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CONTENTS

Study of Impurities and their Effect on the Physico-Chemical Properties of Ionic Liquids <i>Ing. Jan Rotrekl</i>	5
Solute-Solvent Interaction in Systems of Ionic Liquids with Molecular Solvents <i>Ing. Maja Čanji</i>	7
NMR Aerosolomics: A Convenient Route to Organic Aerosol Analysis <i>Ing. Štěpán Horník</i>	9
Formation and Transformation of Atmospheric Aerosol in Atmospheric Boundary Layer <i>Mgr. Adéla Holubová Šmejkalová</i>	11
Separation of Raw Biogas by Membrane Processes <i>Ing. Michal Žák</i>	13
Synthesis of Amidoazahelicenes by Photocyclization of Aromatic Amides <i>Ing. Lubomír Váňa</i>	14
Photochemical Synthesis of Novel Bidentate Aromatic Ligands <i>Martin Kos</i>	15
Transition-Metal Complexes Bearing Helical Phosphines and their Catalytic Activity <i>Ing. Tomáš Beránek</i>	16
Preparation of New Helically Chiral Flavins as Possible Photocatalysts <i>Ing. Martin Jakubec</i>	17
Flow Photoreactor for Cyclization Reactions <i>Ing. Pavel Jakubík</i>	19
Preparation of Nanocrystalline Titania Thin Films and Aerogels by using Modified Supercritical Carbon Dioxide <i>Ing. Marie Cerhová</i>	20
Comparison of $\text{Ca}(\text{OH})_2$ and NaHCO_3 as Sorbents Suitable for Dry Flue Gas Treatment at Temperatures Below 250 °C <i>Ing. Boleslav Zach</i>	22
Possibilities of High Temperature Desulphurization of a Producer Gas <i>Ing. Jiří Brynda</i>	24

Characterization of Bottom Ash from Czech Waste-to-Energy plants	
<i>Ing. Aneta Krausová</i>	26
Preparation of Magnesium Silicide from Scrap for Hydrogen and Pure Silicon Production	
<i>Ing. Jakub Bumba</i>	28

Study of Impurities and their Effect on the Physico-Chemical Properties of Ionic Liquids

Student: Ing. Jan Rotrekl

Supervisor: Ing. Magdalena Bendová, Ph. D.

The primary aim of the present study is to characterize thermo-physically three novel ionic liquids 1-(2-(2-ethoxyethoxy)ethyl)-3-alkylimidazolium with the bistriflate anion, where the alkyl stands for pentyl, isopentyl or neopentyl. For this purpose thermodynamic and transport properties such as density, heat capacity, electrical conductivity, and viscosity are studied.

The purity of an IL follows from the quality of the precursors used in synthesis. To get an IL of highest purity, *e. g.* for spectroscopic use, extreme care must be taken to control purity in each step of the synthesis, which leads to an elevated cost of the product. For most of the applications, however, a less demanding synthesis protocol is sufficient. Different synthesis approaches typically lead to ILs with diverse levels of impurities and intensity of colouring. However, the origin of the colour is not well known. It is assumed that the concentration of these species is in the ppb range and they have no impact on physico-chemical properties [1].

If a colourless IL is required, a simple purification method is recommended [1]. The IL is diluted with dichloromethane (1:1 per volume in this study) to decrease the viscosity. The solution is stirred with active carbon for a given time and afterwards passed through a column with aluminium oxide. The solvent is then easily entirely removed under vacuum [2].

This purification method was used in this study. As colouring was not always removed in a single step, the procedure was repeated several times, leading to significant changes in the measured properties in each of the steps.

Even though it is widely accepted that the colouring of ILs has negligible influence on the properties [1], our new results seem to be in contradiction with such findings. Therefore it was necessary to identify the impurities and their quantity and link them with observed changes in measured properties. Ion chromatography was used to analyze inorganic residues. To analyze the organic compounds, NMR spectroscopy was used. Because the original concentration of impurities in ILs was lower than the detection limit of NMR, the impurities

were first concentrated using aluminium oxide in a solid phase extraction.

