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CONTENTS

4

Supercritical Fractionation of Volatiles and Non-volatiles from Different Plant Sources

Student: Ing. Martin Topiař
Supervisor: Ing. Marie Sajfrtová, Ph. D.
Supervising Expert: Ing. Helena Sovová, CSc.

Many green plants contain biologically active substances that are or could be used in pharmaceutical or food processing industry. The traditional techniques of isolation of active compounds from plants are steam distillation and extraction by organic solvents. However, these processes show significant disadvantages, including the thermal degradation of unstable substances in case of distillation or a high consumption of organic solvents the traces of which remain in the product on conventional extraction. These drawbacks can be eliminated by application of modern separation techniques such as the supercritical fluid extraction (SFE) using carbon dioxide as a solvent. This technology is suitable especially for obtaining valuable plant isolates with almost the same chemical representation as that of the plant. Moreover, SFE allows for a separation of the isolate into several fractions during the extraction

The focus of this work was on using the SFE combined with different fractionation techniques (additional separator, sorption on silica gel in one step with the extraction) in a range of pressures and temperatures (9–30 MPa, 40–50 °C) to enhance volatiles in extracts from the leaves of eucalyptus. Its essential oil is widely used in cough pills or toothpastes and in addition, several studies proved insecticidal and repellent activity of eucalyptus extract.[1,2] The efficiency of SFE in terms of extract composition and yield was compared with hydrodistillation. The composition of volatiles in the isolates was determined using GC-MS and GC-FID.

The major compounds in the essential oil isolated with the yield 26.7 mg/g were 1,8-cineole (42.6 wt %), α-pinene (10.7 wt %) and globulol (5.9 wt %). The concentration of total volatiles in the extracts varied from 2.8 to 59.5 wt %, depending on the extraction and fractionation conditions. The use of additional separator under conditions of 9 MPa and 0 °C led to separation of cuticular waxes and other high molecular substances from the volatile fraction. The fractionation using silica gel as sorbent was effective in terms of separation of oxygenated

sesquiterpenes, mostly globulol, within the second fraction, which was obtained by extract desorption with pure CO_2 at 30 MPa and 40 °C. The validity of using SFE combined with different fractionation techniques as a method for enhancement of volatiles concentration in the extract was demonstrated, as well as its advantages over simple extraction.

Future work will be focused on a separation of pharmaceutically valuable non-volatile compounds from a plant material, with particular interest in sorption and desorption conditions (time, CO_2 consumption, feed to sorbent ratio). The experiments will be conducted with pure compounds as well as with the extract of defined chemical composition. The obtained thermodynamic data will serve as a basis for a mathematical description of sorption from supercritical solvent.

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Mathematical Model for Pressurized Solvent Extraction from *Leuzea carthamoides*

Student: Ing. Zdeňka Machalová
Supervisor: Ing. Marie Sajfrtová, Ph. D.
Supervising Expert: Ing. Helena Sovová, CSc.

Pressurized solvent extraction (PSE) has become an effective alternative to conventional extraction (Soxhlet extraction, maceration) from plant material. Due to the elevated temperature and pressure, which facilitate better penetration of solvent into the matrix pores, the PSE offers advantages with regard to extraction time, yields and consumption of solvent. In spite of the high temperature above the normal boiling point of solvent, thermo-labile substances are mostly preserved because of the short extraction time (5–20 min). The elevated pressure is mainly used to keep the solvent liquid. The PSE is usually semi-continuous or batch-wise process. In the first case, the pressurized solvent flows through the fixed bed of disintegrated plant material and dissolves the solute. In the case of batch-wise extraction, the extraction column is pressurized with the solvent to desired pressure. After a short period of time (5–20 min), the extraction column is depressurized and solvent is pushed out from the system and trapped into the vial. This process is usually repeated two or three times.

The mathematical modelling of experimental data is important for the prediction of the feasibility of the process. The modelling of the extraction from fixed bed is generally based on differential mass balance equations, which include mass balance of the solute for the fluid phase and mass balance of solute for the solid phase. In the most cases, the distribution coefficient is used as a fitting parameter for experimental data.[1]

Leuzea carthamoides is an adaptogenic plant rich in phytoecdysteroids. The most abundant ecdysteroid in this plant is 20-hydroxyecdysone (20-HE) which is well known for its anabolic and tonic effects on mammals and is used as dietary supplement for muscle growth.[2]

This work concerns PSE from roots of *Leuzea carthamoides* and mathematical characterisation of this process. The PSE experiments were carried out at temperature 80°C, pressure 10 MPa and using methanol or ethanol as solvents. The extraction was semi-continuous with various solvent flow rate (0.5, 1, and 2 ml/min). Soxhlet extraction with

methanol was used for comparison of methods. The concentration of 20-HE in extracts was determined by HPLC coupled with mass spectrometry. The basic mathematical model was applied to fit experimental data.

