TBMCE

2018

1st International Conference on

TECHNOLOGIES & BUSINESS MODELS FOR CIRCULAR ECONOMY

CONFERENCE PROCEEDINGS

EDITORS
MILOŠ BOGATAJ
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University of Maribor Press

University of Maribor

Faculty of Chemistry and
Chemical Engineering

1st International Conference on Technologies & Business Models for Circular Economy

Conference Proceedings

Editors
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November 2018

Title *Naslov*	1st International Conference on Technologies & Business Models for Circular Economy
Subtitle *Podnaslov*	Conference Proceedings
Editors *Uredniki*	assist. prof. Miloš Bogataj, PhD (University of Maribor, Faculty of Chemistry and Chemical Engineering) full prof. Zdravko Kravanja, PhD (University of Maribor, Faculty of Chemistry and Chemical Engineering) full prof. Zorka Novak Pintarič, PhD (University of Maribor, Faculty of Chemistry and Chemical Engineering)
Technical editor *Tehnični urednik*	Jan Perša, M.Eng (University of Maribor Press)
Cover Designer *Oblikovalec ovitka*	Jan Perša, M.Eng (University of Maribor Press)
Graphic material *Grafične priloge*	Autorhs
Conference *Konferenca*	1st International Conference on Technologies & Business Models for Circular Economy
Date and location *Datum in kraj*	September 5th – 7th, 2018, Portorož, Slovenia
Organizing Committee *Organizacijski odbor*	Zdravko Kravanja (University of Maribor, Slovenia), Zorka Novak Pintarič (University of Maribor, Slovenia), Miloš Bogataj (University of Maribor, Slovenia), Andreja Nemet (University of Maribor, Slovenia), Žan Zore (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).
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).

Izdajatelj/*Co-published by*
University of Maribor, Faculty of Chemistry and Chemical Engineering
Smetanova ulica 17,2000 Maribor, Slovenia
https://www.fkkt.um.si, fkkt@um.si

Založnik/*Published by*
University of Maribor Press
Slomškov trg 15, 2000 Maribor, Slovenia
http://press.um.si, zalozba@um.si

Edition *Izdaja*	1st
Publication type *Vrsta publikacije*	e-book
Available at *Dostopno na*	http://press.um.si/index.php/ump/catalog/book/367
Published *Izdano*	Maribor, November 2018

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

CIP - Kataložni zapis o publikaciji
Univerzitetna knjižnica Maribor

330:502.131.1(082(0.034.2)

INTERNATIONAL Conference on Technologies & Business Models for Circular Economy (1 ; 2018 ; Portorož)
Conference proceedings [Elektronski vir] / 1st International Conference on Technologies & Business Models for Circular Economy, September, 5th - 7th, 2018, Portorož, Slovenia ; editors Miloš Bogataj, Zdravko Kravanja, Zorka Novak Pintarič. - 1ed. - Maribor : University of Maribor, 2018

Način dostopa (URL): http://press.um.si/index.php/ump/catalog/book/367

ISBN 978-961-286-211-4

doi: 10.18690/978-961-286-211-4
1. Bogataj, Miloš
COBISS.SI-ID 95522049

ISBN	978-961-286-211-4 (PDF)
DOI	https://doi.org/10.18690/978-961-286-211-4
Price *Cena*	Free copy/brezplačen izvod
For Publisher *Odgovorna oseba založnika*	full prof. Zdravko Kačič, PhD, Rector, University of Maribor

University of Maribor Press

1st International Conference on Technologies & Business Models for Circular Economy

MILOŠ BOGATAJ, ZDRAVKO KRAVANJA & ZORKA NOVAK PINTARIČ

Abstract The 1st 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 2018, we presented the Strategic Research and Innovative Partnership – Network for the Transition to Circular Economy (SRIP-CE) as a platform for establishing a successful long-term public-private 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 2018 was organized by Faculty of Chemistry and Chemical Engineering, University of Maribor and held in Portorož, Slovenia at the Grand Hotel Bernardin from September 5th to September 7th, 2018.

