TBMCE 2021

Book of Abstracts

“Naložbo sofinancirata Republika Slovenija in Evropska unija iz Evropskega sklada za regionalni razvoj”
“This investment is co-financed by the Republic of Slovenia and the European Union Fund for Regional Development”

REPUBLIKA SLOVENIJA
MINISTRSTVO ZA GOSPODARSKI RAZVOJ IN TEHNOLOGIJO

REPUBLIC OF SLOVENIA
MINISTRY OF ECONOMIC DEVELOPMENT AND TECHNOLOGY

"Dogodek poteka pod pokroviteljstvom Ministrstva za gospodarski razvoj in tehnologijo"
"The event is under the patronage of Ministry of Economic Development and Technology"

SPONZORJI / SPONSORS

muflon

Saubermacher Slovenija

ŠTAJERSKA GOSPODARSKA ZBORNICA

SRIP KROŽNO GOSPODARSTVO

Univerza v Mariboru
Fakulteta za kemijo in kemijsko tehnologijo

KEMIJSKI INŠTITUT

REPUBLIKA SLOVENIJA
MINISTRSTVO ZA GOSPODARSKI RAZVOJ IN TEHNOLOGIJO

EVROPSKA UNIJA
EVROPSKI SKLAD ZA REGIONALNI RAZVOJ
NALOŽBA V VAŠO PRIHODNOST

Table of Contents

One-Pot Algae Conversion into Sustainable Biofuel by Catalytic Hydroprocessing

Dana Marinič [a], Brigita Hočevar [a], Miha Grilc [a*], Blaž Likozar [a]

[a] The National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, 1001 Ljubljana, Slovenia

*Corresponding author: Miha Grilc (miha.grilc@ki.si)

Introduction: Environmental problems among with the increasing energy demand, instable fuel prices and limited fossil fuel have led to the growing interest in renewable fuels. Microalgae have recently emerged as a suitable feedstock for biofuel production, mostly because of its high biomass productivity, photosynthetic efficiency and the high accumulation capacity of lipids. Furthermore, it does not require arable land of fresh water, hence it's not a threat to traditional agricultural goods. Low carbon footprint and GHG emissions make biofuel technology even more interesting [1, 2]. The advantage of having high tolerance to CO_2 makes microalgae a promising organism for CO_2 mitigation. The biofuel produced from microalgae is considered carbon neutral, as the CO_2 produced from the biomass combustion can be further used as a fuel for the organism's metabolic activities in the cultivation process [3]. One of the principal bio-fuel pathways used for the biofuel production is hydrothermal liquefaction (HTL). HTL is a thermochemical process, where the biomass is transformed directly into liquid biocrude while using high pressures and temperatures. Due to the high oxygen and nitrogen concentrations in bio-crude and consequently poor product quality, further catalytic hydrotreatment is required [4]. Additional treatment leads to the energy, time and cost prohibitive processes, which limits the options for general use. We carried out the one-pot algae conversion into biofuel by catalytic hydroprocessing.

Methods: The catalytic hydrotreatment of Chlorella microalgae was performed in a cylindrical stainless steel slurry reactor. The reactor was filled with 120 mL of reaction mixture that contained 5 wt% of algae, the rest being solvent. The catalyst $NiMo/Al_2O_3$ mass was set to 25 wt% with respect to the initial mass of microalgae. The system was pressurized with hydrogen to the desired pressure (50 - 20 bar) and heated-up to the desired temperature (300 - 350 °C). The reaction conditions were maintained constant for 4 hours. The reaction mixture was then filtered. The solid samples collected from the filtration were washed three times with dodecane and once with hexane, then analyzed by Fourier transform infrared (FTIR) spectroscopy. The liquid samples collected from the filtration were analyzed by Gas Chromatography − Mass spectroscopy (GC-MS) and by FTIR.

Results: GC-MS analysis revealed that produced bio-oils are a complex mixtures of partially or completely deoxygenated compounds. The most promising experiment using 25 wt% of catalyst at 350 °C of reaction temperature yielded 15 wt% of liquid alkanes with the high selectivity towards pentadecane, hexadecane, heptadecane and octadecane. The spectra confirmed low oxygen and nitrogen content, where the main oxygen compound was nonadecanol. Higher temperature resulted in higher yields. The higher the hydrogen pressure, the more hydrogenation reactions of alkenes occurred. In addition, stricter reaction conditions resulted in lower mass residue, suggesting that the liquefaction was more intense. Among the reduced, oxygenated and sulfided catalyst form, the latter was found to be the most promising. FTIR spectrum of liquid product match quite well with the spectrum of the dodecane, since the solvent represents a high proportion of the product. The major difference were two weak bands around 3700 cm^{-1} and 1070 cm^{-1} which are related to O─H stretching vibration.

Conclusions: Microalgae slurry was successfully processed in a cylindrical reactor at temperature of 300 – 350 °C, hydrogen pressure of 20 – 50 bar and residence times of 4 hours. The catalytic hydroprocessing led to the conversion of microalgae into a complex mixture of diesel like hydrocarbons (C14–C18).

Keywords: microalgae, hydrothreatment, one-pot reaction, carbon neutral biofuel.

References:

1. J. K. Bwapwaa, A. Anandrajb and C. Trois, Possibilities for conversion of microalgae oil into aviation fuel: A review, Renew. Sust. Energ. Rev., vol. 80, 1345-1354, Dec. 2017.
2. F. Delrue, Y. Li-Beisson, P.-A. Setier, C. Sahut, A. Roubaud, A.-K. Froment and G. Peltier, Comparison of various microalgae liquid biofuel production pathways based on energetic, economic and environmental criteria, Bioresour. Technol., vol. 136, pp. 205-212, May 2013.
3. D. Moreira and J. C.M. Pires, Atmospheric CO2 capture by algae: Negative carbon dioxide emission path, Bioresour. Technol., vol. 215, 371-379, Sept. 2016.
4. C. Yang, R. Li, C. Cui, S. Liu, Q. Qiu, Y. Ding, Y. Wu and B. Zhang, Catalytic hydroprocessing of microalgae-derived biofuels: a review, Green Chem., vol. 18, 3684–3699, May 2016.

Pyrolysis Process for Biochar Production to Introduce Circular Economy on Farm

Dušan Klinar [a], Nataša Belšak Šel [a*], Klavdija Rižnar [a]

[a] Scientific Research Centre Bistra Ptuj, Interdisciplinary Research and Development, Slovenski trg 6, 2250 Ptuj, Slovenia

[*]Corresponding author: Nataša Belšak Šel (natasa.belsak.sel@bistra.si)

Abstract: European Commission adopted a new Circular Economy Action Plan on March 2020. This plan is one of the main building blocks of the flagship European Green Deal. Within this action plan, there is a specific section dedicated to Food, Water and Nutrients to address the entire food value chain to ensure the sustainability of the sector - strengthening efforts to tackle climate change, protect the environment and preserve biodiversity.

Biomass plays a special role in the circular economy because it is fully recyclable and used as food, fuel and material. Biomass is a container term for raw materials of vegetable and animal origin. This includes crops from agriculture, water cultivation (such as algae) and forestry, as well as their residual flows in the chain of harvesting, consumption and final processing.

Biochar is the carbon rich product obtained when biomass is thermally decomposed (pyrolysed) in restricted air conditions at temperatures between 350 and 700 °C. Biochar made from woody biomass and field residues has several properties which make a compelling case for its broad use in agriculture. Application of biochar to soil as a technique to improve the quality of soil has emerged in recent years. It has the ability to aid in coping up with the greenhouse gases (GHG) and is helpful for carbon sequestration. Various evidences and studies showed that the utilization of biochar can be extremely useful for the improvement of soil organic carbon, capacity of water holding, stimulating soil microbes, increasing the microbial activity and biomass, decreasing in needs and leaching of fertilizers, availability and retention of nutrients, soil aeration, bettering the growth and yield of crop growth as well as reducing the fluxes of greenhouse gases through anthropogenic activity and increase in sequestering carbon.

Production of biochar from biomass results in several major products: heat, power and, under specific reactor-operating conditions, biochar. Other specifically designed processes could alternatively produce synthesis gas and liquid fuel intermediates as well as biochar. The heat can be used to drive electrical power generation, industrial thermal processes, and to heat schools, hospitals, green houses, and lumber kilns, etc., while the electrical power can be used in these same enterprises for cooling and to

power irrigation pumps. This makes biomass sourced energy production co-optimized with biochar a highly intriguing and desirable outcome.

Different scales of pyrolysis technologies are available in the market, ranging from improved cook-stoves to large industrial plants estimated to process 2000 oven dry tonnes of feedstock per year (odt/yr), 20,000 odt/yr and 100,000 odt/yr in small, medium, and large scales, respectively. The supply of pyrolysis devices on the market, which are suitable for use on small or medium-sized farms, is negligible. In addition, pyrolysis plants require the use of dry biomass, which means that an additional cost is represented by a biomass drying kiln. We have developed a pyrolysis device with a capacity of 20 kg of dry biomass per hour, which has an integrated dryer. The pyrolysis furnace was developed for use on farms, where farmers can produce biochar from their own waste biomass.

The potential benefits of using pyrolysis device for biochar production from biomass can be:
- Development of a biochar industry for agricultural and environmental uses.
- Ability to switch between biochar and bioenergy optimization modes in response to market forces.
- Improved crop productivity.
- Increased water and nutrient holding capacities of biochar-amended soils.
- Begin to reverse losses of carbon to the atmosphere.
- Store stable carbon in soils for centuries to millennia.

Pyrolysis devices has been built and tested to produce biochar on-site with farmers who act as producers and end-users. In doing so, this initiative has been demonstrated a methodology for Slovene agriculture to develop a carbon-neutral approach to the management of undesirable biomass while at the same time increasing farm productivity.

Keywords: pyrolysis process, biochar, biomass, circular economy, farm.

Improving Environmental Performance and Moving Towards a Circular Economy with EMAS

Klavdija Rižnar [a*], Dušan Klinar [a], Nataša Belšak Šel [a*]

[a] Scientific Research Centre Bistra Ptuj, Interdisciplinary Research and Development, Slovenski trg 6, 2250 Ptuj, Slovenia

[*] Corresponding author: Klavdija Rižnar (klavdija.riznar@bistra.si)

Abstract: In many European countries, regulatory and bureaucratic burdens are some of the main obstacles to the companies competitiveness and internationalization. For this reason, the European Commission undertook, since 2005, a long-lasting regulatory process aimed at improving and simplifying the existing legislation, pivoted on the wish to create tangible benefits for citizens, businesses and public administrations. Businesses consider Environmental legislation one of the major sources of administrative and bureaucratic restrictions and "bundles". In many countries (such as Austria, Germany and Italy), simplification has been explicitly and intentionally associated to the companies ability to demonstrate their environmental performances improvement. According to this approach, a significant reduction of bureaucracy, and its related cost, is carried out foremost to the benefit of those businesses, who can prove their commitment toward environmental sustainability, for example through voluntarily EMAS registration or other kinds of environmental certification. These States have, in fact, showed significant results in the spread of environmental management systems, proving that the environmental simplification (or regulatory relief) can play a significant role in the dissemination of tools for environmental sustainability. Thanks to the adoption of EMAS, organizations of any kind and size, besides reducing their raw materials consumption and their impact on the environment, can implement managerial and organizational processes that increase know-how, improve efficiency and, in many cases, develop competitive capabilities. The LIFE BRAVER project is part of this approach, which, originating in Europe, has established itself in many Member States. The main target of the project is to improve environmental legislation through a more effective regulation and the reduction or the streamlining of costs and administrative burdens for EMAS registered organizations. The LIFE BRAVER project has actually encouraged and supported the full integration of EMAS (and other voluntary certification schemes) into the EU Member States environmental legislation, for the purpose to ease its implementation by all organizations. The significance of the LIFE BRAVER project objectives is confirmed by the fact that, so far, many companies took advantage of simplifications and existing incentives in support of EMAS.

Keywords: circular economy, regulatory relief, EMAS.

Novel Approach to Decolorization of Reactive Blue 4 in Wastewater using Functional Cellulosic Fabric in H_2O_2/UV/MnTACN Process

Lidija Tušek [a*], Katja Ribič [b], Lidija Fras Zemljič [b], Julija Volmajer Valh [b]

[a] Scientific Research Centre Bistra Ptuj, Research and Development, Slovenski trg 6, 2250 Ptuj, Slovenia

[b] University of Maribor, Faculty of Mechanical Engineering, Institute of Engineering Materials and Design, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Lidija Tušek (lidija.tusek@bistra.si)

Abstract: Textile wastewater containing reactive dyes pose a serious environmental threat disabling the photosynthesis process of aqueous organisms. Reactive Blue 4 (RB4) is also carcinogenic and toxic; therefore, it should be degraded in the wastewater. Advanced oxidation process (AOP) H_2O_2/UV has been used successfully to decolor and degrade Reactive Blue 4 in our previous work [1].

In this study we investigated the suitable catalyst carrier in the form of a functional textile. The cellulosic fabric was treated with the solution of MnTACN and added to the H_2O_2/UV batch reactor as an advanced catalyst system. In addition, pre-treatments of the cellulosic fabric with acid, which ensures the end-of-chain -COOH groups in the cellulose and treatment with UV/Ozone, which cleans the fibres and improves the accessibility to carboxylic groups were tested to determine their effect on the decolorization of RB4 in AOP.

The results showed that MnTACN applied onto the cellulosic fabric accelerates the decolorization process compared to non-catalytic H_2O_2/UV AOP. The RB4 solution is completely decolored in 20 minutes at room temperature in non-catalytic H_2O_2/UV AOP and in only 10 minutes if functional cellulosic fabric with applied MnTACN is added to the batch reactor. Surprisingly, the decolorization process is almost uninfluenced by the treatment of the fabric made prior to the MnTACN treatment.

The main advantage of this improved H_2O_2/UV/MnTACN decolorization process is that MnTACN in not another pollutant in the wastewater after the treatment but it remains on the textile. This procedure also opens the opportunities for continuous decolorization treatment of textile wastewater.

