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# Aerosol particle formation during summer campaign at rural background site Košetice

*Student: Mgr. Adéla Holubová Šmejkalová*

*Supervisor: Ing. Vladimír Ždímal, Dr.*

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

1 Aerosol particles as a ubiquitous component of the atmosphere sig-  
2 nificantly influence atmospheric characteristics. Atmospheric aerosols  
3 (AA) affect radiation balance, formation of clouds and precipitation,  
4 and visibility. They act either directly due to extinction (scattering and  
5 absorption) of incoming solar radiation on aerosol particles, or indi-  
6 rectly serving as cloud condensation nuclei and affecting radiation bal-  
7 ance due to scattering the radiation on clouds<sup>1,2</sup>. Both effects depend  
8 on AA particles' size and concentration, i.e. on particle size distribu-  
9 tion. New particle formation (NPF) is a key process of the atmospheric  
10 aerosol dynamics influencing particle size distribution; therefore, un-  
11 derstanding of NPF is essential for climate studies. NPF events can be  
12 observed in many different environments and cover diversity of nuclea-  
13 tion mechanisms<sup>3,4,5,6</sup>.

14 This study of NPF in the atmospheric boundary layer was carried  
15 out in summer 2016. The measurement was performed at the Na-  
16 tional Atmospheric Observatory Košetice (NAO Košetice). This obser-  
17 vatory is classified as a background site situated on the NW border of  
18 Vysočina region (49° 34' 24.2'' N, 15° 4' 49.0'' E, 534 m a. s. l.). The data  
19 were collected from 5<sup>th</sup> August to 30<sup>th</sup> September 2016 by two state-of-  
20 the-art instruments. A Particle Size Magnifier (PSM, model A11, Air-  
21 modus) continuously recorded clusters formation in the scanned size  
22 range from 1.2 to 3 nm with 4 minutes time resolution, while a Scan-  
23 ning Mobility Particle Sizer (SMPS, IfT TROPOS) monitored aerosol  
24 number size distribution in the mobility diameter range from 10 to  
25 800 nm each 5 minutes.

26 Based on the SMPS data, the individual days were classified as NPF  
27 event, non-event and undefined, according to the method of Dal Maso  
28 et al. (2005). In order to obtain daily patterns, PSM data were averaged  
29 for all NPF event, and all non-event days. Relations between NPF, daily  
30 variability of meteorological elements, and aerosol particles precursor  
31 concentrations were evaluated.

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# Data Processing of Experimental Results in Systems of Ionic Liquids. Pitfalls and Challenges.

Student: Ing. Jan Rotrekl

Supervisor: Ing. Magdalena Bendová, Ph.D.

1 In previous work a number of physico-chemical properties of  
2 systems with ionic liquids (ILs) was presented. A group of *quasi*-  
3 isomeric 1-butyl-3-alkylimidazolium bistriflimides, where alkyl stands  
4 for pentyl, isopentyl, 3-pentyl, and cyclopentyl was selected in view of  
5 the influence that structural changes might have in tailoring physico-  
6 chemical properties of ILs. Isobaric heat capacity, density, viscosity,  
7 electrical conductivity, or mutual solubility with water have been mea-  
8 sured for the studied ionic liquids as a function of temperature and  
9 the effect of isomerization was clearly observed.

10 Raw data can in some cases be sufficient to assess the relation be-  
11 tween the chemical structure and properties of a substance. This was  
12 *e.g.* the case for the density and heat capacity data in present series.  
13 However, to calculate some derived properties, *e.g.* the isobaric expan-  
14 sivity, data regressed with a suitable function are essential. In this ex-  
15 ample it was found, that the quality and adequacy of the density data  
16 correlation plays a crucial role in determining the isobaric expansivity  
17 temperature dependency. If the correlation is incorrect (which may  
18 not be evident at first sight), the derived properties often show phys-  
19 ically nonsensical shapes. To obtain the best results, a robust linear  
20 regression along the gnostic influence function based on mathematical  
21 gnostics [1] was applied to optimize the correlation parameters for  
22 the experimental data.

