

Catalytic cracking

Aims of the experiment

- To produce petrol and natural gas from paraffin oil through catalytic cracking
- To provide evidence for the formation of low boiling point alkanes based on their flammability
- To understand catalytic cracking as an example of a significant large-scale technical process
- To understand the function of catalysts
- To understand the relationship between the chain length of alkanes and their properties

Principles

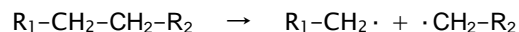
Cracking in chemistry describes the breakdown of an alkane into smaller pieces. Several methods are available for this which proceed via differing mechanisms. They are used by the oil industry to manufacture low boiling point alkanes from the high boiling point fractions of previously distilled crude oil. The main purpose is to obtain high quality petrol derivatives with excellent anti-knock properties. The term "knocking" in an engine refers to the pre-ignition of a petrol-air mixture during compression. This leads to a considerable loss of power and an associated increase in fuel consumption. For an alkane mixture to be a good petrol, it needs on the one hand to be readily flammable, but on the other hand must not spontaneously burn on compression.

The first process for cracking alkanes was thermal cracking. It

has been used on a large industrial scale since as long ago as the 19th century.

Thermal cracking is carried out at temperatures of 500 °C to 1000 °C and at increased pressures. It proceeds via a radical mechanism. It frequently happens that C-H and C-C bonds are cleaved homolytically with increasing temperature. This process is termed pyrolysis.

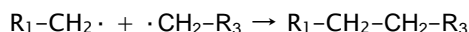
When a C-C bond of a long-chain alkane is broken, fragments of various chain length can result, depending on which bond is cleaved.



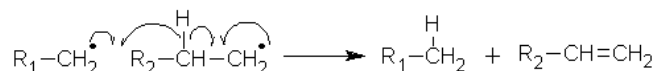
The resulting fragments are radicals. They can react with each other again in a second step. There are various possibilities for this. On the one hand, various fragments can recom-



bine to form new alkanes. In this way, even longer-chain alkanes can result.



On the other hand, the radicals can remove protons from the alkane chain of other molecules. When one of the alkane radicals removes a proton from another radical at the secondary position, an alkene is produced.



All in all, thermal cracking leads to a mixture of alkanes and alkenes of various chain lengths.

The use of catalysts for cracking enables the process to be conducted at the lower temperatures of 400 °C to 500 °C and at normal pressure. Apart from this, the composition of the resulting mixture can be influenced by the choice of catalyst and the reaction conditions. For example, the use of zeolith as a catalyst increases the proportion of branched-chain alkanes, which have better anti-knock properties than non-branched alkanes. Other catalysts used are aluminium oxides and aluminium silicates.

The function of a catalyst is based on the fact that it increases the speed of a reaction by reducing the activation energy required for the reaction. This is facilitated by the fact that the catalyst enables an alternative reaction pathway in which the reaction does not pass through a high-energy transitional state. A catalyst can favour the formation of certain products by selectively increasing the reaction speed only for these reactions.

In contrast with thermal cracking, the exact reaction mechanism of catalytic cracking has not yet been clarified.

As a by-product of catalytic cracking, elemental carbon is also produced which adheres to the catalyst and deactivates it. For this reason, the catalyst must be exchanged regularly and regenerated by burning off the carbon. Burning off the carbon supplies energy for the cracking process.

Risk assessment

Paraffin oil and pearl catalysts are not hazardous substances. A pearl catalyst is an amorphous alumina silica gel consisting of 80% silicon dioxide and 20% aluminium oxide.

During the reaction a mixture of various organic substances is formed, some of which are carcinogenic, mutagenic or poisonous. Contact with the skin of the crack distillate should therefore be avoided. In any case, a lab coat and protective glasses should be worn when performing the experiment.

Both fractions collected are readily flammable. It is possible that elemental hydrogen is contained in some fractions, and for this reason a detonating gas test should be carried out before igniting.

As flammable gases are produced during the experiment, it should in any case be carried out in a fume cupboard. The ground glass surfaces of the apparatus should be greased and joint clips should be used to ensure gas-tightness of the apparatus.

Various crack products



The products can be carcinogenic, mutagenic or poisonous.

They are flammable.

Wear protective glasses and a lab coat!

Equipment and chemicals

- 1 Distillation bridge after Claisen, 250 mm 665 338
- 1 Round-bottom flask 3.3, 250 mL, ST 19/26... 664 301
- 1 Round-bottom flask 3.3, 100 mL, ST 19/26... 664 300
- 1 Beaker, DURAN, 600 mL, nF 664 105
- 1 Support ring for 250 mL round-bottom flask.. 667 072
- 2 Joint clip, plastic from set 665 391ET10
- 1 Glass nozzle, straight 665 237
- 1 Three-way valve, T-shaped, ST nozzles 665 255
- 1 Gas syringe 100 mL, three-way stopcock 665 914
- 1 Chemical thermometer, -10...+220 °C/1 K 666 161
- 1 Heating mantle 250 mL 666 6522
- 2 Laboratory stand II 300 76
- 6 Adhesive magnetic board, 300 mm 666 4660
- 2 Magnetic holder, size 2, 11...14 mm..... 666 4662
- 2 Magnetic holder, size 3, 18...22 mm..... 666 4663
- 1 Magnetic holder, size 1, 9...11 mm..... 666 4661
- 1 Magnetic holder, size 5, 30...32 mm..... 666 4665
- 1 Panel frame C100, two-level, for CPS..... 666 428
- 2 Watch glass dish, 60 mm diam..... 664 153
- 1 Wooden turnings, 200 pcs..... 661 083ET20
- 1 Test tube Fiolax, 16 x 160 mm 664 043
- 1 Test tube holder, wooden, f. 12 tubes 667 052
- 1 Graduated pipette 10 mL..... 665 997
- 1 Pipetting ball (Peleus ball)..... 666 003
- 1 Measuring cylinder 100 mL, with plasticbase 665 754
- 1 Stopcock grease, 60 g..... 661 082
- 1 Paraffin, thick, 100 mL..... 674 0800
- 1 Pearl catalyst, 500 g..... 674 2000
- 1 Iron wool, 50 g..... 671 8400
- 1 Glycerine, 99%, 250 mL 672 1210
- 1 Rubber stopper, one 7 mm hole, 16...21 mm 667 256
- 1 Powder funnel, PP. 65 mm diam..... 604 170

