Topic No 8: Fuel Characteristics and Alternative Fuels.

CONTENTS:

I. Fuels types and resources.

The combustible fuels are designated as hydrocarbons, C_xH_y where x and y = 1….20

Main sources of combustible fuels:

1. Coal is the most extensive resource. It is more difficult to extract and transport than liquid or gaseous fuels. It is not suited for use in modern engines and is used mainly for the production of steam for electrical power.
2. Petroleum-based oils resources are limited. These fuels are intensively used in internal combustion engines because of their high energy density and ease of fuel delivery.
3. Gaseous fuels are easy to transport. These fuels have less energy density. Their reserves are reasonable.

II. Classification of fuels by chemical structure.

- In hydrocarbon molecules carbon atom combines with itself with either single (saturated structures), double or triple bonds (unsaturated structures).
- In addition, hydrocarbons form either straight or branched chain structures and cyclic molecules.

Alkanes (Paraffins) C_nH_{2n+2}

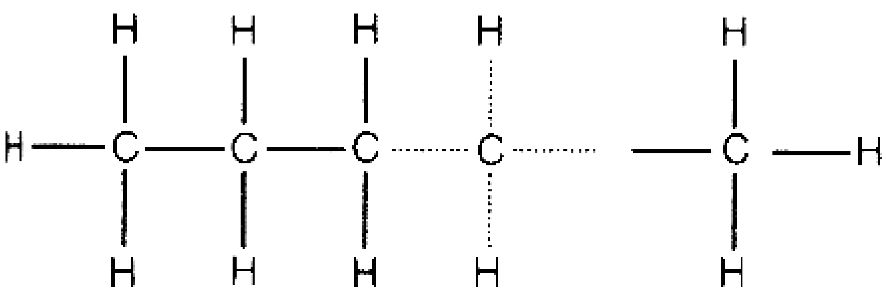


Figure 1. Straight chain (n-) molecules.

Examples: straight chain paraffins are methane CH_4 and octane C_8H_{18}

Alkanes have a high hydrogen content and high heating values. Branched chain types have a more compact structure and have greater resistance to auto-ignition.

II. Classification of fuels by chemical structure.

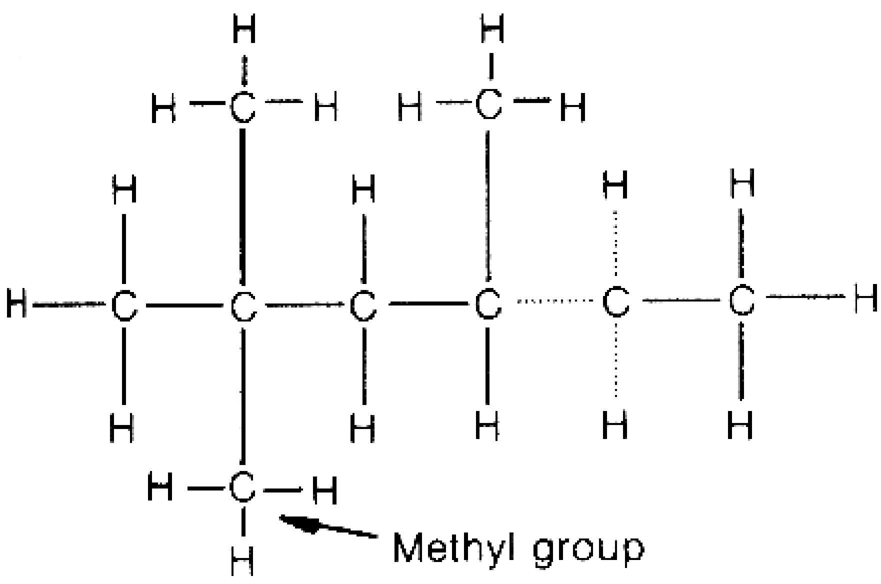


Figure 2.
Branched chain (iso-) molecules.

Some hydrogen atoms are replaced by the group CH_3 (a methyl radical). Example of the isomolecules is iso-octane $C_8H_{18.}$ In isooctane the group CH_3 is attached to the 2 and 4 carbon atoms from the left and is in fact 2,2,4 trimethylpentane.

II. Classification of fuels by chemical structure.

Cyclanes **C_nH_{2n}**

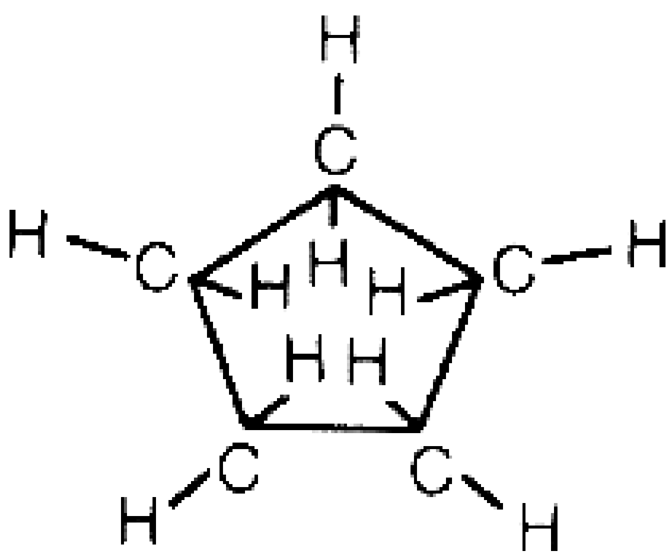


Figure 3. Cyclo molecules.

-These are also often called either cycloparaffins or naphthenes.

-They have closed chain structure and are essentially straight-chain saturated hydrocarbons turned into a ring structure.

-The hydrogen atom at either end is therefore deleted to allow the final C to C bond and can be replaced if the ring is broken. Thus they are unsaturated hydrocarbons.

-An example is cyclopentane C_5H_{10}. Rings having more than 6 atoms of carbon are not common.