Keywords: functional textile, textile wastewater, Reactive Blue 4, manganese catalyst complex MnTACN, advanced oxidation processes H_2O_2/UV.

References:

1. Škodič L, Vajnhandl S, Volmajer Valh J, Željko T, Vončina B, Lobnik A. Comparative Study of Reactive Dyes Oxidation by H_2O_2/UV, H_2O_2/UV/Fe 2+ and H_2O_2/UVV/Fe° Processes. Ozone Sci Eng. 2017;39(1):14–23.

Hydrothermal Decomposition of Multilayer Packaging

Mojca Škerget [a*], Mihael Irgolič [a], Maja Čolnik [a], Željko Knez [a,b]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia

[b] University of Maribor, Faculty of Medicine, Taborska ul. 8, 2000 Maribor, Slovenia

[*]Corresponding author: Mojca Škerget (mojca.skerget@um.si)

Abstract: In 2019 more than one million tons of municipal waste were generated in Slovenia, of which approximately 60 % of this waste was recycled [1]. The largest share of municipal waste is waste packaging of various products (especially food). The amount of packaging waste increases by about 10 % every year, of which more than 90 % is plastic packaging (PP, PE, PET). Depending on the origin, packaging is usually divided into six groups: plastic, metal, paper, glass, wood and multilayer packaging [2]. Multilayer packaging consists of two or more different materials that are not easy to mechanically separate (paper/cardboard, metal foils, tablet blisters, plastic foils). The main advantages of multilayer packaging are its excellent properties (higher strength, lower rigidity, resistance to water vapor and light, lower permeability to gases, …) with lower consumption of materials and with thinner packaging. Tetra Pak is widely used worldwide as an aseptic packaging material. It consists up of three raw materials: duplex paper (75 %), low density polyethylene (LDPE) (20 %) and aluminum (5 %) and usually has been used for liquid food packages of fruit juices and milk [2]. A major problem of these multilayer materials is their recycling [3]. One of a promising chemical recycling method is a hydrothermal process that includes the use of sub- and supercritical water (SubCW and SCW), which is an effective reaction media for the rapid and selective conversion of different waste materials into a wide range of useful products (chemicals, value-added products, alternative energy and fuels). Due to its specific physical and chemical properties, SubCW and SCW has become an alternative to conventional waste management technologies [4]. In this study, the hydrothermal degradation of Tetra Pak waste in SubCW and SCW was investigated. The experiments were carried out in a high pressure and high temperature batch reactor at different temperatures (250-450 °C), reaction times (15-60 min) and by different hydrothermal degradation modes (one- and two step). By hydrothermal degradation of Tetra Pak wastes the gas, bio-oil/oil, solid and aqueous phase products were produced. At the temperature of 250 °C and short reaction time (30 min), the reaction mixture still contained undegraded plastic flakes and some paper mush. By further extension of the reaction time to 60 min the highest yield of the aqueous phase (20 %) products was obtained. The highest yield of bio-oil obtained in the first stage performed at lower temperatures (35 %) was obtained at 300 °C and 60 min. In the second stage performed at higher temperatures, the degradation of

LDPE was significant. The results showed that after one- and two-step degradation of Tetra Pak wastes, the oil yields increase with prolonging time and increasing temperature, while the yields of aqueous phase decrease. The maximum oil yield was obtained after two-step degradation reaction (300 °C, 60 min and 450, 15 min) and it was 66 %. Chemical compositions of bio-oil/oil, the characterization of solid phase (aluminum) and the degraded products in aqueous phase were also determined. The results of this study show that SubCW and SCW present an attractive way for chemical recycling of multilayer packaging waste to useful products.

Keywords: waste, sub- and supercritical water, chemical recycling, multilayer packaging.

References:

1. SURS - Statistični urad Republike Slovenije, https://www.stat.si/StatWeb/ (accessed feb. 16, 2021).
2. A. Korkmaz, J. Yanik, M. Brebu, C. Vasile, Pyrolysis of the tetra pak, Waste Management, 2009.
3. D. W. Dixon-Hardy, B. A. Curran, Types of packaging waste from secondary sources (supermarkets) – The situation in the UK, Waste Management, 2009.
4. Z. Hao, Y. Tao, Q. Chengtun, L. Wanjing, W. Yanfei, Basic Characteristics and Application Progress of Supercritical Water. IOP Conference Series: Earth and Environmental Science, 2020.

Making It Simpler but Better – Sustainable Valorization of Crustaceans Shell Wastes

Filipa A. Vicente [a*], Sónia P. M. Ventura [b], Helena Passos [b], João A. P. Coutinho [b], Ana C. R. V. Dias [c], Mario A. Torres Acosta [d], Uroš Novak [a], Blaž Likozar [a]

[a] National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, 1000 Ljubljana, Slovenia

[b] University of Aveiro, CICECO, Department of Chemistry, 3810 -193 Aveiro, Portugal

[c] University of Aveiro, CESAM - Centre for Environmental and Marine Studies, Department of Environment and Planning, 3810-193 Aveiro, Portugal

[d] University College London, The Advanced Centre for Biochemical Engineering, Department of Biochemical Engineering, London WC1E 6BT, United Kingdom

[*]Corresponding author: Filipa A. Vicente (filipa.andre.vicente@ki.si)

Abstract: The climate change we are currently facing is the reality of the choices we made, and the ones we are about to make will be the turning point for Humanity. The present linear economic model of mine-process-consume-dispose is no longer viable hence triggering scientists to turn to a more Circular economy and seeking the valorization of biomass and residues, searching to improve the Biorefinery concept. Worldwide, there is the production of ~200 billion tons of agricultural and food waste per year that can (and should!) be transformed into new feedstocks. However, converting bio-waste into new feedstocks is still not enough as the current downstream processes are not yet fully sustainable, representing up to 80% of the total manufacturing costs. In this sense, it is imperative to develop more sustainable downstream processes which will enable to build resilient infrastructures, promote inclusive and sustainable industrialization and foster innovation (sustainable development goal #9), following the fundaments of reduce-reuse-recycle. In this work, crustaceans shell wastes were investigated as a renewable feedstock of different products with high commercial interest, such as astaxanthin. Astaxanthin is a natural colorant with well-recognized health benefits. Therefore, this work aimed at the development of an integrated and more sustainable platform for the extraction, isolation and purification of the main shell constituents, namely astaxanthin, minerals, proteins and chitin, while always presenting simple and cheap polishing approaches. At the end, economic and environmental analyses were performed to access the sustainability of the developed integrated platform.

Keywords: circular economy, shell biorefinery, astaxanthin, chitin, sustainable process.

Acknowledgment: This work was funded by the Slovenian Research Agency under research core funding P2-0152; and within the scope of CICECO-Aveiro Institute of Materials projects: UIDB/50011/2020 & UIDP/50011/2020, and CESAM, UIDB/50017/2020 & UIDP/50017/2020, financed by national funds through the Portuguese Foundation for Science and Technology (FCT)/MCTES. A. Dias acknowledges FCT for her contract CEECIND/02174/2017. H. Passos acknowledges FCT under the Scientific Employment Stimulus-Individual Call-CEECIND/00831/2017.

Incorporation of Whey in Cosmetic Products

Maja Bjelošević [a], Blaž Grilc [a], Mirjana Gašperlin [a*]

[a] UL, Faculty of Pharmacy, Pharmaceutical Technology, Aškerčeva 7, 1000 Ljubljana, Slovenia

[*] Corresponding author: Mirjana Gašperlin (mirjana.gasperlin@ffa.uni-lj.si)

Introduction: Whey is a co-product in milk production, and as such represents a high environmental burden. Cosmetology and cosmetic products are one of the fastest-growing scientific areas, which is still rapidly growing with new ranges of cosmetics and increasingly focused towards individual needs and preferences [1, 2]. The aim of the present research work was to develop cosmetic products with whey to ensure zero waste from the processing of milk.

Methods: Three different whey fractions, acid whey, permeate, and flow-through whey in liquid and dried form were incorporated in the composition of shampoo. Shampoo: First, 30 % solution of sodium lauryl sulfate was prepared. In addition, part B was weighed and heated in a water bath at 60 °C. Part A and B were combined and stirred until cooled. At the end, whey was added and pH was adjusted to 4.5-5.5. As a part of stability test, pH (Mettler Toledo GmbH, Switzerland), viscosity (Anton Paar Austria GmbH) and organoleptic evaluation were performed after exposure to 25 and 40 ºC. 2.)
Cleansing gel: First, part A1 was weighed and gradually added into part A2 to provide gelation of xanthan gum. In addition, part B was prepared and part A was slowly added. At the end, preservative and whey were added. As a part of stability test, pH, viscosity and organoleptic evaluation were performed after cyclic exposure to 5, 25 and 40 ºC.

Results: The results show that addition of all three whey fractions leads to production of shampoo and gel in a concentration dependent manner. While for liquid whey the highest amount is up to 20 % (w/w), the optimal concentration for dried whey is 2 % (w/w). During stability study, the pH of shampoos with dried whey stored at 40 °C increased noticeably, while there were no significant changes in other formulations. It was also observed that addition of whey resulted in higher pH values comparing to shampoo without whey. Viscosity was not altered. Since pH did not drastically change after 10 cycles, color and odor of gels were different comparing to gel without whey. According to results, we can conclude that by incorporating whey, the stable cosmetic products with added value can be formed.

Keywords: zero waste, whey, gel, shampoo, cosmetology.

References:

1. G. Secchi, Role of protein in cosmetics, Clinical Dermatology, Jul-Aug, 2008.
2. M. Bjelošević, M. Gašperlin, M. Gosenca Matjaž, Peptidi v kozmetiki-smotrnost njihove uporabe?, Farmacevtski vestnik, 2019.

Biobased Diols from (Hemi)Cellulose and Lignin

Miha Grilc [a*], Brett Pomeroy [a], Rok Šivec [a], Ana Bjelić [a], Blaž Likozar [a]

[a] National Institute of Chemistry, Department of catalysis and chemical reaction engineering, Hajdrihova 19, 1000 Ljubljana, Slovenia

[*]Corresponding author: Miha Grilc (miha.grilc@ki.si)

Introduction: Alcohols containing two hydroxyl groups (diols) are important value-added chemicals in the chemical industry, especially for the production of polyesters, polyurethanes, and alkyd resins. Hitherto diols were solely produced from crude oil (e.g. selective oxidation of unsaturated cyclic or liner hydrocarbons) or natural gas (aldol condensation with formaldehyde), therefore the carbon footprint of subsequent polymer products is substantial and not in accordance with the scopes of the circular economy. At the Department of Catalysis and Chemical Engineering, National Institute of Chemistry, Slovenia, we have developed the technology of producing diols from the building blocks of all three main lignocellulosic biopolymers; i.e. cellulose, hemicellulose and lignin.

Methods and Results: In the first step, the lignocellulosic biomass must be split into its main biopolymers by a suitable fractionation process. There are several fractionation technologies available (e.g. Kraft, Organosolv, Lignosulfonate), each featuring particular pros and cons in terms of product quality and purity, technical maturity, economic feasibility etc. Recently, some promising fractionation technologies emerged for example the one developed in our group by using non-volatile solvents and reactants (ionic liquids or deep eutectic solvents) [1].

After the biopolymers are isolated and/or solubilized they are further depolymerized by hydrolysis (hemicellulose and cellulose) or hydrotreatment (lignin)yielding their monomeric units. Hexoses (pentoses) are the monomeric units of (hemi)cellulose and are readily further converted to HMF-hydroxymethylfurfural (furfural in case of hexoses) in acidified aqueous media. In the ongoing H2020 project BIOSPRINT the production of HMF is being optimized by using a heterogeneous catalyst as an alternative to the use of mineral acids which are difficult to reuse. We have demonstrated that by catalyst engineering and proper selection of process conditions, we can selectively hydrogenate HMF into either unsaturated furanic-diols or tetrahydrofuran-diols using Ni-based catalysts on C or Al_2O_3 support. Stereoselectivity can also be tuned to form tetrahydrofuran-diols in the predominantly cis or trans form, in general above 96 % selectivity can be reached in the formation of furanic diols and 88 % selectivity of tetrahydrofuran-diols (cis and trans mixture), and 72.5 % selectivity of trans-tetrahydrofuran-2,5-diol [2]. The technology has also been patented (LU102760).

Hemicellulose-derived furfural and lignin-derived guaiacyl monomers were also demonstrated to be converted into aliphatic and aromatic diols, respectively [3-5]. So far the selectivities up to 50 % were reached by the catalytic process. On the other hand, a synthetic route (non-catalytic where inorganic reducing agents are consumed during the reaction) to demethylate lignin's guaciacyl monomers is highly selective. Currently, the latter results are confidential, since the process is being developed in collaboration with an industrial partner.

Conclusion: At the conference, the production of valuable bio-based diols either on a linear, aromatic (benzene or furanic ring), or polycyclic backbone is to be presented from various sources. Currently, the developed technologies presented are at various but generally low (<4) technology readiness level (TRL) and are to be developed further.

Keywords: biomass, biorefineries, polymer industry, diols.

Acknowledgments: This research was funded by the Slovenian Research Agency (ARRS) through Programme P2–0152, the research project J2-2492 and postdoctoral project Z2-9200.

References:

1. KISHORE, M. Jhansi L., NOVAK, Uroš, GRILC, Miha, LIKOZAR, Blaž. Natural deep eutectic solvents (DES) for fractionation of waste lignocellulosic biomass and its cascade conversion to value-added bio-based chemicals. Biomass & bioenergy. 2019, vol. 120, p. 417-425.
2. POMEROY, Brett, GRILC, Miha, GYERGYEK, Sašo, LIKOZAR, Blaž. Catalyst structure-based hydroxymethylfurfural (HMF) hydrogenation mechanisms, activity and selectivity over Ni. Chemical engineering journal. 2021, vol. 412, p. 127553-1-127553-18.
3. ŠIVEC, Rok, LIKOZAR, Blaž, GRILC, Miha. Surface kinetics and transport phenomena modelling for furfural hydrotreatment over Pd/C in isopropanol and tetrahydrofuran. Applied Surface Science. 2021, vol. 541, p. 148485-1-148485-15.
4. BJELIĆ, Ana, GRILC, Miha, LIKOZAR, Blaž. Bifunctional metallic-acidic mechanisms of hydrodeoxygenation of eugenol as lignin model compound over supported Cu, Ni, Pd, Pt, Rh and Ru catalyst materials. Chemical engineering journal. 15 Aug. 2020, vol. 394, str. 124914-1-124914-14.
5. BJELIĆ, Ana, LIKOZAR, Blaž, GRILC, Miha. Scaling of lignin monomer hydrogenation, hydrodeoxygenation and hydrocracking reaction micro-kinetics over solid metal/acid catalysts to aromatic oligomers. Chemical engineering journal. 1 Nov. 2020, vol. 399, str. 125712-1-125712-19.

