TBMCE 2019

2nd International Conference on TECHNOLOGIES & BUSINESS MODELS FOR CIRCULAR ECONOMY

CONFERENCE PROCEEDINGS

EDITORS MILOŠ BOGATAJ ZDRAVKO KRAVANJA ZORKA NOVAK PINTARIČ





Faculty of Chemistry and Chemical Engineering

2nd International Conference on Technologies & Business Models for Circular Economy

Conference Proceedings

Editors

Miloš Bogataj Zdravko Kravanja Zorka Novak Pintarič

May 2020

Title Naslov	2 nd International Conference on Technologies & Business Models for Circular Economy
Subtitle Podnaslov	Conference Proceedings
Editors Uredniki	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)
Technical editor Tehnični urednik	Jan Perša (University of Maribor, University Press)
Cover designer Oblikovanje ovitka	Jan Perša (University of Maribor, University Press)
Graphic material <i>Grafične priloge</i>	Authors
Conference <i>Konferenca</i>	TBMCE, International Conference on Technologies & Business Models for Circular Economy
Date and location Datum in kraj	October 24th to October 25th, 2019, Portorož, Slovenia
Organizing Committee Organizacijski odbor	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).
International Scientific Committee Mednarodni znanstveni odbor	Zdravko Kravanja (University of Maribor, Slovenia), Zorka Novak Pintarič (University of Maribor, Slovenia), Miloš Bogataj (University of Maribor, Slovenia), Mojca Škerget (University of Maribor, Slovenia), Mariano Martin (University of Salamanca, Spain), Jiří Klemeš (Brno University of Technology, Czech Republic), Agustin Valera-Medina (Cardiff University. United Kingdom), Petar Uskoković (University of Beograd, Serbia), Elvis Ahmetović (University of Tuzla, Bosnia and Herzegovina), Stefan Willför (Åbo Akademi University, Finland), Adeniyi Isafiade (University of Cape Town, South Africa), Hon Loong Lam (University of Nottingham, Malaysia), Mario Eden (Auburn University, United States of America), Timothy G. Walmsley, (Waikato University, New Zeeland), Tomaž Katrašnik (University of Ljubljana, Slovenia), Blaž Likozar (National Institute of Chemistry, Slovenia), Primož Oven

(University of Ljubljana, Slovenia), Dragica Marinič (Chamber of Commerce and Industry of Štajerska, Slovenia) & Vilma Ducman (Slovenian national building and civil engineering institute, Slovenia).

Published by / Založnik **Co-published by** / Izdajatelj University of Maribor University of Maribor University Press Faculty of Chemistry and Chemical Engineering Slomškov trg 15, 2000 Maribor, Slovenija Smetanova ulica 17, 2000 Maribor, Slovenija https://press.um.si, zalozba@um.si https://www.fkkt.um.si/, fkkt@um.si Edition Publication type 1 st E-book Izdaja Vrsta publikacije Available at http://press.um.si/index.php/ump/catalog/book/472 Dostopno na Published at Maribor, may 2020 Izdano REPUBLIKA SLOVENIJA IP KROŽNO MINISTRSTVO ZA GOSPODARSK GOSPODARSTVO RAZVOLIN TEHNOLOGIIO

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



© University of Maribor, University Press

Text / Besedilo © Authors & editors 2020

This work is licensed under the Creative Commons Attribution-NonCommercial-NoDerivs 4.0 International License. / To delo je objavljeno pod licenco Creative Commons Priznanje avtorstva-Nekomercialno-Brez predelav 4.0 Mednarodna. 4.0 Mednarodna.

https://creativecommons.org/licenses/by-nc-nd/4.0/

```
Kataložni zapis o publikaciji (CIP) pripravili v
Univerzitetni knjižnici Maribor
COBISS.SI-ID 15270915
ISBN 978-961-286-353-1 (PDF)
```

ISBN	978-961-286-353-1 (pdf)
DOI	https://doi.org/10.18690/978-961-286-353-1
Price <i>Cena</i>	Free copie
For publishe r Odgovorna oseba založnika	prof. dr. Zdravko Kačič, Rector of University of Maribor

2ND INTERNATIONAL CONFERENCE ON TECHNOLOGIES & BUSINESS MODELS FOR CIRCULAR ECONOMY

MILOŠ BOGATAJ, ZDRAVKO KRAVANJA &

ZORKA NOVAK PINTARIČ

University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mails: milos.bogataj@um.si, zdravko.kravanja@um.si, zorka.novak@um.si

Abstract The 2nd International Conference on Technologies & Business Models for Circular Economy (TBMCE) 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. In the framework of TBMCE 2019, we presented the Strategic Research and Innovative Partnership - Network for the Transition to Circular Economy (SRIP-CE) as a platform for establishing successful long-term public-private а partnership. 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. TBMCE 2019 was organized by Faculty of Chemistry and Chemical Engineering, University of Maribor and held in Portorož, Slovenia at the Grand Hotel Bernardin from October 24th to October 25th, 2019. The event was under the patronage of Ministry of Economic Development and Technology.

Keywords: circular economy, sustainable development, processes and technologies, circular business models, circular business models.



DOI https://doi.org/10.18690/978-961-286-353-1 ISBN 978-961-286-353-1



Table of Contents

Foundry Wastes as a Potential Precursor in Alkali Activation Technology Barbara Horvat, Alenka Pavlin, Vilma Ducman	1
Evaluation of Fly Ash-based Alkali Activated Foams at Room and Elevated Temperatures Katja Traven, Mark Češnovar, Srečo Škapin, Vilma Ducman	23
An ICT Platform Facilitating Circular Economy Business Models Georgios Tsimiklis, Miltiadis Koutsokeras, Sten-Erik Björling, Wenjie Peng, Sebastien Schmitter, Tim Bartam, Angelos Amditis	35
The Inhibition Effect of Natural Honey on Corrosion of Stainless Steel in a 17 % HCl Solution Regina Fuchs-Godec, Rok Špendl, Urban Bren	47
Use of Supercritical Water for Degradation of Polyethylene Waste Mojca Škerget, Maja Čolnik, Petra Kotnik, Željko Knez	57
Lignin Concentration During Incubation of Chicken Manure with Sawdust and Wheat Straw or Miscanthus Overgrown with <i>Pleurotos</i> <i>Ostreatus</i> Fungi Darja Pečar, Maša Islamčević Razboršek, Franc Pohleven, Andreja Goršek	65
The Deformation of Alkali-activated Materials at Different Curing Temperatures Mark Češnovar, Katja Traven, Vilma Ducman	75
Municipal Waste Composition Analysis – Approaches to and Solutions for Czech Waste Management Jiří Kropáč, Jiří Gregor, Martin Pavlas	85
The Use of Paper Industry Side Products in Construction Barbara Likar, Laura Vovčko	95
Economic Assessment of Waste Oil-in-Water Emulsion Treatment Processes Zorka Novak Pintarič, Marjana Simonič	107

The Influence of Safety Factors on the Optimal Design of Underground Lined Rock Caverns Stojan Kravanja, Tomaž Žula	123
Sustainability Profit Generated by the Optimization of Continuous Beams Tomaž Žula, Stojan Kravanja	133
Pyrolysis – An Alternative Way of Recycling Matevž Roškarič	141
Competence Model for Factories of the Future Tanja Batkovič, Bojan Cestnik, Aleksander Zidanšek, Andreja Abina	159
Education for Zero Waste and the Circular Economy Sector in Europe Peter Glavič, Aida Szilagyi, Isavella Karouti, Achilleas Kostoulas, Oihana Hernaez, Martin Dolinsky, Thomas Schönfelder, Pavel Ruzicka, Gosia Stawecka, Dimitrios Karadimas, Cristina S. Rocha, David Camocho, Bojana Žiberna, Eugenia Atín, Barbara Hammerl, Hans Schnitzer	175
Enzyme Deactivation Using High Pressure Carbon Dioxide Technology Gordana Hojnik Podrepšek, Željko Knez, Maja Leitgeb	205
The H2020 CINDERELA Project — A New Circular Economy Business Model for More Sustainable Urban Construction Alenka Mauko Pranjić, Kim Mezga, Primož Oprčkal, Sebastjan Meža, Ana Mladenovič, Izabela Ratman-Klosińska, Marek Matejczyk, Tomislav Ploj, Matej Kadić, Ainara Garcia Uriarte, Pierre Menger, Douwe Huitema, Niels Ahsmann, Arnout Sabbe, Arjan van Timmeren, Monica Conthe Calvo, Veljko Janjić, Igor Osmokrović, Mario Conci, Matteo Donelli, Enrico Pusceddu, Massimiliano Bertetti, Ignacio Vilela Fraile, Lidia Gullón, Santiago Rosado	211
An Investigation of Waste Material Parameters during Pretreatment Robert Hren, Aleksandra Petrovič, Lidija Čuček, Marjana Simonič	227
Anaerobic Co-digestion of Sewage Sludge and <i>Typha Latifolia</i> and the Impact of Cattle Rumen Fluid on Biogas Production Aleksandra Petrovič, Lidija Čuček, Marjana Simonič	235
Enhanced Inherent Safety Assessment during Heat Exchanger Network Synthesis Anita Sovič, Danijela Urbancl, Zdravko Kravanja, Andreja Nemet	247
Comparative Life Cycle Assessment of Alternative Packaging Materials for Beverages Damjan Krajnc, Zorka Novak Pintarič & Zdravko Kravanja	257

ii

The Difficulties of Designing Technical-Economic Models for Czech Wastewater Treatment Plants Vojtěch Zejda, Jiří Gregor, Jiří Kropáč, Šárka Václavková	273
Catalytic Conversion of Biomass-derived Furfural into Value-Added Chemicals Aleksa Kojčinović, Miha Grilc, Blaž Likozar	285
Transportation Model for Carbon-Constrained Electricity Planning: An Application to the Aluminium Industry	295

Rok Gomilšek, Lidija Čuček, Marko Homšak, Zdravko Kravanja

FOUNDRY WASTES AS A POTENTIAL PRECURSOR IN ALKALI ACTIVATION TECHNOLOGY

BARBARA HORVAT¹, ALENKA PAVLIN² &

VILMA DUCMAN¹

¹ Slovenian National Building and Civil Engineering Institute, Department for Materials, Ljubljana, Slovenia, e-mail: barbara.horvat@zag.si, vilma.ducman@zag.si ² TERMIT, Moravče, Slovenia, e-mail: alenka.pavlin@termit.si

Abstract In this study the amount of amorphous phase of elements useful in alkali activation of waste materials produced by the foundry industry was determined. Waste foundry sands, foundry flue gas and waste casting cores were alkali activated, and waste green ceramics and bottom ash were added to one of the foundry sand samples to shorten the time for producing measurable compressive strength from 1.5 years to 1 week. Keywords: alkali activated material, foundry wastes, compressive strength, upcycling, circular economy.



DOI https://doi.org/10.18690/978-961-286-353-1.1 ISBN 978-961-286-353-1

1 Introduction

The ZAG national building institute and Termit, a mining company, started an upcycling project in 2017 in which different waste materials from several sources were used as precursors in alkali activation (AA) of potential lightweight insulating materials used in the building industry.

Alkali activated synthesis is the process of inorganic materials rich in amorphous Si and Al reacting with alkali (NaOH, KOH, Na-water glass, K-water glass) forming a semi-crystalline polymer structure of Si and Al connected with O bridges. Both Si and Al are in aluminosilicate network as SiO₄ and AlO₄ tetrahedrons that are joined by oxygen bridges. Compensation of the non-natural coordination number of Al is accomplished by amorphous cations from precursor or from an alkali solution (Provis, 2013, Provis and Bernal, 2014, Palomo *et al.*, 1999, Provis, 2014, van Deventer *et al.*, 2010, *Handbook of Alkali-Activated Cements, Mortars and Concretes*, 2015, Provis, 2018).

This technology offers savings to the building industry as a result of low processing costs due to the low temperature curing, and by using waste materials or byproducts instead of raw materials (Palomo and Fernández-Jiménez, 2011); at the same time, these materials have good physical properties and can be fire resistant (Hajimohammadi *et al.*, 2017).

The most thoroughly researched materials for alkali activation are fly-ash (Palomo *et al.*, 1999, Němeček *et al.*, 2011, Fernández-Jiménez and Palomo, 2005, Škvára *et al.*, 2009, Puertas and Ferna, 2003, Puertas *et al.*, 2000), slag (Puertas and Ferna, 2003, Shi and Qian, 2000, Puertas *et al.*, 2000, Pan *et al.*, 2002, Buchwald *et al.*, 2007, Bakharev *et al.*, 1999, Bernal *et al.*, 2012) and metakaolin (Pacheco-Torgal *et al.*, 2008, Němeček *et al.*, 2011, Buchwald *et al.*, 2007, Granizo *et al.*, 2004, Granizo *et al.*, 2000, Bernal *et al.*, 2012, Alonso and Palomo, 2001); however, there are many other waste materials produced by industry and by the demolition of buildings that could be used as precursors.

The focus of our work was to evaluate various foundry wastes upcycling with alkali activation technology into materials that can be used in the building industry. Termit collects these materials from foundries which use their casting cores and quartz sand in order to use these wastes for the rehabilitation of open pits.

Foundry fumes, flue gas and exhaust air (FFG) must be captured in the foundry industry ("European Commission Integrated Pollution Prevention and Control," 2005) because they present a health hazard (Tossavainen, 1976) to foundry workers (lung contamination (Kalliomäki *et al.*, 1979), respiratory disease (Ostiguy *et al.*, 1995, Low and Mitchell, 1985), and potential carcinogenicity (Humfrey *et al.*, 1996)); therefore, it is crucial to immobilize these gases, which can be done with alkali activation (Fernandez-Jimenez *et al.*, 2005b, Khalil and Merz, 1994, Nikolić *et al.*, 2014, Qian *et al.*, 2003, Fernandez-Jimenez *et al.*, 2005a, Guangren, 2002, Yunsheng *et al.*, 2007, Zhang *et al.*, 2008, Shi and Fernández-Jiménez, 2006, Deja, 2002).

Waste foundry sand (WFS) comprises in Termit the largest amount of all collected chemically inert and stable waste materials; therefore, it is logical to find other uses for it. Several studies in the civil engineering field have been conducted with WFS:

- In concrete production, where WFS replaced fine aggregate from 0 % to 100 %, and the water to cement ratio was constant. With increasing amounts of WFS, compressive strength decreased (from 43.6 MPa without WFS, to 32.9 MPa when 60 % WFS replaced fine aggregate, to almost half when only WFS was used – measured on 28th day), while shrinkage and water absorption increased (Khatib *et al.*, n.d.).
- In high-strength concrete production, fine natural sand was replaced with WFS in increments of 0 %, 5 %, 10 % and 15 %. Compressive strength increased with time but decreased with an increase in the ratio of WFS to natural sand. Optimal re-allocation happened at 10 % replacement of fine natural sand with WFS, where a decrease in compressive strength was from 61 MPa to 60 MPa (measured on 28th day). Concrete with more than 5 % WFS showed reduction in water absorption. The particle size distribution of WFS must be arranged to provide similar properties to concrete made with standard fine sand (Guney *et al.*, 2010).

- In ready-mixed concrete production, regular sand was replaced with 0 %, 10 %, 20 %, 30 % and 40 % WFS. Compressive strength and density decreased (from 43.2 MPa to 42.7 MPa when WFS replaced 10 % of the regular sand - measured on 28th day), while water absorption increased with the replacement of sand with WFS. 20 % WFS instead of regular sand does not compromise mechanical properties. Ni, Zn, Cr, F-, total dissolved solids, total organic carbon, and dissolved organic carbon were immobilized well at different pH conditions according to TS EN 12457-4:2004 (Basar and Deveci Aksoy, 2012).
- In concrete production, fine aggregates were partially replaced by bottom ash and WFS in equal amounts from 0 % to 60 %. Compressive strength after 28 days of up to 50 % replacement with WFS and bottom ash was from 29 MPa to 32 MPa (without replacement it was over 35 MPa), and after 1 year it was comparable to the compressive strength of concrete made with just fine aggregates, making 50 % substitution of fine aggregates the highest possible value. The highest compressive strength among all samples with WFS and bottom ash was demonstrated with a sample with 30 % replacement of fine aggregates (Aggarwal and Siddique, 2014).
- In low calcium fly ash alkali activated concrete and in ground granulated blast furnace slab based alkali activated concrete, WFS partially to entirely replaced normal sand, in proportions of 0 %, 20 %, 40 %, 60 %, 80 % and 100 %. A mixture of sand and WFS was added to a mixture of slag/ash and ordinary Portland cement. Whole dry content was alkali activated with 14 M NaOH, Na-water glass and tap water, where the ratio was NaOH(aq):Na-water glass=1:2.3; the mass % (m%) of aggregates to the whole was 76 %, and the m% of alkaline solution was 45 % of powdered binder. The mixture was cured in moulds for 24 h, and compressive strength measured at 28 days, when the alkali activated slag concrete showed higher strength than alkali activated fly ash concrete, no matter the amount of WFS. The highest compressive strength with fly ash concrete was with 60 % of WFS (48.5 MPa), while the highest compressive strength with slag concrete was with 20 % of WFS (above 55 MPa from Fig. 5, Bhardwaj and Kumar, 2019).
- In alkali activation, WFS was used as a precursor and activated with NaOH/KOH of different molarity (6, 8, 10, 12, 14 M), and/or Na-water glass with/without addition of water, cured at room temperature and at 70 °C for 24 h, dried at room temperature and at 110 °C for 24 h, or in a

microwave for 2.3 min. The highest compressive strength was 27.7 MPa gained with only Na-glass water. The addition of water ruined the compressive strength, while drying at elevated temperature or with microwaves increased its value, but at the same time, it severely decreased bending strength (Horvat *et al.*, 2019).

2 Experimental

For research on a laboratory scale, waste casting cores, waste foundry sands, foundry flue gas, a mixture of bottom and fly ash, and waste green ceramics, presented in Table 1 (with sample label and waste label from the Classification list of waste from Official Gazette of the Republic of Slovenia, no. 20/01 Annex 1) were collected from Termit's open waste dumps. The last two waste materials listed were used only as a supplement to foundry sand.

Sample Sample label Waste label Waste casting cores WCC 10 09 06 Waste foundry sand A WFS-A 10 09 08 Waste foundry sand B WFS-B 10 09 08 Waste foundry sand C WFS-C 10 09 08 Foundry flue gas FFG 10 09 10 Mixture of bottom and ASH 10 01 01 fly ash Waste green ceramics WGC 10 12 01

Table 1: Analysed Termit's samples collected from waste dump piles.

Source of labels: Official Gazette of the Republic of Slovenia, no. 20/01 Annex 1

Chemical (X-ray fluorescence; XRF) and mineralogical (X-ray powder diffraction; XRD) analyses were performed on all samples, which were dried to remove H2O with an IR dryer at 105 °C to constant mass, and were afterwards ground in a vibrating disk mill (Siebtechnik) and sieved below 90 μ m.

XRD analysis was performed (Empyrean PANalytical X-Ray Diffractometer, Cu X-Ray source) in steps of 0.0263° from 4° to 70°, under cleanroom conditions, in powder sample holders with an aperture diameter of 27 mm. Mineral analysis, with Rietveld refinement using external standard (pure Al2O3 crystal) to determine the amount of amorphous phase and minerals, was performed with X'Pert Highscore plus 4.1 on XRD data.

Loss of ignition (LOI) was performed on dried powder samples at 950 °C for 2 h in a furnace (Nabertherm B 150) to remove organic compounds and CO2. LOI was determined with the gravimetric method from 2 parallel measurements and corrected with XRF analytical LOI obtained on a fused basis.

For XRF analysis (Thermo Scientific ARL Perform'X Sequential XRF), ignited material was mixed with Fluxana (FX-X50-2, Lithium tetraborate 50 %) in a ratio of 1:10 for Fluxana to lower the melting temperature in a Claisse furnace from The Bee Electric Fusion (to avoid gluing of melt in the platinum vessel, a few drops of LiBr were added to the Fluxana powder mixture). Analysis of the melted disks was performed with OXAS software, and the data were analyzed with UniQuant 5 software.

A scanning electron microscopy (SEM; Jeol JSM-IT500 with tungsten filament cathode) investigation was performed under high vacuum conditions on dried samples.

For alkali activation, samples were dried at 70 °C for 24 h in a WTB Binder dryer without any further treatment if not stated otherwise. 10 M NaOH (Donau Chemie Ätznatron Schuppen, EINECS 215-785-5) and Na-water glass (Geosil, 344/7, Woelner) were mixed in a mass ratio of 1:1, stirred until the liquid became clear, and poured into the sample under constant mixing. The amount of precursor to liquid phase, presented in Table 2, was determined experimentally with a viscometer (Haake PK 100, VT 500, PK2 1.0°), where the limit was the point where viscosity could not be measured any longer due to overload of torque (the WCC sample was ground below 2 different sizes of particles, while samples with smaller particles needed more liquid phase because of enlarged surface area).

m% ratio Sample label	Precursor	10 M NaOH	Na-water glass
WCC ^a	2.5	1	1
WCC ^b	3.3	1	1
WFS-A	4	1	1
WFS-B	3	1	1
WFS-C	3	1	1
FFG	5	1	1
ASH	3	1	1

Table 2: Mass percent ratio of precursor, 10 M NaOH and Na-water glass.

a - ground below < 90 μ m; b - gently ground below < 600 μ m

The WFS-C sample was mixed with ASH in a mass ratio of 1:1, and with ASH and WGC in a ratio of 1:1:1. The mass ratio of mixed dry precursor to 10 M NaOH and Na-water glass was 3:1:1.

Samples were moulded into prisms of 80x20x20 mm3 (sample WCC ground and sieved below 90 µm into prisms of 25x12x12 mm3) and cured at 70 °C for 24 h, or at room temperature. After demolding, they were left to dehydrate and solidify at room conditions for as long as needed, if not stated otherwise (see section 3.2). The compressive strength of alkali activated samples was measured with a compressive and bending strength testing machine (ToniTechnik ToniNORM), and samples were measured by means of SEM (under high vacuum conditions).

3 Results and discussion

Ignition losses at 950 °C of all samples are presented in Table 3.

Laboratory sample label	LOI (950 °C) [%]	LOI (XRF) [%]
WCC	2.5	3.4
WFS-A	5.2	6.5
WFS-B	6.8	7.6
WFS-C	4.0	6.3
FFG	12.7	14.6
ASH	17.7	18.9
WGC	6.5	7.4

Table 3	: LOI	determined	with	gravimetric	method	and o	calculated	from	XRF	data.
I able 5	· LOI	ucterinineu	with	graviniculie	memou	and	calculated	monn.	77171	uata.

The ignition loss of ASH was highest among tested samples (18.9 %) as a result of incomplete combustion in the process. Foundry flue gas has lower LOI (14.6 %), also due to incomplete combustion (from XRF analysis, see Table 4, there is not much CaO and MgO for potential carbonization, which could be the reason for the higher LOI).

All 3 WFS (A, B, C) and WGC have comparable LOI (around 6-7 %), while WCC has the lowest LOI (3 %) because of the high percentage of quartz in the sample (95.7 %, see Table 5).

3.1 Chemical and mineralogical analysis

The amount of different oxides was measured with XRF analysis. The results where the mass percentage of oxides is close to or above 0.1 % are presented in Table 4.

Sample label WCC	Na ₂ O	MgO	Al ₂ O ₃ 2.5	SiO2 95.6	P_2O_5	SO ₃	K ₂ O 0.1
WFS A	0.6	0.6	3.9	90.7			0.3
WFS B	0.2	0.3	3.6	87.7			0.2
WFS C	1.5		0.6	94.0			0.1
FFG	0.7	0.7	8.4	83.5			0.2
ASH	0.3	9.4	10.5	26.9	1.0	2.7	4.1
WGC	03	14	23.1	61.6			44

Table 4: Mass percentage (m% [%]) of oxides measured with XRF.

Table 4: Cont'd.

Sample label	CaO	${\rm TiO_2}$	Cr_2O_3	MnO	Fe ₂ O ₃	ZnO	SrO	BaO
ŴCC	0.1	0.08			0.5			
WFS A	0.9	0.2			1.2			
WFS B	0.5	1.0		0.3	5.0	0.08		
WFS C	0.2	0.08			0.8			
FFG	1.4	0.6			2.2			
ASH	25.3	0.6		0.4	16.8		0.09	0.2
WGC	3.4	0.2	0.8	1.5	1.5			0.4

In all samples, SiO_2 was among the most commonly detected oxides, even in bottom ash, which also had high amounts of CaO, Fe₂O₃, MgO and Al₂O₃. The latter was also present in all samples, where the highest amount, double that compared to ASH, was found in WGC. Other oxides were detected in the samples in quantities of less than 5 %.

Minerals in all precursors determined with Rietveld refinement from XRD are presented in Fig. 1, with the goodness of fit (GOF) below 8.8. All foundry waste materials contain only quartz (from 62 to 96 mass percent); the rest is in the amorphous phase. ASH, on the other hand, contains katoite, quartz, calcite, magnetite and brownmillerite (from highest to lowest amounts), while GWC contains quartz, corundum, ankerite, calcite and magnesioferrite brownmillerite (from highest to lowest amounts).

Elements in precursors (and both mixtures) useful for alkali activation, i.e. elements that are in the amorphous phase, calculated as the difference in mass % between the XRF and XRD results (all elements present in the samples minus all elements in crystalline form), are presented in Table 5. The least promising precursor (containing low amounts of Si and Al) is WCC; among the most promising WFS samples are WFS-B and WFS-C, and the least promising is WFS-A. FFG is more promising for alkali activation compared to ASH, while the most promising material among all of the samples is WGC.



Figure 1: Rietveld refinement of XRD results for a) WCC; WFS b) A. c) B, and d) C; e) FFG; f) ASH; g) WGC.

Element [m%]	Na	K	Mg	Ca	Sr	Ba	Al	Si
WCC	0	0.1	0	0.1	0	0	1.3	0.02
WFS A	0.5	0.3	0.4	0.6	0	0.04	2.0	6.2
WFS B	0.2	0.2	0.2	0.3	0	0.02	1.9	10.1
WFS C	1.1	0.1	0.03	0.1	1	1.04	0.3	2.0
FFG	0.5	0.2	0.4	1.0	0.01	0.04	4.4	10.2
ASH	0.2	3.4	5.7	6.9	0.1	0.2	3.5	6.7
WGC	0.3	3.7	0.2	0	0.02	0.4	8.2	14.0
WFS-C+ASH	0.6	1.8	2.8	3.5	0.04	0.1	1.9	4.4
WFS-C+ASH+WGC	0.5	2.4	1.9	2.2	0.03	0.2	4.0	7.6

Table 5: Mass percent (m,	[%]) of amorphous elemer	nts useful in alkali activation.
---------------------------	--------------------------	----------------------------------

3.2 Mechanical analysis

Compressive strength, one of the most important properties in the building industry, is presented in Table 6, with density, time of solidification and measurement. All three WFS tested exhibited slow reactions, where only WFS-A solidified in a few days (compressive strength was 11 MPa measured after 3 months), while the other two (WFS-B and WFS-C) needed approximately 1.5 years at room conditions (compressive strength after 3 months could not be measured). Addition of ASH to WFS-C reduced the solidification time to 1 week (compressive strength was 3 MPa measured after 3 months), while the addition of GWC to WFS-C and ASH further increased compressive strength to 8 MPa, measured after 3 months. FFG solidified in a day with compressive strength of 10 MPa measured after 3 months. WCC, on the other hand, did not show promising results under mild conditions described in the following section.

l'able 6: Mechanical properties of alkali activate	d material prepared from foundry wastes,
bottom ash and waste	green ceramics.

Sample label	Time of solidification	Time between moulding and measurement	Density [kg/l]	Compressive strength [MPa]
WCC < 90 μm	Did not s	solidify in more that	n 2 years (staye	d rubber-like)
WCC < 600 μm		-	Fell apart	at demolding
WFS-A	< 1 week	3 months	1.6	10.7
WFS-B	~ 1.5 year	~ 1.5 year	1.5	6.1
WFS-C	~ 1.5 year	~ 1.5 year	1.6	12.9
FFG	< 1 week	3 months	1.5	10.5
ASH	< 1 week	3 months	1.3	5.2
WGC	< 1 week	3 months	1.5	25.8
WFS-C+ASH	< 1 week	3 months	1.5	3.2
WFS-C+ASH +WGC	< 1 week	3 months	1.5	8.0

3.3 Microstructural analysis

A SEM micrograph (left magnified 50 times, middle magnified \sim 500 times) of WCC, original and ground, is presented in Fig. 2 (a1 and a2 respectively). In the same Fig., WFS-A (b) and WFS-B (c) are shown. Fig. 3 shows WFS-C (d), FFG (e), ASH (f) and WGC (g). The photos on the right in Fig. 2 and Fig. 3 are photos of the collected samples and samples prepared for AA.

Although there is no significant difference between all 3 WFS under 50 times magnification, there is a difference in the surface when the unground precursors are magnified 500 times; WFS-A has the smoothest surface, WFS-B is slightly rougher, while WFS-C consists mostly of plates and needles.

WCC, gently ground in a mortar with pestle and sieved below 600 μ m, and "WFS" before being used in the foundry industry, gently ground in a mortar with pestle and sieved below 1 mm, are comparable under 50 times magnification to all 3 WFS, from which WFC-B and WFS-C were gently ground in a mortar with pestle and sieved below 1 mm, while under 500 times magnification, the surface of WCC is much smoother. Darker particles of sand have more organic compounds on the surface, which are used to "glue" sand into casting cores. In the sample there were also radiolarians, one marked with a red square in Fig. 2 (a1).

WCC ground in a vibrating disk mill (Siebtechnik) and sieved below 90 µm consisted of mostly "plate-like" rocks with sharp edges.

A mixture of bottom and fly ash (most of it bottom ash) consisted of typical spherical particles (like those found in fly ash), cenospheres (red square in Fig. 3 (f)), mineral aggregates (quartz), (Kutchko and Kim, 2006), and a number of needles aggregated or grown into hedgehog-like structures not found in fly-ash.

GWC consists of plate-like structures with sharp edges, probably ground before further processes in the ceramic industry.

Bottom ash and GWC were gently ground in a mortar with a pestle and sieved below 1 mm for AA.

The SEM of alkali activated materials is presented in Fig. 4, Fig. 5 and Fig. 6; the first two were made from "pure" waste materials, and the latter was made from mixtures of waste materials.

AA of WCC was not successful when the precursor used was ground below $600 \mu m$; the prism fell apart upon demolding and could not support its own weight (see Fig. 4 a1); when the material was ground below $90 \mu m$, the sample foamed, and could be successfully demoulded, but only if the mould used was smaller; however, the material did not solidify in 2 years (it stayed rubber-like). The experiment can not be scaled up under the mild experimental conditions used in this study. For high vacuum SEM, the sample was dried in a vacuum (Fig. 4 a2).

Alkali activated materials from all 3 WFS foamed and looked similar (i.e. sand stones covered with matrix) under low magnification (Fig. 4 b, c left and Fig. 5 d), but there are differences in the matrix itself which are obvious under higher magnification (Fig. 4 b, c and d right).



Figure 2: SEM micrographs of precursors magnified 50 and ~500-times with a photo of precursor before and after preparation for AA: a1) WCC gently ground and sieved below 600 μm (radiolaria is marked with a red square); a2) WCC milled and sieved below 90 μm; WFS from b) WFS-A, and c) WFS-B.



Figure 3: SEM micrographs of precursors magnified 50 and 500 times with photo of precursor before and after preparation for AA: d) WFS-C (inset: enlarged agglomerate of plates and needles); e) FFG; f) ASH (inset: mineral aggregate, quartz; red square: cenosphere); g) WGC.



Figure 4: Photo/SEM micrographs, magnified 50 and 500 times, of alkali activated materials made using: a1) WCC gently ground and sieved below 600 μm; a2) WCC milled and sieved below 90 μm; b) WFS-A, and c) WFS-B.



Figure 5: SEM micrographs magnified 50 and 500 times of alkali activated materials made using: d) WFS-C; e) FFG; f) ASH; g) WGC.

Alkali activated materials from FFG, bottom ash and WGC also appeared to be comparable under low magnification (Fig. 5 e, f and g left), while the matrix itself was similar only for alkali activated materials prepared from FFG and WGC (Fig. 5 e, f and g right), while material from FFG looked huskier, and material from WGC contained a large number of needles (efflorescence of salt). In alkali activated material from bottom ash, cellulose marked with a red square in Fig. 5 f (right) remained from the incomplete combustion of coal, making these materials the least waterproof among all 3 similar samples; it starts to decay in water immediately.

Since alkali activated materials from bottom ash and WGC solidify in a very short time, these precursors were used for the least promising precursor among WFS, WFS-C, according to the amount of amorphous elements needed in alkali activation. The addition of bottom ash to WFS-C, as shown in Fig. 5 h, shortened solidification by more than 5 times, and changed the look of the alkali activated material, while the matrix of the mixture was unique. Addition of WGC to the mixture, shown in Fig. 5 i, shortened the solidification time even more, and left the look of the matrix comparable to that of bottom ash, while the matrix itself changed completely (in the inset SEM micrograph there is cenosphere present from the bottom ash).



Figure 6: SEM micrographs of alkali activated materials made using a mixture of WFS-C and h) ASH; and i) ASH and WGC.

4 Conclusion

Alkali activation of foundry waste has potential in alkali activation as an aggregate, or as a precursor, or even as a potential foaming agent that is an aggregate at the same time. We have shown that with careful selection of precursors, we can control the time of solidification and matrix design, and obtain acceptable compressive strengths.

Acknowledgements

Project No. C3330-17-529032 "Raziskovalci-2.0-ZAG-529032" was granted by the Ministry of Education, Science and Sport of the Republic of Slovenia. The investment is co-financed by the Republic of Slovenia, Ministry of Education, Science and Sport and the European Regional Development Fund.

The Metrology Institute of the Republic of Slovenia is acknowledged for the use of XRF.

References

- Aggarwal, Y., Siddique, R., 2014. Microstructure and properties of concrete using bottom ash and waste foundry sand as partial replacement of fine aggregates. Constr. Build. Mater. 54, 210–223. https://doi.org/10.1016/j.conbuildmat.2013.12.051
- Alonso, S., Palomo, A., 2001. Alkaline activation of metakaolin and calcium hydroxide mixtures: influence of temperature, activator concentration and solids ratio. Mater. Lett. 47, 55–62. https://doi.org/10.1016/S0167-577X(00)00212-3
- Bakharev, T., Sanjayan, J.G., Cheng, Y.-B., 1999. Alkali activation of Australian slag cements. Cem. Concr. Res. 29, 113–120. https://doi.org/10.1016/S0008-8846(98)00170-7
- Basar, H.M., Deveci Aksoy, N., 2012. The effect of waste foundry sand (WFS) as partial replacement of sand on the mechanical, leaching and micro-structural characteristics of ready-mixed concrete. Constr. Build. Mater. 35, 508–515.
 - https://doi.org/10.1016/j.conbuildmat.2012.04.078
- Bernal, S.A., Mejía de Gutiérrez, R., Provis, J.L., 2012. Engineering and durability properties of concretes based on alkali-activated granulated blast furnace slag/metakaolin blends. Constr. Build. Mater. 33, 99–108. https://doi.org/10.1016/j.conbuildmat.2012.01.017
- Bhardwaj, B., Kumar, P., 2019. Comparative study of geopolymer and alkali activated slag concrete comprising waste foundry sand. Constr. Build. Mater. 209, 555–565. https://doi.org/10.1016/j.conbuildmat.2019.03.107
- Buchwald, A., Hilbig, H., Kaps, Ch., 2007. Alkali-activated metakaolin-slag blends—performance and structure in dependence of their composition. J. Mater. Sci. 42, 3024–3032. https://doi.org/10.1007/s10853-006-0525-6
- Deja, J., 2002. Immobilization of Cr6+, Cd2+, Zn2+ and Pb2+ in alkali-activated slag binders. Cem. Concr. Res. 32, 1971–1979. https://doi.org/10.1016/S0008-8846(02)00904-3
- European Commission Integrated Pollution Prevention and Control [WWW Document], n.d. URL http://eippcb.jrc.ec.europa.eu/reference/BREF/sf_bref_0505.pdf (accessed 7.17.19).
- Fernandez-Jimenez, A., Macphee, D.E., Lachowski, E.E., Palomo, A., 2005a. Immobilization of cesium in alkaline activated fly ash matrix. J. Nucl. Mater. 346, 185–193. https://doi.org/10.1016/j.jnucmat.2005.06.006

- Fernández-Jiménez, A., Palomo, A., 2005. Composition and microstructure of alkali activated fly ash binder: Effect of the activator. Cem. Concr. Res. 35, 1984–1992. https://doi.org/10.1016/j.cemconres.2005.03.003
- Fernandez-Jimenez, A., Palomo, A., Macphee, D.E., Lachowski, E.E., 2005b. Fixing Arsenic in Alkali-Activated Cementitious Matrices. J. Am. Ceram. Soc. 88, 1122–1126. https://doi.org/10.1111/j.1551-2916.2005.00224.x
- Granizo, M.L., Alonso, S., Blanco-Varela, M.T., Palomo, A., 2004. Alkaline Activation of Metakaolin: Effect of Calcium Hydroxide in the Products of Reaction. J. Am. Ceram. Soc. 85, 225–231. https://doi.org/10.1111/j.1151-2916.2002.tb00070.x
- Granizo, M.L., Blanco-Varela, M.T., Palomo, A., 2000. Influence of the starting kaolin on alkaliactivated materials based on metakaolin. Study of the reaction parameters by isothermal conduction calorimetry 7.
- Guangren, Q., 2002. Improvement of metakaolin on radioactive Sr and Cs immobilization of alkaliactivated slag matrix. J. Hazard. Mater. 92, 289–300. https://doi.org/10.1016/S0304-3894(02)00022-5
- Guney, Y., Sari, Y.D., Yalcin, M., Tuncan, A., Donmez, S., 2010. Re-usage of waste foundry sand in high-strength concrete. Waste Manag. 30, 1705–1713. https://doi.org/10.1016/j.wasman.2010.02.018
- Hajimohammadi, A., Ngo, T., Mendis, P., Kashani, A., van Deventer, J.S.J., 2017. Alkali activated slag foams: The effect of the alkali reaction on foam characteristics. J. Clean. Prod. 147, 330–339. https://doi.org/10.1016/j.jclepro.2017.01.134
- Handbook of Alkali-Activated Cements, Mortars and Concretes, 2015. . Elsevier. https://doi.org/10.1016/C2013-0-16511-7
- Horvat, B., Ducman, V., Pavlin, A.S., 2019. Waste Foundry Sand as Precursor in Alkali Activation Process. Livar. Vestn. 66, 13.
- Humfrey, C.D.N., Levy, L.S., Faux, S.P., 1996. Potential carcinogenicity of foundry fumes: a comparative in vivo-in vitro study. Food Chem. Toxicol. 34, 1103–1111. https://doi.org/10.1016/S0278-6915(97)00081-1
- Kalliomäki, P.-L., Korhonen, O., Mattsson, T., Sortti, V., Vaaranen, V., Kalliomäki, K., Koponen, M., 1979. Lung contamination among foundry workers. Int. Arch. Occup. Environ. Health 43, 85– 91. https://doi.org/10.1007/BF00378146
- Khalil, M.Y., Merz, E., 1994. Immobilization of intermediate-level wastes in geopolymers. J. Nucl. Mater. 211, 141–148. https://doi.org/10.1016/0022-3115(94)90364-6
- Khatib, J.M., Baig, S., Bougara, A., Booth, C., n.d. Foundry Sand Utilisation in Concrete Production 8.
- Kutchko, B., Kim, A., 2006. Fly ash characterization by SEM-EDS. Fuel 85, 2537-2544. https://doi.org/10.1016/j.fuel.2006.05.016
- Low, I., Mitchell, C., 1985. Respiratory disease in foundry workers. Occup. Environ. Med. 42, 101–105. https://doi.org/10.1136/oem.42.2.101
- Němeček, J., Šmilauer, V., Kopecký, L., 2011. Nanoindentation characteristics of alkali-activated aluminosilicate materials. Cem. Concr. Compos. 33, 163–170. https://doi.org/10.1016/j.cemconcomp.2010.10.005
- Nikolić, V., Komljenović, M., Marjanović, N., Baščarević, Z., Petrović, R., 2014. Lead immobilization by geopolymers based on mechanically activated fly ash. Ceram. Int. 40, 8479–8488. https://doi.org/10.1016/j.ceramint.2014.01.059
- Ostiguy, G., Vaillancourt, C., Begin, R., 1995. Respiratory health of workers exposed to metal dusts and foundry fumes in a copper refinery. Occup. Environ. Med. 52, 204–210. https://doi.org/10.1136/oem.52.3.204
- Pacheco-Torgal, F., Castro-Gomes, J., Jalali, S., 2008. Alkali-activated binders: A review. Part 2. About materials and binders manufacture. Constr. Build. Mater. 22, 1315–1322. https://doi.org/10.1016/j.conbuildmat.2007.03.019
- Palomo, A., Fernández-Jiménez, A., 2011. Alkaline Activation, Procedure for Transforming Fly Ash into New Materials, Part I: Applications 14.

- Palomo, A., Grutzeck, M.W., Blanco, M.T., 1999. Alkali-activated fly ashes A cement for the future. Cem. Concr. Res. 7.
- Pan, Z., Cheng, L., Lu, Y., Yang, N., 2002. Hydration products of alkali-activated slag-red mud cementitious material. Cem. Concr. Res. 32, 357–362. https://doi.org/10.1016/S0008-8846(01)00683-4
- Provis, J., 2013. Alkali activated materials: state-of-the-art report, RILEM TC 224-AAM. Springer, New York.
- Provis, J.L., 2018. Alkali-activated materials. Cem. Concr. Res. 114, 40–48. https://doi.org/10.1016/j.cemconres.2017.02.009
- Provis, J.L., 2014. Geopolymers and other alkali activated materials: why, how, and what? Mater. Struct. 47, 11–25. https://doi.org/10.1617/s11527-013-0211-5
- Provis, J.L., Bernal, S.A., 2014. Geopolymers and Related Alkali-Activated Materials. Annu. Rev. Mater. Res. 44, 299–327. https://doi.org/10.1146/annurev-matsci-070813-113515
- Puertas, F., Ferna, A., 2003. Mineralogical and microstructural characterisation of alkali-activated fly ash/slag pastes 6.
- Puertas, F., MartÂõnez-RamÂõrez, S., Alonso, S., VaÂzquez, T., 2000. Alkali-activated fly ash/slag cement Strength behaviour and hydration products. Cem. Concr. Res. 8.
- Qian, G., Sun, D.D., Tay, J.H., 2003. Immobilization of mercury and zinc in an alkali-activated slag matrix. J. Hazard. Mater. 101, 65–77. https://doi.org/10.1016/S0304-3894(03)00143-2
- Shi, C., Fernández-Jiménez, A., 2006. Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements. J. Hazard. Mater. 137, 1656–1663. https://doi.org/10.1016/j.jhazmat.2006.05.008
- Shi, C., Qian, J., 2000. High performance cementing materials from industrial slags a review. Resour. Conserv. Recycl. 29, 195–207. https://doi.org/10.1016/S0921-3449(99)00060-9
- Škvára, F., Kopecký, L., Šmilauer, V., Bittnar, Z., 2009. Material and structural characterization of alkali activated low-calcium brown coal fly ash. J. Hazard. Mater. 168, 711–720. https://doi.org/10.1016/j.jhazmat.2009.02.089
- Tossavainen, A., 1976. Metal fumes in foundries. Scand. J. Work. Environ. Health 2, 42–49. https://doi.org/10.5271/sjweh.2833
- van Deventer, J.S.J., Provis, J.L., Duxson, P., Brice, D.G., 2010. Chemical Research and Climate Change as Drivers in the Commercial Adoption of Alkali Activated Materials. Waste Biomass Valorization 1, 145–155. https://doi.org/10.1007/s12649-010-9015-9
- Yunsheng, Z., Wei, S., Qianli, C., Lin, C., 2007. Synthesis and heavy metal immobilization behaviors of slag based geopolymer. J. Hazard. Mater. 143, 206–213. https://doi.org/10.1016/j.jhazmat.2006.09.033
- Zhang, J., Provis, J.L., Feng, D., van Deventer, J.S.J., 2008. Geopolymers for immobilization of Cr6+, Cd2+, and Pb2+. J. Hazard. Mater. 157, 587–598. https://doi.org/10.1016/j.jhazmat.2008.01.053

EVALUATION OF FLY ASH-BASED ALKALI ACTIVATED FOAMS AT ROOM AND ELEVATED TEMPERATURES

KATJA TRAVEN¹, MARK ČEŠNOVAR^{1,2}, SREČO ŠKAPIN³ & VILMA DUCMAN¹

¹ Slovenian National Building and Civil Engineering Institute, Department for Materials, Ljubljana, Slovenia, e-mail: katja.traven@zag.si, mark.cesnovar@zag.si, vilma.ducman@zag.si

² International Postgraduate School Jožef Stefan, Ljubljana, Slovenia, e-mail: mark.cesnovar@zag.si

³ Jožef Stefan Institute, Ljubljana, Slovenia, e-mail: sreco.skapin@ijs.si

Abstract Alkali activated materials (AAM) are, in their broadest classification, any binder systems derived by the reaction of an alkali metal source (silicates, alkali hydroxides, carbonates, sulphates) with a solid, amorphous alumosilicate powder (found in precursors such as slag, fly ash and bottom ash). A wide variety of products can be obtained by the alkali activation process and could replace traditional construction products. Among these, alkali activated foams (AAF) represent one of the most promising materials, owing to their economically accessible alumosilicate rich source materials, including industrial waste materials, clean processing, higher added value and most importantly, products with competitive properties. In the present study, the properties of alkali activated fly ash-based foam materials were studied at room temperature as well as at elevated temperatures (up to 1200 °C) in order to develop a durable material in terms of mechanical properties and suitability for high temperature applications.

Keywords: alkali activated materials, fly ash, lightweight foams, porosity, insulating material.



DOI https://doi.org/10.18690/978-961-286-353-1.2 ISBN 978-961-286-353-1

1 Introduction

Alkali-activated materials (AAM), also known as geopolymers or inorganic polymers, in their broadest classification, are any binder systems derived by the reaction of a liquid alkali metal source (silicates, alkali hydroxides, carbonates, sulphates) with a solid, amorphous aluminosilicate powder found in various precursors such as slag, fly ash and bottom ash. When the two components (activator and precursor) are mixed, dissolution and transport of the Al and Si atoms in the alkaline activators takes place first, and then an aluminosilicate network is formed through the poly-condensation of the Al and Si, which can again be amorphous or partially crystallized (Provis & van Deventer, 2013). Besides the chemical composition and the presence of amorphous alumosilicates in precursors as the main requirement for alkali activation, there are several influential parameters that can significantly affect the final mechanical and microstructural properties of the material: the curing regime and ageing (Češnovar et al., 2019), particle size distribution (Traven et al., 2019), type of activator (Chen et al., 2017), Si/Al ratio (Duxson et al., 2005), pH value (Khale & Chaudhary, 2007), etc. Owing to the wide variety of suitable precursors, AAM could be designed to have properties superior to those of conventional binders (Aiken et al., 2017), and when waste material is used as a precursor/activator and a low temperature process is adopted, a reduction of the CO₂ footprint can also be achieved (van Deventer et al., 2012).

A wide variety of products that can be obtained by the alkali activation process (such as blocks, slabs, paving stones, curbs, partitions, refractory materials, materials for specific industrial applications, etc.), and these could replace traditional construction products. Among them, alkali-activated foams (AAF) represent one of the most promising materials to be used as an insulating material in building and construction, on account of their potentially higher added value. The advantage of such materials in comparison with glass or ceramics lies in the lower processing temperatures (up to 100 °C) required to achieve properties similar to those of foamed glass or ceramics, both of which are produced at highly elevated temperatures (above 900 °C). AAF are formed with air voids introduced to a slurry that could be implemented either mechanically, where the alkali-activated material is physically mixed with premade foam, or chemically, using foaming agents such as aluminium (Al), silicon powders, SiC, FeSi alloy, hydrogen peroxide (H₂O₂), NaOCl, sodium perborate, etc. In this case, the chemical blowing agents form gaseous products (such
as O₂ or H₂) and other by-products by thermal decomposition or chemical reaction, as follows (for selected foaming agents):

$$2AI(s) + 2MOH(aq) + 2H_2O(l) \rightarrow 2MAIO_2(aq) + 3H_2(g)$$
(1)

$$2H_2O_2 (l) \rightarrow 2H_2O (g) + O_2 (g)$$
 (2)

The gas bubbles generated either mechanically or chemically are incorporated into the slurry, and when suitable amounts of foaming agent are added, the material is highly porous. Furthermore, stabilizing agents or surfactants can be added to the slurry to decrease the surface tension of the air/slurry system and therefore stabilize the wet foam by reducing the coalescence of bubbles (Korat & Ducman, 2017). The surfactants can be divided into anionic (e.g. sodium oleate, sodium dodecyl sulphate), non-ionic (e.g. Triton X 100) or cationic. This leads to their diverse characteristics and consequently influences the morphology and pore architecture of the foams (Bai & Colombo, 2018). Regardless of the foaming method and/or the type of stabilizing agent, the compressive strength of AAF decreases with a reduction in density and is usually between 1 MPa and 10 MPa in the density range of 360–1400 kg/m³ (Zhang *et al.*, 2014).

In the present study, alkali-activated fly ash-based foam materials were studied in order to develop a durable material in terms of mechanical properties. Samples were assessed for their dimensional stability and thermal resistance, as well as their mechanical/microstructural properties after treatment at 600, 800, 1000 and 1200 °C. Furthermore, these properties directly follow the microstructure of AAF, which is affected by the composition and density (porosity).

2 Experimental

2.1 Materials and AAM/AAF preparation

Fly ash (FA) was obtained from the Thermal Power Plant Šoštanj (Slovenia) and was first characterized by means of XRF, XRD and SEM. The chemical composition of the investigated FA is shown in Table 1, and the results of the mineralogical analysis, along with SEM characterization are shown in Figure 1. Water glass (potassium silicate Betol K 5020 T, produced by Woellner Austria GmbH; $SiO_2:K_2O =$

1.63 mass %; 51.5 mass % aqueous solution) and/or NaOH (produced by Donau Chemie, solid or 41.7 mass % water solution) were used as activators.

Table 1: Chemical composition of fly ash.



Figure 1: Scanning electron microscopy (SEM) image of FA (a); identified phases in FA with their distribution in % (b) and X-ray diffractogram of FA (c).

After analysis of the source material, AAM mixtures with different FA/activator ratios were prepared and designated as shown in Table 2. Mechanical strengths were determined 3 days after curing at a temperature of 70 °C. The mixture showing best performance in terms of mechanical (flexural and compressive) strength (i.e. FA3) was further used for the development of lightweight AAF foamed with 1 mass % of H_2O_2 (hereafter denoted as FA3f). Pores were stabilized with the addition of 1 mass % of sodium dodecyl sulphate (SDS) as a surfactant. The freshly foamed pastes were poured into $20 \times 20 \times 80$ mm³ moulds and cured at 70 °C for 3 days. The hardened AAF (specimen AF3f) were then exposed to elevated temperatures (600, 800, 1000 and 1200 °C; hereafter denoted as FA3f 600, FA3f 800, FA3f 1000 and FA3f 1200, respectively) in order to study their dimensional stability, thermal resistance properties as well as their mechanical and microstructural properties after the heat treatment. The density of all AAF was determined by weighing the individual foams and dividing the resulting weights by the corresponding dimensions of the specimens (i.e. geometrical density).

 Table 2: Composition of different mixtures prepared for the investigation (all in mass %)

 with the calculated (Na+K)/Al/Si ratios in prepared mixtures.

Sample designation	FA	Na ₂ SiO ₃	NaOH	(Na+K)/Al/Si ratio in prepared	
FA1	0.71	0.29	/	0.79/1/2.0	
FA2	0.85	/	0.15	1.3/1/1.53	
FA3	0.73	0.24	0.03	0.91/1/1.93	

2.2 Characterization methods and instruments

The chemical composition of the precursors was determined using a Wavelength Dispersive X-ray Fluorescence (WD XRF) analyser, manufactured by Thermo Scientific ARL Perform X. Mechanical strength (flexural and compressive strength) was determined at 3 days by means of Toninorm test equipment (Toni Technik, Germany), using a force application rate of 0.005 kN/s. XRD of FA was determined using a PANalytical Empyrean X-ray diffractometer with CuK α radiation ($\lambda = 1.54$ Å) at a voltage of 45 kV and a current of 40 mA, in the 20 range from 4° to 70° (scan rate = 0.026°/min). Data was then analysed with X'Pert High Score

Plus diffraction software (PANalytical), using the database PDF 4+2015 RDB powder diffraction files. Rietveld refinement was performed by X'Pert High Score Plus diffraction software. XRD of AAF was determined using D4 Endeavour, Bruker AXS, Karlsruhe (Germany). Dilatometric analysis was performed by means of a Dilatometer Netzsch DIL 402 up to 1000 °C with a heating rate of 5°/min. Microstructural analysis of the precursor as well as hardened AAF was performed by an Ultra plus FESEM, Carl Zeiss (Germany).

3 Results and discussion

The present study was primarily focused on precursor (FA) characterization in order to determine the suitability for alkali activation. According to the XRD analysis, the presence of quartz, magnesioferrite, akermanite-gehlenite, hematite, anhydrite and mullite was confirmed, as well as over 70 % of the amorphous phase needed for the alkali activation process (Figs. 1b and 1c). The presence of favourable alumosilicates was also confirmed by the chemical analysis presented in Table 1. Scanning Electron Microscopy (SEM) was conducted to investigate the morphology of particles (Fig. 1a), which in this case are generally spherical, with a diameter ranging from 1 μ m up to 20 μ m.



Figure 2: Flexural (σ_{FS}) and compressive (σ_{CS}) strength of different AAM mixtures.

To achieve optimal mechanical strengths of hardened AAM, in the next stage of the study focused on the influence of the precursor/activator solution mix ratio. Three mixtures were prepared (Table 2), also taking into account the (Na+K)/Al/Si ratios. Theoretically, the ideal ratio for achieving the best mechanical strength performance is found to be 1/1/1.9 (Duxson *et al.*, 2005). Based on results for the mechanical properties presented in Figure 2, sufficient flexural strength and the maximum compressive strength were found in the case of mixture FA3, which was thus selected for the further development of lightweight AAF. Among all three, the FA3 specimen also exhibited the closest (Na+K)/Al/Si ratio in comparison to the theoretical calculations (Table 2).

In Figure 3, the results of the density and mechanical strength analysis are presented. Before the heat treatment, the specimen FA3f had a density of 0.60 g/cm³ and a compressive strength of 1.24 MPa. The high temperature behaviour was first followed by dilatometry (Fig. 4), and then the samples were exposed to elevated temperatures. As can be seen from Figure 4, the sample first gradually shrank from room temperature to 200 °C; after that, it expanded until 600 °C, and subsequently shrank, sharply and significantly. From nearly 700 °C, it started to expand up to 1000 °C. The test has not been conducted up to higher temperatures, but from Figure 6 it can be seen that vitrification takes place between 1000 °C and 1200 °C.



Figure 3: Flexural (σ FS) and compressive (σ CS) strength and density of the AAF specimens.