The event was under the honorary patronage of His Excellency the President of the Republic of Slovenia Borut Pahor.

Keywords: • circular economy • sustainable development • processes and technologies • circular business models • research and development •

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DOI https://doi.org/10.18690/978-961-286-211-4 ISBN 978-961-286-211-4
Available at: http://press.um.si.

Univerzitetna založba
Univerze v Mariboru

1. Mednarodna konferenca tehnologije in poslovni modeli za krožno gospodarstvo

MILOŠ BOGATAJ, ZDRAVKO KRAVANJA IN ZORKA NOVAK PINTARIČ

Povzetek Fakulteta za kemijo in kemijsko tehnologijo Univerze v Mariboru je organizirala 1. mednarodno strokovno/znanstveno konferenco Tehnologije in poslovni modeli za krožno gospodarstvo (Technologies & Business Models for Circular Economy; TBMCE), ki je potekala od 5. do 7. septembra 2018 v Grand Hotelu Bernardin v Portorožu. TBMCE 2018 je bila namenjena predstavitvi konceptov krožnega gospodarstva in tehnologij ter metodologij, ki prispevajo k preusmeritvi gospodarskih subjektov in družbe kot celote k bolj odgovornemu, tj. krožnemu ravnanju z viri. V sklopu TBMCE 2018 smo predstavili SRIP Krožno gospodarstvo kot platformo za vzpostavitev dolgoročnega uspešnega javno-zasebnega partnerstva z vodilno vlogo deležnikov (v sodelovanju z državo) pri vzpostavljanju verig vrednosti in organiziranju celovite podpore raziskovalni in inovacijski dejavnosti. Konferenčni program je vključeval panelne diskusije, plenarno in uvodna predavanja, ustna predavanja in predstavitve v obliki posterjev s področja tem konference: Trajnostna energija, Biomasa in alternativne surovine, Krožni poslovni modeli, Sekundarne surovine in funkcionalni materiali, IKT v krožnem gospodarstvu, Procesi in tehnologije.

Dogodek je potekal pod častnim pokroviteljstvom predsednika Republike Slovenije Boruta Pahorja.

Ključne besede: • krožno gospodarstvo • trajnostni razvoj • procesi in tehnologije • krožni poslovni modeli • raziskave in razvoj •

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DOI https://doi.org/10.18690/978-961-286-211-4 ISBN 978-961-286-211-4
Dostopno na: http://press.um.si.

Table of Contents/*Kazalo*

Conference Proceedings/*Konferenčni pripsevki*

Univerzitetna založba
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Kako praktično ovrednotiti okoljske vplive proizvoda?

DAMJAN KRAJNC, ZDRAVKO KRAVANJA, ZORKA NOVAK PINTARIČ IN LIDIJA ČUČEK

Povzetek Analiza življenjskega cikla (LCA, Life Cycle Assessment) omogoča ovrednotenje okoljskih vplivov proizvoda ali storitve skozi njegovo celotno življenjsko dobo. Podjetja jo uporabljajo za prepoznavanje priložnosti za zmanjšanje rabe virov in emisij ter optimizacijo poslovnih pristopov. Obstaja nekaj tujih gradiv in referenčnih dokumentov o analizi življenjskega cikla v skladu s standardi ISO, a se večinoma osredotočajo na teoretske osnove, medtem ko pogrešamo več predstavitev praktične izvedbe analize LCA z uporabo ustreznega programskega orodja. Med mnogimi programskimi orodji za izvedbo analize življenjskega cikla, postaja vse bolj uveljavljeno orodje OpenLCA, ki omogoča vizualno privlačno in prilagodljivo modeliranje sofisticiranih ali preprostih modelov in je na voljo kot prosto dostopna, odprtokodna programska oprema.V prispevku bo orodje OpenLCA predstavljeno na didaktično preprostem, praktičnem primeru ocenitve okoljskih vplivov različne embalaže za enkratno uporabo (PET, PC in ALU). Prikazano bo, kako s programom medsebojno primerjati proizvodne sisteme. Predstavljeni bodo cilj in namen, inventarizacija življenjskega cikla, ovrednotenje okoljskih vplivov ter interpretacija rezultatov študije. Na podlagi predstavitve OpenLCA na praktičnem primeru bo podjetje spoznalo uporabno vrednost in zmožnosti orodja. Z njim bo podjetje lažje okoljsko ocenilo svoj proizvod, ga primerjalo z drugimi na trgu, predlagalo različne okoljske scenarije ter prilagodilo svoj model trajnostnega razvoja.