II. Classification of fuels by chemical structure.

Alkenes C_nH_{2n}

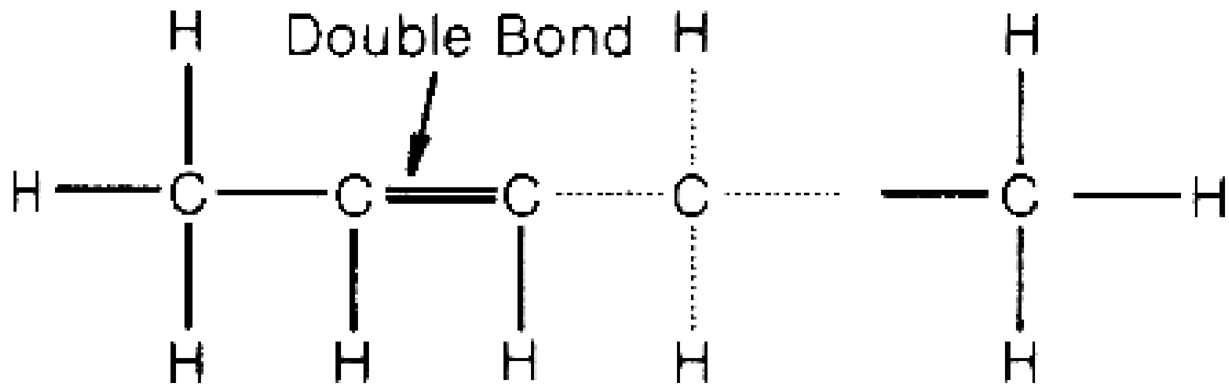


Figure 4. Straight chain (n-) molecules.

These are also called olefins.

They contain one double bond and are open chain unsaturated hydrocarbons.

The double bond may occur between different carbon atoms in large molecules giving a series of different compounds with the same identity.

An example is butene $\mathbf{C_4H_8}$.

II. Classification of fuels by chemical structure.

Alkynes **C_nH_{2n-2}**

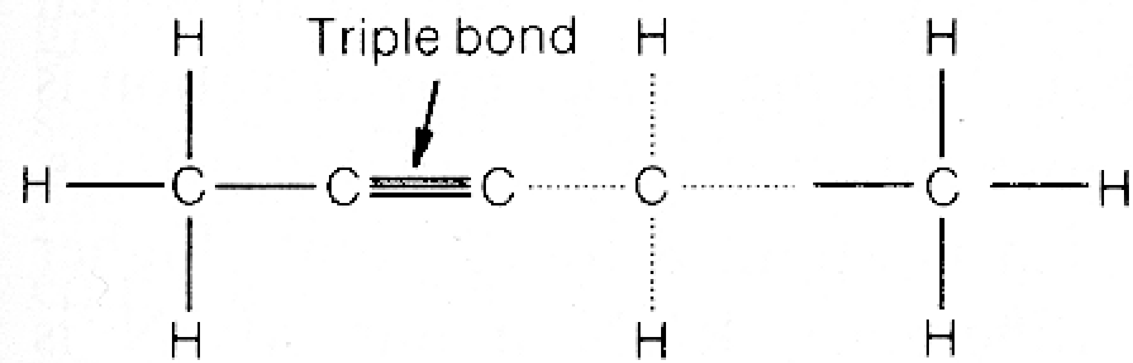


Figure 5. Straight chain (n-) molecules.

-They sometimes are called acetylenes because they are based on the structure of the compound acetylene which is the simplest molecule of the series.

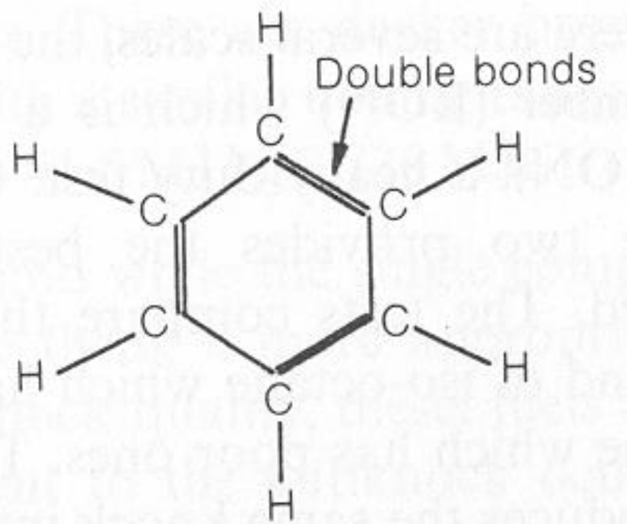
-To expand the series, additional methyl groups replace the hydrogen atoms.

-They all contain one triple bond and are open chain unsaturated hydrocarbons.

-An example is acetylene C_2H_2.

II. Classification of fuels by chemical structure.

Aromatic hydrocarbons C_nH_{2n-6}



They are built up on a basic molecule which is the benzene ring C_6H_6 which contains three double and three single bonds and is a closed chain unsaturated hydrocarbon.

To expand the series, methyl groups replace the hydrogen atom (Figure 7).

Figure 6.
Cyclo molecules.

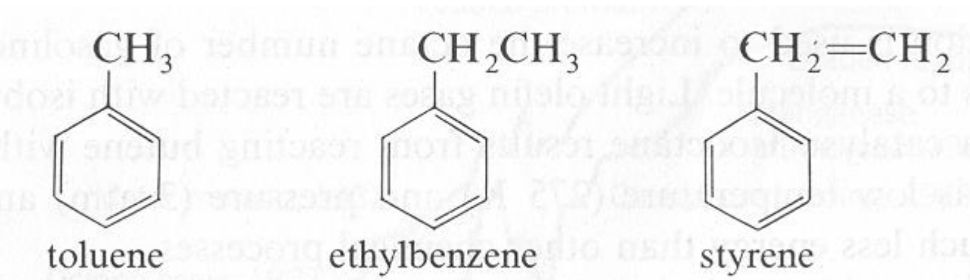
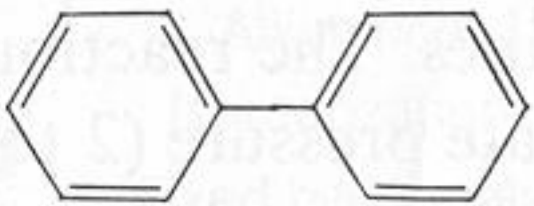
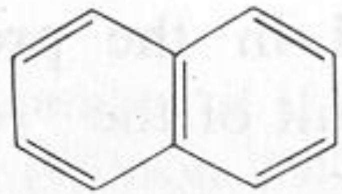


Figure 7. The structure of toluene, ethylbenzene and styrene.

