Separation of crude oil using column chromatography

Aims of the experiment

- Separation of crude oil according to families based on the relevant adsorption properties.
- Understanding the separation principles behind column chromatography
- Understanding the ordering principles of eluotropic series

Principles

Crude oil represents a mixture of various hydrocarbons. The components of the crude oil can be divided into classes based on both their molecular size (chain length) and their molecular structure.

The components of crude oil can be separated by distillation based on their boiling temperatures during preparation. This results in different fractions that can be classified according to boiling ranges. As the molecular size (chain length) is predominantly critical for the boiling properties of the components, we can refer to a separation according to molecular size in simpler terms (refer here to experiment C2.3.3.2).

However, it is also possible to separate the components of crude oil based on their molecular structure. The method that is used is column chromatography.

Crude oil contains saturated alkanes. These can be branched, unbranched, cyclic or chain-like. The same applies to unsaturated alkenes and alkines.

In addition, crude oil contains aromatics of various sizes, as well as hetero-aromatic whose ring structure can include nitrogen, sulphur or oxygen as hetero-atoms.

The hydrocarbons can contain polar groups such as hydroxide, carbonyl or acid functions.

All these properties affect the adhesion properties of the surface materials as well as the solubility of the substances in certain solvents.

This is utilised in column chromatography. The substances to be separated are transported with a mobile phase (solvent mixture) through a stationary phase (in this case aluminium oxide). While the substances to be separated pass through the stationary phase, they are always re-adsorbed by it (they adhere to it) or desorbed (they return to the solution). Substances with a high affinity to the stationary phase tend to spend a longer time in the adsorbed state and less time in the solution. They therefore progress more slowly than substances with a low affinity to the stationary phase.

Solids with polar groups on the surface are usually used as the stationary phase (e.g. silica gel or aluminium oxide). Here the grain size affects the flow resistance of the stationary phase. The smaller the grain size, the higher the flow resistance and the greater the retention of polar substances.

The eluents serving as the mobile phase are ordered in the eluotropic series based on their elution effect. The elution effect is defined as the ability of a solvent to elute a substance. An eluent with a high elution strength E° is able to transport a polar substance faster through the column than an eluent with a low elution strength.

The order of the solvents in the eluotropic series is linked to

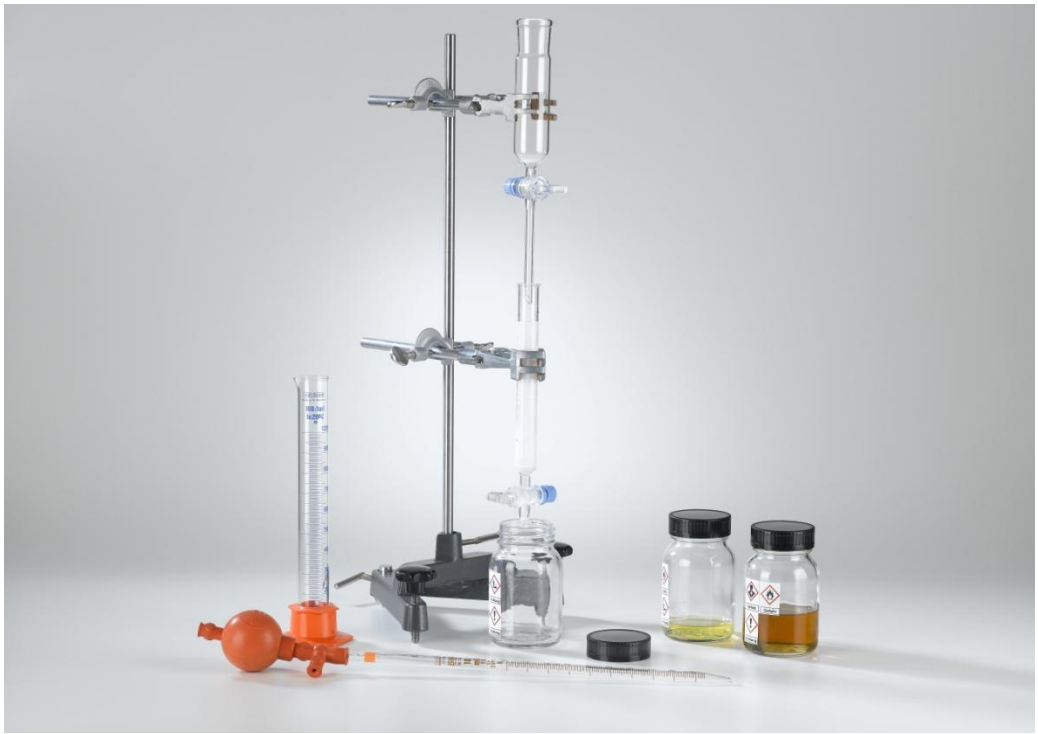

Fig. 1: Experimental apparatus for column chromatography with crude oil

their polarity, but can vary in detail for various stationary phases. The elution strength of an eluent can be set by mixing various solvents.