Ključne besede: • analiza življenjskega cikla • OpenLCA • vplivi na okolje • ocena embalaže • programsko orodje •

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DOI https://doi.org/10.18690/978-961-286-211-4.1 ISBN 978-961-286-211-4
Dostopno na: http://press.um.si.

University of Maribor Press

How to Practically Evaluate the Environmental Impacts of the Product?

DAMJAN KRAJNC, ZDRAVKO KRAVANJA, ZORKA NOVAK PINTARIČ &
LIDIJA ČUČEK

Abstract Life Cycle Assessment (LCA) allows evaluation of the environmental impact of a product or service over its entire life cycle. Companies use it to identify opportunities for reducing resources and emissions and optimizing business approaches. There are some foreign reference documents on the life cycle analysis in accordance with ISO standards, but mostly focus on theoretical basics, while we miss the presentation of the practical implementation of the LCA analysis using the appropriate software tool. Among many software tools for performing life cycle analysis, OpenLCA is becoming an increasingly established tool, which is available as open source software. In the paper, the OpenLCA tool will be presented in a didactically simple, practical case of assessing the environmental impacts of a single disposable packaging (PET, PC and ALU). It will show how to environmentally compare production systems with each other. The goal and purpose, the life cycle inventory, the evaluation of environmental impacts and the interpretation of the results of the study will be presented. In this way it will enable the company to environmentally assess its product, compare it with others on the market, propose different environmental scenarios and adapt its own sustainable development model.

Keywords: • Life Cycle Assessment, • OpenLCA • Environmental impacts • Packaging assessment • Software tool •

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DOI https://doi.org/10.18690/978-961-286-211-4.1 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Kaj je orodje OpenLCA?

OpenLCA je odprtokodna programska oprema, ki jo je razvilo podjetje GreenDelta za oceno življenjskega cikla (LCA) in za študije ocene trajnosti. Kot odprtokodna programska oprema je prosto dostopna na spletni strani projekta (www.openlca.org) brez stroškov licence. LCA je priljubljeno orodje, ki ga uporabljajo podjetja za prepoznavanje priložnosti za zmanjšanje rabe virov in emisij ter optimiranje svojega poslovnega pristopa in sprejemanje odločitev na podlagi gospodarskih in okoljskih meril. Z orodjem OpenLCA je mogoče oceniti ogljični in vodni odtis, načrtovati okolju primernejši proizvod po smernicah eko-dizajna ter pripraviti izjavo o okoljskem izdelku (EPD). OpenLCA je eno najobsežnejših orodij za izvedbo tovrstnih analiz in se pogosto uporablja v trajnostno naravnanih podjetjih in drugih organizacijah. Programsko orodje si je mogoče brezplačno prenesti na povezavi: https://www.openlca.org/download/. Za količinsko opredelitev okoljskih vplivov modeliranega sistema je potrebno v programsko okolje openLCA uvoziti metode ocenjevanja okoljskih vplivov. Metode LCIA »openlca_lcia_methods_1_5_5.zolca« so na voljo v razdelku »Prenosi na spletni strani OpenLCA« (http://www.openlca.org/download_page#LCIA_methods).