After temperature exposure at 600 °C, the density and compressive strength decreased $(0.53 \text{ g/cm}^3 \text{ and } 0.57 \text{ MPa}, \text{ respectively})$. With increasing temperatures (800 °C and 1000 °C), the density remained almost the same, but the compressive strength began to increase (1.88 MPa and 3.82 MPa, respectively), on account of sintering. The highest shrinkage increment and thus density gain (1.31 g/cm³) appeared at 1200 °C. The sintering leads to Na being directly embodied in glass, implying a loss of efflorescence (Hlavacek et al., 2015). The change in crystalline phases was also detected with XRD (Fig. 5), where there was a decrease in quartz intensity, on the one hand, and on the other, the occurrence of new phases (augite, nepheline, anorthite) was observed. Samples fired at 600, 800 and 1000 °C have practically the same density, but compressive strength increases from 0.6 MPa for the sample fired at 600 °C, to 3.8 MPa for the sample fired at 1000 °C, which could be the result of emerging crystalline phases. After firing at 1200 °C, where densification and vitrification occurs, a significant increase was noticed in flexural and compressive strength (19.29 MPa and 56.42 MPa, respectively). The change in volume and colour of FA3f after temperature exposure is shown in Figure 6 and is in compliance with the measurements discussed above.



Figure 4: The dL/L_0 as a function of temperature followed by dilatometry.



Figure 5: X-ray diffractogram of specimens FA3f, FA3f 1000 and FA3f 1200 with the main phases determined and designated as quartz (*), hematite (+), augite (•), nepheline (•) and anorthite (*).



Figure 6: AAF specimens before (FA3f) and after (FA3f 600, FA3f 800, FA3f 1000, FA3f 1200) heat treatment.

AAF samples were also investigated by means of SEM. A comparison of images for samples exposed to different temperatures reveals that heat treatment from 600 °C to 1000 °C (Figs. 7 a–d) does not significantly affect the pores, since they are present in all samples, with a diameter ranging from approximately 100 to 450 μ m. In

addition, it can be seen that the pores are spherical and uniformly distributed. Also, the effect of pore percolation is observed in all 4 samples. In the case of the FA3f 1200 specimen (Fig. 7e), the average pore diameter decreased to approximately $60 \,\mu$ m, again because of sintering.



Figure 7: SEM analysis of a) FA3f b) FA3f 600 c) FA3f 800, d) FA3f 1000 and e) FA3f 1200.

4 Conclusions

This study investigated the sustainability of fly ash from a Slovenian power plant as a precursor in an alkali-activation process. The optimal AAM mixture was further used for lightweight AAF development, which resulted in foam with a density of 0.60 g/cm³ and a compressive strength of 1.24 MPa. These specimen samples were later exposed to elevated temperatures (600, 800, 1000 and 1200 °C) to study their dimensional stability, thermal resistance properties and mechanical/microstructural properties after treatment. The following conclusions were made:

- After exposure to elevated temperatures (600–1000 °C), the density first slightly decreased (0.53 g/cm³) and then significantly increased (1.31 g/cm³) at 1200 °C, because of the sintering process.
- The mechanical properties are reduced when the sample is exposed to 600 °C. Conversely, the mechanical properties increase after exposure in the range of 800–1200 °C, with the maximum compressive strength reached for the FA3f 1200 specimen at 56.4 MPa.
- SEM analysis reveals that the pore structures are not affected when heating the specimens to the temperature of 1000 °C; at 1200 °C the pore diameter is significantly reduced.
- High fire resistance up to 1000 °C enables the use of such AAF in the field of refractory materials.

Acknowledgments

The authors would like to thank the Slovenian Research Agency (ARRS) for the project grant J2-9197: "Synthesis and characterization of alkali-activated foams based on different waste".

References

- Aiken, T. A., Sha, W., Kwasny, J., Soutsos, M. N. (2017), Resistance of geopolymer and Portland cement based systems to silage effluent attack. *Cement and Concrete Research*, 92, 56-65. doi: https://doi.org/10.1016/j.cemconres.2016.11.015
- Bai, C. Y., Colombo, P. (2018). Processing, properties and applications of highly porous geopolymers: A review. *Ceramics International*, 44, 16103-16118. doi: 10.1016/j.ceramint.2018.05.219
- Chen, T.-A., Chen, J.-H., Huang, J.-S. (2017). Effects of activator and aging process on the compressive strengths of alkali-activated glass inorganic binders. *Cement and Concrete Composites*, 76, 1-12. doi: 10.1016/j.cemconcomp.2016.11.011

- Češnovar, M., Traven, K., Horvat, B., and Ducman, V. (2019). The Potential of Ladle Slag and Electric Arc Furnace Slag use in Synthesizing Alkali Activated Materials; the Influence of Curing on Mechanical Properties. *Materials*, 12, 1-18. doi: https://doi.org/10.3390/ma12071173
- Duxson, P., Provis, J. L., Lukey, G. C., Mallicoat, S. W., Kriven, W. M., van Deventer, J. S. J. (2005). Understanding the relationship between geopolymer composition, microstructure and mechanical properties. *Colloid Surface A*, 269, 47-58. doi: 10.1016/j.colsurfa.2005.06.060
- Hlavacek, P., Smilauer, V., Skvara, F., Kopecky, L., Sulc, R. (2015). Inorganic foams made from alkaliactivated fly ash: Mechanical, chemical and physical properties. *Journal of the European Ceramic Society*, 35, 703-709. doi: 10.1016/j.jeurceramsoc.2014.08.024
- Khale, D., Chaudhary, R. (2007). Mechanism of geopolymerization and factors influencing its development: a review. *Journal of Materials Science*, 42, 729-746. doi: 10.1007/s10853-006-0401-4
- Korat, L., Ducman, V. (2017). The influence of the stabilizing agent SDS on porosity development in alkali-activated fly-ash based foams. *Cement and Concrete Composites*, 80, 168-174. doi: http://dx.doi.org/10.1016/j.cemconcomp.2017.03.010
- Provis, J. L., van Deventer, J. S. J. eds. (2013). Alkali activated materials: State-of-the-art Report, RILEM TC 224-AAM. Berlin: Springer/RILEM.
- Traven, K., Češnovar, M., Ducman, V. (2019). Particle size manipulation as an influential parameter in the development of mechanical properties in electric arc furnace slag-based AAM. *Ceramics International*, 45, 22632-22641. doi: https://doi.org/10.1016/j.ceramint.2019.07.296
- van Deventer, J. S. J., Provis, J. L., Duxson, P. (2012). Technical and commercial progress in the adoption of geopolymer cement. *Minerals Engineering*, 29, 89-104. doi: 10.1016/j.mineng.2011.09.009
- Zhang, Z. H., Provis, J. L., Reid, A., Wang, H. (2014). Geopolymer foam concrete: An emerging material for sustainable construction. *Construction and Building Materials*, 56, 113-127. doi: 10.1016/j.conbuildmat.2014.01.081

AN ICT PLATFORM FACILITATING CIRCULAR ECONOMY BUSINESS MODELS

GEORGIOS TSIMIKLIS¹, MILTIADIS KOUTSOKERAS¹, STEN-ERIK BJÖRLING ², WENJIE PENG³, SEBASTIEN SCHMITTER⁴, TIM BARTAM⁵ &

ANGELOS AMDITIS¹

¹ Institute of Communication and Computer Systems, Athens, Greece, e-mail: georgios.tsimiklis@iccs.gr, miltos.koutsokeras@iccs.gr, angelos.amditis@iccs.gr ² Enviro Data, Luleå, Sweden, e-mail: se.bjorling@enviro.se

³ Nottingham Trent University, Advanced Design and Manufacturing Engineering Centre, School of Architecture, Design and the Built Environment, Nottingham, United Kingdom of Great Britain and Northern Ireland, e-mail: wenjie.peng@ntu.ac.uk ⁴ European EPC Competence Center GmbH (EECC), Neuss, Germany, e-mail: schmittner@eecc.info

⁵ GS1 Germany, Cologne. Germany, e-mail: tim.bartram@gs1.de

Abstract The CIRC4Life project aims to develop and implement a circular economy approach through three circular economy business models. In order to support these three business models, around the whole value chain, an ICT platform is created, including various end user tools; central and distributed databases; and external backends. We present the methodology for the system design, the architecture of the ICT platform as well as the main ICT components of the system.

Keywords:

ICT for circular economy, ICT design, Circular Business Models, Circular Economy, Data for Circular Economy.



DOI https://doi.org/10.18690/978-961-286-353-1.3 ISBN 978-961-286-353-1

1 Introduction

The circular economy moves away from the traditional "take-make-dispose" economic model to one that is regenerative by design (Ellen MacArthur Foundation, 2012), (Fellner *et al.*, 2017) and considers the products alongside the value chain. However, existing business models for the circular economy have limited transferability, and there is no comprehensive framework supporting every kind of company in designing a circular business model (Lewadofksi, 2019).

As part of the CIRC4Life (www.circ4life.eu) project, three new circular business models "co-creation of products and services", "sustainable consumption", and "collaborative recycling and reuse" will be created.

The Co-creation of products and services model will bring end-users closer to the design and manufacturing phases by identifying consumer preferences and evaluating product specifications and prototypes via Living Lab to customize end-user requirements. The sustainable consumption model will develop a method to calculate the eco-points of products based on a Lifecycle Assessment: i) assessing the product Lifecycle ii) providing a traceability solution to monitor the product's sustainability along the value chain, and iii) supporting end-users and stakeholders to actively implement the circular economy via awareness raising and knowledge-sharing activities. The collaborative recycling/reuse model will develop a system for stakeholders to interact with each other in order to facilitate the use or reuse of end-of-life products, waste reduction waste implementation of the eco-credits award scheme encouraging people to recycle or reuse.

In trying to identify ICT platforms that could be enablers for the circular economy, one can find in the literature various attempts at online LCA platforms that aim to support products across their Lifecycle (Varghese, 2010),(Ligthart *et al.*, 2019) or to create simplified online approaches for products (Ramos *et al.*, 2016) or deal with how to create simplified LCA approaches for SMEs(Buttol *et al.*, 2012).

On the other hand, LCA tools are not enough to support fully circular business models, and additional tools have been created for the assessment of products at the end of life (Stewart *et al.*, 2011), (Alamerew *et al.*, 2019). Furthermore, cutting-edge technologies such as big data and the internet of things (IoT) have the potential to

leverage the adoption of CE concepts by organizations and society, thus making them more present in our daily lives (Nobre, 2017). However, regardless of the technology used to collect the necessary data, this work proposes a multilayered ICT toolbox as an enabler of circular decisions. The aim of this paper is to identify the needs of Circular Business models, in addition to LCA, and create a single ICT platform that can serve all the stakeholders involved.

2 System Design

To design the ICT platform, an iterative approach comprising three steps was followed. Figure 1 visualizes the iterative procedure, starting from the identification of the end-user requirements, proceeding with the definition of the system/technical requirements and finishing with the system architecture of CIRC4Life.



Figure 1: Methodology for the collection of user requirements, system requirements and definition of the system architecture.

In the following chapters, the actions taken at each of the steps are further elaborated.

2.1 User Requirements

The main purpose behind the collection of end user requirements is to satisfy user needs by introducing the appropriate system specifications into the design of the ICT architecture. A general process comprising four steps, as described by (Maguire *et al.*, 2002) and shown in Figure 2 was used for user requirement collection.



Figure 2: Process for user requirement Analysis.

Information Gathering: The first step of the user requirements analysis is to gather information about the users and stakeholders and the processes that need to be supported by the ICT platform.

User needs Identification: Then the user needs identification was conducted by analysing scenarios and using cases that could be served by the system.

Envisioning and evaluation: In this phase the general architecture of the ICT platform was used as a basis for comparison with the user needs.

Requirements Specification: Finally, the user requirements were formulated considering a generic definition in order to accommodate to the greatest possible extent any future requirements that could derive from newly created Business Models.

Once the user requirements were described, these were categorized in the following categories:

- 1. Design: Aspects relevant to the CEBM of The Co-creation of Products and Services model.
- 2. Use: Aspects relevant to The Sustainable Consumption model.
- 3. Recycle/Reuse: Aspects relevant to The Collaborative Recycling and Reuse model. 4.Generic: Aspects that are generic and relevant to the whole project scope or other non-functional requirements.

Finally, a link to the related ICT system to which the requirement applies is associated with each user requirement. This part was retrofitted after the completion of all the user requirements and the initial system design, being the link to the system requirements and the whole architecture of the system.

2.2 System Requirements

The starting point for the definition of the system requirements was the full list of collected user requirements. A complete list of the characteristics of the TO BE created system was made in order to fully match functional and non-functional user requirements (Robertson & Robertson, 2007). This was the starting point for the draft version of the system requirement, which through an iterative round of ICT design, were formulated to their final version as seen in Figure 3.



Figure 3: CIRC4Life system requirements process.

The system requirements were then formulated as seen in Table 1 to offer a complete view of the system needs and the association to the business models.

Attribute	Description
Unique ID	It identifies each requirement through a unique identifier.
Туре	are considered
	 Functional Requirements (FR): These are the fundamental or essential subject matter of the product. They describe what the product must do or what processing actions it is to take (Robertson & Robertson, 2007).
	 Non-Functional Requirements (NFR): These are the properties that the functions must have. These requirements are as important as the functional requirements for the product's success (Robertson & Robertson, 2007)
Priority	The priority of a requirement is the decision on the importance of the requirement's implementation. The priority depends highly on the specific domain of the application Priority is divided by (Bradner, 1997):
	- MUST: This means that the definition is an absolute requirement of the specification.
	 SHOULD: This means that there may exist valid reasons in particular circumstances to ignore a particular item, but the full implications must be understood and carefully weighed before choosing a different course. COULD: This means that an item is truly optional.
Category	The category is used to aggregate the requirements into coherent sets. The following set of categories shall be used:
	 Product Design
	 Product Usage
	– Recycle/Reuse

Table 1: Table summarizing the format of the system requirements collection.

- Interoperability
- Performance
- Usability
- Reliability
- Security
- Legal
- Openness
- **Description** The description is the intent of the requirement. It is a statement of what the requirement must fulfil.
- **Rationale** The rationale is the reason behind the requirement's existence. It explains why the requirement is important and how it contributes to the system's purpose (provide mapping to the project objectives whenever possible).
- **Fit Criterion** A fit criterion is a measurement for a requirement. It is needed because some requirements are too vague or ambiguous to be properly useful. For example, "The system shall be easy to use" is well-intentioned, but not yet able to be implemented. However, if you add a fit criterion such as "75 % of first-time users shall be able to buy the correct cinema tickets within 90 seconds, without using the help functionality" makes it clear to the designer what is needed to make the product successful. (Robertson & Robertson, 2007)
- **Relevant User** As per the user requirement in the section above

Requirement

(s)

- **Dependencies** Indicate if the requirement depends on another one. Relations between two or more requirements should be traced.
- **Conflicts** Conflicts between requirements imply that there exists contradiction upon system implementation, or one requirement makes the implementation of another requirement less feasible.
- **Comments** Any additional comment or observation regarding the specific requirement. In particular, it should include comments on possible technology limitations or identify aspects that may be only partially relevant to the scope of the project (or even beyond the scope).

Related ICTA mapping towards the system in which the system requirementsystemis implemented

Once the whole system architecture was created, this was retrofitted to the system requirements to ensure that the whole architecture was in accordance with each system requirement.

3 ICT Platform Design

Taking into consideration that the ICT platform is designed to serve new business models that have not yet been verified in the market, the risk of changing user requirements was identified. This problem has been previously analysed even outside the context of ICT (Land ,1982), and a "future analysis" technique was introduced. Within the ICT context, the notion of flexibility in the design in order to consider potential future changes was considered a success factor for any ICT system (Oei *et al.*, 1994). In this context, a tailorable approach for ICT system design was introduced, making it possible to adapt to different users and needs (Stamoulis, 2002). Over the software community, Service oriented Architecture (SoA) was proposed as a way to adapt easily to different providers but also to accommodate any change to the users or the requirements (Bennett, 2000) and (Bugden, 2004). Furthermore, all the advantages of a service system compared to a component-based system were analysed (Elfatatry, 2007).

Considering the above, it was decided to use a SoA approach serving the end user parts of the system, whereas by design the system allows local components to use any other preferred architecture. A similar model is described by (Paik, 2017) as a system with multiple layers which can adapt to changing business models.

3.1 ICT Overview

Considering the above, it was decided to create an Ecosystem of subsystems, with different layers being served by a central platform of SoA architecture.

In this context, a data layer is introduced, which comprises all the data providers to the system, including the Escrow Database of the Products and any other legacy data that could be potentially needed by the projected business models. Three independent modules with business logic serve all 3 CEBMs:

- 1. Recycle/Reuse Module, including the recycling bins
- 2. Traceability Module
- 3. LCA Module

The Core platform of the system includes all the databases needed, in a harmonized data format, the webservice/API manager for service provision and the Access Control manager to ensure security of the whole system.

Finally, four different end user environments provide all the interfaces needed by the system users:

- 1. End Users Toolbox (Consumer Eco Account, Eco Shopping Module)
- 2. Retailer Tool for Eco Accounting
- 3. Impact Assessment Tool
- 4. Stakeholders Interaction Toolbox (Brokerage System, B2B system for Stakeholder Interaction)



Figure 4: Overall ICT system architecture.

As can be seen in the graph above, in order to ease the development and further adaptation/maintenance of the system, few end user tools are merged. This gives the possibility of modular development, which could better serve the 3 CEBMs in the heterogenous context of the four different demonstration cases of the CIRC4Life project.

3.2 ICT Components Overview

The main components of the ICT platform and their main functionality are as follows:

Retailer Tool for Eco Accounting: This tool enables the consumer to buy the product at the store and get the related eco information via a receipt showing both the cash payment information and the eco-point information of each item purchased at the check-out point.

End Users Toolbox: Enables the consumer to view the eco-information related to the consumer's purchasing and recycling activities, such as eco-points and sustainable production information, by scanning the traceability tool (e.g. barcode or QR code) embedded in the product.

Impact Assessment Tool: A system to display the impact of various materials and contribute to the design of new products. The system could also provide information about recycling/reuse of materials.

Stakeholder Interaction Toolbox: A system that allows the interactions of stakeholders around the value chain, offering the possibility of matchmaking and exchange of services and materials.

Traceability Module: Capturing interfaces are used to gather data from the partners and load it into the traceability module. Access applications are developed to transform the data and provide APIs to the platform through which it can be used. Traceability data is used to monitor individual products throughout their lifecycle.

Recycle/Reuse Module: This module is used to capture and store online recycling and reuse data of EoL products such as tablets, lights and meat products, and then reward users for the recycling events.

LCA Module: The tool provides the functions to conduct LCA online to analyse the product's environmental/social impacts through their lifecycle, in order to calculate their impact in a standardized format of ECO points.

Core Platform: A core system backend that handles all the data needed for the eco-Point computation (product purchasing), eco-Credit computation (product recycling), the user transaction history, as well as a SoA that handles all the services needed by the frontend systems.

Data Provider: Database and entry systems that handle interaction with external systems and data entry containing product data and supporting resources describing the product and used as an intermediate data input interface to the core platform.

4 Conclusions

Circular Economy business models require flexible ICT systems that can collect and exchange large amounts of data in a centralized way. Service Oriented Architecture is explored as one of the possibilities for serving multiple users across their buying and recycling habits. Through this iterative approach, it was found that Circular Business Models can be better served through modular systems which can adapt to changing user requirements. Furthermore, such an approach allows the Business Models to consider a large variety of data sources and tools, giving them the opportunity to be further refined. Especially for Circular Business Models that require interaction among stakeholders alongside the value chain, this is an additional enabler.

The architecture discussed here is currently under development and will be demonstrated in the scope of the H2020 funded project CIRC4Life.

This research is part of CIRC4Life, which has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 776503.

References

- Elfatatry, A. (2007) Dealing with change: components versus services, Communications of the ACM CACM Homepage archive Volume 50 Issue 8, Pages 35-39.
- Alamerew, Y.A., Brissaud, D. Correction to: Circular economy assessment tool for end of life product recovery strategies. Jnl Remanufactur 9, 187 (2019).
- Bennett, K., Layzell, P., Budgen, D., Brereton, P., Macaulay, L. and Munro, M. Service-based software: The future for flexible software. In Proceedings of the 7th Asia-Pacific Software Engineering Conference, (Singapore, 2000). IEEE.
- Budgen, D., Brereton, P. and Turner, M. Codifying a service architectural style. In Proceedings of the 28th Annual International Computer Software and Applications Conference, (Hong Kong, 2004). IEEE, 16–22.
- Buttol, P., Buonamici, R., Naldesi, L. et al. Integrating services and tools in an ICT platform to support eco-innovation in SMEs. Clean Techn Environ Policy 14, 211–221 (2012). https://doi.org/10.1007/s10098-011-0388-7
- Clewlow, R. R. (2016). Carsharing and sustainable travel behavior: Results from the San Francisco Bay Area. *Transport Policy*, *51*, 158-164. doi:10.1016/j.tranpol.2016.01.013
- Stamoulis D, Kanellis P, Martakos D (2001) Tailorable information systems: resolving the deadlock of changing user requirements. Journal of Applied System Studies 2/2
- Ellen MacArthur Foundation (2012) Circular Economy [Online]. https://www.ellenmacarthurfoundation.org/
- Fellner J, Lederer J, Scharff C, Laner D (2017) Present potentials and limitations of a circular economy with respect to primary raw material demand. J Ind Ecol 21:494–496
- Land, fF 1982, Adapting to changing user requirements , Available at: https://doi.org/10.1016/0378-7206(82)90039-8
- https://www.circ4life.eu/
- Lewandowski, M. Designing the Business Models for Circular Economy—Towards the Conceptual Framework. *Sustainability* 2016, *8*, 43.
- Ligthart, T.N., Thoden van Velzen, E.U. & Brouwer, M. Int J Life Cycle Assess (2019) EnvPack an LCA-based tool for environmental assessment of packaging chains. Part 1: scope, methods and inventory of tool Int J Life Cycle Assess 24: 900-915. https://doi.org/10.1007/s11367-018-1530-0
- Maguire M., Bevan N. (2002) User Requirements Analysis. In: Hammond J., Gross T., Wesson J. (eds) Usability. IFIP WCC TC13 2002. IFIP — The International Federation for Information Processing, vol 99. Springer, Boston, MA.
- Nobre, G.C. & Tavares, E. Scientometrics (2017), Scientific literature analysis on big data and internet of things applications on circular economy: a bibliometric study, 111,463–492
- Oei, J.L.H., Proper, H.A., and Falkenberg, E.D. (1994). Evolving Information Systems: Meeting the Ever-Changing Environment. Information Systems Journal Vol. 4, pp. 213-233.
- Paik H., Lemos A.L., Barukh M.C., Benatallah B., Natarajan A. (2017) Introduction to Service Oriented Architecture. In: Web Service Implementation and Composition Techniques. Springer, Cham
- Ramos, S., Larrinaga, L., Albinarrate, U. et al. Int J Life Cycle Assess (2016) 21: 710. https://doi.org/10.1007/s11367-015-0980-x
- Robertson, J., & Robertson, S. (2007). Volere Requirements Specification Templatehttp://www11.informatik.uni-erlangen.de/Lehre/SS2015/PR-SWE/Material/volere-template.pdf
- Stewart D, Ijomah W (2011) Moving forward in reverse: a review into strategic decision making in reverse logistics. In: International Conference on Remanufacturing - ICoR, 2011-07-27 - 2011-07-29, University of Strathclyde.
- Verghese, K.L., Horne, R. & Carre, A. Int J Life Cycle Assess (2010) 15: 608. https://doi.org/10.1007/s11367-010-0193-2

THE INHIBITION EFFECT OF NATURAL HONEY ON CORROSION OF STAINLESS STEEL IN A 17 % HCL SOLUTION

REGINA FUCHS-GODEC, ROK ŠPENDL & URBAN BREN

University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: regina.fuchs@um.si, rok.spendl@um.si, urban.bren@um.si

Abstract Floral, chestnut and acacia honey were tested as corrosion inhibitors via the weight loss method. Weight loss measurements for stainless-steel type AISI 304 dissolution were performed in 17.0 % (wt.) HCl containing different concentrations of added natural honey at room temperature, for 4h, 8h, and 24h immersion periods. These measurements were used to calculate the corrosion rate, and percentage inhibition. The highest inhibition effectiveness for SS AISI 304 was between 80-90 % when the concentration of natural honey was higher than 0.5 % (wt.) for the chosen corrosion system. ATR-FTIR analysis by Fourier-transform infrared analysis was used to confirm the presence of some functional groups in the surface adhered film on the metal surface.

Keywords: corrosion, natural honey, green inhibitor, stainless steel, aggressive medium.



DOI https://doi.org/10.18690/978-961-286-353-1.4 ISBN 978-961-286-353-1

1 Introduction

Nowadays, too many products in the food chain industry are discarded and treated as waste without giving this a second thought. Before discarding such products, we should take under consideration the possibility of treating those wastes as reusable materials (Girotto *et al.*, 2015).

In general, it is considered that honey does not have an expiration date. Honey is hygroscopic, meaning that it absorbs water molecules from the surface of the material with which it comes into contact, even from the air. This has the effect of providing almost no free water to be used by microbes and mould. Honey also has a low pH value, creating an environment that is usually too acidic for most microbes. In addition, honey naturally produces hydrogen peroxide when it absorbs moisture, which makes it even harder for bacteria to take hold and "spoil" the honey, even if it is improperly stored. However, if the water content of the honey gets high enough, certain types of yeast can survive and ferment the honey somewhat, creating alcohol and in that sense "spoiling" the honey. If honey has a bad or unpleasant taste, there is no need for it to be discarded; it can be used as a corrosion inhibitor, even in a very aggressive medium. On the other hand, natural honey compounds offer interesting possibilities for corrosion inhibition and are of particular interest because of their safe use and high solubility in water. Several studies have shown the inhibition action of natural or mad honey as a promising corrosion inhibitor for some metals and alloys in various media (Pourzarghan, 2017), (El-Etre, et al., 2000), (Radojčić, 2008).

The inhibition behaviour of natural honey in 17.0 (wt.%) aqueous solutions of HCl on the stainless-steel SS type of AISI 304 was studied using the classic gravimetric weight loss technique at room temperature, and for different immersion times (4h, 8h, and 24h). For this purpose, three different types of honey were used (floral, chestnut and acacia honey). The chosen concentrations of added honey were 0.5 %, 1.0 %, 1.5 % and 2.0 % (wt.). Surface analysis of the resulting film on the metal surface was investigated by ATR-FTIR spectroscopy.

2 Experimental

All the gravimetric tests were conducted in 90 ml of aerated solution of 17.0 (wt.%) HCl at room temperature with different concentrations of added honey for 4h, 8h, and 24h immersion periods. The metal surface was abraded successively, using a circulating device under a stream of water and SiC papers of grades 400, 600, 800, 1000, and 1200, washed thoroughly with doubled distilled water, cleaned ultrasonically in a bath of Milli-Q water, rinsed several times with distilled water, and finally dried using hot air.

They were subsequently weighed for the original weight (w_0) and then hung in the test solution with and without the addition of different concentrations of the inhibitor (natural honey) for 4h, 8h, and 24h at room temperature. The corroded specimens were then removed from the solutions, cleaned with distilled water, dried and weighed again to obtain the final weight (w_1) . The experimental tests were repeated at least three times, until good reproducibility of the data was achieved.

From the weight loss measurements, the corrosion rate (r) was calculated, using the following equation (1),

$$r = \frac{\Delta w \cdot k}{\rho \cdot A \cdot t},\tag{1}$$

A – a total area of the stainless-steel specimen ρ – density of steel t – the exposure time

where $\Delta w = w_0 - w_1$. (w_0 and w_1 are the specimen weight before and after immersion in the test solution). The corrosion rate was calculated in millimetres per year (mm/yr.). The inhibition efficiency measurements were based on the weight loss at the end of the measurement period. The percentage inhibition efficiency (*IE*%) was calculated using the equation (2):

$$IE(\%) = \frac{w - w_i}{w} \cdot 100\%,$$
(2)

where w and w_i are the values of corrosion weight loss of stainless steel in uninhibited and inhibited solutions, respectively. FTIR spectra were recorded to understand the interaction of inhibitor molecules (natural honey) with the metal surface (SHIMADZU-IRAffinity-1).

3 Results and discussion

Representative experimental results for weight loss, corrosion rate and inhibition efficiency for SS AISI 304 at 25 °C at different immersion times and different concentrations of three types of honey are given in Table 1. According to Table 1, it is clear that corrosion rate values of SS AISI 304 in a 17.0 (wt.%) solution of HCl decrease when the concentration of added natural honey increases and increase with time of exposure to the HCl solution.

Table 1: Some corrosion parameters for SS AISI 304 in 17.0 (wt.%) HCl from weight loss measurements at different concentrations of added natural honey after 4h, 8h and 24h exposure to the corrosion medium.

17.0 % HCl + 2.0 % of honey										
t	Chestnut honey				Floral hon	ey		Acacia honey		
(h)	$\Delta w(g)$	r	IE	$\Delta w(g)$	r	IE	$\Delta w(g)$	r	IE	
		(mm/yr)			(mm/yr)			(mm/yr)		
4	0.0036	0.708	85.03	0.0041	0.807	82.95	0.0039	0.767	83.78	
8	0.0077	0.758	88.22	0.0072	0.708	88.98	0.0075	0.738	88.52	
24	0.0196	0.643	90.73	0.0333	1.092	84.25	0.0290	0.951	86.29	

17.0 % HCl + 1.5 % of honey											
t	Chestnut honey			Flower honey				Acacia honey			
(h)	$\Delta w(\mathbf{g})$	r	IE	$\Delta w(g)$	r	IE	$\Delta w(\mathbf{g})$	r	IE		
		(mm/yr)			(mm/yr)			(mm/yr)			
4	0.0037	0.728	84.62	0.0040	0.787	83.37	0.0043	0.846	82.12		
8	0.0087	0.856	86.69	0.0091	0.895	86.53	0.0090	0.886	86.23		
24	0.0253	0.830	88.03	0.0395	1.296	85.01	0.0376	1.233	82.22		

17.0 % HCl + 1.0 % of honey											
t	Chestnut honey				Floral hon	ey		Acacia honey			
(h)	$\Delta w(g)$	r	IE	$\Delta w(g)$	r	IE	$\Delta w(g)$	r	IE		
		(mm/yr)			(mm/yr)			(mm/yr)			
4	0.0044	0.866	81.70	0.0046	0.905	80.87	0.0047	0.925	80.46		
8	0.0099	0.974	84.85	0.0107	1.053	83.63	0.0108	1.063	83.47		
24	0.0332	1.089	84.30	0.0412	1.351	80.52	0.0490	1.607	76.83		

17.0 % HCl + 0.5 % of honey										
t	Chestnut honey				Floral honey			Acacia honey		
(h)	(h) $\Delta w(g)$ r IE			$\Delta w(g)$	r	IE	$\Delta w(g)$	$\Delta w(\mathbf{g})$ r		
		(mm/yr)			(mm/yr)			(mm/yr)		
4	0.0085	1.673	64.66	0.0117	2.165	51.35	0.0108	2.125	55.09	
8	0.0227	2.234	65.26	0.0246	2.460	62.35	0.021	2.066	67.86	
24	0.0882	2.893	58.29	0.0937	3.152	55.69	0.1071	3.513	49.35	



Figure 1: Corrosion parameters: corrosion rate (r), inhibition efficiency (IE%) and weight loss (Δm) for SS AISI 304 from weight loss measurements at different concentrations of added Chestnut honey after 4 h, 8h and 24h exposure to a 17 (wt.%) HCl solution.

The rapid drop in the corrosion rate as the concentration of added chestnut honey increases from 0.5 % to 1 % (wt.) is shown in Figure 1. The same effect can be observed for the other two types of natural honey (Table. 1).



Figure 2: Weight loss against concentration of different types of natural honey for SS AISI 304 after 4h, 8h and 24h exposure to a 17.0 (wt.%) HCl solution.



Figure 3: Inhibition efficiency (*IE*%) against concentration of different types of natural honey for SS AISI 304 after 4h, 8h and 24h exposure to a 17.0 (wt.%) HCl solution.

Results clearly show that *IE* increases with increasing concentration of natural honey (inhibitor), while the weight loss decreases. This could be due to the inhibitor molecules acting by adsorption onto the metal surface. When the concentration of all three types of honey is less than 1.0 (wt.%), the *IE* increases sharply with an increase in concentration, while a further increase causes no appreciable change in performance (Figs.2 and 3).



Figure 4: ATR-FTIR absorption spectra of film obtained from the surface of SS AISI 304 after 8h exposure to 17.0 (wt.%) HCl solution in the presence of 2.0 (wt.%) of acacia honey.

It was reported by (Gerengi, 2014) that the constituent molecules of the honey contain oxygen atoms in functional groups (O–H, C–H, C–O, C=O), which meet the general consideration of typical corrosion inhibitors. The adsorption of these compounds on the metal surface reduces the surface area available for the attack of the aggressive ions from the 17.0 (wt.%) HCl solution.

4 Conclusions:

- The results indicated that the introduction of natural honey obviously minimizes the weight loss and abridged SS dissolution in a 17.0 (wt.%) HCl solution.
- The data obtained from the gravimetric method and ATR-FTIR spectroscopy technique confirm that by increasing the concentration of natural honey, the inhibition efficiency on the SS AISI 304 in a 17.0 (wt.%) HCl medium was increased.
- According to the gravimetric studies, natural honey displayed 80-90% corrosion inhibition efficiency on stainless-steel type AISI 304 in a 17.0 (wt.%) HCl medium when the concentration of natural honey was higher than 0.5 % (wt.) for the chosen corrosion system.

Acknowledgments

This work was financially supported by the Slovenian Research Agency under the research project "Physico-Chemical Processes on the Surface Layers and Application of Nanoparticles".

References

- EL-Etre, A.Y., Abdallah, M., (2000) Natural honey as corrosion inhibitor for metals and alloy. II.Csteel in high saline water. *Corrosion Science*, 42, 731-738.
- Gerengi, H., Goksu, H., Slepski, P. (2014). The Inhibition Effect of Mad Honey on Corrosion of 2007-Type Aluminium Alloy in 3.5% NaCl Solution. *Materials Research*, 17, 255-264. dx.doi.org/10.1590/S1516-14392013005000174
- Girotto, F., Alibardi, L., Cossu, R., (2015). Food waste generation and industrial uses: A review. *Waste Management*, 45, 32-41. dx.doi.org/10.1016/j.wasman.2015.06.008
- Pourzarghan, V., Sarhaddi-Dadian, H., Bakhshandefard, H., (2017). Feasibility study of natural honey use as corrosion inhibitor in protecting the bronze artifacts. *Mediterranean Archaeology and Archaeometry*, 17, 301-309. doi: 10.5281/zenodo.1048935
- Radojčić, I., Berković, K. (2008) Natural honey and black radish juice as tin corrosion inhibitors. Corrosion Science. 50, 1498-1504. doi: 10.1016/j.corsci.2008.01.013
- Yee, J.Y. 2004. A Study on the Inhibitive Effects of Extracts of Honey and Rosmarinus Officinalis L. (Rosemary). M.Scthesis, University of Manchester Institute of Science and Technology, Corrosion and Protection Centre.

USE OF SUPERCRITICAL WATER FOR DEGRADATION OF POLYETHYLENE WASTE

MOJCA ŠKERGET¹, MAJA ČOLNIK¹, PETRA KOTNIK^{1, 2} & Željko Knez¹

¹ University of Maribor , Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: mojca.skerget@um.si, maja.colnik@um.si, petra.kotnik@um.si, zeljko.knez@um.si
 ² University of Maribor , Faculty of Medicine, Maribor, Slovenia, e-mail:

² University of Maribor, Faculty of Medicine, Maribor, Slovenia, e-mail: petra.kotnik@um.si

Abstract The degradation of polyethylene (PE) waste using supercritical water (SCW) has been studied. The colored PE waste was degraded in SCW at 425 °C and 450 °C and at reaction times ranging from 15 min to 4 h, and the effect of temperature and reaction time on product yield was investigated. The degradation products were separated into the oil, gas, aqueous and intermediate phases. The obtained products in the oil and gas phase were analyzed using GC/MS, while the total carbon in the aqueous phase was determined by TOC analyzer. It was found that the oil phase was mostly composed of hydrocarbons, while the gaseous phase contained various gases such as CO2, and light hydrocarbons from C1-C6. TC value in aqueous phase decreased with increases in the temperature and reaction time.

Keywords: polyethylene, waste, supercritical water, recycling, plastics.



DOI https://doi.org/10.18690/978-961-286-353-1.5 ISBN 978-961-286-353-1

1 Introduction

Currently, great attention is being paid to the development of recycling technology for waste packaging, since plastic waste that is not recycled represents a major ecological and economic problem. Production of plastics is expected to increase in the coming years, and waste plastics already pollute drinking water, poison aquatic animals and cause health problems (Anuar Sharuddin et al., 2016; Helmer Pedersen and Conti, 2017). Degradation of plastics is very slow in the natural environment. Plastic waste in the environment can decompose for several hundred years, and consequently, pollution with plastics does not decrease (Anuar Sharuddin et al., 2016; Moore, 2008). Waste plastic can be recycled in many ways. The four main recycling techniques are primary, mechanical (secondary), chemical (tertiary) and quaternary (energy recovery) (Helmer Pedersen and Conti, 2017). Primary recycling refers to the processing of plastics where the product is later used for a purpose similar to that of the original plastics (Achilias et al., 2012; Rahimi and García, 2017). Mechanical recycling or secondary recycling is a process where the polymer is separated from the respective contaminants and can be easily converted into granules with conventional extrusion (Achilias et al., 2012; Rahimi and García, 2017). Chemical or tertiary recycling is a process where waste plastics can be converted into petrochemical components or lead to complete depolymerization to monomers or partial depolymerization to oligomers and other chemical substances. Quaternary recycling or energy recovery is a method where waste plastics are incinerated (Achilias et al., 2012; Helmer Pedersen and Conti, 2017; Rahimi and García, 2017).

One of the most effective methods for chemical recycling is based on the use of sub- and supercritical water, as an environmentally friendly medium. Decomposition of plastics in subcritical and supercritical water is a very effective method for converting plastic waste into a wide range of useful products without expensive and harmful organic solvents (Zhang *et al.*, 2007). Subcritical water (SubCW) is known as hot water under pressure, above boiling point (100 °C) and below the critical point (374 °C, 221 bar). With the increase in temperature and pressure above the critical point, water enters the supercritical area (Haghighi and Khajenoori, 2013; Zhang *et al.*, 2007).

Supercritical water (SCW) provides quick and complete reactions. The increase in degradation of polyethylene in supercritical water is partly due to the dissolution of high molecular hydrocarbons in it. In the supercritical state, water has excellent transport properties (like gases), such as high compressibility, high diffusion coefficient and low viscosity. The ionic product of SCW is also very low. Thus, it is especially suitable for reactions with free radicals, such as decomposition of plastic waste into oil and gasses. In the supercritical state, the dielectric constant of water is as low as for nonpolar organic solvents. SCW thus easily dissolves non-polar organic compounds that are not dissolved in water at room temperature and atmospheric pressure (Su *et al.*, 2004; Zhang *et al.*, 2007).

Polyethylene (PE) is one of the most commonly used plastics in the world and is mainly used for packaging. It is a lightweight, durable thermoplastic with low density and a low melting point. PE is resistant to atmospheric effects and is a good insulator, since it has low electrical and thermal conductivity (Kumar *et al.*, n.d.). Its basic use is in packaging, such as plastic bags, plastic foil, bottles, baby toys, pipes, electrical equipment and more. As a result, it represents the largest share of waste plastic.

The aim of this research was to investigate the degradation of colored PE waste in SCW. The effect of different reaction parameters, such as reaction temperature, pressure and reaction time on products yield was studied.

2 Experimental part

2.1 Materials and apparatus

The colored PE waste (Fig. 1) was used as a raw material. The particle diameter of the PE waste was around 4-5 mm.



Figure 1: The colored PE waste.

The decomposition of colored PE waste in SCW was performed in a high-temperature, high-pressure batch reactor, shown in Figure 2. The experiments were carried out at high temperatures (425 °C and 450°C) and high pressures for different reaction times (15 to 240 minutes).



Figure 2: High temperature, high pressure batch reactor.

The reaction mixture of PE and water in a ratio of 1/5 (g/mL) was transferred to the reactor, and a magnetic stirrer was added. The reactor was tightly sealed, and the thermocouple connected. A heating wire was wrapped around the reactor and insulated with glass wool for faster heating and to prevent heat loss. To prevent oxidation, before heating, the reactor was purged three times with nitrogen. When the reactor reached the desired temperature, temperature was maintained constant until the desired reaction time. After completion of the reaction, the heating wire and glass wool were removed, and the reactor was immediately cooled down in an ice bath. When the reactor cooled to room temperature, the generated gas was discharged into special gas bags. The reactor was disassembled, and the resulting decomposition products transferred from the reactor to the beaker. The oil (or wax) phase was transferred to a container and weighed. 20 mL of dichloromethane was added to the remaining liquid phase, then filtered, as it contained solids, which were dried on filter paper and weighed. The liquid phase mixture was stirred well to separate the phases. In the upper phase, there was an aqueous phase, in the middle an intermediate phase, while the lower phase represented dichloromethane and the
remainder of the oil phase. The lower phase was evaporated on a rotary evaporator to remove the solvent, and the residue was weighed and added to the oil phase.

2.1.1 Products analysis

The oil/wax and gas products were analyzed by gas chromatography coupled to a mass spectrometer (GC/MS), while the content of total carbon (TC) in the aqueous phase was determined with a TOC analyzer.

3 Results and discussion

The decomposition products of PE waste in SCW were separated into the oil, gas, aqueous and intermediate phases. The intermediate phase was formed, since dyes and additives in the PE waste were probably converted into ash particles. Figure 3 shows the effect of temperature and reaction time on the yield of decomposition products. With increasing temperature and reaction time, the yield of gases in all cases increased, while the yield of oil at 450 °C decreased. In the case when PE waste degraded at low temperature (425 °C) and for the short reaction time (15 and 30 min), the yield of oil first increased, owing to the slower degradation of PE waste in SCW, and then with prolongation of the reaction time began to decrease. The highest yield of oil was found at a temperature of 450 °C and a reaction time of 15 min and was higher than 98 %. The oil products contained mostly hydrocarbons (alkanes and alkenes). As the temperature and reaction time increased, the yield of gas products increased from 0.6 to 3.6 %, where at 450 °C and 240 min, the maximum yield of gas was achieved. In the gaseous phase, the CO2 and light hydrocarbons such as methane, ethene, ethane, propene, propane, butene, butane, pentene, pentane, hexene and hexane appeared in detectable content.



Figure 3: Effect of temperature and reaction time on product yield.

In the aqueous phase, determined TC values were higher at temperature of 450 °C than at 425 °C (Fig. 4). At the temperature of 425 °C, the concentration of TC increased with a prolonged reaction time; however, at the higher temperature (450 °C), the concentration of TC decreased with longer reaction times. The reason for this was that organic substances were converted to gases at higher temperatures and longer reaction times.



Figure 4: Total carbon (TC) values of aqueous phase products.

Supercritical water is an excellent medium for degradation of PE waste to useful products. Under the operating conditions researched, the main product was the oil phase that contained mostly alkanes and alkenes. The highest yield of oil was achieved at 450 °C, at a very short reaction time (15 min) and was higher than 98 %. The yield of the gas phase was generally low (< 4 %) and increased with increasing temperature and reaction time. The gaseous and oil phases contained many interesting substances that could be reused (energy, fuel). By this method, the degradation of waste plastics would help to reduce the amount of waste plastics, which burden the environment, and the resulting degradation products could be used for further applications.

Acknowledgment

This work was financially supported by the Slovenian Research Agency (ARRS) in the framework of Research Programmes P2-0046 (Separation processes and product design) and P2-0032 (Process systems engineering and sustainable development).

References

- Achilias, D.S., Andriotis, L., Koutsidis, I.A., Louka, D.A., Nianias, N.P., Siafaka, P., Tsagkalias, I., Tsintzou, G. (2012). Recent Advances in the Chemical Recycling of Polymers (PP, PS, LDPE, HDPE, PVC, PC, Nylon, PMMA). Material Recycling - Trends and Perspectives. https://doi.org/10.5772/33457
- Anuar Sharuddin, S.D., Abnisa, F., Wan Daud, W.M.A., Aroua, M.K. (2016). A review on pyrolysis of plastic wastes. Energy Conversion and Management, 115, 308–326. https://doi.org/10.1016/j.enconman.2016.02.037
- Haghighi, A., Khajenoori, M. (2013). Subcritical Water Extraction, in: Nakajima, H. (Ed.), Mass Transfer - Advances in Sustainable Energy and Environment Oriented Numerical Modeling. IntechOpen. https://doi.org/10.5772/54993
- Helmer Pedersen, T., Conti, F. (2017). Improving the circular economy via hydrothermal processing of high-density waste plastics. Waste Management, 68, 24–31. https://doi.org/10.1016/j.wasman.2017.06.002
- Kumar, A., Gupta, R.K. (2003). Fundamentals of polymer engineering, Second edition, Revised and expanded, New York, Marcel Dekker.
- Moore, C.J. (2008). Synthetic polymers in the marine environment: a rapidly increasing, long-term threat. Environmental Research, 108, 131–139. https://doi.org/10.1016/j.envres.2008.07.025
- Rahimi, A., García, J.M. (2017). Chemical recycling of waste plastics for new materials production. Nature Reviews Chemistry, 1, 0046. https://doi.org/10.1038/s41570-017-0046
- Su, X., Zhao, Y., Zhang, R., Bi, J. (2004). Investigation on degradation of polyethylene to oils in supercritical water. Fuel Processing Technology, Selected Proceedings of the 8th Japan-China Symposium on Coal and C1 Chemistry, 85, 1249–1258. https://doi.org/10.1016/j.fuproc.2003.11.044

Zhang, H., Su, X., Sun, D., Zhang, R., Bi, J. (2007). Investigation on degradation of polyethylene to oil in a continuous supercritical water reactor. Journal of Fuel Chemistry and Technology, 35, 487–491. https://doi.org/10.1016/S1872-5813(07)60030-9

LIGNIN CONCENTRATION DURING INCUBATION OF CHICKEN MANURE WITH SAWDUST AND WHEAT STRAW OR MISCANTHUS OVERGROWN WITH PLEUROTOS OSTREATUS FUNGI

DARJA PEČAR¹, MAŠA ISLAMČEVIĆ RAZBORŠEK¹, FRANC POHLEVEN² & ANDREJA GORŠEK¹

¹ University of Maribor , Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: darja.pecar@um.si, masa.islamcevic@um.si, andreja.gorsek@um.si ² University of Ljubljana, Biotechnical Faculty, Ljubljana, Slovenia, e-mail: franc.pohleven@bf.uni-lj.si

Abstract In this study pre-treatment of wheat straw and Miscanthus with Pleurotus ostreatus fungi was performed. Mixtures of chicken manure with sawdust and fungi overgrown wheat straw or Miscanthus in different ratios (80:20 and 50:50) were incubated for 30 d at room temperature. The concentration of acid insoluble lignin was determined in different time intervals. In the samples with Miscanthus, the concentrations are 5-10 % lower than in the samples with wheat straw. In general, it is not clear that the lignin is degrading during the 30 d incubation. Furthermore, the concentrations of glucose and xylose were determined in initial samples and in samples after 30 d of incubation. On average, the concentration of glucose and xylose slightly decreased after 30 d of incubation. Reduction in the sugar concentrations is attributed to its consumption for the growth and development of fungi during the overgrowing of both substrates.

Keywords: chicken manure, *pleurotus ostreatus*, lignin, glucose, xylose.



DOI https://doi.org/10.18690/978-961-286-353-1.6 ISBN 978-961-286-353-1

1 Introduction

In order to ensure the economic acceptability of the production of "clean" energy from renewable lignocellulosic materials, it is imperative to choose an affordable method or a combination of pre-treatment methods for disruption of the naturally recalcitrant carbohydrate-lignin shields (Paul & Dutta, 2018 and Wyman *et al.*, 2018). One of the possible methods is pre-treatment with fungi (Rouches *et al.*, 2016a). The pre-treatment efficiency depends on the strain of fungi selected and the origin of the biomass (Kucharska *et al.*, 2018). White-root fungi secrete enzymes (laccase and peroxidases) that partially break the bonds in polymer chains of lignocellulosic materials and thus make lignin more readily degradable for microorganisms (Rouches et al., 2016b). Known representatives of white-root fungi strains are Pleurotus ostreatus, Trametes versicolor, Heterobasidion annosum, Irpex lacteus, Phanerochaete chrysosporium, Coriolus versicolor, and others.

During our research we investigated the possibility of increased degradation of sawdust and lignocellulosic biomass in chicken manure using fungal pre-treatment, with the aim of increased biogas production. In this particular study, we tested *Pleurotus ostreatus* as a possible white-rot fungi for lignin biodegradation of two different co-substrates, wheat straw and Miscanthus.

2 Materials and methods

2.1 Materials

All the reagents and solvents used were of analytical grade. Dry pyridine (PYR), methanol (MeOH) and toluene were purchased from Merck (Germany), N-O-bistrimethylsilyl trifluoroacetamide with 1 % of trimethylchlorosilane (BSTFA + 1 % TMCS) and CaCO₃ were from Fluka Chemie (Switzerland), D-glucose (99.5 %), Dxylose (98 %), and phenyl- β -D-glucopyranoside (99 %, ISTD) were supplied by Sigma-Aldrich (Germany). Wheat straw and Miscanthus were harvested in local fields in Slovenia. The chicken manure with sawdust used in this study was freshly collected from a biogas plant (Perutnina Ptuj, Draženci, Slovenia).

2.2 Methods

2.2.1 Fungi pre-treatment

Pre-treatment with white-rot wood decay fungi *Pleurotus ostreatus* was performed in 1 L glass jars filled with wheat straw or Miscanthus previously ground into 2 to 3 cm pieces and some water. The jars were sealed and autoclaved. After sterilization, the cooled substrate was inoculated under sterile conditions with cultured mycelium of an oyster mushroom (*Pleurotus ostreatus*, isolate *P.o.*/strain H35) overgrown on Potato Dextrose Agar (PDA) medium. After 3 weeks, the chicken manure with sawdust was mixed with pre-treated and ordinary wheat and pre-treated straw and ordinary Miscanthus at different mass ratios (80:20 and 50:50). The mixtures were further incubated for different periods of time.

2.2.1 Analysis

Acid-insoluble lignin was determined according to the Klasson method. Briefly, the extraction of a known amount of dry sample was performed in a Soxhlet apparatus using acetone as a solvent. The tube with the sample was transferred to the beaker. Water was added and the contents of the beaker were covered with foil and boiled for 1 h. Afterwards, the tube with the sample was removed from the beaker and dried. A known amount of extracted sample was put in a small beaker and hydrolyzed for 1 day using 72 % H₂SO₄. The solution was then transferred to larger beaker and diluted to a 3 % solution. The beaker was covered with the foil and allowed to boil for 4 h. The solution was cooled to room temperature and then filtered using suction filtration. The mass of dry sample left on the filter paper represents the amount of acid-insoluble lignin. The filtrate was taken and stored for later analysis of monosaccharides. TMS derivatives of monosaccharides were analyzed with a GC-FID system (GC HP Agilent 6890), equipped with a split/splitless injector (HP 6890 Autosampler Injector). Separation of the compounds was carried out on a fused silica capillary column (Agilent HP-5MS UI, $30 \text{ m} \times 0.32 \text{ mm}$ i.d., 0.25 µm film thickness). 1 µL of the sample was injected in split mode (split ratio 7:1). Nitrogen 5.0 (Messer d.o.o.) at a flow rate of 0.2 mL min-¹ was used as the carrier gas. The injector temperature was 250 °C. The temperature program of the column was as follows: 1 min held at 70 °C, then raised to 200 °C

using 2 °C min⁻¹ rate; afterwards, the temperature was increased to 320 °C at 10 °C min⁻¹ rate and, finally, held there for 3 min. The total analysis time was 81 min. The flame ionization detector was operated at 250 °C. The gas flows were as follows: hydrogen 30 mL min⁻¹, synthetic air 300 mL min⁻¹, nitrogen 10 mL min⁻¹. All gases used had a purity of 5.0 (Messer d.o.o.). (Medeiros & Simoneit, 2007, Mejanelle *et al.*, 2002, Ruiz-Matute *et al.*, 2011)

3 Results

3.1 Concentration of acid-insoluble lignin

The incubation of mixtures of chicken manure with sawdust and pre-treated and ordinary wheat straw or pre-treated and ordinary Miscanthus lasted for different periods of time (abbreviations: CMS:S - Chicken Manure with Sawdust to ordinary wheat Straw, CMS:*P.o.* - Chicken Manure with Sawdust to pre-treated wheat straw with *Pleurotus ostreatus* fungi and CMS:M - Chicken Manure with Sawdust to ordinary Miscanthus, CMS:*P.o.* - Chicken Manure with Sawdust to pre-treated Miscanthus with *Pleurotus ostreatus* fungi). The samples were taken t = (0, 5, 9, 14, 19, 23 and 30) day. The concentrations of acid-insoluble lignin for all different mixtures and incubation periods are summarized in Table 1.

It can be seen from Table 1 that there is no clear dependence between lignin concentration and incubation time, regardless of whether the substrate (wheat straw or Miscanthus) was pre-treated or not. The lowest lignin concentration, $w_L = 18.10$ %, was obtained for the wheat straw for two mixtures, CMS:S = 80:20 after 5 d and CMS:*P.o.* = 50:50 after 30 d, and the highest value, $w_L = 25.90$ %, was obtained for the mixture of CMS:S = 50:50 after 23 d. The concentrations of acid-insoluble lignin for the Miscanthus samples were 5-10 % lower than those for the wheat straw samples. The lowest value of lignin concentration ($w_L = 9.20$ %) was obtained for Miscanthus for the mixture of CMS:*P.o.* = 80:20 after 9 d and the highest value ($w_L = 15.60$ %) for the mixture of CMS:*P.o.* = 50:50 after 30 d.

Additionally, the concentrations of monosaccharides were determined in the filtrate that was taken during the determination of acid-insoluble lignin according to the Klasson method. The concentrations of glucose and xylose were determined in the samples after 0 and 30 d of incubation.

Table 3 summarizes concentrations of glucose and xylose for all different mixtures of chicken manure with sawdust and pre-treated and ordinary Miscanthus. We can see that after 30 d of incubation, the concentrations of both monosaccharides, regardless of the substrate used, are lower than at the beginning. We could attribute that to the consumption of glucose and xylose during the incubation period. Fungi could use them for the purposes of nutrition, growth and development. Nevertheless, the concentrations are also lower for samples of substrates not pretreated with fungi. The plausible explanation is that the microorganisms located in chicken manure consume sugar similar to the fungi.