The concentration of 20-HE in extract and total yield of extract were significantly influenced by the type of solvent. Higher extraction yields were obtained using methanol as a solvent. On the contrary, the velocity of solvent flow had a minor effect on the yield of the 20-HE. The model assumed the short extractor, where the concentration difference inside the extractor is negligible and thus the lumped parameter model was used. This model is mathematically identical to the model of ideal mixer.

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Adsorption of Phenol from Aqueous Solution on Various Sorbents

Student: Ing. Martina Matějková
Supervisor: Ing. Olga Šolcová, CSc., DSc.

Nowadays, phenols belong to the most common water pollutants in the industrial effluents thus they have become the significant contaminant of ground waters. The underground coal gasification technology (UCG) belongs, among other, to sources of contaminated phenolic water. Phenolic compounds can be also found in wastewater generated by petroleum and petrochemical, pharmaceutical, plastic, rubber proofing, steel, and phenol production industries.[1] Phenolic compounds have low allowable limits (0.5–1.0 mg/l) in the effluent of industrial water, thus, it is inevitable to remove them from any water by environmentally acceptable ways mainly due to their high toxicity to human and aquatic life.[2]

For this reason, this study is focused on an evaluation of an individual sorbent efficiency and capacity concerning phenol removal from waste and/or industrial water by sorption techniques.

Two types of activated carbons (Supersorbon – extrudates, and Norit – powder) were applied as sorbents for contaminated water treatment. Efficiency of the individual sorbents was tested on model contaminated water with the various phenol concentrations. Applied sorbents were thoroughly characterized by various methods as Nitrogen physical adsorption, Mercury porosimetry and Helium pycnometry. The particle size distribution of Norit was performed by a sieve analysis.

All sorption experiments were carried out under continuous shaking in a laboratory batch arrangement at room conditions. For the exact description of the phenol sorption on activated carbons the kinetic equilibrium and sorption capacity were determined. Sorption activity of Supersorbon and Norit was tested on the phenol removal from the UCG real wastewater.

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Preparation of Nanocrystalline Titania Thin Films by Using Pure and Modified Supercritical Carbon Dioxide

Student: Ing. Marie Cerhová
Supervisor: Ing. Marie Sajfrtová, PhD.
Supervising Expert: Ing. Lenka Matějová, PhD.

Titania films are materials of great interest, as TiO_2 anatase crystal structure shows a high photocatalytic activity, chemical stability, strong oxidation activity, and non-toxicity. Anatase can be used in environmental applications, such as air- and water-purification [1] or for the decomposition of organic compounds.[2] The photocatalytic efficiency of thin films depends not only on their phase composition but also on hydrophilicity, specific surface area, crystallinity and crystallite-size. These properties can be significantly influenced by the preparation method used.

The commonly applied method for the preparation of pure and crystalline TiO_2 thin films is calcination.[3] Nevertheless, this thermal treatment presents some disadvantages, such as recrystallization, excessive sintration, crystallite growth, and a decrease in the specific surface area. Furthermore, the properties or photocatalytic performance cannot be easily controlled.

Therefore, calcination has been combined with supercritical fluid extraction (SFE) or pressurized liquid extraction (PLE). It was found that the pre-treatment using supercritical carbon dioxide ($scCO_2$) proposed for lowering the process temperature of sol-gel derived metal oxide film helps to increase the thermal stability and photocatalytic activity of films.[4]

The motivation of this work is to utilize the SFE for the direct preparation of highly pure TiO_2 thin films without any subsequent thermal processing. Extraction with pure and modified $scCO_2$ was tested and compared with PLE. Different types of liquid solvents (water, ethanol, acetone etc.) were used as $scCO_2$ modifiers at concentrations from 0 to 30 mass %. The effect of extraction temperature (40–150 °C), pressure (10–65 MPa) and the volume (50–200 g) and flow rate (0.3–1.8 g/min) of solvents passed through the extractor on microstructure and purity of TiO_2 thin films were examined.

The prepared thin films were characterized with respect to the (micro)structural properties by Raman spectroscopy. The most promising

thin films were analyzed by means of X-ray diffraction to determine the crystallite size, the phase composition, and the film thicknesses. The contact angles of films were measured to obtain the information about surface wettability.

When pure $scCO_2$ or pressurized hot water was used as the solvent no crystallization occurred. The addition of a small amount of water to $scCO_2$ at optimum extraction conditions (T=150 °C, p=30 MPa) led to the direct crystallization of films. The modification of $scCO_2$ by organic solvents resulted in the removal of organic precursors and thus in the increase of the TiO_2 thin film purity. When SFE was terminated by pure $scCO_2$ drying, the crystal size of 12 nm was achieved.

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Physicochemical Properties of Menthol-Based Imidazolium Ionic Liquids

Student: Ing. Adéla Andresová
Supervisor: Ing. Magdalena Bendová, Ph. D.

