Boiling range distribution and fractionated distillation of petroleum

Aims of the experiment

- To work with crude oil and investigate it
- To determine the boiling range distribution and perform a fractionated distillation of crude oil
- To draw conclusions about the composition of crude oil
- To relate the structure to the properties of chemical compounds

Principles

Crude oil is a natural mixture of substances made up of various hydrocarbons. Included in these are mainly straight-chain and branched-chain alkanes, cycloalkanes and arenes. However, crude oil can have various compositions, depending on where it is found. Therefore, no general statement can be made about its characteristics. Instead, the characteristics of various fractions are determined. But even then we are dealing with mixtures of substances. Over 500 different components have been found to this day, also including organic sulfur compounds and salts. The colour of crude oil can vary from light yellow and light brown up to jet black. Also the smell of crude oil can differ greatly.

Today it is assumed that crude oil was formed thousands of years ago through the decomposition of organic material by bacteria, enzymes and mineral catalysts under pressure and the exclusion of oxygen. It occurs in sedimentary rock layers such as argillite, sandstone and limestone. Crude oil is therefore a fossil raw material.

Crude oil serves above all as an energy source and as a starting material for the chemical industry. The major part of crude oil is used for energy production and for fuels. Only about 7 % of crude oil is used for the production of other goods. The constituents of crude oil are starting materials for paints, varnishes, drugs, washing and cleaning agents as well as plastics and road surfaces, for example.

The pumped crude oil also contains natural gas, water and salts. After the removal of these constituents, it is transported via pipelines to the refineries. Here, fractionated distillation of the crude oil takes place with the help of so-called tube furnaces and fractionating towers (for a detailed description see Experiment C2.3.2.1).

Because of its clarity, the bubble tray column (Experiment C2.3.2.1) is highly suited to be used as a model experiment for the technical distillation of crude oil and for the production of various petroleum ether fractions. If, however, the petroleum, diesel or gas oil fractions are needed for further investigations and it is not wished to perform a vacuum distillation, for example, then this experiment is supplemental and serves as an alternative.

For the fractionated distillation, the liquid in this experiment, the crude oil, is heated in distillation apparatus. Here, the liquid initially evaporates on the surface and changes from the liquid into the gas phase. When after some time the vapour pressure of the liquid is equal to the surrounding pressure, the liquid begins to boil.

The boiling point is measured in the rising vapour. This is

Fig. 1: Experimental apparatus for the distillation of crude oil.

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possible, as the vapour at this point is at a temperature which just prevents it from condensing. It is in equilibrium with the boiling liquid.

In the distillation apparatus, this vapour is converted back to the liquid phase through the cooler. The resulting droplets can be collected in the various fractions.

Crude oil is a mixture of substances. The boiling points of the individual constituents lie at different temperatures. This fact is made use of by the fractionated distillation in order to separate the substances. However, the boiling points of the individual constituents lie so close together that a complete separation is not possible by distillation. Instead, the various fractions can be differentiated based on their boiling point ranges (Tab. 1). The properties of these can be investigated.

Risk assessment

Crude oil is a mixture of many various substances. Included in these are also carcinogenic substances. Therefore contact with the skin should be avoided. Suitable gloves are nitrile protective gloves. Further personal protection clothing should also be worn (goggles, lab coat).

The apparatus should be constructed in a fume cupboard. If this is not possible, it is essential that the resulting waste gases are led into a fume cupboard using a tube. Fire and similar sources of ignition must be moved away.

There is a risk of burning, as the apparatus becomes very hot.

Crude oil (artificial)

Signal word:

Hazard

Hazard statements

H225 Highly flammable liquid and vapour.
H304 May be fatal if is swallowed and enters the airways.
H351 Suspected of causing cancer.
H411 Toxic to aquatic life with long-lasting effects.

Safety statements

P210 Keep away from heat/sparks/open flames/hot surfaces. No smoking.
P233 Keep container tightly closed.
P273 Avoid release to the environment.
P280 Wear protective gloves / eye protection.
P303 + P361 + P353 IF ON SKIN (or hair): Remove/take off immediately all contaminated clothing. Rinse skin with water/shower.
P370 + P378 In case of fire: Use extinguishing powder for extinction.
Do not breathe in the vapours.