	Wh	eat straw		Miscanthus			
<i>t</i> / d	SUBSTRAT	MASS	wl/	SUBSTRAT	MASS	wl/	
	Ε	RATIO	%	Ε	RATIO	%	
	CMS·D a	80:20	20.10	CMS·P	80:20	11.80	
0	CIVI3.1 .0.	50:50	20.70	CIVI3.1 .0.	50:50	15.00	
0	CMS·S	80:20	20.90	CMS·M	80:20	11.20	
	0.00.0	50:50	23.40	0100.01	50:50	14.00	
	CMS·P a	80:20	19.90	CMS·P a	80:20	13.50	
5	CIVI3.1 [*] .0.	50:50	20.80	CIVIS.1 [•] .0.	50:50	14.00	
5	CMS·S	80:20	18.10	CMS·M	80:20	9.50	
	CM0.0	50:50	19.40	CIVIO.IVI	50:50	15.10	
	CMS·P a	80:20	21.30	CMS·P	80:20	9.20	
9	CIVI3.1 [*] .0.	50:50	22.60	CIVIS.1 ⁻ .0.	50:50	15.50	
	CMS·S	80:20	24.20	CMS·M	80:20	10.30	
	CM0.0	50:50	23.20	SUBSTRAT E CMS:P.o. CMS:M. CMS:P.o. CMS:M. CMS:M. CMS:M. CMS:P.o. CMS:M. CMS:M. CMS:M. CMS:P.o. CMS:M. CMS:M. CMS:P.o. CMS:P.o.	50:50	13.80	
	CMS·P a	80:20	25.50	- CMS: <i>P.o.</i> - CMS:M - CMS: <i>P.o.</i> - CMS:M	80:20	15.20	
14	CIVI3.1 [*] .0.	50:50	20.80	CIVIS.1 [•] .0.	50:50	13.30	
17	CMS·S	80:20	22.10	CMS·M	80:20	11.60	
	CM0.0	50:50	21.70	CIVI3.IVI	50:50	15.30	
	CMS·D	80:20	21.10	CMS·D	80:20	13.20	
10	CIVI3.1 [*] .0.	50:50	19.60	CIVIS.1 [•] .0.	50:50	14.50	
17	CMS·S	80:20	26.30	CMS·M	80:20	13.10	
	CW0.5	50:50	23.08	CIVI3.IVI	50:50	15.50	
	CMS·D	80:20	24.80	CMS·D	80:20	10.30	
23	CIVI3.1 [*] .0.	50:50	20.10	CIVIS.1 [•] .0.	50:50	12.50	
23	CMS·S	80:20	25.90	CMS·M	80:20	13.50	
	CIVIO.0	50:50	25.90	- CMS:P.o CMS:M - CMS:P.o CMS:M - CMS:P.o CMS:P.o CMS:P.o CMS:P.o CMS:P.o CMS:P.o	50:50	15.00	
	CMS·D	80:20	22.30	CMS-D -	80:20	11.40	
30	CIVI5:P.0.	50:50	18.10	GIVI5:P.0.	50:50	15.60	
50	CMS·S	80:20	22.10	CMS·M	80:20	11.90	
	CIVIO.0	50:50	24.70	C1V13.1VI	50:50	14.90	

Table 1: Concentrations of acid-insoluble lignin.

	Wheat straw								
<i>t</i> / d	SUBSTRATE	MASS RATIO	WG / %	wx / %					
	CMS:D a	80:20	18.24	10.13					
0	CIVI3. <i>F</i> .0.	50:50	16.74	6.11					
0	CMS.S	80:20	14.72	7.96					
	CIVI5:5	50:50	20.46	10.96					
	CMS:D a	80:20	14.14	6.56					
30	CIVI3. <i>F</i> .0.	50:50	16.55	6.46					
50	CMS·S	80:20	12.73	3.87					
	CIVI5:5	50:50	15.66	7.09					

Fable 2: Concentrations	of glucose a	nd xylose f	or wheat straw	samples.
--------------------------------	--------------	-------------	----------------	----------

The concentration of glucose and xylose for all different mixtures of chicken manure with sawdust and pre-treated and ordinary wheat straw are summarized in Table 2.

Table 3: Concentrations of glucose and xylose for Miscanthus samples.

	Miscanthus								
<i>t</i> / d	SUBSTRATE	MASS RATIO	W _G / %	w _X / %					
	CMS·D a	80:20	14.32	3.94					
0	CIVI3.1 [*] .0.	50:50	39.08	11.27					
0	CMS·M	80:20	24.08	6.98					
	CINIS.INI	50:50	25.36	7.05					
	CMS·D a	80:20	10.01	3.29					
30	CIVIS.1 .0.	50:50	14.58	4.74					
50	CMS·M	80:20	7.56	1.89					
	C1VIO.1VI	50:50	12.41	3.46					

4 Conclusion

In analysing the experimental data set, it was found that the concentration of acidinsoluble lignin for Miscanthus samples was 5-10 % lower than that for the wheat straw samples. In general, it is not clear that lignin in either of these two co-substrates would degrade during the 30 d of incubation.

To confirm this claim, we determined the glucose and xylose concentrations by GC-FID in the filtrate after the Klasson lignin was found. Concentrations of both monosaccharides decreased slightly after 30 d of incubation. This trend could be attributed to the consumption of sugars for the growth and development of fungi during the incubation of both substrates.

The results of this study showed that pre-treatment of wheat straw or Miscanthus with selected *Pleurothus ostreatus* white-rot fungi did not cause the expected biodegradation of lignocellulosic material investigated in this particular study.

Acknowledgments

This work was supported by the Slovenian Research Agency within the project Design of Sustainable and Energy Self Sufficient Processes Based on Renewable Resources. ID L2-7633. We are grateful to Dr. Bojan Pahor as well as to the owners of the biogas plant (Perutnina Ptuj, Draženci, Slovenia) for the supply of inoculum and chicken manure with sawdust.

References

- Kucharska, K., Holowacz, I., Konopacka-Lyskawa, D., Rybarczyk, P. (2018). Key issues in modelling and optimization of lignocellulosic biomass fermentative conversion to gaseous biofuels. *Renewable Energy*, 129, 384-408.
- Medeiros, Patricia M. and Simoneit, Bernd R. T. (2007). Analysis of sugars in environmental samples by gas chromatography–mass spectrometry. *Journal of Chromatography A.*, 1141, 271–278.
- Mejanelle, P. et al. (2002). Gas chromatography-mass spectrometric analysis of monosaccharides after methanolysis and trimethylsilylation. Potential for the characterization of substances of vegetal origin: Application to the study of museum objects. Journal of Chromatography Library, 66, 845– 902.
- Paul, S., and Dutta, A. (2018). Challenges and opportunities of lignocellulosic biomass for anaerobic digestion. *Resources, Conservation and Recycling, 130*, 164–174.
- Rouches, E., Herpoël-Gimbert, I., Steyer, J.P., Carrere, H. (2016a). Improvement of anaerobic degradation by white-rot fungi pretreatment of lignocellulosic biomass: A review. *Renewable and Sustainable Energy Reviews*, 59, 179-198.
- Rouches, E., Zhou, S., Steyer, J.P., Carrere, H. (2016b), White-Rot Fungi pretreatment of lignocellulosic biomass for anaerobic digestion: Impact of glucose supplementation. *Process Biochemistry*, 51, 1784–1792.

- Ruiz-Matute, A. I., et al. (2011). Derivatization of carbohydrates for GC and GC–MS analyses. Journal of Chromatography B., 879, 1226–1240.
- Wyman, V., Henríquez, J., Palma, C., and Carvajal, A. (2018). Lignocellulosic waste valorisation strategy through enzyme and biogas production. *Bioresource Technology*, 247, 402–411.

THE DEFORMATION OF ALKALI-ACTIVATED MATERIALS AT DIFFERENT CURING TEMPERATURES

MARK ČEŠNOVAR^{1, 2}, KATJA TRAVEN¹ & VILMA DUCMAN¹

¹ Slovenian National Building and Civil Engineering Institute (ZAG), Ljubljana Slovenia, e-mail: mark.cesnovar@zag.si, katja.traven@zag.si, vilma.ducman@zag.si ² International Postgraduate School Jozef Stefan, Ljubljana, Slovenia, e-mail: mark.cesnovar@zag.si

Abstract Alkali activation is a chemical process whereby materials rich in aluminosilicate, which dissolves in basic media at room temperature, form binding phases by polycondensation. The alkali-activated materials (AAM) are a promising alternative to binding materials such as cement or other products in civil engineering (van Deventer et al., 2012). This study investigates the early age shrinkage behavior of Slovenian ladle and electric arc furnace slag-based alkali activated materials at different curing temperatures. The dimensions of specimens cured at room temperature and elevated temperatures up to 90 °C were measured over the first 7 hours (every 10 min). The results show that the most shrinkage occurred at the highest temperature, owing to the highest rate of evaporation of liquid content. Loss of mass follows from the drying shrinkage.

Keywords: alkali-activated materials, ladle slag, electric arc furnace slag, shrinkage, cracks.



DOI https://doi.org/10.18690/978-961-286-353-1.7 ISBN 978-961-286-353-1

1 Introduction

Alkali-activated materials (AAM) have been widely studied in recent years because of a desire to produce more sustainable materials with less environmental impact. The high potential of AAM results from the availability of raw materials such as metallurgical slag, fly ash etc., which often accumulate in landfills as industrial byproducts (Natali Murri et al., 2013). Given that alkali activation is a low energy technology, these materials could offer an economic and environmentally friendly alternative to ordinary building materials (Fernandez-Jimenez et al., 2015). Although AAM could be useful as a concrete binder, brick or lightweight insulation material, the composition of the raw material and the processing parameters can strongly affect the physical properties. Most of the factors that influence the micro-structural evaluation and/ or mechanical properties of AAM have, however, already been studied, including raw materials (chemical properties) (Fernandez-Jimenez et al., 2006), Al/Si (composition) ratios (van Jaarsveld et al., 2002), activator (Chen et al., 2017), curing regime and ageing (Češnovar et al., 2019). Shrinkage has been widely studied in the ordinary Portland cement system and is also relevant for AAM. For OPC concrete, it is well known that four types of shrinkage occur: plastic, drying, autogenous and carbonation shrinkage. Plastic shrinkage is an immediate after-effect of casting, when water evaporates. Drying shrinkage is the result of dehydration from the gel pores, and autogenous shrinkage is caused by self-desiccation that is a result of higher capillary forces when smaller pores are formed. Carbonation deformation is the result of the penetration of CO2 from air into concrete, and it has not yet been confirmed in the AAM system. Some studies reported expansion of AAM at certain curing stages, where samples were cured under controlled humidity conditions, so such expansion cannot be the result of autogenous deformation, according to the desiccation theory for OPC (Mobili et al., 2016). Chemical shrinkage or expansion is where the absolute volume change of material occurs as a result of chemical reactions (Lura et al., 2003). The correlation between the deformation and reaction processes was extensively studied by Li et al. with a metakaolin geopolymer system, where three stages of chemical shrinkage occur. Within the first few hours, the dissolution of aluminosilicates causes shrinkage; after approximately 8 hours, the formation of Al- rich products consisting of gels (nano-zeolites) takes place along with expansion and is followed by shrinkage when the Al species are further polymerized with available silicate oligomers to produce an Si-rich network (Li et al., 2019). Deformation associated with the curing of AA pastes at room temperature or

when exposed to a slightly elevated temperature has a strong impact on the mechanical properties of materials (Mastali *et al.*, 2018, Gudmundsson *et al.*, 2013). Different curing temperatures cause autogenous, chemical and drying shrinkage, with cracking and microstructure deformation, especially during alkali activation and in the early stage of curing when chemical reactions and autogenous shrinkage take place. Current studies show that autogenous shrinkage could be more problematic than drying shrinkage because it develops quickly at the time when the strain on the material is low (Nedeljković *et al.*, 2018, Jensen *et al.*, 2001). The overall deformation in AAM is mostly a result of chemical reactions and water evaporation (drying) from the AA pastes. During the AA process, as incorporated water evaporates from the paste at room temperature and with low humidity, the volume of AA bodies reduces, and cracking occurs owing to capillary pressure between wet and dry micropore areas (Mastali *et al.*, 2018, Li *et al.*, 2018).

The goal of the present study was to assess shrinkage and/or expansion during alkali activation of ladle and electric arc furnace slag, and to further investigate the effect of the curing regime (temperature, time) on shrinkage and mass reduction in order to identify possible causes of deformation.

2 Materials and methods

This experimental study used electric arc furnace and ladle slag (hereafter designated Slag A and Slag R) as precursors for alkali activation with potassium water glass (K₂SiO₃, Betol K5020T, Woellner, Germany). Both slags are from Slovenian metallurgical industries. The chemical composition of both slags, analyzed using an X-ray fluorescence instrument (XRF-Thermo Scientific ARL Perform X, USA), is shown in Table 1.

Table 1: Chemical	l composition	of Slag A a	and Slag R u	used for preparation	n of AAM (in w	t. %).
-------------------	---------------	-------------	--------------	----------------------	----------------	--------

	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	Cr ₂ O ₃	MnO	Fe ₂ O ₃	LOI	отн
Slag A	0.13	14.87	8.54	21.05	0.17	20.87	3.76	2.24	11.37	14.15	14.15
Slag R	0.28	23.25	5.20	13.69	0.14	27.85	0.18	0.62	4.64	20.47	20.47

The quantitative determination (Rietveld) of mineral phases made from X-ray diffraction analysis (XRD- Malvern PANalytical Empyrean, NL and UK) confirmed that both slags contained a high percentage of amorphous phase (55 wt.% for A and 35 wt.% for R).

Prior to alkali activation, the slags were milled and sieved to under 63 μ m. Powder size distribution was measured using a CILAS 920 (Cilas, Orleans Cedex, France), and the specific surface area was analysed using a Micromeritics ASAP 2020, (Micromeritics, Norcross, GA, USA). The average particle size diameter was 5.94 μ m, with a specific surface area of 7.61 m²/g for Slag A and 5.45 μ m, with a specific surface area of R.

The A and R slags in a 1/1 mass ratio were activated with 33wt. % K₂SiO₃ using an activator/slag ratio of 0.6. Pastes were prepared by homogenization with an electric lab. Mixer, as shown in Figure 1 and cast in 120 x 120 x 250 mm³ moulds. Mixtures of the same composition were cured under different conditions, one at room temperature and the others at an elevated temperature by heating in a laboratory heat-chamber. After 60 min, all samples were demoulded, except for the one cured at room temperature, which was left in the mould because of its low strain.



Figure 1: Homogenization of AA pastes.

The length of specimens was measured using a micrometer (Mitutoyo, Kanagawa, JPN) and mass reduction by weighing specimens with a laboratory balance with a precision of 10⁻⁴ g (Mettler Toledo, Ohio, USA). The measurements and photographs of specimens were taken every 15 minutes of treatment for the first 400 minutes. Shrinkage was calculated according to equation 1.

$$\Delta l = \frac{l_0 - l}{l_0} * 100(\%) \tag{1}$$

Where Δl is the shrinkage, l is the length of the specimen measured at a given time period and l_0 is the initial length of the specimen after moulding.

3 Results and discussion

The deformation and reduction of mass in AAM for the first 7 hours of curing is presented in Figure 2. Plastic shrinkage occurs immediately after casting the AA paste into a mould and continues for 90 minutes, causing low mass reduction in specimens cured at room temperature. A very low percentage of water evaporated from the surface of the specimen at room temperature and the shrinkage could not therefore be detected. The most shrinkage, of 3.5 and 4 %, was detected in the specimens cured at 70 °C and 90 °C after 60 min of curing, and the mass reduction was 2 and 4 % of the original weight, respectively. After shrinkage, expansion takes place after 70 minutes of curing in all specimens, except for the one cured at room temperature. This phenomenon is attributed to chemical expansion, whereby an Alrich nano-zeolite gel is produced (Li et al., 2019). During this time, the reduction of mass shows that autogenous drying is also present. The expansion due to the chemical process is greater than shrinkage in this time period. For the specimen cured at room temperature, there is no expansion curve in Figure 2a, perhaps because the autogenous shrinkage and chemical expansion compensate for the overall deformation. Moreover, the mass reduction for this specimen presented in the Figure 2b curve at 100 min shows a minimal slope. The difference between curing at room and elevated temperatures could be due to faster water evaporation from the specimens and a higher dynamic of the chemical process where the precursor dissolves in the alkaline media. After approx. 120 min of curing, all the specimens show shrinkage, which is a result of chemical and autogenous or drying shrinkage. The slopes in Figure 2b show the mass reduction for all specimens. As

expected, minimal loss is seen in the specimens cured at room temperature, and mass reduction increases with the elevated temperature.





Specimens were cast in moulds as shown in Figure 3. Pictures of the specimen surfaces studied after various times of exposure and curing at room and at elevated temperature were taken during each measurement and weighing of specimens and are shown in Table 2. They reveal that after the chemical expansion takes place, cracks appear on the surface and inner surface of the specimens and then disappear around the time that expansion with chemical, autogenous and drying shrinkage ends. No specific changes to the surface were observed in specimens cured at room temperature for the first 7 hours. Those cracks that had appeared on the surface of all other specimens after curing for 70 min then totally disappeared at 260 min on the specimen cured at 90 °C and were reduced in size on the specimens cured at lower temperatures. After 300 min of curing, the smaller cracks also disappeared under 50 and 70 °C conditions. Major differences appear with specimens cured at higher temperatures, and that relevance is also shown on the graph in Figure 2b. Specimens treated at room temperature had 4.5 % of shrinkage after 7 hours of curing, while all other specimens resulted in approximately 6 % of shrinkage.



Figure 3: Samples of AA pastes immediately after casting in the moulds.

Curing Time (min) /Temp. (°C)	70	260	300
Room temp.		PH -	++
50		at The	N.
70		+	+
90			4

Table 2: Surface of the specimens as a function of curing time and temperature.

As expected, such deformation and cracks significantly influence the mechanical properties. In our previous study of the development of mechanical strength, it was determined that compressive strength varied from 40 to 58 MPa because of the influence of differences in curing temperature (Češnovar *et al.* ,2019), a phenomenon which is now more understandable in the light of the shrinkage/expansion behavior of such materials.

4 Conclusions

In this study, dimension and weight measurements were employed to investigate the effect of curing on shrinkage and mass reduction after alkali activation of ladle and electric arc furnace slag. The focus was on the formation of cracks during the drying of specimens. Different curing temperatures were used in order to distinguish among possible causes of deformation, such as plastic, chemical, autogenous and drying expansion or shrinkage of specimens after alkali activation. The mass reduction of specimens cured at room temperature for the first 7 hours showed that the evaporation of water represents the smallest contribution when compared to specimens treated at 90 °C. Nevertheless, specimens treated at room temperature had the least shrinkage, with an absolute value of 4.5 %, compared to 6 % of shrinkage after 7 hours of curing in all other specimens. From the specimens' surface, it is obvious that larger cracks are formed with a higher curing temperature, as confirmed by the deformation slope trend for each specimen. Cracks disappear or decrease in size in the same order. The technique used in this study was sufficient to evaluate the overall deformation of the AAM specimens that occurs in the early stages of curing. Further study could determine the individual cause of this deformation, such as chemical shrinkage/expansion or autogenous (ASTM Standard C 1698-09) and drying shrinkage (ASTM Standard C 1608-07).

Acknowledgments

Development of AAM is part of the ERA-MIN FLOW project, which has received funding from the Ministry of Education, Science and Sport (acronym: MIZS) under grant agreement No. C 3330-18-252010

References

- Chen, T.A, Chen, J.H., Huang, J.S. Effects of activator and ageing process on the compressive strengths of alkali-activated glass inorganic binders. Cem. Concr. Res. 2017, 76, 1-12.
- Češnovar, M., Traven, K., Horvat, B., Ducman, V. The Potential of Ladle Slag and Electric Arc Furnace Slag use in Synthesizing Alkali Activated Materials; the Influence of Curing on Mechanical Properties Materials 2019, 12(7), 1173.
- Fernandez-Jimenez, A., Garcia-Lodeiro, I., Palomo, A. Development of new Cementitious Materials by Alkaline Activating Industrial By-Products. 2nd International Conference on Innovative Materials, Structures and Technologies, Materials Science and engineering 2015, 96, 012005.
- Fernandez-Jimenez, A., de la Torre, A.G., Palomo, A. Lopez-Olmo, G., Alonso, M.M., Aranda, M.A.G. Quantitative determination of phases in the alkali activation of fly ash. Part I. Potential ash reactivity. Fuel 2006, 85, 625-634.

- Gudmundsson, J.G., Long-Term Creep and Shrinkage in Concrete Using Porous Aggregate The Effect of Elastic Modulus. Master Thesis, University of Reykjavik, Iceland, 2013.
- Jensen, O.M., Hansen, P.F. Autogenous deformation and RH-change in perspective. Cem. Concr. Res. 2001, 31, 1859-1865.
- Lura, P., Jensen, O.M., Van Breugel, K. Autogenous shrinkage in high- performance cement paste: An evaluation of basic mechanisms, Cem. Concr. Res 2003, 33, 223-232.
- Li, Z., Zhang, S., Zuo, Y., Ye, G. Chemical deformation of metakaolin based geopolymer, Cem. Concr. Res 2019, 120, 108-118.
- Li, Z., Liu, J., Ye, G. Drying shrinkage of alkali-activated slag and fly ash concrete. A comparative study with ordinary Portland cement concrete. In proceedings of the Workshop on Concrete Modelling and Materials Behaviour in honour of Professor Klaas van Breugel, Delft, The Netherlands, 27-29 August 2018, p.p. 160-166.
- Mastali, M., Kinnunen, P., Dalvand, A., Mohammadi Firouz, R., Ilikainen, M. Drying shrinkage in alkali-activated binders – A critical review. Con. Build. Mat. 2018, 190, 533-550.
- Mobili, A., Belli, A., Giosue, C., Bellezze, T., Tittarelli, F. Metakaolin and fly ash alkali-activated mortars compared with cementitious mortars at the same strength class, Cem. Concr. Res. 2016, 88, 198-210.
- Natali Murri, A., Rickard, W.D.A., Bignozzi, M.C., van Riessen, A. High temperature behaviour of ambient cured alkali-activated materials based on ladle slag. Cem. Conc. Res. 2013, 43, 51-61.
- Nedeljković, M., Li, Z., Ye, G. Setting, strength, and Autogenous Shrinkage of alkali-Activated Fly Ash and Slag Pastes: Effect of Slag Content, Materials, 2018, 11, 2121.
- van Deventer, J.S.J., Provis, J.L., Duxson, P. Technical and commercial progress in the adoption of geopolymer cement. Min Eng 2012; 29:89-104.
- van Jaarsveld, J.g.s., van Deventer, J.S.J. Lukey, G.C. The effect of composition and temperature on the properties of fly ash-and kaolinite-based geopolymers. Chem. Eng. Jou 2002, 89, 63-73.

MUNICIPAL WASTE COMPOSITION ANALYSIS – Approaches to and Solutions for Czech Waste Management

JIŘÍ KROPÁČ, JIŘÍ GREGOR & MARTIN PAVLAS

Brno University of Technology, Institute of Process Engineering, Brno, Czech Republic, e-mail: kropac@fme.vutbr.cz, jiri.gregor@vutbr.cz, martin.pavlas@vutbr.cz

Abstract Current trends in European Union waste management (WM) have resulted in the unified European Reference Model on Waste. The European Commission and European Environment Agency commissioned research subjects to develop the model, which covers all 28 EU Member States. Uniform information about municipal waste composition is essential for WM modelling at all territorial administration levels. This paper describes demands for (residual) municipal waste composition analyses in the conditions of Czech WM. Besides legislation and environmental strategies, the main motivation is to assess analyses procedures from the point of view of their economic and technical feasibility. Therefore, the requirements for analyses in a specific purpose context are described, and the main sampling methods are assessed. Typical methods and procedures are identified in the paper. The author's team further develops suggestions to propose optimal and effective waste composition analyses solution for intended purposes in Czech WM context.

Keywords: waste management, municipal waste, waste composition analysis, waste treatment, waste composition analysis methodology.



DOI https://doi.org/10.18690/978-961-286-353-1.8 ISBN 978-961-286-353-1

1 Introduction

Relevant and comparable information about municipal waste (MW) composition is essential for waste management (WM) business models and plans at all territorial administration levels. Current trends in European Union WM have resulted in visions of the Circular Economy and the unified European Reference Model on Waste. The up-to-date background for MW composition analysis is a document called SWA-Tool (iC consulenten ZT GmbH, 2004), which is not obligatory and does not meet current WM requirements.

Therefore, there is a project under the Ministry of Environment of the Czech Republic, leading to a proposal for a new Czech certified methodology. Brno University of Technology, Institute of Process Engineering is the coordinator of this project. The new methodology should enable not only comparison of values from individual studies, but above all statistical evaluation of the expanding dataset of results and subsequent forecasting. Relevant information about MW composition and quality forecasts of future composition are crucial for the development of relevant models and plans in the field of waste management. These include techno-economical models of MW treatment units (e.g. sorting line, transfer station, energy recovery or waste collection system modelling) and complex business models concerning specific investment in waste management.

Current work corresponds to the beginning of the project and consists mainly of testing individual procedures and analysis options. At the same time, work is under way on the design of a statistical background for the subsequent evaluation of relevant knowledge about the composition of MW in a certain region.

2 Methods

There are several differently detailed and variously demanding methods for analysing the composition of MW and residual MW in particular. An important overview is the paper from Dahlén & Lagerkvist (2008), which provides simple descriptions of methodologies from around the world. The paper presents mainly physical sampling procedures; other, rather outdated procedures are also mentioned. The findings from Dahlén & Lagerkvist (2008) are complemented by data from the UK Defra (2008) (Annex 5 - Review of Waste Auditing Methodologies), which includes a tabulated overview of methodologies.

In the USA, methods for determining the composition of waste have been under development since the 1960s. The American Society for Testing and Materials (ASTM) method was last updated in 2016 under ASTM D5231-92 (2016).

In Europe, the European Commission seeks to support a vision of what is called the circular economy, as summarized in the Circular Economy Package from the European Commission (2015). Developments in EU waste management are heading towards an unified European Reference Model on Waste (Eunomia Research & Consulting, 2015). This situation will affect the development of new methodologies for MW composition analyses in individual EU member states. The European situation in recent decades is described in the text below.

2.1 European Municipal Waste Composition Analyses Methodics

The SWA-Tool (iC consulenten ZT GmbH, 2004) is a methodology developed as part of a European Commission project. The aim of the methodology is to standardize the procedures used to determine the composition of MMW across EU states. However, this methodology should not become the European standard. The main document is primarily a comprehensive inventory of related knowledge; detailed descriptions are provided in the annexes. These findings are reflected in 24 general recommendations covering all necessary MW composition study parameters, especially the required accuracy of the study; stratification criteria; collection and sorting procedures for samples; and finally, the statistical background for processing the analysis results.

The French MODECOM methodology (Montejo *et al.*, 2011) (Wavrer P., 2008) recommends a minimum of 5 MW collection vehicles for analyses, with at least 2 tons of waste from each. It is recommended to analyse a 500 kg sample by manual sorting and sieving. This methodology does not specify measurement accuracy.

Finnish Nordtest methodology (1995) and Swedish NSR methodology (1997) - while the original 1995 procedures focused on the number and volume of the MW samples and the sampling procedures, the 1997 NSR methodology focused more on characterization of sorted fractions (Dahlén *et al.*, 2007). The sampling takes place from collection vehicles, with subsequent subsampling.

The Dutch RIVM (1995) is an extensive and detailed method demanding both cost and analysis equipment (Cornelissen & Otte, 1993). It combines manual and mechanical procedures.

The Swiss SAEFL methodology (Swiss Agency for the Environment, Forests and Landscape, 2003) uses specific stratification factors: socio-economic factors, geographical location, tourism, seasonality, waste charging system and the effect of separate collection of biowaste. The Swiss method compiled by Maystre & Viret (1995) deals with detailed analysis of waste samples, especially from a chemical point of view. The main objective of this method is to determine the content of heavy metals in residual MW.

In Austria and Germany, there are methodologies at the level of individual Lands and regions. Usually sampling from collection vehicles is used, followed by a procedure for sorted subsample homogenization and separation. Sorting is done manually and with sieves. The output from such analyses is mostly in German, e.g. Kern & Siepenkothen (2010) and Vogel *et al.* (2009). Currently, standardization of procedures and revision of methodology was carried out in Austria in 2017. Sampling from containers is preferred and stratification procedures are established.

In Scotland, Zero Waste Scotland published Guidance on the Methodology for Waste Composition Analysis (Zero Waste Scotland, 2015). Procedures for determining the number of samples are determined according to the required level of study accuracy. Samples for sorting are taken from collection containers. This method, developed in 2006 under the auspices of the Environment Agency of England and Wales (Burnley *et al.*, 2007), deals mainly with stratification parameters that affect the amount and composition of waste.

In Poland in 2006, a report on the "Determination of the methodology for testing the sieve, morphological and chemical composition of municipal waste" (Jędrczak & Szpadt, 2006) was issued to the Polish Ministry of the Environment. The European SWA-Tool procedures (iC consulenten ZT GmbH, 2004) were referenced and commented on.

2.2 Municipal Waste Composition Analysis Methodics in Czech Republic

Most MW composition information is based on studies related to publicly funded projects, where published project results and related publications can be found. In contrast, local studies for smaller municipalities and internal studies for companies operating in the Czech WM often remain unpublished or are mentioned only in references and short reports.

Therefore, the available MW composition data often represents only partial information that is difficult to compare. However, a large part of the Czech studies refers to the methodology established in 2008 under project SP/2f1/132/08 (Benešová *et al.*, 2008), which is based on the results of an extensive analysis of MW composition (12 measurements in each of the three types of buildings per month throughout 2008). Previous Czech methodologies are the "720/2/00" from 2003 and the "VÚMH", which have been developed since the 1970s.

The main characteristics of the SP/2f1/132/08 method from 2008 (Benešová *et al.*, 2008) are as follows:

- The size of the main sample is based on the load of a collection vehicle and should be 6 to 8 t; the sorting sample should be 200 kg (corresponding to a volume of approximately 1 m3);
- Sampling of the analysed (sorted) sub-sample is recommended by "quartation" the sample from the collection wagon;
- Three to four building types are monitored: rural, villa, mixed (housing estate, small town) and housing estate, large town. The size of the collection areas in the individual building types is recommended;
- Waste sorting is based on screening and manual sorting of above-screen fractions. Three levels of classification are monitored; the first level distinguishes 11 components: paper and board and cardboard, plastics, glass, metals, bio-waste, textiles, mineral waste, hazardous waste, combustible waste, electrical equipment, fine fraction;

2.3 State-of-the-art in Municipal Waste Composition Analyses Methodics

The most significant methodological procedures were identified and are described in the text below.

Stratification (stratification layer) is a procedure for establishing a sampling schedule for a specific locality or region in order to obtain representative data in relation to the aim of the analysis. The procedure consists in dividing the target area into several smaller representative groups (stratification layers) for individual types of monitored factors. Samples from individual groups are obtained proportionally according to the ratio of their total representation in the area. Stratification is a prerequisite for proper statistical planning of experimental and measured data evaluation.

Place of sampling within MW treatment:

- A statistical survey or questionnaire is a complementary approach;
- Sampling of households is expected to be inaccurate when the waste producers know about the experiment being conducted;
- Samples from MW collection containers, e.g. volumes of 120, 240 or 1100 litres; this way is recommended by European SWA-Tool (iC consulenten ZT GmbH, 2004);
- Sampling from collection vehicles and subsequent sub-sampling for manual sorting. This is often used in current studies.
- Sample collection at the waste facility, i.e. homogenized samples from the facility waste bunker.

Homogenization of MW samples and **sub-sampling** for sorting - usually, "quartation" is used to reduce the volume of the sorted sub-sample from the total large-volume sample taken. The disadvantage is the gradual reduction of the homogeneity of the sorted volume and thus its representativeness. Other techniques such as machine cutting or milling may also be used; these are used when it is necessary to obtain a very small sample volume for chemical and physical analysis.

Sorting method - for reasons of economy, time and logistics, manual sorting is the method most commonly used. It is also common to use a sieve with a mesh size of about 40 to 20 mm and to thoroughly separate only the oversize waste fraction. Mechanical sorting may have great potential, which is related, for example, to the cost and safety of human labour and the cost of new technologies. Several mechanical sorting methods can be mentioned:

- Sorting with a grate or sieve in a vibrating or drum design;
- Hydraulic and pneumatic sorting;
- Magnetic separators and electrostatic screens are suitable, for example, for separating ferrous and non-ferrous metals from inert materials;
- Optical sorting systems based on the optical identification of materials (different wavelengths, e.g. UV, NIR, X-Ray, laser, microwaves, spectroscopy) and their subsequent mechanical separation (pneumatically, robotic gripper).

The scope and range of monitored components and sorting levels. The first basic level of classification usually consists of 10 to 20 fractions differentiated by material (e.g. plastics, paper, metals or glass), purpose (e.g. electrical waste, food waste, sanitary waste, complex packaging) or other properties (e.g. fine fractions according to the sieves used, hazardous fractions). Lower classification levels often differ significantly between individual analyses and methodological approaches. In general, the agreement between approaches and methods of categorization and studies is questionable for individual methodologies.

Subsequent **laboratory tests** occur occasionally and focus primarily on sorted MW fractions, their energy parameters or the presence of pollutant precursors.

Studies often do not specify **measurement accuracy** when processing measured data. Mean value, median, standard deviation or coefficient of variation can be used to interpret the results of the analysis.

3 Results

Design of the new methodology is in the initial design phase. Current works corresponds to the beginning of the project and consist mainly of testing individual procedures and MW analysis options. At the same time, work is under way on the design of a statistical background for the subsequent evaluation of relevant knowledge about the composition of MW in a certain region. The socio-economic parameters of the region are monitored along with other factors that may affect local MW composition.

These topics, suggestions and practical demands for residual MW composition analyses in Czech conditions were identified based on the first phase of practical tests:

- Samples from MW collection containers, e.g. volumes of 120, 240 or 1100 litres. This way is recommended by European SWA-Tool (iC consulenten ZT GmbH, 2004), and the least impact on the sample during MW collection and transportation is expected (e.g. transfer of moisture content between MW fractions or volume change by pressing);
- Sorting takes place manually; application of screening analyses is discussed.
 A 40 mm sieve will probably be the most appropriate.
- The first two levels of sorting focused mainly on the material composition of the residual MW mixture and the proportion of packaging materials;
- There will be only recommendations for classification of a third sorting level; this is a possibility for specific aims of individual studies (e.g. studies focused on further treatment and material or energy recovery).
- A possible ash content measurement could be analysed in the winter (heating) season.
- Standard deviations will be part of the results presentation. The methodology will include recommendations for the necessary number of measurements in relation to the accuracy of the analysis.
- Classification of complex, multi-material and contaminated materials will be designed in accordance with the objectives of the methodology, the practical possibilities and the demands of the statistical evaluation.

4 Conclusions

Differently detailed and demanding methods for analysing the composition of MW and residual MW are applicable in the world and in the EU. Data from individual studies can provide varied and difficult to compare information on the composition of MW and especially residual MW, making it difficult to plan the operation of treatment units or complex business models in the field of waste management. Information from a range of countries and regions will gradually be unified in their methodologies, as suggested by development around the European Reference Model of Waste.

A new Czech methodics is proposed by Brno University of Technology, Institute of Process Engineering for the Czech Ministry of Environment. The aim is to offer a methodology that provides basic data for complex statistical processing and enables relevant forecasting of the development of MW composition. In the current working phase at the beginning of the project, demands for residual MW composition analyses in Czech conditions were identified and the first practical tests were carried out.

Acknowledgments

The authors gratefully acknowledge the financial support provided by ERDF within the research project No. CZ.02.1.01/0.0/0.0/16_026/0008413 "Strategic Partnership for Environmental Technologies and Energy Production".

References

- ASTM (2016). Standard Test Method for Determination of the Composition of Unprocessed Municipal Solid Waste (D5231-92). ASTM International, West Conshohocken, USA. https://www.astm.org/Standards/D5231.htm
- Benešová *et al.*, (2008). Metodika vzorkování a analýz skladby směsného domovního odpadu. UK v Praze, Přírodovědecká fakulta, Ústav pro životní prostředí. <http://www.komunalniodpad.eu/download/Metodika_vzorkovani.pdf> (in Czech)
- Burnley S. J., Ellis J. C., Flowerdew R., Prosser H., (2007). Assessing the composition of municipal solid waste in Wales.

<https://www.sciencedirect.com/science/article/pii/S0921344906000620#tbl5>

- Cornelissen A. A. J. & Otte P. F. (1993). Physical investigation of the composition of household waste in the Netherlands. https://www.rivm.nl/bibliotheek/rapporten/776201011.pdf
- Dahlén, L. & Lagerkvist, A. (2008) Methods for household waste composition studies. Waste Management, 28(7), 1100-1112. doi: 10.1016/j.wasman.2007.08.014
- Dahlén L., Vukicevic S., Meijer J.-E., Lagerkvist A. (2007). Comparison of different collection systems for sorted household waste in Sweden. Waste Management 27(10), 1298-1305. doi: 10.1016/j.wasman.2006.06.016

- Defra (2008). Municipal Waste Composition: Review of Municipal Waste Component Analyses -WR0119, Annex 5 – Review of waste auditing methodologies. http://randd.defra.gov.uk/Document.aspx?Document=WR0119_8657_FRA.pdf>
- Eunomia Research & Consulting (2015). Development of a Modelling Tool on Waste Generation and Management - Annex 8: An Overview of the European Reference Model on Waste. http://forum.eionet.europa.eu/nrc-scp-waste/library/eionet-workshops/2015-eionet-workshop-waste-focus-circular-economy-expert-workshop-european/xpert-workshop-european-reference-model-waste/background-documents/overview-reference-model-waste-70-

pages/download/en/1/Annex%208%20of%20the%20IA%20target%20review%20final%20 -%20EU%20Model%20overview.pdf>

- European Commission (2015). Circular-economy package. European Commission, Brussels, Belgium. http://ec.europa.eu/environment/waste/target_review.htm>.
- Jędrczak A., Szpadt R., (2006). Określenie metodyki badan składu sitowego, morfologicznego i chemicznego odpadów komunálních. https://docplayer.pl/9258618-Okreslenie-metodyki-badan-skladu-sitowego-morfologicznego-i-chemicznego-odpadow-komunalnych.html
- Kern M., Siepenkothen H-J. (2010). Restabfallanalysen für die AWSH Abfallwitschaft Südholstein GmbH. <https://www.awsh.de/fileadmin/media/PDFs/AWK/Abfallanalyse_AWSH.pdf>
- Maystre L. Y. & Viret F., (1995). A goal-oriented characterization of urban waste. Waste Management & Research, 13, 207-218. doi: 10.1016/S0734-242X(95)90040-3
- Montejo C., Costa C., Ramos P., del Carmen Márquez M. (2011). Analysis and Comparison of Municipal Solid Waste and Reject Fraction as Fuels for Incineration Plants. *Applied Thermal Engineering*, 31(13), 2135-2040. doi: 10.1016/j.applthermaleng.2011.03.041
- Swiss Agency for the Environment, Forests and Landscape (2003). A survey of the composition of household waste 2001/02.

<https://www.bafu.admin.ch/bafu/en/home/topics/waste/publications-

studies/publications/composition-household-waste-2001-02.html>

- Vogel E., Steiner M., Quickert A. (2009). Siebgestützte Restmüllanalysen im Land Steiermark. http://www.abfallwirtschaft.steiermark.at/cms/dokumente/10168259_4336659/4dfe9a05 /Endbericht%20Steiermark_2008.pdf>
- Wavrer P. (2008). New MSW sampling and characterization methodologies. Proceedings of "Reliable data for waste management". Vienna, Austria. http://www.iwa.tuwien.ac.at/newa2008/presentations/Wavrer_New%20MSW%20sampling.pdf>
- Zero Waste Scotland (2015). Guidance on the Methodology for Waste Composition Analysis. Zero Waste Scotland.

<https://www.zerowastescotland.org.uk/sites/default/files/WCAMethodology_Jun15.pdf>

THE USE OF PAPER INDUSTRY SIDE PRODUCTS IN CONSTRUCTION

BARBARA LIKAR & LAURA VOVČKO

Slovenian National Building and Civil Engineering Institute, Dimičeva ulica 12, Ljubljana, Slovenia, e-mail: barbara.likar@zag.si

Abstract The amount of waste material and side products of various industrial plants is increasing, which leads to waste accumulation and lack of space in disposal landfills. The paper industry, with its side products of paper sludge and ash, faces these same issues. To reduce the accumulation of these materials, we explored the possibility of their use in construction. First, a series of geomechanical tests was conducted on a product consisting of fly ash and bottom ash. Based on the laboratory results, test fields were constructed, where the preparation and installation technologies were tested. The fields were exposed to atmospheric conditions, so durability of the product in the natural environment was proven. Since the composition of both fly ash and bottom ash depends on the paper industry process, continuous monitoring of their characteristics was established.

Keywords: waste

management, municipal waste, waste composition analysis, waste treatment, waste composition analysis methodology.



DOI https://doi.org/10.18690/978-961-286-353-1.9 ISBN 978-961-286-353-1

1 Introduction

Side products of various industrial plants are increasing, which leads to waste accumulation and lack of space in disposal landfills. The same effect is noticeable for the paper industry. The main side product is paper ash, which is a residue from burning material. Normally, ash (paper, coal, etc.) is used in mixtures with soil for stabilisation of various road or embankment layers (Vestin *et al.*, 2012). Sometimes fly ash mixed with clay is used for covering the layers in a landfill, so that a less permeable material is attained (Magnusson, 2005; Toller *et al.*, 2009). In this research, a product prepared only from paper ash is used as the material for embankments and backfill material in geomechanical structures. The use of natural material, from a natural source, in such a case is minimised to zero, and the use of a side product like waste material is maximised. The study was conducted from the engineering point of view.

2 Methods and Material

The study demonstrates the design process for a new product created from a paper industry side product. It includes all the laboratory tests and field measurements necessary before the required documentation for using the products in construction can be issued, as well as the extent of quality control during the construction work.

2.1 Preliminary investigations

A side product from paper industry called paper ash includes 20 % of paper fly ash and 80 % of paper bottom ash by dry mass and was first tested in the laboratory. The parameters for in-built products in structures like embankments or backfill were established with basic geomechanical tests to determine water content (according to standard SIST EN ISO 17892-1:2015) and the Proctor test (according to standard SIST EN 13286-2:2010/AC:2013). The Proctor test, which determines maximum dry density and optimum water content, is one of the most important tests for all embankment or backfill materials. The mineralogical characteristics of the material also need to be defined in the first step. The mineralogical composition of a material is important for predicting its environmental impact, which was later tested with a leaching test. For this, the product was prepared according to the Proctor results, and the leaching test was performed according to standard SIST EN 1744-3:2002,
with chemical analyses following the standards ISO 17294-2:2016(E), SIST EN ISO 12846:2012, ISO 10359-1:1992 and SIST EN ISO 10304-1:2009. When the results of chemical analyses on leaching water reached values lower than critical values according to the document Acceptability of Alternative Materials in Road Construction, Environmental Assessment, Appendix 3 – Limit Values associated with Level 1 Environmental Characterisation, Table 1., column 1., Sétra, France, February 2012, further geomechanical tests were performed. For this material, paper ash, with predicted use as backfill or embankment material in geotechnical structures, shear properties, deformation properties, compression strength and water permeability characteristics needed to be tested. Because these parameters are dependent on the dry density of the material, it is necessary for the samples for geomechanical testing to be prepared at the defined dry density and water content. This means under conditions that correspond to the construction conditions.

2.2 Preliminary test fields

The test fields were planned with all results from the laboratory preliminary tests, to investigate the preparation of the product and the installation process. Three different test fields were constructed with different types of mixing and compaction machinery. The main differences between the test fields concerned the time when the paper ash was installed after mixing: immediately, after 4 hours or after 24 hours. The most useful machinery for mixing the paper ash with water and the compactor for compacting it were determined from the results of field measurements and practical experience. After the test fields were made, field measurements such as water content and density were performed, using a nuclear gauge and strength, using a lightweight deflectometer. Intact samples were also taken for additional laboratory testing: water content and density for the geotechnical part and a leaching test for the chemical/environmental part.



Figure 1: One of the test fields with the compactor.

2.3 Activities while building the structures

All data from preliminary laboratory and field tests was used to prepare the Slovenian National Technical Approval (STS). With this document, the product, paper ash, can be used in construction. The main parameters as well as the procedure to prepare the product and the structures into which it was built are defined in the document. The STS also includes a control plan for the product in the section on preparation, as well as field measurements during construction work and while incorporating the paper ash in layers of embankment or backfill. Regular control of paper ash includes particle size distribution tests, Proctor tests and uniaxial compression tests, and ensures a homogenous product, which leads to homogenous layers. The right machinery also needs to be used for correct installation of paper ash as a compacting material. With field measurements, prescribed by the STS, the criteria for good compaction of layers were checked, and intact samples of in-built paper ash were taken to perform tests of environmental impact – leaching tests.

2.4 Description of the material: paper ash

Paper ash is a burning residue in the boiler, where deinking paper sludge, bark and wood residue from production are burned. Paper ash consists of bottom ash (80 % by dry mass) and fly ash (20 % by dry mass). Fly ash is a dust, with a particle size up to 1 mm, while bottom ash represents grain agglomerates of ash up to 10 mm. The chemical and mineral compositions are similar. Most of the components are in an amorphous phase. Calcite, lime, portlandite and other minerals in minor quantities represent the crystalline components.

Initial Moisture Content, w (%)	0
Specific Gravity, p _s (Mg/m ³)	2.64
Optimum Moisture Content, w _{opt} (%)	51
Maximum Dry density, ρ_{dmax} (Mg/m ³)	0.99
Uniaxial compression strength, Rc (MPa)	0.58
Friction angle after 28 days, f (°)	33
Cohesion after 28 days, c (MPa)	0.5
Particle size distribution	
Gravel content (> 2,0 mm) (%)	0
Sand content (0,063 – 2,0 mm) (%)	13.3
Silt content (0,002 – 0,063 mm) (%)	75.6
Clay content (< 0,002 mm) (%)	11.1

Table 1: Main parameters for paper ash.

The chemical composition of the paper ash was determined by using a Thermo Scientific ARL PERFORM'X Wavelength Dispersive X-Ray Fluorescence Spectrometer (WD XRF).

	Chemical components	%
SiO ₂	Silicon dioxide	11.37
Al_2O_3	Aluminium oxide	8.26
Fe ₂ O ₃	Iron (III) oxide	0.39
CaO	Calcium oxide (lime)	47.94
P_2O_5	Phosphorus pentoxide	0.17
MgO	Magnesium oxide	1.70
K ₂ O	Potassium oxide	0.27
Na ₂ O	Natrium oxide	0.17
TiO ₂	Titanium dioxide	0.18
SO ₃	Sulfite	0.31
LOI		27.26
Cŀ	Chloride	0.065

3 Results

Preliminary laboratory results are shown in Table 1 and Table 2. Results from the preliminary test fields as well as a comparison between results from the test fields and the structure, an embankment, are shown in this chapter.

Table 3 shows results from measuring water content and dry density by nuclear gauge in all three test fields. The main differences between the test fields concern the time elapsed between mixing the paper ash with water and compaction of the material in embankment layers. Each test field was constructed in three 20 cm layers. For the mixing step, special machinery was used, containing a spiral in the excavator spoon. The mixing process, in which the paper ash was mixed with water to the optimum water content, lasted at least 15 minutes. With this process, a homogenous product was prepared. After being mixed, the product was spread into a layer and compacted with a vibrating plate to the correct dry density. For test field No. 2, compaction was done after 4 hours, and for test field No. 3 after 24 hours. For test field No. 3, material was mixed again with additional water, before it was compacted into layers. Dry density and water content were measured for each layer, and intact samples were taken from the final layer. The dynamic deformation modulus was measured on the surface of last layer at different time periods.

Test field No.		1	2	3
Compaction		immediately	after 4	after 24
Compaction			hours	hours
A	Immediately	57.4	35.3	55.1
Average water	After 24 hours	48.1	/	52.0
content (%)	After 28 days	40.7	24.0	38.7
Water content, laboratory (%)	Immediately	49.9	39.0	51.4
Average dry	Immediately	0.99	0.96	0.98
density	After 24 hours	1.02	/	1.00
(Mg/m³)	After 28 days	1.02	0.99	1.01
Dry density,				
laboratory	Immediately	0.98	0.96	0.94
(Mg/m^3)				
Dynamic	Immediately	8.1	17.4	21.3
deformation modulus (MPa)	After 28 days	> 70	33.2	> 70

Table 3: Results from the test fields.

The results show that the dry density in the first and the third test fields are similar, but it is necessary to know that for the third test field, the material was remixed with additional water. That is also why measured water contents are similar. The results for the second test field show lower dry densities as well as lower water content. If the dry density is compared to the results of the Proctor test, it can be concluded that with the correct process of mixing and compaction, at least 96 % compactness was reached. The dry density increased slightly after 24 hours and 28 days, while the water content dropped by approximately 10 %.

The influence of the binding process is more apparent in the difference between the dynamic deformation moduli (*Evd*). While values are low immediately after compaction, they reached more than 70 MPa after 28 days. The exception is test field No. 2, where after 28 days, the dynamic deformation modulus reached values more than 2 times greater. The reason for such behaviour of paper ash could lie in the binding process, which mostly expires in the time between the mixing and compacting steps.

Results of chemical analysis of the leached water sample from the test fields (Table 4) shows that all the values were below critical.

Element	Unit	Critical	Laboratory	Sample
		value	sample	from test
				field
Arsenic (As)	mg/kg d.m.	0.5	< 0.001	< 0.02
Barium (Ba)	mg/kg d.m.	20	2.73	2.6
Cadmium (Cd)	mg/kg d.m.	0,04	< 0.002	< 0.005
Chromium-	mg/kg d.m.	0.5	0.028	< 0.01
all(Cr)			0.028	
Copper (Cu)	mg/kg d.m.	2.0	0.035	0.20
Mercury (Hg)	mg/kg d.m.	0.01	< 0.001	0.0021
Molybdenum	mg/kg d.m.	0.5	0.025	< 0.05
(Mo)			0.025	
Nickel (Ni)	mg/kg d.m.	0.4	< 0.002	< 0.01
Lead (Pb)	mg/kg d.m.	0.5	< 0.005	< 0.05
Antimony (Sb)	mg/kg d.m.	0.06	0.002	< 0.006
Selenium (Se)	mg/kg d.m.	0.1	< 0.003	< 0.01
Zinc(Zn)	mg/kg d.m.	4.0	< 0.005	<0.1
Chloride (Cl ⁻)	mg/kg d.m.	800	81.4	11.7
Fluorite (F ⁻)	mg/kg d.m.	10	<1	<1
Sulphate (SO ₄ ²⁻)	mg/kg d.m.	1000	<10	11.9

Table 4: Chemical analyses of the leached water.



Figure 2: Results from controlling the maximum dry density.

The regular control of paper ash, which includes particle size distribution, Proctor tests and uniaxial compression tests, shows that over the period of one year, all the results are quite similar, mostly in the interval of allowed tolerance (Fig. 2 - Fig. 4).



Figure 3: Results from controlling the unconfiend compression strength.



Figure 4: Results from controlling the particle size distribution.

4 Conclusions

Paper ash, which is a side product of the paper industry, can be used for embankments and as a backfill material in geotechnical structures. However, several laboratory tests and field measurements should be performed before this material is used as a product. The main purpose of the whole process is to define the technology for preparing the right mixture and the right compaction technique to reach the requirements for embankment layers, such as density, water content etc., as well as the requirements for environmental acceptability. With all the preliminary investigations done and the Slovenian National Technical Approval issued, the product needs to be continuously controlled both in a laboratory and in the field during the construction work. Only with quality work and continuous control, it is possible to attain a homogenous product for environmentally friendly and geotechnically acceptable structures.

Paper ash is a light material (twice as light as gravel), with high compression strength and shear parameters, which is great for use in areas where the natural ground has low bearing capacity.

Acknowledgments

The authors would like to thank the whole team from the Department of Geotechnics at ZAG for performing laboratory tests and field measurements.

References

- Acceptability of Alternative Materials in Road Construction, Environmental Assessment, Appendix 3 – Limit Values associated with Level 1 Environmental Characterisation, Table 1., column 1., Sétra, France, February 2012
- ISO 10359-1:1992. Water quality Determination of fluoride Part 1: Electrochemical probe method for potable and lightly polluted water.
- ISO 17294-2:2016(E). Water quality Application of inductively coupled plasma mass spectrometry (ICP-MS) Part 2: Determination of selected elements including uranium isotopes.
- Magnusson, Y. (2005). Environmental systems analysis for utilization of bottom ash in ground constructions. Royal Institute of Technology.
- SIST EN 1744-3:2002. Tests for chemical properties of aggregates Part 3: Preparation of eluates by leaching of aggregates.
- SIST EN ISO 10304-1:2009. Water quality Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate - Technical Corrigendum 1 (ISO 10304-1:2007).
- SIST EN ISO 12846:2012. Water quality Determination of mercury Method using atomic absorption spectrometry (AAS) with and without enrichment (ISO 12846:2012).
- SIST EN 13286-2:2010/AC:2013. Unbound and hydraulically bound mixtures Part 2: Test methods for laboratory reference density and water content Proctor compaction.
- SIST EN ISO 17892-1:2015. Geotechnical investigation and testing Laboratory testing of soil Part 1: Determination of water content (ISO 17892-1:2014)
- Toller, S., Kärrman, E., Gustafsson, J.P., Magnusson, Y. (2009). Environmental assessment of incinerator residue utilisation. Waste Managgement, 29, 2071–7. doi:10.1016/j.wasman.2009.03.006
- Vestin, J., Arm, M., Nordmark, D., Lagerkvist, A., Hallgren, P., Lind, B. (2012). Fly ash as a road construction material. Int. Conf on Environmental and technical implications of construction with alternative materials, WASCON 2012. pp. 1–8.

ECONOMIC ASSESSMENT OF WASTE OIL-IN-WATER EMULSION TREATMENT PROCESSES

ZORKA NOVAK PINTARIČ & MARJANA SIMONIČ

University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: zorka.novak@um.si, marjana.simonic@um.si

Abstract Preliminary economic analyses of three different processes for treating waste oil-in-water emulsions were performed. The aim was to identify the most suitable technology in terms of economic feasibility. Methods were chosen based on trials: evaporation, ultrafiltration laboratory and electrocoagulation. The annual quantity of waste oil-in-water emulsions was determined at $3\ 000\ t/a$, and the value of organic water pollution in terms of chemical oxygen demand (COD) was measured at 30 000 mg/L O2. All three methods would have positive net present values; therefore, the investment would be acceptable. The evaporation process integrated with the final treatment, such as active carbon adsorption, would represent a good compromise solution regarding the fulfilment of environmental requirements and economic efficiency.

Keywords:

waste oil-in-water emulsion, ultrafiltration, evaporation, electrocoagulation, economic analysis.



DOI https://doi.org/10.18690/978-961-286-353-1.10 ISBN 978-961-286-353-1

1 Introduction

The total global market share for cutting fluid management was estimated at 3.5 % to 4 % in 2007 (Sutherland, 2008). Ultimately, emulsions reach the end of their life and must be treated before final discharge. Owing to their oil content, which is limited in waste emulsions, disposal could be a major problem for the environment. The separation of oil and water is much more difficult nowadays than some decades ago, because more and more synthetic additives are used, which prevent simple separation of the two phases in emulsion.

Industrial wastewaters from cutting fluids pose a threat to the environment by affecting the chemical oxygen demand (COD) value, biochemical oxygen demand (BOD), mineral oil content, etc. The pH value has to be equalised to a neutral value (Cheng *et al.*, 2005). The varying content of waste oil-in-water emulsions (WOWE) represents a serious problem. Only when the concentration of oil in the oil-water emulsion is low (oil \leq 50 mg/L), can treatment by sand filter be sufficient to meet regulatory requirements for drinking water (Almojjly *et al.*, 2018). Tubular membranes are frequently used for waste oil-in-water emulsion treatment (Nordin & Jönsson, 2010). A cellulose filter paper-polyvinyl alcohol (cellulose-PVA) membrane was fabricated recently for oil-in-water emulsion separation. The efficiency of synthetic emulsion separation was up to 99 % (Xu *et al.*, 2019).

If the oil phase does not contain hazardous material, it could be used as an energy source in incineration plants. Also, some income is guaranteed by the government in order to stimulate incineration and waste volume reduction. Integrated processes composed of selected separation techniques for given ranges of input COD were proposed by applying parametric analyses within the superstructure approach (Novak Pintarič *et al.*, 2016). The model showed that COD values could be reduced below allowable limits for discharging effluent into surface water.