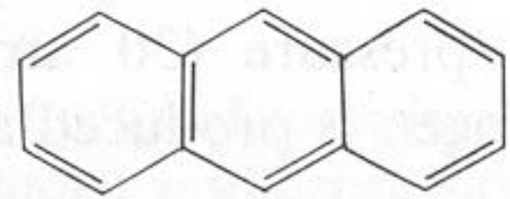
II. Classification of fuels by chemical structure.



biphenyl



naphthalene



anthracene

Figure 8. Examples of two- and three-ring aromatics.

The aromatics have a strong odour and some are the basis for pleasant smelling oils.

They are stable molecules with high knock resistance but are targeted for reduction in fuels because of their carcinogenic potential and high relative reactivity in photo-chemical smog formation.

II. Classification of fuels by chemical structure.

Monohydric alcohols $C_nH_{2n-1}OH$

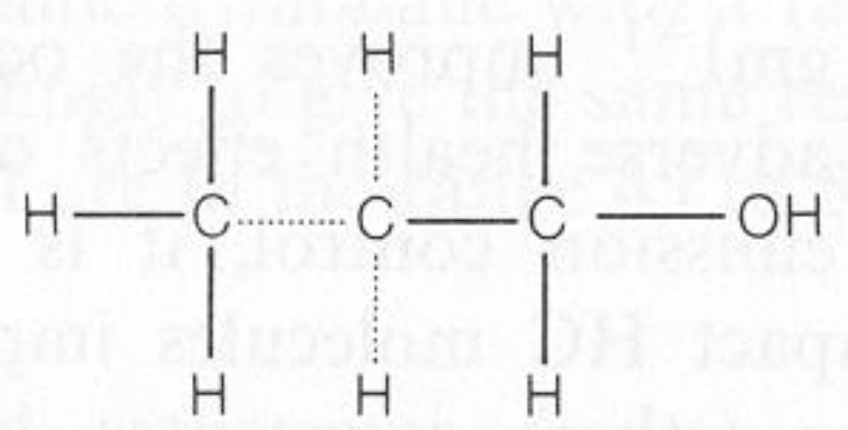


Figure 9. Oxygenates (alcohols).

These are essentially alkanes with one H atom replaced by an OH radical and are one form of a group of fuel compounds known as oxygenates because they contain oxygen.

They are not fossil fuels but may be obtained from them or by fermentation of vegetable matter.

The common types are ethyl alcohol C_2H_5OH and methyl alcohol CH_3OH.

Classification by properties of petroleum-based fuels

Petroleum-based fuels are a blend of many hydrocarbons distilled and reformed in the refining process to give appropriate properties.

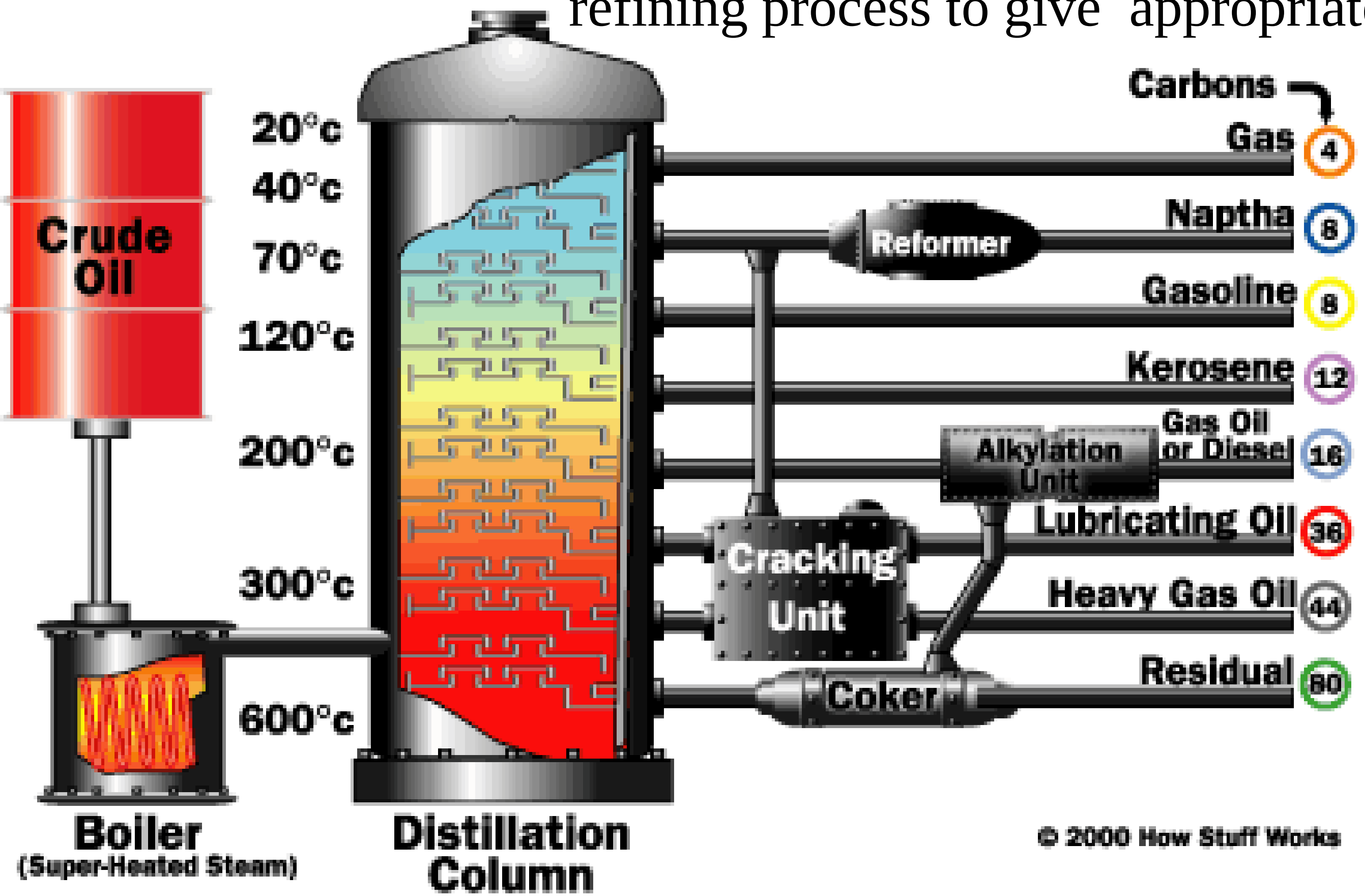


Figure 10. Crude oil Refining process.

