PETROL AND OCTANE NUMBERS

INTRODUCTION

For over a century, the internal combustion engine and its fuel, petrol, have had a major effect on our lives. Despite controversies about traffic congestion, pollution caused by lead compounds amongst others, and large-scale CO_2 emissions contributing to global warming, the importance of petrol is unlikely to diminish for a long time. A study of petrol involves chemistry, pure and applied, so the inclusion of this topic in the new syllabus – with its emphasis on social and applied aspects – is well justified.

PETROL

Petrol is dealt with in Section 5 of the syllabus, which is entitled: "Fuels and Heats of Reaction". As part of the reorganisation and improved presentation of organic chemistry, some hydrocarbon chemistry is dealt with separately from the main organic chemistry component of the syllabus. In particular, the hydrocarbons are being considered in Section 5 as fuels or as sources of fuels. Other hydrocarbon reactions are studied in Section 7. By the time the topic of petrol is reached, the student will have studied:

- Sources of Hydrocarbons
- Structure of Aliphatic Hydrocarbons
- Aromatic Hydrocarbons
- Exothermic and Endothermic Reactions.

OIL REFINING AND ITS PRODUCTS

When crude oil is brought to the refinery, the first process carried out on it is fractionation or fractional distillation. This means that the many compounds in the crude oil mixture are separated according to their different boiling points. Some examples of the resulting fractions and their uses follow:

- Refinery Gas - used to make Liquid Petroleum Gas (LPG)
- Light Gasoline - used to make petrol
- Naphtha - used to make petrol
- Kerosene - used as central heating fuel or to make jet fuel
- Gas Oil - used to make diesel fuel
- Residue Fractions - used to make bitumen for roads.

PETROL COMPOSITION

Petrol is a complex mixture of at least 100 different compounds, mostly hydrocarbons. Most of these are branched-chain alkanes, and some are aromatic compounds.

THE INTERNAL COMBUSTION ENGINE

A number of things happen to the petrol in the internal combustion engine, including:

- Petrol is vaporised
- The vapour is mixed with air
- The petrol-air mixture is compressed
- The mixture is ignited by a spark from the spark plug and burned
- The gases produced by the combustion reaction expand
- Expansion causes the piston to move i.e. kinetic energy is produced.

PREMATURE IGNITION

The greater the extent to which gases are compressed the more they tend to heat up. Sometimes this causes ignition before the spark is produced. This is intended in a diesel engine, where there is no spark plug, but in a petrol engine the occurrence is called auto-ignition or knocking or pinking. This is quite a problem as it can cause loss of power, with obvious danger, or damage to the engine.

It can be prevented in two ways during petrol manufacture:

1. Use of additives
2. Use of a suitable mixture of high-octane compounds.

OCTANE RATING

The octane rating is a measure of the tendency of a fuel to auto-ignite. The lower the octane rating the more likely it is that auto-ignition will occur. Clearly, high-octane fuels are more desirable.

The scale is an arbitrary one. Two compounds were chosen, heptane (C_7H_{16}) and 2,2,4-trimethylpentane ($CH_3C(CH_3)_2CH_2CH(CH_3)CH_3$).

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    H   H   H   H   H   H   H               H  CH3  H  CH3 H
    |   |   |   |   |   |   |               |   |   |   |   |
H – C – C – C – C – C – C – C – H       H – C – C – C – C – C – H
    |   |   |   |   |   |   |               |   |   |   |   |
    H   H   H   H   H   H   H               H  CH3  H   H   H
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heptane — 2,2,4-trimethylpentane

Heptane has a high tendency to auto-ignite, so it was given an octane number of 0. On the other hand, 2,2,4-trimethylpentane has a low tendency to auto-ignite, so it was given a rating of 100.

A mixture of these two compounds containing 95% of 2,2,4-trimethylpentane is said to have an octane number of 95 (2,2,4-trimethylpentane was formerly known as iso-octane, hence the terms "octane number" or "octane rating"). A mixture of compounds with an identical tendency to auto-ignite, under the same conditions of compression, would thus also be given an octane rating of 95. A compound that is less likely to auto-ignite than pure 2,2,4-trimethylpentane would have an octane rating of more than 100.

ADDITIVES

As has been mentioned, the use of additives in petrol manufacture provides a means of preventing knocking. Two types of additive have been in use in recent decades, lead compounds and oxygenates.

Lead compounds e.g. tetra ethyl lead

These work by preventing the type of reactions that cause knocking. They have been in use since the 1920s, but have long been criticised for their harmful environmental effects—the lead compounds present in exhaust fumes are toxic. Their use has been phased out in many countries, and they were banned in Ireland in 2000.

Oxygenates e.g. alcohols or ethers

These compounds work by raising the octane number of the fuel. They cause less pollution, because apart from not containing lead, they produce lower levels of carbon monoxide when they burn. The most commonly used oxygenate is MTBE (methyl tertiary butyl ether). *The systematic name is 2-methoxy-2-methylpropane.* Its octane rating is 118.

HIGH OCTANE COMPOUNDS

Apart from the use of additives, knocking may also be prevented by using a mixture of high-octane compounds in petrol manufacture. Certain molecular features are desirable in ensuring that compounds have high-octane ratings. These are:

a) A high degree of branching
b) Short chain length
c) The existence of rings.