Equipment and chemicals

1	Pocket-CASSY 2 Bluetooth	524 018
1	CASSY Lab 2	524 220
1	NiCr-Ni adapter S, type K	524 0673
1	Temperature probe NiCr-Ni, 1.5 mm	529 676
1	Claisen distillation bridge 250 mm	665 338
1	Bredt distilling receiver	665 354
1	Volumetric flask Boro 3.3, 250 ml	665 301
4	Volumetric flask Boro 3.3, 100 ml	664 300
6	Joint clip, metal, from set	665 397ET10
1	PVC tubing 7 mm diam., 1 m	604 501
2	Hose clamp 8...12 mm	604 460
1	Support ring for round-bottom flask, 250ml	667 072
4	Support ring for round-bottom flask, 100ml	667 071
4	Standard ground-glass stopper, glass	667 227
1	Warning label GHS	61 0771
1	Screw cap, GL 18, mB	667 305
1	Silicone gasket, GL 18/8, set of 10	667 295
1	Protective sleeves for temperature sensors	666 194
1	Heating mantle 250 ml, adjustable	666 6523
2	Laborboy II (laboratory jack-stand)	300 76
1	Beaker, Boro 3.3, 400 ml, squat	664 131
1	Measuring cylinder 100 ml, plastic base	665 754
2	Adhesive magnetic board 500 mm	666 4659
2	Holder, magnetic, size 2, 11...14 mm	666 4662
2	Holder, magnetic, size 3, 18...22 mm	666 4663
1	Panel frame C50, two-level, for CPS	666 425
1	Aluminium, Foil, 1 roll	661 081
1	Stopcock grease, 60 g	661 082
1	Boiling stones 100 g	661 091
4	Watch glass dish, 60 mm diam.	664 153
1	Graduated pipette 10 ml	664 153
1	Pipetting aid 10 ml	666 002
1	Stopwatch, digital	313 12
1	Raw oil (crude oil), 500 ml	674 5810
Recommended for rinsing:		
1	Ethanol, solvent 1 L	671 9720
1	Petroleum ether, 100...140 °C, 500 ml	670 8210
Also required:		
PC with Windows XP/Vista/7/8		
Also necessary for wireless measurement:		
1	Battery for Pocket-CASSY 2 Bluetooth	524 019
1	Bluetooth dongle	524 0031

Set-up and preparation of the experiment

Construction of the apparatus

Note: All glass equipment used in this experiment must be completely dry and must not contain any residual water.

The distillation apparatus, consisting of a Claisen distillation bridge, a 250 ml flask, the Bredt distilling receiver, four 100 ml flasks, a laboratory jack-stand and a heating mantle, is set up on the adhesive magnetic board (see Fig. 1).

Arrange the apparatus such that the distilling receiver stands vertically. If the sloping angle of the cooler is too steep, droplets will run into several flasks. With too shallow an angle, the distillate will flow back from the cooler into the flask.

When setting up, take into account the fact that in the course of the experiment a glass beaker filled with water must be placed on a further laboratory jack-stand under the receiver to cool the distillate that is obtained.

Turn the Bredt distilling receiver such that the drops of distillate that form at the drip nose of the distillation bridge only fall into one volumetric flask of the receiver.

Note: All glass connections must be adequately greased with stopcock grease. Secure the glass connections additionally with a joint clip (metal!).

Connect the distillation bridge to a water tap in reverse flow using tubing and hose clips. Push the temperature probe into the protective sleeve and screw it into the opening of the distillation bridge provided for it using a screw cap with gasket. Following this, connect the temperature probe to the computer via the temperature adapter S and the Pocket CASSY. Attach a piece of rubber tubing to the vent connector of the adapter to discharge the highly flammable gases that develop.

Note: If a vacuum distillation is to be performed subsequently with the residues, all glass equipment, gaskets, etc. must be thoroughly checked and it is absolutely essential that new boiling stones are added.

Performing the experiment

1. Using the measuring cylinder, fill the flask with 100 ml of crude oil, add 3 or 4 boiling stones and reconnect the flask to the distillation apparatus.

2. To improve the heat insulation of the part of the distillation flask protruding from the heating mantle and the distillation attachment, wrap these parts in aluminium foil. This should ensure the highest possible temperature in the receiver flask. For safety reasons, leave a small observation window free.

3. Load CASSY Lab 2 settings.

4. Start the temperature measurement in the software .

5. Now, with a slow flow of cooling water, carefully heat the crude oil by switching on the heating mantle. Set the heating mantle to the "Maximum" setting.

6. To cool the distillate, immerse the receivers in cold water in a glass beaker supported on a further laboratory jack-stand.

7. When the temperature begins to rise and the first droplets are formed, check again that the distillate is only dripping into one volumetric flask of the receiver.

8. Once a distillation temperature of 90 °C has been reached, turn off the water cooling and remove the cooling water from the cooler. This is important in order to prevent the high boiling point constituents from condensing before reaching the distillation bridge and running back into the receiver flask (sudden drop in the temperature curve). When artificial crude oil is used, this might even have to be done at an lower temperature.

9. By turning the Bredt distilling receiver, draw of the fractions in accordance with the following table. Label the volumetric flask accordingly and attach a warning label.

Tab. 1: Fractions of the fractionated crude oil distillation.

Temperature	Constituents
25 - 40 °C	Liquid gases
40 - 70 °C	Petroleum ether
70 - 100 °C	Petroleum ether
100 - 180 °C	Heavy gasoline

Comment: The boiling ranges chosen can be varied at will by combining fractions or changing the temperature ranges.

Note: Bear in mind that while carrying out the experiment, parts of the apparatus can become very hot. Protect your fingers using pieces of rubber tubing slit open or suitable gloves.

10. As soon as all required fractions have been collected, discontinue heating. Lower the heating mantle and carefully remove the aluminium foil with the tweezers.

Caution! The apparatus rod is very hot! Risk of burning! Do not remove the receiver yet! Remove it only after the fractions obtained have cooled down.