This paper presents economic evaluations of WOWE treatment processes. The three most appropriate treatment methods were chosen: evaporation, ultrafiltration and electrocoagulation. Experiments were made on the laboratory scale to determine the operational efficiency of the selected processes, followed by a scale-up to industrial level and economic evaluations. Based on the experimental results, a techno-economic study was performed. Within this study, simulation and design of a WOWE treatment unit was conducted, thus allowing us to establish whether it would be economically profitable to install such plants, and if it would be technically feasible. The treatment unit was designed and engineered to suit WOWE generated from the eastern region of Slovenia. The results provided data for further optimization.

2 Methods

2.1 The existing treatment technology

The annual amount of treated waste oil-in-water emulsion (WOWE) within this study was 1936 tons. The composition of WOWE varied significantly and could achieve input COD values up to 300 000 mg/L. A company used a technology in which waste oil-in-water emulsions were treated by an emulsion-breaking process, achieving an average COD value in treated wastewater of around 30 000 mg/L O₂. The emulsion-breaking process was done by coagulation, using $Al_2(SO_4)_3$ and flocculent (A-100). The pH value was adjusted by using NaOH. The amount of slurry was determined at 324 t/a. Slurry must be dried and then treated by H₂SO₄ to remove water. The dry slurry amount was determined at 216 t/a. The simplified scheme of WOWE treatment is presented in Figure 1. The costs of emulsion breaking are gathered in Table 1. COD was measured in samples in the laboratory using the ISO 6060 standard method. The COD value of the effluent was still very high and needed to be lowered by additional treatment.



Figure 1: Simplified scheme of WOWE pre-treatment.

	TT. 4	Cost per	Amount per	Annual cost,	
	Unit	unit,€	year	€/a	
WOWE	m ³		1972,74		
Al ₂ SO ₄	kg	0.285	25 500	7267.50	
NaOH	kg	0.53	7185	3808.05	
A-100	kg	13.40	53.43	715.96	
H_2SO_4	kg	0.26	9840	2558.40	
Process water	m ³	0.0423	35 033	1481.90	
Compressed Air	m ³	0.0157	12 000	188.40	
El. power	kWh	0.0369	3381.7	124.78	
Power	kW	0.75457	588	443.69	
Emissions	kW/b	0.07444	3381 7	251 73	
Trading	K W II	0.07444	5501.7	251.75	
Process water	_	208 15	12	2497.80	
fixed	_	200.15	12	2477.00	
Water use fee	m ³	0.0732	35 033	2564.42	
Rent	€/a	30	1972.74	59 182.20	
Waste	kg	0.093	292 094	27 164.74	
		Total	l cost €/a	108 249.57	

Table 1: Annual cost of WOWE emulsion breaking.

2.2 Economic evaluations

Environmental tax for pollution load was calculated according to Eq. (1) from the Decree on the environmental tax on pollution due to the wastewater discharge (Decree, 2012).

$$c_{\text{tax}} = c_{\text{EO}} \, \frac{q_{\text{v}} \cdot \gamma_{\text{COD}}}{\gamma_{\text{COD,u}}} \tag{1}$$

where

c_{tax}	tax for environmental pollution (\mathbb{E}/a)
$c_{\rm EO}$	tax for environmental pollution unit $({\ensuremath{\mathbb C}})$
$q_{ m V}$	flowrate of wastewater (m^3/a)

γ_{COD} COD (kg/m³)

 $\gamma_{\text{COD},u}$ environmental pollution unit (50 kg 0_2)

Different criteria were used for evaluating the economic feasibility of certain treatment processes.

Cash flow (C_A) is expressed by Eq. (2):

$$C_{\mathbf{A}} = (1 - t) \cdot (\mathbf{R} - E) + t \cdot D \tag{2}$$

Where

 C_A cash flow (\mathfrak{C}/a)Rrevenue (\mathfrak{C}/a)Eexpenditure (\mathfrak{C}/a)Ddepreciation (\mathfrak{C}/a)ttax rate.

Depreciation (D) is expressed by Eq. (3):

$$D = \frac{I}{n} \tag{3}$$

Where

 $I \qquad \text{investment } (\mathfrak{C}) \\ n \qquad \text{depreciation period (a).}$

Payback time(t_{PB}) is defined by Eq. (4)

$$t_{\rm PB} = \frac{I}{C_{\rm A}} \tag{4}$$

Net present value (NPV) is determined by Eq. (5):

$$NPV = -I + f_{PA} \cdot C_A \tag{5}$$

Where

NPV net present value (\mathfrak{C}) f_{PA} factor of present value (a).

The factor of present value for period (n) at discount rate (p) is calculated by Eq. 6:

$$f_{\rm PA} = \frac{(1+p)^n}{0.1 \cdot (1+p)^n} \tag{6}$$

3 Experimental

Three treatment technologies were tested in order to further decrease the COD value of pre-treated WOWE: evaporation, ultrafiltration and electrocoagulation. These are the most commonly used methods according to the literature (Križan *et al.*, 2013). According to a market survey, it was assumed that the capacity of the treatment process would increase from 1936 t/a to 3000 t/a.

3.1 Evaporation process

An annual quantity of 3 000 t/a and an initial COD value at 30 000 mg/L were assumed. Laboratory experiments determined the WOWE share to distillate at 90 %; therefore, the mass flowrate of distillate was estimated at 2 700 t/a and the flowrate of slurry at 300 t/a. COD in distillate was determined in the laboratory at 1 000 mg/L. Electricity demand was specified by the equipment producer at 60 kWh/m³. Annual demand was calculated at 180 000 kWh/a. Figure 2 represents a simplified process scheme for WOWE treatment by evaporation (EV). Distillate is further transported to a treatment plant (WWTP). The slurry is transported to an incineration plant and burned.



Figure 2: Simplified evaporation process for WOWE treatment.

3.1.1 Capital cost of the evaporation process

The capital cost of an evaporator was obtained from three different suppliers and assessed to an average value of $200\ 000 \notin$. A 30 m³ reservoir is needed for three-day storage of WOWE. The capital cost of the installed tank was estimated at 23 760 \notin . It was calculated that 5.7 t/week of slurry would be produced. The tank volume of slurry storage was estimated at 6 m³ and capital cost at 10 450 \notin .

Total investment was calculated at 234 210 €.

3.1.2 Revenue and operating cost

If the price of WOWE was 100 ϵ/a , the revenue (R), assuming a capacity of 3000 m³/a, would be 300 000 ϵ/a .

Operating costs were as follows:

- electricity at a price of 0.07 €/kWh (Price, 2019)
 180 000 kWh/a · 0.07 €/kWh = 12 600 €/a
- salary for one person: 40 000 €/a
- tax for water emissions was calculated by Eq. (1): $c_{\text{tax}} = 1 404$ €/a

Total cost, i.e. expenditures (*E*), was calculated at 54 004 \notin /a.

3.1.3 Economic criteria

Eq's. 2 to 6 were used for calculation of depreciation D, cash flow C_A , payback time t_{PB} and net present value NPV.

$$D = \frac{234\,210}{10} = 23\,421 \, \text{€/a}$$

The cash flow assuming an 18 % tax rate could be calculated as follows:

$$C_{A} = 205 \ 933 \ €/a$$

 $t_{PB} = 1.14 \ a$
 $f_{PA} = 6.1438$
 $NPV = 1 \ 031 \ 001 \ €$

An *NPV* greater than zero and a payback time of about one year indicate an acceptable investment project for the evaporation process.

3.2 Ultrafiltration process

Fig. 3 presents a simplified scheme of the ultrafiltration process (UF). WOWE flows into the UF cell; a permeate then flows into WWTP, and the concentrate is a waste product that can be incinerated.



Figure 1: Simplified process flow for WOWE treatment by ultrafiltration.

Annual WOWE was the same as with the first treatment (evaporation); 80 % of the initial WOWE is permeate 2 400 t/a and 20 % concentrate 600 t/a. The COD value in the permeate was determined at 7 000 mg/L. It was assumed that specific electricity consumption would be 18 kWh/m³. Annual electrical energy demand is 54 000 kWh/a.

3.2.1 Capital cost of the ultrafiltration process

The capital cost of an ultrafiltration unit was obtained from the supplier: 7 000 €.

The tank for WOWE was the same as for the evaporation process: 23 100 €.

Double the volume was needed for concentrate storage than in the evaporation process, which means 12 m^3 and a capital cost of $14\ 895$ €.

Total investment was calculated at 44 995 €.

3.2.2 Revenue and operating cost

Revenue was the same as in the evaporation process: 300 000 €/a.

Operating costs were as follows:

- electricity: 54 000 kWh/a · 0.07 €/kWh = 3 780 €/a
- salaries: 40 000 €/a
- membrane replacement: the cost of 24 800 \$/a was found in the literature (Cheryan and Rajagopalan, 1998) for 19 059 m³/a. Therefore, for 3 000 m³/a, it was calculated at 2 866 €/a.
- tax for water emissions was calculated by Eq. (1)

$$c_{\text{tax}} = 26 \cdot \frac{2.4 \cdot 7000}{50} = 8\ 736\ \text{€/a}$$

Total cost was calculated at 55 382 ϵ/a .

3.2.3 Economic criteria

$$D = 4 \ 500 \ €/a$$

$$C_{\mathbf{A}} = 201 \ 397 \ €/a$$

$$t_{\mathbf{PB}} = 0.22 \ a$$

$$NSV = -I + f_{\mathbf{PA}} \cdot C_{\mathbf{A}} = -44 \ 995 + 6.1438 \cdot 201 \ 397 = 1 \ 192 \ 348 \ €$$

The ultrafiltration process had an *NSV* greater than zero and a payback time shorter than 1 year, which indicated the investment project for ultrafiltration was acceptable.

3.3 Electrocoagulation process

Figure 4 shows the simplified process of electrocoagulation (EC). Annual WOWE was the same as previously determined. It was established experimentally that 80 % would separate as purified water and 20 % as a slurry. The COD value in purified water was determined at 12 000 mg/L. Electricity demand was estimated at 2 kWh/m³ for a capacity of 3 000 m³/a (Rodriguez *et al*, 2007), yielding an annual demand of 6 000 kWh/a.



Figure 4: Simplified process flow for WOWE treatment by electrocoagulation.

3.3.1 Capital cost of the electrocoagulation process

Capital cost was determined by using a six-tenth factor rule and a reference price of 4 621 778 \$ for equipment with a capacity of 500 gal/min (Hamilton, 2009), which amounted to 141 845 € for the capacity of 3000 m³/a.

Reservoirs for WOWE were assumed the same as for the ultrafiltration process, i.e. 30 m^3 , and $23 \ 100 \notin +14 \ 895 \notin = 37 \ 995 \notin$.

Total investment was estimated at 179 840 €.

3.3.2 Revenue and operating costs

Income is the same as in the other two processes: 300 000 €/a.

Costs:

- electricity: 6 000 kWh/a \cdot 0.07 \in /kWh = 420 \in /a
- salaries: 40 000 €/a
- electrode replacement: aluminium demand is 0.1 kg/m³; the price for aluminium tile was 4 €/kg (Rodriguez *et al.*, 2007), which in our case amounted to 1 200 €/a.
- tax for water emissions was calculated by Eq. (1)

$$C_{\text{tax}} = 26 \cdot \frac{2.4 \cdot 12\ 000}{50} = 14\ 976\ \text{€/a}$$

Total cost was calculated at 56 596 €/a.

3.3.3 Economic criteria

$$D = 17 984 €/a$$

$$C_{A} = 202 828 €/a$$

$$t_{PB} = 0,89 a$$

$$NPV = 1 066 295 €/a$$

Results are gathered in Table 2. All three technologies are economically acceptable at a discount rate of 10 %.

The comparison showed that evaporation has the highest capital cost and electricity demand. This technology was also the most efficient in COD reduction; however, its payback time was the longest and NPV the lowest. The less expensive technology was ultrafiltration, which showed the highest NPV and the shortest payback time. In general, cash flows of all three options were similar at 200 000 \notin /a and the net present values at around 1 000 000.

EV UF EC WOWE flow rate (m^3/a) 3 000 3 000 3 000 COD (mg/L)1 000 7 000 12,000 **Electricity consumption** 60 18 2 (kWh/m^3) Electricity cost (ℓ/a) 12 600 3780420 Total cost (€/a) 56 596 54 004 55 382 44 995 179 840 Capital cost (€) 234 210 Cash flow $(\mathbf{\ell}/\mathbf{a})$ 201 397 205 933 202 828 Payback time (a) 1.14 0.22 0.89 NPV (€) 1 031 001 1 192 348 1 066 295

Table 2: Results of economic evaluation for three technologies.

3.4 Integration of all three technologies with active carbon adsorption

Within laboratory experiments, it was determined that the evaporation process could reduce COD to 1000 mg/L, ultrafiltration to 7000 mg/L and electrocoagulation to 12 000 mg/L. None of these three output concentrations was suitable to discharge treated water into surface water. Therefore, experiments were conducted to further reduce the effluents' COD values by using adsorption on active carbon. It was established that:

- the addition of active carbon in the amount of 2 kg/m³ reduced the COD value of the effluent from the evaporation process from 1000 mg/L to 120 mg/L, which was suitable for discharging into a river.
- the addition of active carbon in the amount of 40 kg/m³ reduced the COD value of the effluent from the ultrafiltration process from 7000 mg/L to 3060 mg/L, and final treatment in WWTP was still needed; however, this meant a lower water emission tax.
- The COD of electrocoagulation effluent was reduced from 12 000 mg/L to 5246 mg/L by using 40 kg/m³ of active carbon. Final treatment in WWTP was still needed at a lower cost.

The investment costs of all three technologies were increased by 10 000 \notin for a filtration vessel with active carbon. The expenditures were increased for purchasing active carbon at a price of 1.5 \notin /kg and removing used active carbon at a price of 0.36 \notin /kg. In the case of ultrafiltration and electrocoagulation, the water emission tax was also calculated because final COD values were above 120 mg/L.

Table 3 present the results of integrated technologies with final treatment using active carbon. The operating costs of ultrafiltration and electrocoagulation integrated with adsorption are high because of their high consumption of active carbon. Net present values are therefore lower than in Table 2; however, the difference is the smallest in the case of evaporation. Evaporation showed the highest NPV, despite large capital cost, but the operating cost was lower and cash flow higher.

	EV+AC	UF+AC	EC+AC
WOWE flow rate (m ³ /a)	3 000	3 000	3 000
COD (mg/L)	120	3 060	5 246
Electricity consumption (kWh/m ³)	60	18	2
Electricity cost (€/a)	12 600	3 780	420
Total cost (€/a)	62 644	229 025	226 727
Capital cost (€)	244 210	54 995	189 840
Cash flow (€/a)	199 028	59 190	63 501
Payback time (a)	1.23	0.93	2.99
NPV (€)	978 578	308 656	200 297

Table 3: Results of economic evaluation for three technologies plus active carbon.

4 Conclusion

This paper presented evaluations of the economic viability of three technologies for treating waste oil-in-water emulsions: evaporation, ultrafiltration and electrocoagulation. The annual amount of WOWE was estimated at 3 000 t/a and initial COD value 30 000 mg/L.

The lowest COD value of the effluent (1000 mg/L) was achieved by the evaporation process; however, its capital cost was the highest, and NPV the lowest, yet still positive. The NPVs for the ultrafiltration and electrocoagulation processes were slightly higher; however, the effluents' COD values were relatively high: 7 000 mg/L and 12 000 mg/L, respectively. The payback period for the evaporation process was slightly above one year, electrocoagulation slightly below, and ultrafiltration only 0.22 years.

When the effluents from these methods were treated by adsorption on activated carbon, only evaporation achieved a final COD value suitable for discharging treated water into a river. NPV decreased by around 5 %, while NPV for combinations of ultrafiltration and electrocoagulation with active carbon decreased by 75 % and 81 %, respectively. Evaporation technology integrated with final adsorption treatment with active carbon represents a good compromise solution between the efficiency of COD reduction and economic viability.

Acknowledgments

The authors acknowledge financial support from the Slovenian Research Agency (Research Programme P2-0032).

References

- Almojily A., Johnson D., Radcliff L. O., Hilal N. (2018) Removal of oil from oil-water emulsion by hybrid coagulation/sand filter as pre-treatment, *Journal of Water Process Engineering* 26, 17-27.
- Cheng C., Phipps D., Alkhaddar R.M. (2005) Treatment of spent metalworking fluids, *Water Research* 39, 4051-4063.
- Cheryan M., Rajagopalan N. (1998) Membrane processing of oily streams. Wastewater Treatment and waste reduction, *Journal of Membrane Science* 151, 13-28.
- Clewlow, R. R. (2016). Carsharing and sustainable travel behavior: Results from the San Francisco Bay Area, *Transport Policy* 51, 158-164.
- Decree (2012) Decree on the environmental tax on pollution due to the waste water discharge (Uredba o okoljski dajatvi za onesnaževanje okolja zaradi odvajanja odpadnih voda, Uradni list RS,. 80/12 and 98/15).
- Hamilton R. (2009) *Evaluation of Lime Softening vs. Electrocoagulation* for Treatment of Produced Water, Prepared for Proprietary Energy Technology Company, Denver.
- Križan J., Petrinić I., Murić A., Simonič M. (2013) Recent developments in membrane treatment of spent cutting oils: a review, *Industrial Engineering Chemical Research* 52(23), 7603-7616.
- Nordin A., Jönsson A. (2010) Influence of module configuration on total economics during ultrafiltration at high concentration, *Chemical Engineeing Research Design* 88, 1555-1562.
- Novak P. Z., Škof G.P., Kravanja Z. (2016) MILP synthesis of separation processes for waste oil-inwater emulsion treatment, *Frontiers of Chemical Science and Engineering* 10 (1), 120-130.
- Price for electrical energy, Cena električne energije. www.zanesljivo.si (access 20. 5. 2019)
- Rodriguez J., Stopić S., Friedrich B. (2007) Continuous Electrocoagulation Treatment of Wastewater from Copper Production, *World of Metallurgy-ERZMETALL* 60 (2), 81-87.
- Sutherland K. (2008) Machinery and processing: Managing cutting fluids used in metal-working, *Filtration & Separation* 45(7), 20-23.
- Xu X., Long Y., Li Q., Li D., Mao D., Chen X., Chen Y. (2019) Modified cellulose membrane with good durability for effective oil-in-water emulsion treatment, *Journal of Cleaner Production* 211, 1463-1470.

THE INFLUENCE OF SAFETY FACTORS ON THE OPTIMAL DESIGN OF UNDERGROUND LINED ROCK CAVERNS

STOJAN KRAVANJA & TOMAŽ ŽULA

University of Maribor, Faculty of Civil Engineering, Transportation Engineering and Architecture Maribor, Slovenia, e-mail: stojan.kravanja@um.si, tomaz.zula@um.si

Abstract This paper presents the influence of safety factors on the optimal design of lined rock caverns (LRC), designed for underground gas storage (UGS). For this system, adequate safety precautions and sufficient strength of the surrounding rock must be ensured. Security steps must be provided for all risks which may occur. This is assured by the inclusion of two special constraints and safety factors into the UGS optimization model. In order to study the influence of safety factor on the system, a parametric mixed-integer non-linear programming (MINLP) optimization of the system is performed for different values of the safety factors. A cost optimization is carried out and GAMS/Dicopt is used. A numerical example at the end of the paper shows the influence of safety factors on the optimal production costs and design of an LRC.

Keywords: Lined rock cavern, Safety factor, Cost optimization, Mixed-integer non-linear programming, MINLP.



DOI https://doi.org/10.18690/978-961-286-353-1.11 ISBN 978-961-286-353-1

1 Introduction

This paper examines the influence of safety factors on the optimal design of a lined rock cavern (LRC) designed for underground gas storage (UGS). The LRC contains gas under high pressure, and the UGS system is usually designed with one or more LRCs. The LRC is normally constructed inside a rock mass. It is comprised of a cylindrically shaped concrete wall which has a steel lining in order to ensure impermeability. The surrounding rock supports the gas pressure; see Stille and Sturk (1994), Sofregaz US Inc. (1999), Brandshaug *et al.* (2001), Chung *et al.* (2003) and Glamheden and Curtis (2006).

We present a continuation of earlier research in which non-linear programming (NLP) optimization of a single gas cavern was described by Kravanja and Žlender (2010) and later extended to optimization of an entire UGS with any number of caverns by Žlender and Kravanja (2011), and to the optimization in different rock environments by Kravanja and Žlender (2012) and Jelušič *et al.* (2019). The latter reference introduced a prediction of the minimal investment costs for the UGSs, with capacities from 10 to 100 million m³ of natural gas, with the help of an adaptive network based fuzzy inference system (ANFIS). Analyses of the LRC/UGS with the ANFIS were reported by Žlender *et al.* (2012, 2013) and Jelušič and Žlender (2014).

For this study, an NLP optimization model of an UGS was developed in which the cost objective function of the system was subjected to geomechanical and design constraints. While the geomechanical constraints assure sufficient strength of the LRC's surrounding rock, the design constraints define the relations between the LRC's dimensions, inner gas pressure and the rock. In Kravanja and Žula (2018), discrete alternatives for rounding the dimensions of the LRC were added to the optimization model and mixed-integer non-linear programming (MINLP) optimization was applied.

According to Žlender and Kravanja (2011) and Jelušič *et al.* (2019), four of the most important risks which may occur during the construction/operation of an LRC and UGS can be prevented by four geomechanical constraints: the strength of the rock mass is sufficient, uplift of the rock above the cavern is prevented, collapse of the rock between the caverns is prevented and deformations of the concrete wall and steel lining are limited (large deformations or destruction of the steel lining are

prevented); see also Kravanja and Žula (2018). These constraints were derived from a series of the finite element method (FEM) analyses using the Hoek-Brown failure criterion; see Hoek *et al.* (2002).

Two of the risks mentioned, uplift of the rock above the cavern and collapse of the rock between caverns, are countered by the inclusion of safety factors into two geomechanical constraints. In order to study the influence of these safety factors on the system, a parametric mixed-integer non-linear programming (MINLP) optimization of the system was performed for different values of these safety factors.

2 MINLP problem formulation

The optimization problem of the lined rock cavern is non-linear, continuous and discrete. Mixed-integer non-linear programming (MINLP) is thus applied. The general MINLP optimization problem is formulated as:

min
$$\chi = f(\mathbf{x}, \mathbf{y})$$

subjected to: $g_k(\mathbf{x}, \mathbf{y}) \leq 0$ $k \in K$
 $\mathbf{x} \in X = {\mathbf{x} \in \mathbb{R}^n: \mathbf{x}^{\text{LO}} \leq \mathbf{x} \leq \mathbf{x}^{\text{UP}}}$
 $\mathbf{y} \in Y = {0,1}^m$

where **x** is a continuous variable and **y** is a discrete (0, 1) variable. Function $f(\mathbf{x}, \mathbf{y})$ is the objective function, which is subjected to (in)equality constraints $g_{k}(\mathbf{x},\mathbf{y})$. At least one function must be non-linear. All functions must be continuous and differentiable.

The optimization model of the LRC is developed according to the above MINLP formulation. The model is comprised of the cost objective function, geomechanical and design constraints, input data (constants) and variables. The design variables (**x**), which are rounded on whole discrete values during the MINLP optimization process, are: the inner diameter of the cavern DCAV [m], the depth of the cavern DEPTH [m], the height of the cavern tube HCAV [m], the thickness of the concrete cavern wall TWALL [m] and the gas pressure PGAS [MPa], see Fig. 1.



Figure 1: Vertical cross-section of lined rock cavern.

3 Safety factors

Adequate safety factors of the LRC/UGS and the strength of the surrounding rock must be calculated/checked. Security steps should be provided for all risks which may be occur. Two risks, uplift of the rock above the cavern and collapse of the rock between caverns, are prevented by the inclusion of two safety factors SF_{up} and SF_{borig} into two geomechanical constraints in the model; see Eqs. (1) - (4). The safety factor against rock uplift above the cavern SF_{up} must be, according to Žlender and Kravanja (2011) and Jelušič *et al.* (2019), greater than a defined minimal value $SF_{up,min}$, see Eq. (1). SF_{up} is defined by Eq. (2). The same holds with the safety factor against rock collapse between two caverns SF_{borig} which must be greater than a defined minimal value $SF_{borig,min}$; see Eq. (3). SF_{borig} is determined by Eq. (4). It should be noted that these two safety factors, Eqs. (2) and (4), were derived as approximation functions from a series of the finite element method (FEM) analyses for different values of inner gases PGAS, depths of the cavern DEPTH and diameters of the cavern DCAV. Coefficients $c_1 - c_3$, $f_1 - f_3$, $g_1 - g_3$, $i_1 - i_3$ and the initial values of safety factors $SF_{up,0}$ and $SF_{borig,0}$ depend on the type of rock in which is the LRC constructed; see these values in Jelušič *et al.* (2019). The initial values of the variables are: $PGAS_0 = 20$ MPa, $DEPTH_0 = 150$ m and $DCAV_0 = 25$ m.

$$SF_{up} \ge SF_{up,min}$$
 (1)

$$SF_{up} = SF_{up,0} \cdot c_1 \cdot \left(\frac{PGAS}{PGAS_0}\right)^{f_1} \cdot c_2 \cdot \left(\frac{DEPTH}{DEPTH_0}\right)^{f_2} \cdot c_3 \cdot \left(\frac{DCAV}{DCAV_0}\right)^{f_3}$$
(2)

$$SF_{horiz} \ge SF_{horiz,min}$$
 (3)

$$SF_{horiz} = SF_{horiz,0} \cdot g_1 \cdot \left(\frac{PGAS}{PGAS_0}\right)^{i_1} \cdot g_2 \cdot \left(\frac{DEPTH}{DEPTH_0}\right)^{i_2} \cdot g_3 \cdot \left(\frac{DCAV}{DCAV_0}\right)^{i_3} \tag{4}$$

The minimal values of safety factors $SF_{up,min}$ and $SF_{boriz,min}$ should be taken to be at least 2. In cases where the LRC/UGS is located in a rural/mountain area, $SF_{up,min}$ and $SF_{boriz,min}$ are usually defined to be 2.5. Here, two questions arise: if we define higher values of safety factors, how much will the investment costs of the LRC increase and what are changes in the LRC's design. The latter is necessary in cases when the LRC/UGS is planned to be constructed close to an urban area. In order to study the influence of safety factors on the system, parametric mixed-integer nonlinear programming (MINLP) optimization of the system is performed for different values of safety factors.

4 Numerical example

A parametric MINLP optimization of the investment costs of a lined rock cavern designed for underground gas storage in Senovo, Slovenia is presented. The parametric optimization was performed seven times for different values of safety factors SF ($SF_{up,min}$ and $SF_{boriz,min}$): from 1 to 6. The UGS in Senovo is planned to be constructed with four LRCs of 5.56 million m³ of natural gas capacity each; see Žlender and Kravanja (2011).

The MINLP optimization model includes similar constraints as in Kravanja and Žlender (2010) and in Kravanja and Žula (2018). Cost items and prices defined in the cost objective function are the same as those used in the project and our previous optimizations; see Table 1. The model is written in GAMS, the General Algebraic Modelling System by Brooke *et al.* (1988). The combinatorics of the MINLP problem is relatively high: altogether 4735 binary variables of alternatives give 1.508·10¹² different LRC structure alternatives. One of them is optimal. This simple parametric cost and rounded dimension optimization is carried out with the GAMS/DICOPT program developed by Grossmann and Viswanathan (2002). Note that comprehensive MINLP problems were usually optimized with MipSyn by Kravanja (2010).

Table 1: Cost items and prices.

Cost item	P	Price		
Upper ground works	2 982 500	EUR		
Underground works	2 798 025	EUR		
Price of the tunnel excavation	2 440	$\mathrm{EUR}/\mathrm{m}^1$		
Price of the tunnel protection	1 340	$\mathrm{EUR}/\mathrm{m}^1$		
Price of the cavern excavation	100	EUR/m ³		
Price of the cavern protection	90	$\mathrm{EUR}/\mathrm{m}^2$		
Price of the cavern drainage	60	$\mathrm{EUR}/\mathrm{m}^2$		
Price of the cavern wall concrete	190	EUR/m ³		
Price of the wall reinforcement	2 000	EUR/t		
Price of the steel lining	920	EUR/m^2		

Table 2: Optimal results for different safety factors SF.

Variable	SF=1	SF=2	SF=2.5	SF=3	SF=4	SF=5	SF=6
PGAS [MPa]	17.5	17.5	17.5	17.5	17.5	17.5	17.5
DEPTH [m]	191.6	191.6	191.6	225.8	314.2	405.8	496.7
DCAV [m]	30.0	30.0	30.0	30.0	30.0	30.0	30.0
TWALL [m]	2.0	2.0	2.0	2.0	2.0	2.0	2.0
HCAV [m]	17.6	17.6	17.6	17.6	17.6	17.6	17.6
$COST_{LRC}$ [M€]	18.22	18.22	18.22	18.33	18.61	18.89	19.19
COST _{UGS} [M€]	72.88	72.88	72.88	73.31	74.42	75.57	76.76

The optimal results for the defined safety factors from SF=1 to SF=6 represent the obtained minimal investment costs from 18.22 to 19.19 million EUR per lined rock

cavern ($COST_{LRC}$) and from 72.88 to 76.76 million EUR per underground gas storage facility ($COST_{UGS}$); see Table 2. All these results exhibit savings of more than 45 % when compared to designs obtained by the classical method (FEM). All dimensions of the caverns and the inner gas pressure are also calculated. Figure 2 presents a diagram of the obtained optimal costs and depths for the UGS Senovo depending on different defined safety factors SF ($SF_{up,min}$ and $SF_{borig,min}$).



Figure 2: Diagram of the optimal costs and depths of the UGS Senovo.

It is somewhat surprising that all variables, except the depth of the cavern, remain the same for all different safety factors. While the optimal costs of the system rise slightly and monotonically, the optimal depths increase significantly for higher safety factors (SF). The results show that if we increase the safety factor from 2.5 to 5.0, the optimal investment costs rise by only 3.7 % although the cavern depth increases 2.1 times (from 191.6 m to 405.8m).



Figure 3: The optimized lined rock cavern, a) SF=2.5, b) SF=5.

5 Conclusions

We examined the influence of safety factors on the optimal design of a lined rock cavern (LRC) designed for underground gas storage (UGS). For this system, adequate safety precautions and sufficient strength of the surrounding rock must be provided. This is assured by the inclusion of two special constraints and safety factors into the UGS optimization model. In cases where the LRC/UGS is located in a rural/mountain area, the safety factor is usually defined as 2.5. However, when the LRC/UGS is planned to be constructed close to an urban area, we have to use higher safety factors. In order to study the influence of safety factors on the system, a parametric mixed-integer non-linear programming (MINLP) of the system is performed for different values of safety factors. Cost optimization is carried out using GAMS/Dicopt. A numerical example at the end of the paper shows that even with doubled safety factors, when the safety factor increases from 2.5 to 5.0, the optimal investment costs rise by only 3.7 %. The design of the cavern shell remains the same, but the cavern depth becomes twice as deep.

Acknowledgments

The authors are grateful for the support of funds from the Slovenian Research Agency (program P2-0129).

References

- Brandshaug, T., Christianson, M., Damjanac, B. (2001). Technical review of the lined rock cavern (LRC) - concept and design methodology: mechanical response of rock mass. US Department of Energy.
- Brooke, A., Kendrick, D., Meeraus, A. (1988). GAMS A User's Guide. Scientific Press, Redwood City, CA.
- Chung, I.M., Cho, W., Heo, J.H. (2003). Stochastic hydraulic safety factor for gas containment in underground storage caverns. J Hydrol, 284, 77-91.
- Glamheden, R., Curtis, P. (2006). Excavation of a cavern for high-pressure storage of natural gas. *Tunnelling and Underground Space Technology*, 21(1), 56-67.
- Grossmann, I.E., Viswanathan, J. (2002). DICOPT Discrete and Continuous Optimizer. Engineering Design Research Center (EDRC) at Carnegie Mellon University, Pittsburgh, PA.
- Hoek, E., Carranza-Torres, C.T., Corkum, B. (2002). Hoek-Brown failure criterion. In: Proc. North American rock mechanics society meeting in Toronto.
- Jelušič, P., Žlender, B. (2014). An adaptive network fuzzy inference system approach for site investigation, *Geotechnical testing journal* 37(3), 400-411. http://www.astm.org/DIGITAL_LIBRARY/JOURNALS/GEOTECH/PAGES/GTJ2012 0018.htm
- Jelušič, P., Kravanja, S., Žlender, B. (2019). Optimal cost and design of an underground gas storage by ANFIS, Journal of natural gas science and engineering, 61, 142-157. doi: 10.1016/j.jngse.2018.11.003
- Kravanja, S., Žlender, B. (2010). Optimal design of underground gas storage. In: WIT Transactions on the Built Environment, 112, 389-399. doi.org/10.2495/HPSM100361
- Kravanja, S., Žlender, B. (2012). Optimization of the underground gas storage in different rock environments. In: WIT Transactions on the Built Environment, 125, 15-26. doi.org/10.2495/OP120021
- Kravanja, S., Žula, T. (2018). MINLP optimization of the underground lined rock. In: Conference proceedings, International Conference on Technologies & Business Models for Circular Economy, 1, 2018, Portorož. 1st ed. Maribor: University of Maribor Press, 149-157. http://press.um.si/index.php/ump/catalog/view/367/345/590-2.
- Kravanja, Z. (2010). Challenges in sustainable integrated process synthesis and the capabilities of an MINLP process synthesizer MipSyn. *Comput Chem Eng*, 34(11), 1831-1848. doi:10.1016/j.compchemeng.2010.04.017
- Sofregaz US Inc. (1999). Commercial potential of natural gas storage in lined rock caverns (LRC). US Department of Energy, Federal Energy Technology Center.
- Stille, H., Sturk, R. (1994). Storage of gas in lined shallow rock caverns conclusions based on results from the Grängesberg test plant. In: Rock mechanics in petroleum engineering, Delft, Netherlands.
- Żlender, B., Kravanja, S. (2011). Cost optimization of the underground gas storage. *Eng Struct*, 33, 2554-2562. doi.org/10.1016/j.engstruct.2011.05.001
- Žlender, B., Jelušič, P., Boumezerane, D. M. (2012). Planning geotechnical investigation using ANFIS. Geotechnical and Geological Engineering, 30(4), 975-989. doi:10.1007/s10706-012-9520-7.
- Žlender, B., Jelušič, P., Boumezerane, D. M. (2013). The feasibility analysis of underground gas storage caverns. Eng Struct, 55, 16-25. doi:10.1016/j.engstruct.2013.01.003.
SUSTAINABILITY PROFIT GENERATED BY THE OPTIMIZATION OF CONTINUOUS BEAMS

Tomaž Žula & Stojan Kravanja

University of Maribor, Faculty of Civil Engineering, Transportation Engineering and Architecture Maribor, Slovenia, e-mail: tomaz.zula@um.si, stojan.kravanja@um.si,

Abstract This paper deals with the optimization of sustainability profit generated by the production of continuous beams. A number of beams designed from three alternative materials, laminated timber, reinforced concrete and structural steel, are considered. Three different optimization models are developed for each of the materials. Furthermore, two different objectives are defined for each material alternative: for economic profit and for sustainability profit (which includes the eco costs of global warming). The design, resistance and deflection constraints of these beams are based on specifications prescribed by Eurocode standards. A mixed-integer non-linear programming (MINLP) approach using GAMS/Dicopt is applied to find most advantageous material alternative for the beams. The results of the numerical analysis clearly show that reinforced concrete beams provide the highest economic profit and the highest sustainability profit.

Keywords: Sustainability profit, GHG emissions, optimization, Mixed-integer non-linear programming, MINLP.



DOI https://doi.org/10.18690/978-961-286-353-1.12 ISBN 978-961-286-353-1

1 Introduction

We present a model for the optimization of sustainability profit generated by the production of continuous beams for civil engineering. Sustainability profit is the sum of economic profit and the eco costs of global warming. A number of beams designed from three different materials, laminated timber, reinforced concrete and structural steel, are included. Furthermore, two different objectives are defined for each material alternative: economic profit and sustainability profit (which includes the eco costs of global warming).

Different techniques and objectives for optimization and sustainability have been introduced. Zaforteza *et al.* (2009) took into account a simulated annealing algorithm (SA) applied with two objective functions, embedded CO₂ emissions and the economic cost of reinforced concrete structures. Camp and Huq (2013) used a hybrid big bang-big crunch algorithm (BB-BC) for the optimal design of reinforced concrete frames to minimize either the total cost or the CO₂ emissions. Alonso and Berdasco (2015) proposed a carbon footprint for sawn timber products. Li *et al.* (2017) presented a topology optimization in order to obtain the best-possible welded box-beam structures that emit less greenhouse gases by using an improved ground structure method (IGSM).

2 MINLP model formulation

It is assumed that a general non-linear and non-convex continuous/discrete optimization problem for the production of continuous beams can be formulated as an MINLP problem:

min
$$\chi = f(\mathbf{x}, \mathbf{y})$$

subjected to: $g_k(\mathbf{x}, \mathbf{y}) \leq 0$ $k \in K$
 $\mathbf{x} \in X = {\mathbf{x} \in \mathbb{R}^n: \mathbf{x}^{\text{LO}} \leq \mathbf{x} \leq \mathbf{x}^{\text{UP}}}$
 $\mathbf{y} \in Y = {0,1}^m$

where **x** is the vector of the continuous variables and **y** is the vector of the discrete (0, 1) variables. Function $f(\mathbf{x}, \mathbf{y})$ is the objective function, which is comprised of the economic and sustainability profits. g_k (**x**,**y**) represents the design, resistance and deflection constraints of the beams.

3 Numerical example

The example illustrates the optimization of 300 equal continuous beams; see Fig. 1. Each beam is a two-span (2L) structure having altogether a length of 2.5.0=10.0 m, subjected to the combined effect of dead-weight, permanent continuous load of 10.0 kN/m (g) and imposed variable continuous load of 12.0 kN/m (q).

Each continuous beam is made from one of three different materials: laminated timber, reinforced concrete and structural steel, see Fig. 2. At this point, a comparison of competitiveness between these three materials was calculated for various material and dimension alternatives, and for two different objectives: optimization of economic profit and of sustainability profit.

For comprehensive topology optimization problems, we usually use the MipSyn program (Kravanja, 2010). Because the optimization problem of beams in this study is a simple discrete and non-linear problem, the Dicopt application (Grossmann, 2002) was selected. Six optimization models (CONBOPT) were developed for a combination of three different materials (timber, reinforced concrete and steel) and two different objective functions. GAMS (General Algebraic Modelling System), (Brooke *et al.*, 1988), was used for mathematical modelling. The objective functions of the models were subjected to design, loading and resistance constraints known from structural analysis. The dimensioning and deflection constraints were performed according to Eurocode specifications: Eurocode 5 (2004) for timber, Eurocode 2 (2004) for reinforced concrete and Eurocode 3 (2005) for steel. The beams were checked for shear, bending moment and lateral torsional buckling resistances as well as for vertical deflections.



Figure 1: Continuous beam.



Figure 2: Cross sections of the continuous beam.

The continuous beam superstructure is comprised of three different materials. The laminated timber beam superstructure consists of 101 different rounded dimension alternatives for the cross-section width and 131 rounded dimension alternatives for the cross-section height. The reinforced concrete beam superstructure contains 7 different concrete grades, 13 standard reinforcing steel bars, 131 rounded dimension alternatives for the cross-section height and 101 rounded dimension alternatives for the cross-section width (rounding up by whole centimeters). In addition, 3 different steel grades, 8 different dimension alternatives of the standard steel plate thicknesses for flanges and webs separately, 1051 rounded dimension alternatives for the width of the flange and 1301 rounded dimension alternatives for the web are included in the steel beam superstructure.

The material and dimension alternatives (binary variables) give 13,231 structure alternatives for the timber beam, 1,204,021 different structure alternatives for the reinforced concrete beam and 262,531,392 different structure alternatives for the steel beam.

Two different objective functions were used for two different defined criteria. The first criterion of optimization includes maximization of economic profit ($P_{\rm E}$ [€]) of 300 equal beams. The economic profit is defined as the sum of the selling price, minus the self-manufacturing material and labor costs and overheads. The objective function was determined for three different materials separately; see Eq. (1). N is the number of continuous beams (N = 300), $C_{\rm s}$ [€] is the selling price of a single continuous beam, and C_{Mi} [€/kg] represents the material unit prices of (*i*∈*I*: laminated timber, impregnation and protection paint for the timber beam; concrete, reinforcing steel bars and formwork slab-panels for the concrete beam and structural steel, electrodes, gas consumption and anticorrosion-resistant paint for the steel beam). ρ_i [kg/m³] is the corresponding unit mass and V_i [m³] is volume. C_{Li} represents the hourly labor costs $[\ell/h]$, t_i [h] are times required for $(i \in I)$: impregnating and painting the timber beam; placing, curing and vibrating the concrete, cutting and placing the reinforcement, paneling the concrete beam, and cutting, welding and painting the steel beam), and f_0 is an indirect cost factor for overheads ($f_0 = 2$). For more detail about cost items used in the economic objective function, see (Jelušič, 2017) and (Kravanja, 2017).

$$\max P_{\rm E} = N \cdot \left(C_{\rm S} - C_{\rm Mi} \cdot \rho_i \cdot V_i - C_{\rm Lj} \cdot t_j \cdot f_{\rm O} \right) \tag{1}$$

The second criterion is the maximization of sustainability profit (P_{SUS} [€]), calculated for 300 beams as the sum of the economic profit and eco costs of global warming (EVR, 2018) caused by beam production. The objective function was determined for three materials separately; see Eq. (2). C_{GW} (€/kg CO₂ eq.) is the price of global warming of 0.116 €/kg CO₂ eq. (EVR, 2018), ρ_k [kg/m³] and V_k [m³] are the corresponding unit masses and volumes, respectively, and f_{CFEFk} is a carbon footprint emission factor ($k \in K$; for the timber beam, reinforced concrete beam and for the steel beam). The carbon footprint emission factors used in the study are 0.69 kg CO₂ eq./kg for timber, 0.11 kg CO₂ eq./kg for concrete, 2.43 kg CO₂ eq./kg for reinforcing steel bars and 1.72 kg CO₂ eq./kg for steel.

$$\max P_{\text{SUS}} = P_{\text{E}} + N \cdot \left(-C_{\text{GW}} \cdot f_{\text{CFEF}k} \cdot \varphi_k \cdot V_k \right)$$
⁽²⁾

Table 1: Results of the continuous beam optimizations.

Criterion		Laminated timber GL24h	Steel S 355	Reinforce d Concrete
1.*	Economic profit (€)	100,638	147,281	179,791
	b (cm)	36.0	14.9	30.0
	h (cm)	38.0	25.7	40.0
2.*	Sustainability profit (€)	86,303	135,623	141,164
	b (cm)	35.0	14.9	30.0
	h (cm)	39.0	25.7	40.0

* 1. Economic profit; 2. Sustainability profit

Table 1 displays the results of the optimization for three different materials and two different objective functions. The results show that concrete beams exhibit the highest economic profit and the highest sustainability profit, while laminated timber beams exhibit the worst results in all criteria.

4 Conclusion

Our analysis of the optimization of sustainability profit generated by the production of continuous beams, calculated using two different objective functions, economic profit and sustainability profit with a mixed-integer non-linear programming (MINLP) approach, clearly shows that reinforced concrete beams exhibit the highest economic profit and the highest sustainability profit.

Acknowledgments

The authors are grateful for the support of funds from the Slovenian Research Agency (program P2-0129).

References

- Alonso, C.M., Berdasco, L. (2015). Carbon footprint of sawn timber products of Castanea sativa Mill. in the north of Spain. *Journal of Cleaner Production*, 102, 127-135. doi.org/10.1016/j.jclepro.2015.05.004
- Brooke, A., Kendrick, D., Meeraus, A. (1988). GAMS A User's Guide, Scientific Press, Redwood City, CA.
- Camp, C.V., Huq, F. (2013). CO₂ and cost optimization of reinforced concrete frames using a big bangbig crunch algorithm. *Engineering Structures*, 48, 363-372. doi.org/10.1016/j.engstruct.2012.09.004
- Eurocode 2. (2004). Design of concrete structures. European Committee for Standardization, Brussels.
- Eurocode 3. (2005). Design of steel structures. European Committee for Standardization, Brussels.
- Eurocode 5. (2004). Design of timber structures. European Committee for Standardization, Brussels.
- Grossmann, I.E., Viswanathan, J. (2002). DICOPT Discrete and Continuous Optimizer. Engineering Design Research Center (EDRC) at Carnegie Mellon University, Pittsburgh, PA.
- Jelušič, P., Kravanja, S. (2017). Optimal design of timber-concrete composite floors based on the multiparametric MINLP optimization. Composite structures, 179, 285-293. doi.org/10.1016/j.compstruct.2017.07.062
- Kravanja, S., Žula, T., Klanšek, U. (2017). Multi-parametric MINLP optimization study of a composite I beam floor system. *Engineering structures*, 130, 316-335. doi.org/10.1016%2Fj.engstruct.2016.09.012
- The Model of the Eco-costs / Value Ratio (EVR). (2018). Delft University of Technology, www.ecocostsvalue.com/. Accessed on: 23 Mar 2018.

PYROLYSIS – AN ALTERNATIVE WAY OF RECYCLING

MATEVŽ ROŠKARIČ

University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: matevz.roskaric@um.si

Abstract In this article we will overview the possibility of using pyrolysis for the reuse of Municipal solid waste (MSW) and sludge. During the pyrolysis process, MSW is transformed to: i) fuel, ii) heat that can be used for drying the sludge or heat conversion to energy, iii) gases that can be burnt for electricity, stored and sold or used to move other generators and iv) some other products. Moreover, pyrolysis can be integrated with other technologies within a large integrated plant converting plastics, sludge and other waste materials into useful products. This work presents preliminary laboratory results of MSW pyrolysis and provide technological options for complex combinations of pyrolysis with other techniques shows promise in the alternative use of MSW and other waste in terms of energy and materials recovery.

Keywords: Municipal solid waste, Pyrolysis, Gasification, Recycling, Integrated circular waste treatment facility.



DOI https://doi.org/10.18690/978-961-286-353-1.13 ISBN 978-961-286-353-1

1 Introduction

In line with advances in technology, we also invented new materials. One of these was plastic, which has many positive effects such as its light weight and versatile use, but it has serious implications for nature. For polymers, it seems logical to assume that we could convert plastic back to fossil fuel, reduce the production of new fossil fuels and also improve the conditions of natural habitats by reducing landfills and other dumping sites that have a negative effect on nature, because of plastic and other garbage that is hard to degenerate (Singh & Ruj, 2016; Thompson, 2009). The majority of plastic is produced for consumers and is sooner or later found in municipal solid waste (MSW). The production of MSW has increased over the years, but the technology to process it is advancing at a slower rate. In 2017, we produced 348 million tons of plastic (PlasticEurope, 2018), of which approximately 50 % is single use (Hopewell *et al.*, 2009).

2 Overview of technologies

With the advancement of technology and construction of cities, the pollution problem is becoming more and more complex. We need to advance in the field of waste management, because we create so much more waste every day that the old methods no longer work at the desired level.

2.1 Recycling

The best ecological treatment, that is commercial, is recycling. This is a process in which waste is treated and converted to new materials and products. With recycling, we have a source of raw materials. This reduces the greenhouse gasses, overall air pollution, water pollution and, above all, it reduces energy usage. The new raw materials can then be processed into new products (Geissdoerfer *et al.*, 2017). However, the quality of the recycled raw materials is not always good. Some materials are harder to recycle or even non-recyclable. Such materials cause problems in the recycling process and need to be separated before the rest is processed.

Plastic presents other problems, like additives which makes them into materials that are hard to recycle or even non-recyclable (Eriksen *et al.*, 2019). The non-recyclable materials are then transported to landfills. Some of the hard-to-recycle materials can be mechanically treated and used in lower quality products. For example, plastic can be shredded and then used in construction materials that can be used as a binder in paving blocks (Agyeman *et al.*, 2019).

2.2 Landfills

Landfills are another option for treating waste like MSW, although the waste loses some of its potential as an energy source and a source of new materials. According to some statistics, nearly 42 % of global waste is buried in landfills (Nizzeto *et al.*, 2016).

The garbage is processed, pressed as compact as possible and buried under the earth, then covered with different materials, to decompose. It decomposes through the process of thermo-oxidation and anaerobic degradation (Webb *et al.*, 2013; He *et al.*, 2019). The idea is that microbes in a controlled space, will decompose complex organic materials. The processes require time, workers and a correctly designed landfill.

One problem is the leaking of leachate. When rain inundates the landfill and percolates through it, it mixes with the dissolved materials and becomes leachate. If not contained properly, the adjacent soil and ground water can become contaminated, and microplastics can be released (Nizzeto *et al.*, 2016; He *et al.*, 2019).

Even if we unburied the waste, because of its physical-chemical properties, like contamination (Quaghebeur *et al.*, 2013) and partial degradation, it is mostly unsuitable, or at least uneconomical to recycle. (Canopoli *et al.*, 2018). There is also the option of using the excavated MSW and processing it to solid recovered fuel (SRF) with some profit (Ventosa *et al.*, 2014). On the other hand, pyrolysis offers an alternative, since some studies have shown that the excavated materials from landfills could be used as feedstock for a pyrolysis reactor. (Canopoli *et al.*, 2018).

2.3 Incineration

Another option is thermal disposal via incineration. In this process, the energy is recovered from the waste in the form of heat with combustion of the organic substances (Lino & Ismail, 2017). The heat can be used to produce electricity or to heat part of a city. From the residue, metals can be extracted and then recycled. During the combustion process, flue gas is formed, which contains many pollutants, such as CO_2 , NO_x , and volatile organic compounds (VOC). Because of these, the flue gas must be cleaned before release into the atmosphere (Al-Salem *et al.*, 2009). However, some emissions are still present using current technologies, and the contamination of heavy metals persists (Wang *et al.*, 2019).

2.4 Gasification

Another form of recycling is gasification. In the process of gasification, organic matter or carbon-based materials are vaporized and transformed into a mixture of carbon monoxide, hydrogen and carbon dioxide at high temperatures. This mixture is also called synthetic gas (syngas). For this to happen, a controlled atmosphere with a gasification agent is needed, like oxygen or steam, and high temperatures of 700 °C or more (Panepinto *et al.*, 2015). Under this condition, syngas is formed, which can be used as a raw material for other products, like methanol or hydrogen, or, most of the time, as a fuel (Panepinto *et al.*, 2015, Higman & van der Burgt., 2008).

With the option of greater energy recovery, gasification plants are used in countries that lack other resources for electrical production, like Japan, or in some Scandinavian countries, which are among the leading countries in waste management (Panepinto *et al.*, 2015). Although it seems like a good alternative, gasification also has problems, like the tar problem. If tars, which can be up to 10 % of yield, are allowed to condensate, they can damage or disable pollution filter systems, and dangerous gases can be released into the atmosphere.

2.5 Pyrolysis

Pyrolysis is another alternative method to manage waste. The whole process happens at high temperature and in an inert atmosphere, like nitrogen. This causes thermal decomposition of the feedstock. The resulting gasses are then cooled to condense to form a liquid, tar, which can be used for fuel or as raw material. Some gases do not condense and can later be used as fuel or raw materials also. The reaction also leaves a solid residue, char, with a high carbon ratio (Sharuddin *et al.*, 2016). Pyrolysis is already used to some degree on a commercial level, but it has the potential to solve many waste problems, because it can be fueled with waste, like non-recycled plastic or MSW. Moreover, the products can then be used again in a different field with a positive energy balance (Abnisa *et al.*, 2014). Even waste excavated from landfills can be used as feedstock for pyrolysis, studies have shown (Canopoli *et al.*, 2018). Also, pyrolysis produces lower SO_x and NO_x emissions (Younan *et al.*, 2016), making the process more economical and ecological. The resulting liquid phases can be used as fuel directly or can be purified. A simple distillation may be enough for mixed plastic to be used as fuel (Wiriyaumpaiwong & Jamradloedluk, 2017).

Generally, for the pyrolysis process, we can use MSW, which differ in composition and type of contamination. Studies have shown that excavated MSW can be used (Canopoli *et al.*, 2018) and that metals like aluminum do not interfere with the process of pyrolysis (Ludlow-Palafox & Ha, 2001). Inorganic molecules can also function as a catalyzer, to reduce the temperature and the energy demand.

Additionally, new technologies are available, like microwave-assisted reactors. In this case, smaller particles of a microwave-absorbent material are mixed with the feedstock. This has the advantage that the heat is equally distributed. (Lam & Chase, 2012).

2.6 Other techniques

They are some new methods in the field of waste treatment that still lack proper research and large-scale applications. For example, there is plasma gasification. It uses plasma to convert organic materials into syngas (Moustakas *et al.*, 2005). Another method for treating MSW is hydrothermal treatment using subcritical water. The water used can have 234 °C and 3 MPa or 295 °C and 8 MPa to recover

MSW (Hwang *et al.*, 2012). Although there are many single methods available, it seems that most have flaws. So, it is only logical that we should combine some of these methods. Some facilities have already been built that first use pyrolysis and then gasification or incineration, for example, in Japan or Norway. Co-pyrolysis of biomass and plastic also shows promising results with lower consumption of energy (Breyer *et al.*, 2017).

2.7 Integrated waste treatment facility

For example, pyrolysis and gasification can be combined, as has been demonstrated in some plants in Japan. Moreover, the feedstocks can be mixed with two different wastes, e.g. the co-pyrolysis of biomass and plastic waste. In South Africa the paper industry creates 1200 tons of waste per month. Most of it consists of paper waste with sludge (PWS), which is rejected by the paper industry. It contains degraded fiber and some plastic waste (Brown *et al.*, 2019). Brown *et al.*, (2019) used rapid pyrolysis for the conversion of this waste. In rapid pyrolysis, the heating rate is a few hundred degrees Celsius per minute. The resulting oil has a higher heating value (HHV) of 22 MJ/kg at a yield of 60 %. The char remnants have an HHV around 20 MJ/kg (Ridout *et al.*, 2016). With this, they could reduce landfill and gain an economic resource.

Other studies have also shown the benefits of using co-pyrolysis, like Jin *et al.* (2019) in their studies of wheat straw and polyurethane. Some modeling has also been done by Oyedun *et al.* (2014), who proved that with the addition of biomass to plastic, we probably create a liquid heat medium and thus decrease energy inputs and costs.

Another modern waste type is sludge. With the increase in wastewater treatment, the amount of sludge is also increasing. For the drying of sludges, several new technologies have been developed, like vacuum drying. Moreover, with the synergistic effects of the biomass and the introduction of sludges into feedstock or pyrolysis, we could reduce energy costs while gaining a new resource. We can also perform pyrolysis of sludge in order to yield an additive for fertilizer (Samolada & Zabaniotou, 2014). With the implementation of these processes, we could also reduce waste water generation via a closed system and even recover heat.

In newer studies, the possibility of solar-assisted pyrolysis has also been analyzed. Ghenai *et al.* (2019) tested it in a laboratory reactor at 500 °C and atmospheric pressure. The tar had the density, dynamics, viscosity, calorific value and chemical structure of diesel fuel. They calculated that the pyrolysis process uses only 52 % of the created solar-grid energy. The rest could be sold at a decent price. With the use of solar panels, greenhouse emissions are also reduced. There is also the possibility of using geothermal energy or other alternative energy sources for the energy demands of the processing plant. With combinations like this, poorer countries with good solar days per year or alternative energy resources could decrease their waste and boost their economy with environmental benefits. For example, in Ghana, waste is a major factor in flooding, because it blocks the canals (Department, 2010) and consequently increases the likelihood of vector borne diseases (Clapp & Swanston, 2009). With pyrolysis, they could solve their problems, as demonstrated by Tulashie *et al.* (2019).

