80	394	40.2	550	13.3	1.2 to 8.0
Toluene [C_7H_8]	0.87	91 C 9 H	110	364	40.6	530	13.4	1.2 to 7.0
Xylene [C_8H_{11}]	0.88	91 C 9 H	144	339	40.6	460	13.7	1.0 to 7.6
Ether [$(C_2H_5)_2O$]	0.72	64 C 14 H 22 O	35	377	34.3	170	7.7	1.7 to 36.0
Acetone $(CH_3)_2CO$	0.79	62 C 14 H 22 O	56	523	28.5	540	9.4	2.5 to 13.0
Ethanol [C_2H_5OH]	0.79	52 C 13 H 35 O	78	904	26.8	420	9.0	3.5 to 15.0
Methanol [CH_3OH]	0.79	38 C 12 H 50 O	65	1110	19.7	450	6.4	5.5 to 26.0

3. Typical Properties of Gaseous Fuels and Hydrocarbons

Substance	Density [kg/m^3]	Main Constituents [% by mass]	Boiling Points [°C]	Specific Calorific Value [MJ/kg]	Ignition Temperature [°C]	Theoretical Air/Fuel Ratio [kg/kg]	Ignition Limits [% by volume of gas in air]
Liquified Gas	2.25	C_3H_8, C_4H_{10}	-30	46.1	400	15.5	1.5 to 15.0
Natural Gas	0.83	50 H 8 CO 30 CH_4	-162	47.7	-	-	-
Hydrogen (H_2)	0.090	100 H	-253	120.0	560	34.0	4.0 to 77.0
Carbon Monoxide (CO)	1.25	100 CO	-191	10.05	605	2.5	12.5 to 75.0
Methane (CH_4)	0.72	75 C 25 H	-162	50.0	650	17.2	5.0 to 15.0
Acetylene (C_2H_2)	1.17	93 C 7 H	-81	48.1	305	13.3	1.5 to 80.0
Ethane (C_2H_6)	1.36	80 C 20 H	-88	47.5	515	17.3	3.0 to 14.0
Ethene (C_2H_4)	1.26	86 C 14 H	-102	14.1	425	14.7	2.8 to 34.0
Propane (C_3H_8)	2.00	82 C 18 H	-43	46.3	470	15.6	1.9 to 9.5
Propene (C_3H_6)	1.92	86 C 14 H	-47	45.8	450	14.7	2.0 to 11.0
Butane (C_4H_{10})	2.70	83 C 17 H	-10	45.6	365	15.4	1.5 to 8.5
Butene (C_4H_8)	2.50	86 C 14 H	-5	45.2	-	14.8	1.7 to 9.0

3 Fuel Composition

3.5 Additives - Chemicals are added to gasoline in very small quantities to improve and maintain gasoline quality.

Examples include: detergents which prevent or clean up carburetor and fuel injector deposits, corrosion inhibitors, antioxidants to reduce gum formation in storage, acetone or similar water absorbents, and ethers such as methyl tertiary butyl ether (MTBE) for increased octane levels.

3 Fuel Composition

3.5.1 Effects of fuel additives

Fuel additive serve two distinct purposes.

- to improve combustion and pollutant emissions,
- to ensure reduced wear and limit deposit formation during the engine life cycle of several hundreds of thousands of miles

3 Fuel Composition

3.5.1 Effects of fuel additives

Figure 2 shows some important fuel-relevant problem areas in a spark-ignition engine

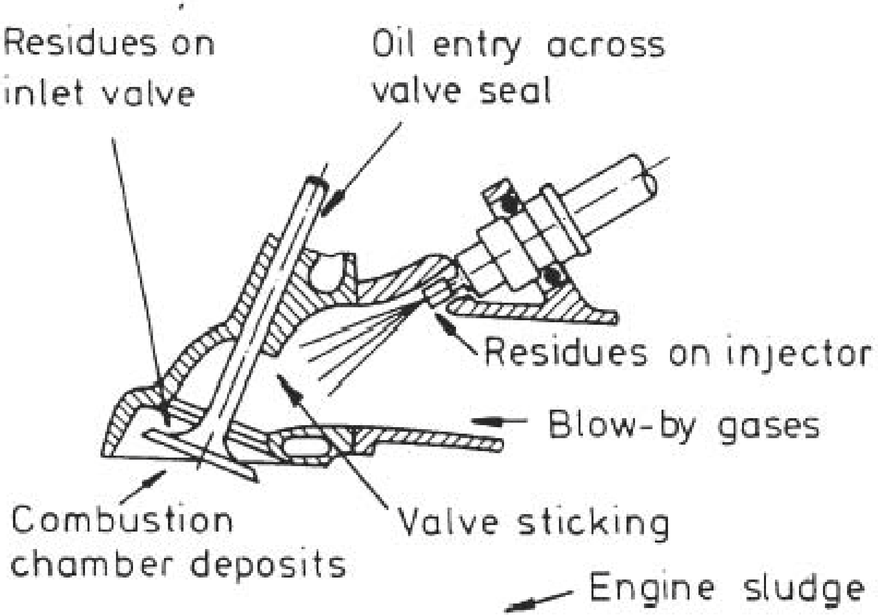


Figure 2 Problem areas related to fuel in a spark ignition engine.