Once cold, the residue can be subjected to a vacuum distillation, if desired. For this, leave the residue in the flask and add fresh boiling stones.

If desired, the fractions can be further analysed (e.g. for viscosity, flammability).

The viscosity can be investigated by drawing up equal volumes of the fractions into a 10 ml graduated pipette and comparing the outflow times. If required, repeat the measurement several times and calculate the mean value.

Observation

After switching on the heating mantle, the temperature in the flask rises and the crude oil begins to boil after several minutes. Vapours rise which repeatedly condense on the wall of the flask and flow back down again.

The vapour rises increasingly higher with time. After a while, the vapour condenses on the protective glass sleeve and heats up the temperature probe. This increase in temperature is recorded.

The vapour streams into the Claisen bridge where it condenses owing to the cooling water and then flows into a volumetric flask via the Bredt distilling receiver.

Evaluation

The evaluation is performed in CASSY Lab 2. A diagram has been prepared for this. In the diagram "Boiling point", the temperature profile of the distillation is first considered.

The appearance of the fractions obtained is recorded in a table.

Result

The measured boiling point of natural crude oil initially increases steeply during the distillation. The slope of the temperature curve lessens during the course of the distillation until a boiling point maximum is reached. After this, the boiling point falls again.

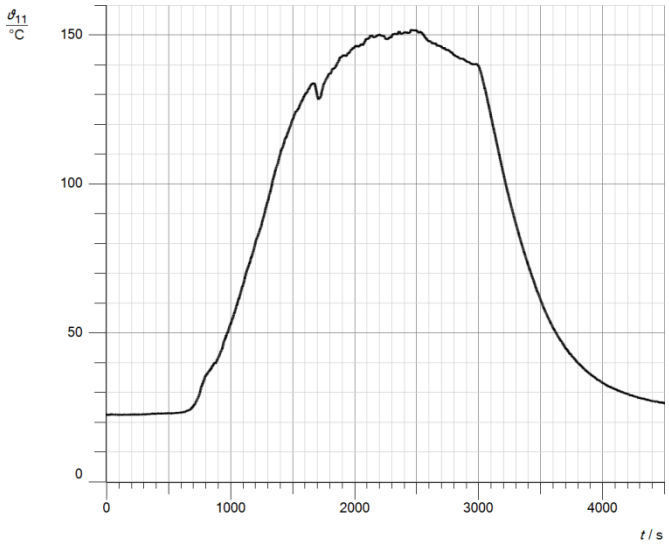

Fig. 2: Temperature profile of the fractionated crude oil distillation.

The boiling point temperature profile can be explained by the composition of the crude oil. As described at the start, crude oil is a mixture of a wide variety of alkanes with different chain lengths. During the course of the distillation, firstly the volatile, short-chain constituents pass from the liquid phase into the gas phase. The long-chain constituents accumulate in the receiver flask. Because of this, the boiling point of the mixture in the flask continuously increases. The slope of the boiling point curve lessens, as the heat capacity of organic compounds increases greatly with temperature. Therefore more energy must be continuously supplied in order to achieve the same temperature increase. Furthermore, cooling through the surroundings also plays a role. The temperature difference to

the surroundings increases, which leads to an increased release of heat.

The curve maximum depends among other things on the power of the heat source, the insulation of the apparatus and the composition of the substance mixture being distilled. After reaching the maximum, the measured temperature falls again, as no more volatile constituents rise from the flask into the gas phase.

Various curve profiles can be observed, depending on the composition of the mixture. Artificial crude oil is a mixture of various fractions whose boiling point ranges must not overlap. In this case, gaps can arise in the boiling point profile which are visible as plateaus in the boiling point graph.

These must not be confused with sudden temperature drops which can arise through return flow when components of the distillate condense again even before reaching the cooler and flow back into the flask (the reason for turning off the cooling at 90 °C).

The fractions collected differ in colour (Tab. 2). The colour differences also depend on the composition of the crude oil investigated.

Tab. 2: Colour differences of the fractions of natural crude oil.

Temperature	Constituents
25 - 40 °C	colourless, cloudy
40 - 70 °C	faint yellow, cloudy
70 - 100 °C	yellow, cloudy
>100 °C	yellow, clear

For the comparison of flammability, it can be expected that the high boiling point fractions are less flammable than the low boiling point fractions because of the lesser content of reactive particles in the gas phase.

Furthermore, high boiling point fractions are more viscous than low boiling point fractions because of the effect of Van der Waals forces between the long-chain molecules. For this reason, they should flow out of the pipette more slowly compared with the low boiling point fractions.

Cleaning and disposal

The individual fractions can be equipped with glass stoppers and kept for further experiments. Rubber stoppers should not be used, as these can be attacked by the vapours of individual fractions. Label the containers with the relevant warning label and collect/store in a cupboard with an extraction system.

Dispose of the residue from the flask in the container for halogen-free organic waste. For cleaning, wash the apparatus and the flask out initially with petroleum ether (100 – 140 °C), and then with ethanol. Dispose of this waste also in the container for halogen-free organic solvent waste. Any stubborn residues can be removed with water, washing-up liquid and a brush.

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