23 In this contribution, a correlation of liquid-liquid equilibrium data  
24 in binary systems of the studied ionic liquids with water was also car-  
25 ried out. To correlate the data on mutual miscibility of ionic liquids  
26 with water the Non-Random Two-Liquid (NRTL) [2] equation was  
27 used in the following form:

$$Q = \frac{G^E}{RT} = x_1 x_2 \left( \frac{\tau_{21} g_{21}}{x_1 + x_2 g_{21}} + \frac{\tau_{12} g_{12}}{x_2 + x_1 g_{12}} \right) \quad (1)$$

28 where  $\tau_{ij} = a_{ij}/T$  and  $g_{ij} = \exp(-\alpha \tau_{ij})$ . This model of excess Gibbs free

29 energy is based on theoretical concepts of the description of the system  
30 on the molecular level. Consequently, its parameters have a physical  
31 meaning. As opposed to empirical models, NRTL allows for a more  
32 reliable description of multicomponent systems using only binary pa-  
33 rameters  $a_{ij}$ . However, the NRTL equation is not linear in its parame-  
34 ters, a non-linear optimization procedure is therefore needed. The pa-  
35 rameter  $\tau_{ij}$  is temperature-dependent, whereas parameter  $a_{ij}$  is usually  
36 fixed to a constant value. However, this often doesn't lead to a suffi-  
37 ciently good description of binodal curves. A temperature dependence  
38 is then used for the  $a_{ij}$  parameter, which makes the optimization more  
39 difficult. Fortunately, even simple functional forms such as a linear de-  
40 pendence can bring about a significant improvement in the quality of  
41 the data fitting. In this study some other forms of temperature depen-  
42 dency of parameter  $a_{ij}$  were also tested.

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# Thermodynamic Properties of Saccharinate-based Ionic Liquids: Comparison of Experimental Data to a Prediction by means of COSMO-RS

*Student: Maja Čanji, MSc.*

*Supervisor: Ing. Magdalena Bendova, Ph. D.*

1 As an overall general aim of this study, thermodynamic properties  
2 of hydrophilic 1-alkyl-3-methylimidazolium-based ILs (n = 4, 6, 8,  
3 10, 16) with a saccharinate (Sac<sup>-</sup>) anion have been investigated. Sac-  
4 charinate is a natural nontoxic anion, contributing to the application  
5 potential of the present ILs series. They were therefore used in a pre-  
6 vious study for a laboratory-scale extraction of glaucine from its plant.<sup>1</sup>  
7 To design an industrial-scale extraction, it is important to have a good  
8 knowledge of the physico-chemical properties in the relevant mixtures  
9 of ILs with molecular solvents.

10 In the present contribution, density of 1-alkyl-3-methylimidazolium  
11 saccharinates (n = 4, 6, 8, 10) and isobaric heat capacity for 1-butyl-3-  
12 methylimidazolium saccharinate were measured in this work for a basic  
13 characterization of the studied ionic liquids. Modelling based on  
14 the COSMO-RS<sup>2</sup> model was used to predict density and heat capacity<sup>3</sup>  
15 for the studied ILs and compared with experimental data. Moreover,  
16 a prediction by means of COSMO-RS of liquid-liquid equilibria<sup>4</sup> for  
17 1-decyl-3-methylimidazolium saccharinate with water was carried out  
18 and compared with a preliminary experiment of its limited miscibility.

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30 diction of IL mixture – A review. *Fluid Phase Equil.* **2010**, *294*, 31–38.

# New Porous Carbon Electrocatalysts Derived from Ionic Liquid for Oxygen Reduction Reaction

*Student: Nikola Zdolšek, MSc.*

*Supervisor: Dr. Tatjana Trtić Petrović, Dr. Biljana Šljukić*

1 In the past few years ionic liquids (ILs) have found application in  
2 nanomaterials design and synthesis, due to unique physicochemical  
3 properties and diversity of cation-anion combination. In the present  
4 work, two porous carbon materials were synthesized by two novel  
5 methods using IL. 1-butyl-3-methylimidazolium methane sulfonate,  
6 with high thermal stability and the melting temperature of 74 °C de-  
7 termined by the HLM method, was used as a medium in ionothermal  
8 carbonization of glucose and as a precursor for synthesis sulphur- and  
9 nitrogen-double-doped porous carbon in direct carbonization of IL.  
10 Carbon materials were characterized by SEM, Raman spectroscopy,  
11 N<sub>2</sub> physisorption at 77 K and X-ray photoelectron spectroscopy.

12 The obtained materials were used as cathodic materials in oxygen  
13 reduction reaction (ORR). Electrocatalytical activity of materials was  
14 examined by cyclic voltammetry in O<sub>2</sub>-saturated 0.1M KOH electrolyte.  
15 The material obtained by direct carbonization of IL showed cathodic  
16 peak at 0.6 V vs. RHE. Detailed investigation was performed using  
17 the linear sweep voltammetry with a rotating disc electrode. Sulphur  
18 and nitrogen-doped porous carbon exhibited very good characteristic  
19 for application for ORR with direct four electron pathway mechanism.  
20 On the contrary, a lower electrocatalytical activity with two-step two-  
21 electron pathway was found for the ionothermal carbon.

