

# TBMCE

# 2022

5<sup>th</sup> International Conference on  
**TECHNOLOGIES & BUSINESS MODELS  
FOR CIRCULAR ECONOMY**

**BOOK OF ABSTRACTS**



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University of Maribor Press





University of Maribor

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Faculty of Chemistry and  
Chemical Engineering

# **5<sup>th</sup> International Conference on Technologies & Business Models for Circular Economy**

Book of Abstracts

Editors

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**Miloš Bogataj**

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September 2022

<b>Title</b> <i>Naslov</i>	<b>5<sup>th</sup> International Conference on Technologies &amp; Business Models for Circular Economy</b>
<b>Subtitle</b> <i>Podnaslov</i>	<i>Book of Abstracts</i>
<b>Editors</b> <i>Uredniki</i>	Sanja Potrč (University of Maribor, Faculty of Chemistry and Chemical Engineering)  Miloš Bogataj (University of Maribor, Faculty of Chemistry and Chemical Engineering)  Zdravko Kravanja (University of Maribor, Faculty of Chemistry and Chemical Engineering)  Zorka Novak Pintarič (University of Maribor, Faculty of Chemistry and Chemical Engineering)
<b>Technical editors</b> <i>Tehnična urednika</i>	Jan Perša (University of Maribor, University Press)  Dunja Legat (University of Maribor, University Press)
<b>Cover designer</b> <i>Oblikovanje ovitka</i>	Jan Perša (University of Maribor, University Press)
<b>Cover graphics</b> Grafika na ovitku	TBMCE 2022, University of Maribor, Faculty of Chemistry and Chemical Engineering and DialogCo d.o.o.
<b>Graphic material</b> <i>Grafične priloge</i>	Authors of proceedings, Potrč, Bogataj, Kravanja, Novak Pintarič, 2022
<b>Conference</b> <i>Konferenca</i>	TBMCE, International Conference on Technologies & Business Models for Circular Economy
<b>Date and location</b> <i>Datum in kraj</i>	September 12 <sup>th</sup> to September 14 <sup>th</sup> 2022, Portorož, Slovenia
<b>Organizing Committee</b> <i>Organizacijski odbor</i>	Zdravko Kravanja (University of Maribor, Slovenia), Miloš Bogataj (University of Maribor, Slovenia), Zorka Novak Pintarič (University of Maribor, Slovenia), Dragica Marinič (Chamber of Commerce and Industry of Štajerska, Slovenia), Andreja Nemet (University of Maribor, Slovenia), Mojca Slemnik (University of Maribor, Slovenia), Mojca Škerget (University of Maribor, Slovenia), Katja Kocuvan (University of Maribor, Slovenia), Samo Simonič (University of Maribor, Slovenia), Klavdija Zirngast (University of Maribor, Slovenia), Sanja Potrč (University of Maribor, Slovenia), Sabina Premrov (University of Maribor, Slovenia) & Sonja Roj (University of Maribor, Slovenia).

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**Published by**  
*Založnik*  
**University of Maribor University Press**  
Slomškov trg 15, 2000 Maribor, Slovenija  
<https://press.um.si>, [zalozba@um.si](mailto:zalozba@um.si)

**Issued by**  
*Izdajatelj*  
**University of Maribor Faculty of Chemistry and Chemical Engineering**  
Smetanova ulica 17, 2000 Maribor, Slovenija  
<https://www.fkkt.um.si/>, [fkkt@um.si](mailto:fkkt@um.si)

**Publication type**  
*Vrsta publikacije*  
E-book

**Edition**  
*Izdaja*  
1<sup>st</sup>

**Available at**  
*Dostopno na*  
<http://press.um.si/index.php/ump/catalog/book/714>

**Published at**  
*Izdano*  
Maribor, September 2022



REPUBLIKA SLOVENIJA  
MINISTRSTVO ZA GOSPODARSKI  
RAZVOJ IN TEHNOLOGIJO



EVROPSKA UNIJA  
EVROPSKI SKLAD ZA  
REGIONALNI RAZVOJ  
NALOŽBA V VAŠO PRIHODNOST

This investment is co-financed by the Republic of Slovenia and the European Union Fund for Regional Development”



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/ Univerza v Mariboru, Univerzitetna založba

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CIP - Kataložni zapis o publikaciji  
Univerzitetna knjižnica Maribor

330:502.131.1(082) (0.034.2)

INTERNATIONAL Conference on Technologies & Business Models for Circular Economy (2 ; 2019 ; Portorož)

5th International Conference on Technologies & Business Models for Circular Economy, [September 12th to September 14th 2022, Portorož, Slovenia] [Elektronski vir] : book of abstracts / editors Sanja Potrč ... [et al.]. - E-knjiga. - Maribor : University of Maribor, University Press, 2022

Način dostopa (URL): <https://press.um.si/index.php/ump/catalog/book/678>  
ISBN 978-961-286-646-4 (pdf)  
doi: 10.18690/um.fkkt.6.2022  
COBISS.SI-ID 120366595

**ISBN** 978-961-286-646-4 (pdf)

**DOI** <https://doi.org/10.18690/um.fkkt.6.2022>

**Price**  
*Cena* Free copy

**For publisher** prof. dr. Zdravko Kačič,  
*Odgovorna oseba založnika* Rector of University of Maribor

**Attribution** Potrč, S., Bogataj, M., Kravanja, Z., Novak Pintarič, Z.,  
**Čitiranje** (eds.). (2022). *5th International Conference on Technologies & Business Models for Circular Economy: Book of Abstracts*. Maribor: University Press. doi: 10.18690/um.fkkt.6.2022

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# Hydrogen-Based Military Energy Hub

URBAN ŽVAR BAŠKOVIČ, MITJA MORI, BOŠTJAN DROBNIČ, ROBERT ŠIPEC,  
TOMAŽ KATRAŠNIK

In recent years, renewable energy has attained a lot of attention due to the pledge to reduce carbon footprint, which was in European Union recently introduced through Green Deal (European Commission, 2019) and later amended with Fit for 55 package (European Commission, 2021). In addition, current energy crisis, which is to a large extent a result of past increasing dependence of Europe on Russian gas, calls for an energy independence. To reduce emissions of greenhouse gasses and secure robust energy supply, a shift from fossil fuels towards renewable energy is essential. One of the promising solutions to implement a higher share of renewable energy into power systems are micro and smart grids, which operate as energy hubs, based on renewable energy sources.

To overcome the issues of electricity supply stability, energy hubs usually incorporate some form of energy storage, which saves energy during production peaks and releases it during production lows. Hydrogen is one of the promising energy vectors, used in energy storage systems since it can be stored for a long time without

degradation. Late developments in hydrogen mobile applications present additional benefit for hydrogen production in energy hubs since it can be directly used to support hydrogen mobility, which is one way towards future sustainability targets for long-haul heavy-duty mobility. Hydrogen fuel-cell technology is namely expected to play an important role in heavy-duty mobile applications in the future and due to its additional specific strategical, operational and tactical aspects, hydrogen vehicles are suitable also for military applications.

To address the above-mentioned challenges and opportunities, this study analyses military-civil collaboration on green energy production and mobility while considering military-specific demands. The overarching goal of the study was to design a hybrid energy positive hub based on renewable electricity production and hydrogen storage within a military base in Kranj, Slovenia, which would fulfil all military standards, among which autonomous operation over 3-, 10- and 30- day periods present a major design restriction. Interconnection between military and civil sectors was established through hydrogen filling stations that could efficiently support local civil hydrogen mobility during non-crisis times as well as military vehicles independently on energy crisis level.

Designed energy hub consists of various energy conversion, storage and management blocks such as photovoltaic powerplant, hydrogen storage tank, fuel cells, Li-Ion battery stack, hydrogen and possibly electric filling stations and a smart energy management system. Energy hub interacts with external hydrogen and electricity networks as a producer or consumer depending on the needs of the system and external factors including hydrogen consumption on filling stations. Sizing of the energy hub components was subjected to a parametric evaluation to provide optimal energy hub design for set demands and following military demands, it can operate autonomously for up to 30 days depending on a yearly season when facing disruptions in external energy supply. The military site with this topology and management can represent a carbon footprint sink in the country because of avoided environmental impacts due to excess green electricity and H<sub>2</sub> distribution to civil sector.

**Keywords:** energy hub, hydrogen, renewable energy, military, mobility.

## Acknowledgement

EU Structural Reform Support Service (SRSS): Ministry of Defence – SRSS (DG Reform) – Support for Sustainable Energy and Mobility in the Slovenian Defence Sector

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<https://doi.org/10.1017/CBO9781107415324.004>
- European Commission. (2021). Fit for 55 package.

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# Interfacial Zones of Fly Ash based Alkali Activated Adhesives

WOLFGANG WISNIEWSKI, VILMA DUCMAN

Adhesive building materials are used to join various components and are often cement based. The high CO<sub>2</sub>-footprint of cement calls for its substitution by more environmentally friendly alternatives such as alkali activated (AA) materials based on industrial wastes such as fly ash or furnace slags. Ideally, such an adhesive forms a chemical bond at the interface with a substrate and additionally interlocks with it mechanically. This interfacial zone (ITZ) presents a critical point in the strength and durability of such composites. Alkaline and alkaline-alkali-earth aluminosilicate hydrates if formed in the ITZ have crucial contribution to its properties (Krivenko et al., 2020).

The presented work addresses the interfaces formed between AA adhesives and concrete, ceramic tiles, a woodbased geopolymer (WDP) and a high density geopolymer (Frankovic et al., 2020). After testing the adhesive properties of a variety of prepared adhesive mixtures, the most promising are selected and the formed interfaces are analysed in detail using electron microscopy. Crack formation and chemical information is evaluated to show that both selected adhesives form very different interfaces to the respective materials.

The interface to concrete implies a good adhesion at low magnifications but a closer look reveals systematic cracking near the interface. The most noteworthy chemical information is an accumulation of K in the adhesive near the interface. The interface to ceramic tiles also implies a good adhesion with fewer cracks, but a chemical reaction is not indicated.

The WDP shows a very heterogeneous interface where either the wood or the geopolymeric matrix are in contact to the adhesive. The wood – adhesive interface shows mechanical interlock as the adhesive fills the pores in the wooden structure. The geopolymer – adhesive interface is characterized by far-ranging cracks but also local mechanical interlocks and areas of direct contact implying a chemical reaction. Similar cracks occur at the HDGP – adhesive interfaces but clear indications of local connections via chemical reactions are located. The formation of a Ca-enriched layer between the HDGP and the adhesive bulk is observed and its microstructure is analysed in detail by advanced electron microscopy.

**Keywords:** alkali activated adhesive, fly ash, interfacial zone (ITZ), pull-off strength, SEM EDXS

### **Acknowledgement**

This research was funded by the Slovenian Research Agency (ARRS) via program P2-0273 “Building structures and materials”.

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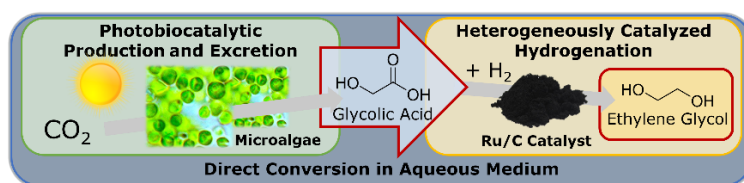
# Ru-Catalysed Conversion of Glycolic Acid Generated via New Green Chemistry

MICHAEL GOEPEL, FLORIAN M. HARTH, CHRISTIAN WILHELM,  
ROGER GLÄSER

To enable the production of established commodity chemicals on the basis of renewable resources, a plethora of challenges in process engineering, catalyst development and the general design of value chains needs to be overcome. In this context the concept of New Green Chemistry (Taubert et al., 2019) exhibits great potential since it allows the production of the platform chemical glycolic acid (GA) without inefficient harvesting steps by using algae directly as microbioreactors, which excrete the glycolic acid into the surrounding medium. Converting the so obtained solutions of the platform chemical GA into value-added product, however, faces the same problems mentioned above as most biomass-based feedstock chemicals. Concerning the value chain, this study focuses on the conversion of GA to ethylene glycol (EG) since its potential use as polymer precursor (Figure 1).

In terms of catalyst design, while Ru was established as promising active phase in the literature for the conversion of biomass-based platform chemical (in aqueous media), less attention has been paid to the influence of supports on catalytic activity. We are therefore investigating the role of the support using Ru-based catalysts for the conversion of aqueous GA solutions, finding out that activity is mainly governed by Ru dispersion and reducibility of the Ru species (Harth et al., 2021). Also bimetallic catalysts combining Ru/C with other noble metals were investigated to further increase catalytic activity. Among the investigated noble metals, Re proved to be most beneficial and the sequence in deposition resulting in the bimetallic catalyst was also found to have strong effect on the catalytic activity.

While producing GA via New Green Chemistry offers multiple advantages, biologically necessary additives in the formed GA solution may lead to new challenges in subsequent processing steps. We therefore also investigated the influence of these additives on the catalytic activity of Ru supported on activated carbon (Ru/C) in the reduction of GA to EG. Results show that some key sulfur-containing molecules are responsible for the majority of activity loss. With this knowledge resulting in the adjustment of the algal based-GA production and some further pretreatment, the processing of real algal-derived GA solutions using Ru/C is possible with moderate yields (Harth et al., 2022).



**Figure 1:** Combination of algal-based photobiocatalytic formation of glycolic acid from CO<sub>2</sub> and sunlight with subsequent heterogeneously catalyzed hydrogenation to obtain industrially demanded ethylene glycol (Harth et al. 2022).

**Keywords:** new green chemistry, biomass, ru-catalysis, bimetallic catalysts, algae, glycolic acid, ethylene glycol

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# Insights into Deactivation of Solid Deoxydehydration Catalysts by Rhenium Leaching

FLORIAN M. HARTH, BRIGITA HOČEVAR, MIHA GRILC, BLAŽ LIKOZAR

The heterogeneously catalyzed removal of oxygen from functionalized compounds is an important process for the production of renewable chemicals and materials from biomass. In recent years, a Re-catalyzed deoxydehydration (DODH) reaction has attracted research attention (Petersen and Fristrup, 2017). It enables the selective removal of vicinal pairs of hydroxyl groups, which is a common feature of sugar-derived chemicals as well as glycerol. The catalytic DODH reaction can, e.g., be applied to obtain adipic acid from sugar-derived feedstocks, a process that was initially developed with molecular catalysts (Li et al., 2014) but lately also heterogeneously catalyzed approaches have been reported for this reaction (Hočevar et al., 2021). What often limits the applicability of solid Re catalysts for DODH reactions is their insufficient recyclability and, in particular, their proneness to leaching of Re, which has been reported in several studies (Denning et al., 2013; Sandbrink et al., 2016; Sharkey and Jentoft, 2019; Meiners et al., 2021).

To understand how material properties and reaction conditions influence Re leaching and catalyst deactivation of solid Re-containing catalysts applied in DODH reactions, we compare and discuss the available literature in this study. It has been shown that, e.g., the support material can significantly influence the stability of supported Re catalysts and in particular TiO<sub>2</sub> has been shown to prevent Re leaching compared to other support materials such as SiO<sub>2</sub> or activated carbon (Sandbrink et al., 2016). Besides, catalyst pretreatment, such as reduction to decrease the amount of soluble Re oxide species, can be used to enhance the stability of DODH catalyst (Hočevár et al., 2021). In terms of reaction conditions, polar solvent have been shown to facilitate Re leaching (Sharkey and Jentoft, 2019). These and other parameters will be critically assessed, in particular regarding the role of the Re oxidation state.