There are about 10^{18} combinations of cations and anions in the structure of ionic liquids (ILs) nowadays, made of a multitude of possible substitution patterns and substituted aromatic or aliphatic groups, and a wide variety of functional groups. The unusual thermodynamic properties of ILs result from the type of cohesive interaction, charge distribution, structuration, and polarity. Even though ionic liquids have found only a limited industrial application so far, their molecular structure and supramolecular organization as a complex, consisting of polar and non-polar domains that is reflected in the complexity of the thermodynamic properties of ILs and ILs mixtures, should be considered.[1] This structural variability of ILs is a motivation for systematic research and structural design, allowing to model or tune ILs with improved property profiles, including a reduced hazard to humans and the environment. The analysis of the thermodynamics data based on morphology of substance as well as the alkyl chain size is used to explore the effect on the ionic liquid properties and their interpretation.

Due to the large scale of possible applications of ILs, the knowledge of a wide range of physicochemical properties of both pure substances and their mixtures is required.[2] For this reason, in a continuation of a research project aimed at a thermodynamic study of 1–[(1R, 2S, 5R)-(−)-menthoxymethyl]-3-alkylimidazolium bis{(trifluoromethyl)sulfonyl}imide ionic liquids, where the alkyl chain length ranges from methyl to dodecyl, thermophysical properties such as density, speed of sound, and heat capacity were measured at a wide temperature range and atmospheric pressure. Experimental volumetric data were used to calculate the isentropic compressibility and isothermal expansion coefficient. In addition, owing to the lack of data caused by the diversity of ILs and the large number of commonly used molecular solvents[3] we decided to determine the excess properties and gain better understanding of the intermolecular interactions via the experimental data of excess molar volumes. A particularity in liquid-mixture behavior was revealed by characterization of excess molar volumes of

selected ILs from the above-mentioned homologous series with acetonitrile and methanol. The dependence of the excess molar volume on the composition of the mixture makes a link between the molecular phenomena and the observed bulk property.

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Influence of Structure of Ionic Liquids on the Properties of their Mixtures with Water

Student: Ing. Jan Rotrekl
Supervisor: Ing. Magdalena Bendová, Ph. D.

Ionic liquids (ILs) represent a group of organic salts with an enormous variability in chemical structure and physico-chemical properties and thus with a broad application potential.[1] However, there is no application without a theoretical base, therefore studies focused on relations between structure and properties are needed.

This contribution reports on a part of the results of a project focused on imidazolium-based ILs with a bis{(trifluoromethyl)sulfonyl}imide anion. The choice of the studied ILs is motivated by a study of the influence of the cation structure on the physico-chemical properties of pure ionic liquids and their mixtures with molecular solvents. For this purpose, four isomeric ILs, namely 1-alkyl-3-butylimidazolium bis{(trifluoromethyl)sulfonyl}imides (abbreviated $[C_4xC_5im][Tf_2N]$, alkyl = pentyl, isopentyl, 3-pentyl, or cyclopentyl) were selected. In a previous work, fundamental physico-chemical properties such as density, isobaric heat capacity, viscosity, electrical conductivity were measured.[2] In this part of the study, the properties of the studied range of ILs in systems with water were investigated.

Due to the hydrophobic character of the $[Tf_2N]^-$ anion, the studied ILs show limited miscibility with water. The solubilities of ILs in water were measured by means of the direct analytical method using a UV/VIS spectrophotometer (Thermo Scientific Helios γ). Solubilities of water in ILs were measured by the cloud-point method. The determined solubilities of bistriflate-based ILs in water are typicaly about 10^{-5} in the mole fraction; this concentration range corresponds to the conditions of infinite dilution.[3] Therefore, the thermodynamic functions of solubilization of the studied ILs in water could be calculated from these data.

Solubility of water in the studied ILs is on the other hand much higher than that of ILs in water, being as high as approx. 0.15 mole fraction units of water. This enabled us to obtain the excess volumes of mixtures in this part of the concentration interval using a DMA 5000 Anton Paar densitometer.

The data obtained in this study clearly show how a subtle variation in the chemical structure, like isomerisation of one substituent on the cation can affect the physico-chemical properties of pure substances and their mixtures.

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Analytical Features of the Optical Biosensor for Glucose Detection

Student: Mgr. Lucie Maixnerová
Supervisor: Ing. Gabriela Kuncová, CSc.

Monitoring of glucose concentration is essential in medicine, food and pharmaceutical industries. MATINOES enzymatic biosensors with the optical oxygen transducer represent a cheap and robust device for monitoring of glucose in bioreactors.

To meet requirements of various applications the biosensor production have to ensure demanded analytical characteristics, such as sensitivity (SN), limit of detection (L_D), limit of quantification (L_Q), and linear dynamic range (LDR).