## *Acknowledgement*

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23 his internship at ICPF and the support to this work provided by the  
24 Ministry of Education and Science of Serbia through project *Physics*  
25 *and Chemistry with Ion Beams*, No. III 45006.

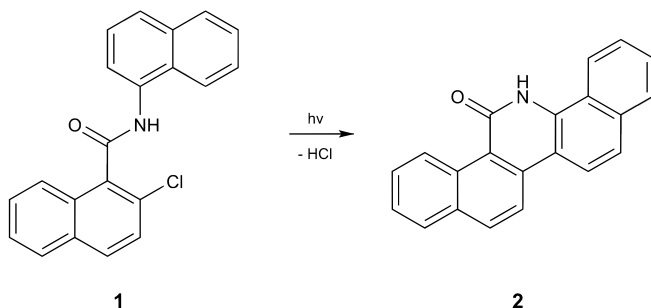
# Synthesis of Amidoazaphenacenes for Applications in Molecular Electronics

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

1 Research and development in organic electronics (OLEDs, OFETs)  
2 based on  $\pi$ -electron network molecules has made rapid progress in  
3 recent years. Phenacenes with their extended two-dimensional  $\pi$ -con-  
4 jugated structure are suitable for this purpose as they can provide  
5 a charge-transporting pathway when arranged into appropriate thin  
6 layer in solid state.<sup>1</sup>

7 This work is focused on preparation of amidoazaphenacenes (e. g.  
8 **2**, Scheme 1). Their amide functional groups can form hydrogen bonds  
9 which have a positive effect on the formation of a stable supramolecu-  
10 lar structure to facilitate the charge carrier transport in thin solid film.<sup>2</sup>

11 Amidoazaphenacenes (e. g. **2**, Scheme 1) were prepared by photo-  
12 cyclization of various *ortho*-chloro-substituted aromatic amides (e. g.  
13 **1**, Scheme 1). This well-known methodology<sup>3</sup> has been used for cy-  
14 clization of small molecules only and we have found it useful also for  
15 a preparation of large phenacene-like systems. The resulting compo-  
16 unds will be subsequently investigated in terms of their material  
17 properties, especially for the formation of the thin film structures ca-  
18 pable of efficient semiconductivity. These findings will be utilized for  
19 the synthesis of other amidoazaphenacenes.



21 Scheme 1. Photocyclization of aromatic amide

### *Acknowledgement*

22 The financial support of the Grant Agency of the Czech Republic  
23 No. 17-02578S is gratefully acknowledged.

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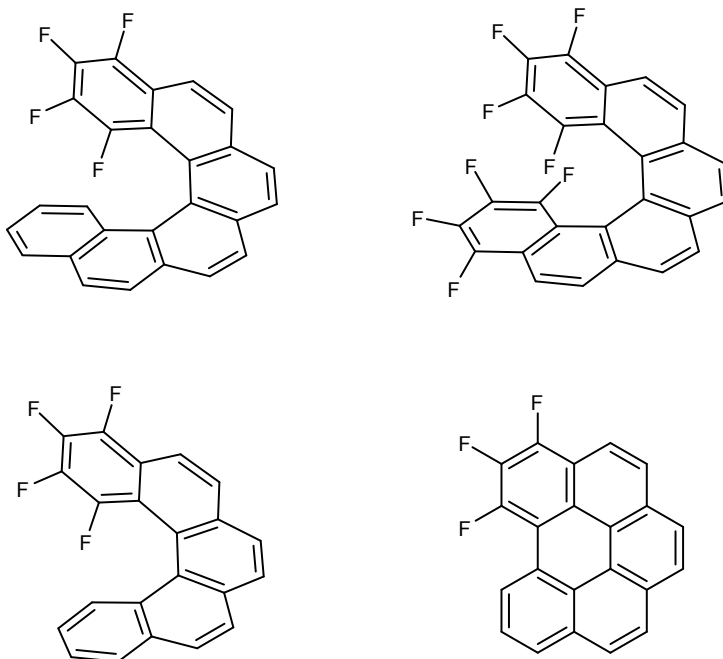
# Preparation of Fluorinated [5]- and [6]Helicenes

*Student: Ing. Pavel Jakubík*

*Supervisor: Ing. Jan Storch, Ph. D.*

*Supervising Expert: Dr. Ing. Vladimír Církva*

1 Introduction of fluorine substituents into the helicene skeleton  
2 is a suitable strategy for enhancing properties required for the con-  
3 struction of optoelectronic devices. The fluorine atoms decrease  
4 C-H/ $\pi$  interactions, which usually organize aromatic molecules in  
5 a solid state, and might contribute to solubility enhancement. Fluorine  
6 substitution is known to modulate aromatic-aromatic interactions  
7 by affecting the HOMO-LUMO gap, changes the electron density of  
8 the  $\pi$ -electron system and results in higher electron mobility. It can  
9 also lead to changes in a chemical reactivity.