Interestingly, the present of the reactant can also play a significant role since it can act as a complexing agent increasing the solubility of Re species in unpolar solvents (Sharkey and Jentoft, 2019). Thus, the DODH reaction appears to be particularly susceptible to Re leaching. However, this phenomenon is also depending on the stage of the reaction and Re leaching and redeposition are occurring at different stages of the catalysts' lifetimes. This indicates the relevance of taking into account the possibility of homogeneously catalyzed reactions that can obscure the mechanism of the reaction. Understanding the phenomenon of Re leaching, on the other hand, also opens the possibility approaches such as release-and-catch catalysis (Sharkey and Jentoft, 2019) as well as in-situ preparation of Re catalysts (Ly et al., 2020).

**Keywords:** heterogeneous catalysis, deactivation, catalyst stability, dehydroxylation

### Acknowledgement

This work was funded by the Slovenian Research Agency (ARRS) under core funding P2-0152 and project number J1-3020. Furthermore, funding from the Young Researchers Programme from ARRS is acknowledged.

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# Pretreatment, Fractionation and Upgrading of Biomass to Platform and Value-Added Chemicals

MIHA GRILC, BLAŽ LIKOZAR

In this conference contribution, the technologies required to convert lignocellulosic biomass into value-added chemicals will be presented. The conversion starts with fractionation of biomass by namely separation of extractives, cellulose, hemicelluloses and lignin. Lignin-first approach initially solubilizes and partly depolymerizes the lignin (after extractives are isolated). Subsequently lignin is precipitated by the anti-solvent addition, while hemicelluloses and their resulting furanics remain dissolved even in highly polar media. Cellulose remains solid and is easily filtered before being further bleached (for fibers) or further hydrolyzed to C6 building blocks.

Cellulose-originating and hemicellulose-based C6 building blocks, namely hexoses are desired to be catalytically converted to platform chemicals 5-hydroxymethylfurfural and/or aldaric acids. Their final functionalization leads highly added products like furanic or tetrahydrofuran diols (BHMTHF) and adipic or furandicarboxylic acid. On the other hand target products from C5 sugars are

furfural, furfuryl alcohol, levulinic acid or gamma-valerolactone. Lignin on the other hand is a promising source of bio-based aromatics. Technologies developed and patented at NIC will be demonstrated at the conference.

**Keywords:** heterogeneous catalysis, biorefinery, fractionation, functionalization

### **Acknowledgement**

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

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# Glucose Oxidation to Glucaric Acid: Microkinetic Modeling of Heterogenous Catalysis

ŽAN LAVRIČ, JANVIT TERŽAN, ANJA SEDMINEK, ANA KROFLIČ,  
BLAŽ LIKOZAR, MIHA GRILC

The use of bio-renewable materials for the production of chemicals which are usually produced from oil, has become important in the last few decades. Glucose, which can be extracted from cellulose and later converted to many useful products, one of them being glucaric acid (Derrien et al., 2017). The latter is commercially produced by nitric acid oxidation, merely because of the low cost of the oxidant. Since the process is not environmentally favorable, heterogenous catalysis was investigated with different gold monometallic and bimetallic catalysts such as AuPt and AuCu. All experiments were carried out in 75 mL Parr reactors under oxygen pressure. The tested catalysts were all based on ZrO<sub>2</sub> supporting material. All catalysts were able to produce some glucaric acid, however AuPt gave the highest yield of the product, reaching 30 % yield. In order to fully understand the key limiting steps of the process, a microkinetic model was composed for a three-phase batch reactor, considering the transfer of oxygen into liquid phase and all of the species from liquid to a solid phase,

where reaction took place. Such description provides an in-depth understanding of the reaction pathway and is able to predict the optimal temperature and time of operation.

**Keywords:** glucose, glucaric acid, bimetallic catalyst, bio-renewable, microkinetic modelling

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# Thermochemical Conversion of Industrial Waste for Sustainable Energy Recovery

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TJAŠA CENČIČ PREDIKAKA, LIDIJA ČUČEK

The steadily increasing demand for energy in recent decades, fluctuating prices and energy-related pollution has led to various initiatives by people, governments and industries to transit towards renewable and alternative energy sources. More sustainable energy can be generated by using various technologies including biochemical and thermochemical processes and various alternative energy sources such as biomass, solar, hydro, geothermal and wind energy (Siwal et al., 2021). In addition, the use of biomass and different types of organic waste for energy recovery contribute to the reduction of greenhouse gas (GHG) emissions, circular economy, and more economically-efficient operation. The most used thermochemical processes for energy recovery from waste biomass are pyrolysis and combustion, while hydrothermal carbonization (HTC) has become increasingly important in recent years. HTC is considered as a promising thermochemical technology for the conversion of wet biomass into solid biofuel, i.e. hydrochar, since drying of biomass

is not required. The hydrochar obtained has higher heating values, better thermal stability, and improved fuel properties compared to the raw biomass (Pauline and Joseph, 2020).

The potential of different biomass types for energy recovery, including various types of organic waste, sewage sludge, agricultural residues and industrial by-products and waste, has previously been investigated using thermogravimetric analysis (TGA) (Magdziarz et al., 2020). The edible oil industry produces large amounts of various by-products and waste, such as spent bleaching earth and various oil press cakes, including sunflower, sesame, hemp, and pumpkin oil cakes. These are energy-rich materials and could be used for energy recovery. In addition, the energy recovered from these waste materials can be reused in oil production, which is energy intensive process. However, despite significant potential of these waste materials for energy recovery, only few studies exist on their use in the HTC process.

In this study, TGA of combustion and pyrolysis of untreated and HTC-treated industrial waste i.e. pumpkin seed oil press cake was performed. HTC was performed at the selected temperature and reaction time in an autoclave reactor with a volume of 300 mL. The raw biomass and hydrochar obtained by HTC were subjected to TGA measurements, which were performed in the temperature range of 25-900 °C and a heating rate of 20 °C/min. To analyze the combustion behavior, the experiments were performed under air atmosphere, while the pyrolysis behavior was studied under inert atmosphere (ensured by N<sub>2</sub> flow). The main properties of the raw biomass and hydrochars obtained from the HTC experiments were studied, such as the calorific value, volatile matter content, and ash content. The changes in carbon content were studied by elemental analysis. Finally, the potential of the tested materials for energy recovery was evaluated.

**Keywords:** energy recovery, industrial waste, hydrothermal carbonization, combustion, pyrolysis, thermogravimetric analysis

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# Urban Water-Food-Energy Interdependences: Solving Urban Challenges Together

MOHAMED HACHAICHI, JAFARU MUSA EGIEYA, NEILL GOOSEN

Around the world, cities are experiencing rapid population growth, increased affluence, urbanization, and economic growth, all of which are constraining how water, food, and energy are used. To achieve sustainable development that advocates enhancing human well-being and reducing poverty, it is necessary to gain a deeper understanding of how water, food, and energy interact in the water-food-energy (WFE) nexus. On the other hand, a diverse array of approaches has been adopted in the circular economy space since applying the WFE nexus, which examines how the utilization of these limited resources interrelate can foster and increase their efficiency for re-use. In the circular economy space, multiple approaches have been applied following the application of the WFE nexus, where the utilization of these limited resources interrelates to make them more efficient for re-use. This study uses machine learning with natural language processing (NLP) and a propensity propagation algorithm to investigate and assess the research corpora of the WFE nexus on both a regional and city level in the last 30 years. The results of a literature review of 32,736 case studies on 2,233 cities indicate that cities with the greatest

potential to encounter resource constraints (WFE limitations) are significantly underrepresented in literature (African and Latin American cities). Therefore, regional and topical bias can lead to the development of more mutual learning links between cities that can contribute to the expansion of WFE policy exchange between the Northern and Southern hemispheres. Additionally, this study shows that cities in the Southern Hemisphere may be able to benefit from knowledge transfer due to their limited urban intelligence programs.

**Keywords:** water-energy-food nexus, machine learning, African cities, Latin American cities, knowledge production, circular economy (minimum 5)

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# Preliminary Study on the Possibilities of Centralized Treatment of Waste Sludge in Slovenia

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ZORKA NOVAK PINTARIČ

In Slovenia, waste sludge was exported abroad until 2019, after which transportation became much more limited and expensive. In Slovenia, only 15 % to 20 % of sewage sludge is treated and disposed of. Some of it is incinerated, about 5 % is processed into geotechnical composites used to fill landfills, and 3 % is used as fertilizer. The remaining 80 % to 85% is exported to other countries. With appropriate technologies, sewage sludge can be converted into heat and various products (Raheem et al., 2018). One of the established technologies is incineration with its variants, while newer technologies include pyrolysis, vitrification, and gasification.

The aim of this work, carried out as part of a student project, is a techno-economic study of three thermal technologies for sludge treatment: incineration, gasification and pyrolysis (Luo et al., 2021). It is assumed that the annual amount of waste sludge in Slovenia is about 80,000 t/yr and contains about 20 % dry matter. In this study,

the problem of sludge was considered from the perspective of the community as a whole, rather than from the perspective of individual companies in the sludge supply chain.

First, various data were collected and calculations of mass balances and composition of products were performed. In the second step, a linear optimization model was developed for the selection of optimal technologies. It included estimates of energy and transportation costs, revenue from the sale of the potential products, and total investment. The optimization was performed with different objective functions: maximizing the economic value of the products and profit, minimizing operating costs (especially energy consumption), and greenhouse gas emissions. Pyrolysis proved to be the optimal choice for maximizing economic performance and gasification for minimizing emissions. Incineration was not selected as the optimal alternative, but had the lowest investment value.

A more detailed economic analysis was performed for pyrolysis. The process was divided into four operations: drying, crushing, pyrolysis, and condensation of the gaseous products. Downstream processing of the products was not considered. The costs of energy, labor, transportation to a central site, and associated greenhouse gas emissions were considered. For centralized processing of 80,000 tons of sludge per year, fixed capital was estimated at 15 million euros and working capital at 4 million euros. It was found that at a discount rate of 10 % and without the sale of pyrolysis products, a net present value of zero is achieved at a sludge price of about 235 €/t. Since the products (bio-oil, syngas, biochar and heat) have some market value, it is realistic to expect that the break-even price of sludge could be further reduced. Decentralized sludge drying and heat integration would also help reduce costs and emissions. It can be concluded that the investment in a pyrolysis plant could be justified because, despite the medium risk, it would allow the sludge to be processed into useful products at a lower cost than the current export price, which is expected to continue to rise.

**Keywords:** sludge, pyrolysis, linear programming, optimal technology, techno economic analysis

## **Acknowledgement**

Funding from the Slovenian Research Agency and the Ministry of Agriculture, Forestry and Food (project V2-2009 and program P2-0414) is acknowledged.

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# Activation and Thermostability of Lipase in Deep Eutectic Solvents

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UROŠ NOVAK

Lipases are a group of water soluble enzymes that catalyse the hydrolysis of ester bonds in lipid substrates with poor water solubility. Some of them have the ability to catalyse esterification, transesterification, aminolysis and acidolysis processes while showing enantioselective properties. Because of their unique features and biotechnological potential they have been employed in many industries (Stoytcheva et al., 2012). Most of these industries use volatile organic solvent – based processes and therefore present a serious concern for their proper usage in terms of green and sustainable technology. Deep eutectic solvents (DESs) present a good alternative because of their low toxicity, biocompatibility and biodegradability (Tan in Dou 2020). Their utilization is in electrochemistry, catalysis and extraction processes. One of many advantages is that they can also provide thermostabilization of commercially important enzymes at elevated temperatures (Bjelić et al., 2020)

Our work is based on studies of lipase B catalytic activity isolated from *Candida antarctica* (Novozym 435). Lipase catalytic activity and stability was primarily obtained at different temperatures and further on at optimum temperature while changing pH value of the incubation buffer. Two milligrams of enzyme was preincubated at a particular temperature (temperature range 30 – 90°C) for 30 minutes in Tris/HCl buffer. Afterwards that the substrate solution was added and the mixture incubated at 37°C. Our experiments showed that the enzyme performs best while being preincubated at 30°C with a steady decrease of activity with the increase of temperature. There was only minimal activity at 80°C and no measurable activity at 90°C, indicating that the enzyme was completely deactivated. Influence of pH was performed at 30°C in McIlvaine buffer with pH ranging from 3 – 8. The highest activity was expressed at pH 5, which can be due to the structure and protonation effect at these particular conditions. We have also done similar experiments to determine activation and thermostability in selected DES. The enzyme was incubated at 30°C for 30 minutes in selected DES. The DES were then diluted, removed and the substrate solution was added to the enzyme to measure the activity. Same experiments were also performed at 80°C. The results showed that the enzyme's activity at 30°C was increased by up to 2-fold and up to 5 to 7-fold at 80°C compared to Tris/HCl buffer. These results show that some of the selected DES mixtures have strong thermostabilizing effects and enable us processes at higher temperatures without significant loss of enzyme function.

**Keywords:** lipase; deep eutectic solvents; activation; thermostability; green technology

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# A Dog Rose Oil Extract as a Potential Green Corrosion Inhibitor

REGINA FUCHS-GODEC

Metallic materials are still the most commonly used group of materials. However, the usability of metals and alloys is limited by a common problem, corrosion. The most successful protective measures already known are coatings, protective paints, smart coatings, self-repairing coatings, protective films formed by adsorption processes, etc., but all in the direction of 'green orientation' and in particular toward a circular economy or waste-free or zero-waste processes. In other words: The waste may be a raw material or, due to a past deadline, be used in one area where that deadline is not relevant. For this reason, the aim of the present work is to study the corrosion inhibition properties of dog rose oil extract (as potential green corrosion inhibitor) in a hydrophobic layer on the copper surface. The chosen corrosive medium was a simulated urban acid rain solution with pH = 5, 3 and 1. The inhibitory effect of dog rose oil extract in a hydrophobic layer on the surface of copper in acidic media was studied by a classical potentiodynamic (PD) method and electrochemical impedance spectroscopy (EIS). The concentrations of added dog rose oil extract were 0.5, 1.0 and 2.0 wt.% in 0.05 mol L<sup>-1</sup> alcoholic solution of

octadecanoic acid. Based on electrochemical measurements, it was shown that the hydrophobic coating of octadecanoic acid alone is not stable in acid rain at pH = 1. The value of inhibition effect is only 70%, while it increases to over 90% when dog rose oil extract is added, depending on the addition of dog rose oil extract.

**Keywords:** copper, green corrosion inhibitor, dog rose oil extract, acid corrosion, EIS, PD

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# Social Life Cycle Assessment of Melamine Etherified Resin Fibre Production

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Social LCA (S-LCA) promotes improving a product's social conditions and overall socio-economic performance throughout its life cycle, encompassing all stakeholders. Despite the social importance of Melamine Etherified Resin (MER) fibres in our daily lives, there has been no comprehensive study to assess the social impacts of the different synthesis routes of MER fibres from different raw materials. This study investigates the social impacts of different synthesis routes for producing MER fibres. The social impact of conventional MER fibre production is analysed by considering the use of raw materials of fossil origin. Two alternative options for producing MER fibres are assessed: Alternative A involves the integration of CO<sub>2</sub> recovery from flue gases, while Alternative B involves the synthesis of wood-based methanol for formalin and further production of MER fibres.

The study assesses the social impact of MER fibre production and verifies whether the alternative synthesis pathways provide more favourable social impacts and demonstrate lower environmental impacts. The social impact assessment is conducted using the openLCA software supported by the SOCA V.1 database [1] for the Ecoinvent v3.3 database [2]. The analysis includes 53 social indicators and reflects the social impacts and associated risk levels for four stakeholder groups: workers, local community, society and value chain actors.

The results are expressed in the medium-risk hours-equivalent unit and compare conventional production with two alternatives. S-LCA results serve as additional sustainability metrics that often get less attention among the three pillars of designing sustainable MER fibre production.

**Keywords:** Melamine etherified resin fibre, Social LCA, SOCA database, Ecoinvent, Social footprint

#### **Acknowledgement**

The authors would like to acknowledge financial support from the Slovenian Research Agency for core research funding No. P2-0412 and the Slovenian Research Agency (project No. J7-3149) and the Czech Science Foundation for a joint SI-CZ project "Design and Management of Sustainable Plastic Value Chains to Support a Circular Economy Transition".