A comprehensive characterization of the impurities will require more experiments tailored to the specific character of ILs. On the other hand, the outcome will be useful in further applications of ILs.

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Solute-Solvent Interaction in Systems of Ionic Liquids with Molecular Solvents

Student: Ing. Maja Čarji

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Ionic liquids (ILs) are molten salts consisting of large, asymmetric organic cations and organic or inorganic anions with a melting point below 100 °C. Numerous combinations of different anions with structurally modified cations can affect their physical and chemical properties. Increasing attention has been paid to room-temperature ionic liquids (RTILs) and their applications as green solvents, since many of them are non-volatile, biodegradable and recyclable materials.¹

In this study, thermodynamic properties of hydrophilic 1-alkyl-3-methylimidazolium-based ILs ($n = 4,6,8,10$) with a saccharinate (Sac) anion have been investigated. The goal of this study was to understand the interactions of ions and their interaction with molecular solvents such as water, methanol, acetone, etc. Saccharinate is a natural nontoxic anion, contributing to a relatively high viscosity of the ionic liquid. Application of highly viscous ILs can be difficult and can be overcome by mixing with some molecular solvents.

The present ILs were used in a previous study for a laboratory-scale extraction of glaucine from its plant.² S-(+)-Glaucine is the main alkaloid component in the *G. flavum* with a wide variety of pharmacological effects including antitussive, contraceptive, anticonvulsant, and neuroleptic-like activities. To design an industrial-scale extraction, it is important to have a good knowledge of the physico-chemical properties in the relevant mixtures of ILs with molecular solvents.

1-Butyl-3-methylimidazolium saccharinate [Bmim][Sac] and 1-Hexyl-3-methylimidazolium saccharinate [Hmim][Sac] were synthesised in this work, whereas 1-octyl-3-methylimidazolium saccharinate and 1-decyl-3-methylimidazolium saccharinate were provided by the group of Prof. Bogdanov.³

So far, density and electrical conductivity were measured in this work for a basic characterization of the studied ionic liquids. Later, volumetric properties and liquid-liquid equilibria in systems of ILs with water and glaucine will be investigated in view of a study of structure-property relationships in these binary and ternary systems, but also from the point of view of the extraction of glaucine.

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NMR Aerosolomics: A Convenient Route to Organic Aerosol Analysis

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

Aerosolomics provides complex evaluation of aerosol composition and compound concentration [1]. It is exploiting metabolomic approach, which is applied to aerosol samples. In our laboratory an NMR method for organic aerosol analysis was developed and tested. The method is focused on water soluble organic compounds (WSOC), which is the least examined group of organic aerosols. In NMR metabolomic approach library ^1H spectra of individual compounds are fitted into the complex ^1H spectrum of a mixture and are subsequently subtracted. This is allowed by the employment of ChenomX software. Since ChenomX is originally a metabolomics software, WSOC are being added to its database continuously. The database currently consists of 120 substances.

Collection of aerosol samples in a high volume cascade impactor together with a special preparation of the sample increased number of identified compounds in every analysed sample. The high volume cascade impactor collects atmospheric aerosols into six stages according to the particle size. Therefore variances in WSOC composition between different particle size samples were found. In this work we present mainly summer 2015 collection of real atmospheric aerosols from Prague – Suchdol.

Major differences were observed in the fraction of carbohydrates and sugar alcohols. Carbohydrate derivatives were found mainly in bigger particle size samples (2.24 – 4.56 μm and 4.56 – 20.00 μm). Other groups of WSOC (mono- and dicarboxylic acids, hydroxycarboxylic acids, oxocarboxylic acids, aromatic compounds or amines) were also thoroughly examined and the results are discussed in this work. The abundance of certain groups of WSOC and the presence of a marker compound can indicate the origin of the aerosol particles.

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Formation and Transformation of Atmospheric Aerosol in Atmospheric Boundary Layer

Student: Mgr. Adéla Holubová Šmejkalová

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Supervising Expert: RNDr. Naděžda Zíková, Ph. D.