In a previous study we demonstrated a dependence of these characteristics on: weight (thickness) of an optically sensitive layer, amount of the enzyme, concentrations of substrates in the reaction medium, and morphology of the sensitive layer[1].

The first aim of my work was to determine boundaries of the above-mentioned parameters as maxima and minima of the weight (thickness) of the layer and the quantity of the immobilized enzyme. Glucose oxidase from *Aspergilus niger* ($37.7 \, KU \cdot g_{solid}^{-1}$) immobilized on Sepabeads® (SPB) coated together with the ruthenium oxygen sensitive complex in the organic-inorganic polymer ORMOCER® were used in all experiments. From process parameters maxima and minima concentrations of oxygen and glucose were detected. The second aim was to prepare biosensors with substantially diverse analytical characteristics via combinations of these parameters. The obtained experimental data will be a base for a detailed mathematical model of MATINOES biosensors (outlined in our previous paper[1]), which we are going to develop in the collaboration with ICT Prague. This model should enable a preparation of MATINOES biosensors with tailor-made analytical features.

The results are summarized in table 1. While maintaining a constant morphology and oxygen concentration of 21 vol. %, SN was in the range from 0.029 to 0.303 $\mu s \cdot L \cdot mmol^{-1}$, L_D in the range from 0.2 to 2.0 $mmol \cdot L^{-1}$, L_Q in the range from 0.7 to 7.0 $mmol \cdot L^{-1}$ and the maximum detectable value of glucose concentration in the range from 2.5

to 16.0 mmol·L^{-1}. Increasing the weight of the layer resulted in an increase of SN, contrary to L_D, L_Q, and LDR that drop. Higher amount of enzyme lead to increase SN in contrast to reduction of L_D, L_Q and LDR. During the measurement, increasing concentration of oxygen from 5 to 100 vol.% caused a decrease of SN and increase of L_D, L_Q, and LDR, respectively.

The analytical features of MATINOES glucose biosensor were varied within one order by changing of enzyme content and the thickness of the sensitive layer.

Table 1: Analytical characteristics of biosensors for glucose detection.

	Minimum value	Maximum value
Weight of optical active layer (mg)	4	16
Weight of immobilized enzyme ($mg_{enzyme}·g_{SPB}^{-1}$)	12.5	350
Sensitivity ($\mu s·L·mmol^{-1}$)*	0.029	0.303
Limit of detection (mmol·L^{-1})*	0.2	2.0
Limit of quantificaion (mmol·L^{-1})*	0.7	7.0
Maximum detectable value of glucose (mmol·L^{-1})*	2.5	16.0

*Detection under 21 vol.% (air), constant morphology of the layer

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Novel NMR Method for Organic Aerosol Analysis

Student: Ing. Štěpán Horník
Supervisor: Doc. Ing. Bohumil Dolenský, Ph. D.
Supervising Expert: Ing. Jan Sýkora, Ph. D.

A novel NMR approach to the analysis of organic aerosol composition was tested. The method is focused on the water soluble organic compounds (WSOC) analysis, which is the least examined group of organic aerosols. So far, the use of NMR technique was limited to so called Functional Group Analysis, in which measured ^{1}H NMR spectra of the WSOC are divided into parts and the entire area is integrated without or with very little identification of individual compounds.[1] Recently, the employment of 2D NMR techniques (COSY, HSQC) was published, however the analysis is rather challenging.[2]

The proposed NMR technique exploits the NMR metabolomic approach, in which the ^{1}H NMR spectra of individual compounds are fitted into the complex ^{1}H NMR spectra. The assignment is based on precise chemical shift of dominant signals of given compound. The library spectrum is subsequently subtracted from the aerosol sample spectrum. For this purpose software ChenomX 8.0 is employed. The key to the detail analysis lies in an extensive database. ChenomX database is primarily intended for metabolite analysis, however ca. 60 compounds can be found also in WSOC fraction. Additionally, the software allows database extension and new compounds can be added.

The suitability of ChenomX was performed both on real atmospheric aerosols and model samples of coal combustion. Up to 30 compounds were found in analyzed samples. Most abundant substances were mono- and dicarboxylic acids (formic, acetic, succinic acid) and their derivatives (lactic acid), followed by carbohydrates, anhydro saccharides and sugar alcohols (levoglucosan, fructose, D-threitol), and amines (methylamine, dimethylamine). The real aerosol sample was also analyzed on four different NMR spectrometers (500, 600, 700, 800 MHz) in order to enhance the resolution and find less abundant substances. The frequencies of the spectrometers were chosen according to the ChenomX database. In the 800 MHz spectrum ca. 50 compounds were identified.

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Combustion of Corn Straw
in a Fluidized-Bed Reactor

Student: Ing. Tomáš Durda
Supervisor: prof. Ing. Vaclav Janda, Ph. D.
Supervising Expert: Ing. Michael Pohořelý, Ph. D.