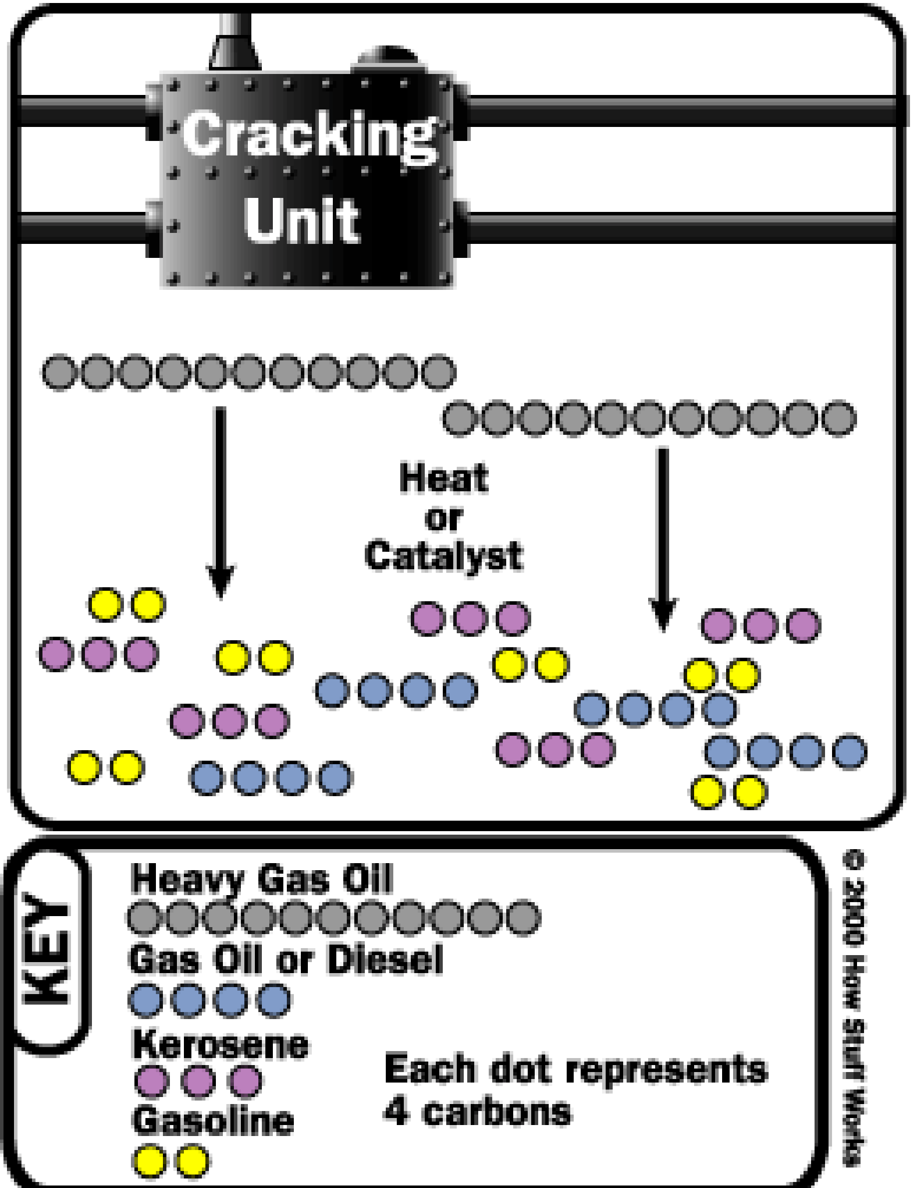


Figure 11. Cracking - breaks large chains into smaller chains.

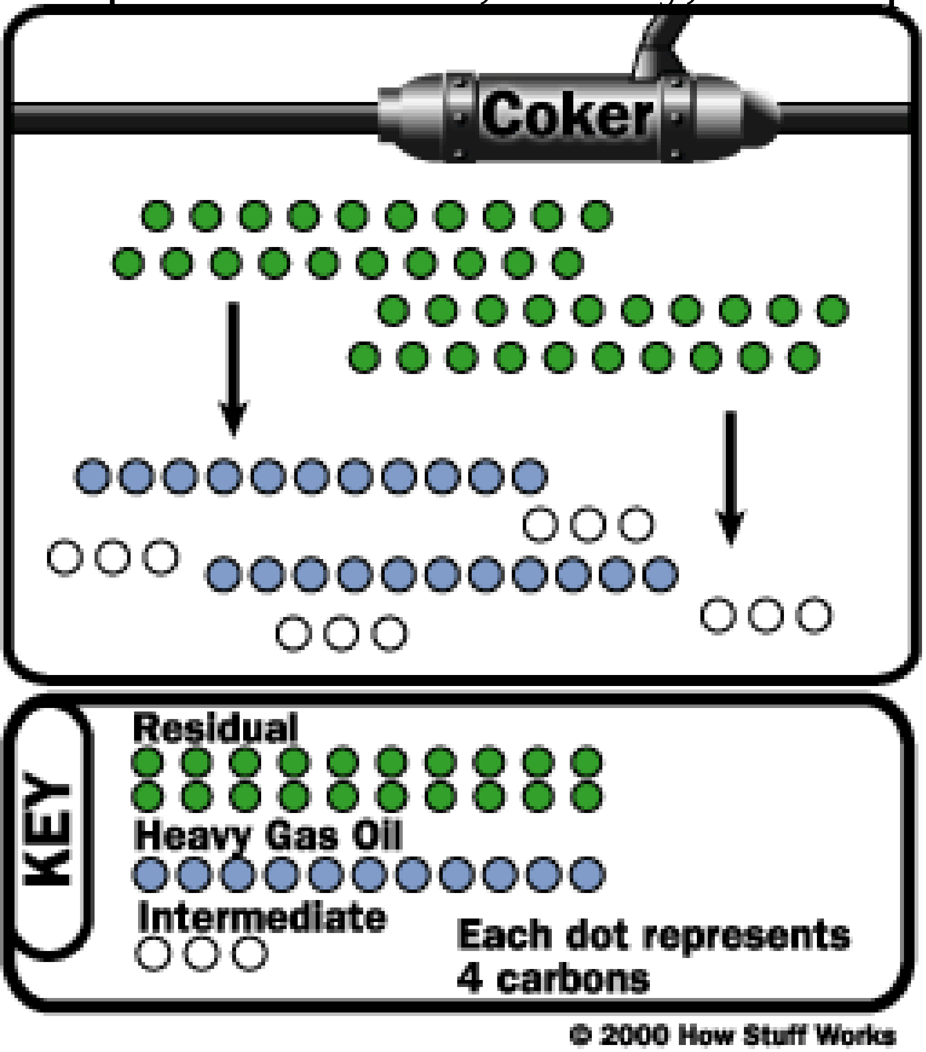
Types of cracking:

•**Thermal** - heating large hydrocarbons at high temperatures until they break apart.

•**steam** - high temperature steam (816 deg. C) is used to break ethane, butane and naptha into ethylene and benzene, which are used to manufacture chemicals.

•**visbreaking** - residual from the distillation tower is heated (482 deg. C), cooled with gas oil and rapidly burned (flashed) in a distillation tower. This process reduces the viscosity of heavy weight oils and produces tar.

Figure 12. Coking - residual from the distillation tower is heated to temperatures above 482 deg.C until it cracks into heavy oil, gasoline and naptha. When the process is done, a heavy, almost pure carbon residue is left (**coke**);



•**Catalytic** coking- uses a catalyst to speed up the cracking reaction. Catalysts include zeolite, aluminum hydrosilicate, bauxite and silica-alumina.

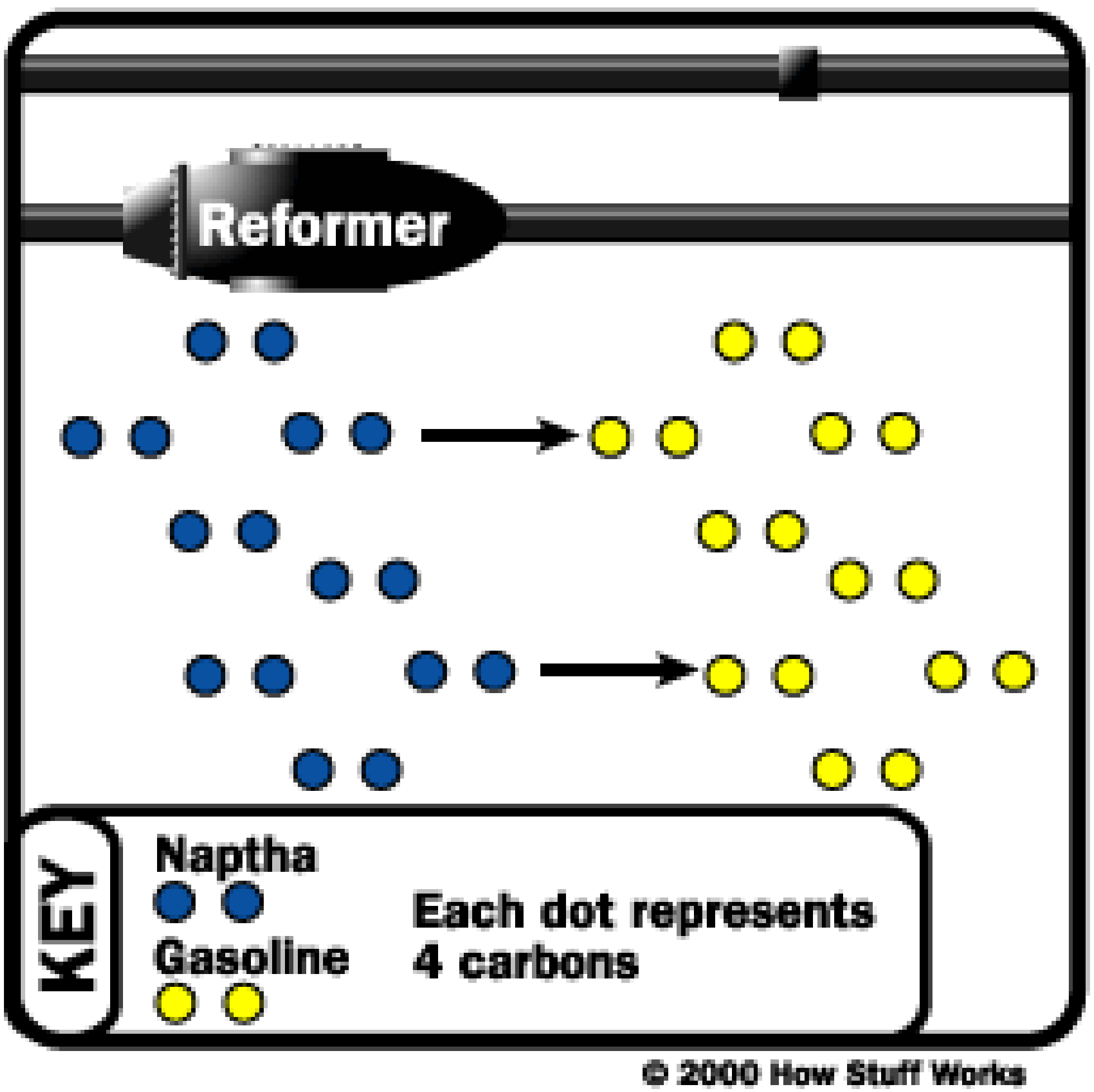


Figure 13. A reformer combines chains.

The major unification process is called **catalytic reforming** and uses a catalyst (platinum, platinum-rhenium mix) to combine low weight naptha into aromatics, which are used in making chemicals and in blending gasoline. A significant by-product of this reaction is hydrogen gas, which is then either used for hydrocracking or sold.