2 Prenos in namestitev

OpenLCA je na voljo za operacijske sisteme Mac, Linux in za 32-bitno in 64-bitno različico sistema Windows. Postopek namestitve se razlikuje glede na operacijski sistem, vendar je precej preprost. Več informacij o namestitvenem postopku je na voljo na naslednji povezavi https://www.openlca.org/wp-content/uploads/2017/04/1.6-Getting-started.pdf. Ko prenesete in namestite programsko opremo, bo navigacijski zaslon prazen. V podoknu za krmarjenje so shranjene informacije o različnih projektih, ki jih ustvarite. Prvi korak je ustvariti novo bazo podatkov. Z desno miškino tipko kliknite podokno za krmarjenje in kliknite »Nova baza podatkov« angl. «New database«. Podajte ime baze podatkov in preverite, ali je gumb »Lokalni« angl. »Local« preverjen/odkljukan. Ustvarjanje lokalnih projektov bo olajšalo izmenjavo in prenos podatkov. Nato kliknite gumb »Celotni referenčni podatki« angl. »Complete reference data« v možnostih vsebine baze podatkov in kliknite »Dokončaj« angl. »Finish«. Vaša nova baza podatkov bo vidna v podoknu za krmarjenje. Opazili boste, da je nova baza podatkov skoraj prazna, razen nekaterih vgrajenih tokov, lastnosti tokov in skupine enot.

3 Inventarizacija življenjskega cikla in metode za oceno okoljskih vplivov

Ko ustvarite novo bazo podatkov, je naslednji korak prenesti in uvoziti bazo podatkov o življenjskem ciklu in metode za oceno okoljskih vplivov. Ti dve podatkovni bazi sta potrebni za izgradnjo svojega openLCA modela.

3.1 Baza podatkov o življenjskem ciklu

Baza podatkov inventarja življenjskega cikla vsebuje niz vhodnih in izhodnih tokov za različne izdelke in sisteme izdelkov, vključno s snovnimi, energijskimi in emisijskimi tokovi. Obstaja več brezplačnih podatkovnih baz, kjer lahko prenesete inventarizacijske podatke življenjskega cikla, vključno z bazo ELCD (Skupni raziskovalni center Evropske Komisije), NREL (Nacionalni laboratorij za obnovljivo energijo), NEEDS (New Energy Externality Development for Sustainability) ipd.

Če želite uvoziti podatkovni niz podatkov o življenjskem ciklu v bazo podatkov, z desno miškino tipko kliknite »proces! Import«. V pogovornem oknu, ki se prikaže, v meniju \ File import izberite Eco Spold 1 in kliknite »Next«. Če želite uvoziti bazo podatkov, se pomaknite do mesta mape, v kateri je bila prenesena baza podatkov, in kliknite mapo s končnico».zip« in kliknite »Next«.

3.2 Metode ocenjevanja okoljskih vplivov

Metode ocenjevanja vplivov življenjskega cikla (LCIA) so potrebne za analizo popisa vplivov, pridobljenih iz modela LCA. Metode ocenjevanja vplivov vzpostavljajo povezavo med emisijami iz proizvodnje produktov oz. obratovanjem procesa in morebitnimi vplivi na okolje. Vsaka metoda ocene okoljskih vplivov vključuje različne kategorije vplivov, ki so specifične za snovi. Na primer, emisije CO_2 in N_2O prispevajo h globalnemu segrevanju, medtem ko emisije H_2S lahko prispevajo k toksičnosti za ljudi. LCIA metode kvantificirajo okoljske posledice teh emisij na podlagi različnih karakterizacijskih faktorjev. Pred modeliranjem LCA je priporočljivo preučiti različnih kategorije okoljskih vplivov v vsaki metodi. Programsko orodje openLCA omogoča tudi spreminjanje metod oz. ustvarjanje novih želenih metod ocenjevanja vplivov na okolje, prav tako pa omogoča tudi vključevanje socialnih indikatorjev v program LCA.