10

11

Figure 1: Fluorinated derivatives of [5]- and [6]helicenes

12 Synthetic strategies to fluorinated helicenes were examined, lead-  
13 ing to tetrafluoro[6]helicene and octafluoro[6]helicene. Different  
14 mechanisms of photocyclization have been tested and compared, pro-  
15 viding interesting insight into the reactivity. An unexpected forma-  
16 tion of side-products has been observed during photocyclodehydroflu-  
17 orination reaction, as well as fluorine atom rearrangement in case of  
18 tetrafluoro[5]helicene. This lead to a need of development of new and  
19 more complicated synthetic approach towards fluorinated helicenes.

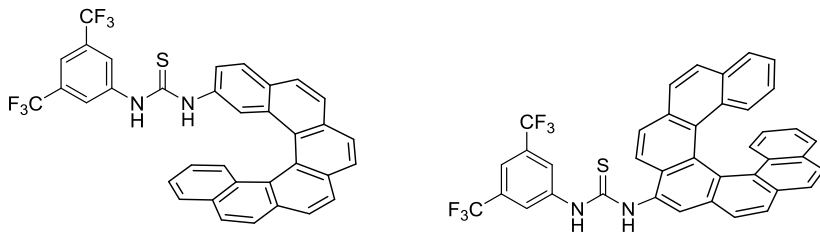
# Helicene-based Thioureas

Student: Ing. Martin Jakubec  
Supervisor: Ing. Jan Storch, Ph. D.

1 Helicenes are compounds of great potential in various fields in-  
2 cluding organocatalysis,<sup>1</sup> thanks to their inherent chirality and sig-  
3 nificant rigidity of their structure. Despite generally good results, the  
4 amount of publications in this area of helicene chemistry is limited.<sup>2</sup>

5 The main goal of this work was to introduce the helicene moiety  
6 into the structure of bis(aryl)thiourea, to prepare a new type of  
7 a helicene-based organocatalyst. Several aryl(helicenyl)thioureas were  
8 synthesized so far. Their ability to form hydrogen-bond complexes  
9 with various types of substrates was verified using NMR and the ac-  
10 tivity of the catalysts is currently being explored.

11 Since the enantioselective organocatalysis requires use of enan-  
12 tiomerically pure compounds, the methodology for resolution of the  
13 starting material, 2-amino[6]helicene, was also explored.



15 Fig. 1: Structures of some of the prepared helicene based thioureas.

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# Transition-Metal Complexes with Helical Phosphines

Student: Ing. Tomáš Beránek

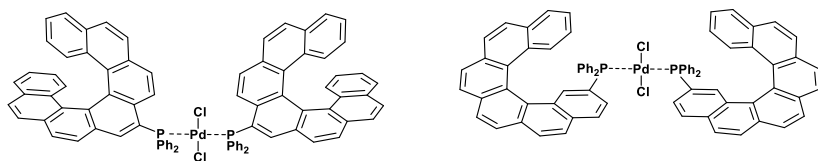
Supervisor: Ing. Jan Sýkora, Ph. D.

Supervising Expert: RNDr. Jaroslav Žádný, Ph. D.

1 Due to their remarkable properties, helicenes are suitable candi-  
2 dates for use in asymmetric catalysis. Among privileged ligands ex-  
3 hibiting central, axial, or planar chirality, the use of helically chiral lig-  
4 ands in transition metal catalysis is still very rare. Although several  
5 pilot experiments have already been carried out in this area, a larger  
6 study of the preparation of complexes bearing helical ligands with cat-  
7 alytically significant metals is still missing<sup>1</sup>.

8 This work follows the synthesis of the palladium (II) complex with  
9 9-phosphanyl[7]helicene, where several structural uncertainties were  
10 clarified. Furthermore, synthetic pathways were investigated to pro-  
11 vide other suitable phosphine derivatives of [6]helicene and their tran-  
12 sition metal complexes. In prepared complexes, the influence of phos-  
13 phine group position on the catalytic activity of helicene complexes  
14 was examined.