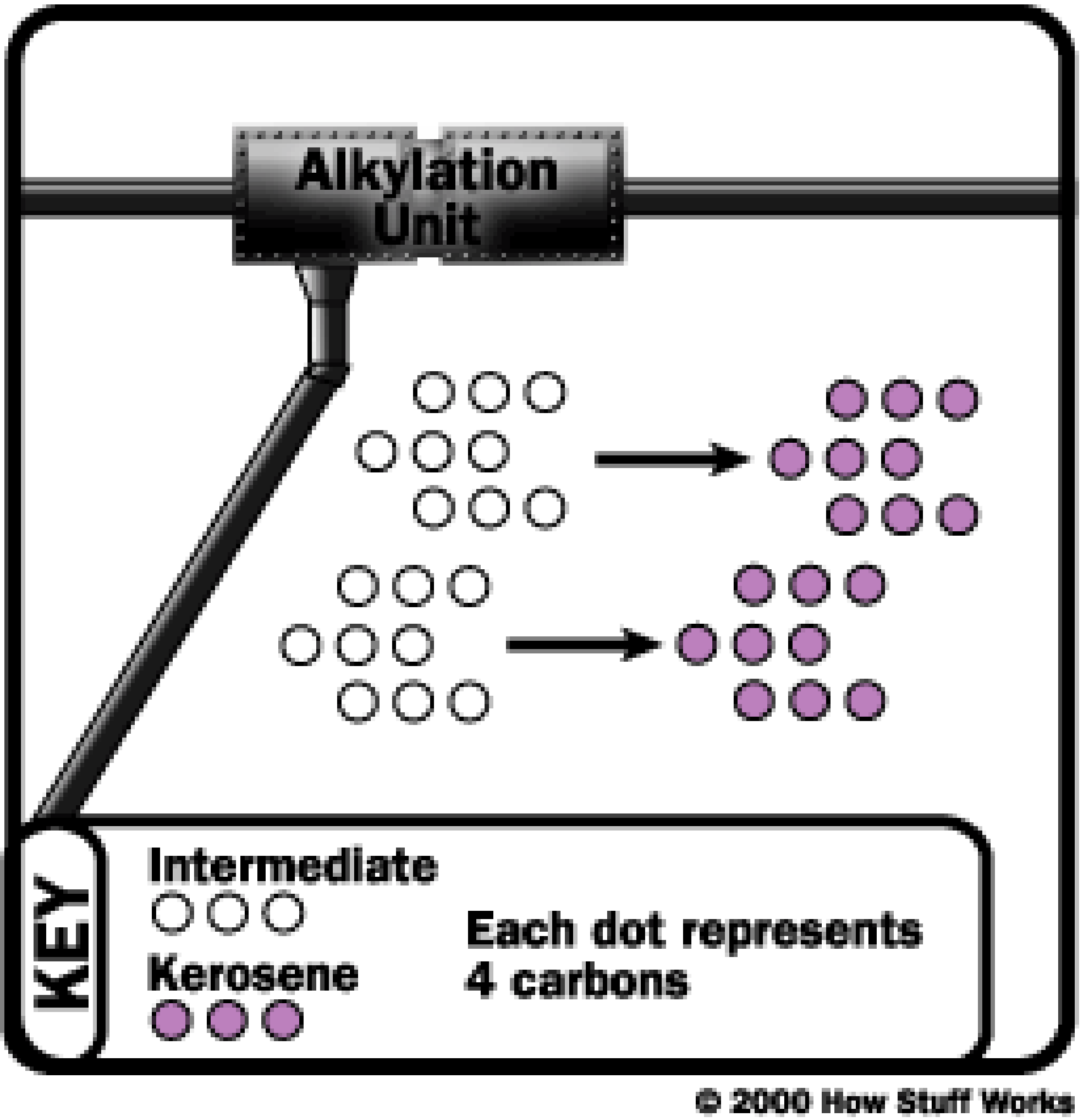


Figure 14. Alkylation – rearrenging chains.

In alkylation, low molecular weight compounds, such as propylene and butylene, are mixed in the presence of a catalyst such as hydrofluoric acid or sulfuric acid (a by-product from removing impurities from many oil products). The products of alkylation are **high octane hydrocarbons**, which are used in gasoline blends to reduce **knock.**

III. Classification by properties of petroleum-based fuels.

The most common groups of petroleum fuels are gasoline, diesel fuels, and fuel oils

Gasoline (petrol): A blend of colourless, volatile liquid petroleum fractions.

- -Boils at 30-200 °C.
- -Relative density ≈ 0.73.
- -A typical average composition – $(CH_{1.85})_{n}$, $n=7$.
- -The fuel is refined to give appropriate octane numbers and volatility.
- -Heating value (lower) ≈ 44MJ/kg (32MJ/l)
- -Most important characteristics are ***volatility*** and ***octane number***.

III. Classification by properties of petroleum-based fuels.

-**Volatility** is the volume percentage that is distilled at or below fixed temperatures.

-If a petrol is too volatile then the petrol forms vapour locks.

-If the fuel is not sufficiently volatile the engine is difficult to start, especially at low temperatures.

-Fuel volatility is specified in BS 4040 to suit climatic conditions.