So, a combination of different methods should give better results. For example, the waste would arrive at an integrated processing facility, where it would be sorted, shredded and dried. With the addition of biomass, the energy demand would be decreased. Also, with solar panels or other alternative energy sources, the energy demand would be decreased.

3 Experimental

Pyrolysis could be an alternative in processing different wastes. In past projects we studied the possibility of treating MSW for the waste management company in Maribor. One option was pyrolysis of the solid recovered fuel (SRF). We studied pyrolysis of polyethylene (PE) and the MSW at different stages of the process. The hypothesis was that, if the SRF contains around 70 % plastic (or at least a major part), which the company claimed that it should have, it should behave like mixed plastic pyrolysis and yield positive results.

3.1 Set-up

We used a laboratory batch type reactor model for investigating the pyrolysis of SRF. Given the limitations of the project, we did not use any inert gases as the carrier gas. The liquid was sampled in the sample tube, where the gas products were burnt at the exit. For a comparison, we used PE.

3.2 Material

For the comparison with SRF, we used PE with high density (HD PE), which was bought at the store. All samples were chopped into smaller pieces to increase the surface for the reaction. For the SRF, we used undried SRF, dried SRF, SRF right after sorting and the SRF with a larger percentage of humus.

3.2.1 Drying

The drying process was carried out at 110 °C for 24 hours. The measured moisture content for SRF was 15 %. We also double-checked the results and dried the SRF in a vacuum oven at 30 °C for 1 day. This time the percentage was 12.61 %, from which we can conclude that the SRF normally have from 10-15 % moisture content.

3.2.2 Composition of SRF

For the optimization of the process, the feedstock composition should be known. For the physical and chemical properties, we used a homogenized air-dried sample with a moisture content of 2.761 %. The 3000 g of the sample were shredded into 2 mm pieces. The tests were carried out at Gorenje Surovina as a standard procedure.

4 Results of SRF and PE HD pyrolysis

All liquids were analyzed by a GC-FID and GC-MS. The gases were not analyzed but were only ignited.

4.1 Results of HD PE

We used 10.64 g of the HD PE feedstock. The temperature was measured at the connecting piece every 30 s to get a temperature trend. For safety reasons, the experiment was conducted at a maximum of 400 °C. According to the literature, we should increase the temperature up to 500 °C or even 600 °C.

We measured the mass of the feedstock and of the products, from which we calculated the mass efficiency (μ) , which describes the ratio between the mass of liquid and gas products to the feedstock, and liquid efficiency, which describes the ratio between the mass of liquid products and the combination of liquid and gas products.

$$\mu = \frac{m_{\rm t} + m_{\rm p}}{m_{\rm s}} = 55.55 \% \qquad \tau = \frac{m_{\rm t}}{m_{\rm t} + m_{\rm p}} = 67.34 \%$$

The mass efficiency of HD PE was 55.55 % which is lower than in the literature. As said before, we were using laboratory distillation equipment and could not go above 400 °C. The liquid itself was clear orange in color, with a strong smell. The liquid and the gases burnt with an intense orange flame.

4.2 Results for SRF

For the calculations, we used dried SRF, although SRF with a larger percentage of biomass has shown great potential for further study.

$$\mu = \frac{m_{\rm t} + m_{\rm p}}{m_{\rm s}} = 49.43 \% \qquad \tau = \frac{m_{\rm t}}{m_{\rm t} + m_{\rm p}} = 55.83 \%$$

In the sample tube, we got two different phases: one a weak yellow and the other a brown-orange phase. We concluded that there was still some moisture left in the SRF, and depending on the type of SRF, we got a water phase with polar organic molecules. We separated the two phases and ignited the brown one, which burnt with an intense orange flame. We also got some solid products in an amount higher than in HD PE. These were ignited and burnt well. If we take the solid products into account, the overall yield increases.

4.3 Analysis of the liquid products

In order to determine the value of the liquid products, we analyzed them in a GC FID (Gas Chromatography - Flame Ionization Detector) and GC MS (Gas Chromatography – Mass Spectrometry). From a previous study, we obtained the caloric value of HD PE, which was 34.8 kJ/g (Roškarič, 2013). For the GC-FID, we used an HP-5 column (5 % phenylmethyl silicone). Then we prepared the temperature program: first heating for 3 min at 35 °C, followed by heating at a rate of 5 °C/min. After 10 min, we reached a final temperature of 280 °C. The whole program took 63 minutes.

The GC FID of HD PE has a typical graphic look, which was expected. From the temperature programs, we can calculate the boiling point of the components. We hoped HD PE and SRF would have similar results. However, the results show fewer components for SRF, which are more together. But we must also say that some of the peaks correspond to that of HD PE, so we do have some similarities.

We also conducted a GC-MS analysis with the same parameters as in GC-FID. The results are shown in the graphs below.



Figure 1: GC MS graph of HD PE.



Figure 2: GC MS graph of SRF.

The GC MS of HD PE was a control group. Its results were, as expected, mostly C6 to C12 aliphatic components, much like in diesel oil. We analyzed SRF and a drop of SRF, which both gave nearly the same results. The library search showed that we got mostly an aromatic system or cyclic system with many heteroatoms, such as oxygen and nitrogen. An inert flow and a different rate of heating in pyrolysis could be more favorable for the aliphatic molecules which were desired. This also shows that the composition of MSW is not always what is said and that it is complex and unpredictable. Before using this oil, we would need to clean it or to install a proper filter for the gases that would be produced during incineration of this oil.

5 Integrated circular waste treatment facility

As shown before, the increase in waste plastic and MSW requires more advanced technologies for their processing. Figure 8 shows an integrated symbiosis plant for transforming wastes into energy, heat and products. The prices are estimated with the help of the computer programs Aspen Plus and Aspen Economics Analyzer and prices by the help of specifications provided by sellers following an internet search.

5.1 Input section

All the waste that comes in, undergoes a separation. With good separation at source, household waste would need only minimum separation. Several techniques can be used for separation, such as manual separation, robotic arms, near infrared (NIR) technology, gravity, magnetic, eddy current and others. If the stream goes to recycling, appropriate recycling procedures are taken. Rejected material then goes back with the other waste into the shredder and later to drying, if necessary.

Feedstocks with different compositions can be applied for different purposes. For example, with more PET in the plastic, more gases are created during pyrolysis (FakhrHoseini & Dastanian, 2013).



Figure 3: Integrated waste treatment plant (Several technologies can be integrated to achieve greater benefit. We can divide them in different sections.)

5.2 Drying of sludge

The investment for the drying facility would be around 1.2 million \notin , with a capacity of 100 tons per day for a 250 m³ reactor. The cost of the cooling water is 52 000 \notin /y and for the heating water 208 000 \notin /y. In an integrated circular waste processing facility, the required heat could be supplied from the cooling water from the pyrolysis or from other available sources in the plant.

5.3 Pyrolysis section

Depending on the size of the plant, different pyrolysis reactors could be used. With more medium-sized or small pyrolysis reactors, we could separately pyrolyze sludge for agricultural usage, MSW, sorted plastic or the recycled plastic, that cannot be recycled again. Two-step pyrolysis could also be an alternative.

The investment for a pyrolysis reactor starts at $500,000 \in$ and can go up to $1,000,000 \in$ for a medium-large reactor. With around 10 t per day, the electrical consumption would be $12,000 \in$ a year. By using alternative energy and heating, we could reduce costs. For example, Lam *et al.* (2013) used microwave-assisted vacuum pyrolysis for plastic waste and cooking oil to achieve the synergistic effect. Moreover, they have proven that a vacuum system is better than a nitrogen flow, because it reduces the boiling point and lowers the temperature of pyrolysis, which saves money.

Investment in a pyrolysis plant that could process 100 t/h, which is 360,000 t per year, would cost 8 million USD \$ in total capital. The operational cost would be 30 million USD \$ per year. The estimated production of oil alone would be 122,927,000 L per year with a cost of production of 0.25 USD \$ per liter (with all the operational costs). With the diesel fuel price of 0.523 USD \$ per liter that they used, the yearly income would be 64 million USD \$. When we subtract 30 million USD \$ of production cost, and if we take into account unexpected costs, transportation and other costs, the profit should still be at least 20 million \$ per year. This is only a scale up of the scale up that they suggested. However, with the additional synergistic benefit of the integrated circular waste treatment plant, the annual cost should decrease.

5.4 Alternative energy sources

In order to reduce operating costs, alternative energy sources can be used. With electrical heating and solar panel systems, the cost of the pyrolysis and the carbon footprint would be reduced. Other alternative sources could be used, like geothermal energy.

5.5 Usage of the products

If sludge alone were pyrolyzed, active carbon could be produced and mixed with fertilizers to increase their effects. The liquid products can be burnt for electricity or used instead of fossil fuels. The tar could also be processed and then polymerized to produce new products. In this way, we would get products with the same high quality as those produced from fresh oil, and the plastic would recycle. Some research was done with promising results in this field (Achilias *et al.*, 2007). The gaseous products can be either processed or burnt for the electricity. The amount of waxes should be minimal, but they can also possess a high calorific value.

5.6 Gasification

The remaining char has two options. It can be burnt or used in the gasification process. With the gasification process, we could produce syngas from the remaining char. Some non-pyrolytic or unrecyclable waste could also be fed to the gasification reactor. It depends on the market demand whether more gaseous, liquid or solid products would be produced.

5.7 Incineration

The remaining waste, char or other products can also be incinerated in the thermal disposal section, where heat is generated and electricity produced. This step can be used for the remainder of the pyrolysis/gasification step and for the dried or pyrolyzed sludges.

6 Conclusions

With the increasing production of waste, like municipal solid waste or plastic waste, many new technologies have been developed to deal with the recovery of strategic resources. These technologies are emerging on the commercial level and will replace the old landfill system or incineration plants. Pyrolysis, gasification and hydrothermal treatment all possess serious potential but are lacking in other respects. Some need more pre-treatment, some are expensive, and for some operational costs are too high. On the other hand, most of them can process a large spectrum of MSW composition, which mechanical recycling does not offer. As has been shown in this study, different feedstock yields different results. The MSW sampled at Gorenje Surovina did not give great results, as compared to other mixed plastic studies. Nevertheless, a slightly different composition or a different reactor could provide better results. Additionally, if we process the MSW at the integrated circular waste treatment facility, many positive synergistic effects occur, so the recovery of resources is better, with lower operational costs. Further studies are required if such a facility is to be built, in order to find the optimum balance between the different techniques that yields the greatest benefit.

Acknowledgements

I would like to thank Prof. Dr Zorka Novak Pintarič for technical and moral support with my article. Thanks also goes to the Faculty of Chemistry and Chemical Engineering in Maribor, which hosted the project that inspired this article, and to all the professors and students that helped with the project.

References

- Abnisa F., Daud W. M. A. W. 2014. "A review on co-pyrolysis of biomass: an optional technique to obtain a high grade pyrolysis oil." *Energy Convers Manage* 87, 71-85.
- Achilias D. S., Kanellopoulou I., Megalokonomos P., Antonakou E., Lappas A. A. 2007. "Chemical Recycling of Polystyrene by pyrolysis: Potential Use of the Liquid Product for the Reproducion of Polymer." *Macromolecular Materials and Engineering.*
- Agyeman S., Obeng-Ahenkora N. K., Assiamah S. M., Twumasi G. 2019. "Exploiting recycled plastic waste as an alternative binder for paving blocks productions." *Case Studies in Construion Materials.*
- Al-Salem S. M., Lettieri P., Baeyens J. 2009. "Recycling and recovery routes of plastic solid waste (PSW): a review." Waste Manage 29, 2625-2643.
- Breyer S., Mekhitarian L., Rimez B., Haut B. 2017. "Production of an alternative fuel by the co-pyrolysis of landfill recovered plastic wastes and used lubrication oils." *Waste Management* 60, 363-374.
- Brown L. J., Collard F. X., Goergens J. F. 2019. "Fast pyrolysis of fibre waste contaminated with plastic for use as fuel products." *Journal of Analytical and Applied Pyrolysis* 138, 261-269.
- Canopoli L., Fidalgo B., Coulon F., Wagland S. T. 2018. "Physico-chemical properties of exavated plastic from landfill mining and current recycling routes." *Waste Managment* 76, 55-67.

- Clapp J., Swanston L. 2009. "Doing away with plastic shopping bags: International patterns of norm emergence and policy implementation." *Environ. Polit.* 18 (3).
- Department, Kumasi Metropolitan Assembly Waste Managment. 2010. "Data for purposes of planning waste management intervention programmes." *Kumasi Waste management Department.*
- Eriksen M. K., Christiansen J. D., Daugaard A. E., Astrup T. F. 2019. "Closing the loop for PET, PE and PP waste from households: Influence of material properties and product design for plastic recycling." Waste Managment 96, 75-85.
- FakhrHoseini S. M., Dastanian M. 2013. "Predicting pyrolysis products of PE, PP and PET using NRTL activity coefficient model." *Hindawi Publishing Corporation* 1-5.
- Geissdoerfer M., Savaget P., Bocken N. M. P, Hultink E. J. 2017. "The Circular Economy A new sustainability paradigm? ." *Journal of Cleaner Production* 143, 757-768.
- Ghenai C., Alamara K., Inayat A. 2019. "Solar Assisted Pyrolysis of Plastic Waste: Pyrolysis oil Characterization and Grid-Tied Solar PV Power System design." *Energy Procedia* 159, 123-129.
- He P., Chen I., Shao L., Zhang H., Lu F. 2019. "Municipal solid waste (MSW) landfill: A source of microplastics? - Evidence of microplastics in landfill leachate." Water Research 159, 38-45.
- Higman C., van der Burgt M. 2008. Gasification. Elsevier.
- Hopewell J., Dvorak R., Kosior E. 2009. "Plastics recycling: challenges and opportunities." *Phil. Trans.* R. Soc. B 364 (1526), 2115-2126.
- Hwang I. H., Aoyama H., Matsuto T., Nakagishi T. 2012. "Recovery of solid fuel from municipal solid waste by hydrothermal treatments using subcritical water." *Waste Managment* 32 (3), 410-416.
- Jin Q., Wand X., Li S., Mikulčić H., Bešenić T., Deng S., Vujanović M., Tan H., Kumfer B. M. 2019. "Synergistic effects during co-pyrolysis of biomass and plastic: Gas, tar, soot, char products and thermogravimetric study." *Journal of the Energy Institute* 92, 108-117.
- Lam S. S., Chase H. A. 2012. "A review on waste to energy processes using microwave pyrolysis." *Energies* 5, 4209-4232.
- Lam S. S., Mahari W. A. W., Yong S. O., Wanxi P., Chong C. T., Ma N. L., Chase H. A., Liew Z., Yusup S., Kwon E. E., Tsang D. C. W. 2013. "Microwave vacuum pyrolysis of waste plastic and used cooking oil for simultaneous waste reduction and sustainable energy conversion: Recovery of cleaner liquid fuel and techno-economic analysis." *Renewable and Sustainable Energy Reviews* 115.
- Lino F. A. M., Ismail K. A. R. 2017. "Incineration and recycling for MSW treatment: Case study of Campinas, Brazil." Sustainable Cities and Society 35, 752-757.
- Ludlow-Palafox C., Ha C. 2001. "Microwave-induced pyrolysis of plastic waste." Ind Eng Chem Res 40, 4749-4756.
- Moustakas K., Fatta D., Malamis S., Haralambous K. 2005. "Demonstration plasma gasification/vitrification system for effective hazardous waste treatment." *Journal of Hazardous Materials* 123, 120-126.
- Nizzeto L., Futter M., Langaas S. 2016. "Are agricultural soil dumps for microplastics of urban origin?" Environ. Sci. Technol. 50 (20), 10777-10779.
- Oyedun A. O., Gebreegziabher T., Ng D. K. S., Hui C. W. 2014. "Mixed-waste pyrolysis of biomass and plastics waste - a modelling approach to reduce energy usage." *Energy* 75, 127-135.
- Panepinto D., Tedesco V., Brizio E., Genon G. 2015. "Environmental Performances and Energy Efficiency for MSW Gasification treatment." *Waste Biomass Valor* 6, 123-135.
- 2018. *PlasticEurope 2018*.
- Quaghebeur M., Laenen B., Geysen D., Nielsen P., Pontikes Y., Van Greven T., Spooren J. 2013. "Characterization of landfilled materials: screening of the enhanced landfill mining potential." *J. Clean. Prod.* 55, 72-83.
- Ridout A. J., Carrier M., Collard F. X., Goergens J. 2016. "Energy conversion assessment of vacuum, slow and fast pyrolysis processes for low and high ash paper waste sludge." *Energy Convers. Manage.* 111, 103-114.
- Roškarič, M. 2013. "V predelavi plastike je prihodnost." *Mladi za napredek Maribora*. Maribor: Mladi za napredek Maribora. 15.

- Samolada M.C., Zabaniotou A. A. 2014. "Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy managment in Greece." Waste Managment 34, 411-120.
- Sharuddin S. D. A., Abnisa F., Daud W. M. A W., Aroua M. K. 2016. "A review on pyrolysis of plastic waste." *Energy Conversion and Management* 115, 308-326.
- Singh R. K., Ruj B. 2016. "Time and temperature depeded fuel gas generation from municipal solid waste." Fuel 80, 1217-1227.
- Thompson R. C., Moore C., J., Saal F. S. V., Swan S. H. 2009. "Plastics, the environment and human health: current consensus and future trends." *Philos. Trans. R. Soc. B. Biol. Sci.* 364 (1526), 2153-2166.
- Tulashie S. K., Boadu E. K., Dapaah S. 2019. "Plastic waste to fuel via pyrolysis: A key way to solving the severe plastic waste problem in Ghana." *Thermal Science and Engineering Progress* 11, 417-424.
- Ventosa I. P., Forn M. C., Sora M. J. 2014. "Urban mining extracting resources from landfill sites." Segur Med Amb N134.
- Wang P., Hu Y., Cheng H. 2019. "Municipal solid waste (MSW) incineration fly ash as an important source of heavy metal pollution in China." *Environmental Pollution* 252, 461-475.
- Webb H. K., Arnot J., Crawford R. J., Ivanova E. P. 2013. "Plastic degradation and its environmental implications with special reference to poly(ethylene terephthalate)." *Poly.* 5, 1-18.
- Wiriyaumpaiwong S., Jamradloedluk J. 2017. "Distillation of Pyrolytic Oil Obtained from Fast Pyrolysis of Plastic Wastes." *Energy Procedia* 138, 111-115.
- Younan Y., van Goethem M. W. M., Stefanidis G. D. 2016. "A particle scale model for municipal solid waste and refuse-derived fuels pyrolysis." *Comput. Chem. Eng.* 86, 148-159.

COMPETENCE MODEL FOR FACTORIES OF THE FUTURE

TANJA BATKOVIČ¹, BOJAN CESTNIK^{2,3}, ALEKSANDER ZIDANŠEK^{1,3,4} & ANDREJA ABINA¹

 ¹ Jožef Stefan International Postgraduate School, Ljubljana, Slovenia, e-mail: tanja.batkovic96@gmail.com, aleksander.zidansek@mps.si, andreja.abina@mps.si
 ² Temida d.o.o., Dunajska cesta 51, Ljubljana, Slovenia, e-mail: bojan.cestnik@temida.si
 ³ Jožef Stefan Institute, Ljubljana, Slovenia, e-mail: bojan.cestnik@temida.si, aleksander.zidansek@mps.si

⁴ University of Maribor, Faculty of Natural Sciences and Mathematics, Maribor, Slovenia, e-mail: aleksander.zidansek@mps.si

Abstract The competence model for the factories of the future connects knowledge, skills and other characteristics necessary for successful work at a given workplace and systematic procedures for their improvement. The purpose of the competence model is to ensure that employees do the right things and that they work successfully. It also strengthens the motivation for life-long learning and intergenerational cooperation. The competencies linked to sustainable development, circular economy, and corporate social responsibility are important components of the competence model. Mismatches in the future skills required for the transition to Industry 4.0 and Society 5.0 are addressed by creating a rich ecosystem of educational approaches and learning materials. An expert system will be developed for the selection of the most appropriate educational approaches for each employee according to the mismatch between their current and desired skills and competencies. In this contribution, the concept of the expert system is presented.

Keywords:

circular economy, competence model, factories of the future, sustainable development, expert system.



DOI https://doi.org/10.18690/978-961-286-353-1.14 ISBN 978-961-286-353-1

1 Introduction

In 1973 David C. McClelland published a study pointing out that, while intelligence affects performance at work, personal characteristics and self-concepts, traits and motives are what make the difference between effective and inefficient work. This phenomenon is noticeable in many areas of the individual's life, including his or her professional career. McClelland defined competencies as characteristics that represent successful performance (McClelland, 1973).

The competence model is used in many areas of human resource management (HRM). A model is a combination of personal characteristics, skills, abilities, knowledge and other individual capabilities that are required for successful and effective performance. It is also important that each competence be clearly defined in the model and include observable or measurable indicators (Skorková, 2016). To establish the model, it is necessary to obtain the relevant information, which can be gathered through surveys, personal interviews and job descriptions.

Meeting the needs of the increasing number of people on Earth using a linear economy seems well beyond the current capacity of our planet. The continued growth of the economy and consumerism is reducing the volume of natural resources that are on the rise, causing habitat loss, species disappearance, and climate changes. This kind of action is not sustainable; therefore, the transformation of the current linear economy into a circular economy is urgently needed. The concept of a circular economy eliminates waste, ensures the longest possible circulation of the product, promotes cascaded use across industries, and provides pure, non-toxic, or at least easier-to-separate inputs and designs, as well as materials with the possibility of reuse and recycling (EMF, 2013).

At the global, EU and Slovenian levels, the concept of a circular economy that is arising from sustainable development activities has become a policy priority (Godina *et al.*, 2018). The foundations of the new business model are more competitive, since they promote sustainable and efficient use and production of resources, green growth, and a low carbon economy. Such a transition offers new challenges and opportunities to transform the economy and create new and sustainable competitive advantages (Lahti *et al.*, 2018).

Companies nowadays also recognize the importance of engaging in corporate social responsibility (CSR). By using CSR, they balance the environmental, social, and economic aspects (Osagie *et al.*, 2014), and this helps to strengthen a brand through philanthropy, social responsibility programs, and volunteer work. It also allows for a stronger connection between employees and the corporation, which contributes to more efficient and successful work (Chen, 2019).

Today's changing problems and challenges of the 4th Industrial Revolution require different thinking, including special, new competencies of employees to manage these challenges. Various competence models are in use for the implementation of needed competencies. In our case, we created the KOC TOP competence model for the factories of the future, with the main aim of ensuring that employees do the right things successfully and deliver as much added value as possible to the organization and society.



Figure 1: The increasing number of publications on the topic of sustainable development, circular economy and corporate social responsibility over the last 20 years (Source: Web of Science).

Looking at the numbers, one can see in Figure 1 that the topics of sustainable development, circular economy, and corporate social responsibility have been getting more and more attractive to researchers and society as a whole over the last 20 years.

In this paper, we present the background of the competence model for factories of the future, which is the basis for the operation of the Competence Center established at the Jožef Stefan International Postgraduate School (IPS). We placed special emphasis on competencies linked to sustainable development, circular economy, and corporate social responsibility, which are important components of the competence model for future factories. In the end, the concept of the expert system is presented, allowing the selection of the most appropriate educational approaches for each employee according to any mismatch between their current and desired skills and competencies, as well as the workplace requirements.

2 Competence model for factories of the future

2.1 Basis for the competence model development

Within the Competence Centre at the IPS, we developed a Competence Model for Advanced Technologies in Factories of the Future (KOC-TOP Competence Model). The KOC-TOP Competence Model incorporates the knowledge (expertise, work experience, and functional knowledge), skills, and other characteristics necessary for successful performance in a given workplace, as well as systematic procedures for improving them. The purpose of the competence model is to ensure that employees do the right things successfully and bring maximum added value to the company, and as a result, contribute to business success. It is used in the selection of training for employees to help the company invest in the most promising competencies and build on their competence strengths. The model describes 1) general competencies that relate to the company culture and values; 2) specific vocational competencies common to the particular profession; and 3) key competencies that are most relevant to each job and represent a competitive advantage for the company. The model includes competencies in the following groups: 1) professional competencies; 2) social competencies; 3) leadership competencies; 4) business competencies; 5) change management; and 6) intercultural

competencies, identified as important by the IPS Competence Center partners (Zidanšek et al., 2018).

The preparation of the competence model is based on the needs of the KOC-TOP Competence Center industrial partners, SRIPs action plans and the educational process in Slovenia. The needs were identified by a specially prepared questionnaire. The partner companies have already introduced competence models in their organizations; therefore, their experience and prepared materials have been included in the construction of the KOC-TOP competence model. An analysis of key competencies for the specific function and workplace of the participating partners was carried out. Project partners first assessed the importance of individual competencies for the workplace through internal procedures. Then they evaluated the level of the employees' competencies and the level of the competencies that are required at a particular workplace. Next, training was selected to improve the required competencies of employees at a workplace (Zidanšek *et al.*, 2018). Some training programs were selected for individuals, others for a group of employees.

The rebirth of industry is one of the priority areas in Europe, especially in the context of smart specialization (S4). The future of all of us depends largely on the complete transformation of current manufacturing plants into smart factories, based on the technologies of the future and the circular economy. The transition to a new era begins with human resources. Therefore, KOC-TOP aims to respond to the needs of companies to introduce the competencies of the future that they need in the era of the 4th Industrial Revolution and Society 5.0, as the boundary between the physical and digital worlds is blurred. Hence, KOC-TOP will motivate employees for lifelong learning and towards digital and cultural literacy to effectively acquire the competencies of the future. The target groups in companies that are involved in the process of additional training for employees and acquiring new competencies are primarily decision-makers, personnel, development managers, innovators, technologists, and production workers. The target groups also include employees of other companies, especially manufacturing companies, and other stakeholders (SRIPs, competent authorities, etc.).

KOC-TOP is based on the action plan of SRIP Factories of the Future (SRIP-TOP), which connects companies with research and education institutions for greater competitiveness and a stronger presence on the global market. SRIP-TOP and KOC-TOP, as a common challenge, are developing employee competencies for Industry 4.0 solutions, notably digitalization, automation, robotics, lean manufacturing, and artificial intelligence. This encourages companies to become more involved in value chains. Of particular importance to the S4 focal area Circular Economy are training in automation, artificial intelligence, and lean manufacturing, to help employees acquire the skills to deploy circular economy technologies in the use of secondary raw materials and waste. For the SRIP Circular Economy, sustainable development competencies are also important, which will improve environmental and social responsibility. For SRIP Smart Cities and Communities (SRIP PMiS), technologies such as cloud computing, open and mass data, embedded smart systems, the Internet of Things and the Internet of the Future are key components. In Figure 2, we summarize the relation between KOC-TOP and Slovenian SRIPs, which have in common not only industrial partners but also competencies for the future.



Figure 2: The relation between the Competence Center KOC-TOP and the Slovenian SRIPs.

2.2 Sustainable development, circular economy and corporate social responsibility in Slovenia, the EU and worldwide

The last four years have been the four hottest on record, and the elevated temperature is due to greenhouse gas emissions (UN, 2019). High temperatures cause the melting of ice, and a rise in sea temperature, which is harmful to coral reefs and other marine life. However, the rising temperature is not the only environmental problem in our economy. Other Environmental problems include water, soil, and air pollution, biodiversity loss, excessive land use, and resource depletion (Meadows *et al.*, 2004; Jackson, 2009, McLellan *et al.*, 2014). Climate change and other environmental problems cause high unemployment in certain parts of the world and poor working conditions (Banerjee & Duflo, 2011), and also exert a negative impact on human health.

Governments, factories, and consumers all over the world are increasingly aware of environmental care and are seeing a strategy in the circular economy that can promote clean growth and improve environmental conditions. As a result, governments are enforcing new pollution and waste control laws, along with strategies that apply throughout the product lifecycle (Ruiz-Real *et al.*, 2018). Global resource consumption is increasing year by year, from 26.7 to 92.1 tons in the last 47 years and 9 % of materials are reused today (De Wit *et al.*, 2019). Global plastics production in 2010 was 270 million tons, and global plastic waste was 275 million tons (Ritchie & Roser, 2018). Increasing international cooperation in environmental policy, a better understanding of environmental challenges, and promoting green solutions are the biggest global challenges of today's society (EU Commission, 2019a).

EU trends from 2010 to 2016 show an increase in waste generation (EEA, 2019a). However, more and more waste is recycled each year: in 2010, 36 % of waste was recycled (EU Commission, 2019b), in 2012, 40 % (EMF, 2015) and in 2016, about 55 % (IUS-INFO, 2019). The central framework for EU and national waste policies is the waste hierarchy. The EU has written The Roadmap to a Resource Efficient Europe, which describes the targets that need to be achieved by 2020 (EEA, 2019a). In 2018, the EU set targets in a new circular economy package, which include setting up separate textile collection by 2025, preparing for the reuse and recycling of waste materials by 2020, and increasing the level of preparation for the recycling and reuse

of municipal waste to 55 % by 2025, 60 % by 2030 and 65 % by 2035 (EEA, 2019b). The EU has a strategy on plastics, which states that by 2030 all plastic packaging on the EU market must be recycled (IUS-INFO, 2019).

In Slovenia, the circular economy represents a great potential for the near future, as there are many untapped natural resources. Slovenia's potential stems from its location, landscape, and cultural diversity (Godina Košir *et al.*, 2018).

By engaging in corporate social responsibility (CSR), companies aim to obtain a balance between the environmental, social, and economic aspects of their business practices. To achieve effective CSR functioning, it is necessary to have employees with the right competencies. Osagie et al. (2014) analyzed the literature and interviewed CSR professionals to establish the required competencies for CER implementation. The competencies obtained were classified into four domains: 1) Cognition-Oriented Competence Domain (Anticipating future developments regarding CSR related challenges, Understanding of the interdependency between systems and subsystems Understanding CSR drivers, CSR standards, and CSR regulations); Functional-Oriented Competence Domain 2) (Leadership competencies, Identifying and realizing CSR related business opportunity, etc.); 3) Social-Oriented Competence Domain (Realizing CSR-supportive interpersonal processes in CSR integration); and 4) Meta-oriented Competence Domain (Ethical normative competencies, Reflecting on personal CSR views and experiences, etc.) (Osagie et al., 2014).

2.3 Concept of the expert system for training support

Nowadays, artificial intelligence (AI) expert systems are applied in many fields. A computer system that emulates the decision-making ability of a human expert can also be used to resolve complex problems in Human Resource Management (HRM). It can significantly contribute to the reduction of costs for organizations as well as to the efficiency of human resources. In the IPS Competence center KoC-ToP, we proposed an expert system for decision support, which can help HRM to select appropriate training for each employee. A preliminary version of the expert system was presented at the 14th SDEWES Conference in Dubrovnik (Cestnik *et al.*, 2019).

Thus, the employee can improve competencies required for their workplaces in an optimal way based on their previous level determined for each competence and the importance value of the competence for each workplace. In Figure 3 we present an entity-relationship model, also called an entity-relationship (ER) diagram. This is a graphic representation of entities and their relation to each other within the proposed expert system, which will be used in computing regarding the organization of data within databases of the information systems. From the diagram, one can see that different relationships and entities have an important role in training selection, evaluation of company progress as well as in the monitoring of employee career development.



Figure 3: An entity-relationship model for the concept of the proposed expert system.

3 Results and Discussion

3.1 Selection of Key Competencies for KOC-TOP 2019

The selection of key competencies is based on the KoC-ToP 2018 Competence Model and the SRIP TOP, SRIP PMiS and SRIP Circular Economy Action Plan. It has been updated in consultation with companies, SRIPs, and other stakeholders. The strategies of companies recognizing changing HRM challenges were also considered when looking for workers and introducing training to acquire the competencies of smart factories at all levels. The challenges of system integration and the introduction of new technologies have been recognized as important and reflect the common needs of the partnership to enhance the professional competencies of digitization, lean manufacturing, automation and robotization, and artificial intelligence. Business competencies have also been recognized as important, especially in managing the introduction of new technologies, personal and leadership competencies, and the competency for sustainable development, including circular economy and social responsibility. The selection of competencies reflects the synergy between professional, business, personal and interpersonal competencies intertwined with digitization as an overarching connector. The project will also contribute to reducing the shortage of key competencies by using the RESPO expert system to ensure that training is maximally effective for each employee and the whole company. In this way, it will help to achieve the goals of companies in the introduction of Industry 4.0 and the complete transformation and rebirth of Slovenian industry.
Table 1: The list of selected competencies appropriate for sustainability, circular economy and corporate social responsibility.

Key competence

Digitization 4.0 (digitalization of infrastructure, augmented and virtual reality, IoT, technological literacy etc.)

Automation and robotization (design, deployment, and use of robots and workflow for factories of the future etc.)

Competencies of digitized lean production (lean & digital lean, mastery of lean thinking, digitization etc.)

Artificial intelligence competencies (machine learning, knowledge technologies, deep learning, computer vision, robot control etc.)

Competencies in research and development (monetization of development projects, innovation culture, rapid prototyping etc.)

Competencies in the field of sensor and measurement systems for factories of the future.

Competencies in the field of sustainable development (environmental protection, circular economy, social responsibility etc.)

Competencies in managing and managing processes, technologies, human resources and organizations in technologically advanced environments.

Business competencies (accounting, financial, bookkeeping etc.)

Managing and implementing change (workflow, technologies, intelligent business models, strategic development etc.)

Quality assurance competencies

Security competencies (technological and cyber security, occupational health, risk management etc.)

Sales competencies (marketing, improving brand awareness, developing aftersales services etc.)

Cognitive competencies (problem solving, critical and systemic thinking, creativity, lifelong learning etc.)

Emotional intelligence competencies (emotional literacy, psychophysical stability, empathy etc.)

Communication skills (communication with colleagues, clients, public speaking, business presentations, foreign languages etc.)

Cultural literacy (learning about cultures of foreign business environments)

3.2 The importance of KOC TOP 2019 for the Slovenian economy

More than 55 partners immediately contacted the consortium. This enormous interest in cooperation represents a commitment for the partnership to develop KOC-TOP into an important platform for the Slovenian economy. The main activities of KOC TOP will be quality training, support for implementation and information, support in the selection of contractors, assistance in reporting and exchange of good practices. We are also planning to hold conferences open to a wider public that will contribute to greater impact of KOC-TOP by presenting challenges and solutions for future factories. Staff will be involved in sharing good practices, enhancing their skills and preparing for the job market in the factories of the future. A special development program for the Factories of the Future (practical guidance and steps) will be developed, which will also be forwarded to ministries with recommendations for further steps. In pursuit of project sustainability, because of the enormous interest shown in cooperation, we will help to ensure that the factory of the future is further supported by real programs for the rapid and quality development of smart factories in Slovenia. Raising employees' competencies will also have a positive impact on the wider social environment, and through selected training, we will strengthen and promote social responsibility and concern for the environment. We also expect the exchange of industry experts with faculties and institutes, so that future generations of employees will be better prepared for the upcoming working conditions in the industry.

3.3 Expert system in practice

The RESPO expert system in its first version was developed for one company's needs. Its functionalities and end-user experience were verified from two different users. One was the HRM personnel in the company, and the second was staff from the Career Center at the IPS. For the evaluation of the RESPO expert system, the HRM personnel in the company first uploaded their competence model from Excel to the system's database. Then, the required levels of competence for each workplace and the levels of competence achieved by each employee were gathered and entered into the system. Next, the list of available future training programs was entered; attached to each of the training opportunities, there was a list of competencies that the training aims to improve. The first version of the expert system correctly

identified the employees' competencies with the highest gap and suggested the most adequate training that should contribute to improvement in those competencies.

The positive response from the Career Center indicates that the developed expert system can, with some modifications, be transferred to the educational systems. It can have an important role when counselling students to select an appropriate study program and obligatory study courses as well as additional training, which could improve their competence for their future jobs. One of the modifications is the incorporation of learning outcomes for each course within the expert system. Therefore, a special comparison was performed at the IPS, in which the competencies from the KOC-TOP competence model were compared with the learning outcome of courses from the Ecotechnologies study program (Batkovič *et al.*, 2019).

The effects of using the expert decision support system will also contribute to a common Career Platform for employees at the Chamber of Commerce and Industry, which seeks to anticipate competence and staffing needs, develop specific competencies and integrate the economy and education, including new employee training programs.

Although the RESPO expert system is still in the pilot phase, we plan to upgrade it and make it available to the interested public. The basic version of the system will be free of charge, and the possibility of custom upgrading will be provided. The KOC-TOP network will outline ways of managing human resources in technologically advanced environments, including with the help of the RESPO expert system, which will aid in the preparation of a special training program. It will also be available to other stakeholders, which will strengthen the cooperation of knowledge institutions with the economy and policymakers.

4 Conclusion

The competence model for the factories of the future was presented. It connects knowledge, skills, abilities and other characteristics necessary for successful work at a workplace within an organization. The purpose of the competence model is to ensure that employees do the right things and that they work successfully and bring as much added value as possible to the organisation and society. It also strengthens

the internal motivation of employees for life-long learning and stimulates intergenerational cooperation. We focus on the competencies linked to sustainable development, circular economy, and corporate social responsibility, which are important components of the competence model. The concept and first responses from practical use were presented for an expert decision support system, which was developed for the selection of the most appropriate training approaches for each employee according to any mismatch between their current skills and the desired skills and competencies as well as workplace requirements. In this contribution, the concept of the expert system is presented.

Acknowledgments

This research was partially supported by The Public Scholarship, Development, Disability and Maintenance Fund of the Republic of Slovenia under the programme "Creative path to knowledge", project acronym RESPO.

References

- Banerjee, A., & Duflo, E. (2011). Poor Economics: A Radical Rethinking of the Way to Fight Global Poverty. NY, USA: PublicAffairs: New York.
- Batkovič, T., Abina, A., Cestnik, B., & Zidanšek, A. (2019), Competencies for Sustainability and Circular Economy. Dubrovnik, Croatia: 14th SDEWES Conference, Proceedings.
- Cestnik, B., Batkovič, T., Kikaj, A., Boškov, I., Ogrinc, M., Smerkol, M., Ostrež, M., Janežič, M., Hasani, N., Kaluža, B., Zidanšek, A., & Abina, A. (2019), *Expert System for Decision Support in Selection of Education.* Dubrovnik, Croatia: 14th SDEWES Conference, Proceedings.
- Chen, J. (2019, February 11). Corporate Social Responsibility (CSR). Retrieved from Investopedia: https://www.investopedia.com/terms/c/corp-social-responsibility.asp
- De Wit, M., Verstraeten-Jochemsen, J., Hoogzaad, J., & Kubbinga, B. (2019). The Circularity Gap Report 2019.
- Ellen MacArthur Foundation (EMF). (2013). Towards the Circular Economy: Economic and Business Rationale for an Accelerated Transition. Ellen MacArthur Foundation. Cowes, UK.
- Ellen MacArthur Foundation (EMF). (2015, September). Europe's Circular-economy Opportunity. Retrieved from McKinsey & Company: https://www.ellenmacarthurfoundation.org/assets/downloads/publications/EllenMacArthu rFoundation_Growth-Within_July15.pdf
- EU Commission. (2019a, January 18). *The Global Circular Economy: 'our aim is transformation'*. Retrieved from EU Commission: https://ec.europa.eu/environment/efe/themes/economics-strategy-and-information-resource-efficiency-international-issues/global-circular_en
- EU Commission. (2019b, March 15). Circular Economy Package Report: Questions & Answers. Retrieved from EU Commission: https://europa.eu/rapid/press-release_MEMO-19-1481_en.htm
- European Environment Agency (EEA). (2019a, July 25). *Waste Generation*. Retrieved from European Environment Agency: https://www.eea.europa.eu/airs/2018/resource-efficiency-and-low-carbon-economy/waste-generation
- European Environment Agency (EEA). (2019b, September 23). Waste Recycling. Retrieved from European Environment Agency: https://www.eea.europa.eu/data-andmaps/indicators/waste-recycling-1#tab-data-references-used

- Godina Košir, L., Korpar, N., Potočnik, J., & Kocjančič, R. (2018). Kažipot prehoda v krožno gospodarstvo Slovenije.
- IUS-INFO. (2019, March 4). EU aktivna na poti v krožno gospodarstvo. Retrieved from IUS_INFO: https://www.iusinfo.si/medijsko-sredisce/dnevne-novice/237771
- Jackson, T. (2009). Prosperity without Growth. Economics for a Finite Planet. London, UK: Earthscan Publications Ltd.
- Lahti, T., Wincent, J., & Parida, V. (2018). A Definition and Theoretical Review of the Circular Economy, Value Creation, and Sustainable Business Models: Where Are We Now and Where Should Research Move in the Future? *Sustainability*, 10, 19. doi: 10.3390/su10082799
- McClelland, D. C. (1973). Testing for competence rather than for "intelligence." *American Psychologist,* 28, 1-14. doi: 10.1037/h0034092
- McLellan, R., Iyengar, L., Jeffries, B., & Oerlemans, N. (2014). Living Planet Report 2014. Species and spaces, people and places. Gland, Switzerland: WWF International.
- Meadows, D., Randers, J., & Meadows, D. (2004). *Limits to Growth. The 30-year update.* London: Routledge.
- Osagie, E. R., Wesselink, R., Blok, V., Lans, T., & Mulder, M. (2014). Individual Competencies for Corporate Social Responsibility: A Literature and Practice Perspective. *Journal of Business Ethics*, 20. doi: 10.1007/s10551-014-2469-0
- Ritchie, H., & Roser, M. (2018, September). *Plastic Pollution*. Retrieved from Our World in Data: https://ourworldindata.org/plastic-pollution
- Ruiz-Real, J. L., Uribe-Toril, J., De Pablo, J. V., & Gázquez-Abad, J. C. (2018). Worldwide Research on Circular Economy and Environment: A Bibliometric Analysis. *International Journal of Environmental Research and Public Health*, 15(2699), 14. doi:10.3390/ijcrph15122699
- Skorková, Z. (2016). Competency models in public sector. Procedia Social and Behavioral Sciences, 230, 226–234. doi:10.1016/j.sbspro.2016.09.029
- United Nations (UN). (2019). UN Climate Action Summit 2019. Retrieved from United Nations: https://www.un.org/en/climatechange/un-climate-summit-2019.shtml
- Zidanšek, A., Abina, A., Beštar, A., Cestnik, B., Dolžan, M., Draksler, T., Srebotnjak Borsellino, M. (2018, October 26). Model kompetenc KoC-ToP. Slovenia.

EDUCATION FOR ZERO WASTE AND THE CIRCULAR ECONOMY SECTOR IN EUROPE

PETER GLAVIČ¹, AIDA SZILAGYI², ISAVELLA KAROUTI³, ACHILLEAS KOSTOULAS³, OIHANA HERNAEZ⁴, MARTIN DOLINSKY⁵, THOMAS SCHÖNFELDER⁶, PAVEL RUZICKA⁷. GOSIA STAWECKA⁸. DIMITRIOS KARADIMAS⁹, CRISTINA S. ROCHA¹⁰, DAVID CAMOCHO¹⁰, BOJANA ŽIBERNA¹, EUGENIA ATÍN⁴, BARBARA HAMMERL⁸ & HANS SCHNITZER⁸ ¹ University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: peter.glavic@um.si, bojana.ziberna21@gmail.com ² CNPCD, Timisoara, Romania, e-mail: aidaszilagyi@cnpcd.ro ³ AKETH_DCT, Trikala, Greece, e-mail: is.karouti@aketh.gr, a.kostoulas@aketh.gr ⁴ PROSPEKTIKER SA, PE Zuatzu, Donostia-San Sebastián, Spain, e-mail: o.hernaez@prospektiker.es, e.atin@prospektiker.es ⁵ EKOrast, Bratislava, Slovakia, e-mail: martin.dolinsky@ekorast.org 6 Atmoterm SA, Opole, Poland, e-mail: schoenfelder@atmoterm.pl ⁷ ENVIROS, s.r.o., Praha, Czech Republic, e-mail: pavel.ruzicka@enviros.cz 8 StadtLABOR, Graz, Austria, e-mail: gosia.stawecka@stadtlaborgraz.at, barbara.hammerl@stadtlaborgraz.at, hans.schnitzer@stadtlaborgraz.at 9 Global Reach, Athens, Greece, e-mail: d.karadimas@vbc.gr

10 LNEG, Lisboa, Portugal, e-mail: cristina.rocha@lneg.pt, david.camocho@lneg.pt

Abstract The Erasmus+ project Education for Zero Waste and Circular Economy started in 2018 to fill a gap in Vocational Education and Training, create a new training course and develop interdisciplinary skills needed for new jobs. The consortium of ten partners from nine European countries intends to produce an interactive platform, comprising a Knowledge Hub, an Online Course and a Diagnosis Tool. One of the first activities of the consortium was to analyse the stateof-the-art in zero waste and circular economy in partner countries. The employment situation was considered, along with experience, qualifications and skills needed for trainees. An overview of the existing training was carried out, including educational methods, types of training organizations, duration of activities, and teachers' and trainers' qualifications. Basic information on the existing curricula and certification processes was reviewed. A special section was devoted to good practices. Links and references have been collected for each partner state.

Keywords: education, zero waste, circular economy, online course, Erasmus+.



DOI https://doi.org/10.18690/978-961-286-353-1.15 ISBN 978-961-286-353-1

1 Introduction

Skills and competences in the field of Zero Waste and Circular Economy (ZW&CE) are becoming extremely important. In 2016, sectors relevant to the CE employed more than four million workers, a 6 % increase compared to 2012. According to the statistics, the European Union (EU) economy still loses a significant fraction of potential "secondary raw materials" in waste streams. In order to avoid that, the EU adopted in 2015 an ambitious programme called "Towards a CE – an economy package to help European businesses and consumers to make the transition to CE", where resources are used in a more sustainable way, boosting global competitiveness, fostering sustainable economic growth and generating new jobs. As part of its continuous effort to transform the European economy into a more sustainable one and to implement the ambitious CE Action Plan, the European Commission (EC) adopted a new set of measures known as the 2018 CE Package. Above all, the CE transition reinforces social and territorial cohesion and favours a balanced distribution of jobs and meeting health and safety standards, while enabling generation of fair and sustainable growth.

The paper provides general information regarding EduZWaCE, an Erasmus+ project that aims to fill the gap in Vocational Education and Training (VET) through the creation of new training courses focusing on ZW&CE. The international consortium consists of ten partners from nine EU countries, with various backgrounds, ranging from Universities to VET centres, and from public organizations to private companies related to ZW&CE. The project is expected to create four distinct Intellectual Outputs by September 2020: a *Knowledge Hub*, an *Online Course*, and a *Diagnosis Tool*, connected through the *Online Platform* of the project.

The paper provides an overview of the current state of the field in the partner countries and the EU28. Major definitions are given, along with a state-of-the-art report related to the organization of training in ZW&CE and good practices in the sector for all partner countries.

1.1 Zero Waste

Waste is unwanted or unusable material. EU waste policy is to turn waste into resources. The waste strategy is based on prevention and recycling. The 7th Environment Action Programme aims to achieve the following: a) reduce waste generation, b) maximise recycling and re-use, c) limit incineration to non-recyclable materials, d) phase out landfilling to non-recyclable and non-recoverable waste, and e) accept waste policy targets in all member states. A Resource Efficiency Roadmap, Raw Materials Initiative, and EU waste legislation have been elaborated by the EC. Additionally, the EC (2010) edited a brochure on the EU approach to waste management (using a life-cycle and waste hierarchy approach).

Zero waste (ZWIA, 2019) is the conservation of all resources by means of responsible production, consumption, reuse, and recovery of all products, packaging, and materials, without burning them, and without discharge to land, water, or air that threatens the environment or human health. ZW refers to waste management and planning approaches that emphasise waste prevention as opposed to end-of-pipe waste management.

ZW is a goal, a process, and a way of thinking that profoundly changes our approach to resources and production. It is not about recycling and diversion from landfills but about restructuring production and distribution systems to prevent waste from being manufactured in the first place. ZW Europe (2019) has laid down rules for the three most important areas of ZW: cities (municipalities), businesses, and life-style.

1.2 Circular Economy

Circular Economy (CE) is inspired by nature, where the output of one being/process becomes an input to another one, and waste does not exist. Many definitions of CE exist (Rizos *et al.* 2017). "CE is an alternative to a traditional linear economy (make, use, dispose) in which we keep resources in use for as long as possible, extract the maximum value from them whilst in use, then recover and regenerate products and materials at the end of each service life" (WRAP, 2019). The overall objective is to "enable effective flows of materials, energy, labour and information so that natural and social capital can be rebuilt" (Ellen MacArthur, 2015). The system diagram in Figure 1 illustrates the continuous flow of technical and biological materials through the 'value circle'.



Figure 1: The circular economy – an industrial system that is restorative by design (Ellen MacArthur, 2013).

CE is central to the achievement of the Sustainable Development Goals (SDGs) and in particular, goal 12 on Ensuring sustainable production and consumption patterns. Products are designed for disassembly and re-use. Closed-loop systems advocate a 'functional service economy' in which manufacturers and retailers shift from selling products to services. Companies maintain ownership of products and act as service providers. Such a model promotes a) more durable products – longer life-span with a lower demand for energy and materials; b) disassembly and refurnishing rather than disposal; and c) new economic opportunities – through product and service shifts.

The EC has adopted a package of measures and legislative proposals to boost sustainable growth and help the EU make the transition towards a more CE. The EU CE package embraces 1) resource efficiency, 2) eco-innovation, 3) secondary raw materials, 4) production (energy and resource efficient CE), 5) smart consumption, and 6) waste prevention and management.

The EU CE Action Plan consists of 54 actions in five priority sectors: plastics, food waste, biomass and bio-based products, critical raw materials, and construction and demolition waste (CDW). The waste recycling targets for 2030 are as follows: 65 % of municipal waste, 70 % of overall packaging, 85 % of E-waste, and 89 % of CDW.

The monitoring framework on CE as set by the EC consists of 10 indicators, some of which are broken down into sub-indicators, divided into the following four thematic areas (Eurostat, 2019a): a) production and consumption, b) waste management, c) secondary raw materials, and d) competitiveness and innovation. France is using a somewhat different set of 10 indicators (SOeS, 2017). *Politico's* (2018) CE index includes 7 out of 10 EU indicators: Germany, UK and France were the leading countries. Czech Republic was 4th, Poland 6th, Slovenia 7th, Austria 9th, Spain 10th, Portugal 16th, Romania 18th, Slovakia 21st, and Greece 26th.

The *Circularity Gap Report* (CGR, 2019) showed that the Gap is not closing. Our world is only 9 % circular. Austria was the first country to elaborate a national CGR (CGR Austria, 2019). The Austrian report used four resource groups: 1) ores, 2) minerals, 3) biomass, and 4) fossil fuels. Material flow analysis included domestic extraction, net imports and recycled material as input, waste after recycling, carbon, vapour and recycled material as output. Mass flows were estimated by applying a combined production- and consumption-based approach. To increase the circularity rate from 9.1 % to 37.4 %, they proposed 1) shifting from fossil fuels to renewable resources, 2) recycling all recyclable waste, 3) sourcing all CDW of old building stocks, and 4) prioritising imports with a higher proportion of secondary content.

1.3 Online courses on ZW&CE

Massive Open Online Courses (MOOCs) about ZW&CE are available on the Internet – see, for example, the MOOC List on ZW (2019), or Ellen MacArthur (2019) courses on CE. The WRAP (2019) course has two levels: a) the Foundation level modules (waste and process mapping, measuring and monitoring, developing an action plan. gaining support, and developing your waste prevention plan), and b) Practitioner level training (resource efficiency and process improvement, behaviour

change, supply chain management and sustainable procurement, Environmental Management System, EMS).

The Solid Waste Association of North America (SWANA) and the California Resource Recovery Association (CRRA) formed a partnership to develop and offer a ZW certification course. It offers an overview of principles and practices in 10 modules including managing organics; financing and funding; contracting and partnerships; collection options and processing technology options (SWANA, 2019).

The KATCH-e (2019) Project (Knowledge Alliance on Product-Service Development towards CE and Sustainability in Higher Education), with a particular focus on the construction and furniture sectors, developed eight learning modules that are linked to each other but can also be used as stand-alone learning and teaching elements in four areas: Basics, Business, Design, and Assessment. Seven tools support the practical implementation of the knowledge and build up skills in companies.

The Finnish Innovation Fund Sintra (2019) helped five Finnish universities to develop nine multidisciplinary courses in different areas of application.

The Action Plan for Scotland, design for CE (Whicher *et al*, 2018) aimed to develop educational materials for cross-university use to increase the importance of circularity in designing undergraduate degrees.

2 Methods

The general methodology of the project was outlined in the project proposal where the expected outcomes were described. The first step in their development was the state-of-the-art review related to current research on ZW&CE in the partner countries. It aimed at outlining the following:

- Current situation of the ZW&CE sector
- Current situation of the organization of ZW&CE education and training

- The best practices emerging.

The consortium gained a better understanding of the sector and managed to point out the areas that allow further expansion for the VET in the ZW&CE sector. In order to refer to a common system, the ideas of NQFs, EQF and ECVET were respected.

A national qualifications framework (NQF) is a formalized structure in which learning level descriptors and qualifications are used to understand learning outcomes. The European Qualifications Framework (EQF) is a common European reference framework whose purpose is to make qualifications more readable and understandable across different countries and systems. According to the review publication (Cedefop, 2017), 34 countries had formally linked their national qualifications frameworks to the EQF.

The EQF is divided into eight levels that cover the entire span of qualifications from those achieved at the end of compulsory education, to those awarded at the highest level of academic and professional or VET and are described by descriptors for the expected knowledge, skills and competences at each level of qualification. In the partner countries, except Slovenia (which has ten levels), NQFs and EQF are totally aligned. Regarding what a learner knows, understands and is able to do, descriptors of learning outcomes are defined in terms of knowledge, skills and competences, relevant to qualifications at that level in any system of qualifications (Table 1).

 Table 1: Knowledge, skills and competences in the European Qualifications Framework (EQF).

Knowledge	Skills	Competences
Knowledge is theoretical and/or factual related to Depth– Understanding and critical thinking	Skills are cognitive (involving the use of logical, intuitive and creative thinking), and practical (involving manual dexterity and the use of methods, materials, tools and instruments) related to breadth and depth – Purpose	Competence is described in terms of responsibility (in relation to others & self-work) and autonomy.

According to the state-of-the-art review, the consortium decided to focus on EQF levels 2 and 5, corresponding to ZW&CE Technician/Worker and Manager jobprofiles, respectively. The EduZWaCE project aims to "create a certification framework for two job profiles – EduZWaCE Skill Card Sets designed to enable further European Credit System for VET (ECVET) certification of the course, to illustrate the skills and competences required for ZW&CE Manager and Worker profiles".

To support the transfer, recognition and accumulation of assessed learning outcomes, the EduZWaCE Curriculum also encompasses technical components of the ECVET, such as the definition of learning outcomes (knowledge, skills and competences) structured into a specific Learning Unit. They can be subject to evaluation and autonomous validation, incorporated into existing systems or qualifications yet to be designed, within the various NQFs. Assigning points to the Learning Units enhances compatibility between different VET Systems and makes it easier for ZW&CE Manager and Worker to obtain validation and recognition of work-related skills and acquired knowledge.

The ECVET (Cedefop, 2016) is one of the important common European tools to support and increase European mobility. ECVET is also meant to support learners on their career and learning paths to a recognized vocational qualification, through transfer and accumulation of their assessed learning outcomes acquired in different national, cultural, and education and training contexts. In a broader sense, ECVET should contribute to promoting lifelong learning and increase the employability of Europeans. The ECVET system is based upon the four concepts:

- Units of learning outcomes
- Transfer and accumulation of learning outcomes
- Learning agreement and personal transcript
- ECVET points.