High-octane compounds can be obtained from low by three processes, each involving the use of catalysts:

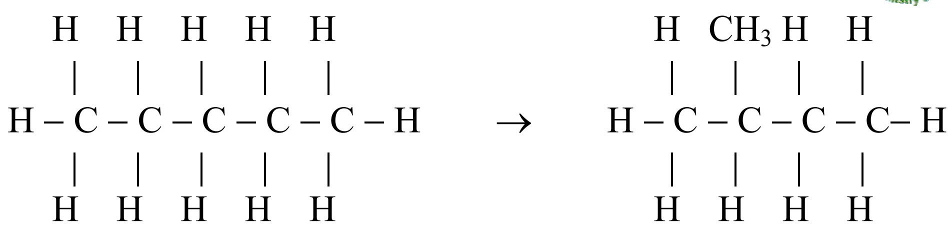
a) Isomerisation
b) Dehydrocyclisation
c) Catalytic cracking.

These processes will be explained in the succeeding paragraphs.

ISOMERISATION

When certain compounds are heated in the presence of a suitable catalyst, a different structural isomer of the particular compound is formed, e.g.

- A straight chain alkane such as pentane (C_5H_{12}), which has an octane number of 62, is heated in the presence of a suitable catalyst
- The chain breaks
- The fragments rejoin to form a branched compound, 2-methylbutane ($CH_3CH(CH_3)CH_2CH_3$), which has an octane number of 93.



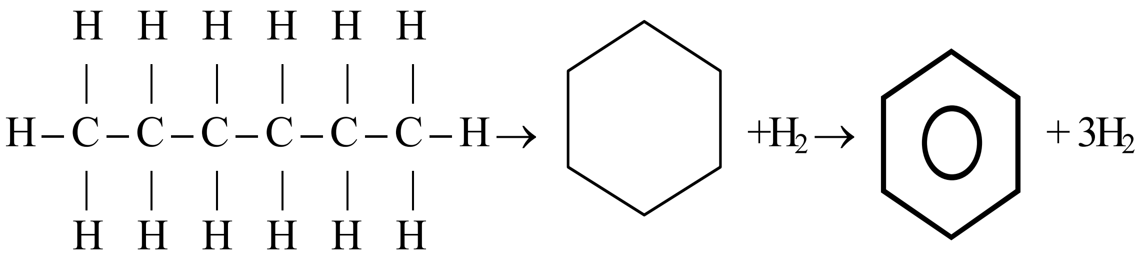
pentane 2-methylbutane

Clearly the product would be a much more suitable component of petrol than the original pentane.

DEHYDROCYCLISATION

This process involves the formation of a ring compound, accompanied by the removal of a valuable by-product, hydrogen gas, e.g.

- A straight chain alkane such as hexane (C_6H_{14}), which has an octane number of 25, is heated in the presence of a suitable catalyst
- The catalyst causes the alkane to change to a cycloalkane e.g. cyclohexane, of octane number 83
  $C_6H_{14} \rightarrow (CH_2)_6 + H_2$
- The catalyst causes the cycloalkane to further change to an aromatic compound, e.g. benzene, of octane number greater than 100
  $(CH_2)_6 \rightarrow C_6H_6 + 3H_2$

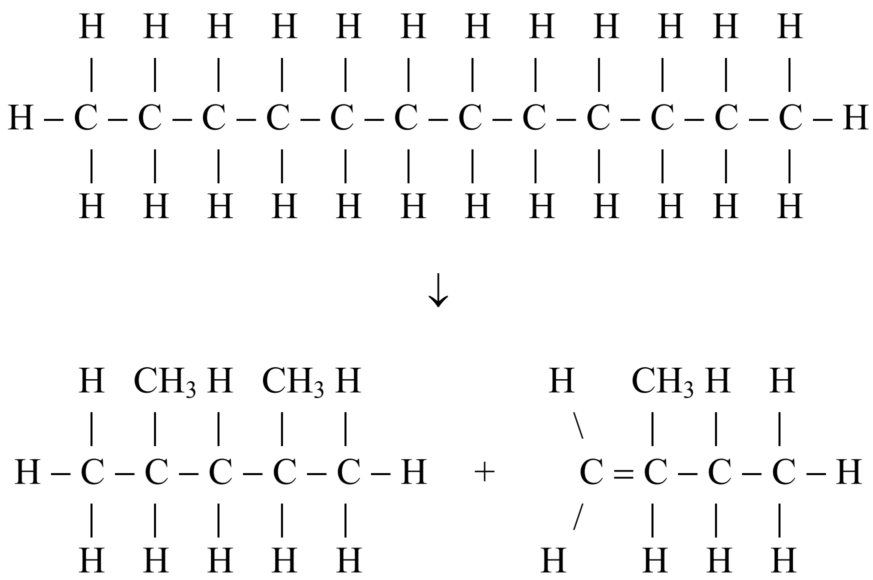


hexane cyclohexane benzene

In terms of octane ratings, the overall effect is to increase from 25 to a number greater than 100. *The same catalyst, platinum dispersed on aluminium oxide, is used for both stages.*

CATALYTIC CRACKING

This process is familiar, as it was included in the 1983 syllabus. It involves taking heavy oil such as kerosene or diesel and heating it to a high temperature in the presence of a catalyst. The large molecule breaks down into several smaller ones, some saturated, some unsaturated e.g.



The unsaturated products are used as feedstock for the polymer industry. The saturated products are usually high-octane branched chain alkanes suitable for making petrol.