COMBUSTION AND FUELS

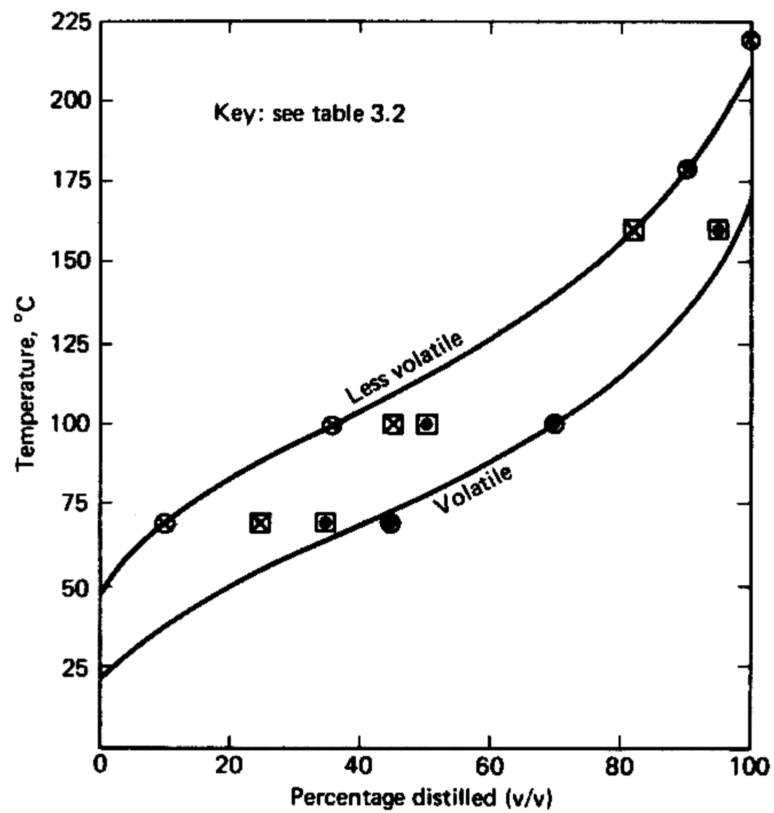


Figure 15. Examples of distillation curves for petrol

Octane number:

The tests compare the antiknock characteristics of the fuel with a blend of **isooctane** which has good antiknock properties and **normal heptane** which has poor ones.

The percentage of isooctane in the blend which produces the same knock intensity as that of the fuel under consideration is termed **octane number**.

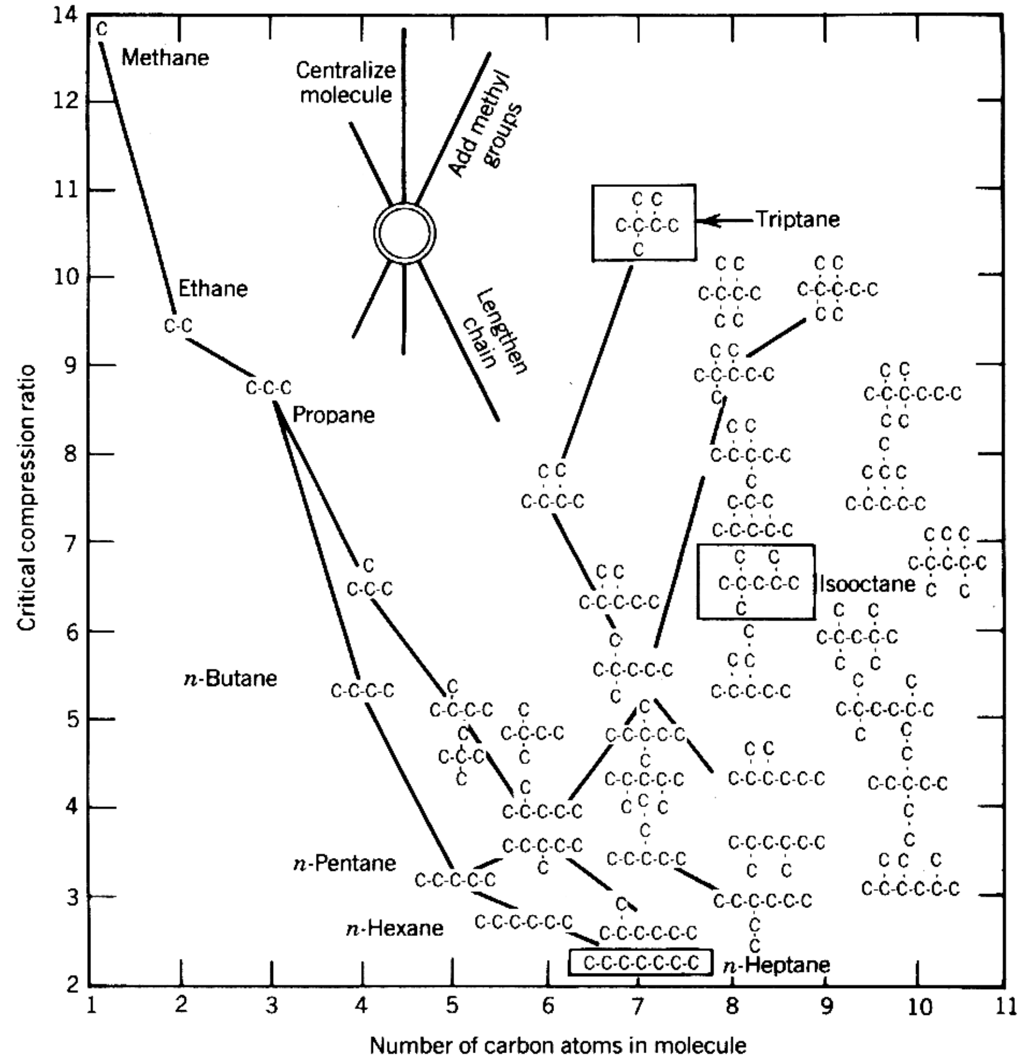


Figure 16. Effect of fuel structure on detonation tendency of paraffinic HC.

Two types of octane number are:
-the **research octane number** (RON) - this is is a light duty test
-the **motor octane number** (MON) – a heavy duty test.

On-road tests indicate that the midpoint between RON and MON provides the best indication of the fuels octane number.

The difference (RON – MON) is called the **fuel sensitivity**, i.e. sensitivity to increased knock under heavy load conditions.

Commercially available petrols have the RON =90-98 (8-10 points higher than MON).

British Standard 7070 defines the specification of unleaded fuel:

Table 1. Octane number requirements of different fuel grades.

Description	RON	MON
Regular unleaded	90	80
Premium unleaded	95	85

Various **additives** can improve the octane rating:
- tetra-ethyl lead (TEL) is phased out in many countries
- compact HC molecules improve the knock rating (alcohol and other oxygenates but much larger quantities than TEL are required.

British Standard 7070 limits the total amount of oxygenates in the content of fuel.

III. Classification by properties of petroleum-based fuels.

Diesel oils: A typical average composition is a $(CH_{1.85})_n$ where *n=11*.

1. Light oils for automotive use. These are brown oils boiling at 180-360°C. Relative density = 0.86. Lower heating value = 42 MJ/kg (35 MJ/1).
2. Heavy oils for stationary or marine engines. These are darker brown, heavy oils. Relative density = 0.87. Boiling range – similar to light oils. Lower heating value =41.5 MJ/kg (36MJ/1).