Additionally required:

Igniter

Set-up and preparation of the experiment

Important: The apparatus should be set up as far as possible to the left in the fume cupboard so that sufficient space remains to the right to displace the piston when introducing gas into the gas syringe.

Screw a thermometer into the right-hand GL fitting of the distillation bridge (see illustration). Screw an end cap onto the left-hand GL fitting. Now attach the distillation bridge to the lower left corner of the magnetic board using a magnetic holder. It is not connected to the cooling water, as air cooling is sufficient.

Grease both flasks, mount them onto the distillation bridge and attach them to the magnetic board using magnetic holders. Secure both of them with a joint clip. The 250 ml flask acts as a distillation flask (left) and the 100 ml flask as a receiver (right).

Place the heating mantle on a laboratory stand under the distillation flask in the bottom left corner of the magnetic

board. Place a water bath on a second laboratory stand under the receiver flask.

Fit a glass nozzle with iron wool to act as blow-back protection. For this, push some iron wool into the tip of the glass nozzle using wooden turnings and press it firmly. The blow-back protection has two functions. Firstly it prevents a flame blow-back into the apparatus, and secondly it reduces the flow speed of the gas produced so that it can be ignited.

Now attach a three-way valve to the distillation flask using a drilled-out silicone stopper and fix it to the magnetic board with a magnetic holder (see illustration). Insert the prepared glass nozzle into the upwards facing outlet of the three-way valve using a drilled-out silicone stopper. Attach the gas syringe to the third outlet of the three-way valve and fix it to the magnetic board with a magnetic holder.

Before starting the experiment, prepare a test tube for the detonating gas test.

Performing the experiment

Note: Operating the apparatus can be made easier by marking the opening direction of the three-way stopcocks on the stopcocks.

Half fill a 100 mL measuring cylinder with pearl catalyst. Place the contents into the distillation flask using a funnel. Then add 10 mL of paraffin oil. Position the three-way valve so that any resulting gas can be led to the outside via the glass nozzle. Raise the heating mantle and the water bath and switch on the heating mantle.

After some time the development of gas can be observed in the flask with the paraffin oil. Collect the gas in a test tube and carry out a detonating gas test to ensure that no hydrogen has been produced. For this, hold a lit wooden shaving in the test tube. If no explosion occurs, then no hydrogen is present and the gas can be lit. If it is not possible to ignite the gas, then the blow-back protection in the glass nozzle must be optimised.

The flame can be extinguished after a short time and the gas led into the gas syringe. Discard the first 100 mL (to flush the gas syringe) and keep the second 100 mL for further analysis. Then lead the gas again to the outside via the glass nozzle and burn it off.

When a sufficient quantity of crack distillate has collected in the receiver flask, lower the heating mantle and switch it off.

To demonstrate that paraffin oil is not readily flammable, place a small amount of it onto a watch glass dish and attempt to light it.

As soon as there is no further gas development in the apparatus, remove the flask with the crack distillate. Place the crack distillate onto a watch glass dish and ignite it. In contrast to paraffin oil, it can be ignited.

Observation

1. A development of gas can be seen in the distillation flask.
2. A black residue forms on the catalyst.
3. Two fractions are produced: gas and crack distillate.
4. Both fractions can be ignited, in contrast to paraffin oil.

Result of the experiment

In the case of alkanes, the boiling point and melting point increase with increasing chain length, while the reactivity is reduced with increasing chain length. Paraffin oil is a mixture of alkanes with an average chain length of 10 to 16 carbon atoms. It is an oil that, although it is flammable, is difficult to ignite.

With catalytic cracking, a mixture of alkanes and alkenes of various chain lengths is formed. Because of the high temperature, the low boiling point constituents rise up into the gas phase, pass through the distillation bridge and cool down continuously in the process. The constituents with a chain length of 1 to 4 carbon atoms are gaseous at room temperature. They pass into the gas fraction, while constituents with a chain length of about 5 to 11 carbon atoms collect in the flask as crack distillate.

Both fractions are readily flammable, as they mainly consist of volatile hydrocarbons with a significantly shorter chain length than paraffin oil.

The blackening of the catalyst is caused by deposits of carbon. These lead to deactivation of the catalyst.

Follow-on experiments

The gas fraction can be analysed by gas chromatography in accordance with the instructions from Experiment C3.2.1.1 "Gas chromatographic analysis on cigarette lighter gas".

The presence of unsaturated hydrocarbons in the crack distillate can be proven using bromine water. However, more crack distillate is needed for this. If required, the experiment can be repeated outside of teaching time using more paraffin oil and correspondingly more catalyst.

Regeneration of the catalyst is an integral part of large-scale catalytic cracking. Anyone who would like to demonstrate this can regenerate the catalyst by burning off the carbon in a stream of oxygen. However, it is important to first let the reaction run to completion so that no paraffin oil remains on the catalyst. The regenerated catalyst can then be used again.

Cleaning and disposal

If the contaminated catalyst is not to be regenerated, it should be placed in the waste container for organic solid waste. Burn off the remains of crack distillate and the gas fraction in the fume cupboard.