Paket metod LCIA, ki so na voljo v programskem orodju openLCA, je obsežen paket različnih metod ocenjevanja vplivov. Družba Triangle Life Cycle Assessment LLC je v sodelovanju z GreenDelta razvila celovit paket z različnimi metodami za oceno vplivov, ki se lahko uporabljajo za bazo podatkov. Če želite te metode ocenjevanja vplivov prenesti v OpenLCA, kliknite na LCIA metode na strani za prenos, angl. »Download page«. Ko jo prenesete, lahko bazo shranite kot datoteko ».zolca«. Datoteke ».zolca« so edinstvene razširitvene datoteke za program OpenLCA - vsakič, ko shranite ali uvozite svojo bazo podatkov morajo biti vaše datoteke v tej obliki. Z desno miškino tipko kliknite zavihek »Ocena učinka«, angl. Impact Assessment. v novi bazi podatkov angl. New database, ki ste jo ustvarili, in kliknite na uvoz, angl »Import«. Izberite možnost \ Database Import (Uvoz baze podatkov) v drugi podmapi. Zdaj se pomaknite do imenika, kjer je bila prenesena datoteka ».zolca« in kliknite na »Dokončaj« angl. Finish.

4 Izgradnja OpenLCA modela

4.1 Razlikovanje med tokovi in procesi v OpenLCA

Elementi baze podatkov, potrebni za modeliranje in primerjavo sistemov izdelkov v openLCA so projekti (Projects), sistemi proizvodov (Product system), procesi (Processes) in tokovi (Flows). Preden začnete graditi svoj model je dobro pojasniti razliko med tokovi in procesi v OpenLCA. Tokovi in lastnosti tokov so osnova za izgradnjo modela OpenLCA in izvedboizračunov. Industrijski sistemi (v tem primeru \Processes (procesi) so v OpenLCA enota sama po sebi z okoljskimi in materialnimi vtoki, ki jih določajo tokovi, in viri, ki jih količinsko kvantificiramo z različnimi tokovi. To olajša analizo proizvodnje več izdelkov iz enega samega procesa.

4.1.1 Tokovi

Tokovi so vsi produkti, snovni ali energetski vtoki in iztoki procesov v sistemu proučevanega produkta. Tok je opredeljen z imenom, vrsto pretoka in lastnostjo referenčnega toka.

OpenLCA razlikuje tri vrste tokov:

- osnovni tokovi: materialni ali energijski tok, ki neposredno ali posredno vstopa v proučevani sistem (npr. surova nafta, emisije v zrak ipd.),
- tokovi proizvodov: material ali energija, ki se izmenjuje med procesi v proučevanem proizvodu,
- tokovi odpadkov: material ali energija, ki zapušča proizvodni sistem.
- Vsak ustvarjen tok mora biti definiran z lastnostmi referenčnega pretoka, kot so masa, prostornina, površina itd. Za isti tok je mogoče določiti tudi več lastnosti pretoka, vendar je treba kot lastnost referenčnega toka izbrati samo eno lastnost toka.

4.1.2 Procesi

Procesi so nizi medsebojno povezanih dejavnosti, ki transformirajo vtoke v iztoke. Vsak proces je opredeljen z iztokom kot količinsko referenco z vrsto pretoka "product flow - tok proizvoda", ki je bodisi izbran ali ustvarjen pri ustvarjanju projekta.

OpenLCA razlikuje dve vrsti procesov:

- enotni procesi: analizirana je najmanjša enota, za katero so količinski opredeljeni vhodni in izhodni podatki in
- sistemski procesi: enota, za katero so vhodni in izhodni podatki združeni.

4.1.3 Projekti

S programom OpenLCA se lahko projekti primerjajo z okoljskimi vplivi različnih proizvodnih sistemov.

4.2 Izgradnja lastnega modela

Vsaka analiza LCA se začne z modeliranjem produktnega sistema. Sistem proizvoda je mogoče ustvariti bodisi iz procesnih podatkov ali z ročnim dodajanje procesov v model, odvisno od količine razpoložljivih podatkov in uporabniških nastavitev.