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# Sustainable Biofuel Production: The Mechanism of Microalgae Liquefaction and Hydrotreatment

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Microalgae have emerged as a promising feedstock for biofuel production. Several approaches have been considered, such as lipid extraction and further transesterification, pyrolysis and hydrothermal liquefaction. However, major challenges lie ahead in order to reach biofuel relative competitiveness with fossil fuels (Yang et al., 2018 and Yang. et al., 2016). The mechanism studies are crucial to better understand chemical reactions. The studies are also essential for further kinetic modelling and optimal operating conditions determination.

Liquefaction and catalytic hydrotreatment of *Chlorella sorokiniana* microalgae were investigated in a three-phase batch reactor over a range of reaction temperatures (200–350 °C), hydrogen pressure (0-5 MPa), dodecane solvent and commercially available bifunctional NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst. Liquid products were sampled in 30-minutes intervals and analyzed by Gas Chromatography – Mass spectroscopy (GC-

MS). The final gas product was analyzed by micro-GC (Agilent 490 Micro GC, TCD detectors equipped with PoraPLOT U and CP-CO<sub>x</sub> columns).

Several intermediates, targeted and side products were detected by GC-MS and micro-GC, that being fatty acids, aldehydes, alcohols, alkanes, alkenes and short chained hydrocarbons. A detailed reaction pathway has been proposed based on experimentally-obtained liquid and gaseous products. Liquefaction and further hydrogenolysis of triglycerides to three fatty acids was followed by hydrodeoxygenation, decarbonylation and decarboxylation to aliphatic hydrocarbons. The yield of hydrocarbons reached 56.5 %, with the products consisting mainly of C15-C18 n-paraffins. The product composition corresponded to the initial algae fatty acid methyl esters profile, which showed that the microalgae were mainly composed of C16 and C18 fatty acids.

**Keywords:** microalgae, biofuel, liquefaction, hydrodeoxygenation, one-pot reaction

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# Quantitative Monitoring of Progress Towards the Circular Economy in Utility Companies

GREGOR UHAN, ZORKA NOVAK PINTARIČ

Circular economy is one of the approaches to solve the problem of resources, waste and emissions, through which the economy can become more environmentally and socially friendly. The concept of circular economy contributes to all dimensions of sustainable development (Ellen MacArthur Foundation, 2013). In order to systematically monitor the progress of businesses and society towards a circular economy, indicators and metrics need to be introduced at the macro and micro levels that allow for visualization, analysis and identification of bottlenecks. In this work, the research focuses on the economic sector of waste management. There is often no comprehensive overview of the progress that individual companies and the sector as a whole are making towards a circular economy. The objective of this work is to demonstrate the implementation of circular economy monitoring in a company engaged in the collection and processing of municipal waste. For this purpose, the

approach developed by Baratsas et al. (2022) was used to evaluate companies at the micro level.

The first phase involved an analysis of three companies that collect municipal waste. The analysis monitored separately collected municipal waste on an annual basis. It was found that rural citizens separate municipal waste to a lesser extent than citizens in larger cities. Although the total number of residents is greater in rural communities than in urban centers, the latter generate more municipal waste because they have more industry, commuters, and tourists.

In the second part, the categories for the company from the urban area were defined, which would be used to measure progress towards the circular economy: waste, water, and emissions. For each category, indicators that the company has been monitoring for several years were selected and transformed into dimensionless metrics and category sub-indices: a) in the "waste" category, the percentage of separately collected municipal waste to the total amount of municipal waste collected; b) in the "water" category, the percentage of treated wastewater to the total amount of industrial wastewater generated; and c) in the "emissions" category, the normalized ratio between the mass of total greenhouse gas emissions and the mass of mixed, non-separated solid waste. The calculated metrics were then combined with the linear average to form the Overall Circularity Index, which is an aggregate indicator for monitoring the transition to a circular economy.

The results were recorded for the monitoring period from 2017 to 2021. It can be seen that the company's Overall Circularity Index improved by about 30 % over this period, with the curve flattening in recent years. The individual categories show a slow but steady improvement in the percentage of separated waste, while the percentage of treated wastewater has increased again in the last two years after a decrease in 2018 and 2019. The emissions category has improved the most. This trend will continue as the company plans to gradually close the landfill in the coming years, which will further contribute to reducing emissions and improving the Overall Circularity Index.

**Keywords:** utility company, waste management, circular economy, progress, overall circularity index, water, emission



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# MSWI Fly Ash as a Secondary Resource for Elements and Construction Materials

GUNVOR M. KIRKELUND, LISBETH M. OTTOSEN

Municipal solid waste incineration (MSWI) plays an important part in waste management strategies, as it significantly reduces the volume of municipal solid waste and the embodied energy can be recovered. Apart from energy, by-products in form of particulate materials such as bottom and fly ash are also produced. Bottom ash is already valorized in several countries, mainly in road construction or embankments, after metals are separated for recycling.

MSWI fly ash is a highly alkaline material that contains high content of soluble salts, and organic and inorganic contaminants and is therefore classified as hazardous waste. The MSWI fly ash is backfilled in mines or disposed of at hazardous waste disposal sites, although these strategies do not promote future recovery of resources in the MSWI fly ash. The potential resources in MSWI fly ash include base metals for industry (for instance Cu, Pb, Zn), critical elements (European Commission, 2020) such as Sb, Ti and REE and ash particles containing Al, Si, Fe and Ca which are eligible for construction materials. Some of these elements have declining natural

reserves or the natural reserves are more difficult to exploit, which means higher exploration costs. Therefore, the MSWI fly ash can be considered a secondary resource for elements and material, however, technology and methods for valorization need to be developed. One strategy to promote resource use from MSWI fly ash is the recovery of elements from the ash and using the MSWI fly ash itself after decontaminating/detoxifying the fly ash by manufacturing products containing the detoxified fly ash (Quina et al. 2018).

For element extraction and separation, an electro-dialytic treatment method was applied to the MSWI fly ash, and removal efficiencies between 80 - 95 % can be obtained for Cd, Cu and Zn. The electro-dialytically treated MSWI fly ash was tested as secondary material in cementitious material, geopolymers or ceramic bricks (Kirkelund et al. 2020, Ebert et al., 2021, Zhan and Kirkelund, 2021, Righi et al. 2022). Mechanical and environmental properties were tested for the different construction material applications. The results show that applying electro-dialytic treatment enhances the material properties of MSWI fly ash, with reduced metal and chloride content, and enriched content of Al, Ca and Si. Mechanical and environmental properties of the construction materials are improved when using the treated MSWI fly ash compared to using the raw untreated MSWI fly ash.

Electro-dialytic treatment has the potential for being a method to extract metals and increase the material properties of MSWI fly ash, so this fly ash can be an important urban mine for resource recovery in the future. This is further explored in the Horizon Europe project AshCycle, where 28 academic and industrial partners from 8 countries join efforts to integrate underutilized ashes into material cycles by industry-urban symbiosis.

**Keywords:** waste-to-energy, resource recovery, cementitious materials, alkali activated materials, ceramics, heavy metals, electro-dialytic extraction

#### **Acknowledgement**

Horizon Europe Grant Agreement-101058162-AshCycle, Erasmus +, Amager Resource Center, Aase og Ejnar Danielsens Fond and China Scholarship Council are all thanked for financial support

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# Circular Economy Approach for Ciprofloxacin Biotransformation in Wastewater Treatment

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Ciprofloxacin (CIP) is one of the most widely used fluoroquinolone antibiotics, which is frequently detected in the effluents of wastewater treatment environments (Rusch et al., 2019). This study focused on CIP degradation with the enzyme laccase. The degradation capability of CIP was determined using high-performance liquid chromatography (HPLC) analysis, which was equipped with a C18 nonpolar reversed-phase bonded column (4.6 nm x 150 mm x 5 µm) and acetonitrile:water as mobile phase (Scherer et al., 2014). In different studies, different methods of CIP degradation were used, such as ultrasonication, the influence of pH and temperature, or by addition of co-existing solutes. However, with the addition of syringaldehyde (Parra Guardado et al., 2019), a method was discovered to perform CIP degradation at room temperature. It was found that the addition of syringaldehyde improved CIP degradation over the same time period.

**Keywords:** laccase, environmental contaminants, ciprofloxacin, biodegradation, wastewater treatment

### Acknowledgement

This work has been fully supported by Slovenian Research Agency Program P2-0046 "Separation Processes and Product Design" and Research Project J2-3037 "Bionanotechnology as a tool for stabilization and applications of bioactive substances from natural sources", as well as by the Ministry of Education, Science and Sport, Slovenia, Research project Contract No. C3330-19-952031.

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# Importance of Water and Energy Integration in Circular Economy Approach

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Global water and energy consumption in various sectors (domestic, agricultural and industrial) will increase in the future due to population and economic growth. Accordingly, there is an urgent need to develop combined water and energy efficient solutions to address this issue in all sectors in line with the circular economy principles. Recent works provided definitions, strategies, and challenges for the circular economy of water (Morseletto et al., 2022), a circular economy framework for resources and waste management in the water and wastewater sector (Smol et al., 2020), and a mathematical approach for the synthesis of a wastewater treatment plant using the concept of circular economy (Ho et al., 2022). Water and energy are important resources used in large quantities in the process industries for various purposes (e.g., washing, cooling, and heating). Their consumption should be minimised in manufacturing processes to reduce operating costs and provide profitable and sustainable solutions. Wastewater generated by these processes

should not be considered as waste because it is a valuable resource for freshwater, energy, and materials. Reusing, regenerating, and recycling wastewater can provide economic and environmental benefits such as reducing freshwater and energy consumption and greenhouse gas emissions and recovering valuable materials from wastewater. To achieve these goals, systematic approaches for water and energy integration should be applied to design optimal water and energy network solutions. In the last several decades, pinch analysis, mathematical programming and hybrid approaches have been successfully applied to design combined water and energy networks with optimal water and energy consumption (Ahmetović et al., 2015, Budak Duhbaci et al., 2021). The main focus of this work is to show the importance of water and energy integration and applications of systematic methods in a circular economy approach for optimising water and energy reuse in manufacturing processes and highlight possible future directions in this research field.

**Keywords:** process integration, process synthesis, systematic methods, resource recovery, sustainable solutions, circular economy

### Acknowledgement

The authors gratefully acknowledge support from the programme for Scientific and Technological Cooperation between the Republic of Slovenia and Bosnia and Herzegovina (Project acronym: "SISUMP", No: 01-1282-1/20) and Erasmus+ programme (Project acronym: "INTERBA", Reference number: 610429-EPP-1-2019-1-AL-EPPKA2-CBHE-JP).

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# Use of Wood Biomass Ash in Prefabricated Concrete Elements

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According to the new package of proposals "Ready for 55%", member states of the European Union (EU) must commit to reducing their emissions by at least 55% by 2030. One of the proposals is the revision of the Directive on the promotion of the use energy from renewable sources (The European Parliament and the Council of the European Union, 2018), which sets a new mandatory target of 40% of energy from renewable sources (RES) compared to the current mandatory share of 32% (European Commission, 2021), with biomass power plants playing a crucial role in achieving this target. On the other hand, many countries have decided to eliminate the use of coal as an energy source for power generation in power plants and focus on the use of energy from biomass, i.e. bioenergy, which is the leader in the EU with a share of up to 60% RES. Heating and cooling account for 75% of the total bioenergy consumption (Eurostat, 2018). According to the annual report of the Croatian Energy Market Operator (CEMO) from 2021, the Croatia has a large number of biomass energy plants: there are even 42 plants with a total installed capacity of 97.068 MW, with which CEMO has signed a contract for the purchase of electricity (CEMO, 2022). Despite the many advantages of biomass energy, especially wood biomass, its combustion generates large amounts of waste - wood

biomass ash (WBA). According to estimates (Milovanović et al), the production of approximately 25.000 tons of WBA per year in Croatia is expected, with the share of ash being 3.1%, which was determined on the basis of surveys in 13 wood biomass power plants in Croatia, i.e. it is estimated that 600.000 tons of WBA will be produced and annually in the whole EU (Bogdan, 2020). However, it should be emphasized that other plants such as paper and pulp mills, furniture factories, tree nurseries, etc. also generate large amounts of WBA. WBA represents a serious environmental hazard if not properly managed because it consists of very small particles that can be airborne (Cheah et al, 2011). Due to excellent chemical, physical and mineralogical properties of WBA (Cheah et al, 2011), (Udoeyo et al, 2006), (Agrela et al, 2018), the sustainability of the precast concrete industry can be improved by using alternative supplementary-cementitious materials (SCM), using WBA as a partial replacement for cement and fine aggregates in low-carbon building materials and products. But, the complex characteristics of each WBA, which depend on the type of wood biomass and combustion technologies used in biomass power plants, as well as the lack of technical and legal regulations, present challenges in converting WBA into a secondary raw material. Therefore, the promotion of recycling, i.e. the transformation of waste from one industry - the energy sector - into raw materials from another industry - the concrete industry - contributes to the realization of the principles of the circular economy.

**Keywords:** wood biomass ash, biomass, fine aggregates, concrete industry

### Acknowledgement

This research was performed as a part of the research project KK.01.2.1.01.0049 „Development of innovative construction products using bio-ash“, which was funded by the European Regional Development Fund.

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# Microkinetics of Bio-Based Furfural Production Using h-beta Zeolite Catalyst in Various Solvents

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BLAŽ LIKOZAR

With the depletion of fossil fuel reserves, the demand for renewable energy sources has increased in recent decades. In addition, environmental pollution is a major global problem. One of the ways to solve this problem is to explore renewable energy sources (Ferreira et al. 2013). Among the various renewable energy sources, biomass has emerged as an affordable source for the production of platform chemicals. Furfural (F) is one of the many platform chemicals that can be produced from biomass, and the global annual production of F is about 652 kilotons (Rachamontree et al. 2020). So far, the production is mostly based on homogeneous catalysis using sulfuric or formic acid as catalysts (Delbecq et al. 2018). However, this process is not only harmful to the environment but can also lead to corrosion and deterioration of process equipment, so a sustainable way for F production needs to be developed. One of the options is to use heterogeneous catalysts such as zeolites

and exploit advantages such as catalyst reusability, environmental friendliness, and the possibility that the process can be carried out continuously (Kim et al. 2011). In this work, the effect of different solvents: methanol, ethanol, i-propanol and dimethyl sulfoxide (DMSO), on F yield is investigated. A commercial H-beta zeolite catalyst with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 28$  was used, and the reaction temperatures were set at 160 °C and 180 °C. The best performance and the highest F selectivity up to 40 mol% were obtained when the reaction was carried out in dimethyl sulfoxide (DMSO) and i-propanol at 140 °C. The selectivity of furfural increases with temperature in each solvent used. The order from highest to lowest yield at a temperature of 180 °C was  $\text{DMSO} > \text{i-propanol} > \text{water} > \text{ethanol} > \text{methanol}$ . A kinetic model for this reaction was then developed. The reaction rate constants and activation energies for each solvent were determined and the phenomenal empirical correlation for the previously calculated kinetic parameters was determined based on the polarity of the solvents.

**Keywords:** biomass, catalysis, zeolite, furfural, xylose, micro-kinetic model

### Acknowledgement

The authors acknowledge financial support from the EU Framework Programme for Research and Innovation Horizon 2020 under Grant Agreement No. 887226 (BioSPRINT) and from the Slovenian Research Agency (research core funding No. P2-0152, J2-2492, J2-1723, and J7-1816).

Also, authors would like to acknowledge funding from the Slovenian Research Agency (ARRS) and the Science Fund of the Republic of Serbia (SFRS) in the form of a joint bilateral project BI-RS/20-21-002. ARRS is also acknowledged for project funding J1-3020.