Oxy-fuel combustion is characterized by the utilization of a mixture of pure O_2 and CO_2-rich gas (from the flue gas recycle). The temperature of combustion process is controlled by CO_2-rich recycle flue gas instead of being modulated by N_2 from the air. The CO_2-rich recycle flue gas ensures the process of fluidization in the case of the fluidized bed technology.

Oxygen is produced from air using well established cryogenic methods. This oxygen enriched air is available in industry as a by-product of nitrogen separation from the air. Nitrogen can be obtained from air using vacuum swing adsorption (VSA), pressure swing adsorption (PSA), or vacuum pressure swing adsorption (VPSA). Enriched air could be used as combustion gas for the combustion with the heat output of 5–50 MWt.

This project is particularly focused on the comparison of the efficiency of the combustion processes and the emission of pollutants in different combustion atmospheres (air, enriched air, pure oxygen with model dry flue gas – CO_2).The present work is focused on the utilization of oxy-fuel and enriched air combustion processes for the combustion of corn straw in the bubbling fluidized-bed reactor. Both processes are compared with the air combustion of corn straw. Fluidized bed temperature was about 750 °C. Fluidized bed material was "ceramsite" (calcined alumosilicate widely available in the Czech Republic). Regarding corn straw combustion with air, we furthermore examined the effect of the replacement of the sand with the ceramsite, as a fluidized bed material, on the efficiency of the combustion processes and then the emission of pollutants. Corn straw combustion with air using the ceramsite showed better results than using the sand, respectively. Concerning the efficiency of corn straw combustion in the different atmospheres (air, enriched air, pure oxygen with model dry flue gas – CO_2) and the emission of pollutants, the best results were achieved when corn straw was burnt in the enriched air atmosphere (30 vol. % of O_2 and 70 vol. % of N_2). The oxy-fuel combustion process of corn

straw (with 21 vol. % of O_2 and 79 vol. % of CO_2) was evaluated as the least effective process. Corn straw combustion by air (21 vol. % of O_2 in 79 vol. % of N_2) led to better results than oxy-fuel combustion with 21 vol. % of O_2 and 79 vol. % of CO_2, but provided worse results than the oxy-fuel combustion with 30 vol. % of O_2 and 70 vol. % of CO_2 and, of course, worse results than the combustion with enriched air.

Possibilities of High-Temperature Desulphurization and Dechloration of a Producer Gas

Student: Ing. Jiří Brynda
Supervisor: Ing. Siarhei Skoblja, Ph. D.
Supervising Expert: doc. Ing. Karel Svoboda, CSc.

Producer gas contains several types of impurities, the limit of which is its further utilization. Depending on the used feedstock and type of gasifier the main impurities are dust, tar, sulphur compounds, HCl, and HF. In producer gas from biomass gasification the main impurities are tar, H_2S, COS, and HCl. In order to use the producer gas in SOFC (solid oxide fuel cells) or Fischer-Tropsch synthesis the concentration of impurities has to be lower than 1 ppmv.[1]

For high temperature desulphurization are commonly used CaO, Fe_xO_y ZnO, CuO, MnO based sorbents. In experimental studies for deep desulphurization, rare earth sorbent such as Ce_2O_3, CeO_2, La_2O_3 have also been investigated. For the evaluation of different sorbents equilibrium concentrations of H_2S and HCl were calculated from thermodynamic data given by Barrin.[2] Input gas composition was 40 vol. % of H_2, 10 vol. % of H_2O, and 30 vol. % of CO_2. At temperatures in the range of 600–800 K ZnO, Ce_2O_3 and La_2O_3 based sorbents are able to ensure output concentrations of H_2S and COS below 1 ppmv and below 0.01 ppmv, respectively. The best equilibrium concentration at 800 K can be achieved by Ce_2O_3. However, trivalent Ce isn't stable and in the presence of CO_2 or H_2O undergoes oxidation to CeO_2 with much higher equilibrium concentration of H_2S. ZnO sorbents are also problematic due to volatility of elemental zinc under reducing conditions.

Producer gas equilibrium concentrations of HCl containing 10 vol. % of H_2O and 100 ppmv of HCl or 10 ppmv respectively, were calculated to predict interferences with HCl during gas desulphurization and the possibility of simultaneous desulphurization and dechloration (de-HCl) by one of these sorbents. ZnO and Ce-based sorbents show a higher equilibrium concentration of HCl. Therefore interferences caused by HCl during desulphurization can be excluded. La_2O_3 exerts the lowest equilibrium concentration of HCl in the producer gas and reacts in temperatures up to 900 K. It should be noted that for deep

de-HCl soda-based sorbents are needed. According to thermodynamic calculation the reaction of Na_2CO_3 with H_2S should be negligible.