Sistem proizvoda vsebuje vse proučevane procese. Sistem proizvoda lahko sestavlja le en proces ali mreža več procesov in je določen z referenčnim procesom. V openLCA se lahko vplivi izračunajo za sistem proizvoda. Referenčni proces sistema proizvoda se uporablja za izračun vplivov za vse povezane procese v zgornjem toku proizvodnega sistema. V sistemu openLCA lahko sistem proizvoda ustvarite samodejno ali ročno. Grafični prikaz modela predstavlja sistem proizvoda in ga je mogoče preprosto spreminjati.

4.2.1 Izdelava sistema proizvoda iz procesnih podatkov

Uporabniki lahko v openLCA ustvarijo nov proizvodni sistem iz obstoječih procesov. Če želite izgraditi sistem proizvoda iz podatkov, ki temeljijo na obstoječih procesih, izberite procesni sistem, ki se nanaša na vaš problem. Na zavihku »Product Systems«(Sistem proizvoda), kliknite na \New product system (Nov produktni sistem) in kliknite »Finish« (dokončaj). V referenčnem zavihku (reference tab) podajte funkcijsko enoto za vašo študijo skupaj z enotami za tokove. V program lahko vključite razne možne predpostavke z dodajanjem opomb v zavihek z opisom »description tab«. Ko imate proizvodni sistem določen, bo grafikon modela prikazal le referenčni procesni sistem. Če želite zgraditi celoten model življenjskega cikla, z desno miškino tipko kliknite na sistem proizvoda, kliknite na Product system / Build Supply chain / Complete, da si ogledate celotno dobavno verigo. Te povezave se lahko spreminjajo glede na želje uporabnika in temeljijo na preučevanem sistemu. V tem programskem oknu je mogoče opraviti večino procesnih sprememb, urejanje in brisanje se lahko opravi glede na naravo problema.

Če želite oceniti okoljske vplive življenjskega cikla kliknite gumb \Calculate (Izračunaj) v zavihku »General Information tab« in izberite metodo alokacije, metodo ocene vplivov ter nastavite normalizacijo ali ponderiranja in pritisnite \Calculate (izračunaj). OpenLCA izračuna okoljske vplive prispevka vsakega koraka v življenjskem ciklu sistema proizvoda. Število in vrsta kategorij vplivov bodo odvisni od vrste metode ocenjevanja vpliva, ki jo izbere uporabnik.

4.2.2 Ročno dodajanje procesov v model

Druga možnost poleg samodejne povezave je ročno dodajanje procesnih tokov v model. Ta možnost je uporabna, če želite spremeniti nekatere tokove v obstoječem sistemu proizvoda, da se ujemajo z opisom procesa. To bo običajno uporabno pri zamenjavi vrste vira in energenta. Ko zgradite dobavno verigo za vaš proces, lahko ročno dodate ali odstranite povezave v procesnem omrežju. Z desno miškino tipko kliknite proces, ki ga je treba premakniti, in izberite \remove connections (odstranite povezave), če želite odstraniti določeno povezavo. Če želite poiskati tokove v smeri toka do določenega procesa kliknite \Search providers for. Če želite dodati nov proces, kliknite \Search recipients for: (Poišči ponudnike). Če povezava ne obstaja, povlecite in spustite referenčni procesni sistem v zavihku »Proces« (Process tab) v vrstici za krmarjenje in nato ustvarite povezave z dodajanjem prejemnikov in ponudnikov.

5 Študija primera

Namen tega primera je ob spoznavanju in uporabi programske opreme openLCA verzija 1.7 predstaviti tipično izvedbo analize življenjskega cikla. Upoštevajte, da to ni celovita analiza LCA, temveč je le primer z navedenimi podatki LCA za namene proučevanja. Številke v tem študijskem primeru so podane le kot primer in niso mišljene kot popolnoma točne. Primer vključuje postopna navodila za modeliranje tokov, procesov, sistemov izdelkov in projektov, da bi količinsko ocenili okoljske vplive.