Research of the Precipitation Mechanism of Fluorides from the Extract after Leaching of the Spent Pot Linings from Alumina Smelting Process

Erik Mihelič [a*], Dušan Klinar [b], Nataša Belšak Šel [b], Klavdija Rižnar [b]

[a] Faculty of Chemistry and Chemical Engineering, University of Maribor, Smetanova 17, 2000 Maribor, Slovenia

[b] Scientific Research Centre Bistra Ptuj, Research and Development, Slovenski trg 6, 2250 Ptuj, Slovenia

[*]Corresponding author: Erik Mihelič (erik.mihelic@student.um.si)

Abstract: The solution of NaF, aluminate - $Al(OH)_4^-$ and the remaining NaOH are collected in the extract after leaching the spent pot linings (SPL) from the electrolysis of the alumina where the primary aluminum is obtained. For the purpose of recycling the solution, fluoride must be removed from the solution into a useful compound such as CaF_2 [1]. In this work, we studied three precipitation methods. One of the methods is precipitation with calcium ions, which are introduced with a solution of calcium hydroxide. We are dealing with two different precipitates, namely $Ca(OH)_2$ and CaF_2. The solubility product of the second ($K_{sp} = 3.9 * 10^{-9}$) is significantly lower than the first ($K_{sp} = 5.5 * 10^{-6}$) [1], which should allow quantitative precipitation of CaF_2. Due to the influence of the common ion - OH^-, complex precipitation conditions occur on the surface of hydroxide particles since there are practically no Ca^{2+} ions in the solution. In order to investigate the influence of hydroxide preparation on precipitation, they were prepared by various methods. Fine lime particles were prepared from $CaCl_2$ and NaOH or precipitation was performed directly by adding a $CaCl_2$ solution to the extract [2]. In the second part of the research, we focused on the development of a method that would most easily determine the equivalent precipitation point of fluoride ions. It was found that direct measurement of the equivalent point by measuring pH or conductivity was not possible. The study found a significant difference in the turbidity of each precipitation, which allows determining the equivalent precipitation point. It turns out that measuring the turbidity of precipitation is a much more useful method than measuring the concentration of fluoride ions with an ion-selective electrode (ISE). The solution is very alkaline, and the ISE for fluorine requires a pH measuring range between 5 and 8, which does not allow direct measurement [3]. We also found that all fluorine does not precipitate quantitatively, as this prevents it from an ionic balance in solution. By analyzing the turbidity, we approached the measurement of the equivalent point,

where we then confirmed the final result by measuring the fluorine using ISE. We also calculated the relative efficiency of different methods of hydroxide formation per degree of fluoride.

Keywords: precipitation, calcium fluoride, equivalent point, turbidity, calcium hydroxide.

References:

1. Mihelič,E. , Razvoj metode za določanje ekvivalentne točke pri obarjanju fluoridov iz ekstrakta po obdelavi izrabljenih katodnih ostankov elektrolize aluminija. Fakulteta za kemijo in kemijsko tehnologijo Maribor, Diplomsko delo, 2020.
2. Tropenauer, B., Klinar, D., Samec, N., Golob, J., Kortnik J., Sustainable waste treatment procedure for the Spent Potlining (SPL) from aluminium production, Materiali in tehnologije, Vol. 53, 277-284, 2019.
3. Tropenauer, B., Klinar, D., Golob, J., Improved understanding of Sodium hydroxide concentration role and kinetic model of cryolite reactive extraction in cathode Spent Pot Linings. Polish J. Chem. Technol, 2021.

Encapsulation of Lactoferrin Isolated from Waste Whey into Hydrogel Beads

Blaž Grilc [a], Maja Bjelošević [a], Mirjana Gašperlin [a*]

[a] UL, Faculty of Pharmacy, Pharmaceutical Technology, Aškerčeva 7, 1000 Ljubljana, Slovenia

[*]Corresponding author: Mirjana Gašperlin (mirjana.gasperlin@ffa.uni-lj.si)

Introduction: Whey, a by-product of the dairy industry, is considered a waste material and represents a burden on the environment. It contains a low proportion of various proteins, but due to the large amounts of waste whey, their absolute mass is not negligible. Various scientific fields are focused on exploiting the potential of whey. Lactoferrin (Lf) is a whey protein that binds iron and has antimicrobial, immunomodulatory and antioxidant effects, thus expressing a number of beneficial effects on human health [1]. The aim of the presented study was to develop and optimize the composition of microcapsules containing Lf based on sodium alginate. Furthermore, determination of the appropriate excipients, encapsulation procedure and drying conditions.

Methods: Aqueous solutions with different ratios of sodium alginate and Lf were encapsulated using an Inotech IE-50 R. As a crosslinking solution 0.5 M CaCl2 was used. The wet hydrogel beads were drained and transferred to a fluid bed dryer. Particle size distribution of dried microspheres was measured by image analysis and Lf content was determined by reverse phase HPLC chromatography. The morphology of the microspheres was assessed with an optical microscope. Excipients for shell porosity reduction were added to the Lf dispersion in proportions of 1-10%. The agglomeration ratio of the dried microspheres was evaluated.

Results: The obtained results showed that when the ratio of Lf to sodium alginate in the initial dispersion increased (i.e., from 1: 1 to 2: 1), the size of the microcapsules increased, however despite the higher proportion of Lf (4: 1), the growth rate of the microcapsules decreases. Due to the porosity of the bead shell, Lf leaked from the core to the crosslinking solution. By testing various excipients, Lf loading in microspheres was increased by three folds. The proportion of agglomerated microspheres was an important parameter in the manufacturing process. With the addition of surfactants, we managed to reduce the agglomeration to less than 5 %.

Conclusion: The results show that by incorporating Lf into a sodium alginate dispersion microcapsule, it can be formulated in a final dosage form for oral use. However, Lf leakage should be further investigated with appropriate formulation composition and inclusion of additional excipients.

Keywords: whey, lactoferrin, microcapsules, sodium alginate, hydrogel beads.

References:

1. Blanca F. Iglesias-Figueroa et al., Int. Dairy J. 89, 37-41, 2019.

Prolonged and Effective Active Properties of Chitosan-Based Biofoils Rich with Japanese Knotweed Extract

Uroš Novak [a*], Katerina Naumoska [b], Urška Jug [b], Ana Oberlintner [a], Blaž Likozar [a]

[a] National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, 1000 Ljubljana, Slovenia

[b] National Institute of Chemistry, Laboratory of Food Chemistry, Department of Analytical Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

[*]Corresponding author: Uroš Novak (uros.novak@ki.si)

Abstract: Japanese knotweed is an alien plant species in Europe and North America, which, due to its fast expansion, poses global ecological damage, leading to displacing autochthonous biodiversity. Moreover, it is causing huge economic harm (e.g. damage to infrastructure). There is an abundant biomass, which consequently produces an excessive amount of biowaste. Eradication techniques are economically and/or environmentally unsustainable. On the other hand, the plant is rich in various secondary metabolites with health-beneficial effects [1,2]. We recently showed that the plant's bark rhizome extract has potent antioxidant activity, which was equivalent to that of vitamin C. Moreover, the antioxidant activity of the plant extract was stable for at least 14 days, which was not the case for vitamin C. Therefore, chitosan biodegradable films enriched with this extract were developed and fully characterized.

Physico-chemical, antimicrobial properties of the foils, as well as the antioxidant effects of the foils coming into contact with food simulants (selected according to EU legislation) and the migration of the extract's bioactive compound/s into the food simulants were tested and will be discussed. The foils are expected to completely biodegrade in the soil environment within 10-14 days [3]. The proposed foils can greatly contribute to zero-waste communities, thus reduce the environmental pollution caused by conventional plastics and further reduce the GHG emissions by using biowaste.

Keywords: bioplastic, extractives, bioactive compounds, active packaging.

References:

1. U. Jug, K. Naumoska, I. Vovk, (-)-Epicatechin-an important contributor to the antioxidant activity of Japanese knotweed rhizome bark extract as determined by antioxidant activity-guided fractionation. Antioxidants, 10, 1-22, 2021.
2. U. Novak, M. Bajić, K. Kõrge, A. Oberlintner, J. Murn, K. Lokar, K.V. Triler, B. Likozar, From waste/residual marine biomass to active biopolymer-based packaging film materials for food industry applications: a review, Physical sciences reviews, 5, 1-24, 2020.

3. K. Kõrge, M. Bajić, B. Likozar, U. Novak, Active chitosan-chestnut extract films used for packaging and storage of fresh pasta, International journal of food science & technology, 55, 3043-3052, 2020.

Adipic Acid from Catalytic Dehydroxylation of Biomass-Derived Mucic Acid

Florian M. Harth [a*], Brigita Hočevar [a], Blaž Likozar [a], Miha Grilc [a]

[a] National Institute of Chemistry, Departmen of Catalysis and Reaction Engineering, Hajdrihova 19, 1001 Ljubljana, Slovenia

[*]Corresponding author: Florian M. Harth (florian.harth@ki.si)

Introduction: Adipic acid is a dicarboxylic acid and one of the most important polymer precursors, in particular for the polyamide industry. A newly developed strategy to produce adipic acid from renewable resources is presented here. Lignocellulose-derived hexoses can be oxidatively converted into aldaric acids (e.g. mucic acid). In the key reaction step, mucic acid then undergoes catalytic dehydroxylation into adipic acid. While Re-based homogeneous catalysts have successfully been used for this reaction, we have developed a heterogeneously catalyzed process using supported Re catalysts. The dehydroxylation gives unsaturated products from which saturated adipic acid can be obtained by subsequent hydrogenation. This combined process was systematically studied using (combinations of) commercially available catalysts and by tuning the reaction conditions.

Methods: Dehydroxylation of adipic acid was performed as batch experiments using a high-pressure autoclave reactor system (Amar Equipment Pvt. Ltd., India). The reactor was loaded with mucic acid, methanol and the catalyst(s), pressurized with nitrogen or hydrogen, heated up to the desired reaction temperature and kept for typically 72 hours. The final reaction mixture as well as intermediate samples were analyzed by GC-MS. On the one hand, different commercially available catalysts were tested. While there was always a solid Re catalyst present (typically Re/C), in some experiments Pd/C was added as a co-catalyst. On the other hand, the reaction conditions were varied, namely the reaction temperature in the range of 120-175 °C and the composition of the gas phase (nitrogen or hydrogen). Typically, the catalysts were reduced ex situ under hydrogen atmosphere at 400 °C prior to the catalytic experiments.

Results: Supported Re catalysts were proven to be highly suitable for the catalytic dehydroxylation of mucic acid. So far, the best results were obtained over Re/C at 120 °C in methanol under nitrogen atmosphere. Up to 93 % of completely dehydroxylated products were obtained. Of particular importance is the role of methanol in this process. It is not only used as the solvent but also serves as the reducing agent in the Re-catalyzed dehydroxylation reaction. Furthermore, it protects the carboxylic groups of the reactant by forming the respective esters.

At low reaction temperature (120 °C) the process is very selective for the fully dehydroxylated product (> 70 % yield), which contains two double bonds. At higher temperatures, however, additional hydrogenation is increasingly enhanced and both partially and fully hydrogenated products are obtained. Hydrogenation can be further promoted by applying a reducing (hydrogen) atmosphere and by adding suitable co-catalysts, such as Pd/C. With these modifications, up to 61 % of adipic acid (in the form of its dimethyl ester) could be obtained.

Recycling experiments revealed that the Re/C catalyst suffered from loss of activity due to Re leaching. By reducing the recovered catalyst before the reuse experiment, this effect could be significantly mitigated and the activity was retained for the first recycling experiment.

Conclusions: The use of solid Re catalysts for the selective catalytic dehydroxylation of mucic acid to adipic acid was investigated. It was shown that the catalysts are reusable and allow for almost quantitative and complete dehydroxylation. Under optimized conditions, 93 % yield of such compounds was obtained. Therefore, the heterogeneously catalyzed dehydroxylation of biomass-derived mucic acid is a promising alternative route towards the renewable production of adipic acid.

Keywords: heterogeneous catalysis, biomass, adipic acid, dehydroxylation.

Acknowledgements: This work was funded by the Slovenian Research Agency (ARRS) under core funding P2-0152 and postdoctoral project Z2-9200. Furthermore, funding from the Young Researchers Programme from ARRS is acknowledged.

References:

1. B. Hočevar, A. Prašnikar, M.Huš, M. Grilc, B. Likozar, B., Angew. Chem. Int. Ed. 60 (2021) 1244.
2. B. Hočevar, M. Grilc, B. Likozar, European Patent Application EP19192802.7 (2019).