In the experimental part of the desulfurization and de-HCl studies, H_2S interference during dechloration was measured. Gas hourly space velocity was around 3000 h^{-1} (standard temperature and pressure). Output gas HCl concentration was about 3 ppmv which shows that it was not affected by H_2S. However a sharp decrease of sorbent capacity was observed, due to the formation of elemental sulfur from H_2S which was investigated under the condition of a model gas with dry nitrogen (without water vapor and hydrogen). The formation of elemental sulfur (S_x molecules) and its adsorption on sorbents plugs sorbent pores. Therefore the presence of hydrogen and water vapor in gas is desirable to suppress this phenomenon.

According to thermodynamic calculations Ce_2O_3 exerts the highest affinity to H_2S and is capable of deep desulfurization at temperatures up to 800 K. Ce_2O_3 can be stabilized by La_2O_3 or MnO addition under common reduction conditions. Therefore Ce_2O_3 sorbents doped by La_2O_3 seem to be promising producer gas sorbents.

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Design of Apparatus for Testing of Catalytic Filters for Flue Gas Treatment

Student: Ing. Boleslav Zach
Supervisor: Ing. Michael Pohořelý, Ph. D.
Supervising Expert: Ing. Michal Šyc, Ph. D.

Flue gas from municipal solid waste incineration contains high concentrations of various pollutants. Treatment of flue gas is therefore required to meet legal emission limits. A lot of research has been dedicated to the topic of flue gas cleaning, most of it, however, associated with large municipal solid waste incineration (MSWI) plants. In areas with low population density, smaller MSWI plants can be the only option if the area of collection is not to be too large, which would increase the costs of transportation. Small MSWI plants are feasible, but the technology has to be adapted to needs of small units.

Catalytic filters can simultaneously remove dust (DeDusting), catalytically destroy organic compounds (DeDiox), reduce nitrogen oxides (DeNOx) as well as (in case a sorbent is fed into the flue gas stream) remove acid compounds from the flue gas (DeSOx). This flue gas cleaning system is called *4D filtration*. Apart from being simple and relatively cheap, this flue gas cleaning system does not produce any wastewater. *4D filtration* therefore seems to be most suitable for small MSWI plants because wastewater treatment system is very expensive to build and to operate. In fact, *4D filtration* is primarily intended for small MSWI plants with processing capacity of around 5 tons per hour (10 MW$_{th}$).

The aim of this presentation is to describe an apparatus for testing of catalytic filters and for determination of optimal conditions for the operation of such filters. This apparatus has been designed and is currently being constructed.

The apparatus consists of four parts: retort burner with a screw feeder, duct system 1, filtration reactor (baghouse), and duct system 2. The essential part of this apparatus is the baghouse, in which four catalytic filter elements are placed. The filter elements can be made of PTFE or ceramic. Based on the baghouse, proportions and details of other parts of the apparatus were calculated. Flue gas is produced in the retort burner with the screw feeder. The feed are either wooden pellets or pellets of model waste. The flue gas is cooled in an air cooler,

from which the gas stream continues through the duct system 1 into the baghouse. The duct system 1 is provided with welded-on fittings used for feeding of pollutants, ash, and sorbent, as well as sampling. On the surface of the filters in the baghouse, the sorbent together with ash create a filter cake. The gas flows through the filter cake where it comes into contact with the sorbent. The duct system 2 (provided with welded-on fittings for sampling) leads the gas from the baghouse into a water cooler. The condensate formed in the water cooler is collected in condensate vessels. The gas subsequently flows through a straight pipe, where the gas flow stabilizes. The stable gas flow is necessary for an accurate measurement of flow-rate in the ultrasonic gas flowmeter. The flow-rate is set by a blower placed downstream of the ultrasonic gas flowmeter.

Using this apparatus, we are going to be able to study the effects of following parameters on *4D filtration:* temperature, type of filter (fibre, ceramic etc.), sorbent properties, gas flow-rate, and fly ash characteristics.

Comparison of Summer and Winter Highly Time-Resolved Submicron Aerosol Composition Measured at a Suburban Site in Prague

Student: Ing. Lucie Kubelová
Supervisor: Ing. Vladimír Ždímal, Dr.
Supervising Expert: Ing. Jaroslav Schwarz, CSc.

Atmospheric aerosols play an important role in many processes such as climate change, air quality degradation, and decrease of visibility. To understand their impact in detail it is important to have a description of their properties such as mass composition and size distribution.[1] The compact-Time of Flight-Aerosol Mass Spectrometer (c-ToF-AMS) is a modern scientific instrument that provides us with such descriptions with high time-resolution.[2]

We analyzed c-ToF-AMS data from a summer (20. 6.–31. 7. 2012) and winter (8. 1.–19. 2. 2013) measurement campaign at a suburban site Prague-Suchdol. The observed chemical composition with dominating organics in both seasons was in accordance with previous measurements at this site.[3] The modal diameter of size distribution occurred at higher values during episodes of increased total concentration and decreased temperature. Furthermore, we compared the AMS data with organic carbon elemental carbon field analyzer (OC/EC) measurement. This comparison together with analysis of particular organic fragments revealed that winter aerosol was less oxidized and more influenced by biomass burning. Such characteristics point to an influence of local domestic heating in winter.