In the experiment presented here, a sample of crude oil is separated according to families by using various eluents with increasing elution strength. Five fractions result from this: Asphaltenes, non-aromatics, mono-aromatics, di-aromatics and poly-aromatics, as well as polar components.

Risk assessment

The solvents used and the petroleum are all harmful or toxic. The experiment should therefore be carried out under a fume cupboard. Laboratory coats, goggles and gloves made from nitrile must be worn when performing the experiment. Take special care when handling methanol, as it is very toxic and even nitrile gloves cannot provide adequate protection.

n-hexane

Signal word: Hazard

Hazard statements

H225: Highly flammable liquid and vapour.

H304: May be fatal if is swallowed and enters the airways.

H361f: Suspected of damaging fertility.

H373: Causes damage to organs through prolonged or repeated exposure.

H315: Causes skin irritation.

H336: May cause drowsiness or dizziness.

H411: Toxic to aquatic life with long-lasting effects.

Safety statements

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P240: Ground/bond container and receiving equipment.

P273: Avoid release to the environment.

P301+P310: IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.

P331: Do NOT induce vomiting.

P302+P352: IF ON SKIN: Wash with plenty of soap and water.

P403+P235: P403 Keep cool and store in a well ventilated place.

n-heptane

Signal word: Hazard

Hazard statements

H225: Highly flammable liquid and vapour.

H304: May be fatal if is swallowed and enters the airways.

H315: Causes skin irritation.

H336: May cause drowsiness or dizziness.

H410: Very toxic to aquatic life with long-lasting effects.

Safety statements

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P273: Avoid release to the environment.

P301+P310: IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.

P331: Do NOT induce vomiting.

P302+P352: IF ON SKIN: Wash with soap and water.

P403+P235: P403 Keep cool and store in a well ventilated place.

Toluene

Signal word: Hazard

Hazard statements

H225: Highly flammable liquid and vapour.

H361d: Suspected of damaging the unborn child.

H304: May be fatal if is swallowed and enters the airways.

H373: Causes damage to organs through prolonged or repeated exposure.

H315: Causes skin irritation.

H336: May cause drowsiness or dizziness.

Safety statements

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.

P301+P310: IF SWALLOWED: Immediately call a POISON CENTER or doctor/physician.

P331: Do NOT induce vomiting.

P302+P352: IF ON SKIN: Wash with soap and water

Dichloromethane

Signal word: Caution

Hazard statements

H315: Causes skin irritation.

H319: Causes serious eye irritation.

H335: May cause respiratory irritation.

H336: May cause drowsiness or dizziness.

H351: Suspected of causing cancer.

H373: Causes damage to organs through prolonged or repeated exposure.

Safety statements

P261: Avoid breathing dust/fume/gas/mist/vapours/spray.

P281: Use personal protective equipment as required.

P305+P351+P338: IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

Methanol

Signal word: Hazard

Hazard statements

H225: Highly flammable liquid and vapour.

H331: Toxic if inhaled.

H311: Toxic in contact with skin.

H301: Toxic if swallowed.

H370: Causes damage to organs.

Safety statements

P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking. P233: Keep container tightly closed. P280: Wear protective gloves/protective clothing/eye protection/face protection.

P302+P352: IF ON SKIN: Wash with soap and water. P309+P310: IF exposed or you feel unwell: Immediately call a POISON CENTER or doctor/physician.

Equipment and chemicals

8	Small separating chamber 250 ml	665 563ET5
1	Measuring cylinder 100 ml, ...	665 754
1	Funnel Boro 3.3, 100 mm diam.....	665 005
1	Wash bottle, PE, 250 ml	661 242
1	Beaker, Boro 3.3, 250 ml, squat	664 130
1	Wide-mouth bottle, clear glass, 50 ml.....	602 283
1	Graduated pipette 10 ml	665 997
1	Pipetting ball (Peleus ball)	666 003
1	Chromatography column 235 x 20 mm Ø	665 592
1	Dropper funnel, glass, 75 ml, SB 29	665 073
1	Stand base, V-shaped, small.....	300 02
1	Stand rod 47 cm, 12 mm diam.....	300 42
2	Bosshead S	301 09
2	Universal clamp 0...80 mm.....	666 555
1	Powder funnel, PP 100 mm diam.....	665 025
1	Spoon-ended spatula, SS, 180 mm	666 966
1	Beaker, Boro 3.3, 100 ml, squat.....	602 022
1	Warning labels, GHS.....	661 0771
1	Compact balance 440-3N, 200… 0.01 g .	667 7977
1	n-heptane, 250 ml	672 1810
1	n-hexane, 250 ml	672 2210
1	Toluene, 250 ml	675 2100
1	Methanol, 250 ml.....	673 2700
1	Dichloromethane, 500 ml	671 6590
1	Aluminium oxide, 250 g.....	670 2900
1	Acetone, 1L.....	670 0410
1	Stopcock grease, 60 g	661 082
1	Crude oil, artificial, 1 L.....	674 5810

Set-up and preparation of the experiment

Note: The stopcocks of the glass apparatus are greased and checked for permeability before the experiment.