3 Fuel Composition

3.5.2 Additive for gasoline engine

Most important additives that have a direct effect on combustion are “anti-knock products”. Additives containing metals are designed to improve combustion (combustion enhancers).

Deposits will accumulate on the valve heads that act like a sponge during cold starting and cause the air-fuel mixture to become leaner.

At full throttle, the deposits reduce the cylinder charge and thus cause power losses.

3 Fuel Composition

3.5.3 Additive for diesel engines

Additives, for diesel engine, concentrates on improving combustion, reducing deposit formation during combustion of the fuel and keeping the injectors clean.

Three group of additives are used for diesel engines:\

Cetane number enhancers: Increasing the cetane number by using cetane number enhancers means that ignition lag is reduced, i.e. ignition is advanced.

Extensive research has proven that increased additive concentration help to reduce HC, CO and particulate emission by a significant degree without causing NOx emission to increase.

When the cetane number was increased by ten units, HC emissions dropped by up to 80%, CO emissions were up to 50% lower and particulate emissions were reduced by up to 30%. Combustion noise is also reduced considerably.

3 Fuel Composition

Combustion enhancers: Combustion enhancers act directly on the combustion process.

This effect is achieved both in clean and in coked engines, Unburned hydrocarbons and particulates are reduced by a significant degree whereas CO and NOx emissions remain unchanged.

Multifunctional diesel additive: This additive pack includes components for corrosion protection, demulsification and reducing the foaming tendency.

Oxidation inhibitors and detergents are used to keep the injectors clean.

After run with the additive pack, HC emissions had dropped and CO and particulates were more lower without causing any significant increase of NOx emissions.

4 Basic Combustion

Basic definitions

- ‘combustion’ reactions are one form of chemical reaction
  1. combustion is defined as the oxidation of a ‘fuel’, with large amounts of released energy
  2. the oxidiser is in most cases air (or more specifically, O2 in air) because of its abundance.
  3. a ‘fuel’ is any material (mostly Hydrocarbons that store energy in their chemical bonds. Highest energy storage per unit mass or unit volume (in liquid form)) that can be burned to release energy. Hydrocarbon fuels of the form C_xH_y are the most common.

4 Basic Combustion

Basic definitions

- many hydrocarbon fuels are mixtures of many different hydrocarbons although they mainly consist of the following:
  - gasoline ~ octane, $C8H18$
  - diesel ~ dodecane, $C12H26$
  - methanol = methyl alcohol, $CH3OH$
  - LNG (liquefied natural gas) ~ methane, $CH4$
  - LPG (liquefied petroleum gas) ~ propane, $C3H8$

4 Basic Combustion

Composition of air

- on a molar (or volume) basis, *dry* air is composed of:
  - 20.9% oxygen O2
  - 78.1% nitrogen N2
  - 0.9% CO2, Ar, He, Ne, H2, and others
- a good approximation of this by molar or volume is: 21% oxygen, 79% nitrogen
- thus, each mole of oxygen is accompanied 0.79/0.21 = 3.76 moles of nitrogen.

4 Basic Combustion

Composition of air

- at ordinary combustion temperatures, N2 is inert, but nonetheless greatly affects the combustion process because its abundance, and hence its enthalpy change, plays a large part in determining the reaction temperatures.
    1. this, in turn, affects the combustion chemistry, as we shall see later.
    2. also, at higher temperatures, N2 does react, forming species such as oxides of nitrogen (NOx), which are a significant pollutant.

4 Basic Combustion

Stoichiometry and air/fuel ratios

- the amounts of fuel and air taking part in a combustion process are often expressed as the ‘air to fuel’ ratio:

$$AF = \frac{m_{air}}{m_{fuel}}$$

where:

- m_{fuel}, m_{air} = mass of fuel or air (kg),
- equivalent, and widely used, terms to the AF are the fuel/air ratio FA , the equivalence ratio, ϕ, and the ‘lambda’ ratio λ:

$$\phi = \frac{1}{\lambda} = \frac{FA}{FA_{stoich}}$$

4 Basic Combustion

- It is important to define what measure is being used in describing the relationship between A/F and other parameters.
- Keys for remembering the trends in each measure of A/F is:

Measure	**Leaner Combustion**	**Richer Combustion**
A/F	Bigger	Smaller
F/A	Smaller	Bigger
λ	Bigger	Smaller
ϕ	Smaller	Bigger

4 Basic Combustion

Thermodynamics of Combustion

- When molecules undergo chemical reaction, the reactant atoms are rearranged to form new combinations (oxidized). The chemical reaction can be presented by reaction equations. However, reaction equations represent initial and final results and do not indicate the actual path of the reaction, which may involve many intermediate steps and intermediate species. This approach is similar to thermodynamics system analysis, where only end states and not path mechanism are used.
- The dissociation of the products into species with a higher enthalpy of formation occurs in many combustion reactions of practical importance. In such cases, the temperature of the products is lower than the undissociated temperature, because some of the energy released by the original combustion reaction is absorbed by endothermic, dissociative reactions.