Extraction of Fungitoxic Compounds from Low-Quality Wood Biomass

Viljem Vek [a], Ida Poljanšek [a], Angela Balzano [a], Miha Humar [a], Primož Oven [a*]

[a] University of Ljubljana, Biotechnical Faculty, Dpt. of Wood Science and Technology, Jamnikarjeva 101, 1000 Ljubljana, Slovenia

[*]Corresponding author: Primož Oven (primoz.oven@bf.uni-lj.si)

Abstract: The contribution summarizes the published results of research activities focused on the development of bio-based preservatives. Wood preservatives used in this study were founded on the use of plant polyphenols as fungitoxic compounds. Nonstructural components of wood, i.e. flavonoids, lignans and stilbenes, were extracted from wood of broken trees and from wood of less-utilized tree species. Thus, we included in the investigation wood biomass of the lowest quality, which has no relevant value on the market and is often used only as cellulose wood or energy source. Targeted phenolic compounds were extracted from pine knotwood (Pinus sylvestris and Pinus nigra) and black locust heartwood (Robinia pseudoacacia) by Soxhlet extraction with acetone. All the extracts were qualitatively and quantitatively evaluated by gravimetry, spectrophotometry and chromatography. Individual compounds were purified by flash chromatography, according to the method based on the use of more environmentally friendly non-chlorinated solvents. The extracts were colorimetrically analyzed for antioxidant properties by measuring free radical scavenging activity. Less durable beech and Scots pine sapwood was impregnated with the prepared bio-based preservative solutions in a vacuum-pressure chamber. After impregnation, the retention of the extracts in the wood matrix was examined gravimetrically, and with confocal laser microscopy and scanning electron microscopy. Antifungal properties of the extractives were determined with measuring in vitro inhibition of fungal growth and resistance of impregnated wood to fungal decay. Hydrophilic extracts of wood from injured pine trees and black locust inhibited the development of fungi and fungal decay of wood, and showed antioxidant activity. The results of the research show that low quality wood of broken trees and wood of less-utilized tree species represents a potential source for extracting natural bioactive compounds. Phenolic extracts of low-quality wood biomass show application potential, not only as fungistatic or antioxidant agents in wood preservatives, but also in the field of packaging and dietary supplements. In this context, we will also briefly present our applied project that was granted by Slovenian Research Agency.

Keywords: low-quality wood biomass, extraction, phenolic compounds, fungal inhibition, natural antioxidants.

Challenges and Applications of Microreactor Technology

Aleksandra Verdnik [a], Zdravko Kravanja [a], Zorka Novak Pintarič [a*]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Zorka Novak Pintarič (zorka.novak@um.si)

Abstract: In the last two decades, there has been an increasing trend towards the development and use of flow systems in microreactors. Their characteristics, such as rapid mixing, good temperature control, short residence times, and high surface-area-to-volume ratio, bring some advantages to chemical processing. Flow chemistry offers many improvements over batch processes, especially in terms of faster mass and heat transfer, lower energy consumption, higher process safety, access to a wide range of reaction conditions, higher yields, better selectivity, reduced use of toxic and hazardous chemicals, performance of heterogeneous catalyses and multistep reactions. In addition, flow chemistry and continuous processes can be a solution to make chemical syntheses greener and more sustainable [1].

The aim of this work is to evaluate the commercial potential of microreactors and their Technology Readiness Level (TRL) for industrial applications, especially in the field of green chemicals and technologies, sustainable development and circular economy. At the Faculty of Chemistry and Chemical Engineering in Maribor, the acquisition of microreactors is planned within the RIUM project. The main goal in the near future is to combine mathematical optimization of microprocess systems and practical implementation of various process configurations in microreactor equipment.

A review of the literature [2] has shown that applications of microreactors in chemical engineering are rapidly evolving. Microprocess systems are well established at the laboratory level, pilot applications are being developed, and there are still relatively few industrial applications. Most applications relate to the synthesis of organic compounds, fine chemicals and pharmaceuticals. Microreactors allow complex multiphase chemical reactions (gas, liquid, solid phase) to be easily carried out. Organic syntheses effective in microreactors are: Grignard reactions, hydrogenation, Diels-Alder reactions, chlorination, fluorination, oxygenation, and nitration reactions. The advantages of microsynthesis over batch reactors are considerable; for example, nitration reactions are often problematic in a batch reactor because they are extremely exothermic. In microreactors, the heat generated is efficiently dissipated due to the high heat transfer coefficient [3]. Another example is the synthesis of nanoparticles, which is relatively complex and expensive in conventional processes, while efficient synthesis of both inorganic and metal nanoparticles has been reported for flow systems. The use of microreactors has also been extended to biosynthesis and biochemical processes as well as polymerization reactions. In the field of green and

sustainable chemistry, the synthesis of biofuels, mainly biodiesel from vegetable oils, was carried out in microreactors [2, 3].

Microprocess systems can be an alternative to batch processes, especially in terms of higher selectivity and higher efficiencies with lower energy consumption. They allow the performance of different types of synthesis and make the processes safer and more efficient. In this paper, the main challenges in the development of industrial microprocess applications are presented, namely: achieving larger capacities [4], more efficient separation, regulation, analytics, automation and integration, scale-out, etc. There are also uncertainties in estimating costs and investments, lack of experience in operating in industry, the lifetime of microprocess equipment, the need to extend applications to other areas such as food, transportation, etc.

Keywords: microreactor, flow chemistry, microprocess engineering, applications, challenges.

Acknowledgements: The authors are grateful for financial support from the Slovenian Research Agency (program P2-0032 and project J7-1816) and the Republic of Slovenia, the Ministry of Education, Science and Sport and the European Union under the European Regional Development Fund (project RIUM, contract number C3330-20-952000).

References:

1. Haswell, S. and P. Watts, Green chemistry: Synthesis in micro reactors. Green Chemistry - GREEN CHEM, 2003. 5: p. 240-249.
2. Suryawanshi, P.L., Gumfekar, S.P., Bhanvase, B.A., Sonawane, S.H., Pimplapure, M.S., A review on microreactors: Reactor fabrication, design, and cutting-edge applications. Chemical Engineering Science, 2018. 189: p. 431-448.
3. Bojang, A.A. and H.-S. Wu, Design, fundamental principles of fabrication and applications of microreactors. Processes, 2020. 8(8): p. 891.
4. Hessel V., Creative Energy-Energy Transition, European Roadmap of Process Intensification, Technology Report, Technology: Micro-Channel Reactor. https://bit.ly/3rgRUoY, accessed 16. 07. 2021.

Techno-Economic Analysis of Chemical Recycling of Waste PET

Jan Drofenik [a], Aleksandra Verdnik [a], Nejc Poprijan [b], Zorka Novak Pintarič [a*]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Zorka Novak Pintarič (zorka.novak@um.si)

Abstract: Recycling of waste PET (polyethylene terephthalate) is very important as it saves 20 % - 30 % of non-renewable energy resources [1]. Recycling also reduces greenhouse gas emissions while significantly reducing the generation of plastic waste. The most common method for recycling PET is mechanical recycling. The problem that occurs with multiple mechanical recycling is that the quality of the plastic decreases with each subsequent cycle. PET can also be recycled by a chemical process to the base molecules terephthalic acid (TA) and ethylene glycol (EG). Today, TA is an important raw material in the market for the production of polyester fibers, bottles and PET films. The production volume of TA is increasing year by year. The classical TA production process is the so-called Amoco process, in which fossil-based p-xylene is oxidized with compressed air in acetic acid medium in the presence of a corrosive catalyst Co/Mn/Br [2].

In this study, the production of TA by the fossil-based process was compared with the production of TA from waste PET by chemical recycling process. The latter takes place in two stages. In the first stage, a reaction takes place between the waste PET and NaOH in a stainless steel batch reactor. The products of this reaction are EG and sodium terephthalate. In the second stage, a reaction takes place between sodium terephthalate and hydrochloric acid, producing TA and sodium chloride. Based on the literature, process flow sheets for both processes were developed [2-3]. Based on the data on the amount of waste PET in Slovenia, the annual production capacity of TA was estimated to be 2000 t/a. Using these data, a techno-economic analysis for the process of TA production by chemical recycling of waste PET was performed using the program Aspen Process Economic Analyzer. The costs of raw materials, utilities and depreciation of the process units were taken into account.

The cost of chemical recycling of waste PET was estimated and compared with the market price of TA obtained by the Amoco process. A preliminary techno-economic analysis has shown that the cost of chemical recycling is currently higher than the market price of TA, which is derived from fossil sources. This shows that considering economic factors alone often does not work in favor of the use of renewable resources.

In the future, it would be desirable to perform a computer simulation of the chemical recycling of PET in the Aspen Plus program, to perform a process heat integration, and to analyze the environmental impact of the waste-based process compared to the fossil-based process.

Keywords: chemical recycling, terephthalic acid (TA), amoco process, waste PET, techno-economic analysis.

References:

1. Shen, L., et al., Life cycle energy and GHG emissions of PET recycling: change-oriented effects. The International Journal of Life Cycle Assessment, 2011. 16(6): p. 522-536.
2. Cao, N., E. Chang, and M. Kaufman, New Terephthalic Acid Process. 2011.
3. Vakili, M. and M.H. Fard, Chemical recycling of poly ethylene terephthalate wastes. World Appl Sci J, 2010. 8(7): p. 839-46p.

Assessing the Impact of Organic Farming and Conservation Agriculture on the Environment and Food Self-Sufficiency

Jan Drofenik [a], Bojan Pahor [a], Zdravko Kravanja [a], Zorka Novak Pintarič [a*]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Zorka Novak Pintarič (zorka.novak@um.si)

Abstract: The food supply chain is a large and complex system that has a major impact on the environment and the population. It is regulated by national and European regulations. The most important of these is European Green Agreement, whose main goal is to achieve climate neutrality by 2050. An important part of European Green Agreement is the Farm-to-Fork Strategy, which sets the EU's targets for agriculture and food. Under this strategy, the EU aims to reduce the use of chemical and hazardous pesticides by 50 %, reduce nutrient losses (especially nitrogen and phosphorus) by 50 %, reduce the use of mineral fertilizers by 20 % and reduce the sale of antimicrobials in the EU by 50 % by 2030. This strategy also aims to allocate 25 % of agricultural land to organic farming by 2030 [1].

In this study, two alternative methods of agricultural production were considered: organic farming, characterized by the non-use of synthetic chemicals, and conservation agriculture, characterized by minimal or reduced tillage. The values of total level of self-sufficiency, level of self-sufficiency for human consumption, the amount of greenhouse gas (GHG) emissions, the amount of fertilizers used, and the amount of nitrogen input to the soil in different scenarios were compared. Based on these five parameters, the situation in Slovenian agriculture in 2030 was quantitatively assessed in the cases where: a) 25 % of agricultural land would be allocated to organic farming instead of the current 7.7 %, b) 15 % of agricultural land would be allocated to organic farming and 10 % to conservation agriculture. In both cases, consumption of red meat and meat products was reduced and some vegetable production was shifted to greenhouses. Due to the reduced consumption of red meat and meat products, the production of beef and meat products from beef would decrease by 2030, while the production of pork and meat products from pork would increase, as the current self-sufficiency level of meat and pork products is low. As a result of these changes, the demand for animal feed has changed, so the surplus land that was previously dedicated to animal feed production has been allocated to the production of food for humans.

The analysis has shown that the values of total level of self-sufficiency and the level of self-sufficiency for human consumption are much higher in the case b) where 10 % of the agricultural land is devoted to conservation agriculture. However, the condition

of reducing the use of mineral fertilizers by 20 % is not met. It would be fulfilled in scenario a) where 25 % of agricultural land is devoted to organic farming. In scenario a) the reduction of nitrogen input to the soil is higher than in scenario b). The reduction in GHG emissions is about the same in both cases, about 11 %.

The results show that appropriate combinations of organic and conservation agriculture, together with a change in eating habits towards lower consumption of red meat and production of some vegetables in greenhouses, could lead to gradual compliance with the requirements concerning the reduction of emissions and the use of synthetic fertilizers. In addition, the level of food self-sufficiency for humans could be improved even with the expected population growth.

Keywords: food supply chain, organic farming, conservational agriculture.

References:

1. European Union. (2020). Farm to Fork Strategy - For a Fair, Healthy and Enviromentally-Friendly Food System, from https://ec.europa.eu/food/system/files/2020-05/f2f_action-plan_2020_strategy-info_en.pdf, accessed 14th July 2021.

In-Situ FTIR Monitoring of Enzyme Catalysed Triacetin Hydrolysis

Darja Pečar [a*], Nina Belina [a], Andreja Goršek [a]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Darja Pečar (darja.pecar@um.si)

Abstract: In this study enzyme catalyzed triacetin hydrolysis was performed. Lipase from porcine pancreas was used as a biocatalyst. Hydrolyses were conducted in phosphate buffer (c = 0,05 mol/L) at (25, 30 and 35) °C, different amounts of lipase (0.2, 0.4 and 0.6) g and pH = (6, 7 and 8). The reaction progress was monitored by in-situ ReactIR 702L from Mettler Toledo, which allowed the real-time quantification of produced diacetin. The results revealed that the highest conversion was achieved at 35 °C, 0.6 g of lipase and pH = 7 and 8. Furthermore, the kinetic analysis of this reaction was conducted. The obtained experimental data have been described by Michaelis-Menten kinetic model. Calculated reaction rate constants were lower at lower temperatures and lower amounts of added enzyme. They vary between 489.9 and 2298.8 s-1. Average Michaelis-Menten constants were 103.9, 104.8 and 238.3 mol/L and activation energies 104.2, 109.3 and 64.3 kJ/mol for 0.2, 0.4 and 0.6 g of enzyme, respectively.

Keywords: kinetics, FTIR, hydrolysis, triacetin, diacetin.

Optimization of Bacterial Cellulose Production by *Komagataeibacter Hansenii*

Kaja Kupnik [a,b], Mateja Primožič [b], Željko Knez [b,c], Maja Leitgeb [b,c*]

[a] University of Maribor, Faculty of Mechanical Engineering, Research group of textile chemistry, Smetanova ulica 17, 2000 Maribor, Slovenia

[b] University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory for Separation Processes and Product Design, Smetanova 17, 2000 Maribor, Slovenia

[c] University of Maribor, Faculty of Medicine, Taborska ul. 8, 2000 Maribor, Slovenia

[*]Corresponding author: Maja Leitgeb (maja.leitgeb@um.si)

Abstract: Cellulose is one of the most abundant available renewable polymer sources and it is mostly of plant, animal and bacterial origin. Bacterial cellulose (BC) is produced by various strains of the Gram-negative bacteria, but most prominent BC-producer is genus *Komagataeibacter* (formerly known as *Acetobacter*, *Gluconacetobacter*), group of acetic acid bacteria. BC has the highest purity and does not contain contaminant molecules or by-products such as hemicellulose, lignin and pectin. Precisely because of its purity and other exceptional mechanical properties, such as biocompatibility, ultrafine and porous network structure with high water holding capacity and large surface area, it has attracted many researchers in various scientific fields. Low cytotoxicity and ability to form a variety of structures, including aerogels, films, foams, and membranes are an additional advantage for many applications in the cosmetics, pharmaceutical, paper, (bio)medicinal, and food industries [1].

