Chem Factsheet

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Cracking, Reforming and Isomerisation

You have already studied the separation of crude oil into its components by **fractional distillation**. This method of separation is dependant on the different **boiling points** of the various fractions. But this is only the first stage in petroleum refining. To maximise the economics of the process, the production of the most valuable fraction needs to be enhanced. Obviously demand and income from petrol (gasoline) is very high and so the refinery conditions are geared to maximise the production of this fraction.

One of the fractions, the **naphtha fraction**, does not have very many uses. It is too volatile to be used as a lubricant and it does not have very good burning qualities. Naphtha does not make a very good fuel so, to the refinery operator, producing lots of naphtha is not a very good thing. Different processes are applied to this fraction in particular to produce much more valuable compounds.

1. Cracking

Cracking involves the breaking up of large alkane molecules to form smaller ones. There are two types.

(a) **Thermal cracking** uses **high temperatures** (800°C) and so is **energy intensive**. It is used on the **residue (tar)** obtained at the bottom of the tower.

(b) **Catalytic cracking** uses a catalyst and is used on some of the **distillates** obtained further up the tower. The catalyst used is called a **zeolite** catalyst. These are compounds of complex **aluminosilicates** that occur both naturally and are made synthetically. Due to the presence of the catalyst **lower temperatures** are used and so a saving is made on energy usage.

During cracking **an unsaturated compound** is always formed. Below is an example of a cracking reaction

$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

This is decane (an alkane) - one of the molecules that might be in the naphtha fraction. It is not a good fuel for petrol engines

↓

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$ + $CH_2{=}CH_2$

This is octane. It is a good fuel for petrol engines. It is saturated.

This is ethene. It is unsaturated. It is more reactive than an alkane and a valuable raw material

For the refinery operator, cracking is a two-win process. He gets both a more valuable compound for use in petrol blends and also an alkene which, being more reactive, can be used as an **intermediate** in the synthesis of other compounds such as poly(ethene) and ethanol. Before going onto the next two sections, we need to consider combustion a little more – particularly what happens to the fuel inside a petrol engine.

You have probably been to a garage and seen numbers on the petrol pumps e.g. '95 Ron' - this is the **octane number** of the petrol. But what does number this mean?

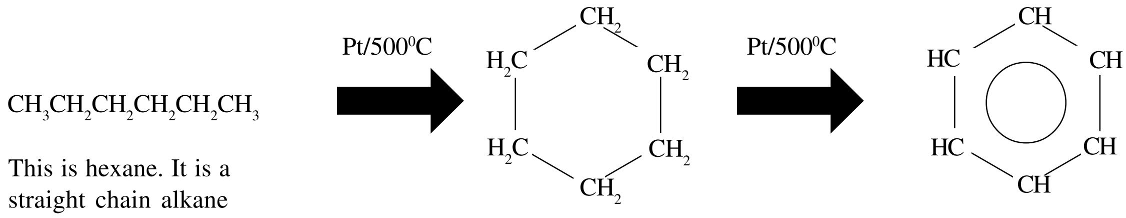
Petrol engines basically work by compressing an air/petrol mixture and then igniting it with a spark from a spark plug. The fuel then burns and the hot gases produced push down a piston. This downward push is then converted to kinetic energy that finally arrives at the wheels of the car making it move. However, conditions can arise by which the fuel can ignite **before** the spark occurs. This is called **auto-ignition**. When auto-ignition occurs, instead of having a smooth burn, the fuel literally **detonates** and is heard as a loud rattle. This is called **'knocking'** (or pinking'). Knocking is not good. At worst, it can lead to a hole forming in the top of the piston (very expensive!) ; at best, a fall off in performance and poor fuel consumption (very expensive!). If allowed to continue, both malfunctions will occur (very, very expensive!!). Most cars these days have an **anti-knock sensor** connected to a computer that, when it detects knocking in the engine, will induce a change in engine conditions and stop the knocking. But the engine can only be adjusted within a small range and so it is important that the right fuel is put into the petrol tank.

Some fuels have a **very low ability to resist knocking - such a fuel is heptane.** This alkane is given an **octane rating of 0.** Now, this is when things get confusing! The compound **2,2,4-trimethylpentane is not octane** - but it does contain eight carbon atoms. It used to be called **iso-octane** and so the label 'octane' has stuck. This compound has a **very high ability** to resist knocking and so is given an **octane rating of 100**. A fuel rated with an octane rating of 95 will perform as if it was composed of 95% 2,2,4-trimethylpentane and 5% heptane. The fuel may not actually contain these amounts as other substances are blended in, but the fuel will behave as if it does. It is possible to obtain fuels with octane ratings greater than 100.