4.1 Combustion Reaction of Hydrocarbon in O_2

- Oxyfuel combustion, that is burning in pure oxygen, is also used to further raise the products temperature, in gasifiers (reformers), or to avoid the formation of nitric oxides.

$$C_nH_m + \left(n + \frac{m}{4}\right)(O_2) \rightarrow nCO_2 + \frac{m}{2}H_2O$$

4.1 Combustion Reaction of Hydrocarbon in O_2

Combustion Stoichiometry

If sufficient oxygen is available, a hydrocarbon fuel can be completely oxidized, the carbon is converted to carbon dioxide (CO_2) and the hydrogen is converted to water (H_2O).

The overall chemical equation for the complete combustion of one mole of propane (C_3H_8) is:

$$C_3H_8 + aO_2 \rightarrow bCO_2 + \underset{\text{\# of moles}}{\underset{\uparrow}{c}}\underset{\text{species}}{\underset{\uparrow}{H_2O}}$$

Elements can not be created or destroyed so

carbon balance gives $b = 3$

hydrogen balance gives $2c = 8 \rightarrow c = 4$

oxygen balance gives $2b + c = 2a \rightarrow a = 5$

Thus the above reaction is:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$$

4.2 Combustion Reaction of Hydrocarbon in Air

- Air contains molecular nitrogen N2, when the products are low temperature
- the nitrogen is not significantly affected by the reaction, it is considered **inert**.
- The complete reaction of a general hydrocarbon C_nH_m with air is:

$$C_nH_m + \left(n + \frac{m}{4}\right)(O_2 + 3.76N_2) \rightarrow nCO_2 + \frac{m}{2}H_2O + 3.76\left(n + \frac{m}{4}\right)N_2$$

- The above equation defines the **stoichiometric** proportions of fuel and air.

4.2 Combustion Reaction of Hydrocarbon in Air

$$C_nH_m + \left(n + \frac{m}{4}\right)(O_2 + 3.76N_2) \rightarrow nCO_2 + \frac{m}{2}H_2O + 3.76\left(n + \frac{m}{4}\right)N_2$$

- In complete, stoichiometric combustion of hydrocarbons, the products are water and carbon dioxide.
- Even with stoichiometric combustion, carbon monoxide and nitric oxides form, as well very small amounts of hydrocarbons and their fragments (PAH).
- The amount of CO, NOx and “CH” in the products depend on the fuel, combustion conditions, nature of the combustion process, and how fast the products are cooled.

4.2 Combustion Reaction of Hydrocarbon in Air

There is no complete combustion !

The amount of CO, NOx and “CH” in the products depend on the fuel, combustion conditions, nature of the combustion process, and dissociation of the products.

$$C_nH_m + \left(n + \frac{m}{4}\right)(O_2 + 3.76N_2) \rightarrow$$

$$(n-\alpha)CO_2 + \left(\frac{m}{2} - \beta\right)H_2O + 3.76\left(n + \frac{m}{4} - \frac{\gamma}{2}\right)N_2$$

$$+\left[\alpha CO + \beta H_2 + \gamma NO_x + some O_2\right]$$

dissociation products

4.2 Combustion Reaction of Hydrocarbon in Air

4.2.1 Combustion Stoichiometry

$$\left(A/F\right)_s = \frac{1}{(F/A)_s} = \frac{\left(1+\frac{(m/n)}{4}\right)(32+3.76\cdot 28)}{12+(m/n)\cdot 1}$$

Note above equation only applies to stoichiometric mixture

For methane (CH_4), m/n = 4 → $(A/F)_s$ = 17.2

For octane (C_8H_{18}), m/n = 2.25 → $(A/F)_s$ = 15.1

4.2 Combustion Reaction of Hydrocarbon in Air

Combustion Stoichiometry

Example: For propane (C_3H_8) n= 3 and m= 8

$$C_3H_8 + (5)(O_2 + 3.76N_2) \rightarrow 3CO_2 + 4H_2O + 3.76(5)N_2$$

The stoichiometric mass based air/fuel and fuel/air ratio is:

$$(A/F)_s = \frac{1}{(F/A)_s} = \frac{\left(n + \frac{m}{4}\right)\overline{M}_{O_2} + 3.76\left(n + \frac{m}{4}\right)\overline{M}_{N_2}}{n\overline{M}_C + m\overline{M}_H}$$

Substituting the respective molecular weights and dividing top and bottom By n = one gets the following expression that only depends on the ratio of the number of hydrogen atoms to carbon atoms *(m/n)* in the fuel.

$$(A/F)_s = \frac{1}{(F/A)_s} = \frac{\left(1 + \frac{(m/n)}{4}\right)(32 + 3.76 \cdot 28)}{12 + (m/n) \cdot 1}$$

4.2 Combustion Reaction of Hydrocarbon in Air

4.2.2 Fuel Lean Mixture

- Fuel-air mixtures with more than stoichiometric air, **excess air**, can burn.