Therefore, the production of BC by *Komagataeibacter hansenii* by optimizing the cultivation parameters was performed. Two different complex production media, the effect of added inoculum volume, the concentration of the carbon source in the fermentation medium, the influence of light or darkness, and the cultivation period were tested in order to obtain the highest BC yield. Additionally, Fourier-transform infrared (FTIR) spectroscopy was used to analyze the molecular composition of the produced BC. The results of the research showed successful production of BC by *K. hansenii* and combination of different parameters was selected for optimal BC production resulting in the highest yield.

Keywords: optimization, FTIR, bacterial cellulose, production.

References:

1. Kupnik, K.; Primožič, M.; Kokol, V.; Leitgeb, M. Nanocellulose in Drug Delivery and Antimicrobially Active Materials. Polymers 2020, 12, 2825, doi:10.3390/polym12122825.

Preparation of Advanced Products from Waste Sludge by Pyrolysis and Their Potential Fertilizer Applicability

Olivija Plohl [a*], Dušan Klinar [b], Lidija Fras Zemljič [a]

[a] University of Maribor, Faculty of Mechanical Engineering, Smetanova ulica 17, 2000 Maribor, Slovenia

[b] Scientific Research Centre Bistra Ptuj, Research and Development, Slovenski trg 6, 2250 Ptuj, Slovenia

[*]Corresponding author: Olivija Plohl (olivija.plohl@um.si)

Abstract: Nowadays, the final treatment and disposal of waste sludge is an expensive and environmentally harmful problem. Some traditional disposal routes for sewage sludge are coming problematic, so the challenge for sewage sludge managers is to find cost-effective and innovative solutions while responding to environmental, regulatory and public pressures [1, 2]. Recycling and utilization of sewage sludge waste are the preferred options for sustainable development, so innovative and efficient technologies are an essential step in sewage sludge recycling [3]. Due to its high mineral value, it can be used, for example, as a fertilizer and offers the possibility of returning the nutrients (nitrogen, phosphorus, etc.) to nature [4]. So far, there are several sludge treatment methods to reduce the weight and volume of the sludge, as well as to reduce the potential health hazards associated with the disposal and handling of this sludge, but usually these conventional methods require a furnace, an additional support system, fuels, trained personnel and precautions against potential fire and safety hazards, while the flue gas emissions and the leachates of the ash are a potential threat to the environment. On the other hand, sludge pyrolysis is an attractive field of research to obtain chemically valuable products and solid biochar from waste sludge [5] that can be used as fertilizers. For this purpose, the sludge from the wastewater treatment plant was dehydrated using low pressure technology and then pyrolyzed in a laboratory scale unit to obtain various products. The dehydrated and solid fraction of biochar from the sludge were characterized by X-ray powder diffraction (XRD), the presence of functional groups was investigated by infrared spectroscopy, the specific surface area was determined by BET, while the morphology was determined by scanning electron microscopy (SEM). In addition, inductively coupled plasma-optical emission spectroscopy (ICP-OES) was performed to determine the physicochemical parameters in dehydrated sludge and solid pyrolized sludge in the form of biochar. Finally, the produced biochar was used in different growth tests to evaluate its fertilizer activity. The results indicate a promising application of pyrolyzed sludge in the form of biochar in the agricultural sector.

Keywords: pyrolysis, biochar, waste sludge, sludge recycling, potential fertilizer.

References:

1. B. Bratina, A. Šorgo, J. Kramberger, U. Ajdnik, L.F. Zemljič, J. Ekart, R. Šafarič, From municipal/industrial wastewater sludge and FOG to fertilizer: A proposal for economic sustainable sludge management, J. Environ. Manage. 183 (2016) 1009–1025. doi:10.1016/j.jenvman.2016.09.063.
2. Q. Zhang, J. Hu, D.J. Lee, Y. Chang, Y.J. Lee, Sludge treatment: Current research trends, Bioresour. Technol. 243 (2017) 1159–1172. doi:10.1016/j.biortech.2017.07.070.
3. G. Mininni, A.R. Blanch, F. Lucena, S. Berselli, EU policy on sewage sludge utilization and perspectives on new approaches of sludge management, Environ. Sci. Pollut. Res. 22 (2015) 7361–7374. doi:10.1007/s11356-014-3132-0.
4. L. Lamastra, N.A. Suciu, M. Trevisan, Sewage sludge for sustainable agriculture: Contaminants' contents and potential use as fertilizer, Chem. Biol. Technol. Agric. 5 (2018) 1–6. doi:10.1186/s40538-018-0122-3.
5. E. Agrafioti, G. Bouras, D. Kalderis, E. Diamadopoulos, Biochar production by sewage sludge pyrolysis, J. Anal. Appl. Pyrolysis. 101 (2013) 72–78. doi:10.1016/j.jaap.2013.02.010.

Challenges at Upscaling from Laboratory to Industrial Level in Wool2Loop Project

Majda Pavlin [a], Barbara Horvat [a], Vilma Ducman [a*]

[a] Slovenian National Building And Civil Engineering Institute, Department for materials, Dimičeva ulica 12, 1000 Ljubljana, Slovenia

[*]Corresponding author: Vilma Ducman (vilma.ducman@zag.si)

Abstract: The aim of the Wool2Loop project is to use mineral wool waste to develop several products at pilot level, including a façade panel. The recipe for this was developed at ZAG and, in addition to the main precursor, which is rock wool, also contains other additives: electric arc furnace slag, metakaolin, lime and quartz sand. A homogenized mixture of dry reagents was activated with NaOH dissolved in Na-water glass, cured at room temperature and demoulded after 24 hours. At laboratory scale, the results were promising, but when upscaling to industrial level at company Termit d.d., new challenges appeared: the appearance of a porous structure, the decrease in mechanical strength, the curvature of the plates after a few weeks after molding, and efflorescence became more evident. Therefore, parameters such as different particle sizes in the batches, a stronger vibrating table, different curing regimes and the addition of lime were investigated. Their influences were followed by measuring the slump test, curvature and mechanical strength. SEM, XRD, FTIR and MIP were used to evaluate the results and support the findings. Our investigations revealed that the most important parameter in the selection of the mix design was the particle size of the mineral wool, which affects the need for alkali activators, which subsequently causes more efflorescence, contributes to the reduction of mechanical strength and causes an increase in curvature. In addition, the vibration and demoulding process contributed to the microstructure and pore size distribution, while the curing regime of larger specimens must be strictly controlled in terms of temperature and humidity to prevent curvature of the panels. This paper aims to emphasize that upscaling involves many technological parameters that are not so clearly expressed at the laboratory level, but which must be taken into account for successful upscaling.

Keywords: waste mineral wool pre-treatment, alkali-activated material, particle size, curing regime, curvature.

Zeta Potential as a Useful Parameter for Characterization of Bio-Based and Biodegradable Coatings

Tjasa Krasevac Glaser [a*], Olivija Plohl [a], Thomas Luxbacher [b], Lidija Fras Zemljič [a]

[a] Faculty of Mechanical Engineering, University of Maribor, Laboratory for Characterization and Processing of Polymers (LCPP), Smetanova ulica 17, 2000 Maribor, Slovenia

[b] Anton Paar GmbH, Particle characterization and surface charge, Anton Paar Strasse 20, AT-8054 Graz, Austria

[*]Corresponding author: Tjasa Krasevac Glaser (tjasa.glaser@um.si)

Abstract: Biocoatings present a new challenge for different applications as well as the environment, where natural biobased coatings are welcome due to their biodegradability and nature-friendliness. Biocoatings are particularly important in curbing the spread of antibiotic resistance, which is a major problem in the EU. In addition to developing natural based biocoatings, it is also important to understand their effectiveness on different base materials. Since most coatings act at the interface, it is extremely important to study the surface properties of the functional material, i.e., after the coating has been applied. One important surface property is the surface charge as a crucial parameter for enhancing or suppressing the interaction between dissolved compounds in an aqueous solution and solid surfaces. When various materials are brought into contact with an aqueous solution, they generally acquire a surface charge at the solid-liquid interface through various processes such as ionization, ion adsorption, or ion dissolution [1]. Surface charge plays an important role in determining the interactions of materials with liquid non-biological as well as biological components. The surface zeta potential (SZP), which is primarily used as an indicator of the surface charge of solids, is a valuable parameter for comparing material surfaces before and after surface treatment, as well as their charging behaviour in an aqueous solution [1, 2]. Thus, SZP is a key parameter for the understanding of surface properties and for the development of new specialized materials based on applications of biocoatings, e.g., biomaterials or implants. It simultaneously provides insights into the surface chemistry of the (modified) material and valuable information on the interactions with charged species. The measurement of streaming potential (or alternatively streaming current) is the direct approach to SZP. A pressure gradient is applied between the two ends of a capillary flow channel, which generates the fluid flow and the streaming potential signal [3]. In this way one can use SZP to characterise the charging behaviour of the surface and to obtain information of the isoelectric point. In this paper, various materials modified with bio-based and biodegradable coatings (e.g., polysaccharide-based coatings) are presented in terms of their surface charge behaviour. SZP analyses were performed for various

modified materials using biocoatings such as potential packaging materials, personal protective materials, as for example protective masks, and silicone or stainless-steel materials as medical devices. It has been shown that SZP analysis on macroscopic materials is an important method to qualify properties of these new materials for various applications and to follow the success of material functionalization using biocoatings.

Keywords: surface zeta potential (SZP); biobased coatings; modified materials; surface charge; streaming potential.

References:

1. R.J. Hunter, Zeta potential in colloid science: Principles and applications, Academic Press, London, 1981.
2. D.J. Shaw, Introduction to colloid & surface chemistry, 4th Editio, Butterworth-Heinemann, Oxford, 1992. doi:10.1007/s13398-014-0173-7.2.
3. V. Ribitsch, C. Jorde, J. Schurz, H.J. Jacobasch, Measuring the zeta potential of fibers, films and granulates, Prog. Colloid Polym. Sci. 77 (1988) 49–54.

A Simultaneous Optimisation Method for Plant Operating Variables and HEN of a Natural Gas Purification Process

Bohong Wang [a*], Yang Zhang [b], Min Zeng [c], Petar Varbanov [a], Yongtu Liang [b], Jiří Jaromír Klemeš [a]

[a] Sustainable Process Integration Laboratory – SPIL, NETME Centre, FME Engineering, Brno University of Technology - VUT Brno, Technická 2896/2, 616 69 Brno, Czech Republic

[b] China University of Petroleum Beijing, College of mechanical and storage and Transportation Engineering, National Engineering Laboratory for Pipeline, Safety/Beijing Key Laboratory of Urban Oil and Gas Distribution Technology, Fuxue Road No.18, Changping District, Beijing, 102249, China

[c] Xi'an Jiaotong University, Key Laboratory of Thermo-Fluid Science and Engineering, Ministry of Education, China

[*]Corresponding author: Bohong Wang (wang.b@fme.vutbr.cz)

Abstract: As an essential part of Heat Integration, the Heat Exchanger Network (HEN) plays a vital role in large-scale industrial fields. The optimisation of HEN can increase energy efficiency and considerably save the operating and investment cost of the project. This study presents a novel approach for simultaneous optimisation of plant operating variables and the HEN structure of a natural gas purification process. The reuse of existing heat exchangers is considered in the method to extend the life cycle of the equipment to contribute to the circular economy. The objective function is the total energy consumption of the studied process. A two-stage method is developed for optimisation. In the first stage, a Particle Swarm Optimisation (PSO) algorithm is developed to optimise variables including tower top pressure, tower bottom pressure, and reflux ratio on the HEN, thereby changing the initial temperatures of cold and hot streams in the HEN. In the second stage, a shifted retrofit thermodynamic grid diagram (SRTGD)-based model and the corresponding solving algorithm is applied to retrofit the HEN. The case study shows that the optimal operating conditions of towers and temperature spans of heat exchangers can be solved by the proposed method to reduce the total energy consumption. The case study shows that the total energy consumption is reduced by 39.6 %.

Keywords: Heat Integration, Heat Exchanger Network, Natural Gas Purification Process, Particle Swarm Optimisation.

Advanced, Virtually Supported Design of Small Scale Mono-Incineration Plants for Circular Economy

Anton Žnidarčič [a], Tomaž Katrašnik [a], Tine Seljak [a*]

[a] University of Ljubljana, Faculty of mechanical engineering, Aškerčeva 6, 1000 Ljubljana, Slovenia

[*]Corresponding author: Tine Seljak (tine.seljak@fs.uni-lj.si)

Background: Introduction of circular economy requires dedicated waste treatment solutions to ensure highest possible material and energy recovery with the lowest or near-zero emissions. Practical and efficient ways to achieve this are presented by thermal treatment. As highly variable properties of various waste materials lead to different thermal decomposition characteristics, introduction of mono-incineration plants is encouraged [1], as it enables tailoring to specific physical and chemical properties of selected waste, facilitating the downstream recovery of residuals. Due to the variable quantities of various waste materials, and the fact that circular economy guidelines address whole treatment chain, it is also necessary to develop solutions on various scales, including small scale plants for locally closed treatment loops. While these reduce logistic costs and increase social acceptance, they at the same time exhibit high sensitivity to process parameters due to complex waste characteristics combined with low thermal power output and dimensional constraints [2].