Atmospheric aerosols are natural components of the atmosphere but they are also produced by the anthropogenic activity. Their presence in the atmosphere has influence on radiation balance, clouds and precipitation formation, and visibility. Therefore the study of the aerosol formation, their behavior and composition is very important. Especially for climate change research, detailed knowledge about the influence of aerosols on the state of the atmosphere is necessary. Although aerosols are able to absorb and/or scatter radiation, they have generally cooling effect on the atmosphere.^{1,2,3}

The aim of this work is to study the formation of new atmospheric aerosol particles and their transformations in the planetary boundary layer. The experimental data will be measured at the Collocated station Košetice – Křešín u Pacova. The station consists of a 250 m tall atmospheric tower, and professional meteorological and air-quality station. By measuring aerosol properties both on the tower and at the ground using advanced aerosol instrumentation, the atmospheric aerosol concentration fluxes will be assessed, and the changes in physical and chemical properties of the aerosol in the boundary layer will be characterized.

The station is a core of the research infrastructure ACTRIS-CZ run by the Czech Hydrometeorological Institute (CHMI) in close cooperation with Global Change Research Institute (GCRI), Research Centre for Toxic Compounds in the Environment (RECETOX) and Institute of Chemical Process Fundamentals (ICPF). CHMI provides a professional meteorological and air quality station operated since 1988, GCRI offers its 250 m tall Atmospheric tower yielding vertical profiles of meteorological parameters and greenhouse gases, RECETOX adds its expertise on persistent organic pollutants, and ICPF takes care of the aerosol component.

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Separation of Raw Biogas by Membrane Processes

Student: Ing. Michal Žák

Supervisor: Ing. Pavel Izák, Ph. D., DSc.

Recently, purification of raw biogas has attracted a great attention of the research community. Possibility of effective waste utilization for cheap biofuel production has enormous ecological and economical benefits.

In this work are compared a water-swollen thin film membranes and composite hollow fiber membrane modules. Effective separation of carbon dioxide from methane in raw biogas is case study. A fundamental part of the project lies in pilot plant verification of the membrane gas separation based on our patent (CZ303106) by hollow fibres modules. The subject of the future doctoral thesis is the determination of permeation properties of raw biogas by spiral wound modules and hollow fibres modules. On the basis of the results the most economically promising system is now further developing for the commercial utilization in the industry.

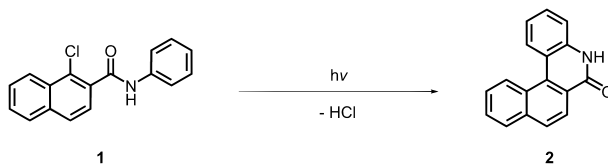
The most promising system is also modelled in two ways, first, chemical engineering model is already compared in this work. Developing of the second model, physical chemistry one, which will be describing the behaviour of moisture in raw biogas, is also already in progress.

Synthesis of Amidoazahelicenes by Photocyclization of Aromatic Amides

Student: Ing. Lubomír Váňa
Supervisor: Dr. Ing. Vladimír Církva

Azahelicenes and their derivatives have gained interest, because of their remarkable properties and chemical behavior predetermining them for different applications (optoelectronics, light-harvesting, or asymmetric catalysis).¹

This work is focused on exploration of photocyclization possibilities of various aromatic amides to amidoazahelicenes (e.g. **2**, Scheme 1) — azahelicene precursors. This well-known methodology² has been used for cyclization of small molecules only and we have found it useful also for preparation of large helicene-like systems. Various aromatic *ortho*-substituted (R = -OMe or -Cl) amides (e.g. **1**, Scheme 1) were prepared in order to study their cyclization under UV-irradiation. These findings will be utilized for the synthesis of other amidoazahelicenes.