- With excess air you get **fuel lean** combustion, the extra air appears in the products in unchanged form.

$$C_nH_m + \gamma(n + \frac{m}{4})(O_2 + 3.76N_2) \rightarrow nCO_2 + \frac{m}{2}H_2O + dN_2 + eO_2$$

where for fuel lean mixture have excess air so $\gamma > 1$

- Above reaction equation has two unknowns (d, e) and we have two atom balance equations (O, N) so can solve for the unknowns

4.2 Combustion Reaction of Hydrocarbon in Air

4.2.3 Fuel Rich Mixture

- Fuel-air mixtures with less than stoichiometric air can also burn.
- With less than stoichiometric air you get **fuel rich** combustion, there is insufficient oxygen to oxidize all the C and H in the fuel to CO_2 and H_2O.
- Get incomplete combustion where carbon monoxide (CO) and molecular hydrogen (H_2) also appear in the products.

$$C_nH_m + \gamma(n + \frac{m}{4})(O_2 + 3.76N_2) \rightarrow aCO_2 + bH_2O + dN_2 + eCO + fH_2$$

where for fuel rich mixture have insufficient air → $\gamma < 1$

- Above reaction equation has three unknowns (*a, b, d, e, f*) and we only have two atom balance equations (*C, H, O, N*) so cannot solve for the unknowns unless additional information about the products is given.

4.2 Combustion Reaction of Hydrocarbon in Air

4.2.4 Off-Stoichiometric Mixtures

The **equivalence ratio**, ϕ, is commonly used to indicate if a mixture is stoichiometric, fuel lean, or fuel rich.

$$\phi = \frac{(A/F)_s}{(A/F)_{mixture}} = \frac{(F/A)_{mixture}}{(F/A)_s}$$

stoichiometric	$\phi = 1$
fuel lean	$\phi < 1$
fuel rich	$\phi > 1$

Stoichiometric mixture:

$$C_nH_m + \left(n + \frac{m}{4}\right)(O_2 + 3.76N_2) \rightarrow \text{Products}$$

Off-stoichiometric mixture:

$$C_nH_m + \frac{1}{\phi}\left(n + \frac{m}{4}\right)(O_2 + 3.76N_2) \rightarrow \text{Products}$$

4.2 Combustion Reaction of Hydrocarbon in Air

Off-Stoichiometric Conditions

Other terminology used to describe how much air is used in combustion:

150% stoichiometric air = 150% theoretical air = 50% excess air

$C_3H_8 + \gamma(n + \frac{m}{4})(O_2 + 3.76N_2)$ $\gamma = 1.5$ → mixture is fuel lean

Example: Consider a reaction of octane with 10% excess air, what is ϕ?

The stoichiometric reaction is:

$$C_8H_{18} + 12.5(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + 47N_2$$

10% excess air is:

$$C_8H_{18} + 1.1(12.5)(O_2 + 3.76N_2) \rightarrow 8CO_2 + 9H_2O + aO_2 + bN_2$$

16 + 9 + 2a = 1.1(12.5)(2) → a = 1.25, b = 1.1(12.5)(3.76) = 51.7

$$\phi = \frac{(A/F)_s}{(A/F)_{mixture}} = \frac{12.5(2)(4.76)/1}{1.1(12.5)(2)(4.76)/1} = 0.91$$

4.2 Combustion Reaction of Hydrocarbon in Air

- Consider the combustion of octane, C8H18. Under ideal conditions, all of the hydrocarbon fuel consumed by the engine would be converted to CO2, H2O, and N2. Since ambient air contains approximately 21% oxygen and 78% nitrogen by volume, each mole of oxygen consumed involves (78/21) = 3.7 moles of N2.
- With this information, the ideal combustion equation for a fuel such as octane can be written by balancing the number of moles of each constituent on either side of the combustion equation:
- C8H18 + (12.5)O2 + (12.5)(3.7)N2 --> (8.0)CO2 + (9.0)H2O + (47.0)N2

4.2 Combustion Reaction of Hydrocarbon in Air

- Hence, ideal combustion of octane produces approximately 13% carbon dioxide, 14 % water vapor, and 73 % nitrogen. However, actual vehicle exhaust gas also contains unburned hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NOx), aldehydes, and various other constituents. The emissions in exhaust as it leaves the engine are called engine-out or feedgas emissions; they are carried through a catalytic converter, and the net output to the air is called tailpipe emissions.