Objectives and results: The work presents the virtual design approach for the development of advanced small scale waste mono-incineration plants for wastewater sludge. The novelty of the approach is that it includes multiple steps, from improved description of a certain waste material thermal decomposition, to the computationally efficient, yet highly accurate 3-D CFD simulations, which consider detailed chemical kinetics. The steps thus provide a bottom up description of a waste material combustion characteristics, and are described as follows:

- A thorough description of material thermal decomposition under various conditions is obtained, considering and combining experimentally and literature-available data.
- A 0-D model, respecting obtained data alongside mass and energy balance constraints is applied to determine potential composition range of emitted volatiles under certain conditions.
- Definition of suitable fuel surrogates, relying on 3-D CFD simulations with detailed chemical kinetics, which are validated with experimentally obtained data.
- Creation and validation of waste material and system operating conditions oriented reduced reaction mechanisms, which enable accurate, yet efficient 3-D CFD system scale combustion simulations.

While first three steps provide the means for improved waste material combustion modelling and are described in [2], the final step enables its application on a system scale and is presented in detail in [3]. This work integrates and couples all steps, resulting in a tool for highly robust description of complex waste material mono-incineration. This can be used to design a specific system and optimize its operation in various combustion conditions, ensuring the highest material and energy recovery levels. To depict the capability of the tool, the effect of increased moisture content in wastewater sludge is evaluated in terms of reaction zone length in a prototype sewage sludge mono-incineration plant. With a set of simulations, suitable system response was defined for dry sludge (13.3 wt.% moisture content) and for sludge with increased moisture content (30 wt.%). With OH radical as an identifier of reactive zone length, the model mandates an increase in air-fuel ratio, altered through higher secondary combustion air mass flow in order to maintain a similar volume and elongation of the reactive zone. This results in an increased air-fuel ratio from 1.8 to 2.0 without compromising the spatial distribution of heat release rate and thus maintaining similar system efficiency. With fluctuations in sludge moisture content which depend mostly on upstream processing and energy availability for drying, the flexibility of the system in terms of permissible moisture content can be determined as well.

Keywords: combustion, waste treatment, small scale incineration, numerical model, mono-incineration.

Acknowledgements: The authors acknowledge the financial support from the Slovenian Research Agency (research core funding No. P2-0401 – Energy engineering, project funding Z2-1862 – Zero footprint combustion for green energy generation) and Ministry of Education, Science and Sport through programme CelCycle. Support of COST action CM 1404 (SMARTCATS) is also acknowledged.

References:

1. Schnell M., Horst T., Quicker P.: Thermal treatment of sewage sludge in Germany: A review, Journal of Environmental Management, 2020, Vol. 263.
2. Žnidarčič A., Seljak T., Katrašnik T.: Surrogate model for improved simulations of small-scale sludge incineration plants, Fuel, 2020, Vol. 280.
3. Žnidarčič A., Katrašnik T., Zsély I.G., Nagy T., Seljak T.: Sewage sludge combustion model with reduced chemical kinetics mechanisms, Energy Conversion and Management, 2021, Vol. 236.

Development of FTIR, UV and Fluorescence Based Analytical Methodology for Lignin Characterisation

Rok Pogorevc [a], Tina Ročnik [a], Miha Grilc [a*], Edita Jasiukaitytė-Grojzdek [a], Blaž Likozar [a]

[a] National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Hajdrihova 19, 1000 Ljubljana, Slovenia

[*]Corresponding author: Miha Grilc (miha.grilc@ki.si)

Introduction: Lignin is composed of three different phenylpropanoid units which are the source of aromatic rings which could be substituted at different position [1]. Lignin is synthesized using three monolignols, specifically sinapyl alcohol (syringyl (S)), coniferyl alcohol (guaiacyl (G)) and p-coumaryl alcohol (H) [1,2]. During the polymerisation monolignols are coupled forming specific lignin motifs. The most important lignin inter-unit linkages are β-O-4, β-5 and β-β [2]. Fractionation is one of the promising ways to produce lignin with particular properties (molecular weight, structural features). Several fractionation processes, that use different solvents, have been developed [1]. The aim of this paper is to characterize lignin fractions with different analytical methodologies to analyse depolymerisation, which was previously confirmed with NMR and SEC/GPC. One of the analytical methodologies used in this paper is Fourier-transform infrared spectroscopy (FT-IR), which is a powerful tool to characterize lignin relatively fast. This can in turn be used to control the process and validated product quality [3]. Furthermore, UV and florescence are also analytical techniques that can be utilized to characterize lignin fractions.

Methods: Fractionation used in this paper was done by adding different volumes of water to isolated lignin liquid composed of dissolved lignin and ethanol to isolate lignin with specific molecular weight. These fractions were then dried and characterised by Nuclear magnetic resonance (NMR), Size exclusion chromatography (SEC/GPC), FTIR, UV and florescence.

Results: NMR results indicate that adding more water to the lignin liquid decreases the number of the most important lignin motifs, which was also confirmed by analysing lignin fractions with SEC/GPC. SEC/GPC curves show higher molecular weights at the fraction 1 compared to fraction 5. The comparison of FT-IR curves for the first to the last fraction show a clear decrease of the peak at 1026 cm^{-1}, which is specific for the β-O-4 linking motif [4]. This indicates that the number of these linkages is decreasing as more water is added to the lignin liquid, which is in line with the NMR results.

Conclusions: The overall correlation of the analytical data (FT-IR, UV fluorescence, NMR, SEC) allowing to characterize lignin fractions faster and easier will be presented and discussed.

Keywords: lignin, molecular weight, FTIR spectroscopy, fractionation, UV.

Acknowledgements: This work was funded by the Slovenian Research Agency (ARRS) under core funding P2-0152 and project J2-2492.

References:

1. L. Cuiyun, S. Chuanling, W. Guanhua, J. Hongyu and M. Litong "A novel and efficient process for lignin fractionation in biomass-derived glycerol-ethanol solvent system," Industrial Crops and Products, vol. 111, pp. 201-211, aug. 2017.
2. C. W. Lahive, P. C. J. Kamer, C. S. Lancefield and P. J. Deuss "An Introduction to Model Compounds of Lignin Linking Motifs; Synthesis and Selection Considerations for Reactivity Studies," ChemSusChem, vol. 13, pp. 4238-4265, 2020.
3. C. G. Boeriu, D. Bravo, R. J. A. Gosselink and J. E. G. van Dam "Characterisation of structure-dependent functional properties of lignin with infrared spectroscopy," Industrial Crops and Products, vol. 20, pp. 205-218, 2004.
4. M. Yáñez-S, B. Matsuhiro, C. Nuñeza, S. Panb,C. A. Hubbellb, P. Sannigrahib and A.J. Ragauskas "Physicochemical characterization of ethanol organosolv lignin (EOL)from Eucalyptus globulus: Effect of extraction conditions on themolecular structure," Polymer Degradation and Stability, vol. 110, pp. 184-194, sept. 2014.

COVID-19 Pandemics: Influence on Circular Economy

Jiří Jaromír Klemeš [a*], Yee Van Fan [a], Peng Jiang [b], Petar Varbanov [a]

[a] Sustainable Process Integration Laboratory – SPIL, NETME Centre, FME Engineering, Brno University of Technology - VUT Brno, Technická 2896/2, 616 69 Brno, Czech Republic

[b] Sichuan University, Department of Industrial Engineering and Engineering Management, Business School, 610064, Chengdu, China

[*]Corresponding author: Jiří Jaromír Klemeš (klemes@fme.vutbr.cz)

Abstract: The COVID-19 has been swiping the world. By mid-August 2021, close to 205 M confirmed cases of COVID-19 and reaching 4.5 M deaths in 222 countries had been reported to the World Health Organization. By comparing the early 2020-2021 COVID-19 outbreak and the 1918 flu pandemic, this pandemic might get more deadly than the most severe previous pandemic. Many measures such as quarantine, social distancing and lockdown have been set to mitigate the coronavirus infection. The pandemic has had profound influences on the Circular Economy in many industries, including agriculture, manufacturing, finance, education, healthcare, sports, tourism and food. With the rapid development of global vaccination, the light at the end of the tunnel has been seen. On the other hand, there has been growing uncertainty about the influence of the new strains, e.g. the delta variants. The industry and business are on the way to understand the complicated impacts on the Circular Economy and identify emerging opportunities triggered by COVID-19 pandemics. The way ahead demands a continuous analysis of all novel emerging opportunities under careful balancing of savings and increasing demands. Not all novel smart, high-tech remote/contactless options are energy efficient, and each of them should specifically balance in case-specific conditions. The economic disruptions have been facilitating faster changes and stronger creativity. Innovations meet both cultural and material requirements for acceleration. Old and traditional structures preventing the income of novel technologies are weakening. The old economy has been collapsing, and the novel "clusters" of innovation are becoming the core of a novel emerging economy. This had been happening during the past three centuries. It has been witnessed five substantial's "waves" regularly causing economic destructions and related re-clustering. The first wave was driven by employing the power of water, and the steam power was the second wave. Coal and electricity brought the third wave, the fourth exploiting oil and gas, and the fifth wave was triggered by digital transformation. It is the opportunity that the humans are presented at the start of the sixth immense wave of innovation, which is driven by renewable energy combined with e-mobility, e-health, e-activities and e-services, smart-city technology and the number of activities listed, including hydrogen energy. And this wave has been strongly initiated by the pandemics. For example, e-business is accelerating by the movement restriction and

contactless preference in daily life to contain the virus. The surges in need for single-use plastics and packaging in combating the pandemic have also raised the practicability of eliminating single-use materials. The outcomes emphasised that diversifying solutions to achieve the needed objective is vital to improving susceptibility and providing higher flexibility in minimising environmental footprints instead of a complete ban. However, more comprehensive research for the alternative solution (e.g. reusable option) towards low energy consumption without compromising the effectiveness should be offered and advocated. The concern, design (recycling/reuse friendly) and the end of life cycle management toward a Circular Economy have also been initiated further by pandemics due to sudden challenges in handling the increasing waste (e.g. masks, packaging, Personal Protection Equipment - PPE). It is interesting to see that the new waves are, in most cases, coincided with some crises or critical situations where the society has been mobilising all possible researches strongly to overcome. COVID-19 pandemic revealing the vulnerability of current global systems where many voices have been calling for a response to shape the post-COVID-19 world. In embracing these opportunities, a Circular Economy transition could be realised sustainably. These COVID-19 consequences have brought new challenges to the Circular Economy efforts. The surge of e-commerce and home deliveries and the sharply increased use of PPE caused a significant rise in the use of plastics – mostly single-use. Another issue is the need for embedding safety measures in all business processes – including good delivery, for alleviating the concerns about infection. The challenges have several dimensions. The efficiency of reverse logistics of single-use packaging has to be improved significantly in the short run. As a longer-term solution, novel multi-use packaging and containers would be necessary, optimising the number of reuse cycles and the logistics.

Keywords: circular economy, sustainability, materials innovation, energy demands, COVID-19.

Acknowledgements: The authors gratefully acknowledge financial support from the EU project Sustainable Process Integration Laboratory – SPIL, funded as project No. CZ.02.1.01/0.0/0.0/15_003/0000456, by Czech Republic Operational Programme Research and Development, Education, Priority 1: Strengthening capacity for quality research.

References:

1. Ellen MacArthur Foundation, 2020, The circular economy: a transformative Covid-19 recovery strategy: How policymakers can pave the way to a low carbon, prosperous future. accessed 7 August 2021.
2. Fan Y.V., Jiang P., Hemzal M., Klemeš J.J., 2020. An update of COVID-19 influence on waste management. Science of The Total Environment, 754,142014.
3. Jiang P., Fu X., Fan Y.V., Klemeš J.J., Chen P., Ma S., Zhang W., 2021. Spatial-Temporal Potential Exposure Risk Analytics and Urban Sustainability Impacts related to COVID-19 Mitigation: A Perspective from Car Mobility Behaviour, Journal of Cleaner Production, 279, 123673.

4. Jiang, P.; Klemeš, J.J., Fan, Y.V., Fu, X., Bee, Y.M. 2021, More Is Not Enough: A Deeper Understanding of the COVID-19 Impacts on Healthcare, Energy and Environment Is Crucial. Int. J. Environ. Res. Public Health, 18, 684. Doi: 10.3390/ijerph18020684
5. Jiang, P.; Fan, Y.V., Klemeš, J.J.; 2021, Impacts of COVID-19 on energy demand and consumption: Challenges, lessons and emerging opportunities, Applied Energy 116441
6. Jiang, P., Klemeš, J.J., Fan, Y.V., Fu, X., Tan, R.R., You, S., Foley, A.M., 2021. Energy, environmental, economic and social equity (4E) pressures of COVID-19 vaccination mismanagement: A global perspective, Energy, 121315.
7. Klemeš, J.J., Fan, Y.V., Tan R.R., Jiang P., 2020, Minimising the present and future plastic waste, energy and environmental footprints related to COVID-19, Renewable and Sustainable Energy Reviews, 127, 109883.
8. Klemeš, J. J., Fan, Y. V., Jiang, P., 2021. Plastics: friends or foes? The circularity and plastic waste footprint. Energy Sources, Part A: Recovery, Utilisation, and Environmental Effects, 43(13), 1549-1565.
9. Klemeš, J.J., Fan, Y.V., Jiang, P., 2021. COVID-19 pandemic facilitating energy transition opportunities, International Journal of Energy Research, doi: 10.1002/er.6007
10. Klemeš, J.J., Fan, Y.V., Jiang, P., The Energy and Environmental Footprints of COVID-19 Fighting Measures–PPE, Disinfection, Supply Chains. Energy. 2020: 118701.
11. Klemeš, J.J., Jiang, P., Fan, Y.V., Bokhari, A. Wang, X.C., 2021. COVID-19 pandemics Stage II – Energy and environmental impacts of vaccination, Renewable and Sustainable Energy Reviews, 150, 111400.