15 Attempts on enantiomeric resolution of prepared helicenes were  
16 also carried out.



18 Figure 1 – Transition-metal complexes with helical phosphines

19 *This work was supported by the Technology Agency of the Czech Republic*  
20 *(TA04010082).*

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# Progress in Synthesis of Aza-helicenes

Student: Martin Kos

Supervisor: Dr. Vladimír Církva

1 Creation of helical compounds with unique structural attributes  
2 and properties remains in focus of many researchers. Recent litera-  
3 ture reveals many examples of exploiting helical structures as molecu-  
4 lar springs<sup>1</sup>, selenoids<sup>2</sup>, tweezers<sup>3</sup>, motors<sup>4</sup>, dye-sensitized solar cell  
5 materials<sup>5</sup>, OLED<sup>6</sup>, and so on. In recent years, the preparation of hetero-  
6 helicenes has been studied extensively in order to exploit the unique  
7 properties of these molecules<sup>7</sup>. However, azahelicenes were not elab-  
8 orated sufficiently and only a few reports have described the synthe-  
9 sis of such compounds despite their possible applications in various  
10 branches of chemistry.

11 Herein we report synthesis of series of novel aza- and diaza-he-  
12 licenes, which were prepared mainly by photocyclization of correspon-  
13 ding imine precursors. Reaction conditions (solvent, photocatalyst,  
14 type of UV, use of water scavenger) of photocyclization were opti-  
15 mized and enhanced. Usage of TEMPO (2,2,6,6-tetramethyl-piperidin-  
16 1-yl)oxyl) as oxidizing agent lead to improvement of yields up to 72%.

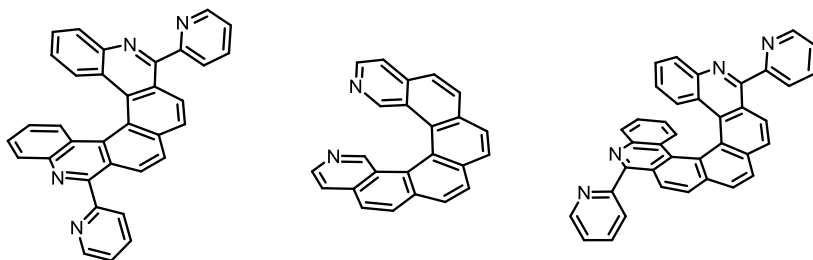


Figure 1

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# Preparation of Magnesium Silicide and Magnesium Germanide from Waste for Material recovery

*Student: Ing. Jakub Bumba*

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

1 The increasing world production of electronics requires a huge  
2 amount of rare ultrapure elements, mainly conductors and semicon-  
3 ductors. The requirement for high purity is also the reason of their  
4 high price. The lifetime of the first generations of PV panels based on  
5 polycrystalline or monocrystalline silicon has come to an end, nowa-  
6 days. The old PV panels still contain a quantity of silicon with purity  
7 over 90%. However, this purity is insufficient for their reuse as semi-  
8 conductors even in new PV panels. Impurities such as silicon oxide,  
9 dopants and conductors e. g. B, P<sub>2</sub>O<sub>5</sub>, Si<sub>x</sub>N<sub>y</sub>, Ag, Al, Cu, Sn, signifi-  
10 cantly complicate their recycling process.

11 Germanium is a similarly essential component for glass, used in  
12 telecommunication optic fibres, infrared optics, semiconductors and  
13 electronic circuitry.

14 To cover a high demand of silicon and germanium, it is crucial  
15 to recover them from scrap. However, the established recycling pro-  
16 cesses use a high amount of energy, dangerous chemicals, and expen-  
17 sive technological processes. In addition, the obtained products with  
18 insufficient quality require subsequent refining procedures.

19 For this reason this work is focused on low-temperature recycling  
20 processes of silicon and germanium. These processes utilize old PV  
21 panels as raw material for ultrapure silicon, or low purity germanium  
22 for subsequent ultrapure germanium production. The first step of the  
23 silicon recovery process is based on magnesium silicide (Mg<sub>2</sub>Si) prepa-  
24 ration by a direct thermal synthesis from elements. Milled PV panels  
25 and magnesium scrap were used as raw materials. Different PV pan-  
26 els were tested under various reaction conditions. The resulting pro-  
27 ducts were characterized by X-Ray Diffraction (XRD) and Scanning Elec-  
28 tron Microscopy (SEM) with Energy Dispersive X-Ray Spectroscopy  
29 (EDX) and then hydrolysed by phosphoric acid to yield silicon hy-  
30 drides (silanes) in the second step. Silane was then thermally decom-  
31 posed into ultrapure silicon and hydrogen in the last step of the pro-  
32 cess. The formation of silanes and their subsequent decomposition was

33 studied by the Fourier Transform Infrared Spectroscopy (FTIR) and  
34 Gas Chromatography – Mass Spectroscopy (GC-MS). The first step of  
35 mentioned process for silicon recovery was also tested for germanium.  
36 Formation of magnesium germanide ( $\text{Mg}_2\text{Ge}$ ) was successfully con-  
37 firmed by XRD and SEM/EDX.