The eluents are each poured into small separating chambers. The following are required: (1) 50 ml n-hexane, (2) a mixture of 90 ml n-hexane and 10 ml toluene, (3) 110 ml toluene and (4) a mixture of 50 ml methanol and 50 ml dichloromethane. The measuring cylinder is flushed using the wash bottle filled with acetone each time after use. The result impure acetone is collected in a beaker.

The sample is prepared. For this, weight out 500 mg crude oil in a 50 ml wide-mouth bottle. Add 20 ml n-heptane for precipitation of the asphaltenes. Allow the samples to stand for some time and continue setting up the experiment.

Fasten the chromatography column on the stand using a bosshead S and universal clamp. Fill the column. For this, continually fill some n-hexane and allow aluminium oxide to trickle in using the powder funnel and spoon spatula. Make sure that no gaps or breaks form. Remedy these by knocking, if necessary. The column is filled to approx. 3 cm below the edge.

Note: The column should not be allowed to become dry at any time, as otherwise cracks can form.

Fasten the dropper funnel above the column on the stand using the bosshead S and universal clamp.

Performing the experiment

Decant the solvent (n-heptane) from the prepared crude oil sample into a 100 ml beaker. The asphaltenes should remain behind at the edge of the screw cap glass.

The solvent contains the maltenes. Add these fully onto the column and allow to seep in. Make sure that the column does not become dry during this.

Pour the various eluents (1-4) into the dropper funnel in succession using a funnel. Adjust the stopcocks of the dropper funnel and column so that both drip at about the same speed. If necessary, recalibrate from time to time. Make sure that the column filling is not swirled up. If need be, lower the dropper funnel slightly.

Collect the eluates of the four eluents in small separating chambers for further experiments.

Observation

1. During elution with (1) n-hexane, a yellow phase initially migrates through the column. A brown edge remains behind.

2. A yellow phase is also leached out with (2) n-hexane toluene 1:9.

3. The fractions of (3) pure toluene and (4) 1:1 methanol-dichloromethane are brown.

4. After adding the last eluent the column is again grey-white.

Result

The asphaltenes represent components of the crude oil that are insoluble in short-chain alkanes. They must be removed before column chromatography by precipitation with n-heptane, as they clog the pores of the column and hence prevent further flow.

The crude oil components dissolved in the n-heptane are referred to as maltenes. After applying the maltenes onto the column, begin by eluting with n-hexane. The non-polar non-aromatics are contained in this fraction. They have the least affinity to the stationary phase and are quickly leached from the column with n-hexane, which has only a low elution strength ($E° = 0.00$).

The elution strength of the mixture comprising n-hexane and toluene is between the elution strength of the individual components n-hexane ($E° = 0.00$) and toluene ($E° = 0.22$). The smaller aromatics are consequently eluted, while the larger aromatics and polar components continue to adhere to the stationery phased, thereby moving only very slowly through the column. The yellow colour can originate from organo-sulphur compounds or smaller aromatics.

With toluene ($E° = 0.22$), the larger aromatics are then leached from the column. The colour of the fraction is brown, which allows us to conclude a mixture of differently coloured aromatics.

Finally, the polar components of the crude oil are also eluted with a mixture of methanol ($E° = 0.73$) and dichloromethane ($E° = 0.30$). This fraction also has a brown colour, which allows us to conclude that some of the polar components are aromatics.

The column is again grey-white after this. The components of the crude oil should therefore have been eluted for the most part.

It is to be noted that column chromatography has limited accuracy as a separation method. In particular, the molecule classes to be separated can become intermixed in the individual classes due to overloading effects. The loss of some components can occur due to irreversible adsorption or during evaporation of the solvent.

Follow-up experiments

Column chromatography provides a rough separation of the individual fractions of crude oil. It is then possible to examine the resultant fractions in more detail using further chromatographic methods, such as gas chromatography (GC), high-performance liquid chromatography (HPLC) or thin-layer chromatography (TLC). The solvent can be extracted with a rotary evaporator for this, if necessary. It must be borne in mind that a loss of high-boiling components can also occur.

Column chromatography can also be combined with fractioned distillation (experiment C2.3.3.2) in order to attain both a separation according to molecular size as well as a separation by molecular class.

Cleaning and disposal

The fractions are stored in sealed bottles for further use. The solvents can be recovered by distillation, if required. Otherwise they are disposed of in the container for organic solvent waste. Solutions containing dichloromethane must be disposed of in a special container for organic solvent waste containing halogens.

The column material can be disposed in the container for inorganic solids after drying under a fume cupboard.