Framework for Optimization of Wastewater Treatment Handling Various Types of Wastewater Using AOP and Coagulation/Flocculation Processes

Andreja Nemet [a*], Miloš Bogataj [a], Zdravko Kravanja [a]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Andreja Nemet (andreja.nemet@um.si)

Abstract: Optimization of wastewater treatment in industry with batch processes is in itself a challenging task as the planning must take into account at what time, which type of wastewater should be treated in a given treatment process. If the treatment process consists of advanced oxidation process (AOP) and coagulation/flocculation process (CFP) the sequence of these two processes is also a matter of decision. The AOP process mainly breaks down the large pollutant molecules into smaller molecules thought oxidization, while in the CFP these pollutants are removed. Using the AOP process first, followed by the CFP might seems more reasonable at first glance, but large amount of pollutants could result in an inefficient AOP process. On the other hand, performing CFP first could lead to an inefficient CFP because the large molecules do not coagulate/flocculate or coagulate/flocculate only very slowly. In this study, a framework for wastewater treatment optimization was developed. The two most important issues wastewater treatment are considered. The first issue is the composition and the amount of wastewater production entering the wastewater treatment plan. For this purpose, a detailed description of wastewater generation and collections systems should be made. After the data collection, the data reconciliation and simulation of the total wastewater generation and collection system, including information about the wastewater composition, should be performed. The second important issue of optimization is the efficiency of wastewater treatment. For this purpose, a detailed description of the treatment process should be made. The important step in the wastewater treatment process description is to conduct laboratory experiments to determine the efficiency of each treatment process for different types of wastewater. Ideally, all wastewater types should be tested, but this is often impossible due to the wide variety of products washed from the tanks in the production line. Therefore, different wastewaters should be grouped based on their similar composition. This selection is critical to obtain representative samples for each group. After the grouping, the laboratory experiment should be conducted using design of experiments to obtain statistically acceptable results. In the final step, the results of both important issues are incorporated into the optimization using a mathematical programming approach, considering the amount and composition of the wastewater is considered and the efficiency of each step of the treatment process

in any order. The developed framework represents a systematic way to improve the wastewater treatment processes, which is inevitable when trying to optimize wastewater treatment processes on an industrial scale.

Keywords: flocculation, optimization, wastewater treatment plant, AOP.

Production of Hydrochar from Pumpkin Seed Oil Press Cake by Hydrothermal Carbonization

Aleksandra Petrovič [a*], Tjaša Cenčič Predikaka [b], Lidija Čuček [a]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[b] Ikema d.o.o., Institute for chemistry, ecology, measurements and analytics, Lovrenc na Dravskem polju 4, 2324 Lovrenc na Dravskem polju, Slovenia

*Corresponding author: Aleksandra Petrovič (aleksandra.petrovic@um.si)

Abstract: Hydrothermal carbonization (HTC) is regarded as a promising thermochemical technology to convert wet biomass into solid biofuel at mild temperature conditions of up to 300 °C [1]. The process is complex as involves several simultaneous reactions including dehydration, condensation, hydrolysis and polymerization, but offers several advantages, such are drying of biomass is avoided, products in the form of hydrochar or liquid fertilizer are produced, and relatively low investment cost is required [2]. The main product hydrochar exhibits higher heating values compared to raw biomass and has better fuel properties with higher energy efficiency. Hydrochar is suitable for the removal of pollutants such as heavy metals, antibiotics and dyes from wastewater due to its high absorption capacity. Besides, it could be used as a functional material for the synthesis of various carbonaceous materials and supercapacitors due to its high specific surface area. Furthermore, promising nutrient content, water holding capacity and ability of carbon sequestration makes it usable as an organic amendment to improve physical properties and fertility of the soil [3].

Various biomass types could be applied for HTC process, such as agricultural, industrial and other waste, such as sewage sludge and digestate. Among industrial waste, oil cakes are promising sources for hydrochar production. Oil cakes produced during oil extraction from oilseeds typically contain high protein and fiber content, and are rich in nutrients such as phosphorous, calcium and kalium. Due to relatively high nutritional value, they could be utilized as animal feed or green manure for plants growth, while high carbon content makes them usable for production of carbon-rich solid fuel in the form of biochar or hydrochar. Up to now few studies were performed where oil cakes such as sesame, sunflower and few others were exposed to hydrothermal treatment and have shown promising results regarding hydrochar production [4]. Literature review showed that no study exists on hydrothermal carbonization of pumpkin seed oil press cake, which could be generated during oil extraction from pumpkin seeds of pumpkin species Cucurbita pepo L. var. oleifera or

var. styriaca. This type of oil cake is in Europe available mostly in Pannonian region, particularly in countries such are Austria, Hungary, Croatia and Slovenia.

The aim of this study was to investigate the impact of various operating parameters of hydrothermal carbonization on hydrochar formation from pumpkin seed oil cake. HTC experiments were conducted in an autoclave reactor at two different temperatures (200 and 250 °C) and two different reaction times (2 and 5 h). The main characteristics of biomass and obtained hydrochars were determined, such as biochar yield, pH, a calorific value, the volatile matter content, the ash content, and others. According to the characteristics of the obtained hydrochars, optimal conditions for hydrochar production from the above-mentioned oil cake were suggested.

Keywords: hydrothermal carbonization, hydrochar, characterisation, oil industry waste, pumpkin seed oil press cake.

References:

1. Silva, R. D. V. K.; Lei, Z.; Shimizu, K.; Zhang, Z., Hydrothermal treatment of sewage sludge to produce solid biofuel: Focus on fuel characteristics. Bioresource Technology Reports 2020, 11, 100453.
2. Shan, Y.-Q.; Deng, X.-Q.; Luque, R.; Xu, Z.-X.; Yan, L.; Duan, P.-G., Hydrothermal carbonization of activated sewage sludge over ammonia-treated Fenton sludge to produce hydrochar for clean fuel use. Green Chemistry 2020, 22, (15), 5077-5083.
3. Celletti, S.; Bergamo, A.; Benedetti, V.; Pecchi, M.; Patuzzi, F.; Basso, D.; Baratieri, M.; Cesco, S.; Mimmo, T., Phytotoxicity of hydrochars obtained by hydrothermal carbonization of manure-based digestate. Journal of Environmental Management 2021, 280, 111635.
4. Khan, M. A.; Alqadami, A. A.; Wabaidur, S. M.; Siddiqui, M. R.; Jeon, B.-H.; Alshareef, S. A.; Alothman, Z. A.; Hamedelniel, A. E., Oil industry waste based non-magnetic and magnetic hydrochar to sequester potentially toxic post-transition metal ions from water. Journal of Hazardous Materials 2020, 400, 123247.

Footprint Assessment of Hydrothermal Decomposition of Melamine Etherified Resin Fibre

Timotej Vidovič [a], Maja Čolnik [a], Mojca Škerget [a], Lidija Čuček [a], Jan Puhar [a], Annamaria Vujanović [a*]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Annamaria Vujanović (annamaria.vujanovic@um.si)

Abstract: A rapid growth in plastic consumption has been seen worldwide in recent years. Many industries have used plastics in various functions and in many aspects, which also increased the production of plastic-related waste. Large quantities of plastic waste leak into the environment and consequently causing not only significant environmental, but also economic damage. There are many different types of plastic materials, which can be divided into thermoplastic and thermosetting materials. Thermoplastic materials, such as e.g. polyethylene terephthalate (PET) can be re-melted which makes it easier to recycle. On the other hand, thermoset plastic materials cannot be remelted, so this type of waste is usually incinerated or disposed in the environment, which causes significant environmental burdens. Melamine resins are resistant thermoset plastic materials made from melamine, urea and formaldehyde by condensation polymerization. Cross-linked polymers cannot be remelted or reformed hence materials recycling is difficult or even could be impossible. That is the reason they mainly end up in landfills after their life cycle. Among promising methods to resolve the environmental plastic pollutions are hydrothermal processes which have a low impact on environment. To convert waste into materials, fuels and chemicals, water at high temperature and pressure is used as a main process medium. Under this condition the water remains in liquid or supercritical state. A chemical decomposition of melamine etherified resin (MER) fibres and related environmental implications are studied in this work. The decomposition takes place in a hydrothermal reactor with water at subcritical conditions. Environmental footprints and recycling opportunities for the above-mentioned product are analyzed, and later compared regarding different decomposition temperatures. Footprint assessment is performed mainly using OpenLCA software and various databases. Environmental comparison of the processes is evaluated regarding to GHG, nitrogen, phosphorus, energy, human toxicity potential and ecological footprints.

Keywords: hydrothermal processes, LCA, Melamine Etherified Resin (MER), environmental evaluation.

Maximum Power Output of Organic Rankine Cycle Powered by Multiple Heat Sources

Monika Dokl [a], Lidija Čuček [a*]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Lidija Čuček (lidija.cucek@um.si)

Abstract: In recent decades, various heat sources such as waste heat and renewable heat from sources such as solar, biomass, geothermal and heat from heat pumps have been used to generate electricity besides conventional electricity production. However, significant amounts of heat remain in a form of low-grade heat, which is difficult to recover. Among the numerous heat recovery technologies, organic Rankine cycle (ORC) has already proved to be a promising method for utilizing low and medium quality heat. In this study, a novel ORC superstructure is proposed and optimized for utilizing multiple heat sources. Except for the input data related to a case study, most of the process streams data are described by variables to be optimized such as temperatures, pressures, flowrates and energy flows. The thermodynamic properties of selected suitable fluids are summarized in correlations obtained as functions of pressure and/or temperature. The best utilization of the available thermal energy is achieved by maximization of power output of the system. Further, the economic performance of optimized system is investigated. The results show successful integration of the proposed ORC design and multiple heat sources, as well as its applicability in a selected case study.

Keywords: organic rankine cycle, mathematical programming, multiple heat sources, maximum power output.

CO_2 Hydrogenation to Methanol over Nanoshaped Pd/CeO_2 Solids: Effect of Exposed Surfaces on Catalyst Performance

Matevž Roškarič [a*], Gregor Žerjav [a], Rohini Khobragade [a], Martin Košiček [b], Janez Zavašnik [b], Nataša Novak Tušar [a], Albin Pintar [a]

[a] National Institute of Chemistry, Laboratory for Environmental Sciences and Engineering, Department of Inorganic Chemistry and Technology, Hajdrihova 19, 1001 Ljubljana, Slovenia

[b] Jožef Štefan Inštitut, Department of Gaseous Electronics, Jamova 39, 1000 Ljubljana, Slovenia

[*]Corresponding author: Matevž Roškarič (matevz.roskaric@ki.si)

Abstract: Global CO_2 emission is steeply increased as a consequence of the extensive reliance on the combustion of fossil fuels in the eons of prosperity for the urbanization and industry rebellion. CO_2 is not benevolent to the atmosphere as it is marked as a greenhouse gas with severe detrimental environmental impacts anticipated like climate change, a rise in the atmospheric temperature, acidification of oceans and so forth. Therefore, recycling of CO_2 to the industrially valued products and carbon-neutral fuels like methanol through the hydrogenation reaction is the most prominent option [1]. Over the last few decades, the ternary $Cu/ZnO/Al_2O_3$ catalyst system was extensively explored in industries for CO_2 hydrogenation; nevertheless, an excess of water formation leads to the limited activity and poor selectivity as well as sintering of active phase with the resulting catalyst deactivation [2]. This implies that novel catalytic formulations are needed.

Herein, we report on the performance of Pd/CeO_2 catalysts with four different ceria morphologies, i.e. polyhedral, rod, cube and polygonal, for catalytic CO_2 hydrogenation to methanol. All the synthesized catalysts were investigated using N_2 physisorption, SEM-EDX, TEM, HR-TEM, XRD, H_2-TPR, CO_2-TPD and Py-TPD. Among all, 5 wt.% Pd/CeO_2-NPH (polyhedral) catalyst with ({111} and {110}) crystalline facets showed the highest CO_2 hydrogenation activity as compared to Pd/CeO_2-NR (rod) ({111} and {100}), Pd/CeO_2-NPG (polygonal) {111} and Pd/CeO_2-NC (cube) {100} samples. The highest specific surface area and high extent of surface oxygen vacancies were observed in the case of Pd/CeO_2-NPH catalyst. It is also inferred that the Pd/CeO_2-NPH catalyst showed CO_2 conversion of 9%, selectivity of S(CO) 23%, selectivity of $S(CH_3OH)$ 77% and space time yield of STY (CH_3OH) 1.2 (g/(gcat. h)) at 50 bar pressure and 260 °C with the flow rate of 50 ml/min of reaction gas (CO_2/H_2, 1:3). The results revealed strong metal-support interactions by forming the $PdxCe_{1-x}O_{2-\delta}$ linkage that improved the formation of surface oxygen vacancies and

CO_2 activation on the CeO_2 support, and promoted dissociation of H_2 on the Pd metal. In-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were carried out for the best performing Pd/CeO_2-NPH catalyst at the optimum reaction conditions to investigate the formation of reaction intermediates during the methanol synthesis reaction. The results revealed the formation of bidentate and monodentate carbonates on the CeO_2 support, which immediately decomposed to form the formate species. Further, the formate was rapidly hydrogenated to crucial methoxy species followed by the formation of methanol and CO product. There was no clear evidence for the abundance of formic acid intermediate during in-situ DRIFT experiments, which leads to the formate reaction mechanism pathway. In contrast, the Pd/CeO_2-NC catalyst with exposed {100} facets showed slow formation of the methoxy intermediate during the reaction, which explains lower activity for methanol production.

Keywords: methanol, CO_2 hydrogenation, Pd/CeO_2, morphology, in-situ DRIFTS.

References:

1. A. Goeppert, M. Czaun, J.P. Jones, G.K. Surya Prakash, G.A. Olah, Chem. Soc. Rev. 43 (2014) 7995-8048.
2. J. Nakamura, T. Fujitani, S. Kuld, S. Helveg, I. Chorkendorff, J. Sehested, Science 357 (2017) eaan8074.

