Fractionated petroleum distillation with a bubble tray column

Aims of the experiment

- To work with crude oil and investigate it
- To perform a fractionated distillation of crude oil
- To learn about a bubble tray column
- To understand what happens in a refinery
- 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 where it is found. Therefore, no general statement can be made about its characteristics. Instead, the characteristics of various fractions are described. 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.

Crude oil is a fossilised raw material which mainly serves as an energy source and as a starting material for the chemical industry. The constituents of crude oil are, for example starting materials for paints, varnishes, drugs and washing and cleaning agents. In petrochemistry, however, only around 7 % of crude oil is used for the production of goods. The remainder is used for energy production and for fuels.

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.

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 takes place, among other processes.

This involves heating the crude oil to 400 ° C under normal

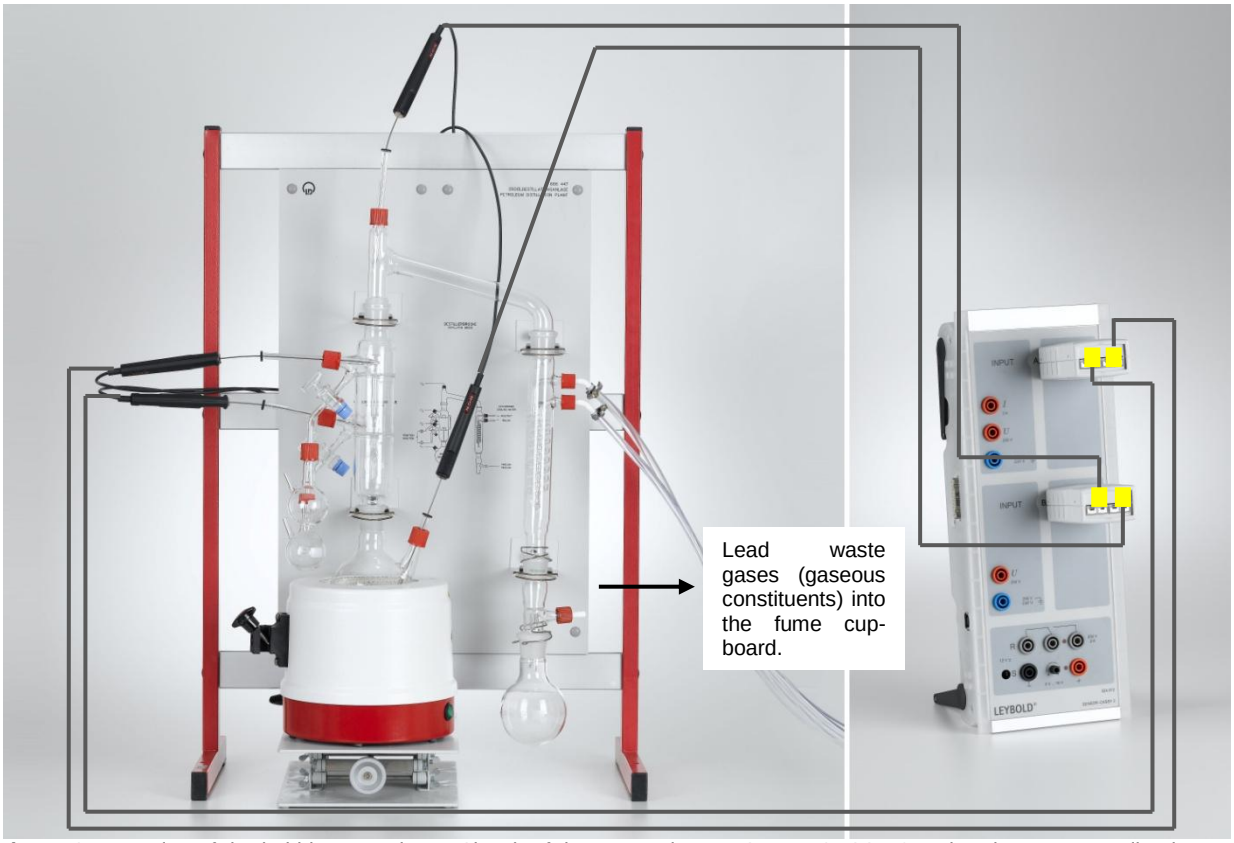

Fig. 1: Construction of the bubble tray column. Sketch of the connections to Sensor-CASSY 2 and to the waste gas line in a fume cupboard.