Scheme 1. Photocyclization of aromatic amide

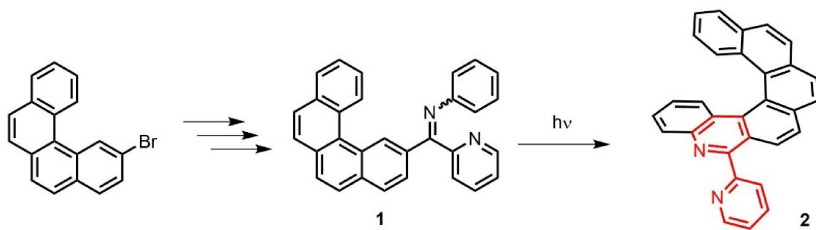
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Photochemical Synthesis of Novel Bidentate Aromatic Ligands

Student: Martin Kos
Supervisor: Dr. Vladimír Círka

Transition metal complexes bearing 2,2'-bipyridine ligands are widely utilized in many fields of research, particularly in photocatalysis [1] or as chromophors in dye-sensitized solar cells [2]. This work is focused on the synthesis of such ligands containing extended polyaromatic systems, mainly pyridyl-aza[n]helicenes and pyridyl-aza[n]phenacenes. The synthetic strategy is illustrated on preparation of 6-pyridyl-5-aza[6]helicene (**2**) (scheme 1). The imino specie **1** readily undergoes a photocyclization reaction in presence of Lewis acid to furnish the corresponding aza[6]helicene **2**. In this manner various aza[n]helicenes and aza[n]phenacenes were prepared. Synthesis of corresponding Ru(II) complexes is in progress in our laboratory.



Scheme 1

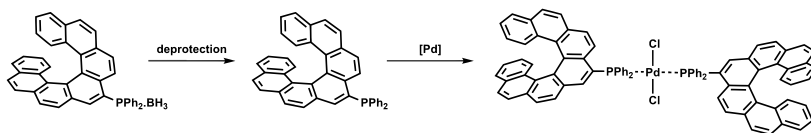
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Transition-Metal Complexes Bearing Helical Phosphines and their Catalytic Activity

Student: Ing. Tomáš Beránek
Supervisor: Ing. Jan Sýkora, Ph. D.
Supervising Expert: Ing. Jan Storch, Ph. D.

Helicenes represent polyaromatic molecules with unique optical and electronic properties. Due to them they can be applied in many fields of research.¹ Surprisingly, the coordination chemistry of helicenes and their use as chirality inducers is still strongly under-developed.² Among privileged ligands exhibiting central, axial or planar chirality, the use of helically chiral ligands in transition metal catalysis is still very rare. Herein, we are focusing on helical phosphines potentially usable in homogeneous asymmetric catalysis. Based on previous results,³ a methodology for preparation of transition metal complexes bearing helical phosphine ligands in their racemic form was developed and such compounds were fully characterized. (Scheme 1).



Scheme 1

Prepared palladium complex was successfully tested in series of Suzuki reactions. Course of the reactions was studied depending on electronic and steric effects of substrates. The preparation of other helicene ligands in their racemic and non-racemic forms is in progress in our lab.

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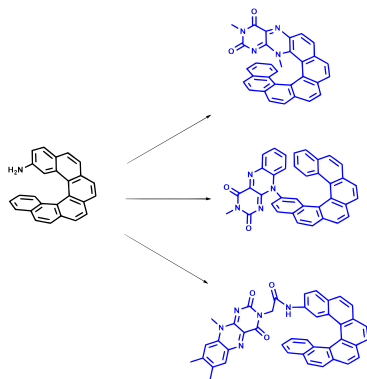
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Preparation of New Helically Chiral Flavins as Possible Photocatalysts

Student: Ing. Martin Jakubec
Supervisor: Ing. Jan Storch, Ph. D.
Supervising Expert: Doc. Ing. Jan Vacek, Ph D.

Flavins are well known photoactive compounds, which were previously employed as catalysts and photocatalysts in various types of reactions, *i.e.* oxidations¹ or [2+2] photocycloadditions². Introduction of a chiral selector might induce enantioselectivity in reactions of suitable prochiral substrates. In this case, helicenes are used not only as chiral selectors, but also for their interesting optical properties.

The main goal of this work was to explore synthetic pathways leading to preparation of new helically chiral flavohelicenes (scheme 1). Several different structures with both flavin and helicene moiety can be prepared using 2-amino[6]helicene as a precursor. Some photo- and electrochemical properties were measured to determine the applicability of these compounds.



Scheme 1: Potential helicene-based flavins.