Valorization of Agricultural Digestate for Ammonia Recovery under Uncertainty

Klavdija Zirngast [a], Lidija Čuček [a], Zdravko Kravanja [a], Zorka Novak Pintarič [a*]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Zorka Novak Pintarič (zorka.novak@um.si)

Abstract: This contribution presents a sensitivity analysis for the synthesis of flexible supply networks for producing electricity from biogas, and processing a low-quality digestate into more valuable products, while considering uncertain input data. Besides the use of dry and wet digestates from biogas plants as fertilizers [1], this contribution considers the production of concentrated nitrogen fertilizers through a two-stage vacuum evaporation. Such fertilizers are of higher values compared to the digestate, as they are richer with nitrogen and lower in water content, thus also reducing the cost of transport [2]. Production of ammonium sulfate by vacuum evaporation process and adding sulfuric acid is considered. The process is heat-integrated with biogas process, reducing consumptions of external utilities for two-stage evaporation to practically zero [3]. The problem is formulated as a mixed integer linear programming (MILP) model, with the main objective to maximize the economic profit. To account for uncertainty, decomposition methodology is applied which consists of several steps that gradually lead from nominal process structure obtained at fixed values of uncertain parameters to more flexible process that accounts for deviations in uncertain parameters [4]. The proposed approach for the synthesis of biogas supply network producing heat, electricity and higher-value fertilizers is demonstrated on an illustrative case study of up to nine agricultural biogas plants in Slovenia.

Keywords: mathematical programming, supply networks synthesis, uncertainty, biogas supply network, concentrated nitrogen fertilizer.

Acknowledgements: The authors acknowledge financial support from the Slovenian Research Agency (core research funding No. P2-0032 and P2-0412 and projects No. J7-1816 and N2-0138).

References:

1. Egieya, J.M., Čuček, L., Zirngast, K., Isafiade, A.J., Pahor, B., Kravanja, Z. 2018. Synthesis of biogas supply networks using various biomass and manure types. Computers & Chemical Engineering, doi: 10.1016/j.compchemeng.2018.06.022.
2. Chiumenti, A., da Borso, F., Chiumenti, R., Teri, F., Segantin, P. 2013. Treatment of digestate from a co-digestion biogas plant by means of vacuum evaporation: Tests for process optimization and environmental sustainability. Waste Manage, 33, 1339-1344.

3. Novak Pintarič, Z., Bogataj, M., Pahor, B., Simonič, M. 2020. Preliminary design of optimized heat integrated two-stage vacuum evaporation for processing digestate from biogas plant. Thermal Science, 283-283.
4. Zirngast, K., Kravanja, Z., Novak Pintarič, Z. 2018. A Robust Decomposition Methodology for Synthesis of Flexible Processes with many Uncertainty Parameters – Application to HEN Synthesis. Chemical and Biochemical Engineering Quarterly, accepted for publication.

Bio-Based Polyester Resins for Coatings

Nataša Čuk [a*], Martin Ocepek [a], Radmila Wollrab [a]

[a] Helios Tblus Količevo, d.o.o., Synthetic resins, Količevo 65, 1230 Domžale, Slovenia

[*]Corresponding author: Nataša Čuk (natasa.cuk@helios.si)

Abstract: Helios produces a wide range of products such as coatings for the metal industry, industrial wood coatings, powder coatings, road markings, refinish, decorative coatings and synthetic resins. In addition, Helios is developing new products and solutions based on the principles of environmental care and sustainability. Customer demands and Helios strategy are to increase bio-based content in produced materials since we expect significant demand for bio-based polymers and coatings. Helios is also a member of the Strategic Research and Innovation Partnership (SRIP), a network for the transition to a circular economy.

In recent years, the potential replacement of fossil-based chemicals, using inexpensive and renewable starting materials, is being increasingly explored with the aim of developing a more sustainable bio-based economy. Most efforts are focused on the preparation of bio-based monomers for polymer synthesis [1]. The simplest case is the so-called drop-in approach where raw material derived from biomass is identical to fossil-based one [2]. Nevertheless, in coatings, the cost-performance ratio is the most important element and therefore the balance of bio-based content against performance and costs needs to be considered [3,4].

We have focused our research on the development of bio-based saturated polyester resins. Polyester resins offer excellent properties such as durability, weather resistance, fast curing, excellent corrosion resistance, low temperature curing, impact resistance and flexibility. They are used in industrial, can & coil, automotive, flexible packaging coatings, enamel coatings and other coatings.

The focus was put on two types of resins: firstly, the development of polyester resins for 2K PUR systems using monomers produced from renewable resources such as succinic acid, sebacic acid, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol and others, and secondly, the development of polyester resins for coil coating application based on 2,5-furandicarboxylic acid, recycled terephthalic acid and isosorbide.

Keywords: bio-based resins, FDCA, recycled terephthalic acid, succinic acid, sebacic acid.

References:

1. https://www.mdpi.com/journal/polymers/special_issues/ biodegradable_biobased_polyesters.
2. European Coatings Technology Forum, Coatings from Renewable Resources. Berlin, 2017.
3. European Coatings Journal, Issue 4, 2016.
4. European Coatings Journal, Issue 4, 2018.

Increasing the Efficiency of a Renewable Energy System within the EU through Energy Integration within Sectors

Sanja Potrč [a], Andreja Nemet [a], Lidija Čuček [a], Zdravko Kravanja [a*]

[a] University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, 2000 Maribor, Slovenia

[*]Corresponding author: Zdravko Kravanja (zdravko.kravanja@um.si)

Abstract: Increasing energy demand and the associated environmental impact require a rapid transformation of the energy system. To accelerate the transition to a renewable energy system, synergies between renewable energy production, energy efficiency improvement and technology development must be achieved. This contribution presents the synthesis of renewable energy supply networks to achieve 100 % renewable energy supply within the EU by 2050. The generation and supply of renewable electricity, heat, first, second and third generation biofuel, hydrogen and bioproducts from different renewable energy sources are considered. A dynamic mixed-integer linear programming model is formulated with maximization of the sustainability net present value [1] as the objective, considering yearly, monthly, daily and hourly time periods. Our previous study [2] is extended with energy integration within the end-use sectors to reduce primary energy consumption and thus increase the efficiency of the system. The results reveal the impact of electrification of the road transport sector, residential sector and services. Heat pumps powered by renewable electricity are expected to be a key technology for meeting heating demand in the residential and service sectors, accounting for about 60 % of final consumption. All sectors combined are expected to almost double current electricity demand by 2050. Biomass CHP is also expected to increase by 2050, providing 33 % of the residential sector's heat demand. Coal-fired thermal power plants are expected to be gradually replaced by cogeneration systems

Keywords: energy efficiency, sustainability, renewable energy, supply networks synthesis.

References:

1. Ž. Zore, L. Čuček, D. Širovnik, Z. Novak Pintarič, Z. Kravanja, Maximizing the sustainability net present value of renewable energy supply networks, Chemical Engineering Research and Design 131, 245-265, 2018.
2. S. Potrč, L. Čuček, Ž. Zore, Z. Kravanja, Synthesis of Large-Scale Supply Networks for Complete Long-term Transition from Fossil to Renewable-based Production of Energy and Bioproducts, Chemical Engineering Transactions 81, 1039-1044, 2020.

Extraction of Phosphorus from Municipal Sludge and Use of Residue in Construction Sector

Primož Oprčkal [a*], Ana Mladenović [a], Alenka Mauko Pranjić [a]

[a] Slovenian National Building and Civil Engineering Institute, Dimičeva ulica 12, 1000 Ljubljana

[*]Corresponding author: Primož Oprčkal (primoz.oprckal@zag.si)

Abstract: Approximately 38,000 tonnes of municipal sludge (dry mass) are produced annually in Slovenia. Most of it is exported, and there is often no traceability in term of further management. What remains in the country goes partly into incineration, and partly is recycled into construction products and used for geotechnical applications. It is expected that in the future, in parallel with the increase in the capacity and efficiency of wastewater treatment, the amount of sludge generated will also increase. It is for certainly expected that extraction of phosphorus and possibly other nutrients out of sludge will come into force in the coming years in the EU and on the national levels. Phosphorus is on the list of critical raw materials and is one of the raw materials on which the EU is almost entirely dependent on imports.

There is intensive research in the field of selective extraction of phosphorus from sewage sludge incineration ash, which is in many EU countries already regarded as an alternative future source of phosphorus. However, due to high content of potentially toxic metals, which are usually leached from the ash during extraction process, it is still a matter of research on how to obtain quality and pure phosphate substances in economically and environmentally acceptable way. Bioleaching of phosphorus from sewage sludge can on the other hand represent a sustainable solution, by which it can be achieved relatively selective extraction of phosphorus and other nutrients (N, organic carbon) from sludge. Simultaneously, organic contaminants from sludge are degraded and are not present in the extracting solution, while metals in the large part remain the solid residue after extraction.

The recycling of the residues after phosphorus extraction is carried out by mixing a specific amount of calcium ash and the sludge. In the process of hydration and hydrolysis, the pH value rises to about 12, resulting in the destruction of pathogenic microorganisms and organic pollutants from the sludge. New mineral phases are also formed, which chemically immobilize potentially dangerous elements. Composites must be prepared with an optimal water content to achieve a consistency suitable for installation in the geotechnical fill, by compactions and installation in layers. This approach has many advantages such as relatively simple and economically acceptable recycling and installation, and the possibility of using large quantities of sludge together and locally available alternative additives, e.g. ashes.

Keywords: sewage sludge, extraction of phosphorus, construction composite, recycling, material recovery.

Drava River Sediment Management by Hydropower Company DEM

Mojca Božič [a], Vilma Ducman [b*], Mitja Kolar [c], Karmen Fifer Bizjak [b], Boštjan Gregorc [a]

[a] Dravske elektrarne Maribor, Obrežna ulica 170, 2000 Maribor, Slovenia

[b] Slovenian National Building and Civil Engineering Institute, Dimičeva ulica 12, 1000 Ljubljana, Slovenia

[c] Faculty of Chemistry and Chemical Technology, University of Ljubljana, Večna pot 113, Slovenia

[*]Corresponding author: Vilma Ducman (vilma.ducman@zag.si)

Abstract: Drava River Hydropower Company (DEM) is the owner of eight large hydropower plants and three small hydro power plants on river Drava in Slovenia. There are six hydropower plants in Alpine region, constructed in the form of river cascades. The total length of artificial accumulation lakes is 72 km, with a surface area of 15.1 km^2 and volume of 52 million m^3 of water. In the Pannonian region, Drava River hosts five hydroelectric power plants, of which two are in Slovenia and operated by DEM. The total length of the derived channels associated with these plants is 21 km, while the total length of the plants' artificial accumulation lakes is 27 km, with a surface area of 34.1 km^2 and volume of 44 million m^3. The total length of the "new river canals" is about 102 km. Sediment management is one of the most important maintenance measures implemented by DEM at the accumulation basins of hydroelectric power plants on the Drava River.

Current practice of sediment management is locally oriented, meaning that sediments are removed only in the identified problem areas. Sediment removal is carried out in the way that sediment is pumped from the bottom of river reservoir and placed where it does not obstruct the river flow and is not harmful in any other way. Removed sediment is thus mostly deposited along the riverbanks or used for construction of artificial islands in the riverbed. Because of the lack of space in the Drava River valley for sediment deposition and new imposed regulations, there is an urgent need for new solutions in sediment management.

Therefore, DEM and involved projects partners are researching new solution for use of sediment as a natural and renewable resource for new value-added product production, and thus enable the retraining of sediment from waste into a renewable source of production, e.g. brick material, alkali activated material, embankment filling material etc.

Meeting Five Editors in Chief – How to Increase your Publication Result and Success

Jiří Jaromír Klemeš [a*], Petar Sabev Varbanov [a]

[a] Sustainable Process Integration Laboratory – SPIL, NETME Centre, FME Engineering, Brno University of Technology - VUT Brno, Technická 2896/2, 616 69 Brno, Czech Republic

[*]Corresponding author: Jiří Jaromír Klemeš (klemes@fme.vutbr.cz)

Abstract: **'Publish or perish' (POP)** is a phrase that describes the pressure put on academics to publish in scholarly journals rapidly and continually as a condition for employment (finding a job), promotion, and even maintaining one's job as defined by Imad A. Moosa in his monograph from 2018. In the Oxford Dictionary of Phrase and Fable, 'publish or perish' is used to refer to an attitude or practice existing within academic institutions, whereby researchers are put under pressure to produce journal publications in order to retain their positions or to be deemed successful. The POP issue is primarily relevant to those working in academic institutions (called academics, academic researchers, or just researchers). This is a condensed description of how important are publication activities. This has been already widely practised by world-leading universities in the past century, however with the nearly exponential growth of researchers and also scientific journals becomes one of the key issues.

This workshop presentation gathered a wide range of editors serving a variety of journals and world-leading publishers to be available to share their experience with the attendees:

Editors in Chief:

1. JOURNAL OF CLEANER PRODUCTION, Elsevier
2. CLEANER ENGINEERING and TECHNOLOGY (CLET) - Elsevier - GA
3. CLEANER CHEMICAL ENGINEERING (CLCE) - Elsevier - Golden Access
4. CLEANER ENERGY SYSTEMS (CLES) - Elsevier - Golden Access
5. CHEMICAL ENGINEERING TRANSACTIONS, AIDIC Milano, Italy

Associate, Subject and European Regional Editors:
JOURNAL OF CLEANER PRODUCTION, Elsevier
INTERNATIONAL JOURNAL OF ENERGY RESEARCH, Wiley
ENERGY, Elsevier
CLEAN TECHNOLOGIES AND ENVIRONMENTAL POLICY, Springer

The topics to be discussed cover at least briefly: writing a potential successful scientific manuscript, selection of a right journal and their metrics, various types of paper submission, Selecting and using the right references, similarity and plagiarism, correct

novelty reasoning and presentation of the proposed methods and the results, proper conclusions writing, how to handle the reviewing process, final proofing, presentation and promotion of the published paper. Examples of successful publications will be given, with analysis of the features leading to their high impacts.

The Workshop is going to be followed by dedicated consultations of specific and individual features.

Acknowledgements: Support provided by the project "Sustainable Process Integration Laboratory – SPIL", project No. CZ.02.1.01/0.0/0.0/15_003/0000456 funded by EU "CZ Operational Programme Research and Development, Education", Priority 1: Strengthening capacity for quality research.

References:

1. Moosa I A, Publish or Perish, Perceived Benefits versus Unintended Consequences, 2018, Elgar online, doi: /10.4337/9781786434937.00007.
2. The Oxford Dictionary of Phrase and Fable, 2006, Oxford University Press, doi: 10.1093/acref/9780198609810.001.0001.

Author Index

Š

T

V

W

Z

Ž