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pressure in a so-called tube furnace (see Fig. 2). The majority of it evaporates immediately. The vapour-liquid mixture formed here enters into a first fractionating tower. This contains numerous trays with openings ("caps"). The evaporated fractions rise upwards, cool down and return to a liquid state on the various trays. On each tray, a fraction collects that is within a certain boiling point range. As it is hottest at the bottom of the tower, the fractions with the highest boiling points collect here. The fractions thus obtained can be run off continuously from the various trays. The fractions obtained during distillation are roughly divided according to Table 1.

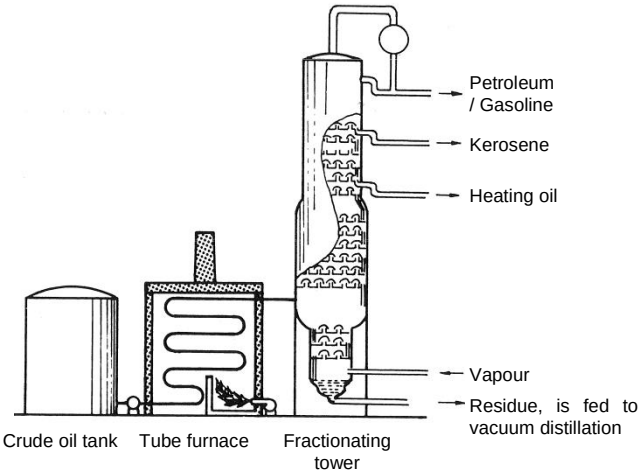

Fig. 2: Illustration of fractionated crude oil distillation under normal pressure.

At a temperature of 400 °C, not all fractions of petroleum can be completely separated at normal pressure. However, the temperature should also not exceed 400 °C, as many hydrocarbons decompose upwards of this point. The residue from the first distillation is therefore passed into a second distillation tower which is under reduced pressure. The constituents evaporate at lower temperatures in this vacuum distillation.

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

Temperature	Constituents
≤ 35 °C	Gases (methane, ethane) and liquid gases (propane, butane)
35 – 100 °C	Petroleum ether
100 – 180 °C	Heavy gasoline
180 – 250 °C	Kerosene
250 – 400 °C	Heating oils
400 – 550 °C	Wax distillate (spindle oils, lubricating oils)
> 550 °C	Vacuum residue for bitumen

In the following experiment, a simplified distillation of crude oil will be carried out under normal pressure in a bubble-tray column. The bubble-tray column has two trays on which therefore two fractions can be collected. In this case we will obtain mixed fractions of the fractions shown in the table. The fractions obtained differ in appearance, viscosity, flammability and soot formation when burnt. These properties will be investigated as part of the experiment.

Risk assessment

Crude oil, also the artificial type, 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 rubber 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.

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.

Precautionary 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	Crude oil distillation, CPS	666 447
1	Panel frame C50, two-level, for CPS	666 425
3	PVC tube 7 mm diam., 1 m	604 501
5	Hose clamp, 8...12 mm	604 460
1	Heating mantle 500 mL, adjustable	666 6533
1	Laboratory stand	300 75
4	Temperature probe NiCr-Ni, 1.5 mm	529 676
4	Sleeve for temperature probe, set	666 194
2	NiCr-Ni adapter S, type K	524 0673
1	Sensor-CASSY 2	524 013
1	CASSY Lab 2	524 220
1	Measuring cylinder 250 mL	665 755
1	Aluminium foil, 10 m	661 081
1	Safety screen	667 605
1	Tweezers, pointed 130 mm	667 026
3	Conical flask 100 mL, SB 19	664 241
3	Cork stopper	667 281
1	Warning labels	661 0771
3	Evaporating dish	608 311
3	Wooden turnings, from set	661 083ET20
1	Stopcock grease, 60 g	661 082
1	Crude oil, artificial, 1 L	674 5840
or	crude oil, 500 mL	674 5810
1	Boiling stones 100 g	661 091

Also required:

1	PC with Windows XP/Vista/7/8
1	Labo igniter

Set-up and preparation of the experiment

Construction of the apparatus

1. Place the CPS crude oil distillation equipment into the panel frame.

2. Place the glassware into the CPS panel as described on the panel.

Make sure that all glass connections and stopcock taps are adequately greased with stopcock grease. Secure the glass connections additionally with a joint clip.

3. Also connect the water cooler as described on the CPS panel. For this, the cold water should flow from bottom to top.

The tubes connected to the cooler and those on the water tap must be secured with hose clamps to prevent the tubes from coming off.