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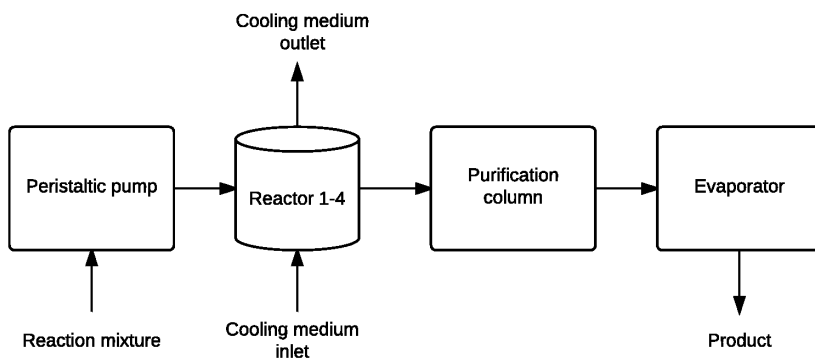
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Flow Photoreactor for Cyclization Reactions

Student: Ing. Pavel Jakubík
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[n]Helicenes and [n]phenacenes have attracted a considerable attention due to their unique electronic and optical properties. Applications in various fields of applied research require a steady supply of material in a sufficient quantity at reasonable price. Their preparation is generally easy to scale up to multigram, or even tens-of-gram scale. A weak point of scaling up is the photoreaction, which is dependent on concentration and irradiation intensity.

In the quest of our investigation in this field, we have assembled a fully functional flow reactor based on a working prototype. The accessible amount of [n]helicenes and [n]phenacenes prepared has increased several times. This was achieved not only due to a larger irradiated volume over the prototype, but also thanks to an advanced purification method, which facilitates the reaction mixture work-up and yields material ready for final crystallization without a further intervention.



Reactor setup scheme

Preparation of Nanocrystalline Titania Thin Films and Aerogels by using Modified Supercritical Carbon Dioxide

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Supervisor: Ing. Marie Sajfrtová, Ph. D.

Supervising Expert: Ing. Lenka Matějová, Ph. D.

Titanium dioxide has been extensively investigated for its promising applications in the form of thin films in solar cell [1] and also as a monoliths (blocks) for solar energy conversion [2]. The most important use of titania is associated with photocatalysis [3, 4] or as supporting material in the catalytic reactions [5]. Owing to the high photocatalytic activity, TiO_2 is an effective, easily available, relatively inexpensive and chemically stable photocatalyst. The photocatalytic activity of TiO_2 strongly depends on the structural properties such as crystal phase composition and crystallite size.

A commonly used method for the preparation of pure and crystalline TiO_2 is calcination (thermal treatment) [6, 7]. Nevertheless, this thermal treatment has some disadvantages such as excessive sintering, crystallite growth, recrystallization, or uncontrollable destruction of highly-porous structure of titania, commonly accompanied by the decrease of the surface area as well as of porosity.

The crystallization technique using modified supercritical carbon dioxide (SFC) opens up the possibility to prepare directly crystalline and highly pure nanostructured TiO_2 [8, 9] without any subsequent thermal treatment.

The motivation of this work is to utilize the SFC for the preparation of nanocrystalline titania thin films and aerogels of high purity. The crystallization with pure and modified scCO_2 by water (5–30 wt. %) and/or organic solvent (10 wt. %) was tested. The temperature (40–150 °C), pressure (10–30 MPa) and the volume of CO_2 (50–200 g) passed through the extractor were optimized with respect to the microstructure and purity of TiO_2 thin films and aerogels.

The purity and crystallinity of prepared TiO_2 thin films and aerogels were estimated by Raman spectroscopy. The crystallite size and the phase composition were determined by X-ray diffraction. Textural properties of aerogels such as the surface area and the pore-size distribution were characterized by nitrogen physisorption and helium pycnometry measurements.

Both, TiO₂ thin films and aerogels prepared with pure scCO₂ were amorphous. The crystallization of TiO₂ thin films was achieved at 150 °C with 100 g of scCO₂ modified by 30 wt. % of water. In case of aerogels, the temperature of 40 °C and lower concentration of water in scCO₂ (5 or 15 wt. %) were sufficient for the crystallization. The best results in terms of crystallization and the purity of titania were obtained during the process combine scCO₂, water and organic solvent.