#### *Acknowledgement*

38 The financial support of the Grant Agency of the Czech Republic  
39 No. 15-14228S is gratefully acknowledged.

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# Reaction Kinetic Study of Heterogeneous Hydrogenations for 3D-printed Catalysts

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*Supervising Expert: Petr Stavárek, Ing. PhD*

1 This work focuses on a reaction kinetic study of three-phase hydro-  
2 genation reactions. Two model catalytic hydrogenations are studied  
3 in a batch reactor equipped with a catalyst basket. Catalysts for both  
4 reactions are used in the form of cylindrical pellets. The goals of this  
5 work are to study the kinetics and reaction mechanism, as well as the  
6 determination of the reaction kinetic parameters. In the current stage  
7 of the investigation different reaction conditions are tested. A basic  
8 set of experimental data was collected that investigated the effect of  
9 temperature. The experiments consisted of several hour-long exper-  
10 iments with continuous sampling in about 20 min long intervals. In  
11 this manner, the time-concentration profiles were collected for differ-  
12 ent operating conditions. The repeated data series with fixed reaction  
13 conditions (temperature, hydrogen pressure) have revealed a notice-  
14 able deactivation of the catalyst used. Data are evaluated by a mathe-  
15 matical kinetic model to determine the kinetic parameters of the indi-  
16 vidual reaction steps. The kinetic model that describes the investigated  
17 reaction should enable detailed modeling of the optimum shape of the  
18 catalyst support. The main innovation and challenge of the project un-  
19 der which this work is carried out is to 3D print the optimum foam  
20 structure as a catalyst carrier. The second challenge is to find the best  
21 properties of the catalyst for the hydrogenation reactions. The anti-  
22 cipated innovation involves enhancement in energy efficiency, mass and  
23 heat transfer, and last but not least in catalytic performance.

## *Acknowledgement*

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25 zon 2020 research and innovation program under grant agreement  
26 No: 680414.

# Hydrodynamic Behavior of Bubbles in Slot Channels

*Student: Kingsley Ezeji, MSc.  
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1 Vertical movement of gas bubbles in liquid phase is of enormous  
2 significance in a number of industrial operations such as electrolytic  
3 cells, filtration devices, and heat exchangers.<sup>1</sup> The movement of these  
4 gas bubbles is capable of providing the stirring required for fluid mix-  
5 ing. However there is very little published data on the hydrodynamic  
6 behavior of such bubbles in inclined rectangular channels.

7 We present results of laboratory experiments investigating the dy-  
8 namics of air bubbles rising in stagnant or co-flowing liquid (water)  
9 in inclined channels of rectangular cross-sections. The experiments  
10 were conducted in a basic Plexiglas channel (1300 × 240 × 20 mm, in  
11 length ( $L$ ), width ( $W$ ), and height ( $H$ ), respectively). Different channel  
12 geometries ( $H = 5, 10$  and  $20$  mm;  $W = 20 \div 240$  mm) were obtained  
13 by insertion of suitably varied plates into the basic channel. Channel  
14 inclinations were ranging from  $\alpha = 5^\circ$  (almost horizontal) to  $90^\circ$  (ver-  
15 tical). Measurements and data analysis were carried out with the use  
16 of a high speed video camera system and image processing technique  
17 providing information on the bubble shape (bubble length  $L_B$  and vol-  
18 ume  $V_B$  and bubble rise velocity  $U_B$ ). The specific impact of channel  
19 geometry, orientation and inclination on the shape, stability, and ve-  
20 locity of rising bubbles was studied and discussed.

21 The results obtained in all studied channel configurations suggest  
22 that large bubbles (with  $L_B/W < 1/2$ ), reach a final rise velocity  $U_B$ ,  
23 which is no more sensitive to further increase in the bubble size. In  
24 vertical channels, this final bubble velocity depends on the channel  
25 perimeter  $P$  and a universal velocity scaling based on the Froude num-  
26 ber  $Fr = U_B/\sqrt{gP}$  can be recommended. In inclined channels with thin  
27 slots, this scaling remains valid. But in this case only the axial compo-  
28 nent of gravity is considered  $Fr = U_B/\sqrt{g \sin \alpha P}$ . In inclined channels  
29 with large slots, where bubbles are more deformed and streamlining  
30 effect more pronounced, this scaling does not hold. To obtain univer-  
31 sal scaling in this case, it becomes necessary to also take into account  
32 the transverse component of gravity. The velocity of bubbles rising

33 in co-flowing liquid exhibits a linear dependency on the mean liquid  
34 velocity ( $U_{TB} = C_L \cdot U_{TB} + U_{TB,0}$ )<sup>2</sup> with the distribution coefficient  
35  $C_L$  ranging between 1 and 1.5, depending on the inclination angle and  
36 channel height.