4. A laboratory stand and a heating mantle can now be placed under the flask (500 mL).

5. If the apparatus is not in a fume cupboard: attach a tube to the side tap of the feed and secure using a hose clip in order to lead the waste gases into a fume cupboard (see Fig. 1).

6. Insert the NiCr-Ni temperature probe into its protective sleeve and then insert it into the apparatus at the marked location.

7. Now insert the four temperature probes into two NiCr-Ni adapters S and connect these to the A and B inputs on the Sensor-CASSY 2 (see Fig. 1).

8. Connect the Sensor-CASSY 2 to the PC and start the CASSY Lab 2 software.

9. Load the settings for CASSY Lab 2. Do not start the measurement yet.

10. For the measurement, the two adapters must be selected by clicking on them in the graphic. Four temperatures will now be recorded.

Preparation

1. In order to determine also the volume percentages of the individual fraction yields at the end of the experiment, 150 mL of the crude oil (synthetic) are measured exactly in a measuring cylinder and placed into the 500 mL flask.

2. Now 6 - 8 boiling stones are added to the flask to prevent superheating (bumping). The flask is then re-connected to the apparatus.

Performing the experiment

1. Start the temperature recording in CASSY Lab 2 and raise the heating mantle to the point where the flask is not pushed upwards but is well surrounded.

2. Enclose the upper part of the flask that is not surrounded by the heating mantle and the initial section of the bubble tray column in aluminium foil. This facilitates the distillation, as the rising vapour does not cool as quickly because of the insulation. In this way, it can reach the first bubble tray and condense on it. Leave a small peephole free so it is still possible to observe the oil.

3. Check the water cooling again and then switch on the heating mantle. Here, the "minimum" setting is sufficient. Should superheating (bumping) or any other incident nevertheless occur during the distillation, the heating mantle can be lowered immediately using the laboratory stand.

4. At the same time, start the temperature recording in CASSY Lab 2.

5. After a few minutes, liquid will collect initially on the first tray of the bubble tray column and then on the second tray. Only after this should the fractions be removed, on no account before. The droplet speed when removing the fractions should be about 1 droplet per minute. Because of the Liebig cooler, vapours will also be collected that do not condense on the bubble trays.

6. The experiment can be discontinued when the temperature in the flask, the sump temperature, is about 240 °C. At this temperature, sufficiently large fractions should have been collected.

7. The individual fractions can now be investigated for colour, viscosity and soot formation on burning:

   a. Describe the colour and viscosity of the fractions qualitatively and record the findings in a table.

   b. For investigation of the soot formation and the flammability, burn off all three fractions each in a separate evaporating dish. For this, place a small amount of the fraction in an evaporating dish and ignite it with glowing wooden turnings. Record the soot formation and the flammability in a table.

Observations

After switching on the heating mantle, the temperature rises in the flask (technical jargon: "sump") and the crude oil begins to boil after a few minutes. Vapours rise upwards which repeatedly condense. The first vapour-liquid mixture arrives at the first tray after about 10 minutes. The vapours reach the second bubble tray after a few more minutes and liquid is collected here also.

A proportion of the vapours does not condense on either of the bubble trays. The temperature of these vapours is measured at the top of the apparatus, the so-called top temperature. This is the last to increase.

Fractions can be removed when the temperature on both bubble trays remains constant (in this case after about 25 minutes).

If the distillation is allowed to run longer, then further increases in temperature of both bubble trays and of the top temperature can be observed. Only at this point will it also be possible to collect a fraction after the cooler.

Evaluation

Fractionated distillation

For investigation of the fractionated distillation, the temperature profile of the individual fractions is evaluated (see Fig. 3).

Initially only the sump temperature rises continuously. Following this, the temperatures of the first and second trays rise. The top temperature is the last to increase. At these individual points in time, the liquid-vapour mixture has reached these temperature probes and liquid is collected on the trays. An equilibrium between vapour and liquid is reached on each tray. After this equilibrium has been reached, these temperatures remain constant within certain limits.

The first bubble tray contains a fraction with a boiling point range of about 80 - 100 °C. This corresponds to light gasoline with a higher boiling point. The fraction on the second bubble tray has a boiling point range of 50 - 70 °C and is also one of the light gasolines. The fractions that could be collected after the cooler have a boiling point of 25 - 35 °C and could consist of liquid gases, such as propane and butane. The liquid on the first bubble tray has a temperature of about 80 - 95 °C at equilibrium, that on the second bubble tray has a temperature of about 50 - 70 °C. These are the boiling point ranges of the two fractions. The boiling point range of the top fraction is determined by the top temperature. This fraction only condenses when it is well cooled, as its boiling point is around 35 °C.