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# Hydrogenation of Dibenzyl Toluene over Heterogeneous Nickel Doped Catalyst

FILIP BERGELJ, BRETT POMEROY, BLAŽ LIKOZAR

Liquid organic hydrogen carriers (LOHC) are a new technology on the hydrogen energy market that has a lot of possibilities, such as storing hydrogen in a safer manner than ordinary methods, without high pressures or low temperatures (Brückner, N. et al., 2014) Organic compounds are hydrogenated, stored in the liquid phase, and then dehydrogenated when hydrogen gas is needed. This also allows the use of already existing energy infrastructures. Of these LOHC, dibenzyl toluene has emerged as one of the best options, due to its chemical and physical properties. It can absorb a lot of hydrogen, it is safe and non-expensive (Asif, F. et al, 2021). The hydrogenation reaction is a heterogeneous reaction with liquid substrate, solid catalyst, and hydrogen gas. It is conventionally performed on noble metal catalysts, which are very active but expensive. This work aims to research the option of using cheaper catalysts for this reaction, such as ones based on nickel (Ding, Y. et al., 2021).

The experiments were performed in stainless steel reactors with temperature and pressure control. The commercial nickel catalyst is supported on alumina and was beforehand reduced in a tube furnace in flow of hydrogen gas at 400 ° for three hours. Dibenzyl toluene was diluted in tetrahydrofuran and the catalyst was added, then the reactor was filled with hydrogen gas. As the goal is not only to obtain the yield and selectivity of the reaction, but also the kinetic parameters, many different parameters were tested.

The temperature range for the reaction was 170 °C – 210 °C, the pressure of hydrogen gas 25 bar, 50 bar and 75 bar. Other than that, the tests performed also included different ratios of substrate/solvent, stirring rates and amount of catalyst. Results showed that the reaction mechanism with the nickel catalyst is the same as with the noble metal (Ru/Al<sub>2</sub>O<sub>3</sub>) catalyst, showing three separate stages of hydrogenation, one for each of the aromatic rings. No detectable amounts of side products were found in these reactions. With the right conditions, the majority of dibenzyl toluene can be hydrogenated, although only to the first and second stage, while the noble metal catalyst can hydrogenate it fully to the second stage and partially to the third in the same amount of time.

This research shows that nickel-based catalysts are a viable option for hydrogenation of liquid organic hydrogen carriers. In further research, improved nickel catalysts will be synthesized to extend the scope of the hydrogenation further.

**Keywords:** LOHC, heterogenous catalysis, hydrogenation, transition metal, dibenzyl toluene

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# Identifying Circular Potential of a Business Model

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**Introduction.** Since the mid-1990s, firms have been experimenting with new ways of doing business, which has led increasing research interest for business models. Among interpretations of the meaning and function of “business models” emerged from the management literature (Ref.: 24, Massa et. al, 2016) here **business models are understood as a conceptual representation of how a business functions.** An ongoing debate about the relationship between business models and strategy, however, does not provide sufficient clarity, whether a business model of a firm is considered to be a target (or ideal) representation of its repeatable business conduct or a representation of the firm’s current practice. In the examination of a firm’s degree of circularity this dilemma is essential. While we can measure the level of the circularity of an economy (Ref.: 11, 31, 33), we understand a firm to be circular to the extent, to which it successfully engages into the circular processes within and economy in which it operates. Such an organisation has the potential and the ability to successfully interact with other actors along the value chain to closing, slowing and narrowing loops of resource flows (Ref.: 1, 4, 5, 20, 21, 22). This ability generally requires changes of the business model in use (Ref.: 1, 2, 3, 16, 17, 18, 19, 21). Therefore, we claim that from the perspective of a circular business model

transformation (Ref.: 16, 24, 27, 29), a firm increases its circularity through a transformational process, by enhancing both its circular business model potential and developing capabilities to seize it. We develop this underlying assumption in a simplified version of the “Circularity Assessment Score”, or the CAS model.

**Methods.** The CAS figures as a useful composite assessment tool of a firm’s circularity focusing on its business model. On one dimension we evaluate circular potential in a context of a value chain, while on the other one, we assess the commitment to demonstrated by managerial abilities and overall organisational practices combined are evaluated, which are needed to seize the circularity potential.

We aim to verify the understanding of the concept of the circular business model potential laid upon the evaluation of the target business model a firm pursues. This exercise does not seem to be straightforwardly simple. Therefore, a test study helps us validate the usefulness of the CAS and identify potential interferences. Results contribute to the validation of the CAS and are further used to elaborate the model and its adaptations to various industry contexts, in which we aim to examine the relationship between the circularity of a firm and the value creation. Over 50 respondents representing large, medium and small firms were attracted through various digital channels to fill in the questionnaire (26 questions, of which 16 sum up to the score, freely available on-line (Ref.: 6). 15 respondents were interviewed in-depth and analysed.

**Results.** The findings clarify how to avoid ambiguities between the actual level of the business model as applied in an observed firm and its circular business model potential, identified in the early stage of research (Ref.: 13). Furthermore, they provide useful hints and suggestions for the preparation of a more advanced CAS model.

**Conclusions.** A clear understanding of “circularity potential” evaluated by the use of the target circular business model is a significant theoretical contribution allowing to use it generally in further research. Distinguishing the potential from the actual level of circularity reached by a certain the business model is crucial for impartial assessment. This helps the validation of the CAS and examine the relationship between the level of circularity and the economic value creation.

**Keywords:** circular economy, target business model, circularity potential, economic value creation

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# Material Digital Twin: How Optimized Mass Flow Control Increases Circular Economy

MARKO BOJINOVIĆ, JAKA BURJA, GREGA KLANČNIK, LUKA KRAJNC

The following study presents advantages of having a detailed mass flow control in the production companies in heavy industry. Digital twin is widely considered the best possible solution for process and material related control and optimization of individual industrial processes by considering the actual technology used by the end user, incorporating its material component which is affecting the products quality. This is a key factor in this endeavour, and it produces significant advantages for circular economy. Knowledge on how much material, related also to quality of entering materials, is possible to introduce and how much material exits with all relevant yields for particular technological process is a key to optimize internal and external processes. For the efficient optimization it is necessary to have exact information on the quantity, type (chemical composition), granulation and specific characteristics i.e. radioactivity at each individual process step. Digital twin also enables companies to do simulations for optimization without disturbing the actual production and technological processes.

In this presentation a case study for digital material flow for a company dealing with significant amounts of internal and external recycled material in heavy industry will be presented. The comparison between existing and optimized material flows shows a significant improvement in material flow. In addition, also data collection points and data acquisition protocols will be presented. And finally, implementation of new measuring and production equipment based on analysis of bottlenecks will be presented.

**Keywords:** digital twin, material flow, process optimization, circular economy, data acquisition

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# The Problem of Municipal Sewage Sludge as a Renewable Energy Source in the Circular Economy

ERIK MIHELIČ, DUŠAN KLINAR, KLAVDIJA RIŽNAR

It is known that large quantities of MSS (Municipality sewage sludge) are generated in municipal wastewater treatment plants, for which we do not currently have a suitable recycling process. MSS is nowadays transported mainly to incineration, which requires a high cost. For the circular economy, new opportunities appear to introduce alternative methods of MSS treatment, which are economically and energetically interesting since the dry matter of MSS contains up to 18 MJ of renewable energy. On the other hand, we face the problem of sludge as wet material which is unsuitable for use in any thermal processes like pyrolysis or incineration for energy generation. Since the amount of water in untreated MSS is approximately 75%, it is necessary to find appropriate solutions to dry MSS in the way of the most energy and environment-efficient alternative.

The problem of an environmentally acceptable drying system of MSS regarding CO<sub>2</sub> emissions and heat utilization is studied. The most used method of drying with hot air generates heat with natural gas from the pipe. The second method involves the use of a heated utility. This method is technologically interesting because it is a thermally integrated process. With the heat pump, water from evaporation during drying is condensed. As a result, the latent heat of vaporization energy ( $\Delta H_{\text{vap}}$  2200 kJ/kg) can be reused to heat the drying air. Both methods of MSS drying were finally compared with composting sludge treatment. Interest is to find an alternative that is the most environmentally friendly and produces minor CO<sub>2</sub> emissions.

The MSS energy value is evaluated as a renewable energy source. Due to the high water content of the MSS, the drying process is the key factor for this purpose. The key approach is to eliminate MSS as waste and use it as a renewable energy source simultaneously. Such an approach represents a winning situation by applying a circular economy.

**Keywords:** MSS, drying of MSS, heat utilisation, CO<sub>2</sub> emissions, MSS destruction

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# Recovery of a Clean Phosphorous from Sewage Sludge Ash by an Electrodialytic Process

LISBETH M. OTTOSEN, PERNILLE E. JENSEN, GUNVOR M. KIRKELUND

Sewage sludge incineration is extensively practiced in European countries such as the Netherlands, Austria, and Germany, where legislative developments prohibit the direct spreading of sewage sludge on agricultural land. These and other countries opt for mandatory P recovery from the sewage sludge ash (SSA) from incineration since this type of ash has a very high phosphorous concentration (about 10% per weight). Since P is on the EU list for critical raw materials, this element should be recovered from the ash, but no technology is yet implemented for such recovery. This work focuses on the development of an electrodialytic method for the recovery of P from SSA.

Electrodialytic extraction is a method that combines ion-exchange membranes and an applied electric field. It can be used for the extraction of P from SSA with minimum use of chemicals. Instead, the input of this method is energy, preferably from renewable sources (and maybe even excess energy), and the input during the process causes a low environmental burden.

The electro-dialytic cell has two compartments, each with an electrode. The compartments are separated by a cation exchange membrane (CEM) (Ottosen et al., 2013). The SSA is suspended in water in the compartment with the anode. When applying the electric DC field to the electrodes, the electrical conductance is converted to ionic conductance at the electrode/electrolyte interface. The SSA suspension will gradually acidify due to electrolysis at the anode ( $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2(\text{g}) + 2\text{e}^-$ ). During the acidification, heavy metals and P are dissolved from the SSA. Still, whereas the positively charged heavy metals are transported by electromigration over the CEM and concentrate in the cathode compartment, the extracted P remains dissolved in the dispersion solution as negatively or uncharged species. With this, simultaneous P extraction and heavy metal separation are obtained.

Recovery of more than 80% P in the anolyte has been obtained. The heavy metal content relative to P by far met the limiting values for using industrial wastes as fertilizers (Ottosen et al., 2016).

It is advantageous to consider the added value from the potential utilization of the residual SSA when aiming to optimize the P extraction processes (Li et al., 2018). Next to the simultaneous extraction and separation of elements, EDR offers the advantage that the treated SSA potentially can be used as a partial replacement for cement in concrete (Kappel et al., 2018) or as a partial clay replacement in fired clay bricks (Ottosen et al., 2020). Thus, through EDR, the SSA is separated into a clean P resource and a particulate material, which can be used as a secondary resource in the production of construction materials.

**Keywords:** phosphorous, sewage sludge ash, critical raw material, secondary resource, electro-dialysis

#### **Acknowledgment**

Horizon Europe Grant Agreement-101058162-AshCycle, the Danish EPA, and BIOFOS are thanked for their financial support.

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# Optimization of Renewable Energy Supply Networks for Achieving Regenerative Energy System Design in the EU by 2050

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ZDRAVKO KRAVANJA

In order to limit the temperature rise to well below 2 °C and thus mitigate the effects of climate change, current measures at the global level are insufficient and too slow. Since most greenhouse gas emissions are released from energy production and use, accelerating the transformation of the energy system is crucial to achieving the goal of net-zero carbon emissions by 2050 (International Energy Agency, 2020).

This contribution, therefore, presents a stepwise transition to a sustainable energy system in the EU by 2050, aiming to reach the state of annual net-zero carbon emissions or even go beyond carbon neutrality. For this purpose, a mixed-integer linear programming (MILP) model was developed, achieving balanced solutions between the environmental, economic, and social pillars of sustainability. In order

to obtain a regenerative system design, an assessment and prediction of the Earth's long-term CO<sub>2</sub> emission self-sequestration and atmospheric CO<sub>2</sub> concentration were evaluated as functions of future anthropogenic CO<sub>2</sub> emissions. The results show that, taking into account the Earth's self-regenerative capacity, carbon emissions neutrality in the EU could be achieved as early as 2039 by reducing CO<sub>2</sub> emissions by 69% from 1990 levels with a selection of appropriate technologies, making the transition sustainable and economically feasible.

**Keywords:** energy transition, renewable energy system, supply network optimization, carbon emissions neutrality, regenerative development

### **Acknowledgment**

The authors gratefully acknowledge the financial support from the Slovenian Research Agency (PhD Research Fellowship Contract No. 1000-19-0552, Core Research Funding No. P2-0414 and P2-0421, and Projects No. J7-1816, N2-0138, and J7-3149), financial support from the Grant Agency of the Czech Republic under Project No. 21-45726L, and the HORIZON 2020 project RESHeat based on Grant Agreement No. 956255.

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# Recyclability of Recycled Concrete Products in Cements

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The Circular Economy not only implies the recycling of waste to obtain secondary raw materials that can be used in new products, but also to the eventual disposal of the wastes coming from the end-of-life of this recycled products. Thus, the design of the recycled products should focus the very end of these products and their recycling opportunities.

About 500 million tons of CDW are generated annually in the EU. CDW is one of the priority waste streams in the EU, with a target of 70% recycling by 2020 set in the Waste Framework Directive. That means that when the target is reached, Europe will produce 350 million tons of recycled products. How to recycle these recycled products will turn into a major issue.

This research addresses the recycling possibilities of a concrete product that contains coarse concrete aggregate as recycled material. The use of this finely milled product is proposed as an active addition to cement that already includes by-products in their composition.

The partial substitution of cement by secondary raw materials contributes positively to the reduction of waste dumping and to the reduction of greenhouse gas emissions. However, the substitution rates of secondary raw materials are higher in concrete aggregates (20%) than in cements. The dosage of a concrete includes approximately three times more coarse aggregate than cement. This means that the amount of waste that can be incorporated into recycled concrete is greater if it is done as coarse aggregate than if it is added to cement. The main advantage of the partial substitution of cement lies in the reduction of CO<sub>2</sub> derived from the decarbonization process of the cement raw materials.

Initially, small proportions of substitution of the milled concrete by cement (5, 7 and 10 %) are planned with the aim to assess the potential advantages of its use, the impact of the substitution on the technical requirements of the product application and the potential limitations that must be imposed for an adequate use of the new eco-cement.

These small substitutions can cause a reduction in CO<sub>2</sub> production related to the decarbonation of calcium carbonate (CaCO<sub>3</sub>) as a raw material for cement. Initially, this reduction is estimated to nearly 38-76 kg of CO<sub>2</sub> per ton of produced cement. On the other hand, it is recommended to propose a test plan that determines the dosage limits for the additions according to their impact on the mechanical behavior of the new products, and consequently a test plan has been designed and it is suggested to define the concrete additions.

**Keywords:** circular economy, cement, concrete, recycling

#### **Acknowledgment**

The authors thank the Fundación Gómez Pardo for its support to the research and development of this publication.

This article has been partially funded by Cinderela project which has received funding from the European Union's Horizon 2020 research and innovation Programme under grant agreement N°776751.