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Comparison of $\text{Ca}(\text{OH})_2$ and NaHCO_3 as Sorbents Suitable for Dry Flue Gas Treatment at Temperatures Below 250 °C

Student: Ing. Boleslav Zach

Supervisor: doc. Ing. Michael Pohořelý, Ph. D.

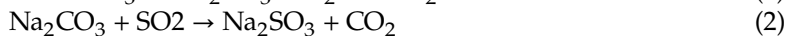
Supervising Expert: Ing. Michal Šyc, Ph. D.

Flue gas treatment is a very important part of every Waste-to-Energy (WtE) plant. Currently, dry flue gas treatment methods are very popular because they are not burdened by wastewater production. Frequently, there are attempts to simplify the process, lower the capital costs, operating costs, and the production of residues classified as hazardous waste.

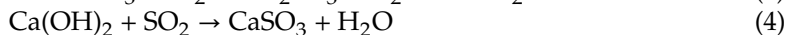
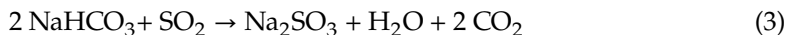
Simultaneous removal of multiple pollutants offers a big potential for simplifying of dry flue gas treatment. However, the individual processes have different optimal conditions. To operate dry flue gas treatment at compromise conditions, properties of sorbents have to be known.

$\text{Ca}(\text{OH})_2$ and NaHCO_3 are the most common sorbents for dry removal of acidic gases from flue gas at low temperature and were, therefore, chosen for comparison. The most important factors are temperature and flue gas humidity.

The properties of NaHCO_3 are great for sorption of SO_2 and HCl and the sorption process works sufficiently regardless of the process temperature and flue gas humidity. Firstly, NaHCO_3 in flue gas decomposes to Na_2CO_3 , which then reacts with the acidic gases. Equations (1) and (2) describe the decomposition reaction of NaHCO_3 and its reaction with SO_2 respectively. During this decomposition, H_2O and CO_2 leave the sorbent and cause the formation of surface structures suitable for sorption of acidic gases. Although this surface is smaller than surfaces of some calcium based sorbents, high reactivity of Na_2CO_3 formed *in situ* in flue gas enables its use with low stoichiometric excess ratio (1.1–1.4). The disadvantages of NaHCO_3 are its relatively low reactivity towards HF , water solubility of air pollution control residues, and price.



$\text{Ca}(\text{OH})_2$ is commonly used with higher stoichiometric excess ratio (usually 2.0–2.5). On the other hand, calcium is bivalent. Therefore, in comparison with NaHCO_3 , theoretically only the half of the amount of substance is necessary for removal of the same amount of SO_2 , HCl , or HF , as can be seen from equations (3) and (4). The mass of used NaHCO_3 and $\text{Ca}(\text{OH})_2$ is, therefore, similar despite of the big difference in stoichiometric excess ratios.



The sorption rate of HCl on $\text{Ca}(\text{OH})_2$ is, in comparison with NaHCO_3 (Na_2CO_3), an order of magnitude lower and to reach the emission limits, the flue gas treatment has to be conducted under suitable conditions. A suitable temperature for removal of acidic gases by calcium based sorbents is connected to the content of H_2O in flue gas. The reaction rate is very good in the vicinity of dew point but the process conditions shouldn't be too close to the dew point to avoid condensation. The advantages of $\text{Ca}(\text{OH})_2$ are better reactivity towards HF , very low water solubility of air pollution residues, and low price in comparison with NaHCO_3 .

Acknowledgements

This research was conducted within Waste to Energy Competence Centre funded by the Technology Agency of the Czech Republic (project TE02000236) and was co-financed from specific university research (MSMT No 20-SVV/2016).

Possibilities of High Temperature Desulphurization of a Producer Gas

Student: Ing. Jiří Brynda

Supervisor: Ing. Sjarhei Skoblja, Ph. D.

Supervising Expert: Doc. Ing. Karel Svoboda, CSc.