Lead compounds particularly 'tetraethyl lead, $[Pb(C_2H_5)_4]$' were found to significantly increase the octane rating of fuels (If a fuel has a very high octane rating it means that higher compressions can be used and more power obtained from the engine.) but because of environmental issues lead petrol is not used today.

2. Reforming

Reforming is important because many useful intermediates are produced. **Platinum or platinum/rhodium** catalysts are used. Very often **cyclic** or **aromatic** compounds are formed.



This is hexane. It is a straight chain alkane

This is cyclohexane. It is a cyclic alkane.

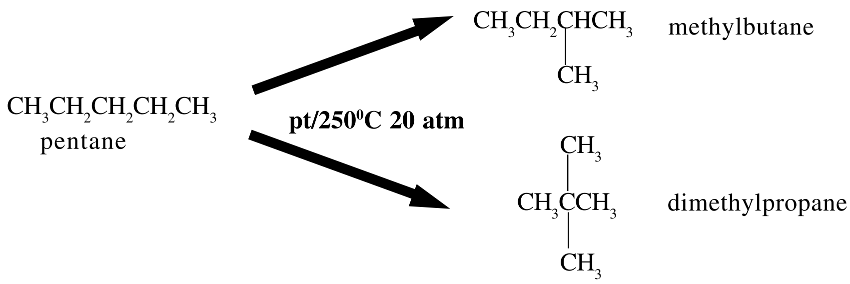
This is benzene. It is an aromatic compound.

Note that during reforming, the **number of carbon atoms does not change;** the number of hydrogen atoms **does** change. Very often hydrogen is given off as a by-product. The change from hexane to cyclohexane gives 1 mole of hydrogen gas and the change from cyclohexane produces 3 moles of hydrogen gas. This amount of hydrogen is significant and can be sold as a product; for instance, to manufacture ammonia.

3. Isomerisation

Isomers are compounds with the **same molecular formula** but with **different structural formula.** In this process then, the number hydrogen and carbon atoms are **the same in both reactant and product.** In terms of refining practice, isomerisation is used to **induce branching** into hydrocarbon chains because branching has been found to produce **better burning characteristics** than hydrocarbons with straight chains.

Isomerisation involves a platinum catalyst, temperatures of about 250ºC and pressures of about 20atm. The process is usually applied to C-4 and C-5 straight chain alkanes.



Practice Questions

1. Complete the following equations which represent cracking reactions.

   (a) $C_{15}H_{32} \rightarrow C_4H_8 +$

   (b) $C_{10}H_{22} \rightarrow C_8H_{18} +$

   (c) $\rightarrow C_3H_6 + C_9H_{20}$

2. What alkanes would you need to form…?
   (a) Cyclopropane
   (b) Cycloheptane

3. What are the possible structures and names for the isomerisation products of (a) hexane and (b) heptane?

Answers

1. (a) $C_{11}H_{24}$ (b) C_2H_4 (c) $C_{12}H_{26}$

2. (a) Propane (b) heptane

3. (a) 2-methylpentane: $CH_3CH_2CH_2CH(CH_3)CH_3$
   3-methylpentane: $CH_3CH_2CH(CH_3)CH_2CH_3$
   2,2-dimethylbutane: $CH_3CH_2C(CH_3)_2CH_3$
   2,3-dimethylbutane: $CH_3CH(CH_3)CH(CH_3)CH_3$

   (b) 2-methylhexane: $CH_3CH_2CH_2CH_2CH(CH_3)CH_3$
   3-methylhexane: $CH_3CH_2CH_2CH(CH_3)CH_2CH_3$
   2,2,-dimethylpentane: $CH_3CH_2CH_2CH(CH_3)_2CH_3$
   2,3-dimethylpentane: $CH_3CH_2CH(CH_3)CH(CH_3)CH_3$
   2,4-dimethylpentane: $CH_3CH(CH_3)CH_2CH(CH_3)CH_3$
   3,3-dimethylpentane: $CH_3CH_2CH(CH_3)_2CH_2CH_3$
   2,2,3-trimethylbutane: $CH_3CH(CH_3)CH(CH_3)_2CH_3$

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