Learning outcomes are used as a basis for credit transfer and accumulation. They do not dependent on the learning process, the content of teaching or the learning context. Therefore, it is possible to compare learners' achievements in different settings or contexts. The learning outcomes and the approach chosen for identifying them will depend on the specific qualifications system or context, enabling the provider of the training to design and describe the units overall. However, irrespective of the selected approach, learning outcomes should be designed so that they can be clearly understood by the actors involved: achieved during mobility, assessed abroad and recognized when the learner returns to the home institution.

ECVET points are a numerical representation of the overall weight of learning outcomes in a qualification and of the relative weight of units in relation to the qualification. Together with units, descriptions of learning outcomes and information about the level of qualifications, ECVET points can support the understanding of a qualification. The number of points allocated to a unit provides the learner with information concerning the relative weight of what he has accumulated. It also provides the learner with information concerning what remains to be achieved.

Each Learning unit is expected to correspond to 1 ECVET point – in total each course will be certified with 5 ECVET points.

3 Results and discussion

3.1 State-of-the-art in zero waste

Global annual waste generation is expected to jump from 2.01 Gt (billion tonnes) to 3.4 Gt over the next 30 years (The World Bank, 2019). At least 33 % of that is not managed in an environmentally safe manner. Worldwide, waste generated per person averages 0.74 kg/d (kilogram per day) but ranges widely, 0.11–4.54 kg/d. Global waste composition is: food and green 44 %, paper and cardboard 17 %, plastic 12 %, glass 5 %, metal 4 %, rubber & leather 2 %, wood 2 %, other 14 %. Global treatment and disposal of waste distribution: open dump 33 %, landfill (unspecified) 25.2 %, *recycling* 13.5 %, incineration 11.1 %, sanitary landfill (with

landfill gas collection) 7.7 %, composting 5.5 %, and controlled landfill 3.7 %. It is estimated that 1.6 Gt of CO_2 equivalent greenhouse gas emissions were generated from solid waste treatment and disposal in 2016, or 5 % of global emissions.

EU-28 waste generation per inhabitant was 4950 kg/a in 2016, and included the following waste fractions: CDW 38 %, mining and quarrying 25 %, manufacturing 10 %, energy 3 %, other economic activities 18 %, and households 8 %. In partner countries, the mass of waste generated per capita was the highest in Romania (9,0 t/a) followed by Austria (7,0 t/a), Greece (6,7 t/a), Poland 4,8 t/a, Spain (2,8 t/a), Slovenia (2,7 t/a), Czech Republic (2,4 t/a), Slovakia (2,0 t/a), and Portugal (1,4 t/a).

Recycling is the process of converting waste materials into new materials and objects. It can prevent the waste of potentially useful materials and reduce the consumption of fresh raw materials, thereby reducing energy usage, air pollution (from incineration), and water pollution (from landfilling). Fractions of recycling (Eurostat, 2019b) are high in CDW (89 %), medium in overall packaging waste (67 %), and low in recycling municipal waste (46 %), plastic packaging (42 %), and e-waste (41 %). Regarding the total waste recycling fractions, Austria is in the 1st group, Slovenia in the 2nd one, Poland in the 3rd, Portugal, Czech Republic and Spain in the 4th, and Slovakia, Greece and Romania in the last one (Fig. 2). High recycling rates are a precondition for the CE. In urban solid waste recycling, the situation is very much the same.

In *Austria,* the annual mass rate of waste continues to increase. According to the Austrian Federal Waste Management Plan 2017, around 4.2 Mt of municipal waste was generated from households and similar establishments – an increase of 6.8 % compared to 2009. Approximately 10 Mt of CDW accrued in 2015 in Austria. The average was 1160 kg per person. The mass of excavated materials and soils was approximately 32.8 Mt. In 2015, 420 plants were available for treating CDW. Approximately 9.7 Mt of CDW and excavated materials were treated in these plants. A new waste prevention program has been published by the BMNT ministry in 2017, supporting environmental goals by defining targets for avoiding waste, reducing pollutants and establishing CE.

In the *Czech* Republic, 34.5 Mt/a waste was generated in 2017. 80.4 % of it was recovered as waste to material, and 3.6 % as waste to energy. Recycling of packaging waste achieved 73.7 %; 98 % of CDW was materially recovered. While 49.6 % of municipal waste was recovered, 45.4 ended in landfills. Municipalities have to ensure separate collection of paper, plastic, glass, metals and biodegradable municipal waste. Separation and recycling centres, operated by municipalities, accept bulky waste (e.g. old furniture), metals, bio-waste, fats and oils, hazardous waste, household appliances, tyres, small CDW, and other waste that cannot be separated in small containers.



Figure 2: Total waste recycling fractions in Europe 2016 (Eurostat).

In *Poland*, environmental education is crucial for the success of transformation towards ZW&CE. Research on sustainable consumption indicates that the level of consumer awareness is still low. Pricing is still almost the only criterion when making consumer decisions. In this context, it is important to focus education on changing consumer behaviour by raising their awareness of environmental protection and

developing their knowledge about rights in access to information about the product and the producer to minimize the impact of products during their lifecycle.

Portuguese material productivity in 2016 was $1.08 \notin/t$, which is half the European average (2.07 \notin/t). The Portuguese economy tends to accumulate materials in its territory, since more materials are extracted and imported than exported, thus accumulating stocks of materials, mainly in real estate. In 2014, extraction plus imports represented 202 Mt of materials, of which 93 Mt were accumulated in stock and 109 Mt left the economic circuit as emissions and exports. Regarding the production of waste in 2016, urban waste production per inhabitant was 454 kg/a, with a recycling rate of 40.4 %, below the European average (43.7 %). However, waste production in Portugal is lower than the European average: the total dredged waste and contaminated soil reached 1184 kg/a, 69 % of the EU average.

Romania is far behind in terms of implementation of the CE principles. Landfilling continues to be the prevalent management practice, with only 13.3 % of waste recycled. Consequently, the collection targets for waste packaging, waste electric and electronic equipment, and waste batteries and accumulators are not met, and the circular material use rate is the lowest in Europe. The key challenge is the inability to sort all waste. There are many reasons for that, starting with the continuous changing of legislation and its poor implementation, the failure of various key actors in taking responsibility, ineffective extended producer responsibility schemes, and low levels of awareness and education. Inadequate practice in reporting, collecting, integrating and evaluating data, and the slow implementation of policy and economic instruments are serious barriers to enhancing waste prevention and reduction, and transition to CE.

In *Slovakia*, interest in ZW has increased among the broader public and younger generation. There are various growing ZW communities even outside the big cities, and an increasing number of shops. E.g. a Facebook group *ZW Slovakia* has close to 12 000 followers. There are various start-ups and social enterprises focusing on upcycling fashion, and producing bags and bottle holders using recycled textiles. Fashion brands that focus on clothing rental and swapping are coming. In 2019, a conference *Slovakia Goes ZW* was organized in Stara Trznica, again with various Slovak companies and e-shops present.

In 2017, *Slovenia* produced 483 kg of municipal waste per capita including 60 kg of food waste; 70 % of waste is separated. The system is similar to the Czech one. ZW Europe reported that Slovenia was the best performing EU country, with the lowest mass of residual waste, just 102 kg per capita in 2014.

187

Spanish companies are proving to be up to the challenge of CE and have launched programs of all kinds: ensuring the durability of products, recovering resources within the value chain, extending the life of the product, marketing products as services, etc. In this new panorama, companies have begun to rethink their production processes in order to minimize waste generation.

3.2 State-of-the-art in circular economy

Eurostat is following the CE results by using 16 indicators and calculating their normalized values for each member state. The best results have been achieved by Netherlands, Belgium and Slovenia. Austria is 5th, Poland 9th, Spain 14th, Portugal 15th, Slovakia 17th, Romania 22nd, and Greece 24th. There are no data available for the Czech Republic. CE ranking in Europe is presented in Figure 3.

The circular material use fraction (rate) of total material use in EU-28 reached 11.7 % in 2016 (Eurostat, 2018). Netherlands managed 29 %, Austria 10.6 %, Poland 10.2 %, Slovenia 8.5 %, Spain 8.2 %, Czech Republic 7.6 %, Slovakia 4.9 %, Portugal 2.1 %, Romania 1.5 % and Greece 1.3 %.



Figure 3: Circular Economy Ranking in the EU26.

3.2.1 Organization of training sessions

In partner countries, ad hoc seminars, scientific and professional conferences are organized; web platforms, books, and e-manuals are available; no regular and systematic education is taking place from the elementary level to tertiary education. In some of them, new MSc courses are starting in 2018 and 2019 at university level.

In *Austria* an International Masters Programme on CE has recently been introduced at Graz University.

In *Czech* Republic, the VET course on CE was organized by the University of Chemistry and Technology in Prague in 2017/18. The aim of the course is to offer specific knowledge in the field of CE, which will influence activities from product development and production, recycling technology, waste management, marketing, and environmental protection, to social issues, and business responsibility. The course is suitable for waste management, CSR experts, environmental ecologists and

managers determining the strategies chosen to ensure business resilience and new strategies. The course is officially accredited as Lifelong learning instruction.

189

In *Portugal*, the following courses were identified at the university level:

- A new curricular unit on "Product Design in CE" at the University of Aveiro (KATCH-e, 2019)
- A post-graduate course "CE Environment as a Competitiveness Factor" at Lusófina University
- A training unit at the University of Porto (Faculty of Engineering).
- Courses (e.g. "Training on CE" provided by SGS) and workshops (e.g. workshops on circular design, circular business models, life cycle perspective on CE and managing CE provided by LNEG and IAPMEI) have also been organized.

In *Slovakia*, the levels of EQF are unified with the National levels published by the Ministry of Education.

- In primary and secondary school education (Levels 1-4), training for the CE is not approached in a systemic way. Elementary schools may join as associated parties in various EU funded projects or can join initiatives organized by local/municipal authorities in the region.
- Post-secondary education (Level 5) this level of education was omitted in the strategy document of the Ministry of Environment. Similarly, no initiatives are being performed in relation to this target group.
- 3) University studies the only existing accredited study program in "CE" is offered by the Slovak University of Agriculture in Nitra.
- 4) Informal education training in CE is being offered in the form of internationally recognized project initiatives (e.g. Interreg Danube Transnational Programme MOVECO) or as initiatives of national agencies or local NGOs (e.g. Open Source CE days organized by EKOrast). The target groups are university students, teachers and entrepreneurs.

3.2.2 Characteristics of training for the circular economy

Training sessions are *organized* by research/project groups, regional/national chambers of industry and commerce, universities, R&D institutes, competence/technology centres, local communities, ministries (regional and national ones), NGOs, media, or service providers. They are also given as a part of another course or degree; e.g., formal CE education is organized by the Slovak University of Agriculture in Nitra; however, the systemic approach towards sustainable development is best embraced by the Slovak University of Technology.

The *duration* of training is 1–2 days for seminars, up to 2 years for a university degree. For example, in Portugal, the module "Product Design in a CE" curricular unit at the University of Aveiro takes 1 semester, while the "CE – Environment as a Competitiveness Factor" post-graduate course at Lusófona University lasts 1 year.

Trainers are professionals, environmental consultants, R&D team members, ministries, universities, institutes, competence centres, technology centres, or companies. They are not employed as VET teachers of ZW & CE.

3.2.2 Curriculum content

A Master's course on CE exists in *Spain*, and a course on environmental management and sustainability in *Greece*.

In 2017 the *Portuguese* Ministry of Environment presented the National Strategy of Environmental Education 2020 with three thematic pillars, one of them being CE (APA, 2017).

In Austria, several courses are offered:

 Vocational training for Waste Disposal and Recycling Experts by the Federal Economic Chamber (WKÖ)

- Courses are offered by the Austrian Water and Waste Management Association (ÖWAV) in CDW, waste management, municipal waste management, construction law, and waste management law
- International Master's Programme on CE at the University of Graz.

In Czech Republic several course blocks on CE are offered.

In most partner countries, there are no certification processes.

3.3 Good practices in circular economy

Austria

- *1) RepaNet Initiative* (Re-Use- und Reparaturnetzwerk Österreich), launched in 2004 to increase the supply of repaired products and the demand of repair and rental services.
- 2) BauKarussell, the first Austrian cooperation that addresses reuse in buildings on a large scale. Together with property developers, the consortium removes selected materials and products to make them available for new buildings. The operational work is performed by employees from social enterprises. These unemployed people gain jobs, training and support to find their way back to the labour market.
- *3) Re-Use Box*, the first collection system for reusable small goods to be distributed to the population at several points in Graz. The collected goods are sorted by the participating social economy enterprises and prepared for reuse in the reuse shops.
- 4) A *Reuse shop* at the resource park in Leibnitz, Styria, offers the possibility to sell used, but still well-functioning household and garden equipment, books, toys, decorative items, and much more.

Greece

- 1) ReWeee Project (Reducing Waste Electrical and Electronic Equipment, WEEE) aims to prevent the creation of WEEE and to demonstrate that WEEE can be efficiently sorted and reused.
- 2) Close the loop in ceramic industry: Valorisation of various types of inorganic and organic wastes as substitutes for clayey raw material. The quality of extruded and pressed ceramic products was evaluated for their properties and the environmental impact.
- 3) HYDROUSA, Demonstration of water loops with innovative regenerative business models for the Mediterranean region will provide innovative, regenerative and circular solutions for (1) nature-based water management of Mediterranean coastal areas, closing water loops; (2) nutrient management, boosting the agricultural and energy profile; and (3) local economies, based on circular value chains. The services lead to a win-win-win situation for the economy, environment and community within the water-energy-foodemployment nexus.

Poland

- 1) 5 Fraction Coalition a transparent pictogram system for packaging in Poland.
- BREAM certification of Skanska buildings a developer with a recycling rate of 97 % in 2018.
- *3) Think*, eliminate everything that you don't need Studio 102, based on the 5R approach (Refuse/Reduce/ Reuse/Repurpose/Recycle).

Czech Republic

- 1) Strategy Circular Czechia 2040 under preparation
- 2) Several bottom-up initiatives

193

3) CE course.

Portugal

- 1) The National Action Plan for the Circular Economy, with strategies and mechanisms to implement CE;
- 2) The *ECO.nomia Portal*, a knowledge sharing platform promoting CE, tools, funding opportunities, examples of best practices, etc.
- 3) The Research and Innovation Agenda on CE
- 4) Five regional agendas
- 5) *Funding opportunities for CE*, such as an Environmental fund to support CE projects, an EC Voucher to fund companies in small EC projects, etc.
- *6)* The *EcoLab*, a collaborative laboratory on CE to promote cooperation between academia and companies in transition to CE, with a particular focus on industrial biotechnology, green chemistry and eco-design
- 7) Several national R&D projects.

Romania

- 1) The use of sludge for agricultural purposes
- 2) A law on food donation.

Slovenia

- 1) SMEs' Green action plan for transition to CE
- 2) Indicators, methods and tools for measuring CE

3) Use of eco-design for SMEs in civil engineering.

Spain

1) Circular business training (furn360.eu)

2) Resources offered by Ihobe, the Environmental Basque Agency.

3.4 Intellectual Output 1

The **Knowledge Hub** supports the development of interdisciplinary skills needed for new jobs in this area. It is an interactive online resource centre, gathering selected information to enable circular projects and ideas to be used and applied as inspiration coming from existing best cases and success stories.

VET teachers, professionals from companies and other users will have access to this open education resource, with tailored information in a structure that will allow further enclosure by all partners of newly released information, which is continuously being developed in the area of ZW&CE.

The taxonomy of the Knowledge Hub includes relevant content about CE, waste and ZW concept, critical raw materials, circular design, etc., available in literature, standards and legislation, books, good practices, case studies, presentations, videos, software, methods, tools and other relevant resources. It has a user-friendly structure and functionalities, and because of its concept and architecture, it is easily transferable to other educational systems and topics.

3.5 Intellectual Output 2

The EduZWaCE platform is developed on the open source of Moodle, an elearning platform designed to provide trainers, administrators and learners with a reliable, secure and integrated system of personalized learning environments. Moodle is provided freely as Open Source software that anyone can adapt, extend or modify for commercial or non-commercial projects without any licensing fees, and benefit from the cost-efficiencies and flexibility. Moodle's multilingual backbone ensures that there are no linguistic limitations to learning online. The community has started translating Moodle into more than 120 languages, and users can easily localize their Moodle approach, along with plenty of resources, support and community discussions available in various languages, including those of the project partners.

Moodle (2019) is used as technical base in almost 20 million online courses. It is one of the best open source learning management systems, offering a plethora of features in comparison to other providers (Capterra, 2019). The system allows a wide range of different possibilities from which the project will use the following:

- The Quiz option to test trainees
- The features of Forum, Chat and Teleconference to ensure communication between trainers and trainees
- The possibility to assess trainers by surveying them in order to improve the quality of course organization.

The possibilities of the open source learning management system will be used in the EduZWaCE platform by a modular approach to use exactly those features that fulfil the multifunctional and collaborative needs in the area of administration, the platform itself and the course content.

3.6 Intellectual Output 3

The **ZW&CE on-line course** targets two jobs: the Manager, and the Technician/Worker.

3.6.1 Focus group 01

ZW&CE Manager is a professional able to asses resource use, waste generation, and product lifecycles, and to develop, implement and monitor CE projects in a company. He/she should be able to perform systems evaluation by identifying its indicators and the actions needed to improve or correct performance, relative to the goals of the system, monitor organization performance in material resource/waste

management, and propose improvements or take corrective action. A Manager's tasks would be to assess resource consumption and waste generation, develop material and waste balances in the company, assess root causes of material inefficiencies and waste, generate, evaluate and implement waste reduction options, evaluate companies' products and propose ways of greening them, perform circularity assessment in a company, propose circular solutions for products, operations and services, and propose/evaluate new circular business models. Considering that companies are acting within a value chain, networking and cooperation with actors from the value chain are requirements.

Entry requirements correspond to the EQF level 5 completed by the interest in acquiring specialized knowledge in ZW&CE. It requires at least one year's work experience in resource and waste management, production operations, specialised factual and theoretical knowledge within the field of waste and resource management and specific production operations. A comprehensive range of cognitive and practical skills required to solve abstract problems and develop creative solutions are also desired.

As for learning outcomes, the individual shall demonstrate mastery of acquired learning outcomes in accordance with certain performance criteria and context conditions. Five learning units are being developed: 1) Introduction to CE, 2) Material and resource efficiency, 3) Circular design, 4) Value creation in CE, Circular business models, and 5) Self-assessment and co-creation of circular solutions. Their content is elaborated in sub-sections, e.g. for learning unit (4): a) Self-assessment tools – benefits and limitations, b) Assessment of product environmental performance, c) Assessment of material flows and waste streams in production processes, and d) Cooperation within value chains.

The knowledge skills and competencies are presented in Table 2. Performance criteria and workloads in hours can be added. The learning outcomes for the content in sub-sections are organized the same way.

Knowledge	Skills	Competences
Depth: The learner has knowledge in design of CE procedures and their applicability in practice in the development of	Breadth and depth: The learner is able to apply the design methodology with a circularity approach, applying strategies and tools aiming to develop new and	Responsibility (relation to others & self-work): The learner is able to carry out projects individually if he/she has adequate knowledge of specific methods in line with product and service development.
and services.	innovative circular solutions	He is able to manage and establish the link between other team members and review their work from a methodological and practical
and critical thinking:	The learner is able	point of view.
The learner understands the concepts of design for CE and the	to apply practical strategies and tools to solve specific problems and challenges faced by	The learner will be able to transfer the knowledge and skills to their own project and to implement it.
strategies for implementation.	an actual design problem.	Autonomy: High level of autonomy.

Table 2. Learning Outcomes.

Main action / achievement	Workload
The learner will have an understanding of the role of design and	
designers in the CE model and become acquainted with circular	
design concepts and strategies, be able to select and apply them,	25 hours
design and develop processes, products and services in a holistic	
manner.	

.

3.6.2 Focus group 02

Training material for focus group 2, to be developed within the EduZWaCE Project, is designed for technicians and workers from reuse, repair and recycling centres who are interested in acquiring knowledge and new skills in the field of reuse and CE.

Since CDW is the largest waste stream in the EU in volume (EPRS, 2015), the main focus of this EduZWaCE training programme will be on CD sector. In this context a comprehensive training manual ("Qualified workers for the reuse of CD materials") will be developed.

This qualified worker carries out an assessment of reusable CDW streams prior to demolition and renovation of buildings. The aim is to facilitate and maximize recovery of materials and components from demolition or renovation of buildings and infrastructures for beneficial reuse, without compromising safety measures and practices. In the EU context, this task could be performed by trained workers within the reuse parks and recycling and waste collection centres, as well as construction or demolition companies.

By the end of the course, participants should be familiar with different types of reusable CD materials as well as techniques of dismantling and material recovery. The course will combine theory with practical examples and assignments. It will be divided into five learning units: 1) Introduction, 2) Furniture, 3) Construction elements, 4) Electric equipment in buildings, and 5) Conduct of an assessment of reusable CD materials

The introductory learning unit will give an overview of aspects such as the following: What is an assessment of reusable construction and demolition materials (purpose, target groups, added value, etc.)? What are the major steps in conducting such an assessment? A summary of best practices in cities will then be presented. The subsequent learning units (2–4) will focus on selected reusable materials and elements, i.e. furniture, construction elements and electric equipment in buildings, providing information on different dismantling and material recovery techniques (including instructions, videos, graphics, etc.). At the end of the course (learning unit 5), a fictitious assessment of a building will be performed by the course participants. They will be given an opportunity to perform the assessment within the framework of a focus group and under guidance of an expert in the field of circular economy.

The requirement for entering the course is completion of Level 2 of the EQF.

3.7 Intellectual Output 4

The ZW&CE Diagnosis Tool, developed within the EduZWaCE project, is considered to be a useful self-assessment tool for companies (in particular SMEs) that will help them investigate opportunities for circular economy solutions in their specific context. The company will be able to identify the most effective opportunities for improvements in terms of circularity, as well as the overall sustainability performance, and to choose the most effective leverage points and feasible measures leading to both an improvement in circularity and efficient allocation of its limited resources.

In order to optimise improvement measures and actions, it is important to review the whole system of a business in a consistent way; therefore, all levels of a company need to be assessed in a systematic way, including the physical level (products, production processes), the information level (management systems) as well as the governance level (business strategy, stakeholders relations).

Understanding of the main materials (and energy) flows and waste streams is the key to assessing the company's situation in relation to circularity; in this regard, the internal circular economy opportunities are addressed in a first step based on the following elements:

- Level of integration of circular economy objectives into the core business strategy and business models;
- Key materials used, risks and opportunities related to these and relevant waste flows;

- Real costs of materials and waste flows, including non-product output related costs;
- Actions already implemented towards circularity.

At the same time, the external opportunities of circular economy will be assessed. These will address, in particular, the life cycle perspective of products, and opportunities within value chains and with other stakeholders (e.g. industrial symbiosis).

The main feature of the Diagnosis Tool is the holistic approach, which is manageable at the SME level. In contrast to other methodologies that provide a diagnosis in this field, our tool is strictly based on a need-driven approach. Instead of assuming that any existing tool can produce the desired positive changes, the Diagnosis Tool focuses first on improvement potential within the given company, and only after that, does it assign suitable measures that address this potential to be further developed by the company.

The tool will be made available in the Collaborative Section of the Platform to be used for free by companies and circular economy experts. We expect about 10 companies per partner to be logged in on the Platform and use the Diagnosis Tool during the project lifetime.

Apart from the Platform, the Diagnosis Tool will also be closely linked with the other intellectual outputs. The tool users will have a possibility to explore received recommendations through the resources of the Knowledge Hub, as well as to learn more about actual topics in the On-line Course.

4 Dissemination

The results of the project need to achieve maximum impact: they should radiate as widely as possible so that the valuable lessons and experience gained by one group can benefit others. Moreover, what is learned from a project should inform future policy. All this can happen only if connections are made between the project partners and the wider community. The key means of connecting with the target audience is

the process of communication and dissemination. Three types of audience have been defined at individual, local and national, EU and global levels: 1) Dissemination inside and outside an organization will tackle project partners and users. 2) Dissemination at local and national levels will target potential users: key players in VET, teachers' associations, VET learners/students and employees, universities and research institutions, NGOs, innovators and sustainability experts, company representatives, industrial associations, clusters on one side, and local and regional policy makers, on the other side; 3) Dissemination at the European and global levels will address European and international organisations and institutions, policy makers, academia, NGOs and international networks with varied interests, from education and awareness creation, to policy development and support.

Dissemination is carried out according to the Plan for Communication and Dissemination, having as its main objective to communicate the project objectives, collect feedback and contributions from the target audience, and disseminate results, technical achievements and innovations. The project portal plays a central role in communication and dissemination of the project ambitions and results, while communication by social media is of great importance. The outcomes of the project, any tangible resources, products, deliverables and outputs resulting from the funded projects, will also be available for dissemination purposes at the Erasmus+ Project Results Platform and the EduZWaCE platform (https://www.eduzwace.eu/).

New CE phenomena bring to the forefront new managerial challenges as they evoke cooperative attitudes in situations that used to be fully competitive. If the business success of circularity is based on successful collaboration of previously unlinked industries, then there is a need to forecast how this cooperation could turn out.

In CE, there is a disproportionally larger number of collaborative incentives and needs than ever before. This is well documented by recycling, reuse, recovery, restoration or revitalisation projects. The issue of cooperation is significantly present as a key-enabling driver for sharing ideas, testing approaches or constant improvements.

5 Conclusions

Earth Overshoot Day (2019) moved from August 1 last year to July 29 this year, the earliest ever. This is the day when humanity has used nature's budget for the entire year. This means that humanity is now using nature 1.75 times as fast as the planet's ecosystems can regenerate. Carbon dioxide emissions currently make up 60 % of humanity's demand on nature. The partner countries' overshoot days occur even earlier: Austria, April 9; Czech Republic, April 17; Slovenia, April 27; Poland, May 15; Greece, May 20; Slovakia, May 22; Portugal, May 26; Spain, May 28, and Romania, July 12.

The warming up of land and oceans is causing faster and more abundant water evaporation and many extreme events: record-breaking heat waves with fires, droughts, melting of polar ice and glaciers, and sea level rise, tornadoes, typhoons, powerful storms, hail, floods, and land-slippage. Biodiversity is reduced by species extinction. Food production is lowered and woods are endangered. Hydro energy production is reduced; river transport is stopped. Many people are killed in extreme events, and the number of climate refugees is rising. Education for ZW&CE can help slow climate change and reduce the scarcity of materials.

"Decoupling environmental degradation from economic growth by doing more and better with less" is needed. Slower growth, or even *degrowth*, particularly in the developed countries, is required to stay within planetary limits. Degrowth requires changes in consumption patterns (habits, behaviours, and life styles), better prediction mechanisms, reduction in consumption levels, and changes in infrastructure. It is also called *strong sustainable consumption*. Education for degrowth is badly needed, and education for ZW&CE can be very helpful as a first step.

Our research has shown that universities have started to introduce courses on CE, but curricular units on ZW are very scarce. VET education is even less developed – there are no curricula, no courses, no teachers and no students to do the jobs of the future; the only exception seems to be Austria. The younger generation is requiring changes towards degrowth that can be connected with education to yield synergies. In contrast with schools, there are many bottom-up initiatives and good practices that can be integrated into education for ZW&CE.

References

- APA, Agência Portuguesa do Ambiente (2017). National Strategy of Environmental Education 2020. https://apambiente.pt/_zdata/DESTAQUES/2017/ENEA/AF_Relatorio_ENEA2020.pdf (accessed 29.07.2019).
- Capterra, 2019, 11 Best Free and Open Source LMS Tools for Your Small Business. https://blog.capterra.com/top-8-freeopen-source-lmss/#12 (accessed 15.04.2019).
- Cedefop, 2016. ECVET in Europe: monitoring report 2015. Luxembourg: Publications Office. Research paper; No 56. http://dx.doi.org/10.2801/946187 (accessed 25.07.2019).
- Cedefop, 2017. National qualifications framework developments in Europe 2017.Luxembourg: Publications Office. http://data.europa.eu/doi/10.2801/029873 (accessed 25.07.2019).
- Circularity Gap Report, 2019, Circle Economy. https://docs.wixstatic.com/ugd/ad6e59_ba1e4d16c64f44fa94fbd8708eae8e34.pdf (accessed 21.07.2019).
- Circularity Gap Report Austria, 2019, Alstof Recycling Austria. https://www.ara.at/fileadmin/user_upload/Downloads/Circularity_Gap_Report/CGR_Austria_Endversion.pdf (accessed 21.07.2019).
- Earth Overshoot Day, 2019. https://www.overshootday.org/eod2019-july-29/ (accessed 30.07.2019).
- EduZWaCE, (2019), Analysis of zero waste and circular economy sectors in Europe. https://www.eduzwace.eu/index.php/the-material/intellectual-output-3 (accessed 25.07.2019).
- Ellen MacArthur Foundation (2013), Towards the Circular Economy. https://www.ellenmacarthurfoundation.org/assets/downloads/publications/Ellen-MacArthur-Foundation-Towards-the-Circular-Economy-vol.1.pdf (accessed 11.07.2019).
- Ellen MacArthur Foundation (2015), Towards a Circular Economy: Business Rationale for an Accelerated Transition". https://tinyurl.com/zt8fhxw (accessed 11.07.2019).
- Ellen MacArthur Foundation (2019), Freely accessible learning offerings Massive Open Online Courses (MOOCs) https://www.ellenmacarthurfoundation.org/resources/learn/courses (accessed 18.07.2019).
- EPRS, 2015, European Parliamentary Research Service, Understanding waste streams Treatment of specific waste. http://www.europarl.europa.eu/EPRS/EPRS-Briefing-564398-Understanding-waste-streams-FINAL.pdf (accessed 29.07.2019).
- European Commission, 2008. The raw materials initiative meeting our critical needs for growth and jobs in Europe. https://eur-lex.europa.eu/legal-

content/EN/TXT/PDF/?uri=CELEX:52008DC0699&from=EN (accessed 18.07.2019).

- European Commission, 2010. Being wise with waste: the EU approach to waste management. http://ec.europa.eu/environment/waste/pdf/WASTE%20BROCHURE.pdf (accessed 10.07.2019).
- Eurostat, 2019a, Indicators used to monitor the progress towards the circular economy. https://ec.europa.eu/eurostat/web/circular-economy/indicators (accessed 19.07.2019).
- Eurostat, 2019b. Circular economy indicators. https://ec.europa.eu/eurostat/web/circulareconomy/indicators/main-tables (accessed 10.07.2019).
- KATCH-e, 2019, Overview of the KATCH-e Modules and Tools. www.katche.eu (accessed 29.07.2019).
- MOOC List, 2019, Zero Waste MOOCs and Free Online Courses. https://www.mooclist.com/tags/zero-waste (accessed 19.07.2019).
- Moodle, 2019. www.moodle.org; https://moodle.net/stats/ (accessed 02.07.2019).
- Politico, 2018, Ranking how EU countries do with the circular economy.
 - https://www.politico.eu/article/ranking-how-eu-countries-do-with-the-circular-economy/ (accessed 21.07.2019).

- Rizos, V., Tuokko, K., Behrens, A., 2017. The Circular Economy, A review of definitions, processes and impacts. https://circular-impacts.eu/sites/default/files/D2.1_Review-of-definitionsprocesses-%26-impacts_FINAL.pdf (accessed 11.07.2019).
- Sintra, 2019, Multidisciplinary study module on the circular economy. https://www.sitra.fi/en/projects/multidisciplinary-study-module-circular-economy/ (accessed 20.07.2019).
- SOeS, 2017, The Monitoring and Statistics Directorate, 10 Key Indicators for Monitoring the Circular Economy, https://www.statistiques.developpementdurable.gouv.fr/sites/default/files/2018-10/datalab-18-economie-circulaire-Edition-2017anglais.pdf (accessed 19.07.2019).
- SWANA, 2019, Zero Waste Principles and Practices. https://swana.org/Training/CourseCatalog/PlanningManagement/ZeroWastePrinciplesand Practices.aspx (accessed 19.07.2019).
- The World Bank, 2019. Trends in solid waste management. http://datatopics.worldbank.org/what-awaste/trends_in_solid_waste_management.html (accessed 10.07.2019).
- Whicher, A., Harris, C., Beverly, K., Swiatek, P., 2018, Design for circular economy: Developing an action plan for Scotland, J. Clean. Prod. 172, 3237–3248.
- WRAP, 2019. Waste & Resource Action Programme UK. http://www.wrap.org.uk/aboutus/about/wrap-and-circular-economy (accessed 10.07.2019).
- Zero Waste Europe, 2019. What is zero waste? https://zerowasteeurope.eu/what-is-zero-waste/ (accessed 10.07.2019).
- ZWIA, 2019. Zero waste definition. Zero Waste International Alliance. http://zwia.org/zero-wastedefinition/ (accessed 10.07.2019).
ENZYME DEACTIVATION USING HIGH PRESSURE CARBON DIOXIDE TECHNOLOGY

Gordana Hojnik Podrepšek¹, Željko Knez^{1,2} & Maja Leitgeb^{1,2}

 ¹ University of Maribor, Faculty of Chemistry and Chemical Engineering, Laboratory for Separation Processes and Product Design, Maribor, Slovenia,
 e-mail: gordana.hojnik@um.si, zeljko.knez@um.si, maja.leitgeb@um.si
 ² University of Maribor, Faculty of Medicine, Maribor, Slovenia, e-mail: zeljko.knez@um.si, maja.leitgeb@um.si

Abstract For some foods, low enzyme activity is desirable in order to stabilize the quality of the product. High enzyme activity adversely affects food quality, causing enzymatic browning in vegetables and fruits and degradation of starch in grains, and enzymatic reactions cause redness, occlusion and oxidation processes in flour. During storage of whole wheat flour, lipids can influence the quality of the flour through enzymatic hydrolysis, which is catalyzed by lipases (Budisa et al., 2014). Our research focused on the use of scCO2, which has attracted particular attention in research and technology because of its "green" (i.e., sustainable) properties with the possibility of reusability of CO2 while pursuing a circular economy approach (Li et al., 2016). Enzyme deactivation by scCO2 treatment at different pressures, temperatures and exposure times of wheat flour was performed.

Keywords: Supercritical technology, supercritical carbon dioxide, enzyme deactivation, high pressure, reusability of CO2.



DOI https://doi.org/10.18690/978-961-286-353-1.16 ISBN 978-961-286-353-1

1 Introduction

Flour, a product obtained in the process of grain milling, is one of the most important raw materials in the food industry. Flour is indispensable for the production of a wide variety of staple products such as bread, pasta, cakes, and biscuits. Flour must be of satisfactory quality for processing to obtain acceptable end products (Sujka *et al.*, 2017). Many of the bioactive compounds present in food products, such as enzymes, anthocyanins and vitamin C, are thermo-sensitive and are destroyed by heat treatment. High temperature also affects the fresh flavor of fruits and other products. Therefore, it is necessary to use efficient non-thermal preservation techniques in food production.

Because of the development of undesirable chemical changes in flour during storage, deactivation of enzyme activities may be an appropriate strategy to extend shelf life and maintain the functional properties of whole wheat flour. Previous studies have used different thermal processing methods, including steaming, microwave heating, and passing through infrared and gamma radiation to decrease enzymatic activities (Poudel *et al.*, 2018).

For instance, deactivation using $scCO_2$ is a promising non-thermal method to significantly decrease enzyme activity through the combined effect of high pressure of up to 65 MPa with mild heating of up to 50 °C. Enzyme deactivation using $scCO_2$ processing is usually connected with lowering the products' pH combined with physical disruption of the enzymes (Marszalek *et al.*, 2019).

2 Experiments

The chemicals and reagents used in this study were distilled water, white wheat flour type 500, carbon dioxide (99.5 % purity, Messer, Ruše). Ethanol, phosphoric acid, sodium chloride, Coomassie-Brilliant Blue G250 and acetonitrile were supplied by Merck, while chicken egg albumin, sodium acetate, acetic acid and p-nitrophenyl butyrate were supplied by Sigma. α -amylase enzymes from *Aspergillus oryzae* were obtained from Sigma and lipase from *Aspergillus niger* was obtained from BioChemics. All other chemicals used in the laboratory were of analytical grade.

The following experimental methods were used in the study:

- Time optimization of enzyme extraction, where the optimal conditions for the extraction of enzymes from wheat flour were determined. The optimal shaking time and method of centrifugation of the sample were experimentally determined in order to obtain the highest concentration of proteins present in the supernatant after centrifugation.
- Determination of protein content in flour was estimated using the Bradford dye binding method with bovine serum albumin as the standard, measured on a UV-spectrophotometer at a wavelength of 595 nm.
- Determination of enzyme activity: White wheat flour was selected for this study since it is most commonly used in bakery products. After the examination of previously published scientific studies, we decided to determine the activity of the desired and undesired enzymes which are most often present in different types of flour. In the study, we investigated the activity of α -amilase and lipase enzymes. The activity of individual enzymes was determined based on enzymatic activity assays using a UV-spectrophotometer method at different wavelengths.
- Deactivation of enzyme using high-pressure reactor and determination of residual enzyme activity after scCO₂ treatment. In order to determine the effect of scCO₂ on the activity of enzymes in white wheat flour, free enzymes (α-amilase and lipase) were exposed to different conditions in a high-pressure batch reactor (200 bar and 300 bar at 35°C). Then, white wheat flour was exposed under the same conditions in a high-pressure batch reactor. Later, enzymes were extracted from scCO₂ treated wheat flour, where the supernatant was used to determine the enzyme activity. For comparison, the enzyme activity of untreated flour was determined. Residual activities of treated wheat flour were correlated to the native enzyme activity, taken as 100 %.

3 Results

Optimization of enzyme extraction from white wheat flour was performed during the research. Different times and methods for obtaining the supernatant had a significant influence on protein concentration in the sample. The protein concentration was determined by direct measurement of protein content in the remaining supernatant after extraction.

Optimal conditions and the highest protein concentration were achieved with a single centrifugation (step 3) at a shaking time of 90 minutes.

The influence of scCO₂ on the residual activity of enzymes was investigated after 3 hours of treatment time at 200 bar and 300 bar at 35°C. Deactivation of the α -amylase enzyme occurred after 3 hours at 200 bar. As can be seen from Tab. 1, deactivation of α -amylase is further increased at 300 bar. Lipase achieved half-life of the enzyme at treatment time after 3 hours and 300 bar.

Furthermore, the influence of scCO₂ on the residual activity of enzymes in white wheat flour was investigated after 3 hours of treatment time at 200 bar and 300 bar at 35°C. Comparing the results from Tab. 1, similar behavior of enzymatic activities of free enyzme and enzymes in white wheat flour under the same conditions and treatment with scCO₂ was observed. Residual activity of α -amilase decreased at 200 bar and further decreased at 300 bar. Also, inactivation of the lipase enzyme is less effective in white wheat flour than in the free enzyme, since it remains 75 % at 300 bar.

Table 1: Residual activity after deactivation of pure enzyme and enzyme in flour sample in scCO2.

Enzyme	Residual activity [%]			
	200 bar, 35 °C, 3 hours	300 bar, 35 °C, 3 hours		
pure α-amylase	11.7	6.8		
pure lipase	125.8	53.4		
α-amylase in sample	2.8	2.6		
lipase in sample	97.1	75.8		

A sample of white wheat flour was studied using FTIR spectroscopy, which offers qualitative and quantitative determination of food macro components such as proteins, lipids, saccharides, and water. FTIR spectroscopy, which relies on absorption of infrared radiation by oscillating molecules, is increasingly applied in food research (Sujka *et al.*, 2017). Several bands characteristic of proteins, fats, carbohydrates and water were observed in the flour spectrum. An intense band in the 3600–3200 cm⁻¹ range is generated by the stretching vibration of O–H bonds. Bands in the 3000–2800 cm⁻¹ range are caused by stretching vibrations of C–H bonds. Proteins were observed in the 1,600 cm⁻¹ to 1,700 cm⁻¹ range by bands caused by amide I bonds and 1,550 cm⁻¹ to 1,570 cm⁻¹ by amide II, respectively (Mohan Kumar *et al.*, 2019). The spectral region between 1500 and 900 cm⁻¹ is called the fingerprint region because of the unique patterns characteristic of given samples. The assignment of spectral bands to vibrations generating these bands is presented in Fig. 1.



Figure 1: FTIR spectrum of white wheat flour.

4 Conclusions

Because of the negative effects of enzymes on flour quality, we decided to deactivate the α -amylase and lipase enzymes which are present in flour. The effect of process parameters (pressure and exposure time) on the activity of enzymes in flour was investigated. Protein concentration in flour was determined using the Bradford

method. scCO₂ affects the activity of enzymes, and the activity of certain enzymes in flour is significantly lower after exposure to certain pressures and temperatures, compared to the activity of enzymes in flour that was not exposed to scCO₂.

Acknowledgments

This work was supported by the Ministry of Education, Science and Sport of Slovenia within the research project: contract No. C3330-19-952031.

References

- Budisa, N., Schulze-Makuch, D. (2014). Supercritical Carbon Dioxide and Its Potential as a Life-Sustaining Solvent in a Planetary Environment. *Life*, 4, 331-340.
- Li, B., Zhao, L., Chen, H., Sun, D., Deng, B., Li, J., Liu, Y., Wang, F. (2016). Inactivation of Lipase and Lipoxygenase of Wheat Germ with Temperature-Controlled Short Wave Infrared Radiation and Its Effect on Storage Stability and Quality of Wheat Germ Oil, *PLoS ONE*, 11(12).
- Marszałek, K., Doesburg, P., Starzonek, S., Szczepańska, J., Woźniak, Ł., Lorenzo, J., Skąpska, S., Rzoska, S., Barba, F. (2019). Comparative effect of supercritical carbon dioxide and high pressure processing on structural changes and activity loss of oxidoreductive enzymes, *Journal* of CO₂ Utilization, 29, 46-56.
- Mohan Kumar, B.V., Sarabhai, S., Prabhasankar, P. (2019). Targeted degradation of gluten proteins in wheat flour by prolyl endoprotease and its utilization in low immunogenic pasta for gluten sensitivity population, *Journal of Cereal Science*, 87, 59-67.
- Poudel, R., Rose, D.J. (2018). Changes in enzymatic activities and functionality of whole wheat flour due to steaming of wheat kernels, *Food Chemistry*, 263, 315-320.
- Sujka, K., Koczoń, P., Ceglińska, A., Reder, M., Ciemniewska-Żytkiewicz, H. (2017). The Application of FT-IR Spectroscopy for Quality Control of Flours Obtained from Polish Producers, *Journal* of *Analytical Methods in Chemistry*, 9 pages.

THE H2020 CINDERELA PROJECT — A NEW CIRCULAR ECONOMY BUSINESS MODEL FOR MORE SUSTAINABLE URBAN CONSTRUCTION

ALENKA MAUKO PRANJIĆ¹, KIM MEZGA¹, PRIMOŽ OPRČKAL¹, SEBASTJAN MEŽA¹, ANA MLADENOVIČ¹, IZABELA RATMAN-KŁOSIŃSKA², MAREK MATEJCZYK², TOMISLAV PLOJ³, MATEJ KADIĆ³, AINARA GARCIA URIARTE⁴, PIERRE MENGER⁴, DOUWE HUITEMA⁵, NIELS AHSMANN⁵, ARNOUT SABBE⁶, ARJAN VAN TIMMEREN⁶, MONICA CONTHE CALVO⁶, VELIKO JANJIĆ⁷, IGOR OSMOKROVIĆ⁷, MARIO CONCI⁸, MATTEO DONELLI⁹, ENRICO PUSCEDDU¹⁰, MASSIMILIANO BERTETTI¹⁰, IGNACIO VILELA FRAILE¹¹, LIDIA GULLÓN¹² & SANTIAGO ROSADO¹² ¹ Slovenian National Building and Civil Engineering Institute, Laboratory for stone, aggregates and recycled materials, Ljubliana, Slovenia, e-mail: alenka.mauko@zag.si, kim.mezga@zag.si, primoz.oprckal@zag.si, sebastjan.meza@zag.si, ana.mladenovic@zag.si ² Institute for Ecology of Industrial Areas, Katowice, Poland, e-mail: i.ratman-klosinska@ietu.pl, m.matejczyk@ietu.pl ³ Nigrad, komunalno podjetje, d. d., Maribor, Slovenia, e-mail: tomislav.ploj@nigrad.si, matej.kadic@nigrad.si ⁴ Fundación Tecnalia Research & Innovation, Parque Científico y Tecnológico de Bizkaia, Derio – Bizkaia, Spain, e-mail: ainara.garcia@tecnalia.com, pierre.menger@tecnalia.com, ⁵ KplusV, Science Park 402, (Science Park UvA), Amsterdam, The Netherlands, e-mail: d.huitema@kplusv.nl, n.ahsmann@kplusv.nl ⁶ TUDelft, Faculty of Architecture and the Built Environment, Department of Urbanism, Chair of Environmental Technology and Design, Delft, The Netherlands, e-mail: arnout.sabbe@tudelft.nl, a.vantimmeren@tudelft.nl, m.conthecalvo-24@tudelft.nl 7 Bexel Consulting, Beograd, Serbia, e-mail: veljko.janjic@bexelconsulting.com, igor.osmokrovic@bexelconsulting.com ⁸ Opencontent, via Galilei, Trento, Italy, e-mail: mario.conci@opencontent.it 9 Bocconi University, Milano, Italy, e-mail: matteo.donelli@unibocconi.it 10 Polo Tecnologico di Pordenone, Pordenone, Italy, e-mail: enrico.pusceddu@polo.pn.it, massimiliano.bertetti@polo.pn.it 11 AEDHE, Madrid, Spain, e-mail: innovacion@aedhe.es 12 Foundation Gómez Pardo, Madrid, Spain, e-mail: ireccion.tecnica@fgomezpardo.es, santiago.rosado@fgomezpardo.es Abstract The municipal sector and different industries, including

construction and demolition activities in urban areas, generate waste streams that could provide excellent secondary raw materials (SRM) to replace traditional raw materials in construction applications. The CINDERELA project develops a business model (CinderCEBM) aided by a one-stop-shop (CinderOSS) service to help construction companies increase profit and deliver value by using SRM from urban waste streams in building and civil engineering applications. The model and the platform will be tested in different socio-economic environments to ensure technological, systemic and economic viability across Europe through demonstrations involving manufacturing and construction with the use of SRM-based materials supported by building information modelling (BIM) and advanced solutions combining disruptive technologies (3D printing) and SRM cascading recycling systems (phosphorus extraction from wastewater prior to sewage sludge use in construction).

Keywords: CINDERELA project, circular business model, secondary raw materials, waste recycling, urban construction.



DOI https://doi.org/10.18690/978-961-286-353-1.17 ISBN 978-961-286-353-1

1 Introduction

The construction sector is one of the largest consumers of raw materials; therefore, an increase in raw material efficiency in construction is of great importance. According to OECD data (2018), the construction sector is expected to more than double between 2017 and 2060 globally, with its use of materials increasing to almost 84Gt in 2060. In Europe, the construction sector, including buildings, consumes about half of all raw materials and energy extracted and one third of the total amount of water used. At the same time, construction waste accounts for one third of all waste generated (European Commission, 2014). Construction is also an important economic sector, representing ca. 9 % of Europe's GDP and directly employing 18 million Europeans (European Commission, 2019). With these numbers, the transition of the construction sector from linear to circular is a major step towards making the European economy more sustainable.

The construction sector presents enormous potential for implementing circular economy business models that will facilitate a decrease in its environmental impact and encourage resourceful use of materials. Such an approach envisages, among other things, the use of secondary raw materials (SRM) recovered by recycling of different waste types generated in urban areas, including construction and demolition waste (CDW), industrial waste, waste from extractive and processing activities and some waste types generated by municipal sector (for example, sewage sludge from urban wastewater treatment, and heavy fractions remaining from municipal waste treatment). This approach provides a pathway to new consumption patterns and value chains relevant for urban areas where valuable raw materials can be recovered for construction purposes. New patterns include the use of cascading recycling approaches, e.g. extraction of critical raw materials (CRM) such as phosphorus (P) from wastewater before it enters the treatment plant, so that the sewage sludge as process residue can be later used as SRM for construction without losing the value of the phosphorus contained in it. Other approaches combine techniques offered by disruptive technologies such as robotic 3D printing to use plastic recycled as SRM from municipal waste for manufacturing construction

A. Mauko Pranjić, K. Mezga, P. Oprčkal, S. Meža, A. Mladenovič, I. Ratman-Kłosińska,
M. Matejczyk, T. Ploj, M. Kadić, A. Garcia Uriarte, P. Menger, D. Huitema, N. Absmann,
A. Sabbe, A. van Timmeren, M. Conthe Calvo, V. Janjić, I. Osmokrović, M. Conci, M.
Donelli, E. Pusceddu, M. Bertetti, I. Vilela Fraile, L. Gullón & S. Rosado:
The H2020 CINDERELA Project — A New Circular Economy Business Model for More
Sustainable Urban Construction

elements of advanced geometries and design as elements of small urban infrastructure.

Building and infrastructure construction in urban regions are very important activities linked with intense urbanisation and consequent expansion of cities. It is estimated that by the year 2050, nearly 86 % of the world's population in developed regions (64 % in less developed regions) is expected to live in urban areas (UN DESA, 2012). This means intense investments in infrastructure and buildings and revitalisation of urban space, including transformation of degraded areas. Many urban centres across Europe are already the scene of intensive construction works because of increasing numbers of inhabitants and services. At the same time, cities are geographically and administratively closed units (using short transport routes), and generate large quantities of various waste types, with a potential of the use as SRM for construction. All these features make urban environments an excellent "living laboratory" for verifying the effectiveness of sustainable construction and circular economy models based on SRM.

Sustainable urban construction based on closed local raw material circulation from waste to products is the main topic of the CINDERELA research and demonstration project entitled New Circular Economy Business Model for More Sustainable Urban Construction.

2 The CINDERELA project

2.1 About the project

CINDERELA is a 4-year large scale demonstration project implemented under the flagship of the European Union's Horizon 2020 research and innovation programme (contract no. 776751). The goal of the project is to make circular economy an industrial concept in the construction sector. CINDERELA is coordinated by the Slovenian National Building and Civil Engineering Institute and involves 13 partners from seven European countries (Slovenia, Spain, Italy, Poland, Serbia, The Netherlands and Croatia): NIGRAD, Foundation Gómez Pardo,

TECNALIA, AEDHE, Polo Pordenone, Opencontent, Bocconi University, IETU, BEXEL, TUDelft, KplusV and 6.MAJ. A multidisciplinary consortium jointly designs and demonstrates under real conditions a CINDERELA circular economy business model (CinderCEBM) based on the manufacturing and application of SRM-based construction materials which are recovered from local waste streams.

2.2 Building a new circular business model – CinderCEBM

Companies need a solid framework for creating and innovating circular business models that combine economic profits with environmental and social values. A CinderCEBM is the central theme of the CINDERELA project that, on one hand addresses the environmental challenge of waste management, and on the other offers sustainable and profitable urban construction solutions for businesses based on the recycling of various wastes. With appropriate technologies that are sufficiently simple, economically viable, financially acceptable and technically compatible with existing construction and production equipment, waste (Figure 1) can be recycled into SRM-based construction products that have the appropriate characteristics for their intended use. New circular business models have a better environmental footprint than conventional products, while offering a similar price point. In this respect, the most promising SRM-based construction products are recycled and manufactured aggregates, building composites (green concrete, geotechnical composites, asphalt) and recycled soil. The largest quantities of recycled waste can be used in low grade applications, such as geotechnical embankments and fillings. On the other hand, upcycling (recycling into products of higher quality or value than original, such as green concrete) is considered as more desirable; however, the uptake of waste is generally lower than in the case of downcycling.

A. Mauko Pranjić, K. Mezga, P. Oprčkal, S. Meža, A. Mladenovič, I. Ratman-Kłosińska,
M. Matejczyk, T. Ploj, M. Kadić, A. Garcia Uriarte, P. Menger, D. Huitema, N. Ahsmann,
A. Sabbe, A. van Timmeren, M. Conthe Calvo, V. Janjić, I. Osmokrović, M. Conci, M.
Donelli, E. Pusceddu, M. Bertetti, I. Vilela Fraile, L. Gullón & S. Rosado:
The H2020 CINDERELA Project — A New Circular Economy Business Model for More
Sustainable Urban Construction



Figure 1: Construction and demolition waste (CDW) is one the most voluminous waste streams in the urban environment.

In support of the CinderCEBM, circular business model, the project is developing a multiservice CINDERELA "one-stop-shop," called CinderOSS. CinderOSS combines many different services that can help entrepreneurs implement and accelerate their waste-to-construction product circular business model, as well as helping governments and other stakeholders in participating or stimulating these business models. CinderOSS offers information on product development services, market creation, including complementary measures, proposals for new regulatory and administrative procedures and information about the production and construction of circular construction products with the associated Building Information Modelling (BIM) libraries. Finally, CinderOSS will include a digital marketplace called the CINDERELA Digital Business Ecosystem (CinderDBE), where waste-to-product flows are traced, offering transparency and an efficient environment for stakeholders to meet and trade materials.

Both CinderCEBM and CinderOSS will be tested in real environments in six European countries (Spain, Italy, Slovenia, Croatia, Poland and the Netherlands). Through the basic conditions for the implementation of a business model, such as the prices of waste handling and of SRM, the availability of materials, nontechnological barriers (such as legislation and social acceptance of SRM) and incentives, will be checked.

2.3 Assessing waste-to-resource opportunities in urban and peri-urban areas

Getting the right information on the types, location, availability and flows of SRM as well as the actors behind them is a critical enabler of CinderCEBM. Using an innovative, open source, GIS supported tool named GDSE (Geodesign Decision Support Environment), CINDERELA provides a holistic protocol for material flow analysis in urban and peri-urban areas. The tool is used to predict optimal waste-toproduct solution based on waste availability, quantity and location. For example, the tool combines a list of the NACE (Nomenclature des Activités Économiques dans la Communauté Européenne) codes of the economic activities with the appropriate codes from European List of Waste (LoW) and actors that generate them with the support of the ORBIS database (2018). The tool provides a material flow analysis representing waste stocks and flows (Figure 2).



Figure 2: Visualization of the outcomes of the GDSE tool - left a Sankey diagram and right a Sankey map with an activity based spatial material flow analysis for selected waste streams in Maribor and surrounding municipalities, Slovenia.

This initial step of setting a business model in a local environment using analysis of existing waste flows was tested in six selected urban areas and regions in Europe: in the Maribor area (Slovenia), Istria (Croatia), Basque country (Spain), Amsterdam Metropolitan Area (the Netherlands), Trento area (Italy) and Katowice area

A. Mauko Pranjić, K. Mezga, P. Oprčkal, S. Meža, A. Mladenovič, I. Ratman-Kłosińska,
M. Matejczyk, T. Ploj, M. Kadić, A. Garcia Uriarte, P. Menger, D. Huitema, N. Ahsmann,
A. Sabbe, A. van Timmeren, M. Conthe Calvo, V. Janjić, I. Osmokrović, M. Conci, M.
Donelli, E. Pusceddu, M. Bertetti, I. Vilela Fraile, L. Gullón & S. Rosado:
The H2020 CINDERELA Project — A New Circular Economy Business Model for More
Sustainable Urban Construction

(Poland). Within the investigated regions, the largest quantities of suitable waste streams to be used as SRM for construction products included different fractions of CDW (group 17 from LoW such as concrete, brick, ceramic, mixture of CDW, and dredging spoil), waste generated by the municipal sector (heavy fraction after municipal solid waste treatment or sewage sludge from wastewater treatment), and other waste reflecting the local economy/industry (mining waste, waste from thermal processes (slags and sludges), and others).