- The ratio of air mass to fuel mass is called air fuel ratio (A/F). The stoichiometric or theoretical A/F is defined as the minimum amount of air that supplies sufficient oxygen for the complete combustion of all the carbon, hydrogen and any other elements in the fuel that may oxidize. For example, the stoichiometric A/F for the ideal combustion of octane can be calculated as follows:

4.2 Combustion Reaction of Hydrocarbon in Air

On a molar basis:

$$(A/F)\text{mole} = \frac{(12.5 \text{ moles } O_2 + 47.0 \text{ moles } N_2)}{(1 \text{ mole of fuel})}$$

$(A/F)\text{mole} = 59.5$ mole air/mole fuel

On a mass basis:

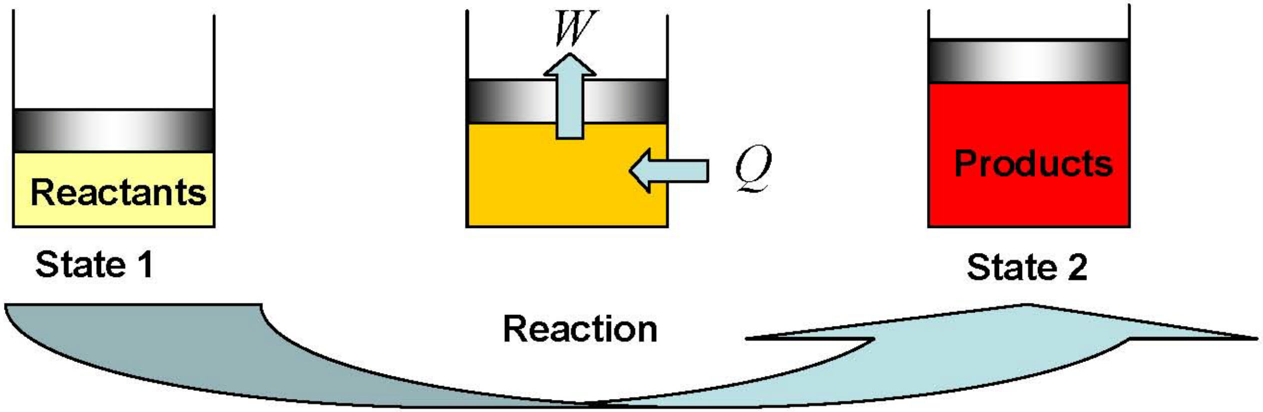
$$(A/F)\text{mass} = \frac{(59.5 \text{ mole air/mole fuel})*(28.97 \text{ kg/mole air})}{(114.2 \text{ kg/mole fuel})}$$

$(A/F)\text{mass} = 15.0$ kg air/kg fuel

4.3 First Law Analysis for Reacting System

Consider a constant pressure process in which n_f moles of fuel react with n_a moles of air to produce n_p moles of product:

$$\underbrace{n_f F + n_a A}_{\text{Reactants}} \rightarrow \underbrace{n_p P}_{\text{Products}}$$



Applying First Law with state 1 being the reactants at P_1, T_1 and state 2 being products at P_2, T_2:

$$Q = \Delta U + W$$

$$Q_{1\to 2} = (U_2 - U_1) + P(V_2 - V_1)$$

4.3 First Law Analysis for Reacting System

$$Q = (U_2 - U_1) + P(V_2 - V_1)$$

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= H_2 - H_1$$

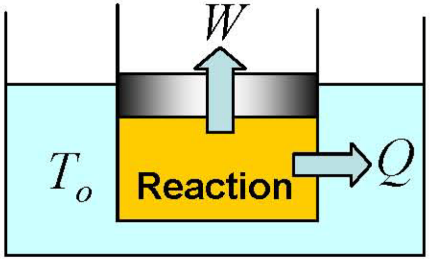
$$= H_P - H_R = \sum_P n_i \bar{h}_i (T_p) - \sum_R n_i \bar{h}_i (T_R)$$

$H_P < H_R$ $Q < 0$ exothermic reaction

$H_P > H_R$ $Q > 0$ endothermic reaction

5 Heat of Combustion

Consider the case where the final temperature of the products is the same as the initial temperature of the reactants (e.g., calorimeter is used to measure Q).



$$P_1 = P_2 = P_o$$
$$T_1 = T_2 = T_o$$

The heat released under this situation is referred to as the **enthalpy of reaction, ΔH_R**,