The authors gratefully acknowledge the financial support from the Slovenian Research Agency (PhD

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# Influence of Feather Composites on the Removal of VLC from Water

MARJANA SIMONIČ, LIDIJA FRAS ZEMLJIČ, SIMONA STRNAD

As a waste, feathers are undoubtedly sufficient in quantity, easily accessible and inexpensive, and also boast many physicochemical properties, which can be used to their advantage for various applications. By reusing waste feathers, the resulting amount of waste thus contributes to the development of more environmentally friendly products. The purpose of the research was to investigate the possibility of using waste feathers as an adsorbent material for the removal of volatile lipophilic compounds (VLC). The influence of the feather and two composites of feather/zeolites material on the adsorption capacity was studied. The addition of zeolites would contribute to easier handling of the composite material for adsorption. Karl-Fisher titration, ATR-FTIR spectroscopy, and EDXRF X-ray fluorescence spectroscopy were applied for analyses. The adsorption properties of the materials and composites were determined by the ASTM F726-12 standard. Based on the obtained results, we found that the structure of the feathers significantly affects the adsorption ability, due to the larger active surface of cut feathers compared to whole feathers. If feathers were packed into cotton material the adsorption was more efficient compared to the viscose-packed feathers. Comparing the two materials, the use of cotton is a more environmentally friendly

material in terms of the final treatment of the waste generated. With the addition of zeolites, the mass of adsorbed oil decreased in all cases, compared to composites prepared only with feathers. Thus, we can conclude that the loose-cut feathers, without the addition of zeolites, showed the highest adsorption efficiency for volatile lipophilic compounds.

**Keywords:** waste feather, FTIR adsorption, lipophiles, ASTM

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# Reuse of Filter Dust from Container Glass Production

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In the production of inorganic non-metallic materials, a large part of the process waste is separated from the processes and remains unused. For its valorisation, the waste needs to be further processed to achieve the desired properties. An example of such waste is filter dust from container glass production (hereinafter FD), collected at the electrostatic or cloth flue gas filters. The solid filtration residue, namely FD, is considered as hazardous waste, since it contains a significant amount of selenium<sup>1</sup>. Selenium is added to the glass mixture as physical de-colorizer, which compensates the green colour of iron that enters the mixture through raw materials. Due to the relatively high variations of selenium concentrations, FD is not easy to use as secondary raw material in production of extra flint glass and is presently handed over to an authorized contractor for the removal of hazardous waste.

To demonstrate the feasibility of using FD as a secondary raw material in extra flint glass production, we developed (1) a sampling method for FD, (2) a homogenization method to prevent fluctuations in SeO<sub>2</sub>, (3) analytical methods for determining the

selenium concentration in FD before reuse in the glass mixture. In addition, we developed a mathematical model that predicts the amount of  $\text{SeO}_2$  wt.% in FD from process parameters, such as glass melt temperature and retention time, initial  $\text{SeO}_2$  concentration in the batch, glass pull etc.

Finally, an industrial trial of returning FD to the raw material mixture was performed. Selenium was introduced into the mixture with both FD and decolorizing agent ( $\text{Na}_2\text{SeO}_3$ ). During the experiment, the colour of bottles was monitored organoleptically and the amount of selenium in the mixture was adjusted with addition of  $\text{Na}_2\text{SeO}_3$  to ensure an acceptable colouring. We found that FD as a secondary raw material could replace at least 50 % of the primary raw material  $\text{Na}_2\text{SeO}_3$ . Herewith achieving a 41 % closed loop recycling rate of FD.

**Keywords:** glass industry, extra flint glass, filter dust, secondary raw materials, selenium dioxide, XRF analysis

#### **Acknowledgement**

This work was carried out under SEKUMAT project, co-funded by RS and EU from European regional development fund.

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# ENCOURAGE – Sustainable Waste Management

KLAVDIJA RIŽNAR, DUŠAN KLINAR, ŠTEFAN ČELAN

The transition to a sustainable and climate-neutral economy requires significant investment throughout the EU. Most areas are particularly vulnerable to the effects of climate change and requires integrated and coordinated actions towards socio-economic transformation. Moreover, the COVID19 pandemic has significantly affected the society. It is important to provide unique support across Europe to students, entrepreneurs and innovators dedicated to developing innovative solutions to societal challenges.

Waste management is an important dimension of environment protection. According to the Waste Framework Directive 2008/98/EC, waste management strategies must aim primarily to prevent the generation of waste. The waste should be treated as secondary raw material, reused, recycled, recovered or used as an energy source. As a final resort, waste should be disposed of safely by incineration or in landfills. EU countries are facing the problem of practical skills for sustainable implementation of Waste Management as well as lack of knowledge on how to implement the requirements of the established legislation. Among the problems that

municipalities face is the lack of sufficient education of its staff, in order to understand the economic, social and environmental benefits of reuse and recycling and the existing solutions.

The aim of ENCOURAGE is the education of the target groups (representatives from waste or environmental department within municipalities, public enterprises in charge of waste management, VET schools, decision makers) for sustainable waste management in line with the national and EU policies and in long-term contributing to the development and management of waste resources on both a local and global scale.

Objectives are focused on the:

- Development and implementation of new and innovative professional courses for the waste sector in line with EU Waste Framework Directive.
- Improvement of the level of competencies and skills at municipality level in the field of sustainable waste management.
- Minimalization of the gap between the needs for new knowledge, lack of educational programs and challenges of target groups in sustainable waste management.

In this research benchmarking analysis of skills and competences, needs and challenges for sustainable waste management was carried out. The objective was to provide assessment of the current situation regarding the skills and competences of the target groups in sustainable waste management, and their needs and challenges they are facing in practical implementation of the waste management legislation requirements.

In order to understand which is the best waste management practices that will overcome the shortcomings for the target groups, detailed needs analysis has been performed in terms of a comparative analysis of the current good practices in waste management in EU and in the pilot countries (Slovenia, Poland, Cyprus, Greece, N. Macedonia), which are incorporated within their strategic documents in waste management. The analysis has been focused on the skills and competences, needs and challenges of the target groups – employees working in the waste sector in

municipalities, with special focus on GAP analysis and their needs and challenges in the field of sustainable waste management, and the employees working in the waste sector in decision makers, their needs, and challenges in developing methodologies and making legal decisions related to proper waste management.

**Keywords:** climate change, waste management, sustainability, courses, Erasmus+

### Acknowledgement

Project ENACOURAGE (2021-1-PL01-KA220-VET-000030417) has been funded with support from the European Commission (ERASMUS+).



Co-funded by the  
European Union



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# Twin Transformation in Helios Resins: Linking Sustainability and Digital Technology

RADMILA WOLLRAB, MARTIN OCEPEK, NATAŠA ČUK

Driven by the regulations and consumers, an ever increasing push towards sustainability and a reduced carbon footprint has inevitably influenced the resins industry. This transition to green business is not seen as a challenge in Helios Resins but as the industry's obligation, which must act responsibly at all levels to promote the spread of sustainable technologies. It is known that Helios Resins is investing in the research and development of new bio-based resins produced from bio-monomers obtained from a huge range of biological carbon sources. Moreover, we are already using monomers that are partially or entirely bio-based in our conventional products, mostly polyesters.

Going further, one of our strategies is to connect digital transformation and Industry 4.0 with sustainability. How can we combine two of the most important trends currently in the chemical industry and use Industry 4.0 tools to improve resource consumption rate and reduce waste and pollution?

One of the obvious first steps in linking the two is the implementation of predictive maintenance in manufacturing. Predictive maintenance is a proactive maintenance strategy aiming to detect and solve performance equipment issues before they occur by collecting data from sensors, analyzing, and making prediction models. It is clear how this type of maintenance benefits companies from an economic standpoint by significantly reducing costs associated with machine failure and unplanned outages. But this approach can also have a positive environmental impact. On one hand, predictive maintenance extends the lifespan of machinery, therefore minimizing the end-of-life waste (Bonilla et al, 2018). On the other hand, halting a chemical process due to machine failure and aside from an established protocol can cause out-of-control CO<sub>2</sub> emissions into the atmosphere (Fant, 2021). And lastly, misalignment of any mechanical equipment leads to energy loss so implementing a predictive maintenance strategy reduces energy waste and optimizes energy consumption (Banyai, 2021).

Here, we use the opportunity to present Helios Resins' approach to the intersection of Industry 4.0 and sustainability and the tremendous value it holds.

**Keywords:** sustainability, Industry 4.0, predictive maintenance, energy management, circular economy

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# Advanced Functional Keratin-Based Particles Synthesized from Recycled Keratin from Feather Biowaste

LIDIJA TUŠEK, ANJA MEŠL, LIDIJA FRAS ZEMLJIČ, OLIVIJA PLOHL,  
MAJA ČOLNIK, MOJCA ŠKERGET

Chicken feathers are considered waste from the poultry meat processing industry, which produces several million tonnes of feathers each year [Barman et al., 2017]. Only a small portion of the feathers are processed into valuable products such as feather meal for livestock and fertilisers; the majority are disposed of by incineration or burial. Innovative waste management technologies need to be explored to reduce the environmental impacts caused by the production and disposal of poultry feathers.

Chicken feathers are mainly composed of keratin and should be considered as a biocompatible and biodegradable protein resource. Keratin has been used to produce fibre composites and can be processed into gels, films, nanoparticles, and microparticles with the necessary modifications [Chilakamarry et al., 2021].

Our previous study has shown that subcritical water extraction of poultry feather waste at 180 °C and 20 bar for 1 h is a successful method to isolate keratin [Tušek et al., 2022]. This research focuses on the development of advanced keratin-based particles from recycled keratin by subcritical water extraction. To investigate the complexation ability of keratin, three polyelectrolytes with different functional groups were used for particle synthesis at specific pH values, namely alginate with carboxyl groups, chitosan with amino groups, and penta-ionic sodium tripolyphosphate (TPP) with phosphate groups. DLS analysis showed that complex formation between keratin/alginate and keratin/chitosan resulted in microparticles, and colloidal particles were formed only in the case of keratin/TPP. The ATR-FTIR spectra of the particles indicate that electrostatic interactions were the driving force for complex formation between keratin and oppositely charged polyelectrolytes. Keratin has antioxidant activity that deteriorates with the addition of alginate, chitosan, and TPP, as measured by the spectrophotometric method using ABTS reagent. Over a longer period of time (4 weeks), the absorbance approaches zero, which means that all free radicals are inhibited.

The keratin/TPP particles, which were found to be optimal, were further tested as a drug delivery system for the model drug amoxicillin. UV/VIS spectroscopy showed that amoxicillin was successfully encapsulated (69.24%) and slowly released up to 96% over 6 hours. This type of particles therefore has a promising application as a delivery system with simultaneous antioxidant and potentially antimicrobial properties.

**Keywords:** recycling, keratin, chicken feathers, waste biomass, subcritical water extraction, microparticles, nanoparticles, drug delivery system, encapsulation

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Zbornik povzetkov = Book of abstracts: Slovenski kemijski dnevi 2022 = 28th Annual Meeting of the Slovenian Chemical Society: 21.-23. september 2022, Portorož, Portorose, Slovenija. Ljubljana: Slovensko kemijsko društvo, 2022.

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# Development of Green Coatings Approaches for Medical Devices

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This work deals with the development, production, and testing of multifunctional and environmentally friendly bio-based coatings for urethral catheters (made of polyvinyl chloride (PVC) or thermoplastic elastomers (TPE)). The working hypothesis was that the novel coatings will ensure superior antibacterial properties while maintaining low surface friction.

The multifunctional coatings were applied to the catheters by activating the catheter surface with a gas plasma in a first step, which allowed better adhesion of the biobased multifunctional coatings in a second step. The coatings were prepared from anionic and cationic polysaccharide macromolecular solutions that are biodegradable, non-toxic, and human and environmentally friendly (Park et al., 2018, Park et al., 2022). Both types of coated catheters were analyzed by the following methods: a) contact angle measurements: wettability; Fourier transform infrared

spectroscopy – attenuated total reflectance ATR-FTIR and X - ray photoelectron spectroscopy XPS: elemental composition. The stability of the coating was followed by desorption experiments: i.e., the catheters were placed in a physiological solution for 10 minutes and the desorption bath was analyzed by UV-VIS experiments. The antimicrobial properties were analyzed by the ASTM E 2149 standard method. It has been shown that the coating mainly increases the hydrophilicity on the surface and the contact angle decreases to 30. Moreover, the coatings are applied in larger quantity on the surface with previous plasma activation. More so, in this case, desorption is negligible compared to non-plasma activated and further coated catheters. Coating with cationic polysaccharides was also found to have antimicrobial capacity against Gram-positive *S. aureus*.

Nowadays, most commercial coatings of catheters are based on synthetic organic chemistry, so the application of these coatings is very important to replace synthetic polymers, which are widely used in biomedical implants and devices, with natural polymers such as polysaccharides. These are biocompatible and have no side effects on humans or the environment. The application of these coatings is very promising and can be used for other polymer-based medical devices such as tympanic tubes, dialysis tubes, etc., in addition to catheters.

**Keywords:** catheters, green coatings, polysaccharides, plasma, activation

#### **Acknowledgement**

We are grateful the Slovenian Research Agency for financial support (research program P2-0118 and project L2-3163).

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# Recycling of Keratin-Rich Poultry Feather Waste for Keratin - Based Nanofibers Production

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MOJCA ŠKERGET

Waste materials such as wool and chicken feathers are among the most polluting industrial wastes that are generated in large quantities every day. Waste chicken feathers contain 91% keratin, making them adequate source of this important biopolymer (Tesfaye et al. 2017, Sharma et al. 2016). However, most extraction processes are still ecologically questionable. In particular, the processes to develop high value-added applications focusing on biomedical materials remain a major challenge. In this study, nanofibers were prepared from isolated/recycled keratin. First, we extracted keratin from chicken feather waste by hydrothermal decomposition of feathers with subcritical water, which is an environmentally friendly and green technique. The presence of keratin in the aqueous solution was confirmed by ATR-FTIR analysis, and then the molecular weights were determined by SDS-PAGE electrophoresis. The molecular weights of the aqueous keratin solution were determined in a range between 1 kDa and 14 kDa. The aqueous keratin

solution was analysed for protonated and deprotonated groups by potentiometric titration, the zeta potential was measured at different pH values of the solution, the particle size was determined by the DLS method, and the keratin concentration in the solution was determined by the Bradford method. To prepare the nanofibers, the keratin solution was mixed with polyethylene oxide (PEO) in different proportions, and the nanofibers were spun by electrospinning and examined under an optical microscope. We also spun nanofibers from mixtures of PEO/keratin/alginate and PEO/keratin/chitosan in different volume ratios. The PEO/keratin/alginate and PEO/keratin/chitosan blends were analysed for conductivity and viscosity, as well as the degree of antioxidation using the ABTS spectroscopic method. The determined optimum PEO content for nanofiber formation is 70 %. Nanofibers from PEO/keratin/alginate and PEO/keratin/chitosan blends formed more easily and better when alginate is present. PEO/keratin/chitosan and PEO/keratin/alginate and pure keratin nanofibers also have antioxidant properties, and thus can be used as wound dressings for the cases, where antioxidant activity is important to control wound oxidative stress and thereby accelerate wound healing. Nanofibers, especially those made from biocompatible or biodegradable biobased materials, show great potential for biomedical and healthcare applications due to their unique combination of properties and intrinsic functionalities. The large surface area per unit mass, high porosity and small pore size between fibers associated with the structure of nanofibers are the main properties that make them superior to their micro and macro counterparts made of the same material.

**Keywords:** recycling, keratin, chitosan, alginate, electrospinning, nanofibers

#### **Acknowledgement**

We are grateful the Slovenian Research Agency for financial support (research programs P2-0118 and P2-0421).

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# Degradability of Different Types of Plastics in a Simulated Marine Environment

SELESTINA GORGIEVA, KLEMENTINA PUŠNIK ČREŠNAR, LARA LIZI, LIDIJA  
FRAS ZEMLJIČ, SILVO HRIBERNIK

Plastics have outstripped most manufactured materials and have long been under scrutiny from an environmental perspective, as leaving plastics in the environment causes major environmental problems as they often end up in ecosystems where they are not wanted. Particularly critical are the oceans, from which plastics are more difficult to remove and have negative impacts on marine animals that become entangled in the debris, creating the problem of nano/microplastics entering the food chain (Oliveira et al, 2020; Niaounakis, 2017).

To develop a material which degrades faster and has a less negative impact on the environment, biodegradable plastics have been developed and are increasingly replacing fossil plastics.