Another important consideration for establishing key business processes related to CinderCEBM is the valorisation of waste potential for recycling into SRM-based construction products. CINDERELA is developing a set of criteria for the recycling of waste into SRM-based products for different intended uses in construction works, such as composition, quantity, quality, availability and recyclability of waste. For three case studies (Maribor with surrounding municipalities in Slovenia, Istria in Croatia and the Madrid – Henares corridor in Spain) laboratory testing of the selected waste (Figure 3) was performed in order to valorise their potential as SRM for the construction sector.



Figure 3: Visual appearance of mixed CDW (waste code 17 09 04 from LoW), and soil and stones (waste code 17 05 04) from Slovenian and Croatian case studies.

2.4 Design, development and testing of construction works with SRMbased products

CINDERELA focuses primarily on construction works (that is, building and civil engineering works (European Parliament and the Council, 2011)) with the application of SRM-based construction products and materials such as recycled aggregates (aggregates from recycled CDW), manufactured aggregates (aggregates from recycled industrial waste, originating from processes involving thermal or other modification), building composites (such as green concrete (Figure 4) with recycled and manufactured aggregate, geotechnical composites using sewage sludge and other wastes (Figure 5), asphalt with addition of aggregate from reclaimed asphalt) and recycled soil originating from selective excavation of soil. For the recycled wastes, CINDERELA defines a set of end-of-waste (EoW) criteria (such as limiting values of elements in leachate from composites) for different intended use of final products. As a measure stimulating the demand side of the CinderCEBM, the criteria will be incorporated into the CinderOSS.



Figure 4: Green concrete with reclaimed bituminous (left) and tar asphalt (right).

A. Mauko Pranjić, K. Mezga, P. Oprčkal, S. Meža, A. Mladenovič, I. Ratman-Kłosińska,
M. Matejczyk, T. Ploj, M. Kadić, A. Garcia Uriarte, P. Menger, D. Huitema, N. Ahsmann,
A. Sabbe, A. van Timmeren, M. Conthe Calvo, V. Janjić, I. Osmokrović, M. Conci, M.
Donelli, E. Pusceddu, M. Bertetti, I. Vilela Fraile, L. Gullón & S. Rosado:
The H2020 CINDERELA Project — A New Circular Economy Business Model for More
Sustainable Urban Construction



Figure 5: Composite from sewage sludge and ash.

Laboratory test data of SRM-based construction products will serve a double purpose; firstly, to design and establish modular as well as mobile pilot production plants for recycled and manufactured aggregates, building composites and recycled soils, and secondly, to demonstrate their use in large scale pilot demonstrations involving geotechnical works for revitalisation of a degraded area, construction of small scale facilities and for road construction. To build trust and encourage designers of and investors in construction works to use SRM-based products, BIM libraries will be developed. They will include all relevant data on SRM-based construction products (including mechanical properties, type of incoming materials, chemical and mineralogical composition, and environmental impact) to enable the use of the BIM tools for designing, constructing, managing and demolishing (reuse and recycling) of construction work with SRM-based materials during their life span. Through BIM, the CINDERELA pilot demonstrations, which will be built in Slovenia, Spain and Croatia, will showcase the added value of using SRM-based construction materials compared to traditional raw material based products.

Demo 1: Extraction of valuable materials - phosphorus extraction

Phosphorous (P) is one of 27 CRMs in Europe for which supply security is at risk and economic importance is high. The current P extraction approach is usually implemented in centralised wastewater treatment plants (or up the chain), as a measure to reduce the operational and maintenance costs of the utility by preventing the clogging of the wastewater collection and treatment infrastructure with struvite. However, the approach is not wide-spread, because the recovered P-product is relatively new to the market and poses problems for utilities in terms of storage, valorisation and market uptake. In the CINDERELA project, P, along with other nutrients important for agriculture, is recovered directly from separately collected urine in the form of liquid fertilizer. The complete nutrient recovery (CNR) system consists of stabilization, purification and concentration of the urine. A CNR approach has a number of important advantages nitrogen and other valuable secondary nutrients (boron, iron, nickel, etc.) are recovered along with the phosphate; the full waste is treated, with full removal of micropollutants, pathogens, and bad odour from urine; a liquid high-grade organic fertilizer is produced, which can be used directly for hydroponics/urban farming, and distilled water is obtained as a valuable by-product. After the CNR process, urine enters the sewage path again where sewage sludge without the extracted P and other nutrients can still be recycled into SRM-based construction products, generating value as input material. Modular and mobile units for extraction of nutrients from urine will be tested in Amsterdam (The Netherlands) and in Maribor (Slovenia). To showcase the full cascading recycling approach, sewage sludge, after phosphorus extraction, will be applied to production of SRM-based construction materials (geotechnical composite) at the Umag demonstration pilot.

Demo 2: Pilot production of SRM-based construction products

Some recycled materials, such as recycled aggregates, are already used in European construction; nevertheless their use, especially in countries with an abundance of natural aggregate, has not yet become an everyday business. The potential of many other waste materials remains unexplored, in particular when taking into A. Mauko Pranjić, K. Mezga, P. Oprčkal, S. Meža, A. Mladenovič, I. Ratman-Kłosińska,
M. Matejczyk, T. Ploj, M. Kadić, A. Garcia Uriarte, P. Menger, D. Huitema, N. Ahsmann,
A. Sabbe, A. van Timmeren, M. Conthe Calvo, V. Janjić, I. Osmokrović, M. Conci, M.
Donelli, E. Pusceddu, M. Bertetti, I. Vilela Fraile, L. Gullón & S. Rosado:
The H2020 CINDERELA Project — A New Circular Economy Business Model for More
Sustainable Urban Construction

consideration their immense possibilities in terms of mass flows and synergic effects for production of new construction composites.

Three pilot production plants of SRM-based construction products in Maribor, Umag and Madrid will be developed as part of the CinderCEBM demonstration. In these pilot plants, different types of wastes will be recycled into SRM-based construction products, which will be later used in construction pilot demonstrations. All pilot plants are designed to be modular and mobile with capacities of 10,000 tons/year on average and a maximum of 70 tons/day. They will be a combination of crushing, screening and mixing devices combined, depending on the type of the final product.

3D printing of street furniture with recycled plastics from municipal solid waste is another demonstration of innovative technology and use of materials within the CINDERELA project. To demonstrate the potential of this material and technology together, CINDERELA will develop a 3D printed building component that will showcase the principles and benefits of circular economy, especially when focusing on the manufacturing process with the use of disruptive technologies. This will be a small scale project, demonstrating the potential development of production of SRMbased construction materials in the future.

<u>Demo 3: Large-scale demonstrations of construction with SRM-based</u> <u>construction products</u>

In order to demonstrate the business case and technical feasibility, large scale construction pilots with SRM-based construction products will be implemented in Maribor, Umag and Madrid, using sustainable building materials produced during the project. BIM will be utilized to support all phases of designing (Figure 6), constructing, using and reusing/recycling of construction works (or part of them), from the preliminary planning of work to facility management and deconstruction. For each of the projects, case-study analyses – clash detection, quantity take-offs, 4D (model-based time planning), 5D (model-based time and cost planning), and 6D facility maintenance (model-based maintenance planning) will be performed.



Figure 6: Planning of information-supported pilot construction in the CINDERELA project.

Geotechnical works

The largest quantity of SRM-based construction products replacing virgin materials can be utilized in the case of different geotechnical works. Revitalization of degraded urban areas through geotechnical works will be performed using the following steps: (1) site surveying and sampling, (2) analysis of existing materials (natural soils, anthropogenic soil, including dumped materials), (3) excavation and separation of waste materials, (4) recycling of waste and production of SRM-based construction products, and (5) construction and revitalization of the site. SRM-based material will be placed in layers and compacted in order to reach adequate intrinsic properties for geotechnical works. During the revitalization process, monitoring equipment will be installed for monitoring of eluates in piezometers. The monitor readings will be recorded directly into the BIM.

Construction of demo facilities

In Maribor, a one storey facility will be built with the use of SRM-based construction products. The facility will include a conference room, a laboratory, offices, toilet facilities and a stairway to the roof. The floor and the walls will be made of green concrete made with recycled aggregates. The foundation floor will be prepared and

222

A. Mauko Pranjić, K. Mezga, P. Oprčkal, S. Meža, A. Mladenovič, I. Ratman-Kłosińska,
M. Matejczyk, T. Ploj, M. Kadić, A. Garcia Uriarte, P. Menger, D. Huitema, N. Ahsmann,
A. Sabbe, A. van Timmeren, M. Conthe Calvo, V. Janjić, I. Osmokrović, M. Conci, M.
Donelli, E. Pusceddu, M. Bertetti, I. Vilela Fraile, L. Gullón & S. Rosado:
The H2020 CINDERELA Project — A New Circular Economy Business Model for More
Sustainable Urban Construction

fortified with the use of recycled soil; thermal insulation under the foundation will be made of recycled brick or glass. In Umag, a fence surrounding a degraded area will be constructed using modular prefabricated building blocks made of green concrete with recycled and manufactured aggregate, and in Madrid, a small facility will be constructed as a ground floor building. It will serve as the main control room for delivery of waste and the entrance to a waste treatment plant. The construction materials will include reused construction elements (doors and windows) and recycled aggregates recovered from the demolition of an existing building.

Road construction

SRM-based construction products developed in the CINDERELA project can successfully replace virgin materials and decrease the environmental impact of road construction/maintenance works. Recycled aggregate is excellent material for subgrade and base courses, and manufactured aggregates and reclaimed asphalt for surface courses. In Maribor, Umag and Madrid, a road construction project will take place after revitalization of degraded areas is completed.

2.5 Environmental, economic and social assessment

To ensure that the business model will deliver not only economic but also environmental and social added value, CinderCEBM will be assessed using life cycle approaches including environmental Life Cycle Assessment (LCA) and related methods such as Social Life Cycle Assessment (S-LCA) and Life Cycle Costing (LCC). This comprehensive assessment will help to evaluate how the new solutions proposed in CinderCEBM compare with the current "business as usual" situation in terms of environmental added value, economic viability and social implications. To facilitate their marketability, confirm innovation and performance along with the environmental benefits, new SRM-based construction products and technologies will also be assessed using the environmental technology verification (ETV) approach.

2.6 The role of stakeholders in the CINDERELA model and service

In order to further improve the model and service, stakeholders, actors and potential end-users for CinderCEBM and CinderOSS will be engaged. Through project activities, different target groups can acquire new knowledge and skills for more sustainable waste management and their use in construction in urban environments. Local, regional and national decision makers will be provided with information on new circular services and materials, value chains and decision-making tools. Policy makers will receive information about various barriers and incentives and proposals for new incentives for the circular economy. Waste holders will become more competitive by introducing new business models that include recycling waste into construction products rather than landfilling. Waste managers and processors as well as construction companies, as potential users of CinderOSS, will be the first to receive information on how a business model works in different environments, thereby increasing the chances of setting up a comparable model in their own environment. Construction companies, the most important players in sustainable urban construction, will receive information on the production of sustainable construction products based on SRM, their properties, methods of installation and maintenance, as well as BIM-supported tools for more modern and faster construction. The project is also of interest to the general public, which the partners see as an important player in the implementation of new circular models, since it depends to a large extent on their active participation and acceptance.

3 Conclusions

Sustainable urban construction, based on the closed local circulation of raw materials from waste-to-products, is an opportunity for many actors in urban areas, as well as for the general public. However, despite the potential advantages of circular approaches in the construction sector involving recovery and use of SRM from urban waste streams, it is still a challenging task to implement for many companies because of lack appropriate knowledge, technologies, good practices and incentives. For Europe, the CINDERELA project brings many new developments, innovations and a solid knowledge base that can stimulate demand and supply, and encourage A. Mauko Pranjić, K. Mezga, P. Oprčkal, S. Meža, A. Mladenovič, I. Ratman-Kłosińska,
M. Matejczyk, T. Ploj, M. Kadić, A. Garcia Uriarte, P. Menger, D. Huitema, N. Absmann,
A. Sabbe, A. van Timmeren, M. Conthe Calvo, V. Janjić, I. Osmokrović, M. Conci, M.
Donelli, E. Pusceddu, M. Bertetti, I. Vilela Fraile, L. Gullón & S. Rosado:
The H2020 CINDERELA Project — A New Circular Economy Business Model for More
Sustainable Urban Construction

actors with circular ambitions involved in the construction sector to take action and bring circular business models into real life. In Slovenia, where the circular economy is one of the main domains of Smart Specialisation Strategy, testing the new business models and services that will emerge from the project is of particular interest to city managers, as well as industry and entrepreneurs, because of the country's small size in terms of geography and administration, as well as openness to new, more sustainable products and services. In this way, Slovenia can further strengthen its position as a frontrunner in the transition from linear to circular economy providing an example to other European cities, and becoming an important player and competitor in global sustainable development.



This project has received funding from the European Union's Horizon 2020 research and innovation program under grant agreement No 776751



References

- European Commission. (2014). Resource efficiency opportunities in the building sector. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions, COM(2014) 445 final, Brussels.
- European Commission. (2019). New rules for greener and smarter buildings will increase quality of life for all Europeans. https://ec.europa.eu/info/news/new-rules-greener-and-smarter-buildingswill-increase-quality-life-all-europeans-2019-apr-15_en
- European Parliament and the Council. (2011). Laying down harmonized conditions for the marketing of construction products and repealing. Council Directive 89/106/EEC, Regulation (EU) No 305/2011, 9 March 2011.
- OECD. (2018). Global Material Resources Outlook to 2060: Economic Drivers and Environmental Consequences, OECD Publishing, Paris. doi.org/10.1787/9789264307452-en
- ORBIS database. (2018). https://www.bvdinfo.com/en-gb/our-products/data/international/orbis
- UN DESA. (2012). World Urbanization Prospects: The 2011 Revision, United Nations, Department of Economic and Social Affairs, Population Division, New York.

226

AN INVESTIGATION OF WASTE MATERIAL PARAMETERS DURING PRETREATMENT

Robert Hren, Aleksandra Petrovič, Lidija Čuček & Marjana Simonič

University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: robert.hren1@student.um.si, aleksandra.petrovic@um.si, lidija.cucek@um.si, marjana.simonic@um.si

Abstract Pretreatment of biomass and waste is important for its efficient utilization as biofuels and/or biochemicals. In this study, two different pretreatment techniques are discussed: physico-chemical (thermal, at elevated temperature) and biological (fermentation) with the addition of rumen fluid. Analyses were performed on sewage sludge, riverbank grass (Typha latifolia) and their combination (ratio 1:1). Various parameters were measured in the liquid phase, such as chemical oxygen demand (COD), amounts of nitrogen, phosphorus and potassium (NPK analysis), total organic carbon (TOC), conductivity and pH value, and composition of CH4, O2, CO2 and H2S in the gas phase. The values of parameters in the liquid phase were analyzed before and after pretreatment, while in the gas phase parameters were measured only after pretreatment.

Keywords:

Waste materials, sewage sludge, riverbank grass, pretreatment of waste, determination of parameters.



DOI https://doi.org/10.18690/978-961-286-353-1.18 ISBN 978-961-286-353-1

1 Introduction

Lignocellulosic biomass is an abundantly available renewable resource and includes agricultural and forest residues, energy crops and some components of municipal, agricultural, forestry and various industrial waste (Soccol *et al.*, 2019). Because of its wide availability, its conversion in biorefineries into biofuels, biochemicals and biopolymers has attracted much attention. Lignocellulosic materials are mainly composed of cellulose, hemicellulose and lignin and form complex cell walls which are resistant to degradation (Oh *et al.*, 2015). Pretreatment can help in delignification of biomass while making biomass more susceptible to saccharification by improving its digestibility (Hendriks *et al.*, 2009). Various pretreatment techniques exist, such as chemical, physico-chemical, physical and biological and integrated processes combining different techniques (Kumar *et al.*, 2017).

The goal of this study is to explore the effects of different pretreatment methods on the values of analyzed parameters. Two different pretreatment techniques were applied: biological treatment using rumen fluid (38.6 °C, duration of 8 days) and physico-chemical treatment with elevated temperature (80 °C, duration of 5 days). Various parameters were tested in the liquid (chemical oxygen demand – COD, amounts of nitrogen, phosphorus and potassium – NPK, total organic carbon – TOC, conductivity and pH value) and gas phases (composition of CH₄, O₂, CO₂ and H₂S). Cuvette tests were used for measuring the values of most parameters (COD, NPK, NH₃, and TOC) before and after pretreatment, sensors were used for measurements of conductivity and the pH value, and gas analyzers were used for measuring concentrations of gases.

2 Materials and methods

The following materials were used:

- Riverbank grass Typha latifolia;
- Sewage sludge;
- Rumen fluid.

Samples were prepared in triplicate with all samples containing 6 wt.% of solids based on average dry matter (DM) content. The following set of samples were analyzed:

- Untreated samples (denoted as "Before" in Figures);
- Riverbank grass (denoted as "T");
- Sewage sludge (denoted as "B");
- Grass and sewage sludge in a ratio of 1:1 (denoted as "T+B");
- Sewage sludge and 50 ml of rumen fluid (denoted as "B+V");
- Riverbank grass and 50 ml of rumen fluid (denoted "T+V");
- Grass and sewage sludge in a 1:1 ratio with 50 ml of rumen fluid (denoted as "T+B+V").

Two pretreatment methods were tested, pretreatment with the addition of rumen fluid and thermal pretreatment. All batch assays were maintained at mesophilic conditions in a heated bath filled with deionized water. Temperature was set at rumen temperature of 38.6 °C (Turbill *et al.*, 2011) by using a Thermo ScientificTM SC100 immersion circulator. Biological pretreatment was performed for 8 days, while thermal pretreatment was performed for 5 days at 80 °C.

Several parameters were tested in the liquid phase, such as chemical oxygen demand – COD, nitrogen, phosphorus and potassium – NPK, ammonia content, total organic carbon – TOC, conductivity and pH value. For the determination of most parameter values before and after pretreatment, samples were firstly diluted and measured with QUANTOFIX® test strips, and further analyses were performed using a PF-12^{Plus} photometer and NANOCOLOR® tube tests (COD, NPK, NH₃ and TOC). Pasco sensors were used for measurements of conductivity and the pH value, and an Optima7 Biogas gas analyzer for measuring concentrations of gases in the gas phase (CH₄, CO₂, O₂ in %, and H₂S in ppm). Dry solids were determined by drying a certain mass of material to constant weight. C/N ratio was determined according to Eq. (1):

$$C/N = \frac{TOC}{TN} \tag{1}$$

3 Results and discussion

Figure 1 shows the results of measurement of NPK concentration. The highest NPK values were obtained for the combination of grass and sludge. This sample has the highest value of potassium, as well as high values of nitrogen and phosphorus. The smallest values were obtained for untreated samples and grass samples. It is notable that NPK content decreased with the addition of rumen fluid. With thermal pretreatment (80 °C), concentrations of P and K decreased, while the concentration of N increased. Similar results in terms of N concentration were obtained previously (Risberg *et al.*, 2013). For the purpose of further digestate use as fertilizer, a combination of grass and sludge is suggested because of its higher NPK values. However, an important consideration for digestate's further use are the heavy metals, pathogens and persistent organic pollutants (POPs) contained in sludge (Zhang *et al.*, 2017).



Figure 1: NPK concentrations.

Figure 2 further shows the C/N ratio, which is important for optimal growth of microorganisms (Bedoić *et al.*, 2019). The highest value is exhibited by rumen fluid and grass before pretreatment. The C/N ratio for all pretreated samples is between 4 and 7. For optimal growth of microorganisms, the C/N ratio of feedstocks should be between 20 and 30; otherwise, inhibition could occur (Wang *et al.*, 2019). C/N ratios considerably different than those suggested have been reported previously (Risberg *et al.*, 2013).



Figure 2: C/N ratio.

Figure 3 shows the composition of CH₄, CO₂, O₂ (in %) and H₂S (in 1/100 ppm) in the gas phase. CH₄ increased most significantly when rumen fluid was added to the samples. The highest CH₄ value was obtained in B+V samples as a result of fermentation, and thus the growth rate of methanogenic bacteria increased (Budiyono *et al.*, 2014). At higher temperatures (80 °C) no CH₄ was observed, as fermentation typically occurs up to 65 °C (Sunny & Joseph, 2018). Further, it could be seen that the most H₂S was produced in grass samples with the addition of rumen fluid. Higher H₂S concentrations are mainly the results of bacterial degradation under anaerobic conditions (Long *et al.*, 2016).



Figure 3: Gas composition.

4 Conclusions

The aim of this study was to test different pretreatment methods and to analyze how pretreatment influences the values of parameters. Two pretreatment methods were applied, biological and thermal pretreatment; sewage sludge and riverbank grass (*Typha latifolia*) were used as raw materials.

The results show that COD values increased during pretreatment, with the riverbank grass showing the highest increase. The highest NPK values were observed in samples of combined sewage sludge and riverbank grass. With the addition of rumen fluid, the concentration of K increased significantly, while samples containing sewage sludge showed higher values of P and N when compared to grass samples. Also, the concentration of ammonia was especially high in samples which contained sewage sludge; however, at higher temperatures, the concentration of ammonia decreased in all samples. In the samples containing sewage sludge and/or rumen fluid pretreated at 38.6 °C, significant concentrations of CH₄ were observed in the gas phase. Also, concentrations of H₂S were significant, especially in samples which contained rumen fluid. On the other hand, when pretreatment was performed at 80 °C, no CH4 and insignificant amounts of H2S were produced. For all samples containing grass, a significantly acidic environment was established, and conductivity increased when pretreatment was performed at 38.6 °C. Most of the parameters changed during pretreatment; however, the advantage of specific pretreatment techniques should be further tested for production of bioproducts.

Acknowledgments

The authors acknowledge financial support from the Slovenian Research Agency (research core funding No. P2-0412 and P2-0032).

References

- Bedoić, R., Čuček, L., Ćosić, B., Krajne, D., Smoljanić, G., Kravanja, Z., Ljubas, D., Pukšee, T., & Duić, N. (2019). Green biomass to biogas–A study on anaerobic digestion of residue grass. *Journal of Cleaner Production, 213*, 700-709.
- Budiyono, B., Widiasa, I. N., Johari, S., & Sunarso, S. (2014). Increasing biogas production rate from cattle manure using rumen fluid as inoculums. *International Journal of Science and Engineering*, 6(1), 31-38.
- Hendriks, A., & Zeeman, G. (2009). Pretreatments to enhance the digestibility of lignocellulosic biomass. *Bioresource Technology*, 100(1), 10-18.

233

- Kumar, A. K., & Sharma, S. (2017). Recent updates on different methods of pretreatment of lignocellulosic feedstocks: a review. *Bioresources and Bioprocessing*, 4(1), 7.
- Long, Y., Fang, Y., Shen, D., Feng, H., & Chen, T. (2016). Hydrogen sulfide (H2S) emission control by aerobic sulfate reduction in landfill. *Scientific Reports*, 6, 38103. doi:10.1038/srep38103
- Oh, Y. H., Eom, I. Y., Joo, J. C., Yu, J. H., Song, B. K., Lee, S. H., Hong, S. H., & Park, S. J. (2015). Recent advances in development of biomass pretreatment technologies used in biorefinery for the production of bio-based fuels, chemicals and polymers. *Korean Journal of Chemical Engineering*, 32(10), 1945-1959. doi:10.1007/s11814-015-0191-v
- Risberg, K., Sun, L., Levén, L., Horn, S. J., & Schnürer, A. (2013). Biogas production from wheat straw and manure–impact of pretreatment and process operating parameters. *Bioresource Technology*, 149, 232-237.
- Soccol, C. R., Faraco, V., Karp, S. G., Vandenberghe, L. P., Thomaz-Soccol, V., Woiciechowski, A. L., & Pandey, A. (2019). Lignocellulosic bioethanol: current status and future perspectives. In *Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels* (pp. 331-354): Elsevier.
- Sunny, S. M., & Joséph, K. (2018). Review on factors affecting biogas production. International Journal For Technological Research In Engineering, 5(9), 2347-4718.
- Turbill, C., Ruf, T., Mang, T., & Arnold, W. (2011). Regulation of heart rate and rumen temperature in red deer: effects of season and food intake. *Journal of Experimental Biology*, 214(6), 963-970.
- Wang, X., Yang, R., Guo, Y., Zhang, Z., Kao, C. M., & Chen, S. (2019). Investigation of COD and COD/N ratio for the dominance of anammox pathway for nitrogen removal via isotope labelling technique and the relevant bacteria. *Journal of Hazardous Materials*, 366, 606-614.
- Zhang, X., Wang, X.-q., & Wang, D.-f. (2017). Immobilization of heavy metals in sewage sludge during land application process in China: A review. *Sustainability*, 9(11), 2020.

ANAEROBIC CO-DIGESTION OF SEWAGE SLUDGE AND *TYPHA LATIFOLIA* AND THE IMPACT OF CATTLE RUMEN FLUID ON BIOGAS PRODUCTION

Aleksandra Petrovič, Lidija Čuček &

Marjana Simonič

University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: aleksandra.petrovic@um.si, lidija.cucek@um.si, marjana.simonic@um.si

Abstract This study investigated the potential for anaerobic codigestion of sewage sludge and the Typha latifolia plant in biogas production. The impact of cattle rumen fluid added to reaction mixtures was also investigated regarding biogas production. Four different combinations of these substrates were tested. The anaerobic digestion studies were performed in 1 L batch reactors under mesophilic conditions, with a hydraulic retention time of 55 days. The results showed that co-digestion of sewage sludge and the Typha latifolia plant significantly enhanced biogas production in comparison with mono-digestion of sewage sludge, since the total amount of biogas produced increased by almost 50 %, from 385 up to 578 mL of biogas/g of dry matter. The highest amount of biogas (614 mL/g of dry matter) was produced when cattle rumen fluid was added to the mixture, suggesting that rumen microorganisms exerted a positive effect on substrate degradation.

Keywords:

anaerobic co-digestion, biogas production, sewage sludge, *typha latifolia*, cattle rumen fluid



DOI https://doi.org/10.18690/978-961-286-353-1.19 ISBN 978-961-286-353-1

1 Introduction

Sewage sludge (SS), a by-product of wastewater treatment, could, if not properly treated, create huge environmental risks, given the presence of pollutants such as pathogens, heavy metals and dioxins. On the other hand, it is rich in nutrients (nitrogen, phosphorus, potassium, etc.), and thus offers great potential for recovering these nutrients to become valuable products (Kacprzak *et al.*, 2017). In Europe, about $10 \cdot 10^6$ t/y dry matter (DM) of sewage sludge is produced (Milieu Ltd, 2008). As a result of more stringent requirements for water treatment, its production is increasing in all European countries. Thus, there is increasing pressure and challenge to find better treatment and disposal methods for this waste (Bianchini *et al.*, 2016).

Commonly used technologies for energy and/or resource recovery from sewage sludge include anaerobic digestion, incineration, pyrolysis and gasification (Raheem *et al.*, 2018). Anaerobic digestion is among the more widely employed processes for sludge stabilization, owing to its relatively high methane production capacity, lower energy consumption, and the ability to deactivate pathogens in biomass (Montalvo *et al.*, 2017). In order to balance the C/N ratio, which significantly impacts biogas production, sewage sludge could be co-digested with various organic substrates such as a range of food wastes (Mehariya *et al.*, 2018), animal wastes (Borowski *et al.*, 2013) and other organic wastes (Elalami *et al.*, 2019). The *lignocellulosic* plant *Typha latifolia*, which grows in or near water and is widely used for wetlands to remove nitrate, ammonia and heavy metals from (waste)water, represents one of the renewable substrates that could be applied in anaerobic co-digestion (Hu *et al.*, 2006).

Anaerobic digestion performance depends on many factors, especially since methanogens, the microorganisms mainly responsible for the methane production during anaerobic digestion, are sensitive to contaminants and can easily be inhibited (Paulo *et al.*, 2015). A similar microbial consortium can be found in the stomachs of ruminant animals (Neshat *et al.*, 2017). Various authors have claimed that rumen microbial cultures have shown good prospects for anaerobic digestion of lignocellulosic materials because of their ability to increase the hydrolysis of lignocellulosic substrates (Čater *et al.*, 2014), such as cattail (Hu & Yu, 2006) and corn straw (Jin *et al.*, 2018).

The aim of this study was to examine the potential of sewage sludge and *Typha latifolia* grass (cattail) for anaerobic co-digestion and to investigate the impact of cattle rumen fluid (microbial consortium) on biogas production.

2 Material and methods

2.1 Substrate characteristics

Sewage sludge containing 18.47 % total dry solids was taken from a local municipal wastewater treatment plant, while the *Typha latifolia* grass was gathered near the Dravinja riverbank. The inoculum was obtained from a local biogas plant that produces biogas from poultry manure, and rumen fluid was acquired from a nearby slaughterhouse. Before being used in the experiments, the rumen fluid was filtered through fabric to remove larger particles. The *Typha latifolia* grass was cut into pieces (with a size of approximately 0.8 cm x 0.4 cm).

The basic characteristics of sewage sludge, *Typha latifolia* grass, inoculum and cattle rumen fluid were determined before performing anaerobic digestion, such as total dry solids content (TS), water content, total nitrogen (TN) content, total phosphorus (TP) content and total carbon (TC) content (Table 1). The following analytical methods were used: SIST EN 16168:2013 for determining total nitrogen content, SIST EN 1885:2009 for the total phosphorus content, SIST EN 13137:2002 for total carbon content and SIST EN 14346:2007 for the dry matter content.

Parameter	Sewage sludge	<i>Typha</i> latifolia grass	Inoculum	Cattle rumen fluid
Total dry solids (TS, %)	18.47	11.11	8.02	2.42
Water content (%)	81.53	88.89	91.98	97.58
Volatile solids (% TS)	80.06	/	/	/
TN (% TS)	7.83	3.48	3.65	3.67
TP (% TS)	0.94	0.30	0.33	0.06
TC (% TS)	45.71	46.65	28.61	31.27

Table 1: Basic characteristics of the substrates.

2.2 Anaerobic digestion studies

The anaerobic digestion studies were performed in 1 L batch reactors with a working volume of 600 mL and a retention time of 55 days. Four different reaction mixtures were prepared in two parallel batches (Table 2):

- Mixture 1 containing inoculum and sewage sludge (samples S1, S2) in a ratio of 1:1;
- Mixture 2 consisting of inoculum, sewage sludge and the *Typha latifolia* grass (samples SG1, SG2) in a ratio of 2:1:1;
- Mixture 3 containing a mixture 1 + 50 mL of cattle rumen fluid (samples SR1, SR2);
- Mixture 4 containing a mixture 2 + 50 mL of cattle rumen fluid (samples SGR1, SGR2).

Reaction mixture	Inoculum (g TS)	Sewage sludge (g TS)	<i>Typha latifolia</i> grass (g TS)	Cattle rumen fluid (mL)
S1, S2 (Mixture 1)	15	15	/	/
SG1, SG2 (Mixture 2)	15	7.5	7.5	/
SR1, SR2 (Mixture 3)	15	15	/	50
SGR1, SGR2 (Mixture 4)	15	7.5	7.5	50

Table 2: The composition of reaction mixtures.

30 g of total solids per 500 g of liquid were added to each reactor. Thus, the dry matter content of each reaction mixture was 6 wt.%. For all mixtures 1-4, the ratio between inoculum and substrates for anaerobic digestion was 1:1. (15 g: 15 g). To achieve a dry matter concentration of 6 wt.%, a buffer solution (Angelidaki *et al.*, 2009) was added to each reaction mixture. After preparing the mixtures, the reactors (filter flasks for vacuum use, sealed with PTFE septa) were placed into a heating bath and flushed with inert argon gas for about 30 s to achieve anaerobic conditions. A constant temperature of 42 °C (mesophilic conditions) was maintained by using an immersion circulator (Thermo ScientificTM SC100). The flasks were hand-mixed daily for about 30 s.

Biogas production was measured daily by a water displacement method, while pH and conductivity were measured periodically. Wireless pH and conductivity sensors (Pasco) were used for this purpose, whereas around 4 mL of the samples were taken for analysis from the reactors using a 5 mL syringe with a needle. After the analysis, the samples were returned to the flasks. The composition of biogas produced was tested with an Optima 7 Biogas analyser.

3 Results and discussion

Anaerobic digestion depends on various operating parameters such as temperature, pH, system configuration, substrate composition and hydraulic retention time (Fang *et al.*, 2020). In the following, the results obtained in mono- and co-digestion of sewage sludge (SS) and *Typha latifolia* grass are presented in regard to some of these operating parameters.

3.1 Biogas production and the effect of hydraulic retention time (HRT)

Hydraulic retention time significantly affects biogas production, digestion rate, microbial flux and the C/N ratio of the digestate (Mehariya *et al.*, 2018). The volume of biogas produced in regard to hydraulic retention time in mono-digestion of sewage sludge is shown in Figure 1a) (samples S1 and S2), while results from the co-digestion experiments are shown in Figures 1b), c) and d).



Figure 1: Volume of biogas produced regarding HRT in the case of: a) mono-digestion of SS; b) co-digestion of SS and *Typha latifolia* grass; c) co-digestion of SS and rumen fluid; and d) co-digestion of SS, grass and rumen fluid.

The majority of the biogas was produced in the first 15 days of the experiment; between days 16 and 35, significantly smaller amounts of biogas were measured, while after 35 days, the values were almost negligible. In the co-digestion of SS and rumen fluid (samples SR1, SR2; Fig. 1c), characteristics similar to those in the monodigestion of SS were observed, except that between days 10 and 20, slightly more biogas was produced. This suggests that rumen fluid microorganisms and enzymes did contribute significantly to sludge decomposition.

When SS was co-digested with the *Typha latifolia* grass (samples SG1, SG2; Fig. 1b), up to 50 % higher biogas yield was noted, as compared to the SR1 and SR2 samples or to the S1 and S2 samples. The reason for improved biogas yield could be the improved C/N ratio of the substrate with the addition of grass. Co-digestion with organic substrates like *Typha latifolia* in comparison with mono-digestion offers better digestibility, better nutrient availability (Grosser *et al.*, 2018), increased pH buffering capacity and dilution of toxic substances such as ammonia (Fang *et al.*, 2020).
The highest biogas yield was achieved with the mixture of SS, grass and rumen fluid (samples SGR1, SGR2; Fig. 1d). For this sample, even after 25 days of the experiment, biogas yield was still relatively high. The microbial communities in rumen fluid increase the hydrolysis of lignocellulosic substrates and the production of fatty acids (Čater *et al.*, 2014). Rumen microorganisms comprise ~10⁸-10¹⁰ methanogens/g, with great potential in biogas production (Jin *et al.*, 2018). The systems containing rumen microorganisms showed improved degradation efficiency and conversion rate (Hu & Yu, 2006).

Average cumulative volume of biogas produced for all the samples (in mL/g of dry matter) is shown in Figure 2. The lowest biogas production was obtained in monodigestion of SS (samples S), 385 mL/g, while in the case of co-digestion with grass, it was 578 mL/g, an improvement of almost 50 %. With the addition of cattle rumen fluid to the mixture of SS and grass, total biogas production increased even more (6 % more), achieving the highest value among all tested reaction mixtures (614 mL/g of dry matter). Similarly, the addition of rumen fluid slightly improved biogas yield during mono-digestion of SS (7 %).



Figure 2: Total volume of biogas produced (mL)/g of dry matter.

3.2 Impact of C/N ratio

The optimal C/N ratio for anaerobic co-digestion is around 20 and might differ according to the operating temperature and type of substrate used (Ma *et al.*, 2018). SS typically has a lower C/N ratio (6–9), which can be improved by mixing with substrates with a higher C/N ratio (18-22), such as food wastes (Awe *et al.*, 2018). The C/N ratio for SS in this study was 5.8, and the C/N ratio of *Typha latifolia* grass was 13.4 (see Table 1), which means that mixing these two substrates improved the C/N ratio of SS and increased biogas yield. The C/N ratio of rumen fluid amounted to 8.5 (see Table 1), but since the rumen fluid was added only in small quantities, its impact was not significant to the overall C/N ratio.

3.3 pH impact

The majority of studies show that temperature (Obulisamy *et al.*, 2016) and pH value are among the key parameters in the anaerobic digestion process (Fang *et al.*, 2020). The system's performance is highly dependent on its buffering capacity, which can be attained through the addition of a buffering agent (Mehariya *et al.*, 2018). pH values for all the studied reaction mixtures for each parallel batch separately are shown in Figure 3.



Figure 3: pH values for reaction mixtures with retention time for: a) first parallels and b) second parallels.

pH values in all reaction mixtures increased in the first 10 days of the experiment. In the case of mono-digestion of SS (samples S1, S2), after 10 days the values were relatively stable. These stable values could be due to the buffering agent that was added to each reaction mixture. Similar trends were observed for samples SR1 and SR2, where rumen fluid was added to the SS. For both, the pH values were mainly below 8.0. For co-digestions of SS and *Typha latifolia* grass (samples SG and SGR), changes in pH value were more significant (a higher increase initially, and a greater decrease at the end of the experiment). The highest pH values were measured in samples SG1 and SG2 and were 8.4 and 8.58. The pH values are just within the optimal pH range, which is between 7 and 8.5 (Fernández-Cegrí *et al.*, 2012); thus, no greater inhibition effect was observed during these experiments.

4 Conclusions

In this study the potential of anaerobic co-digestion of sewage sludge and the *Typha latifolia* plant with/without the addition of rumen fluid was investigated. Monodigestion of SS (samples S) produced the lowest biogas yield, 385 mL/g of dry matter, which is compared to previous studies in the literature, higher than the average amount reported, which is 350 mL/g of dry matter (Grosser & Neczaj, 2018). Thus, the results of this study are comparable with those from similar systems and show good prospects for further investigation.

Co-digestion of SS with *Typha latifolia* grass enhanced biogas production compared to mono-digestion of SS by almost 50 %. The addition of cattle rumen fluid slightly improved the process, since it increased biogas production by 6-7 %. However, greater improvements were expected. Thus, it would be interesting to further study the influence of the quantity of cattle rumen fluid added to the samples on biogas and digestate production.

Acknowledgments

The authors would like to acknowledge Slovenian Ministry of Education, Science and Sport (project No. C3330-19-952041) and the Slovenian Research Agency (research core funding No. P2-0412 and P2-0032) for financial support, and the IKEMA d.o.o. company for their support in chemical analytics and consultancy in the field of sewage sludge management.

References

Angelidaki, I., Alves, M., Bolzonella, D., Borzacconi, L., Campos, J., Guwy, A., Kalyuzhnyi, S., Jenicek, P., & Van Lier, J. (2009). Defining the biomethane potential (BMP) of solid organic wastes and energy crops: a proposed protocol for batch assays. *Water Science and Technology*, 59(5), 927-934.

- Awe, O. W., Zhao, Y., Nzihou, A., Minh, D. P., & Lyczko, N. (2018). Anaerobic co-digestion of food waste and FOG with sewage sludge – realising its potential in Ireland. *International Journal of Environmental Studies*, 75 (3), 496 - 517. doi:10.1080/00207233.2017.1380335f
- Bianchini, A., Bonfiglioli, L., Pellegrini, M., & Saccani, C. (2016). Sewage sludge management in Europe: a critical analysis of data quality. *International Journal of Environment and Waste* Management, 18 (3), 226 - 238.
- Borowski, S., & Weatherley, L. (2013). Co-digestion of solid poultry manure with municipal sewage sludge. *Bioresource Technology*, 142, 345-352. doi:https://doi.org/10.1016/j.biortech.2013.05.047
- Čater, M., Zorec, M., & Marinšek Logar, R. (2014). Methods for Improving Anaerobic Lignocellulosic Substrates Degradation for Enhanced Biogas Production. Springer Science Reviews, 2(1), 51-61. doi:https://10.1007/s40362-014-0019-x
- Elalami, D., Carrere, H., Monlau, F., Abdelouahdi, K., Oukarroum, A., & Barakat, A. (2019). Pretreatment and co-digestion of wastewater sludge for biogas production: Recent research advances and trends. *Renewable and Sustainable Energy Reviews*, 114, 109287. doi:https://doi.org/10.1016/j.rser.2019.109287
- Fang, W., Zhang, X., Zhang, P., Wan, J., Guo, H., Ghasimi, D. S. M., Morera, X. C., & Zhang, T. (2020). Overview of key operation factors and strategies for improving fermentative volatile fatty acid production and product regulation from sewage sludge. *Journal of Environmental Sciences*, 87, 93-111. doi:https://doi.org/10.1016/j.jes.2019.05.027
- Fernández-Cegrí, V., de la Rubia, M. A., Raposo, F., & Borja, R. (2012). Impact of ultrasonic pretreatment under different operational conditions on the mesophilic anaerobic digestion of sunflower oil cake in batch mode. Ultrasonics Sonochemistry, 19(5), 1003-1010. doi:10.1016/j.ultsonch.2012.02.001
- Grosser, A., & Neczaj, E. (2018). Sewage sludge and fat rich materials co-digestion Performance and energy potential. *Journal of Cleaner Production*, 198, 1076-1089. doi:https://doi.org/10.1016/j.jclepro.2018.07.124
- Hu, Z.-H., & Yu, H.-Q. (2006). Anaerobic digestion of cattail by rumen cultures. *Waste Management,* 26(11), 1222-1228. doi:https://doi.org/10.1016/j.wasman.2005.08.003
- Jin, W., Xu, X., Yang, F., Li, C., & Zhou, M. (2018). Performance enhancement by rumen cultures in anaerobic co-digestion of corn straw with pig manure. *Biomass and Bioenergy*, 115, 120-129. doi:https://doi.org/10.1016/j.biombioe.2018.05.001
- Kacprzak, M., Neczaj, E., Fijalkowski, K., Grobelak, A., Grosser, A., Worwag, M., Rorat, A., Brattebo, H., Almås, Å., & Singh, B. R. (2017). Sewage sludge disposal strategies for sustainable development. *Environmental Research*, 156, 39-46. doi:https://doi.org/10.1016/j.envres.2017.03.010
- Ma, H., Guo, Y., Qin, Y., & Li, Y.-Y. (2018). Nutrient recovery technologies integrated with energy recovery by waste biomass anaerobic digestion. *Bioresource Technology*, 269, 520-531. doi:https://doi.org/10.1016/j.biortech.2018.08.114
- Mehariya, S., Patel, A. K., Obulisamy, P. K., Punniyakotti, E., & Wong, J. W. C. (2018). Co-digestion of food waste and sewage sludge for methane production: Current status and perspective. *Bioresource Technology*, 265, 519-531. doi:https://doi.org/10.1016/j.biortech.2018.04.030
- Milieu Ltd. (2008). WRc, RPA and DG Environment; Environmental, Economic and Social Impacts of the Use of Sewage Sludge on Land. *Final report for the European Commission*.
- Montalvo, S., Cahn, I., Borja, R., Huiliñir, C., & Guerrero, L. (2017). Use of solid residue from thermal power plant (fly ash) for enhancing sewage sludge anaerobic digestion: Influence of fly ash particle size. *Bioresource Technology*, 244, 416-422. doi:https://doi.org/10.1016/j.biortech.2017.07.159
- Neshat, S. A., Mohammadi, M., Najafpour, G. D., & Lahijani, P. (2017). Anaerobic co-digestion of animal manures and lignocellulosic residues as a potent approach for sustainable biogas production. *Renewable and Sustainable Energy Reviews*, 79, 308-322. doi:https://doi.org/10.1016/j.rser.2017.05.137

- Obulisamy, P. K., Chakraborty, D., Selvam, A., & Wong, J. W. C. (2016). Anaerobic co-digestion of food waste and chemically enhanced primary-treated sludge under mesophilic and thermophilic conditions. *Environmental Technology*, 37(24), 3200-3207. doi:10.1080/09593330.2016.1181112
- Paulo, L. M., Stams, A. J. M., & Sousa, D. Z. (2015). Methanogens, sulphate and heavy metals: a complex system. Reviews in Environmental Science and Bio/Technology, 14(4), 537-553. doi:10.1007/s11157-015-9387-1
- Raheem, A., Sikarwar, V. S., He, J., Dastyar, W., Dionysiou, D. D., Wang, W., & Zhao, M. (2018). Opportunities and challenges in sustainable treatment and resource reuse of sewage sludge: A review. *Chemical Engineering Journal, 337*, 616-641. doi:https://doi.org/10.1016/j.cej.2017.12.149

ENHANCED INHERENT SAFETY ASSESSMENT DURING HEAT EXCHANGER NETWORK Synthesis

Anita Sovič, Danijela Urbancl, Zdravko Kravanja & Andreja Nemet

University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: anita.sovic.93@gmail.com, danijela.urbancl@um.si zdravko.kravanja@um.si, andreja.nemet@um.si

Abstract This study aims to accurately assess the inherent safety of a heat exchanger network during synthesis in the early stage of design. It is a challenging task, as for accurate estimation of mass present in the heat exchangers, detailed design is required. An iterative procedure was used, synthesizing the heat exchanger network (HEN) first, followed by a detailed design of each heat exchanger separately and, finally, updating the heat exchanger network synthesis model based on the designs of the heat exchangers. For both the synthesis and the heat exchanger design, mixed-integer nonlinear programming (MINLP) models were used. The results show the impact of accurate sizing of exchangers for individual heat transfers, as the results varied by up to 73 % in risk assessment, while the net present value of the HEN before and after detailed heat exchanger design remained essentially the same.

Keywords: mathematical modeling, heat exchanger network, inherent safety, process optimization, process synthesis.



DOI https://doi.org/10.18690/978-961-286-353-1.20 ISBN 978-961-286-353-1

1 Introduction

The Circular Economy provides great benefits for society as well as for the environment, but only when planned carefully. The processes in a Circular Economy are closely connected to each other; hence, much depends on each one, so it is crucial that each process operates properly. Also, the consequences reach far beyond the limits of each process. One of the most important aspects of operability is the safety of the processes. Process safety must be considered during the planning, installation, and operation of plants. Special attention should be paid to inherent safety, presenting all the potential hazards in each process resulting from substances used, process conditions, equipment, and process design. As the major decisions that heavily influence the inherent safety of a plant are made during the early stages of planning, inherent safety must be taken into account in those stages (Kletz, 1996).

There has been a great deal of work done on developing and testing inherent safety indexes; however, only a few studies have been done in the area of process synthesis considering inherent safety.

In this study, the aim is to enhance the assessment of inherent safety (risk) indexes during Heat Exchanger Network synthesis by considering the exact geometry of each Heat Exchanger type.

2 Methodology

A three-stage approach was used to synthesize a HEN using enhanced safety assessment. A superstructure approach based on mathematical programming was used to synthesize the HEN.

In Step 1, the initial HEN model synthesis was performed, as described in Nemet *et al.* (2017), using estimated area density factors for volume, mass and, consequently, for risk indicator assessment. After obtaining an initial HEN, each heat exchanger was optimized separately, based on the selected type of heat exchanger.

In Step 2, models for determining the optimal geometry of each heat exchanger were developed using descriptions from Goričanec *et al.* (2008), Goričanec (2015), Goričanec and Trop (2016). In this work, only shell type, tube type and plate type heat exchangers were considered. The models for heat exchangers took into account: i) the proper Ft correction factor for heat exchanger logarithm mean temperature, ii) appropriate velocity and pressure drop within pipes and on the shell side, iii) type of flow (laminar, turbulent, transitional) and iv) number of passes. For shell and tube heat exchangers, we also took into account the: i) inner and outer radius of the pipe, ii) the pipe arrangement (triangle and quadratic), iii) standardized number of pipes.

In the last Step 3, the updated correction factors, volume-to-area ratio, and heat transfer coefficient were used to obtain the final HEN.



Figure 1: Work flowsheet presenting the three-step approach.

2 Case study

The procedure was tested on an illustrative case study. The input data is presented in Table 1. As can be seen, all the main properties of the substances are required to enable the detailed geometry optimization of heat exchangers as well as the risk assessment.

	Hot streams		Cold streams	
Property	H1	H2	C1	C2
Supply temperature / K	490	550	330	390
Target temperature /K	400	510	400	440
Heat capacity flowrate / kW K ⁻¹	44	27	20	30
Heat transfer coefficient / W m-	0.144	0.244	0.144	5.944
1K-1				
Boiling temperature at 1 bar /K	338	112	82	20
LC 50 /mg m ⁻³	26,000	13,000	5,348	1,227
State	gas	gas	gas	gas
Flammable	yes	yes	yes	yes
Energy, released at explosion/ kJ	4 670	142	10	2 253
kg-1				
Density / kg m ⁻³	45	18.6	49	16
Dynamic viscosity / kPa s	0.0151	0.01761	0.0167	0.0153
Specific heat / J kg ⁻¹ K ⁻¹	5 270	3 000	1 045	14 490
Conductivity / W m ⁻¹ K ⁻¹	0.0741	0.0741	0.0240	0.239
Thermal resistance / K m ² W ⁻¹	0.00036	0.00036	0.00036	0.00036

Table 1: Input data for entire HEN synthesis.

2.1 Initial HEN synthesis - Step 1

Figure 2 presents the HEN obtained using the initial HEN synthesis. The HEN consists of one shell and tube exchanger and two plate heat exchangers.





2.2 Optimization of each heat exchanger- Step 2

Figure 3 presents the masses of substances present in the heat exchanger in relationship to its geometry. Figure 3a presents the shell and tube heat exchanger with a triangular distribution of tubes having an inner diameter of 19.05 mm, while Figure 3b presents the results with a triangular distribution of tubes and an inner tube diameter of 25.4 mm. Figure 3c presents the result of a quadratic distribution of tubes with an inner diameter of 19.05 mm.



Figure 3: Mass present in the heat exchanger at different geometries, when triangular tube distribution with a) 19.05 mm tube inner diameter, b) 25.4 mm tube inner diameter and c) quadratic tube distribution with 19.05 mm tube inner diameter in various tube lengths.

The smallest mass was present in a heat exchanger with 5 m tube length, in a triangular arrangement where the inner diameter of the tubes was 19.05 mm. Therefore, this solution was taken as the optimal geometry.

For plate heat exchangers, a sensitivity analysis was performed considering the width and the height of the plates for heat exchange between streams H1-C1 and H1-C2. The mass of the heat exchanger in the first exchange is presented in Figure 4a, while the second is presented in Figure 4b.



Figure 4: Mass of material in a plate heat exchanger between streams a) H1-C1 and b) H1-C2.

In Figure 4a, the smallest mass present in the heat exchanger between H1-C1 is in the one with a plate dimension of 0.5×0.75 m, while from Figure 4b the smallest mass present in the heat exchanger is in one with plate dimensions of 1×1.5 m.

2.3 Updated HEN synthesis- Step 3

The overall HEN synthesis was performed again after obtaining the optimal design of each heat exchanger. The updated data is presented in Table 2.

Table 3 provides a comparison between a HEN obtained by initial synthesis and synthesis with the updated model.

	Initial model	Updated model		
Logarithm mean temperature correction factor				
Shell and tube (H2-C1)	0.8	0.958		
Plate (H1-C1)	1	1		
Plate (H1-C2)	1	0.988		
Ratio between volume and area / m ³ m ⁻²				
Shell and tube (H2-C1)	0.055	tube: 0.00326 shell:		
		0.00196		
Plate (H1-C1)	0.00143	0.001726		
Plate (H1-C2)	0.00143	0.001756		
Heat transfer coefficient / W m ⁻¹ K ⁻¹				
Shell and tube (H2-C1)	H2: 0.244, C1: 0.144	0.1198		
Plate (H1-C1)	H1: 0.144, C1: 0.144	0.2203		
Plate (H1-C2)	H1: 0.144, C2: 5.944	0.2046		

Table 1: Comparison of the data used in the initial and the updated model.

Table 3: Comparison of selected results between designs obtained with the initial and the updated model.

	Initial	Updated	Difference	Difference
	model	model		/%
				Area /m ²
Shell and tube (H2-				
C1)	38.91	12.72	26.19	67.3
Plate (H1-C1)	185.26	128.86	56.41	30.4
Plate (H1-C2)	95.02	59.99	35.03	36.9
				Toxicity
Shell and tube (H2-				
C1)	1.6987×10-6	6.7065×10-7	1.0280×10-6	60.5
Plate (H1-C1)	1.8100×10-5	1.5475×10-5	2.6251×10-6	14.5
Plate (H1-C2)	1.1277×10-5	3.0168×10-6	8.2602×10-6	73.2
Flammability				
Shell and tube (H2-				
C1)	5.0962×10-7	2.0120×10-7	3.0842×10-7	60.5

A. Sovič, D. Urbancl, Z. Kravanja & A. Nemet: Enhanced Inherent Safety Assessment during Heat Exchanger Network Synthesis

Plate (H1-C1)	1.6158×10-6	1.3814×10-6	2.3439×10-7	14.5	
Plate (H1-C2)	3.3831×10-6	9.0503×10-7	2.4781×10-6	73.2	
Explosiveness					
Shell and tube (H2-					
C1)	2.5473×10-9	1.0057×10-9	1.5416×10-9	60.5	
Plate (H1-C1)	1.4177×10-8	1.2121×10-8	2.0565×10-9	14.5	
Plate (H1-C2)	3.5050×10-	1.2330×10-	2.2721×10-		
	10	10	10	64.8	
Net present value/					
k€	4131.643	4132.372	0.729	0.0138	

3 Conclusions

We have developed a method using a three-step approach for detailed heat exchanger design and, consequently, a more accurate risk assessment during HEN synthesis. In each step, a MINLP model was used. As the results indicate, for a basic trade-off between operating cost and investment using Net Present Value (NPV) as a criterion, the initial model for HEN synthesis provides acceptable results, as the difference between the initial and the updated HEN models in NPV is negligible. However, when a comparison of the risk assessment is performed, the differences are larger: up to 73 % difference was obtained in the risk assessment indicator. This leads to the conclusion that for accurate risk assessment, detailed heat exchanger geometry must be considered.

Acknowledgments

The authors acknowledge financial support from the Slovenian Research Agency, program P2-0032 and project J7-1816.

References

- Kletz, T.A. (1996). Inherently safer design: The growth of an idea. Process Safety Progress, 15(1), 5-8. doi: 10.1002/prs.680150105
- Nemet, A., Klemeš, J. J., Moon, I., Kravanja, Z. (2017). Safety Analysis Embedded in Heat Exchanger. Network Synthesis, *Computer and Chemical Engineering* 107, 357-380, doi: 10.1016/j.compchemeng.2017.04.009.
- Goričanec, D., Črepinšek Lipuš L. (2008). Prenos toplote. Fakulteta za kemijo in kemijsko tehnologijo, *Univerza v Mariboru*, Maribor.
- Goričanec, D. (2015) Mehanika fluidov I. Fakulteta za kemijo in kemijsko tehnologijo, Univerza v Mariboru, Maribor.

255

Goričanec, D., Trop, P. (2016) Procesne naprave. Fakulteta za kemijo in kemijsko tehnologijo, U*niverza v Mariboru*, Maribor.

COMPARATIVE LIFE CYCLE ASSESSMENT OF ALTERNATIVE PACKAGING MATERIALS FOR BEVERAGES

DAMJAN KRAJNC, ZORKA NOVAK PINTARIČ & ZDRAVKO Kravanja

University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: damjan.krajnc@um.si, zorka.novak@um.si, zdravko.kravanja@um.si

Abstract The study assesses the potential environmental impact of several widely used packaging systems: polyethylene terephthalate bottles, glass bottles and aluminium cans. The functional unit was defined as packaging necessary for distribution of 1000 L of beverage. The reference flow also included labels and closures, transport packaging (corrugated cardboard, trays, disposable foil and wooden EUR pallets). Data were sourced from Ecoinvent 3.2 and ELCD 3.2 databases as well as beverage manufacturers. OpenLCA software was used for LCA modelling. The environmental impacts were estimated using the CML 2001 method. Under the assumptions made in this study, drinks packaged in PET bottles have the lowest environmental impact, followed by aluminium cans. Extraction of raw materials for primary packaging has the highest environmental impact, while the end-of-life and transport phases affect the results less than expected.