Important characteristic of the diesel oils: **cetane number** (indicates how readily the fuel self-ignites), **viscosity**, **cold filter plugging point** (at low temperatures the high molecular weight components form a waxy deposit), **the flashpoint** (the temperature to which the liquid has to be heated for the vapour to form combustible mixture with air at atmospheric pressure).

III. Classification by properties of petroleum-based fuels.

Cetane number of the fuel specifies its anti-knock quality in the CI engine. If an engine runs on a fuel with too low cetane number, there will be diesel knock. Diesel knock is caused by too rapid combustion and is the result of a long ignition delay period, since during this period fuel is injected and mixes with air to form a combustible mixture. Ignition occurs only after the pressure and temperature have been above certain limits for sufficient time, and fuels with low cetane numbers are those that self-ignite readily.

The cetane number is obtained from a comparative test in which the original fuel is compared with a mixture of normal cetane, ($C_{16}H_{34}$) rating 100 and αmethyl-napthalene ($C_{11}H_{10}$) rating 0. The proportion of cetane in the comparative fuel gives the cetane number of the fuel under test.

Values which are typical of a good quality fuel are in the range 45 to 50.

Additives in diesel fuel to improve the cetane number are referred to as ignition accelerators. Their concentrations are greater than those of antiknock additives used in petrol. Additives in diesel fuels are amyl nitrate $C_5H_{11}ONO_2$ (addition of 1% quantity by volume improves cetane number of the diesel fuel by 6 units), ethyl nitrate $C_2H_5ONO_2$ and ethyl nitrite C_2H_5ONO.
In very cold conditions special pre-heaters and an addition of volatile fuels with high cetane numbers, such as ether are used to start a diesel engine.

The properties of different fuel oils are specified in BS2896.

Table 2. Specifications for diesel fuels in accordance with BS2896

		BS 2869 Class A1	Class A2
Viscosity kinematic at 38 deg.C (cantistokes)	Min Max	**1.5** **5.0**	**1.5** **5.5**
Cetane number	Min	**50**	**45**
Carbon residue % by mass on 10% residue	Max	**0.2**	**0.2**
Distillation recovery at 350 degC, % by volume	Min	**85**	**85**
Flashpoint, closed (deg.C)	Min	**56**	**56**
Water content, % by volume	Max	**0.05**	**0.05**
Sediment, %	Max	**0.01**	**0.01**
Ash, % by mass	Max	**0.01**	**0.01**
Sulphur, %	Max	**0.03**	**0.03**
Copper corrosion test	Min	**1**	**1**
Cold filter plugging point (deg.C), max	Summer Winter	**-4** **-15**	**0** **-9**

III. Classification by properties of petroleum-based fuels.

Fuel oils: They are used in industrial furnaces and in large marine diesels. This fuel is very viscous and requires heating. It is a brownish, black oil. Relative density = 0.95. Lower heating value = 40 MJ/kg (38 MJ/1).

IV. Classification by properties of gaseous fuels.

Natural gas: is predominantly methane (CH_4), also contains other gases which may include ethane, propane, butane and heavier HC in the form of condensate. Methane and ethane can be liquefied at very low temperatures. Generally liquefaction (to LNG) is impractical. The gases are stored for use as CNG at 15 MPa to 25 MPa. Methane is a clean burning gas (it has a high H/C ratio) and it is safe, easily handled fuel. It has a low laminar flame speed and therefore does not ignite easily. It is lighter than air and disperses readily. Lower heating value = 47 MJ/ kg.

IV. Classification by properties of gaseous fuels.

Liquefied petroleum gas: The main components are propane C_3H_8 and butane $C_4H_{10.}$ Under pressures of 1 MPa these become liquid at atmospheric temperature. LPG is easier to store and handle in comparison with LNG.

Boiling points at atmospheric pressure are: propane -42 °C, butane -0.5 °C.

The majority of LPG (about 70%) occurs as well gas often alongside NG from which it is separated and contains only paraffin hydro-carbons.

LPG is not a safe fuel because of its easy evaporation and density greater than air.

Relative density of the liquid is about 0.51 (propane) to 0.58 (butane).

The lower heating values = 46 MJ/kg.

IV. Classification by properties of gaseous fuels.

V. Classification by properties of alternative fuels:

Alcohols (methanol, ethanol, propanol, butanol), Hydrogen, Biogas, Synthetic fuels, Nitrogen hydrides (ammonia NH_3, hydrazine N_2H_4).

Alcohols. The most commonly available are methanol and ethanol. They are used as fuels or for blending petrol as a fuel extender or octane improver. High methanol content fuels are under consideration and this requires design changes in order to optimise SI engine performance. They have high latent heat, high boiling point and flash point. Production is, for ethanol, by processing vegetable matter and, for methanol, by wood distillation, or by chemical formation from natural gas or coal.

Biogas is mainly methane, like NG

V. Classification by properties of alternative fuels:

Hydrogen is a most attractive fuel with a high heating value. Its density is very low. Hydrogen is difficult to store, has a very high flame velocity and low ignition energy and must be handled with great care. It escapes through seals very easily but disperses readily. The wide flammability limits allow quality control (by varying the fuel/air ratio) which is more efficient than quantity (throttling) control. The low ignition energy may cause abnormal combustion, for example, preignition from surfaces or particles.

- ***Synthetic fuels*** – these are synthetic oxygenates such as MTBE and ETBE (methyl, ethyl tertiary butyl ether). They are derived from methyl and ethyl alcohol respectively via ethers. They are more expensive than the alcohols but have better characteristics for use in IC engines. Other synthetic petrols may be derived from coal or NG either via methanol or by hydrogenation of coal.

V. Classification by properties of alternative fuels:

Nitrogen hydrides (ammonia NH_3, *hydrazine* N_2H_4)

These are synthesized from nitrogen and hydrogen.
Ammonia is toxic but is readily identifiable through its distinct smell.

Nitrogen hydrides have good antiknock properties which allow compression ratios of up to about 12 in otherwise conventional SI engines.

The energy densities are low and they are relatively expensive.