Producer gas contains several types of impurities, which limit its further utilization. Depending on the used feedstock and gasifier type the main impurities are tar, dust, sulphur compounds, HCl, and HF. In producer gas from biomass gasification the main impurities are tar, H₂S, COS, and HCl. In order to use the producer gas in SOFC (solid oxide fuel cells) or Fisher-Tropsch synthesis the concentration of impurities must be lower than 1 ppmv.

Sorbents currently used for high temperature desulfurization are based on CaO, Fe_xO_y, ZnO, CuO. Fe_xO_y and CaO based sorbents are not capable to achieve sufficiently low output H₂S concentration at high temperatures. ZnO and CuO sorbents are problematic due to undergoing reduction at high temperatures. This reduction causes the formation of volatile elemental zinc in the case of zinc sorbents and reduction of active CuO to less active Cu₂O and Cu which exerts inferior desulfurization activity. For this reason new substances for high temperature desulfurization are being examined. The easiest way to assess the desulfurization potential of different substances at different conditions is according to their thermodynamic data. According to thermodynamic calculations several rare earth oxides such as Ce₂O₃ and La₂O₃ seem to be suitable for deep high-temperature desulfurization. These calculations suggest that Ce₂O₃ and La₂O₃ are able to ensure output concentrations of H₂S and COS below 1 ppmv and 0.01 ppmv, respectively, in the temperature range of 600–800 K and gas containing 40 vol. % of H₂, 10 vol. % of H₂O and 30 vol. % of CO₂. For a more complex thermodynamic calculation, methods based on the minimization of free Gibbs energy have to be applied. These more complex and accurate calculations suggest a possibility of oxidation of Ce₂O₃ in the presence of CO₂ or H₂O to CeO₂, which has a much higher equilibrium concentration of H₂S. Complex thermodynamic calculations suggest a formation of inactive and thermally stable oxy-carbonate La₂O(CO₃)₂ in presence of CO₂.

In the experimental part of the desulfurization studies, H₂S sorption on CeO_x/Al₂O₃ and La₂O₃/Al₂O₃-based sorbents was examined at the temperature 727 K at different gas compositions. First tests were carried out in gas without any oxidizing agent containing only H₂ and N₂. Prepared CeO_x/Al₂O₃ sorbent was reduced prior to each desulfurization experiment. This step indicated to be crucial for sorbent activity and capacity. These experiments proved possibility of high temperature desulfurization with Ce-based sorbent. But even with a sorbent prereduced by a gas with 50% vol. of H₂, the sorbent was capable to attain output H₂S concentration below 1 ppmv for only 2.5% of relative time of sorption. Slightly better results were attained when the reduction step was carried out at temperature 827 K for one hour in a gas consisting of 90 vol.% of H₂ and 10 vol.% of CH₄. To find the extent of reduction, both reduced and non-reduced CeO_x based sorbent were analyzed by XPS (x-ray photoelectron spectroscopy). According to the results of the analysis the non-reduced sorbent contains 51% of Ce^{IV} and 49% of Ce^{III} compared to 35% of Ce^{IV} and 65% of Ce^{III} in the reduced sorbent. In the following experiments, a sorbent prepared and prereduced in this way was tested in dry producer gas: CO₂ = 14.4 vol.%, CO = 39.4 vol.% and H₂ = 46.2 vol.% with 250 ppmv of H₂S.

Experiments with the reduced CeO_x-based sorbent did not proved any desulfurization activity in wet nor in dry producer gas, even though that XPS analysis proved that both reduced and nonreduced sorbent does contain active Ce₂O₃. This is caused by an immediate reoxidation of reduced cerium oxide by H₂O and CO₂ in producer gas. For application of the CeO_x-based sorbent in desulfurization of producer gas it is necessary to prepare a stabilized Ce₂O₃. The possibilities of stabilization of Ce₂O₃ will be investigated in the following experiments.

Characterization of Bottom Ash from Czech Waste-to-Energy plants

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Supervising Expert: Ing. Michal Šyc, Ph. D.