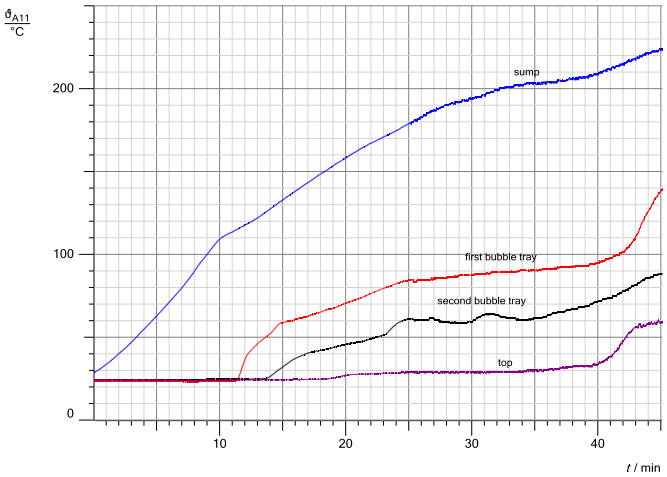

Fig. 3: Temperature profile of the fractionated bubble tray distillation.

Investigation of the individual fractions

For the evaluation, the three fractions obtained are differentiated according to colour, viscosity, flammability and soot formation (see Tab. 2).

The fraction after the cooler (top fraction) is colourless and very volatile. The fraction from the second bubble tray is non-volatile and highly viscous. However, it is still colourless. The fraction on the first bubble tray is light yellow in colour, less volatile and more viscous.

Tab. 2: Difference between the fractions.

	Sump	1. Tray	2. Tray	Top
Boiling point range [°C]	>100	80 – 100	50 – 70	<35
Colour	dark brown	light yellow	colour-less	colour-less
Viscosity	High			Low
Flamma-bility	Slow			Rapid
Soot for-mation	Large			Low

To differentiate between the fractions, a small amount of each is taken and ignited on an evaporating dish. It takes increasingly longer, starting with the top-fraction to the fraction in the first bubble tray, until the individual liquid ignites. The flames are also increasingly sooty in the same order.

Result

Fractionated distillation

An equilibrium is repeatedly reached on the individual trays of the column during the entire distillation. On each tray, the same quantity of substance changes to the gaseous state and also condenses. For this reason, the boiling point of the fraction remains constant.

After about 40 minutes, the top fraction from the 150 mL of crude oil has completely evaporated. This is seen through rapid temperature increases at this point in time. This applies analogously to the fractions on both trays. The fraction on the first bubble tray is then collected on the second tray, that of the second tray in the top fraction.

Fractionated crude oil distillation is normally carried out on a continuous basis. Here, such exhaustion of a fraction is counteracted though suitable control technologies.

Investigation of the individual fractions

The different properties of the individual fractions are based on the molecules contained within them. One can generally say that the boiling point of a compound increases with the size of its molecules. Therefore, a fraction with a high boiling point contains molecules with a large chain length. Apart from the actual weight of the molecules, the increasing boiling point is also based on increasing interactions between the individual molecules. With increasing chain length, the so-called van der Waals forces increase. These act between the C atoms or their electrons and cause the molecules to be attracted. The larger the number of electrons per molecule, the greater are the van der Waals forces. Thus the molecules are no longer able to change into the gaseous state so easily.

Fractions with a high boiling point have a higher viscosity. This is also connected with the van der Waals forces. The individual large molecules can flow past each other only slowly, because they are attracted to one another. The viscosity increases.

The increased soot formation with fractions with a high boiling point has a different cause. On combustion of the individual fractions, the same amount of oxygen is always available, but the number of carbon atoms to be burned increases. Therefore not all carbon atoms are able to react with oxygen. Instead, they become visible as soot.

Cleaning and disposal

Store the individual fractions in conical flasks with cork stoppers for further experiments. Rubber stoppers should not be used, as these can be attacked by the vapours of individual fractions. Attach an appropriate warning label to the conical flask and store in accordance with the technical regulations for combustible substances.

The chemicals and products used in the experiment are classed as hazardous waste according to the European Waste Catalogue (EWC). If recycling is not possible, the waste must be disposed of in accordance with local authority regulations. For this, collect the used boiling stones in a plastic bag together with any oil-contaminated paper towels. Also collect completely emptied containers that have not dried out as well as crude oil residues and dispose of these together as special waste.

Roughly clean the distillation flask if it is to be used for further crude oil experiments. If necessary, glow it out under the fume cupboard.