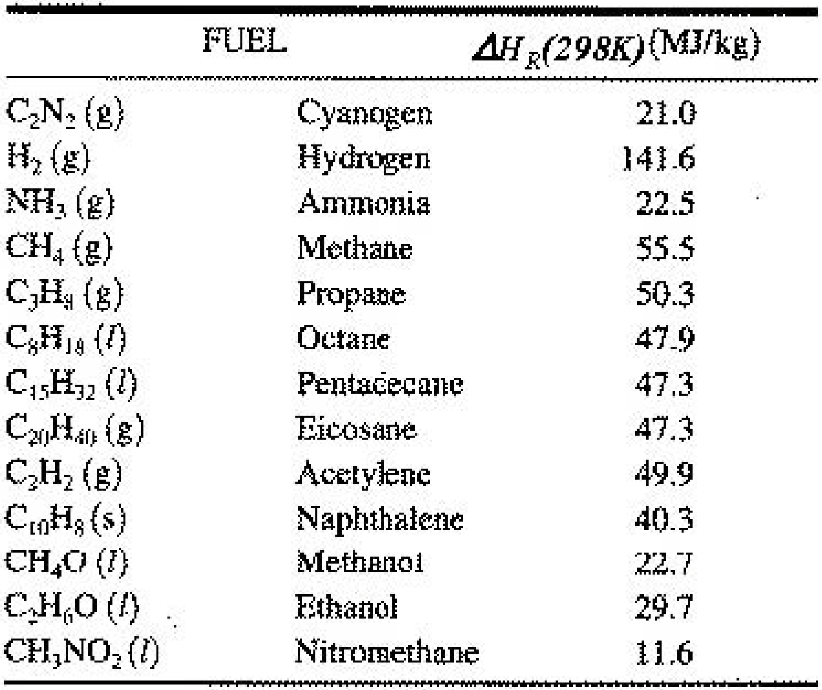
$$\Delta H_R = \sum_P n_i \bar{h}_i(T_p) - \sum_R n_i \bar{h}_i(T_R)$$
$$= \sum_P n_i \bar{h}_i(T_o) - \sum_R n_i \bar{h}_i(T_o) \quad \text{units : kJ per kg or kmol of fuel}$$

5 Heat of Combustion

The maximum amount of energy is released from a fuel when reacted with a stoichiometric amount of air and all the hydrogen and carbon contained in the fuel is converted to CO_2 and H_2O

$$C_nH_m + \left(n + \frac{m}{4}\right)(O_2 + 3.76N_2) \rightarrow nCO_2 + \frac{m}{2}H_2O + 3.76\left(n + \frac{m}{4}\right)N_2$$

This maximum energy is referred to as the **heat of combustion** or the **heating value** and it is typically given per mass of fuel

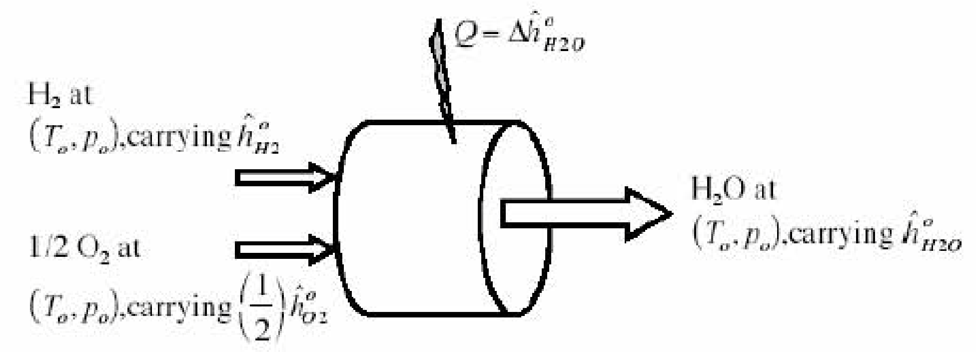


FUEL		$\Delta H_R(298K)$(MJ/kg)
C_2N_2 (g)	Cyanogen	21.0
H_2 (g)	Hydrogen	141.6
NH_3 (g)	Ammonia	22.5
CH_4 (g)	Methane	55.5
C_3H_8 (g)	Propane	50.3
C_8H_{18} (*l*)	Octane	47.9
$C_{15}H_{32}$ (*l*)	Pentadecane	47.3
$C_{20}H_{40}$ (g)	Eicosane	47.3
C_2H_2 (g)	Acetylene	49.9
$C_{10}H_8$ (s)	Naphthalene	40.3
CH_4O (*l*)	Methanol	22.7
C_2H_6O (*l*)	Ethanol	29.7
CH_3NO_2 (*l*)	Nitromethane	11.6

5 Heat of Combustion

- The amount of heat transferred out this reaction, when burning at constant pressure is also known as the enthalpy of reaction.