#### *Acknowledgment*

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38 damentals under the Internal Project IGA No. 880513.

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# High-Temperature Desulfurization of a Producer Gas by La- and Ce-based Oxides

*Student: Ing. Jiří Brynda*

*Supervisor: Ing. Sjarhei Skoblja, Ph. D.*

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

1 The deep high-temperature desulfurization of a producer gas  
2 is a necessary step to efficient power production by solid oxide fuel  
3 cells. The sorbents currently used for such desulfurization are mostly  
4 based on ZnO and CuO, which deteriorate above 773 K<sup>1</sup>. Based on  
5 thermodynamic calculations<sup>2</sup>, we decided to test the possibility of us-  
6 ing sorbents containing La and Ce oxides. The prepared sorbents con-  
7 tained either La<sub>2</sub>O<sub>3</sub> or nonstoichiometric cerium oxide CeO<sub>x</sub> (x=1.5–2)  
8 on an alumina support. The sulphur capacity and desulfurization ef-  
9 ficiency of both sorbents were tested at 773 K in various gas mixtures  
10 containing reducing gases (e.g. H<sub>2</sub>, CO) and H<sub>2</sub>S as the model sul-  
11 fur compound. These preliminary laboratory tests implied that each  
12 sorbent was capable of high desulfurization efficiency. Next, exper-  
13 iments performed in artificial producer gases (CO, H<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O,  
14 N<sub>2</sub> and H<sub>2</sub>S) of varying compositions showed the negative influence  
15 of increasing amounts of CO<sub>2</sub> and H<sub>2</sub>O, as well as the importance  
16 of pre-reduction in the case of the cerium-based sorbent. Thus, the  
17 application of La- and Ce-based sorbents for deep high-temperature  
18 desulfurization seems to be feasible for producer gases with low con-  
19 centrations of CO<sub>2</sub> and H<sub>2</sub>O.

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# Preliminary Evaluation of Sewage Sludge Biochar Composition and Mass and Energy Balance of the Sludge Pyrolysis

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*Supervising Expert: Sjarhei Skoblia, Ph. D.*

1 Biochar is a solid material obtained from the thermochemical con-  
2 version of biomass in an oxygen-limited environment.<sup>1</sup> Biochar can be  
3 used, for example, as soil amender/conditioner, or active carbon ad-  
4 sorbent. Its production sequesters carbon into a stable form, there-  
5 fore it mitigates greenhouse gas emissions. Based on the feedstock  
6 biomass material and biochar properties, biochar for soil application  
7 may be classified as fertilizer, liming material, soil improver, growing  
8 medium, agronomic additive or plant biostimulant.<sup>2</sup>

9 With regard to a relatively high content of nutrients (N, P, K,  
10 Ca, Mg), sewage sludge is a potentially suitable material for biochar  
11 production by pyrolysis and the produced biochar may be consid-  
12 ered as a fertilizer. Due to thermal treatment, sludge biochar con-  
13 tains significantly low-to-no amounts of pathogens and organic (mi-  
14 cro)pollutants, which are recently of concern in terms of the agri-  
15 cultural use of sewage sludge. In addition, pyrolysis, together with  
16 combustion and gasification, is a highly convenient treatment route  
17 for sewage sludge since it leads to a remarkable volume reduction of  
18 the waste.<sup>3</sup>

19 The pyrolysis experiments were performed in a quartz reactor,  
20 nitrogen being supplied to attain oxygen-free atmosphere. Sewage  
21 sludge from Brno-Modřice municipal wastewater treatment plant was  
22 pyrolyzed at temperatures 400, 500, 600, 700 and 800 °C. Biochar (solid  
23 residue), liquid (tar) fraction, and pyrolysis gas were weighed and  
24 analyzed to obtain the mass and energy balance and to describe the  
25 basic properties of biochar. With an increase in pyrolysis tempera-  
26 ture, biochar yield decreased from 61% (400 °C) to 46% (800 °C), which  
27 is attributed to more organic material decomposition at higher tem-  
28 peratures. Consequently, the gas yield increased. Soil nutrients (P,  
29 K, Ca, Mg) that are mostly bound to thermally more stable mineral  
30 fraction were concentrated in the biochar.