In this study, biodegradable (polylactic acid, chitosan-coated polylactic acid, and starch-based) and non-biodegradable (polypropylene) plastic samples were exposed to a simulated marine environment and observed over a period of 190 days. Gravimetry, goniometry, Fourier transform infrared spectroscopy – attenuated total reflectance ATR-FTIR, X-ray diffraction, thermogravimetric analysis and optical microscopy were applied to assess the potential degradation events and patterns.

The results confirm the intrinsic stability of polypropylene in the simulated marine environment, in contrast to other biodegradable samples studied. PLA and starch-based plastics show a higher mass loss, increased hydrophilicity, and chemical degradation over time due to functional end groups seen in the spectra of ATR-FTIR. At the end of the experimental work, we conclude the importance of using complementary analytical methods to determine biodegradability, which will give us an insight into the changes in the samples studied.

**Keywords:** plastics, PLA, PP, starch, marine environment, degradability

#### **Acknowledgement**

The authors would like to acknowledge the financial support from Slovenian Research Agency and Textile Chemistry and Advanced Textile Materials Program (P2-0118).

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# Production of Lignocelulitic Enzymes from *Pleurotus Ostreatus* Cultivated on Waste Materials

MATEJA PRIMOŽIČ, KATJA VASIĆ, ŽELJKO KNEZ, MAJA LEITGEB

**Introduction.** Forest and agricultural waste can be a major development and “zero waste”, ecological opportunity and can be served as substrates for medicinal mushrooms cultivation such as *Pleurotus ostreatus*. This can lead to the realization of a "zero waste economy". (Diaz and Diaz-Godinez, 2022; Kumla et al., 2020).

**Methods:** The cultivation of *P. ostreatus* fungi on a solid medium composed from different agriculture waste (cabbage, carrot, apple, potato, beech bark etc.) was performed. The influence of substrate composition on cultivation of *P. postreatus* and on the activity of enzymes from extracts obtained from fungi mycelium was studied. Extracellular enzymes, produced by *P. ostreatus* were immobilized in the form of cross-linked enzyme aggregates (CLEAs).

**Results.** The highest protein concentration in mycelium extract was detected in the medium composed from wheat bran + carrots. A very high total protein concentration also contained enzyme extracts from fungi mycelium grown on wheat bran + apple, wheat bran + lettuce and wheat bran + cherry. The highest enzyme immobilization efficiency (88%) in the form of CLEAs was achieved when the mycelium extract was obtained from a medium containing wheat bran + carrots.

**Conclusions.** Media, composed from different agriculture wastes, provide the necessary nutrients for successful cultivation of *P. ostreatus*. Substrate composition of medium for *P. ostreatus* cultivation influenced the total protein concentration in obtained extracts. Extracellular enzymes produced by *P. ostreatus* were successfully immobilized in the form of CLEAs with high immobilization efficiency.

**Keywords:** enzymes, isolation, *Pleurotus ostreatus*, agriculture wate, environmental sustainability

#### Acknowledgement

This research was supported by the Slovenian Research Agency within the frame of program P2-0046 (Separation Processes and Production Design) and project No. J2-3037 (Bionanotechnology as a tool for stabilization and applications of bioactive substances from natural sources).

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# Nanocellulose from *Polypodiophyta* Fern for Environmental Sustainability

KATJA VASIĆ, ŽELJKO KNEZ, MAJA LEITGEB

**Introduction.** As a new emerging sustainable nanomaterial, nanocellulose (NC) is gaining immense attention over the past decades, due to its potential in production of high-value products for environmental, biomedical and pharmaceutical industries, as well as in packaging and storage formulations for food related industries (Dhali et al., 2021; Guo et al., 2020; Jiang et al., 2021).

**Methods.** The isolation of cellulose nanofibers from ferns (class *Polypodiopsida*) was achieved by chemo-mechanical method. The chemical processes involved alkali treatment, bleaching and acid hydrolysis, and the mechanical fibrillation was performed via grinding. In the study, prolonged treatment was performed. Structural and morphological analysis were carried out by SEM, EDS, and FT-IR. Thermal stability of NC fibers was investigated by TGA and DSC, while particle sizes were determined by DLS.

**Results.** Structural and morphological analysis, as well as thermal analysis gave supporting evidence for successful removal of hemicellulose and lignin in all samples. However, a reduction in degree of polymerization and particle sizes (27-60 nm), as well as the most consistent particle sizes were evident, while using prolonged treatment of bleaching.

**Conclusions.** NC obtained is a potential candidate for further process optimization. Product development with optimization is crucial in adding value to derived NC, which is necessary in developing advanced and feasible NC-based materials to overcome increasing economic and environmental concerns.

**Keywords:** nanocellulose, isolation, plant material, *Polyodiophyta*, environmental sustainability

#### Acknowledgement

This research was supported by the Slovenian Research Agency within the frame of program P2-0046 (Separation Processes and Production Design) and project No. J2-3037 (Bionanotechnology as a tool for stabilization and applications of bioactive substances from natural sources).

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# Biomass Derived Hexose Dehydration over Solid Acid Catalyst in Different Solvent Systems

ANA JAKOB, MIHA GRILC, BLAŽ LIKOZAR

Alternative resources have over last decades gained more attention, due to the major increase in energy consumption and continuous depletion of fossil fuels. Therefore, the exploration of the sustainable carbon source lead towards utilization of widely abundant lignocellulosic biomass feedstock (R. J. Van Putten et al., 2013). Lignocellulosic biomass valorisation holds a prominent potential for the production of value-added products, such as green chemicals. Therefore, glucose, the most dominant saccharide of cellulose and hemicellulose biomass fraction is regularly used as a substrate to produce various platform chemicals, including HMF (hydroxymethylfurfural) (L. Zhu, et al., 2020). The valorisation of bio-based polysaccharides (hemicellulose/cellulose) commonly includes the step of hydrolysis, followed by acid catalysed dehydration of monosaccharides (T. D. Swift, et al., 2016). The process itself is known to be troublesome due to its low efficiency. The challenge of low product (HMF) selectivity usually lays in enhanced formation of by-products, which tends to be especially pronounced in aqueous environment. Therefore, the aim was

to investigate and explore the effect of organic solvents addition on the hexoses (glucose and fructose) dehydration reaction to increase the selectivity of the desired product, HMF. The challenge of lignocellulosic biomass conversion is additionally signified due to the low glucose reactivity in comparison to its respective isomer, fructose (Xu Siquan et al., 2019). Focusing to resolve the mentioned challenges and enhance the glucose-fructose isomerization, various commercial and in-house solid acid catalyst were synthesised, varying the Brønsted and Lewis acidity. Sugar dehydration experiments were performed in 75 mL batch reactors at the temperature of 130 °C. All of the reactions were conducted under 10 bars of N<sub>2</sub>. To monitor the concentration of the reactants/products as a function of time, samples were taken in time intervals of 1 h. The collected samples were quantified using ultra high-performance liquid chromatography (UHPLC), where substrates (glucose and fructose) were quantified by using RI detector, while quantification of HMF was performed by UV-VIS detector, at specific wavelength. The addition of organic solvents to water media enabled to significantly increase the final HMF yield at relatively low operational temperatures. Furthermore, increasing the amount of organic solvent (DMSO/GVL) in the reaction media considerably increased the HMF selectivity, although being less pronounced in case of GVL. Catalyst screening demonstrated the best performance of ion-exchange resins, with a strong Brønsted acidity in all of the tested solvent system. The deposition of different metals on the catalyst support enabled the crucial step of glucose-fructose isomerization. Although, the product selectivity and distribution tended to be significantly dependent on the amount of the introduced organic solvent and promotion of the catalyst with different metal ions.

**Keywords:** saccharide, dehydration, lignocellulose, hydroxymethylfurfural, catalysis

#### **Acknowledgement**

The authors would like to appreciatively acknowledge the financial support of by the Slovenian Research Agency (Program P2-0152 and the project Z2-9200).

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# Environmental Impact Assessment of Novel Nanocrystalline Cellulose Production

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JANEZ TURK, ANJA LEŠEK

Life Cycle Assessment (LCA) was applied to evaluate environmental performance of the nanocrystalline cellulose produced by means of depolymerisation, bleaching and rinsing of cotton fibers. Two procedures of the nanocrystalline cellulose production process were considered. First is the baseline procedure, where diethylene glycol from all three rinsing cycles was reused; the diethylene glycol from first rinsing cycle in the process of depolymerisation, while the diethylene glycol from second and third rinsing cycles in the rinsing process of the next production series. Diethylene glycol, after being reused in rinsing process of the next production series was considered as a waste material, which could be combusted in gas turbine power plant. In case of second (alternative) procedure of the nanocrystalline cellulose production, the diethylene glycol from first rinsing cycle was directly combusted in gas turbine power plant. Only diethylene glycols from second and third rinsing cycles were reused again for rinsing in next production series, before

being combusted in gas turbine. Results of LCA show that the production of 1 kg of dry nanocrystalline cellulose is associated with 63.7 kg CO<sub>2</sub> equivalent emissions in case of baseline production procedure and with 65.9 kg CO<sub>2</sub> in case of alternative production procedure. Diethylene glycol is the major contributor to global warming potential and fossil depletion potential in life cycle of the nanocellulose. While electricity requirements and glycerine represent environmental hotspots regarding fifteen of eighteen impact categories included in ReCiPe 2016 impact assessment method. Comparison of two different production procedures shows relatively low difference regarding environmental performance of nanocrystalline cellulose, however, the preference is given to baseline production procedure.

**Keywords:** LCA, cellulose, nanocrystals, pilot production, green chemistry, cascade use

#### **Acknowledgement**

The research was co-financed by EU Structural Funds in Slovenia. The programme is placed within priority area S4 - The natural and traditional resources for the future, Networks for the transition to the circular economy. The authors also wish to acknowledge the financial support provided by the Slovenian Research Agency (Research Core Funding No. P2-0145 and No. P2-0273).

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# Microwave Irradiation of Alkali-Activated Metakaolin Slurry

BARBARA HORVAT, BRANKA MUŠIČ, MAJDA PAVLIN, VILMA DUCMAN

More than 40% of the man-caused carbon footprint originates from conventional building and civil engineering. As a result, alternatives are being explored that use waste materials to replace raw materials, reduce the energy required for production, and require less time to transform reagents into the final product.

One of the solutions for replacing conventional building material is alkali-activated material (AAM), which use as the precursor waste materials such as fly ash, slag, mineral wool, etc. AAMs are synthesized below 100 °C and in just a few hours to a few days. Curing time and energy consumption can be reduced even further if microwave irradiation is used at the initial stage of the alkali-activation process. Microwaves volumetrically raise the temperature, increase the dissolution rate and rapidly make amorphous Si and Al available for the formation of the aluminosilicate network (ASN).

In this framework, metakaolin was alkali-activated with Na-water glass in the ratio that according to the literature (Duxson et al., 2005) gives the highest possible compressive strength (amount of substance Si:Al=1.9:1) while still avoiding efflorescence (amount of substance Na:Al $\leq$ 1). The slurry was irradiated with microwaves of power of 100 W and 1000 W for 1 min immediately after moulding. One sample was in an open mould, the second was permanently closed to avoid dehydration while sample was irradiated. Both were compared to non-irradiated samples, that were cured at room temperature.

TGA/DSC was performed on all samples 12 min after the ingredients were mixed and compared to the more than 1-year-old non-irradiated sample. Fresh samples were followed until constant results.

Mechanical strengths were measured at 3 days and 28 days, while leaching was performed only on 28-day-old samples to estimate the environmental impact of AAMs prepared with and without microwave irradiation.

**Keywords:** alkali-activation, metakaolin, microwaves, TGA/DSC, leaching

### **Acknowledgement**

This work is part of the ARRS project of dr. Barbara Horvat and was financially supported by the Slovenian Research Agency under Grant no. J2-3035.

This work is part of the postdoc project of dr. Majda Pavlin and was financially supported by the Slovenian Research Agency under Grant no. Z2-3199.

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# Catalyzed Degradation of Polyethylene Terephthalate

ŽIGA SAMSA, DARJA PEČAR, ANDREJA GORŠEK

In this research catalyzed degradation of polyethylene terephthalate was performed. For that purpose, ZSM-5 zeolite was synthesized as an acid catalyst. For its characterization N<sub>2</sub> adsorption, scanning electron microscopy, NH<sub>3</sub> temperature programmed desorption, differential scanning calorimetry, thermogravimetric analysis, dynamic light scattering and Fourier transform infrared spectroscopy were utilized. Degradation reactions were performed in high pressure crucibles using differential scanning calorimeter at different temperatures (200, 250 and 300) °C and time intervals (2.5, 5, 10 and 15) min. Samples were analyzed using high performance liquid chromatography coupled with UV-VIS detector. The results revealed that the highest conversion was achieved at 300 °C and 10 min. The analysis of obtained results showed that despite the differences in conversions were not as high as expected, reactions with the catalyst were slightly more effective than without it. For the future work, we plan to finetune the synthesis procedure to obtain more active catalyst. And for the upgrade of the study the kinetic analysis of the reaction will be conducted.

**Keywords:** degradation, catalyst, ZSM-5, polyethylene terephthalate

### **Acknowledgement**

We would like to thank the Slovenian Research Agency (ARRS) for co-financing the research project "Planning and management of sustainable value chains of the production of plastic materials for the transition to a circular economy" with the code J7-3149.

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# Design and Management Solutions for Sustainable Plastic Value Chains

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YEE VAN FAN

Plastic pollution has emerged as one of the highly discussed global environmental problems recently, especially under the increasing usage during the global pandemic. The problem spans land, ocean, and air pollution via macro-, micro-, and nano-plastics. Despite the availability of different technologies to mitigate the environmental footprint of plastics and their waste, the deployment has been hampered by different challenges. The methods developed for the optimal design and operation of entire plastics value chains under the Circular Plastics Project [1] will be presented. These include machine learning and Pinch Analysis, life cycle assessments targeted for recycling and upcycling, integration of renewable resources, waste and end-of-life plastic materials, and energy implications of recycling. The preliminary results indicate maximum theoretical recycling rates of 38 % for PET, 100 % for polyethylene and 92 % for polypropylene, while accounting for energy implications can reduce these maximum values.

**Keywords:** plastic waste, sustainable value chain, optimisation, environmental footprint

### Acknowledgement

The research was supported by the GACR (Grant Agency of the Czech Republic) under No. 21-45726L and from the Slovenian Research Agency for project No. J7-3149.

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# Increasing the Efficiency and Integration of Renewable Energy Sources to Address Energy Crisis

JIŘÍ JAROMÍR KLEMEŠ, PAWEŁ OCLON, YEE VAN FAN, PETAR VARBANOV

The energy crisis intensifies, especially in Europe, as gas prices surge. IEA warns that world is experiencing the first truly global energy crisis in history and will be particularly challenging in coming months where the Russia's role on natural gas security is apparent [1]. The civic sector and, notably, buildings require about 40% of the overall energy consumption, and this is directly related to the released emissions, including GHG. There is a well-proven need for reduction of GHG Footprint as well as the air pollutants (Ox, O<sub>3</sub>, VOC, PMs). Buildings can utilise renewable energy sources in different ways [2], including on-site or distributed energy supply. Renewable energy, including solar energy, heat pumps, geothermal, biomass and wind energy, attracts increasing attention to buildings to coming closer to sustainable buildings.