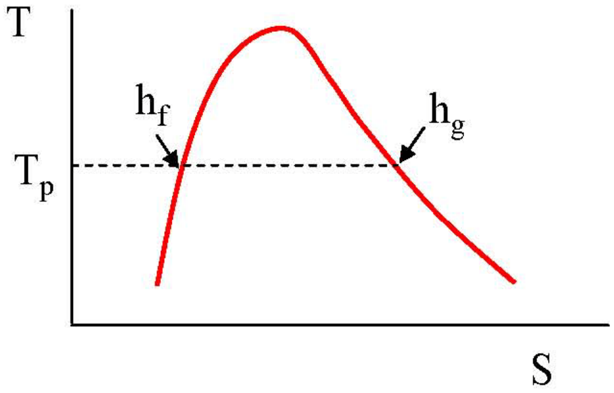
$$H_2+\frac{1}{2}(O_2+3.76N_2)\rightarrow H_2O+\frac{3.76}{2}N_2 \quad \left\|+\Delta\hat{h}^o_{H2O}\right\|$$



- For most hydrocarbon the maximum enthalpy of reaction per unit mass of fuel, or heating value, is 45 -50 MJ/kg, for hydrogen it is 123 MJ/kg.

5 Heat of Combustion

There are two possible values for the heat of combustion that can be calculated depending on whether the water in the products is taken to be in a liquid or vapor state.



From steam tables:

$$h_{fg} = h_g - h_f > 0$$

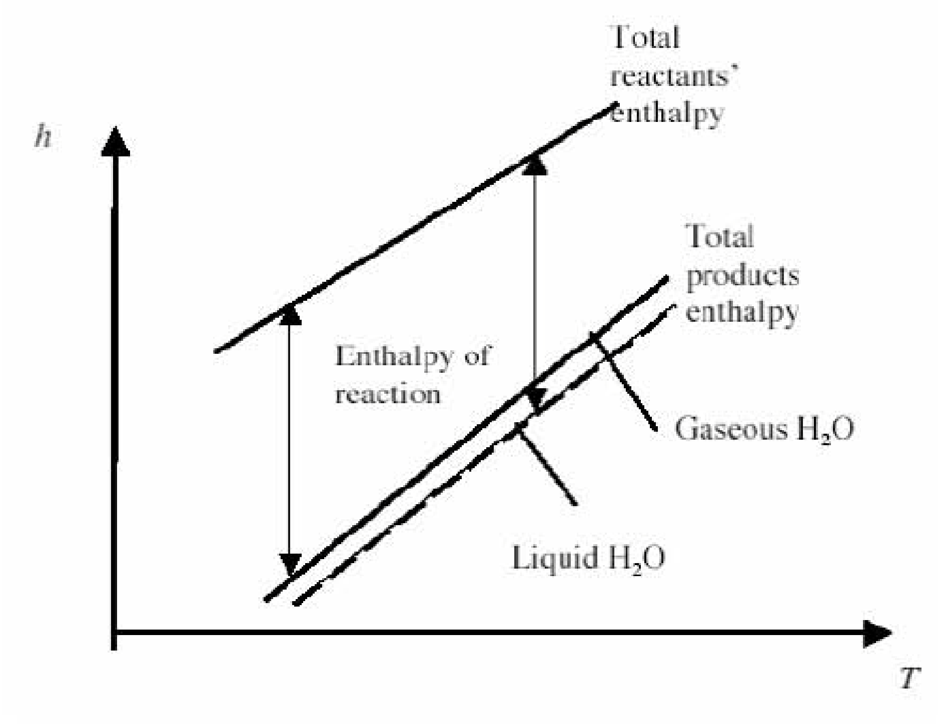
$$\Delta H_R = H_P - H_R < 0 \quad \text{(exothermic)}$$

The term **higher heat of combustion** is used when the water in the products is taken to be in the liquid state

The term **lower heat of combustion** is used when the water in the products is taken to be in the vapor state