Keywords: life cycle assessment, packaging materials, beverage, environmental impacts, OpenLCA.



DOI https://doi.org/10.18690/978-961-286-353-1.21 ISBN 978-961-286-353-1

1 Introduction

Packaging contributes significantly to the environmental impact of product manufacturing. The packaging life cycle is often longer than the product itself and it often has greater environmental impact than the product does. Packaging is thus one of the most intensely studied areas of Life Cycle Assessments (LCA). LCA enables us to evaluate the environmental impacts of packaging throughout the life cycle of production, from raw material extraction through material processing, production, distribution, use, repair and maintenance, to eventual disposal or recovery. Using LCA, it is possible to identify key process stages of manufacturing that have the greatest environmental impact. Since this analysis focuses on the entire life cycle, it prevents shifting the environmental burden from one stage of the life cycle to another (i.e. from production to raw material production).

In the research cooperation of our university with Slovenian companies, there is growing interest in performing LCA of selected products, or even the entire company. LCAs are increasingly being recognized as a tool for improvement and innovation, and a way of reducing environmental impact. In line with these trends, we expect that the use of life cycle thinking in leading Slovenian companies will intensify in coming years. Those companies that have already set out to perform an LCA analysis often face many practical questions about approaching practical life cycle assessment.

Therefore, we aim to promote LCA analysis as currently the most suitable method for assessing environmental impacts. There is extensive research on the environmental assessment of different packaging systems for different products (Saleh Y., 2016; Hischier *et al.*, 2010; Pagani *et al.*, 2015; Amienyo *et al.*, 2013; Navajas *et al.*, 2017). However, the purpose of this study is to assess the potential environmental impact of disposable beverage packaging available on the Slovenian market. It provides a practical example of evaluating the packaging systems of polyethylene terephthalate bottles (PET), glass bottles (GL) and aluminium cans (ALU). The value of this research is not only in the results of the analysis; it is also intended to provide supporting information for easier and more intensive use of LCA analysis. This will provide businesses with a tool to support decision making on environmental policy and make it easier to choose from different production options with comparable characteristics. In case of interest, we will present this study and similar examples as part of a professional training workshop on LCA using the OpenLCA software tool.

2 Materials and methods

2.1 Aim and scope of the study

Our aim is to evaluate the environmental impact of the following packaging systems: polyethylene terephthalate bottles (PET), glass bottles (GL) and aluminium cans (ALU). The analysis was performed on some of the most commonly used 0.500 L containers.

Six indicators of potential environmental impacts were considered in the analysis: global warming potential (IPCC, 2013), ozone depletion (WMO, 2006), acidification (Hauschild and Wenzel, 1998) and eutrophication (Heijungs *et al.*, 1992). The reference units concerned are kg CO₂ equivalent, g CFC-11 eq., g SO₂ eq. and g PO₄ eq.

The environmental impact assessment of packaging was carried out using OpenLCA 1.9.0 software. The study was conducted according to the methodology of life cycle assessment ISO 14044: 2006 (ISO, 2006).

2.2 Functional unit

The functional unit was defined as the packaging required to fill and distribute 1000 L of beverage to the point of sale. The reference flow of the production system included beverage packaging (aluminium can, glass and PET bottles, labels and closures) as well as transport packaging (corrugated cardboard, trays, disposable foil, wooden EUR pallets) required for filling and distribution of 1000 L of drink.

2.3 System boundaries

The geographical boundary of the study is within the typically used production processes and waste management practices within the EU. We assessed the potential environmental impacts of the entire life cycle of each packaging system approach (cradle-to-grave). This means that the packaging systems included all stages from raw material extraction to final waste processing. The waste management processes evaluated were disposal, recycling and incineration. Due to lack of data, the following activities were excluded from the system boundary:

- production and packaging of the beverage and its ingredients,
- mass flows contributing less than 1 % to total mass flows,
- transportation of consumers to buy drinks.
- The life cycle of the beverages is shown in Figure 1. The systemic boundary of the study includes the following stages of the life cycle:
- production of primary packaging, including bottles, aluminium cans, PET bottles, aluminium and polymer caps (HDPE), Kraft paper and polypropylene (PP) labels; production of secondary packaging materials, including corrugated cardboard, Kraft paper, low density polyethylene (LDPE) and wooden pallets,
- waste management: recycling and disposal,
- transport of raw materials, packaging materials and transport of the beverage to the retailer along the life cycle.

The product itself, i.e. drink, was not included in the analysis. This means that the filling process was also not studied.





3 Life cycle inventory

The LCI (Life Cycle Inventory) quantifies the use of resources (energy and materials) and environmental emissions associated with a specific product life cycle.

3.1 Process diagrams

This section presents process diagrams created with OpenLCA 1.9. Figure 2 shows the process diagram of the life cycle of aluminium packaging, Figure 3, the diagram of glass packaging and Figure 4, the diagram of production of PET packaging.



Figure 2: Process diagram of the life cycle of aluminium packaging.



Figure 4: Process diagram of the life cycle of PET

Figure 3: Process diagram of the life cycle of glass.

3.2 Inventory data and assumptions

Inventory data were obtained from the Ecoinvent 3.2 databases (Ecoinvent, 2016) and the European reference Life Cycle Database of the Joint Research Center, Version 3.2 (ELCD, 2015) and beverage manufacturers.

Primary production data were obtained from the literature, including quantities of primary and secondary packaging materials (Amienyo *et al.*, 2013; Klöpffer *et al.*, 2011). The types and quantities of primary and secondary packaging are summarized in Table 2. Bottle closures are made of 84 % aluminium alloy and 16 % low density polyethylene (LDPE) (Amienyo *et al.*, 2013). Green packaging glass made from a mixture of primary and secondary raw materials (average European situation based on the BAT document EU-IPPC on BAT on the Glass Industry (Scalet *et al.* 2013) was considered for the analysis of the bottles. Aluminium cans are made of primary and secondary aluminium.

PET bottles are made from 80 % virgin material and the rest from recycled PET fibres, as is the case with Zala water (Pivovarna Lasko Union, 2019). The stoppers are made of high-density polyethylene (HDPE) and the LDPE label.

As shown in Table 2, secondary packaging includes various materials and systems such as cardboard, LDPE foil and wooden EUR pallets.

The analysis considered the transport routes (Table 1) for individual transportation stages/sections. The distances considered were chosen according to our own assumptions and they do not represent the real case distances. However, they were included in the analysis to determine the indicative contribution of transport to the overall environmental impacts of the analysed system. The analysis considered transport by 16-32 ton trucks, EURO 5.

Transportation routes	Segment	Distance [km]
Level 1	from raw material production to	230
	production site	
Level 2	from the production site to the	30
	filling of the drink	
Level 3	from central warehouse to point of	133
	sale	
Level 4	from the point of sale to the waste	20
	centre	
	TOTAL:	413

Table 1: Considered transport routes for individual transportation stages/sections.

Amount Amount Packaging components Packaging components Packaging components Amount [kg/FU] [kg/FU] [kg/FU] ALU GL PET PRIMARY PACKAGING 34.19 PRIMARY PACKAGING 966.04 PRIMARY PACKAGING 56.95 Body (52 % recycl. ALU) 26.60 Glass (35 % recycl. green GL) 960.00 Bottle (PET) 49.3 Closure (ALU) 5.70 Closure (84 % alu alloy and 16 % 4.04 Closure (HDPE) 6.03 LDPE) Labels (Kraft paper) Coatings 1.83 2.10 Labels (LDPE) 1.62 0.06 Inks Sulfuric acid 0.40 SECONDARY PACKAGING SECONDARY PACKAGING SECONDARY PACKAGING 14.31 28.79 9.61 Corrugated cardboard Corrugated cardboard 13.60 25.20 Corrugated cardboard 8.90 Foil (LDPE) Foil (LDPE) Foil (LDPE) 0.71 3.59 0.71 Pallets (mass in kg) Pallets (mass in kg) 25.0 Pallets (mass in kg) 25.0 25.0 EUR EUR Pallet type Pallet type EUR Pallet type Number of bottles per pallet 1848 Number of bottles per pallet 320 Number of bottles per pallet 960 Number of pallets per FU Number of pallets per FU 0.54 3.13 Number of pallets per FU 1.04

Table 2: Specifications of the estimated aluminium (ALU), glass (GL) and plastic (PET) packaging system.

4 Life cycle impact assessment

The aim of this phase is to transform inventory results into different types of environmental impacts. Impact categories considered in the Life Cycle Impact Assessment (LCIA) include acidification, eutrophication, global warming and ozone depletion. LCI-derived emissions and resources were assigned to each of these impact categories. They were then converted to indicators using factors calculated from EIA models (EC, JRC and IES, 2011). The OpenLCA software tool was used to model the LCA. Environmental impacts were assessed using the CML 2001 method.

4.1 Results

Table 3 shows a comparison of the packaging systems analysed for each environmental category. Figure 5 shows a comparison of the packaging systems analysed for different environmental categories. Bottle production contributes most to the impacts in virtually all the estimated impact categories (except in the ozone depletion category, where can production has a greater impact). This is because of the higher mass of bottles and the energy-intensive process to maintain the high temperatures required in the furnaces. Bauxite, used as a source of aluminium in cans, is a major contributor to the ozone depletion indicator. PET bottles show the least environmental impact in all categories. Their lower impact can be attributed to the lower impacts of material and production and their mass. This also reduces the effects of transport and end-of-life disposal.

Based on these results, it can be concluded that the glass bottle making process has the greatest environmental impact, since it contributes most to almost all categories of environmental impacts. This is followed by the production of aluminium cans.

Table 3: Comparison of analysed packaging systems for individual environmental categories.

Impact Category	ALU	GL	PET	Unit
Acidification Potential	2.72	7.56	1.27	kg SO ₂ eq.
Eutrophication Potential	0.77	1.08	0.17	kg PO4 eq.
Global Warming Potential	419.30	930.32	245.50	kg CO ₂ eq.
Ozone Depletion Potential	0.17	0.12	0.02	g CFC-11 eq.



Figure 5: Comparison of the analysed packaging systems for individual environmental categories (relative result).

Figure 6 shows the contributions of each process phase to the global warming potential (GWP). The individual phases are divided into the production of packaging, closures, secondary packaging, labels, transport and waste management (GWP is used as an example as one of the impact categories).

Extraction of raw materials and their transformation into primary packaging contributes most to the environmental profile of beverage packaging systems. Therefore, attention must be paid to the selection of packaging material in the environmental planning of packaging. Nevertheless, the production of secondary packaging is also important. Further, it can be observed that the end of life and the transport phase affect the final values of the indicators less than would be expected.



Figure 6: Contributions of individual process phases to global warming potential (GWP).

5 Conclusion

We evaluated the impact of three packaging systems for the distribution of 1000 L of pre-filled beverage (cans, plastic and glass with a single unit filled with 0.5 L).

The results show that the production phase contributes most to the overall environmental impacts of global warming potential (around 90 %). Therefore, this phase needs to be addressed most and packaging should be designed according to eco-design guidelines. The main factors behind this result are the type and amount of material used. There is a likely correlation between bottle weight and environmental impact. However, this is not true for aluminium cans, which are the lightest in weight but nevertheless have a greater environmental impact than PET bottles. It should be noted that the single use system has been evaluated as one of the most common practices. Considering the bottle return system, glass bottles are likely to exhibit lower environmental impact, but additional bottle cleaning processes, return transport etc. would have to be considered in this case. Our analysis shows that PET bottles are the least burdensome among the systems evaluated, followed by aluminium cans and finally non-returnable glass bottles.

References

- Accorsi R., Versari L., Manzini R. 2015. Glass vs. plastic: life cycle assessment of extra-virgin olive oil bottles across global supply chains. Sustain. 7:2818-40.
- Amienyo D., Gujba H., Stichnothe H., Azapagic A., 2013. Life cycle environmental impacts of carbonated soft drinks. Int J Life Cycle Assess, 18:77–92.
- EC (European Commission), JRC (Joint Research Centre) in IES (Institute for Environment and Sustainability): International Reference Life Cycle Data System (ILCD) Handbook-Recommendations for Life Cycle Impact Assessment in the European context. First edition November 2011. EUR 24571 EN. Luxemburg. Publications Office of the European Union; 2011.
- EcoInvent. EcoInvent database 3.2. as implemented in OpenLCA 1.9.0., 2016.
- ELCD European reference Life Cycle Database of the Joint Research Center. Version 3.2 from October 2015.
- Guinée, J. Handbook on Life Cycle Assessment; Kluwer: Alphen aan den Rijn, The Netherlands, 2002.
- Hauschild M., Wenzel H. 1998. Environmental assessment of products. Scientific background, vol. 2, 1st ed. Chapman & Hall, London, UK.
- Heijungs R., Guinée J.B., Huppes G., Lankreijer R.M., Udo de Haes H.A., Wegener Sleeswijk A., De Goede H.P. 1992. Environmental life cycle assessment of products: guide and backgrounds (part 1). Centre of Environmental Science, Leiden, The Netherlands.
- Hischier R., Althaus H.J., Werner F. 2010. Developments in wood and packaging materials life cycle inventories in Ecoinvent. Int. J. Life Cycle Assess. 10:50-8.
- IPCC (Intergovernmental Panel on Climate Change). 2013. Climate Change 2013: the physical science basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, Cambridge, UK and New York, NY, USA.
- ISO International Organization for Standarization. ISO 14044:2006 EnvironmentalManagement, Life Cycle Assessment, Requirements and Guidelines; International Organization for Standarization: Geneva, Switzerland, 2006.
- Jenkin M.E., Hayman D.G. 1999. Photochemical ozone creation potentials for oxygenated volatile organic compounds: sensitivity to variations in kinetic and mechanistic parameters. Atmos. Environ. 33: 1275-93.
- Klöpffer W., Rechberger H. and Eickhoff U., 2011. Ökobilanz von Getränkeverpackungen in Österreich Sachstand 2010, Ifeu- Institut für Energie- und Umweltforschung Heidelberg GmbH, www.ifeu.de
- Navajas A., Uriarte L. in Gandía L. M., 2017. Application of Eco-Design and Life Cycle Assessment Standards for Environmental Impact Reduction of an Industrial Product. Sustainability 2017, 9(10), 1724.
- Pagani M., Vittuari M., Falasconi L. 2015. Does packaging matter? Energy consumption of pre-packed salads. Br. Food J. 117:1961-80.
- Pivovarna Laško Union, 2019. Voda Zala, https://www.zala.si/druzbena-odgovornost (27. 09. 2019).
- Saleh Y., Comparative life cycle assessment of beverages packages in Palestine. Journal of Cleaner Production 131, Pages 28-42, 2016.
- Scalet B. M., Garcia M. M., Sissa A. Q., Roudier S., Delgado S. L., 2013. Best Available Techniques (BAT) Reference Document for the Manufacture of Glass European Commission EUR 25786
 – Joint Research Centre – Institute for Institute for Prospective Technological Studies. Luxembourg: Publications Office of the European Union.

- WMO (World Meterological Organization). 2006. Scientific assessment of ozone depletion. Global ozone research and monitoring project Report No. 50. WMO, Geneva, Switzerland.
- World Resources. 1992. Guide to global environment. Available from: http://www.wri.org/publication/world-resources-1992-93.

272

THE DIFFICULTIES OF DESIGNING TECHNICAL-ECONOMIC MODELS FOR CZECH WASTEWATER TREATMENT PLANTS

VOJTĚCH ZEJDA¹, JIŘÍ GREGOR¹, JIŘÍ KROPÁČ¹ & ŠÁRKA VÁCLAVKOVÁ²

¹ Brno University of Technology, Faculty of Mechanical Engineering, Brno, Czech Republic, e-mail: 133939@vutbr.cz, jiri.gregor@vutbr.cz, kropac@fme.vutbr.cz ² Institute of Chemical Process Fundamentals of the CAS, Prague, Czech Republic, email: vaclavkova@icpf.cas.cz

Abstract This paper describes the main points that must be faced when preparing a methodology for a techno-economic model of a wastewater treatment plant (WWTP). The model and the design are meant to be applied to real WWTP technologies in the Czech Republic. Most of Czech WWTPs combine mechanical and biological processes to treat wastewater. The main waste product of all wastewater treatment processes is sewage sludge (SS), which is typically a semiliquid mixture of organic and inorganic substances. The paper summarises the basic research on the WWTP models, presents the basic structure of the techno-economic model and describes the basic input data sets, which are crucial for the analysis of real WWTPs. The aim is to propose the structure and design of a techno-economic model that will be sufficiently variable and can evaluate the mechanical equipment of the WWTP together with the variable composition of wastewater.

Keywords: circular economy, wastewater treatment plant, technicaleconomic model, pollution, pollution prevention.



DOI https://doi.org/10.18690/978-961-286-353-1.22 ISBN 978-961-286-353-1

1 Introduction

An analysis of the current state of technologies used at municipal WWTPs in the Czech Republic in connection with corresponding energy efficiencies is one of the objectives of our research activities. Our aim is to create a mathematical tool that will enable the analysis of different WWTPs systems. This paper discusses the available background materials and selects the key input data needed to create the relevant computational model.

1.1 Motivation

The tightening of rules on surface water quality (EC, 1991) led municipalities in the Czech Republic to build or to adjust their own WWTP over the past decade. Rules requiring cleaner effluent of WWTP entering surface waters also brought the need for adjustment to and modernisation of existing WWTP technology and equipment. Moreover, it is expected that current and upcoming European directives (EC, 2018) reflecting the circular economy principles, which aim to maximise the energy and material utilisation of waste materials, will call for further adjustments to and investment in municipal WWTP technologies. Newly built operating technologies, mainly those with lower treated water volumes, are nevertheless facing problems with the fulfilment of limits given by surface water protection rules, problems that needs to be solved prior to further technology adjustment. It is a common practise in central European countries, for the operator of WWTP to be the municipality itself, where the responsible officers are often not experts in available technologies. In such a system, it is difficult for an operator to identify causes of operating trouble or to find a suitable solution (Fiala, 2017). Operators of larger WWTPs (usually more than 10,000 inhabitants equivalent) are then often interested in energy savings and in seeking energy sustainable processes at the operated WWTP. Over dimensioning of WWTP technology is a widespread problem among Czech WTTPs. This is commonly caused by original assumptions of a greater burden of treatment plants by industrial wastewater from different companies, which, however, in many cases don't work today. Implementation of the new European directives seems very complicated in the context of this situation.

1.2 Problem analysis

To identify the causes of existing problems, it is necessary to analyse thoroughly the current situation, which will help to identify appropriate measures as well as to define space for potential investment.

Although analyses with similar objectives have been made in the past (Estrada, 2011), materials available for our study were very limited. The previously available analysis was related either to the evaluation of a specific WWTP or to a comparison of a certain part of the technology among several WWTPs being operated by one operator. In some cases, available analyses of a specific WWTP containing many different tests were made to evaluate possible modernisation or optimisation of a specific WWTP. Other available materials are typically WWTPs annual reports (Sedláček, 2017). The available materials used mathematical models to assess the efficiency, operating costs, and economic return of selected modernisation options. The comparison of the different technological options may be used as feedback for basic design of future technology adjustments. Another available source is a study by Nesměrák (2010) containing a statistical evaluation and characterisation of measured flows, concentrations and material composition of influent and effluent water from several dozen WWTPs. Data on wastewater pollution by medicines were processed similarly (Svoboda et al., 2009). In terms of energy balance, attention in the Czech Republic is focused mainly on small WWTPs (Holba, 2017) and also on modern sludge management approaches by requirements of the circular economy (Hartig, 2018). Materials available from other European countries consider, for example, a modernisation of WWTP operations in Italy, which was done in accordance with the objectives of the circular economy and was described by Bianco (2018). The problem of selecting the most suitable innovative equipment was addressed in a study that describes the development of a programming tool for the analysis of WWTPs flows according to data from two real Danish WWTPs (Bozkurt, 2016). Spain assessed the complex efficacy of 49 WWTPs, where operating costs were not related only to the amount of pollutants removed but also to the pollutants' environmental importance (Castellet, 2016). All of these studies made analyses of the WWTP processes, but their motivations were different from our purposes.

There is no existing universal tool to help analyze the efficiency of the machinery in wastewater treatment plants in the Czech Republic. Creating this tool is the key aim of our research activities. This article deals with finding and analyzing key parameters that are common to most WWTPs in the Czech Republic.

2 Model description

To design a properly working technical-economic model, the individual computational sections must correspond fully to real technological processes and machinery. WWTP combining mechanical and biological stages of treatment are the most common utilities for municipal wastewater treatment in the Czech Republic. However, the type and dimension of each machine are unique for each WWTP. Similarly, equipment for sludge handling technology is unique to each WWTP, and the choice of technology depends on the size of the WWTP. The aim of our research is to create a model to cover the entire portfolio of equipment that could potentially be used in the Czech Republic. This will allow the creation of a model from the real scheme of any Czech WWTP. If the resulting computational model is to be universal, it is necessary to thoroughly decompose the individual sections of the whole process and describe all interaction links. In the first step, it is necessary to create relevant material balances of real Czech WWTPs and subsequently link these with corresponding energy balances.

2.1 Mass balance

Analysis of the pollution of influent wastewater is necessary to properly analyse the role and significance of the individual WWTP facilities. The influent water of municipal WWTP generally contains in four wastewater sources (parts of mass balance):

- a) Domestic wastewater
- b) Wastewater from agriculture
- c) Industrial wastewater
- d) Rainwater.

276
The ratio between these four streams depends on the location of the plant. The proportion of streams can be estimated only by indirect calculations. It could reasonably be presumed that there will be a significant proportion of agricultural wastewater in a small rural WWTP, while an urban WWTP plant will include a larger share of industrial wastewater. The proportion of rainwater depends primarily on the type of sewerage system. To design the WWTP technology, it is very important to thoroughly analyse potential pollution sources and their proportional ratio in influent water. However, the presumed sources of pollution considered when the WWTP was built may have changed or be defunct at this moment. This situation causes operating problems and often has adverse effects on the overall economy. For the technical-economic model, it is crucial to know the presumed influent water pollution when WWTP was designed, as well as the current composition of the influent wastewater. Figure 1 illustrates transforming individual types of pollution in the purification process.



Figure 1: Transforming individual types of pollution in the common wastewater purification process.

The contaminants suggested in Figure 1 are typically present in all municipal wastewater, regardless of the origin. Therefore, it is appropriate to include these in the formation of the primary model. Other types of pollution do not have to occur in all wastewaters, or occur to such a small extent that these are not relevant for the WWTP technology — lately, medicine contamination of municipal wastewater has increased. However, no relevant treatment technologies are available, to the author's knowledge. Therefore, technologies allowing for minimisation of medicine contamination are not included in the proposed model.

After determining the standard pollution of the wastewater, it is possible to focus on the WWTP technology itself. As already mentioned, in the Czech Republic the process of municipal wastewater treatment could be divided into a mechanical stage, a biological stage and sludge processing. A diagram of a standard municipal WWTP is shown in Figure 2. The scheme in Figure 2 proposes all individual operations, their common order in WWTP technology as well as their mutual material links.

The mechanical stage should be able to catch all the floating impurities that come with the wastewater. In terms of model creation, it is remarkable that the composition of machinery in this stage is practically the same for all sizes of WWTP. They differ only in their rated capacity, i.e. the volume of wastewater that can be cleaned and the volume of individual impurities that can be separated. Some differences then occur in additional treatment equipment and possible handling of the trapped dirt.

Given this simplification of the considered water pollution, it can be stated that elimination of dissolved pollution by microorganisms is the aim of the biological stage. There are many variations in composition and shape of the activation tanks and their machinery (mixers and aeration) used in WWTPs. The size of the technology depends on the level of wastewater pollution. As a consequence of increasing pollution, WWTPs were forced to adapt the biological stage technology and increase its efficiency (in what is called intensification). This has often brought the need to add additional chemical agents (e.g. iron salts or methanol) into the process. The action of microorganisms leads to the formation of activated sludge, which is separated in settling tanks. Part of this sludge is returned to the process, while the rest of the sludge (referred to as excess or secondary) is discharged to sludge processing.



Figure 2: Scheme of a standard urban wastewater treatment plant.



Figure 3: Energy consuming operations.

Sludge management facility design is individual for each WWTP. The common practice in the Czech Republic is that sludge from a small WWTP is transported for subsequent processing to a larger facility. Sludge dewatering technology represents practically the entire sludge management at small WWTPs. This causes problems when making the balance of large WWTP sludge processing, as it is practically impossible to distinguish between the sludge produced by a large WWTP's own technology and the sludge brought from the surrounding small WWTPs. In a balance of larger WWTPs, the amount of sludge processed by sludge management facility will correspond to the sum of its own sludge production and sludge delivered from smaller WWTPs. At larger WWTPs, sewage sludge is commonly treated by anaerobic digestion, where biogas is produced as a secondary product of the reaction. The resulting biogas is further utilized as a source of energy at the WWTP. The digested sludge is dewatered and analysed. If the level of contaminants present in sludge complies with the rules given for agricultural use of sludge, the sludge is then transported to farmers.

2.1 Energetic balance

To build an energetic balance, it is essential to identify the key machine components that are necessary for the operation of the WWTP. These are shown in Figure 3. The number of pump stations is individual for each WWTP and depends on the geographical location. A WWTP built on a slope wouldn't need any pump stations, in contrast to a treatment plant built on the plain.

It is evident that electricity consumption plays a crucial role in energy balance. The energy intensity of specific operations is highly individual. Since there are mainly rotary electrical machines at WWTPs, their power input depends on the equipment power output and on their efficiency, which is negatively affected by outdated concepts and insufficient maintenance.

The heat energy is added to electricity consumption in the large WWTPs for heating of anaerobic digesters. Commonly, heat energy from combustion produces biogas is used in the cogeneration unit. However, no Czech WWTP has yet managed to create enough energy from biogas to completely cover WWTP energy consumption.

3 Resulting knowledge

The analysis of the material and the energy balance resulted in the following findings, which must be taken into account for the creation of a technical-economic model. It is important to give the input parameters appropriate significance for the device at the beginning. The real parameters of the influent wastewater and the real volume of collected impurities are important parameters for the design model at the

280

mechanical stage. The dissolved pollution load, which is essential to determine the amount of air supplied and the mixing rate, is important for designing a model of the biological treatment stage. The amount and composition of sewage sludge are crucial for sludge management. The high content of organic substances has a positive effect on the production of biogas and thus on the subsequent energy balance.

The composition of mechanical-technological treatment equipment may be considered uniform for all WWTP types, but several possible variants must be considered for the biological treatment stage. However, machinery in sludge management could be so variable that global typing is unrealistic. It follows that the mathematical model of the mechanical stage can only be simplified by listing machines installed and their dimensions according to the flow capacity and the amount of collected impurities. Several technology modifications with different variations of the particular installed equipment need to be considered for the biological treatment stage model. In the case of sludge management, it will be necessary to mathematically analyse each operation separately, even in several variants according to a particular technical design. It would be possible to create a real sludge management scheme of any WWTP from these modelled operations with sufficient credibility.

The energy consumption of individual devices would need to be converted to a certain characteristic power parameter for the energy model. However, it is necessary to obtain a large amount of data on specific devices from real plants, but only by comparing such specific wattages could one assess the energy condition of a given plant.

4 Discussion

As mentioned above, several simplifications have been made to create the primary model. The first proposed simplification is a shortening of the list of pollutants in wastewater. An even greater simplification could be made in the context of the circular economy. Only pollution with organic substances and phosphorus compounds is interesting from the point of view of secondary material utilisation of waste materials. One of the main goals of intensive research activities worldwide is to identify the most efficient means of wastewater treatment processing. Our technical-economic model will be a useful tool to define the best possibilities for implementing the results of this research into specific WWTP operations. It can be assumed that it is not possible to predict the economic impact of any adjustments to a particular operation without an assessment of the energy and technological level of the given technology.

5 Conclusions

The paper deals with the potential for creating a universal technical-economic model of WWTP. The goals that the model aims to fulfil were defined. Furthermore, common wastewater pollution was analysed, and the consequences of present pollution on WWTP technology were described. The technology itself was then thoroughly analysed in terms of material and energy balance. The resulting conclusions clearly defined possibilities for modelling the specific technological units and outlined the input data necessary to create an initial technical-economic model.

We are still receiving input data from WWTP operators, and this study is very helpful to define the necessary and key parameters that will be crucial for further activities.

Acknowledgements

The authors gratefully acknowledge the financial support provided by ERDF within the research project No. CZ.02.1.01/0.0/0.0/16_026/0008413 "Strategic Partnership for Environmental Technologies and Energy Production.

References

- Bianco M., 2018. Circular Economy and WWTPs: Water Reuse and Biogas Production. In: Gilardoni A. (Ed.), *The Italian Water Industry: Cases of Excellence*, Springer International Publishing, Cham, Switzerland, ISBN 978-3-319-71336-6, 237–257.
- Bozkurt H., Van Loosdrecht M.C.M., Gernaey K.V., Sin G., 2016. Optimal WWTP Process Selection for Treatment of Domestic Wastewater – A Realistic Full-Scale Retrofitting Study. *Chemical Engineering Journal*, 286, 447–458.
- Castellet L., Molinos-Senante M., 2016. Efficiency Assessment of Wastewater Treatment Plants: A Data Envelopment Analysis Approach Integrating Technical, Economic, and Environmental Issues. *Journal of Environmental Management*, 167, 160–166.
- EC, 1991. Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment, <eur-lex.europa.eu/eli/dir/1991/271/oj> accessed 15. 3. 2019.
- EC, 2018. Directive (EU) 2018/851 of the European Parliament and of the Council of 30 May 2018 amending Directive 2008/98/EC on waste (Text with EEA relevance), <eurlex.europa.eu/eli/dir/2018/851/oj> accessed 15. 3. 2019.

- Estrada J.M., Kraakman N.J.R.B., Muñoz R., Lebrero R.A, 2011. Comparative Analysis of Odour Treatment Technologies in Wastewater Treatment Plants. *Environ. Sci. Technol.*, 45(3), 1100– 1106.
- Hartig K., Jonášová S., 2018. Sludge and Circular Economy, Water Management, <vodnihospodarstvi.cz/kaly-a%E2%80%AFcirkularni-ekonomika/>, accessed 13.03.2019. (in Czech)
- Holba M., Matysíková J., 2017. Energy economies in small municipal sewage treatment plants, *Waste Forum 2017*, Hustopeče, Czech Republic, 111,1–5. (in Czech)
- Nesměrák I., 2010. Basic statistical characteristics of distribution of flows, concentrations and material flows on influent and effluent from municipal wastewater treatment plants, Vol. 1, T. G. Masaryk Water Research Institute, Praha, Czech Republic. (in Czech).
- Sedláček J., 2017. Evaluation of WWTP Ostrá 2016, Annual Report. Hydrotech, Ostrá, Czech Republic. (in Czech)
- Svoboda J., Fuksa J.K., Matoušová L., Schönbauerová L., Svobodová A., Váňa M. Šťastný V., 2009, Pharmaceuticals and sewage treatment plants - disposal options and real data, *Water Management*, Praha, Czech Republic, 9–12. (in Czech)

284

CATALYTIC CONVERSION OF BIOMASS-DERIVED FURFURAL INTO VALUE-ADDED CHEMICALS

ALEKSA KOJČINOVIĆ, MIHA GRILC & BLAŽ LIKOZAR

National Institute of Chemistry, Department of Catalysis and Chemical Reaction Engineering, Ljubljana, Slovenia, e-mail: aleksa.kojcinovic@ki.si, miha.grilc@ki.si, blaz.likozar@ki.si

Abstract Lignocellulosic biomass represents the most promising substitute for fossil resources and their ever-growing conversion to fuels and chemicals. It can be processed in various ways, thus yielding a variety of products. The most preferable technique is hydrolysis, which can transform cellulose and hemicellulose into second-generation biofuels and platform chemicals, such as furfural. Heterogeneously catalyzed liquid-phase hydrotreatment of furfural will be presented as one of the potential routes for converting furfural to bio-based functionalized furans, lactones, furfuryl ethers and alkyl levulinates. Development and optimization of these processes involved thorough investigation of reaction conditions and the nature of catalysts on the activity and selectivity towards the desired products and their detailed analytical characterization.

Keywords: circular economy, biomass, catalysis, furfural, hydrotreatment.



DOI https://doi.org/10.18690/978-961-286-353-1.23 ISBN 978-961-286-353-1

1 Introduction

In recent history, the modern lifestyle has placed consumption and the availability of resources at the core of its nature. Those resources come mostly from fossil fuels, which have a very long regeneration time; with such intense consumption, they will be depleted in a short time. These trends have led to a linear economy, with onetime consumption of goods and their assumed destruction or exhaustion upon completed usage. However, a more responsible approach is circular economy, which replaces the concept of "consumer" with that of "user". Users get the benefit of utilizing the good, after which it is returned to the circle for additional applications.

The concept of cycling is visualized in Figure 1. Explaining the benefits of the circular economy through four concepts: 1. The power of the inner circle refers to minimizing the use of materials in circular economy with respect to that of linear economy. This is visualized with the tighter circle, which would lower the need for refurbishing, remanufacturing and changing the properties of the used material for further usage, while increasing the savings on additional materials, labor, capital, energy and externals such as greenhouse gases, water, toxicity, etc.; 2. The power of longer cycling refers to maximizing the length of each cycle and/or the number of consecutive cycles. This could be done though repair, reuse, or remanufacturing, which would avoid new resources being directed to the manufacturing of a brand new product; 3. The power of cascaded use refers to expanding reuse across various other industries, with minimal change to product's nature; 4. The power of pure inputs refers to fact that purity of materials increases collection and redistribution efficiency, while maintaining product quality (The Ellen MacArthur Foundation, 2012).



Figure 1: Four core values of circular economy (The Ellen MacArthur Foundation, 2012).

Since fossil fuels are not being replenished as fast as they are being utilized, proper replacement is needed. The most suitable substitute is lignocellulosic biomass. Since this type of biomass is not edible (therefore does not compete with the food sector), is easily regenerated, and could be utilized with the application of minor changes to existing technologies, it is considered the most valuable feedstock in the biorefinery concept. Lignocellulose is composed of cellulose (40-50 %), hemicellulose (25-35 %), and lignin (15-20 %), depending on its source (Alonso *et al.*, 2012). It mostly refers to the biomass obtained from agricultural waste residues (rice straw, wheat straw, corn stover, hulls, plant residues, etc.) or urban biomass (branches, leaves, forest residue, construction/demolition wood). In these terms, Slovenia represents a high-potential location for versatile biorefinery, as it is third in Europe (after Finland and Sweden) in terms of relative forest coverage (Area of Wooded Land, 2019). In addition, Slovenia has strong existing chemical, agricultural and wood-processing industries; therefore, there is more incentive to utilize existing raw materials, while providing new value-added products to the market.

With such ubiquitous potential sources of raw material, as well as its miscellaneous composition, biomass can be processed in a variety of ways while also producing diverse types of products. Some of those processes include harsh conditions used for pyrolysis, gasification, or liquefaction, while a preferable route is through hydrolysis (Figure 2.). With such systems, small, adaptable biorefineries are sought for extraction of a wide assortment of products acquired from every part of the lignocellulosic biomass: extractives, cellulose, lignin, and hemicellulose. One such refinery is Tanin Sevnica d.d. Tanin valorizes the hemicellulosic part of the forest by wood processing of residual biomass. After hemicellulose isolation and subsequent hydrolysis to C5 cyclic sugars (xylose, mannose, glucose, galactose), acid-catalyzed dehydration of pentoses produces furfural (Figure 3.) (Li *et al.*, 2016).



Figure 2: Scheme of lignocellulosic hydrolysis.

Furfural is a bio-based model compound that can be further upgraded to a wide array of value-added, bio-based chemicals and biofuels. Its functionalities (furan ring and aldehyde group) allow numerous possible reactions: reduction, oxidation, decarbonylation, acetalization, aldol condensation, etherification, esterification, hydrogenolysis, ring-opening, etc. Numerous reviews have been published on catalytic upgrading of furfural over various metal catalysts (Sharma *et al.*, 2013; Šivec *et al.*, 2019); however few report thorough experimental study of the influence of reaction conditions on catalyst activity and selectivity, followed by multiscale modeling.

This study had the aim of developing a potential reaction mechanism for furfural hydrotreatment over molybdenum-based catalysts. Optimization of reaction conditions was carried out in a batch reactor involving three different MoO_3 catalysts and a MoO_2 catalyst. The results were compared to those of Ni and Pd supported on alumina support. All collected samples were analyzed by gas chromatography for identification and quantification of the products, which were later used for constructing the reaction mechanism.



Figure 3: Scheme of hemicellulose hydrolysis to xylose and subsequent dehydration to furfural.

2 Experimental Part

All experiments were performed in a 300 mL stainless steel autoclave, equipped with the magnetically driven Rushton turbine impeller (Figure 4.). Hydrotreatment experiments on furfural were done at temperatures of 150-200 °C and a hydrogen pressure of 5 MPa for 5 hours, over various catalysts. The catalysts in use involved three MoO₃ provided by three different manufacturers (ABSCO Ltd., Fluorochem, Honeywell-Fluka, and Sigma-Aldrich), MoO₂, and alumina-supported Ni and Pd. The gaseous phase was continuously analyzed by an Agilent 490 Micro Gas Chromatographer, while liquid phase samples were collected and analyzed later by Shimadzu Ultra QP2010 Gas Chromatographer with Mass Spectrophotometer for identification, and a Flame Ionization Detector for quantification.

3 Results

After screening all the catalysts under these reaction conditions, all the products were analyzed by gas chromatography, and the potential reaction mechanism was proposed, as in Figure 4. The results suggested that isopropanol hydrogenates furfural to furfuryl alcohol even at room temperature without the presence of the catalyst, but in rather minor quantities. However, in the presence of the catalyst, furfuryl alcohol (FAL) was observed in more significant quantities, which then allow the metal's activity to further upgrade FAL, thus leaving concentrations of furfuryl alcohol at lower amounts. Alumina-supported nickel and palladium catalysts showed higher activity compared to that of MoO_x, regardless of the reaction conditions. It was observed that, in addition to FAL, Ni/Al₂O₃ catalyzed the hydrodeoxygenation reaction, thus producing 2-methylfuran (MF), while Pd/Al₂O₃ further hydrogenated the furan ring, thus producing tetrahydrofurfuryl alcohol (THFA).



Figure 3: High pressure mixing reactor with stainless steel autoclave.

There were no significant differences in activity or selectivity among the four molybdenum oxide catalysts, regardless of their differences in manufacturing or oxidation state. It was observed that furfural undergoes the acetalization reaction at room temperature with isopropanol, thus forming di-isopropoxymethylfuran, which is reversible back to furfural. Yet again, furfural undergoes hydrogenation from isopropanol, yielding furfuryl alcohol. It was observed that, under medium temperatures (175 °C), the major product is isopropyl furfuryl ether, with minor concentrations of the ring-opening product, isopropyl levulinate (IPL). At higher temperatures, IPL becomes the major product, while an additional reaction took place. While hydrogenating furfural, isopropanol converts to acetone, which then undergoes aldol condensation with furfural, thus forming furfuryl acetone.



Figure 4: High pressure mixing reactor with stainless steel autoclave.

4 Conclusions

The modern lifestyle, current technological advances, and the latest environmental policies require a shift from linear economy to circular economy. In such a system, products manufactured and used will be more efficiently designed, require less material input, will be used longer, will permit use in different niches with minor adjustments, and lastly, will pose less harm to the environment while being used and upon their discarding.

Biomass represents the most promising substitute for fossil energy, which currently represents the principal source for fuels and chemicals, as well as the greatest reason for climate change and pollution. Lignocellulosic biomass can be fragmented to its constituent components, lignin, cellulose, and hemicellulose, and then further upgraded to various value-added chemicals. Hemicellulose can undergo hydrolysis to produce pentane sugars, which can be dehydrated in the presence of an acid catalyst to furfural. In the presence of secondary alcohols, furfural can easily be converted to furfuryl alcohol, and then further upgraded to various value-added chemicals, depending on the nature of the catalyst. Ni and Pd catalysts catalyze hydrodeoxygenation and hydrogenation reactions, respectively. Molybdenum oxide catalysts had lower activity and selectivity, while producing furfuryl acetone and the ring opening product, isopropyl levulinate. Consequently, IPL could be used in this way as a fragrance and flavonoid additive, or further upgraded to fuel additive compounds.

Further studies should involve process optimization and subsequent microkinetic and DFT modeling in order to better understand, describe, and predict the behavior of the catalytic system. Thorough characterization of the catalysts is also beneficial in order to correlate activity and selectivity to the nature of the catalyst. Additionally, bifunctional/bimetallic catalysts should also be investigated to potentially lower the number of reaction steps needed, and/or the required time and energy.

Acknowledgments:

The authors gratefully acknowledge financial support by the EU Framework Programme for Research and Innovation Horizon 2020 under Grant agreement no. 814416 (ReaxPro) and the Slovenian Research Agency (research core funding P2-0152 and basic postdoctoral research project Z2-9200).

References

- The Ellen MacArthur Foundation. Towards a Circular Economy Economic and Business Rationale for an Accelerated Transition. Greener Manag Int 2012, *97*.
- Alonso, D.M., Wettstein, S.G., Dumesic, J.A., Bimetallic Catalysts for Upgrading of Biomass to Fuels and Chemicals. *Chem. Soc. Rev.* 2012, 41, 8075-8098.
- Area of Wooded Land. European Commission Eurostat. 43% of the EU is covered with forests. Acc. 07.10.2019. https://ec.europa.eu/eurostat/web/products-eurostat-news/-/EDN-20190321-1
- Li, X., Jia, P., Wang, T., Furfural: A Promising Platform Compound for Sustainable Production of C4 and C5 Chemicals. *ACS Catal*. 2016, *6*, 7621-7640.
- Sharma, R.V., Das, U., Sammynaiken, R., Dalai, A.K., Liquid phase chemo-selective catalytic hydrogenation of furfural to furfuryl alcohol. *App. Cat. A.* 2013, *454*, 127-136.
- Šivec, R., Grilc, M., Huš, M., Likozar, B., Multiscale Modeling of (Hemi)cellulose Hydrolysis and Cascade Hydrotreatment of 5-Hydroxymethylfurfural, Furfural, and Levulinic Acid. Ind. Eng. Chem. Res. 2019, 58(35), 16018-16032.

294

TRANSPORTATION MODEL FOR CARBON-CONSTRAINED ELECTRICITY PLANNING: AN APPLICATION TO THE ALUMINIUM INDUSTRY

ROK GOMILŠEK^{1, 2}, LIDIJA ČUČEK², MARKO HOMŠAK³ & ZDRAVKO KRAVANJA²

1 Talum Inštitut d.o.o., Kidričevo, Slovenia, e-mail: rok.gomilsek@talum.si 2 University of Maribor, Faculty of Chemistry and Chemical Engineering, Maribor, Slovenia, e-mail: rok.gomilsek@talum.si, lidija.cucek@um.si, zdravko.kravanja@um.si 3 Talum d.d., Kidričevo, Slovenia, e-mail: marko.homsak@talum.si

Abstract Aluminium production is one of the most highly energy-intensive processes and consequently one of the largest sources of greenhouse gas (GHG) emissions. A large portion of these emissions are indirect emissions, owing to consumption of electricity. Various Process Integration techniques have been developed for energy consumption and/or GHG footprint targeting and reduction. In this paper, a transportation model for carbon-constrained electricity planning is proposed. The model is applied to specific aluminium products, slugs and evaporators, and implemented within a General Algebraic Modelling System (GAMS) environment. The proposed model calculates optimal allocation of electricity sources to reach the CO2 emission benchmark set by the European Union. Results show that meeting the CO2 emission benchmark will increase costs by 26 % when current electricity prices are considered.

Keywords: carbon emission pinch analysis, GHG emissions, transportation model, aluminium industry, benchmark.



DOI https://doi.org/10.18690/978-961-286-353-1.24 ISBN 978-961-286-353-1

1 Introduction

Primary aluminium is produced by the electrolytic reduction process, where aluminium is separated from the alumina (Al_2O_3) within a cell. The current is passed from the anode to the cathode during this process (Kvande, 2014). According to data from the International Aluminium Institute (World Aluminium, 2019), on average, 14,210 kWh of electricity was used to produce 1 t of primary aluminium in 2018. This makes aluminium production one of the most highly energy-intensive processes and consequently one of the largest producers of greenhouse gas (GHG) emissions. A large portion of these emissions are indirect emissions, which is the result of electricity consumption, while direct GHG emissions are also considerable. Direct emissions could be reduced by a using higher share of secondary aluminium, by implementation of carbon capture technology, by using inert anodes and other strategies, while indirect GHG emissions could be reduced by changing energy sources toward renewable and other low-carbon sources of electricity (Gomilšek *et al.*, 2019).

Various Process Integration techniques have been developed for reduction of the GHG footprint. One promising technique is Carbon Emission Pinch Analysis (CEPA), which was first introduced by Tan and Foo (Tan & Foo, 2007). CEPA is a Pinch Analysis (PA) procedure for identifying the minimum number of low- or zero-carbon energy sources needed to achieve the specified emission limit/target (Tan & Foo, 2007). CEPA methodology has been further extended and applied to the analysis of energy sectors in the Philippines (Foo *et al.*, 2008), Ireland (Crilly & Zhelev, 2008), New Zealand (Atkins *et al.*, 2010), the USA (Walmsley *et al.*, 2015), China (Jia *et al.*, 2016), Nigeria (Salman *et al.*, 2019) and other countries. It has also been applied to systems at different scales, extended through the use of alternative metrics and footprints, and has been integrated with Input-Output Analysis to include economic aspects (Tan *et al.*, 2017).

Various approaches exist for the synthesis and retrofit of Process Integration (PI) systems, such as heat and mass exchanger networks (HENs and MENs), and carbon management networks. Approaches could be based on heuristics, on thermodynamic insights (PA), on numerical optimization (Mathematical Programming – MP) and on hybrid or combined approaches (Čuček *et al.*, 2019). The most widely used approach to carbon-constrained planning is the PA approach

(CEPA). Often it is combined with MP as part of a hybrid approach (Tan & Foo, 2007). A mathematical formulation has also been developed in the form of what is called a crisp model, minimizing the total amount of the zero-emission energy resource (Tan & Foo, 2007).

In this study, a transportation model for carbon-constrained electricity planning is proposed, which enables the use of various optimization criteria to guide the search. The transportation model for carbon-constrained electricity planning has been applied to specific aluminium products, slugs and evaporators, and implemented within a General Algebraic Modelling System (GAMS) environment.

2 Model development

Several methods based on MP exist for solving PI problems. The transportation model (Cerda *et al.*, 1983) was one of the first problem formulations, while various MP formulations followed, such as the transhipment and expanded transhipment models (Papoulias & Grossmann, 1983), the stage-wise problem (Yee & Grossmann, 1990) and several others (Čuček *et al.*, 2019). Since both mass and energy are extensive properties, the transportation model is a suitable method for solving carbon-constrained electricity planning problems.

In the model, two main sets are defined:

- Set *i* represents various energy sources, e.g. fossil, nuclear and renewable;
- Set *j* represents various products. In this study, two specific products from aluminium production are considered. These are slugs and evaporators, which are both produced by the company.

The transportation model comprises supply and demand nodes. The supply nodes represent the supply or availability of various energy sources (a_i). The demand nodes represent the demand or consumption of electricity (b_j). The amount of electricity from supply to demand (x_{ij}) is a positive variable. Eq. (1) specifies that availability of energy sources must be greater than or equal to the sum of electricity consumed for all *j* products considered for every energy source *i*.

$$\sum_{j} x_{ij} \le a_i \quad \forall i \tag{1}$$

The sum of electricity consumption of energy sources from supply to demand must be equal to the electricity consumed by each product *j*, as shown in Eq. (2):

$$\sum_{i} x_{ij} = b_j \quad \forall j \tag{2}$$

CO₂ emissions from electricity use for producing the considered amounts of products (E_j) are calculated with Eq. (3), where x_{ij} is multiplied by the emission factors of energy sources *i* (F_j) for each product *j*:

$$\sum_{i} x_{ij} \times F_i = E_j \quad \forall j \tag{3}$$

The fraction of electricity source *i* used for producing each product *j* (w_{ij}) is calculated by Eq. (4):

$$w_{ij} = \frac{x_{ij}}{b_j} \quad \forall \ i, j \tag{4}$$

The objective considered is minimization of costs (OBJ), which is calculated by Eq. (5) by multiplying x_{ij} with the cost of energy source *i* (P_i):

$$OBJ = x_{ij} \times P_i \quad \forall \ i, j \tag{5}$$

3 Results and discussion

The carbon-constrained electricity planning problem has been solved for two aluminium products, slugs and evaporators, applying the proposed transportation model and a GAMS modelling environment. Three different scenarios were performed:

 Scenario 1 (Current): CO₂ emissions for every product are fixed to actual values, since they represent the current case, with defined fractions of energy sources.

- Scenario 2: Fractions of energy sources are relaxed, and CO₂ emissions are fixed to new values to meet the requirements of the benchmark set by the European Union (European Commission, 2019), which should be achieved for each product separately.
- Scenario 3: Similar to that in Scenario 2; however, the overall emission benchmark should be achieved.

The carbon footprint composite curves for the second and third scenarios are shown in Figure 1 and Figure 2, where the current case (current electricity mix to satisfy consumption) crosses the benchmark line in both scenarios. Consequently, electricity sources with smaller emission factors (nuclear and/or renewable) should replace fossil resources in the electricity mix. Moreover, in both scenarios 2 and 3, the benchmark has been achieved. Only nuclear energy has been selected, owing to both the smaller emission factor and the price, compared to those for renewable sources. It should be noted that, for reasons of confidentiality, the values of emissions are normalized, where the value of 1 represents the current emissions.



Figure 1: CO₂ footprint composite curve for Scenario 2.



Figure 2: CO₂ footprint composite curve for Scenario 3.

The total cost of the process for all three scenarios considered is presented in Table 1, where it can be seen that costs for both scenarios 2 and 3 are increased by 26 %, compared to the base case. These higher costs are due to the increased share of nuclear energy, which is more expensive than fossil energy. Similarly, as in Figures. 1 and 2, the values of costs are normalized.

Table 1: Total	cost	of various	scenarios.
----------------	------	------------	------------

	Current	Scenario 2	Scenario 3
Z	1	1.26	1.26

4 Conclusions

This paper presents a transportation model for carbon-constrained electricity use for producing aluminium slugs and evaporators. The proposed model calculates optimal allocation of electricity sources to reach the CO₂ emission benchmark. It was shown that the cost of electricity supply would increase by 26 % over current prices of electricity if the company wants to meet the requirements of the CO₂ emissions benchmark.

300

In the future, the model will be expanded with predictions of future prices of electricity sources, a more detailed electricity consumption mix, more detailed electricity pricing, and to include consumption of other energy sources for heating and cooling.

Acknowledgments

The authors are grateful for funding support from the companies Talum d.d. and Talum Inštitut d.o.o. and from the Slovenian Research Agency (research core funding No. P2-0412 and P2-0032).

References

- Atkins, M. J., Morrison, A. S., Walmsley, M. R. W. (2010). Carbon Emissions Pinch Analysis (CEPA) For Emission Reduction in the New Zealand Electricity Sector. *Applied Energy*, 87, 982-987. doi: 10.1016/j.apenergy.2009.09.002.
- Cerdá, J., Westerberg, A. W., Mason, D., Linnhoff, B., (1983). Minimum Utility Usage in Heat Exchanger Network Synthesis. *Chemical Engineering Science, 38 (3),* 373-387. doi: 10.1016/0009-2509(83)80156-0.
- Crilly, D., Zhelev, T. (2008). Emissions targeting and planning: An application of CO2 emissions pinch analysis (CEPA) to the Irish electricity generation sector. *Energy*, 33, 1498-1507. doi: 10.1016/j.energy.2008.05.015.
- Čuček, L., Boldyryev, S., Klemeš, J. J., Kravanja, Z., Krajačić, G., Sabev Varbanov, P., Duić, N. (2019). Approaches for retrofitting heat exchanger networks within processes and Total Sites. *Journal of Cleaner Production*, 211, 884-894. doi: 10.1016/j.jclepro.2018.11.129.
- European Commission. Commission delegated regulation (EU) 2019/331 of 19 December 2018 determining transitional Union-wide rules for harmonised free allocation of emission allowances pursuant to Article 10a of Directive 2003/87/EC of the European Parliament and of the Council. Brussels: Official Journal of the European Union, 2019.
- Foo, D. C. Y., Tan, R. R., Ng, D. K. S. (2008). Carbon and footprint-constrained energy planning using cascade analysis technique. *Energy*, 33 (10), 1480-1488. doi: 10.1016/j.energy.2008.03.003.
- Gomilšek, R., Čuček, L., Homšak, M., Kravanja, Z. (2019). Towards GHG Emissions Neutrality of Aluminium Slug Production: An Industrial Study, accepted manuscript for 22nd Conference Process Integration, Modelling and Optimization for Energy Saving and Pollution Reduction – PRES'2019, 20 – 23 October 2019, Crete, Greece.
- International Aluminium Institute. Current IAI statistics, Primary aluminium smelting energy intensity. http://www.world-aluminium.org/statistics/primary-aluminium-smelting-energy-intensity/ (accessed: 7.9.2019).
- Jia, X., Li, Z., Wang, F., Foo, D. C. Y., Tan, R. R. (2016). Multi-dimensional pinch analysis for sustainable power generation sector planning in China. *Journal of Cleaner Production*, 112 (4), 2756-2771. doi: 10.1016/j.jclepro.2015.10.102.
- Kvande, H. (2014). The Aluminium Smelting Process. Journal of Occupational and Environmental Medicine, 56, S2-S4. doi: 10.1097/JOM.00000000000154.
- Lee, S. C., Ng, D. K. S., Foo, D. C. Y., Tan, R. R. (2009). Extended pinch targeting techniques for carbon-constrained energy sector planning. *Applied Energy*, 86 (1), 60-67. doi: 10.1016/j.apenergy.2008.04.002.
- Papoulias, S. A., Grossmann, I. E., (1983). A structural optimization approach in process synthesis-II: Heat recovery networks. *Computers & Chemical Engineering*, 7 (6), 707-721. doi: 10.1016/0098-1354(83)85023-6.

- Salman, B., Saifuddin, N. M., Foo, D. C. Y. (2019). Carbon emissions pinch analysis (CEPA) for energy sector planning in Nigeria. *Clean Technologies and Environmental Policy*, 21 (1), 93-108. doi: 10.1007/s10098-018-1620-5.
- Tan, R. R., Foo, D. C. Y. (2007). Pinch analysis approach to carbon-constrained energy sector planning. *Energy*, 32, 1422-1429. doi: 10.1016/j.energy.2006.09.018.
- Tan, R. R., Aviso, K. B., Foo, D. C. Y. (2017). Economy-Wide Carbon Emissions Pinch Analysis. *Chemical Engineering Transactions*, 61, 913-918. doi: 10.3303/CET1761150.
- Walmsley, M. R. W., Walmsley, T. G., Atkins, M. J. (2015). Achieving 33% renewable electricity generation by 2020 in California. *Energy*, 92, 260-269. doi: 10.1016/j.energy.2015.05.087.
- Yee, T. F., Grossmann, I. E. (1990). Simultaneous optimization models for heat integration-II. Heat exchanger network synthesis. *Computers & Chemical Engineering*, 14 (10), 1165-1184. doi: 10.1016/0098-1354(90)85010-8.



Faculty of Chemistry and Chemical Engineering

OCTOBER 24TH TO OCTOBER 25TH 2019, PORTOROŽ, SLOVENIA