This presentation has been dealing with those issues to suggest progress towards sustainability and solutions to mitigate the energy crisis. Several challenging issues have been recognised and are pointed out:

- i. Acceptable cost and Return on Investment would make the Renewable Energy System (RES) competitive without or with minimum subsidies.
- ii. Follow the traditional observation: Simple is beautiful and usually efficient.
- iii. Minimised full GHG Footprints as well as Poisonous Pollution Footprints covering the period from the cradle to the grave, i.e. Influence afterlife and the trade-off of potential indoor pollution arise from the enhanced energy efficiency. Minimising emissions based just on the operation spot can provide distorted pictures.
- iv. Integration of various renewable energy sources (wind, hydro, solar) with heat and electrical energy storage systems, with grid and also backup sources of energy.
- v. Integration of Underground Thermal Energy Storage (UTES) including heat accumulators and Borehole Thermal Energy Storage (BTES) with Heat Pumps for Building Heating/Cooling
- vi. Based on the efficient integration, smart energy management. The electricity preferably is synchronised by production and consumption, and only the excess of the electrical energy produced from RES to be stored.
- vii. The produced electricity has highly changing emissions content over the day and different parts of the year, and it is preferable to use energy with lower emissions content.
- viii. The footprint effects can be attributed eco-cost, which will help in evaluating the sustainability and the economic feasibility of the arrangements for renewable energy use in buildings, with long-term heat storage comprehensively
- ix. Renewable energy could be cleaner by tackling at the end of life management and maintenance stages

**Keywords:** renewable energy, system integration, energy crisis and supply, heating, cooling and ventilation, building

#### **Acknowledgement**

The financial support from the Horizon 2020 project RESHeat – Grant agreement No. 956255 is acknowledged.

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# Plastic Waste Management Strategies for Tourism-Generated Plastic Waste in Three European Countries

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The tourism sector has been highlighted as a significant source of environmental burdens, as it is responsible for around 12 % of the global carbon footprint (Arora, 2021). These environmental impacts are partially brought on by the use and waste disposal of single-use plastics products by visiting tourists, as many of the frequently polluting single-use plastics such as disposable toiletries or food packaging are sourced from tourism activities. In certain European coastal communities heavily dependent on tourism, visitors can cause up to a 40 % surge in marine litter, which is almost entirely comprised of plastic (Alessi and Di Carlo, 2018). The plastic footprint of tourism and consequent management of waste plastic therefore requires addressing as the tourism sector aims to transition towards a zero-waste future. This paper reviews plastic waste management strategies in the case studies of France, Italy, and the UK, which all represent countries with a high volume of annual tourist stays. The study takes into account the fluctuating plastic waste generated by tourism

across different seasons in the three countries. In this way, the current state of the transition towards zero-waste tourism and the countries' handling of tourism-related plastic waste is quantified. Results show the benefits of plastic waste management strategies particularly in Italy and the UK, where focus is on circular avenues of polymer recycling and incineration for recovery of heat and electricity. These strategies are determined to be key ways of unburdening the environment by reducing the demand for virgin polymer production as well as for production of heat and electricity. Therefore, waste management strategies in Italy and the UK, where around 45 % of plastic packaging waste is already recycled, present a promising outlook regarding tourism and plastic waste.

**Keywords:** tourism plastic footprint, plastic waste management, zero-waste strategies, plastic recycling, energy recovery

### Acknowledgement

The authors would like to acknowledge the financial support from the Ministry of Education, Science and Sport of Republic of Slovenia and the European Regional Development Fund for project No. 5442-1/2018/106, the Slovenian Research Agency for the project J7-3149 "Design and Management of Sustainable Plastic Value Chains to Support a Circular Economy Transition". The authors are also grateful for the support from the Slovenian Research Agency for Core Research Funding No. P2-0412 and P2-0421 and Project N2-0138.

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# Social and Environmental LCA of Tourism – A Case Study

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The environmental impacts of tourism have been studied extensively regarding both case studies and the global consequences of tourism, where it is understood that tourism generates significant environmental burdens. However, studies so far have not investigated the social sustainability pillar or tourism in combination with its environmental sustainability. This paper presents the combined environmental and social Life Cycle Assessment (LCA) for a case study of a tourist group traveling from Canada on an 8-day trip across the European countries of Croatia, Slovenia, and Italy. Four key domains of tourism are assessed: (i) tourist transport by air from Canada to Europe as well as the return trip to Canada, (ii) leisure activities during the trip including bus transport, (iii) hotel accommodation, and (iv) food consumption. Environmental impacts are assessed using eleven impact categories, where direct emissions as well as upstream impacts of the entire tourist trip are accounted for. Social LCA assessment considers tourism's influence on the well-being of tourism sector workers and local communities, as well as other groups within the value chain. Results for both environmental and social LCA highlight the

dominant impact of air transport, which remains a large area of concern on the global tourism scale. Less significant impacts are generated by the domains of bus transport, hotel accommodation and food consumption. However, the areas of hotel accommodation and food consumption present viable alternative scenarios which could mitigate environmental impacts. By encouraging both tourism service providers and tourists themselves to modify their behavior, the first steps towards reducing the negative burdens of tourism could be achieved.

**Keywords:** tourism plastic footprint, plastic waste management, zero-waste strategies, plastic recycling, energy recovery

### **Acknowledgement**

The authors would like to acknowledge the financial support from the Ministry of Education, Science and Sport of Republic of Slovenia and the European Regional Development Fund for project No. 5442-1/2018/106, the Slovenian Research Agency for the project J7-3149 “Design and Management of Sustainable Plastic Value Chains to Support a Circular Economy Transition”. The authors are also grateful for the support from the Slovenian Research Agency for Core Research Funding No. P2-0412 and P2-0421 and Project N2-0138.

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# Biodegradation of Bio-Based Polymeric Materials in Water Environment Using Respirometric Method

BETI VIDMAR, BLAŽ LIKOZAR, UROŠ NOVAK

Environmental challenges are not only critically linked to sustainability of ecosystems, but also increase risks to food, energy and water security on a global scale. Given the vast amount of single use plastic pollution created by overuse around the world. Thus efforts have spurred to create innovative strategies for regulation, managing plastic waste, consumer education and development of biodegradable alternative materials. Solutions for plastic pollution must be considered in the context of the whole plastics value chain, since the demand for it is increasingly annually by 4 % (Rosenboom et al., 2022). One of the main examples is plastic used for food wrapping made of polyethylene, which is chemically inert and hydrophobic material. Therefore, microorganisms in environment have no appropriate mechanism to digest synthetic plastics (Zeenat et al., 2021).

In the past 10 years many different polysaccharides from various natural sources, mainly cellulose, starch, chitosan, agar, alginate, etc. were used for development of eco-friendly packaging materials. Despite their great potential, their commercial use for now is limited due to their poor barrier and mechanical properties, thermal instability in comparison to the conventionally used plastics (Shah et al., 2021).

The aim of our study was to improve the drawbacks of using natural polymers by the use of composites and nano-sized materials based on biopolymers like nanocellulose mixed into alginate matrix. The materials will be chemically modified to tailor their chemical and physical properties as well as their biodegradation potential. The design is focused on bio-based plastic materials that would be readily biodegradable, which we tested using microbes from selected natural sources. Main source for biodegradation testing was performed water mixed with active sludge from wastewater plant and with added alginate/nanocellulose biocomposite materials. The controllable biological degradation using standard BOD method in a hermetically closed bottle (Oxitop) monitoring changes in pressure resulting from oxygen consumption over the incubation period was employed. Furthermore, the evaluation of biochemical characterization of enzymatic activity, biodegradation kinetics and molecular approach to characterize and classify microbial communities involved in the polysaccharide foils biodegradation process was done. Moreover, the morphological studies using scanning electron microscopy and FTIR on new and degraded materials was performed to compare their structure and the presence of functional groups and molecular bonds, that cause the biodegradation. Using chemical and microbiological approaches a better understanding of microbial background of biodegradation and correlation between microbial consortia and physio-chemical parameters have been established.

**Keywords:** polysaccharide foils, biodegradation, enzymatic biodegradation activity, microbial communities

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# Facade Panels: From Raw Materials to Final Product

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Mineral wool is one of the most widely used insulation materials in the world. It therefore represents a big problem after its enduse as it takes up a lot of space in landfills due to its low density. About 2.55 million tons of mineral wool waste was produced in 2020 in the European Union (Väntsi and Kärki 2014) and there is a need to recycle this waste. Mineral wool is usually divided into stone or glass wool which differ in their chemical composition and production which includes different ingredients.

Under the Wool2Loop project (“WOOL2LOOP” 2019) started in June 2019 and to be completed in October 2022, our consortium is developing and producing various products based on the alkali activation technology in which mineral wool is used as the main raw material (Yliniemi et al. 2016). Alkali-activation is based on a chemical reaction which can produce final products with similar or better properties than concrete or ceramic-type products.

The Slovenian National Institute for Building and Civil Engineering (ZAG) and Termit are responsible for the production of façade panels in Slovenia. A mixture of stone wool based façade panels was developed and designed at ZAG while their manufacture was performed at Termit. The mix design was changed twice to get a final product that is durable, with less porosity than at the beginning. Unfortunately, there is still efflorescence on the panels due to an incomplete dissolution of the mineral fibers and the associated sodium excess in the mixture. The mechanical properties reached compressive strengths of up to 60 MPa and bending strengths of about 20 MPa. The particle size and the organic binder of the mineral wool waste determine the workability and thus the final properties of the façade panels. Insufficient grinding of the material e.g. leads to a very dense mixture and causes lower mechanical properties due to a reduced dissolution of the material. As façade panels are applied outdoors, leaching tests were also performed but revealed no major difference between the different batches although their mechanical properties varied greatly. The elements Cr, As, and Mo exceed the legal inert waste limits in most samples.

Nevertheless, recycling waste mineral wool through the alkali activation reaction remains one potential way to use this waste material and produce durable end products with good mechanical properties.

**Keywords:** waste mineral wool, facade panels, alkali-activation, durability, recycling (minimum 5)

### Acknowledgement

H2020 project Wool2Loop has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No. 821000. The opinions expressed in this document only reflect the authors' view and in no way reflect the European Commission's opinions. The European Commission is not responsible for any use that may be made of the information it contains. We acknowledge financial support from the Slovenian Research Agency, Slovenia, through project No. Z2-3199 »The immobilisation and leaching of toxic trace elements in alkali-activated materials prepared from locally available waste and by-products«.

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# Optimization of Organic Rankine System Utilizing Multiple Low Temperature Heat Sources: Comparison of Separate and Cascade Designs

MONIKA DOKL, LIDIJA ČUČEK

The decarbonization of the energy system and the development of a power sector based largely on renewable energy sources are crucial to gradually reduce greenhouse gas emissions. Furthermore, the integration of renewable energy sources leads to numerous benefits such as decentralized production and improved energy security. Among the various energy conversion technologies to transform renewable energy into useful products, the organic Rankine cycle (ORC) is widely used as it can be applied to heat sources with a wide temperature range. With different ORC configurations, more efficient recovery of thermal energy from a multi-grade heat sources can be achieved. A cascade ORC system with two ORC loops driven by solar radiation, geothermal heat and waste heat from aluminium production is proposed to better match the diverse heat sources. In order to utilize different heat

sources at low temperature levels, the operating conditions of the system are described by variables to be optimized, such as temperatures, pressures, mass and energy flows. The thermophysical properties of the fluids in the system such as ethylene glycol-water mixture, organic fluid R245fa, and cooling water are included as functions of temperature and/or pressure. Optimization is performed in terms of maximum power generation and the thermodynamic performance of separate and cascade designs is compared.

**Keywords:** organic rankine cycle, multiple low temperature heat sources, geothermal heat, solar energy, waste heat, thermodynamic optimization, maximum electricity production, separate and cascade designs (minimum 5)

#### **Acknowledgement**

The authors are grateful for funding support from the Slovenian Research Agency (research core fundings No. P2-0412 and P2-0421 and projects No. N2-0138 and J7-3149).

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# Development and Technical Assessment of Alkali Activated Roofing Tiles

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Within the Recover+ project a new type of slate-looking roofing tile has been developed by alkali activation of an Fe-rich slag. Three main challenges that needed to be overcome before entering the large scale production were: paste flowability vs. tile warping, tile porosity and efflorescence.

The mix-design was optimised at lab-scale and subsequently adjusted for a pilot production. The roofing tiles were produced in a two step casting procedure, using a silicon mould and vigorous vibration. An oven curing was performed at 50 °C for three days.

The obtained tiles were used to make an outdoor roof panel in order to follow their behaviour in-situ for a certain period of time, and alongside the slates were also tested in the laboratory using the provisions of European standard EN 491 for technical evaluation of concrete roofing tiles (EN 491, 2011). Following tests were performed:

- mechanical resistance (transverse strength),
- water permeability, and
- freeze-thaw resistance.

Results have confirmed that roofing tiles developed within the project reached comparable performance then commercially available products. Comparing results for technical parameters of Recover+ roofing tiles with the commercial ones it was noticed that mechanical resistance still could be improved; this would be possible either by increasing the thickness of the slates or by different regime of curing (Češnovar et al., 2019).

**Keywords:** alkali activated materials, Fe slag, roofing tiles, durability, transverse strength, freeze-thaw resistance

### **Acknowledgement**

This research was funded by EIT Raw Materials project Recover+ no.16365.

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# The Effect of Various Bases as Reactants on Homogeneously Carboxylated Phenol

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The production of new C-C bonds through carboxylation reactions using CO<sub>2</sub> as a reactant represents one of the most promising routes in Carbon Capture and Utilization (CCU) practices. The CO<sub>2</sub> fixation reactions are advantageous reactions in CCU processes since newly formed compounds have higher atom and energy efficiency. Carboxylic acids are one of the most abundant and important type of compounds, which find their role in various industries and reaction paths. The Kolbe-Schmitt reaction is a two-step process of production of salicylic acid, involving the reaction between the strong base (hydroxides/carbonates) and the phenol, followed by the carboxylation of the produced metal phenoxide. In this study, it was found that NaOH, KOH, and Na<sub>2</sub>CO<sub>3</sub> are active bases for a two-step Kolbe-Schmitt method, while K<sub>2</sub>CO<sub>3</sub> is active only using the Marasse method, involving direct reaction between the phenol, the base and the CO<sub>2</sub>. The results have shown that the usage of KOH results with the highest selectivity towards the salicylic

acid (SA), while besides the SA, other obtained products include 4-hydroxybenzoic acid (4HBA) and the dicarboxylic product of 4-hydroxyisophthalic acid (4HiPh).

**Keywords:** phenol, salicylic acid, carboxylation, CO<sub>2</sub>

### **Acknowledgement**

Authors gratefully acknowledge financial support by the Slovenian Research Agency (P2-0152 and J2-1723).

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# Investigation of PET Plastic Waste Degradation

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Plastic waste significantly pollutes aquatic ecosystems, especially aquatic animals that get caught in larger pieces of plastic and often consider smaller pieces as food. When they swallow plastic particles, they often can no longer digest normal food and die (Thushari and Senevirathna, 2020). Humans ingest plastic containing toxic substances through the food chain, which can be detrimental to long-term health (Ašmonaitė 2019). In a resolution adopted in 2021 (European Parliament, 2021), urgent action is called for to reduce aquatic pollution, limit the use of single-use plastics and promote sustainable and biodegradable materials. Understanding the impacts of conventional plastics on various aquatic habitats is critical for the development of new materials.

This research focuses on tracking plastic waste (PET films and PET fibers) using Toxicity characteristics following Characteristic Leaching Procedure (TCLP)-SW-846 Test Method 1311 (EPA, 1992) to determine the mobility of both organic and inorganic analytes present in samples. Water obtained by the TCLP process was tested for simple qualitative properties (turbidity, conductivity, and chemical oxygen demand (COD) of the samples) before and after the filtration process. The water after filtration was also analyzed for particle size distribution by determining the hydrodynamic radio using the principles of dynamic light scattering. It has been shown that particles of colloidal size (less than 1  $\mu\text{m}$ ) are found in the filtrate, while analysis of PET fibres by optical microscope revealed that fragmentation into micro- and nanofibers occurred, while in case of PET films no fragmented particles were found.

The results are shown in Table 1.