5 Heat of Combustion

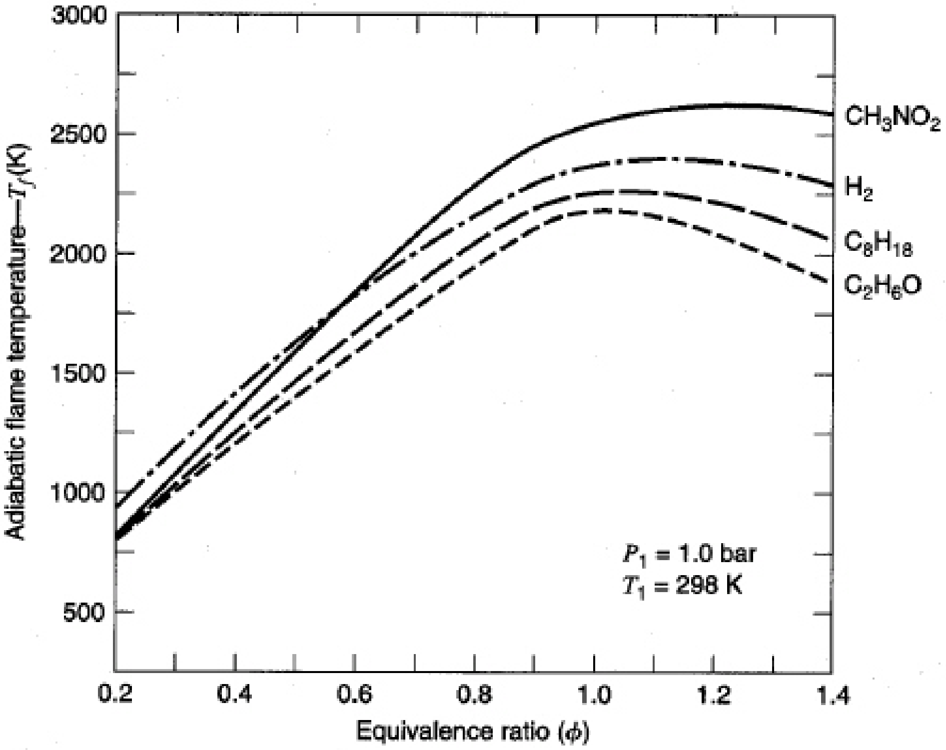
HHV vs. LHV



- This is also the Higher Heating Value (HHV), if water in the products is in the liquid phase, or the Lower Heating Value (LHV), if it is in the gaseous phase (getting either depends on T and p of the process).

Adiabatic Flame Temperature

- Consider the case where the cylinder is perfectly insulated so the process is adiabatic (*Q= 0)*
  - For a constant pressure process, the final products temperature, *T_a, is known* as the **adiabatic flame temperature (AFT).**



Effects of Fuel-air mixture on Constant Pressure Adiabatic Flame Temperature with products at equilibrium

Stoichiometric mass of air for complete combustion of a fuel $(AF)_s$,(kg of Air/kg of Fuel)

$$AF)_s = 11.51\ C\% + 34.48(H_2\% - O_2\%/8) + 4.31\ S\%$$

- **Example**: Find the $AF)_s$ for heptane (C_7H_{16}).

Molecular weight of heptane = 7*12+16*1 = 100 kg

C% = 7x12/100=84%, H_2% = 16x1/100=16%,

O_2% = 0.0, S% = 0.0 :::

$AF)_S$ = 11.51x0.84 + 34.48x0.16 = 15.18 (kg of air / kg of fuel)

Actual Air-Fuel Ratio $AF)_a$ and Excess Air

- Note: for practical cases, it is common practice to use more air than stoichiometric amount to increase the chances of complete combustion or to control the temperature of the combustion chamber. **Excess Air** must be supplied (more than AF)s) as the mixing of air and fuel **is not perfect**.
- **% Excess air = [{AF)a – AF)s} / AF)s] x 100**
- A mixture with an excess air is termed **weak mixture & poor or lean**. And one that has a deficiency of air is termed **rich mixture**.
- For SI engine, $AF)_a$ ~ (12 – 20) depending on the operating conditions (e.g., accelerating, cruising, starting etc.)
- For CI engines, $AF)_a$ ~ (18 – > 30) due to poor mixing of fuel and air.

Engine Exhaust Analysis
Determination of AF in an engine during operation

- It is common practice to analyze the exhaust of an IC engine.
- The control system of a modern *smart automobile engine includes sensors that continuously monitor the* exhaust leaving the engine. These sensors determine the chemical composition of the hot exhaust by various **chemical, electronic, and thermal methods**. This information, along with information from other sensors, is used by the **engine management system (EMS)** to regulate the operation of the engine by controlling the air-fuel ratio, ignition timing, inlet tuning, valve timing, etc.
- Repair shops and highway check stations also routinely analyze automobile exhaust to determine operating conditions and/or emissions. This is done by taking a sample of the exhaust gases and running it through an **external analyzer.**
- When this is done, there is a high probability that the exhaust gas will cool below its dew point temperature before it is fully analyzed, and the condensing water will change the composition of the exhaust. To compensate for this, a *dry analysis can be performed* by first removing all water vapor from the exhaust, usually by some thermo-chemical means.

The Analytical Procedure to Determine the Actual Air-Fuel Ratio AF)$_a$

1. Write the combustion equation:

$$X(\frac{x}{12}C + \frac{y}{2}H_2) + YO_2 + 3.76YN_2 = aCO_2 + bCO + cO_2 + dH_2O + eN_2$$

- Where x, y, a, b, c & d are known,
- X, Y & d are unknown.

2. By applying required balances, X and Y are determined

3. AF)$_a$ = (32 Y) / (0.232 X)

Notes

- M = Molecular weight , N = number of moles.
- Molecular weight of air; M_{air} = 28.97 kg/kmol
- Mass = moles x molecular weight; m = NxM
- $AF)_{by\ mass} = AF)_{by\ vol} \times (M_{air}/M_{fuel})$
- Where, $AF)_{by\ vol}$ is the $(N_{O2} + N_{N2})$ in the equation of combustion of a fuel.
- λ- ratio $\{AF)_a/AF)_s = m_{air,a}/m_{air,s}\}$ is also called 'percentage of theoretical air'.
- The subscripts: a = actual, s = stoichiometric.