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# Dry Flue Gas Treatment: Preparation for Experimental Campaign and Preliminary Experiments

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

1 Flue gas treatment is a very important part of every Waste-to-Energy (WtE) plant. Currently, dry flue gas treatment methods are very  
2 popular because they are not burdened by wastewater production.  
3 Frequently, there are attempts to simplify the process, lower the capital costs, operating costs, and the production of residues classified  
4 as hazardous waste.  
5

6 Simultaneous removal of multiple pollutants has a big potential for  
7 the simplification of dry flue gas treatment. However, individual processes have different optimal conditions. Therefore, the knowledge of  
8 the influences of various conditions on individual processes is crucial.  
9 To be able to test these influences, a unit has been built.  
10

11 Before we could start the experiments, it was necessary to test all  
12 sections of the unit. We have tested the stability of the flue gas composition, pressure and flow rate measurements, filter cake formation,  
13 cleaning of filters, and regulation of temperature and pressure at various places of the unit.  
14

15 We have also successfully tested the addition of sulfur (dissolved  
16 in toluene) to wooden pellets that we use as fuel for flue gas production. Last three experiments showed very close conversion rates of  
17 sulfur from fuel to flue gas. We are, therefore, able to set the concentration of SO<sub>2</sub> in produced flue gas. Also, the influence of the pollutant  
18 addition on the mechanical durability of used pellets was measured.  
19

20 Dosing of sorbent particles (milled to approx. 10 μm) into the flue  
21 gas turned out to be difficult. We have made a dosing system out of  
22 an icing mesh sifter, stepper motor, valve, and a funnel. The character of dosed particles makes it difficult to set reliably a specific feeding  
23 rate. It is, however, possible to weigh the whole feeding system any-  
24 time during an experiment, which allows us to measure the real feeding  
25 rate and to test different feeding rates without having to stop the  
26 experiment.  
27  
28  
29  
30  
31

32 During recent experiments, all parts of the unit were running.  
33 However, the main objective of these experiments was to complete our  
34 methodology and to verify its suitability for following experiments.  
35 The main experimental campaign will follow in June and July.

# Use of Water-Modified Supercritical Carbon Dioxide for Direct Preparation of Crystalline Monolithic TiO<sub>2</sub> Aerogels

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1 TiO<sub>2</sub> forms three crystalline phases (anatase, brookite, rutile), of  
2 which anatase is the most investigated because of its high photocat-  
3 alytic activity. Due to its chemical stability, strong oxidation activity  
4 and non-toxicity, anatase is used especially for air- and water-purifica-  
5 tion.<sup>1</sup> Titania aerogels in the monolithic form have been extensively  
6 applied for the various applications such as solar energy conversion<sup>2</sup>  
7 and photocatalysis.<sup>3</sup> The use of TiO<sub>2</sub> for a given application depends  
8 not only on its phase composition, but also on specific surface area,  
9 crystallinity and crystallite-size. These properties can be significantly  
10 influenced by the preparation method used.

11 Crystalline and pure TiO<sub>2</sub> aerogels are commonly prepared by  
12 calcination accompanied by an uncontrollable porous structure de-  
13 struction, decrease of surface area, as well as porosity.<sup>4</sup> Also the pho-  
14 tocatalytic performance cannot be easily managed. Using supercriti-  
15 cal carbon dioxide (scCO<sub>2</sub>) seems to be a promising way to obtain  
16 crystalline and pure TiO<sub>2</sub> monoliths without any subsequent ther-  
17 mal treatment.<sup>5,6</sup> With this gentle method the structural, textural and  
18 physicochemical properties can be better controlled.

19 We studied a combination of supercritical CO<sub>2</sub> and water for the  
20 preparation of crystalline and pure nanostructured TiO<sub>2</sub> without any  
21 thermal processing. The effect of temperature (40–100 °C) and pres-  
22 sure (10–30 MPa) on the purity, structural and textural properties  
23 was investigated. The prepared aerogels were characterized with re-  
24 spect to the (micro)structural properties by Raman spectroscopy and  
25 X-ray diffraction. The textural properties such as specific surface area,  
26 content of mesoporous and volume of microporous were determined  
27 from nitrogen physisorption and skeletal density by helium pycnom-  
28 etry measurements.

29 The pressure of 10 MPa did not cause any crystallization. When the  
30 pressure increased, crystallization to anatase and brookite occurred.  
31 Increasing the temperature resulted into a decrease of specific surface

32 areas, change of the monoliths' colour from white to yellow, and into  
33 the more fragile blocks.

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