**Table 1: Analysis of water obtained in TCLP before and after the filtration process**

	Blank	PET films	PET fibers
Parameter before   after filtration			
Turbidity (NTU)	0.05   0.02	0.29   0.26	15.93   1.21
Conductivity ( $\mu\text{S}/\text{cm}$ )	0.757   2.53	4.82   5.34	6.89   6.55
COD (mg/L O <sub>2</sub> )	< 3   < 3	< 3   < 3	72   8.5
Particles-plastic released on filter (mg)	/	0.3	3.2
Plastics mass loss (%)	/	0.099	0.199
Particle size after filtration (nm)	/	929	819

From the results, fragmentation into micro and nano particles is much more pronounced in the water-based fiber sample of PET, resulting in higher sample turbidity, conductivity, and release of plastic particles. In addition, PET fibres lose more mass compared to PET films. This indicates that PET fibers are much more susceptible to degradation, resulting in higher COD values compared to those for PET film-based water samples, implying a higher organic contaminant content.

**Keywords:** plastics, degradation, aquatic environment, fragmentation, PET films, PET fibers, toxicity characteristics



## Acknowledgement

The authors would like to acknowledge financial support from the Slovenian Research Agency (project No. J7-3149 and core research funding No. P2-0421, P2-0118 and P2-0412) and the Grant Agency of the Czech Republic under Project No. 21-45726L.

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# Selective Catalytic Conversion of 5-HMF to Diols and Triols

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## Introduction

Hydroxymethylfurfural (HMF) is a critical platform chemical with incredible potential that can be made from renewable resources, specifically lignocellulosic biomass [1]. Due to the fact that HMF consists of three relevant functionalities (an aldehyde, an alcohol, and furan ring), a wide variety of bio-based chemicals can be produced that are highly desirable in the polymer industry [2]. Hydrogenation has been identified as the most encouraging catalyst conversion route to convert 5-HMF to high value chemicals. Usually, hydrogenation is carried out at moderate temperatures (180-250°C), elevated hydrogen pressures (30-50 bar), in the presence of a heterogeneous catalyst [3]. Considering catalysts that have been recognized to be highly active for hydrogenation, transition metal catalysts are favourable as they are economically advantageous, although, they generally require supplementary promoters to improve performance and tune product selectivity. Nickel supported on alumina was chosen alongside ceria as the promoter to alter the acidity of the

catalyst to finely tune product selectivity towards diols (BHMF/BHMTHF) and triols (1,2,6-hexanetriol).

## Methods

Catalytic activity tests were carried out in 75 mL batch reactors where liquid samples were collected, and quantified using a GC-FID, to plot product concentrations as a function of time. Several catalyst characterization methods were performed including temperature-programmed reduction (TPR), SEM, TEM, in addition to temperature-programmed desorption (TPD).

## Results

A reaction network based on all detectable products during catalytic activity experiments has been proposed and validated. A detailed kinetic model has also been described that demonstrates the impact different types of active sites (metallic and acidic) have on product selectivity and the influence ceria as the promoter had on catalyst activity and selectivity.

## Acknowledgement

Authors acknowledge financial support by the EU Framework Programme for Research and Innovation Horizon 2020 under Grant agreement no. 814416 (ReaxPro) and the ARRS (Programme P2-0152 and postdoctoral research project Z2-9200).

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# Advances in Biopolymer Science and Technology Aiming Towards Resilience and Zero-Waste Circular Bioeconomy

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ANA OBERLINTNER, BETI VIDMAR, PETRA JERIČ, BLAŽ LIKOZAR

We are entering a ‘storm’ of climate change and biological resource constraints. The earlier companies, cities, and countries plan ahead and prepare themselves for the predictable future, the better their chance of thriving. Taking into account the planet Earth Overshoot Day for 2022 was 28<sup>th</sup> of July and marks the date when humanity’s demand for ecological resources and services in a given year exceeds what Earth can regenerate in that year. This deficit has related to liquidating stocks of ecological resources and accumulating waste, primarily carbon dioxide in the atmosphere” (Earth Overshoot Day 2022). Step towards new logic resilience and sustainability through exploring renewable biomass and waste streams not only to replace current practice but foremost pursue a way of delivering new value products and energy following the zero-waste concept by closing the loops, reducing the material and

emission footprint and protecting the environment and resources for the future generations. In that respect the evaluation of the biorefinery concepts offering a rich spectre in valuable compounds from the abundant renewable local resources was put in our focus (Vicente et al., 2022). A special case studies for building a circular bioeconomies from the waste being available in quantities for commercial valorisation, will be showcased. Additionally an overview of technologies was also assessed for more sustainable and environmentally friendly and circular approaches. Highlight the recently developed lab scale sustainable alternative processes, which greatly lowered the environmental burden of produced waste the environmental footprints and the energy demand distribution of different cradle to gate routes will be presented.

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# Characterization of Solid Residue Obtained After Enzymatic Hydrolysis of Textile Waste

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The increasing waste quantities reached 2.17 million tons of textile waste produced in 2018 (Eurostat, 2022). The majority of this waste is still not recycled but mixed with other Municipal Solid Waste (MSW) and co-incinerated or landfilled (EEA, 2022). This makes textile waste an important area for introduction of circular economy solutions, where various processes have already been proposed. A very promising one is the enzymatic hydrolysis (EH), in which textile polymers are decomposed into various valuable monomers in a biochemical process under the influence of enzymes. Aside bio-based polymers, the process has been recently adapted also to perform decomposition of polyester/cellulose blends (Quartinello et al, 2018). While the research is currently focused on increasing the process efficiency, its solid residue is still a subject of thermal treatment by incineration or co-incineration in large scale devices (Xu et al, 2021). As the EH process requires heat energy, there is an emerging important possibility to apply remaining solid

residue as an energy source, allowing the closing of the material and energy loops and thus introduce a truly circular economy solution.

The current state of the art largely disregards treatment of the solid residue, leading to the lacking description of the relevant solid residue properties and its behavior during thermal treatment processes. Thus, the first ever study to determine both the physical and chemical properties of the material before and after EH was conducted with the aim to provide required data for proposal of suitable thermal treatment process. The study first defines the bulk density and compressibility to determine handling requirements. Then, chemical composition is defined using FTIR and combined with the moisture analysis, obtained with coulometric titration. This data also serves in validation of higher and lower heating values, obtained with adiabatic calorimeter. Crucial data on thermal decomposition behavior is generated with TGA measurements. Two different textile waste materials were considered, the unused waste sanitation textile (cotton, non-woven) and the cotton spinning waste. The results were benchmarked with properties of other waste and biomass derived fuels, which showed that the most similar materials to the EH solid residue are wood shavings and MSW. This provides useful orientation regarding material handling and its introduction into thermal treatment process.

To provide additional information for decision making related to design and control of the thermal treatment process itself, the study also includes the analysis of the expected combustion properties with the use of 3D CFD combustion modeling. The combustion properties were modelled for both the solid residue and the entry material using surrogate model approach, which allows for detailed combustion description of the volatiles that are expected to be generated during thermal decomposition at different conditions. With this, the study presents the first ever analysis of the chemical, physical and combustion properties of the EH solid residue. It thus provides the crucial data for the design of efficient thermal treatment solutions for closing the energy and material loops in the area of textile recycling.

### **Acknowledgement**

The work is part of the Poly Circularity (Poly Krožnost) project, funded by the Slovenian Ministry of Economic Development and Technology and by the European Union through the European Regional Development Fund.

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# Automated Design of Experiments Within a Conceptual Framework for the Design and Synthesis of Microprocess Systems

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Microprocess systems are an increasingly important area for process intensification in chemical production and a promising tool for process automation and optimization. The principle of Design of Experiments (DoE) is widely used to optimize reactions, which is also being studied in the field of flow systems. Recently, many studies have been conducted on the topic of self-optimization of flow systems, including an integrated online analysis tool with feedback control loop that uses an optimization algorithm to repeatedly generate new conditions until an optimum is reached. The aim of this work is to review the state of the art in automated optimization of flow processes and the analytical tools required to improve the experimental part of our previous study, which discussed a conceptual framework for microprocess design and synthesis through a combined laboratory approach

(microdevices) and mathematical programming (MIPSYN-Global) (Verdnik et al., 2022).

To find the optimal operating parameters of chemical reactions, several experiments under different reaction conditions must be performed to reach the optimum, which can be time consuming. To enable faster optimization, a self-optimization platform consisting of laboratory equipment with analytical tools, computer software, and an optimization algorithm was developed (Rodriguez-Zubiri et al., 2022). It turned out that flow systems (consisting of a pump, flow reactor, temperature controller, backpressure controller, etc.) are ideal for self-optimization of reactions precisely because of their small size. They allow integration of analytical tools and adjustment of operating parameters such as flow rate, temperature, and pressure (Holmes et al., 2016).

A literature review has shown that the main monitoring techniques, using analytical instrumentation to monitor chemical reactions in flow reactors, are as follows: On-line high performance liquid chromatography (HPLC), mass spectrometry (MS), gas chromatography (GC), and in-line infrared spectroscopy (FTIR), ultraviolet-visible spectroscopy (UV-vis), and nuclear magnetic resonance spectroscopy (NMR) (Rodriguez-Zubiri and Felpin, 2022).

In addition to flow systems and analysis tools, there is also a need for optimization algorithms and computer software. Self-optimization algorithms allow us to reduce the number of experiments to reach the optimum. The most common single objective algorithm is Stable Noisy Optimization by Branch and FIT (SNOBFIT) (Jeraal et al., 2021), which has been successfully used to optimize chemical reactions of organic compounds in flow reactors. In practice, it is necessary to optimize several criteria simultaneously, e.g., to maximize product yield and minimize process costs. The Thompson Sampling Efficient Multi-Objective (TS-EMO) algorithm is most commonly used for multi-objective optimization of chemical processes (Schweidtmann et al., 2018). The most common software for automating chemical reactions with one of the algorithms is based on LabVIEW, which is integrated with Matlab (Bédard et al., 2018).



To achieve effective optimization of the chemical process, various combinations of interactions between temperature, pressure, and reaction time must be considered. Automated flow reactors with integrated analysis and feedback control represent an important tool for determining optimal operating parameters in the chemical process industry. In this way, the efficiency of laboratory experiments would be improved in a combined laboratory/mathematical programming approach to the design and synthesis of microprocess systems.

### **Acknowledgement**

The authors are grateful for financial support from the Slovenian Research Agency (program P2-0414 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).

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# Life Cycle Assessment of Blended Cements with Wood Biomass Ashes

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Cement industry is one of the most important economic sectors in the Europe, as it supplies several key value chains. It is identified as high impact intermediary products and Energy Intensive Industry (EII) as according to *European Green Deal and Masterplan for a competitive transformation of EU energy-intensive industries enabling a climate-neutral, circular economy by 2050*. Greater circularity of materials represents a major opportunity for transforming these industries into environmentally friendly, carbon-neutral, resource-efficient, and circular industries. This has already been recognized in the cement industry: Today's commercially available cements typically contain an average of about 20% cementitious substitutes - mainly finely ground limestone, granulated blast furnace slag or fly ash from coal-fired power plants. It is estimated that the use of these and similar cement substitutes can reduce CO<sub>2</sub> emissions from cement production by about 400 million tons per year (Juenger and Siddique, 2015) (Scrivener et al., 2016).

On the other hand, a large portion of mixed waste streams are still disposed of in landfill. Incineration ashes belong to this category. Incineration ashes are generated from the combustion of various materials/fuels, and several types can be distinguished: Municipal Solid Waste Incinerator Ash (MSWI), ashes from incineration of sewage sludge (sewage sludge ashes – SSA) and wood biomass ashes (WBA), which is generated when wood biomass is used as a renewable resource in power plants. The status of certain types of these wastes in the EU depends on the regulations and practices of individual member states. In Croatia, only WBA is produced. The trend of increasing of new power plants poses a problem for WBA management. It is estimated that the total amount of WBA in the existing biomass plants in Croatia is 25,414 tons per year (Milovanović et al., 2019).

For a circular economy and a sustainable society, it is important to put the incineration ash to good use. This is possibility by activating all relevant actors in the value chain to develop synergies and partnerships in the development of an ash-based system solution. This is one of the main objectives of the new European project »*AshCycle – Integration of underutilized ashes into material cycles by industry-urban symbiosis*«. The sustainability performance of innovative products and technologies will be captured using the life cycle assessment (LCA) tool. In this study, the life cycle analyses of two cement blends with wood biomass ash are compared with those of commercially available cement. In addition, technical and logistical challenges of using new materials in cement sector have been identified.

### Acknowledgement

This research was performed as a part of the European project Horizon Europe Grant Agreement No 101058162 ‘AshCycle – Integration of underutilized ashes into material cycles by industry-urban symbiosis’.

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# Adsorption of Heavy Metals Using Magnetic Nanoparticles and External Magnetic Field

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**Introduction:** Heavy metals are common pollutants of water and soil, therefore pose a huge risk for ecosystems due to their non-degradable nature (Bhateria and Singh, 2019). The magnetic field assisted adsorption is a non-conventional method employed in the removal of water pollutants (Flores López et al., 2018). It can be performed using magnetic nanoparticles (MNPs), modified with different organic polymers. Polysaccharides have been extensively employed in synthesis of MNPs as coating materials for constructing an adsorptive material, mainly due to its high adsorptive ability, low cost, renewability, biodegradability, biocompatibility and ease of modification (Vasić et al., 2020; Almomani et al., 2020).

**Methods:** Chitosan MNPs were synthesized by the co-precipitation method, using ferric and ferrous ions, and later functionalized with chitosan by microemulsion technique. Such synthesized MNPs were used as the adsorptive material for efficient removal of Cr(VI) ions. Adsorption of Cr(VI) ions was optimized with and without an external magnetic field, while when using the external magnetic field, the amount of the absorbent (30 and 50 mg of MNPs) and magnetic field strength (50, 100 and 200 mHz) were optimized.

**Results:** The optimum conditions for Cr(VI) ions adsorption using chitosan functionalized MNPs were found to be while using an external magnetic field in a batch system. The highest adsorption efficiency after 2h (94.2%) was achieved when using 50 mg of MNPs with the frequency of the electric current through the coil set to 100 mHz.

**Conclusions:** Chitosan functionalized MNPs were found to be an effective adsorptive nanomaterial for efficient removal of Cr(VI) ions from aqueous solutions using an external magnetic field and show great potential for use in wastewater treatments.

#### Acknowledgement

This research was supported by the Slovenian Research Agency within the frame of program P2-0046 (Separation Processes and Production Design), program P2-0114 (Applied electromagnetics) and project No. J2-3037 (Bionanotechnology as a tool for stabilization and applications of bioactive substances from natural sources).

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# 5<sup>TH</sup> INTERNATIONAL CONFERENCE ON TECHNOLOGIES & BUSINESS MODELS FOR CIRCULAR ECONOMY: BOOK OF ABSTRACTS

SANJA POTRČ, MILOŠ BOGATAJ, ZDRAVKO KRAVANJA,  
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**Abstract** The 5th International Conference on Technologies & Business Models for Circular Economy (TBMCE) was organized by the Faculty of Chemistry and Chemical Engineering, University of Maribor in collaboration with the Strategic Research and Innovation Partnership - Networks for the Transition into Circular Economy (SRIP- Circular Economy) and Chamber of Commerce and Industry of Štajerska. The conference was held in Portorož, Slovenia, at the Grand Hotel Portorož from September 12th to September 14th, 2022. TBMCE 2022 was devoted to presentations of circular economy concepts, technologies and methodologies that contribute to the shift of business entities and society as a whole to a more responsible, circular management of resources. The conference program included panel discussions, plenary and keynote sessions, oral and poster presentations on the following topics: Sustainable energy, Biomass and alternative raw materials, Circular business models, Secondary raw materials and functional materials, ICT in Circular Economy, Processes and technologies. The event was under the patronage of Ministry of Economic Development and Technology.

**Keywords:**

circular economy, sustainable development, processes and technologies, circular business models, research and development



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