Bottom ash presents the majority of all solid residues from waste-to-energy (WtE) plants and contains significant amount of valuable components that can be recycled such as ferrous scrap, non-ferrous metals, or glass. Metals and glass recovery followed by the reuse of residual fraction as a construction material can be an appropriate option for bottom ash treatment. Important benefits of bottom ash recycling for the plant operator are also the reduced costs for landfilling and revenues from obtained metals. In the Czech Republic, most of the bottom ash is landfilled, which is not in accordance with contemporary trends and its material reutilization should be preferred.

Bottom ash usually contains around 5–13% of ferrous scrap, 2–5% of non-ferrous metals, 15–30% of glass and ceramics, 1–5% of unburned organics, and 50–70% of mineral fraction.^{1, 2, 3, 4} Several incineration plants in Europe are equipped with systems for metal recovery, mostly based on magnetic separation of ferrous scrap and non-ferrous metals separation by eddy-current separator. Separation of glass is a rather unique technology and is based on optical sorting systems.

Our study summarizes the composition of bottom ash from two WtE plants in the Czech Republic. Bottom ash with particle size over 2 mm was characterized by combination of manual and mechanical analyses (e.g. magnetic separation, sieving, grinding, etc.). Bottom ash with particle size under 2 mm was analysed using scanning electron microscopy, to find its composition and to determine the form of comprised metals.

The composition of dry bottom ash from Czech WtE plants ranged as follows: 10–24% of glass, 1.8–5.2% of ceramics and porcelain, 0.3–1.0% of unburnt organic matter, 12–17% of magnetic fraction, 1.1–4.5% of Fe scrap, 1.3–2.4% of NFe metals. Residual fraction formed by ash and minerals together with fraction of particles under 2 mm varied between 54–67%. Various content of recoverable materials were found in bottom ash samples from different WtE plants. Therefore, we performed an analysis of incinerated waste with respect to the plant waste

collection area (urban vs. rural or mixed), type of incinerated waste (commercial or municipal), intensity of separate collection, etc. Based on the results, we found that type of incinerated waste had crucial impact on the bottom ash composition. Especially the amount of incinerated commercial waste which usually does not contain any recoverable materials. The determination of waste and thus bottom ash composition can be decisive in the period of considering instalments of technology for metals or glass recovery.

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Preparation of Magnesium Silicide from Scrap for Hydrogen and Pure Silicon Production

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Supervisor: Ing. Olga Šolcová, CSc., DSc.

Nowadays, there is an effort in chemistry to maximally utilize materials and energy without pollutant or toxic waste production. Photovoltaic panels (PV) belong to systems which use only solar energy to generate electricity in commercial and residential applications. PV panels have become very popular because they work without noise, material consumption and pollutants with government support. Their efficiency can exceeds 19% and lifetime 25 years. It is known, that up to 97% of contained semiconductors (mainly silicon) can be recovered. Nevertheless, the purity of regenerated silicon is usually not enough sufficient for semiconductor applications even for new PV panels. Troubles with purity and usage are also connected with recovered magnesium from automotive scrap.

This work is focused on preparation of magnesium silicide to purify silicon *via* waste-free route. Magnesium silicide was successfully prepared by the reaction between silicon from PV panels and magnesium from scrap. The synthesis was tested under various temperature, reaction time and atmosphere. Prepared samples of magnesium silicide were characterized by X-Ray diffraction, Raman spectroscopy, Scanning Electron Microscopy with Energy Dispersive X-Ray spectroscopy and compared with commercial standard. Magnesium silicide was then hydrolysed by phosphoric acid. Gaseous product (mixture of silanes) was characterized by Gas Chromatography – Mass Spectroscopy. The only by-product of hydrolysis is magnesium phosphate; a desired fertilizer. Prepared silane was thermally decomposed over hot platinum wire. Decomposition of silane into pure silicon and hydrogen was indirectly confirmed by Fourier Transform Infrared Spectroscopy. The mentioned process for silicon purification provides high purity silicon, hydrogen and magnesium phosphate. All three steps of process was successfully verified. The recovered high purity silicon can be used even for semiconductor applications. The obtained hydrogen can serve as a source of energy and magnesium phosphate can increase agricultural yields.

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