The daily cycles of the main species were influenced mainly by two factors. First, the dilution effect caused by the boundary layer height and second, photochemical reactions leading to the formation of secondary aerosol. To assess the influence of the backward air mass trajectories, the trajectories were divided into clusters according to their shape and origin. In winter, maritime air masses were connected to generally lower concentrations of aerosol with an increased share of nitrate and decreased share of organics. On the contrary, arrival of winter continental air masses coincided with atmospheric aerosol with an increased share of organics and sulphate.

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Source Apportionment of Submicron Particles Deposited in Regional Lung Measured at an Urban Background Site in London

Student: Tuan V. Vu, MSc.
Supervisor: Prof. Roy M. Harrison; Dr. Juana Mari Delgado-Saborit
Supervising Expert: Dr. Vladimir Zdimal; Dr. David C. S. Beddows

Aerosol particles not only provide information about atmospheric processes, but also have an important influence upon human health. Exposure to ambient aerosols is found to be associated with an increase in mortality, asthma exacerbation, and cardiovascular effects in both epidemiological and toxicological studies.[1] As a result, urban particulate matter has been of much concern in recent years. The object of this study was to identify the sources of submicron particles and identify which source is most responsible for particles deposited in the human respiratory system.

Particle number size distributions (PNSD) were measured by a Scanning Mobility Particle Sizer (TSI, USA), covering the size range 16.5- 604 nm operated by the Department for Environment, Food and Rural Affairs (DEFRA) at an urban background site in London (North Kensington) during 2012. Using PNSD data, Positive Matrix Factorization (PMF) was applied to identify and apportion the sources of particle number.[2] Total regional lung doses of particles from each source were calculated based on the ICRP model[3] from the data obtained by PMF. From PMF results, six main sources of particles were found, including local traffic emission (26.6 % by number), aged traffic emission (29.9 %), diffuse urban (28.3 %), nucleation (6.5 %), secondary aerosol I (1.7 %), and secondary aerosol II (6.9 %). Based on the ICRP model, the total deposition fraction of submicron particles for the above listed sources in the human respiratory tract was 0.57, 0.41, 0.24, 0.68, 0.21, and 0.23, respectively. In terms of source apportionment of particles deposited in the lung, Table 1 shows source contributions of particles (%) in the extra-thoracic (ET), tracheo-bronchial (TB), and alveolar (AL) regions and total lung. Traffic emissions were the main source of particle number deposited in both regional and total lung, accounting for from 63.4 to 68.9 % of total deposited particles. This was followed by the diffuse urban (16.9 %) and nucleation (10.8 %).

Table 1. Sources contribution of particles (%) in in the extra-thoracic (ET), tracheo-bronchial (TB), and alveolar (AL) regions and total lung.

| Source	AL	TB	ET	Total
Local traffic emission	36.6	40.1	36.7	37.3
Aged traffic emission	31.2	28.8	26.6	30.3
Diffuse urban	17.5	14.2	16.9	16.9
Nucleation	10.0	12.9	12.5	10.8
Secondary I	0.8	0.6	1.6	0.9
Secondary II	3.8	3.4	5.7	3.9

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Synthesis of Aza-Aromatic Compounds by Photocyclodehydrogenation Reaction of *N*-Aryl Imines

Student: Ing. Martin Kos
Supervisor: Dr. Ing. Vladimír Církva

Photocyclodehydrogenation reaction of stilbene-like molecules is one of the most important methods of synthesis of polyaromatic compounds such as carbohelicenes, heterohelicenes and phenacenes[1] which are promising materials for usage in optoelectronics (OLED, OFET). Incorporation of nitrogen atom to their structure could benefit from enhanced solubility and ability to make complex with transition metals. Unlike stilbenes, few examples of photocyclization of imines are published in the literature[2] with disadvantages of low yields and the requirement to use strong acid as solvent. We found out that a salt of the *N*-phenyl-benzophenone imine (**1**) and tetrafluoroboric acid (HBF$_4$) is readily converted after irradiation to 6-phenylphenanthridines (**2**) (Scheme 1). Various substituted asymmetrical benzophenone imines **1** (X = H, F, Cl, Br, Me, OMe, NO$_2$; Y = CH, N) were prepared to determine regioselectivity of reaction (isomers **2a** or **2b**). The gained knowledge will be used for preparing of more complex polyaromatic molecules.
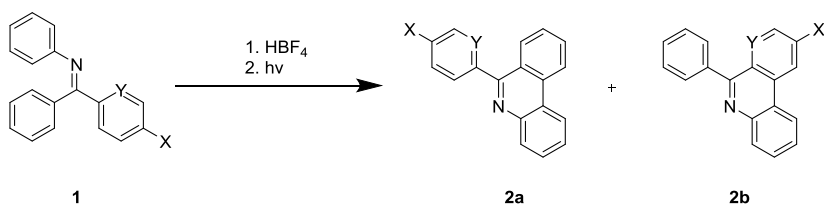
Scheme 1. Photocyclodehydrogenation reaction of *N*-aryl imines

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Preparation of soluble [*n*]phenacene derivatives

Student: Ing. Pavel Jakubík
Supervisor: Ing. Jan Storch, Ph. D.

[*n*]Phenacenes are group of polycyclic aromatic hydrocarbons, which are isomeric form of linear [*n*]acenes. Owing to their conjugated π-electron system, both of these groups are suitable for use in opto-electronic. For utilization in these applications, solubility in common organic solvents is desired. In case of [*n*]phenacenes, which are generally poorly soluble, increase in solubility is achieved by suitable substitution. Compared to unsubstituted [*n*]phenacenes, currently prepared derivatives: 1,2,3,4-tetrafluoro[5]phenacene, 2-aza[5]phenacene, 2,9-diaza[5]phenacene and 12,13-diaza[5]phenacene (Figure 1) show significantly increased solubility.

Batch arranged photocyclization reaction is not effective in terms of time consumption and purity of resulting products, which limits its use for large-scale synthesis. Due to this fact, a prototype of flow photocyclization apparatus was designed, allowing time-effective photocyclization in a multi-gram scale, which is crucial for future research of [*n*]phenacenes.
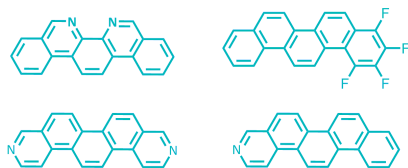

Figure 1. Prepared [*n*]phenacenes with increased solubility

# Progress in Helicene Stationary Phases

Student: Ing. Martin Bernard
Supervisor: Ing. Jan Sýkora, Ph.D.
Supervising Expert: Ing. Jan Storch, Ph.D.

Curious structure of helicenes, inherently chiral *o*-condensed pol-yaromatic compounds, grants them several interesting properties (e. g. high α value). Typically, silica can be modified by various organic species; however using the unique helicene motif as a chiral selector brings some complexity to this field of interest.

We prepared silica-based phases modified by various racemic helicenes used for preliminary testing of their general properties and one stationary phase covered with pure enantiomer of 9-amino[7]helicene. We have proposed and tested a few chiral racemic compounds for their potential separation using mentioned stat. phase. We achieved one positive result (sign of resolution; see scheme below); however the model compound is pretty much useless and just showed us structural
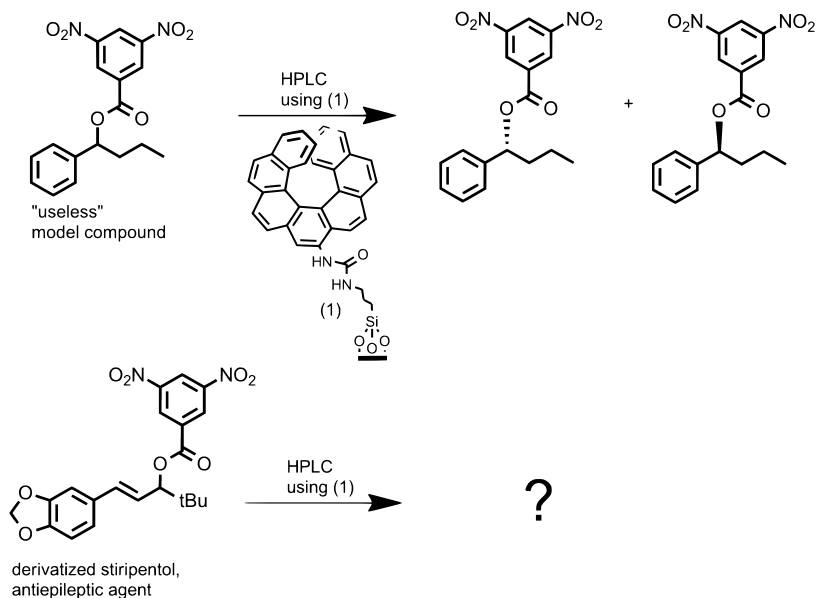
specifics needed for these resolution. For example, the model compound shares some structural motifs with stiripentol, chiral antiepileptic agent exhibiting eutomeric *in vivo* properties.[1]

Furthermore, we have improved one racemic stationary phase using stable 2-amino[6]helicene (compare with unstable 9-amino[7]helicene in phase (1), problems connected with unstability of this material were discussed last year). Results of testing this phase in non-chiral HPLC are satisfying so far; chiral HPLC testing is in progress. Hopefully, the resolution of stiripentol derivative will be discussed during oral presentation.

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