Navedeni primer temelji na »bazi podatkov ELCD 3.2«, ki je brezplačno na voljo na spletnem mestu družbe Nexus (https://nexus.openlca.org/databases). Po korakih nam ta vodič pomaga razumeti delo z OpenLCA. Če potrebujete več informacij, si lahko preberete na strani http://www.openlca.org/, kjer najdete najnovejši uporabniški priročnik ter povezave do učnih videoposnetkov.

5.1 Cilj, obseg in omejitev tega primera

5.1.1 Definicija cilja

Cilj te študije primera je primerjava okoljskih vplivov treh različnih materialov za 500 ml embalaže za vodo. Embalaža je izdelana iz PET (polietilen tereftalata), PC (polikarbonat) in ALU (aluminija).

5.1.2 Opredelitev področja uporabe

Pri načrtovanju analize življenjskega cikla najprej začnemo z definiranjem funkcijske enote. V tem primeru imajo vse vrste pakiranja PET, PC in ALU enako funkcijo: vsebovati in zaščititi pijačo - vodo. Torej bi lahko funkcijsko enoto opredelili kot embalaža za 500 ml vode. Prva možnost bo imenovana »PET embalaža«, druga »PC embalaža« in tretja »ALU embalaža«. Da bi se izognili prezapletenim modelom v tej študiji primera, v tej študiji ne bomo upoštevali tesnjenja in zamaška, temveč le jedro telesa embalaže. Meje sistema te ocene vključujejo proizvodnjo, porabo in odstranjevanje embalaže.

5.1.3 Omejitve

V tej študiji primera nimamo natančnih podatkov o proizvajalcu in uporabljamo omejeno bazo podatkov. Zato nekatere podatke ni mogoče najti v podatkovni bazi in je potrebno uporabiti približke in določene predpostavke. Natančno težo pločevinke in steklenice, porekla aluminija, trenutnega deleža recikliranja, transporta ter nekaterih drugih procesov je mogoče predpostaviti ali oceniti. Kljub temu pa lahko dobimo dober vtis o možnih vplivih na okolje. Ta študija ni izdelana z namenom sodelovati v razpravi o različnih materialih za embalažo, temveč zgolj prikazuje funkcije in zmožnosti programske opreme OpenLCA ter predstavlja tipičen primer okoljskega načrtovanja.

5.2 Izgradnja in primerjava sistemov

5.2.1 Podatki o bazi podatkov in namestitev

Pri ocenjevanju življenjskega cikla je potrebno pridobiti dostop do podatkovne zbirke ali sestaviti lastne inventarizacijske podatke. Ta študija primera temelji na podatkovni bazi ILCD, platformi Evropske Komisije za oceno življenjskega cikla proizvodov.

Če želite namestiti bazo podatkov, lahko prenesete bazo podatkov s spletne strani openLCA (https://nexus.openlca.org/), pri čemer so nekatere baze plačljive in nekatere brezplačne, podatkovna baza ELCD je brezplačna. Če želite bazo dodati v bazo podatkov openLCA, kliknite desno tipko miške v okno »Navigation” in izberite »Import database«, nato izberite preneseno bazo in jo uvozite. Nato lahko začnete z izvedbo študije.

5.3 Ustvarjanje novega toka

Če želite ustvariti mapo s tokovi »Flows«, z desno miškino tipko kliknite na mapo elementov »Flows«, izberite »Add new child category« in jo poimenujte, npr. »Embalaža s pijačo«. Ker imamo tri vrste embalaže, bomo ustvarili tri podmape: »Tokovi – PET«, »Tokovi – PC« in »Tokovi – ALU«.

Najprej bomo ustvarili nov tok v mapi »Tokovi – PET«. Z desno tipko miške kliknite zraven »Tokovi – PET« in izberite »New flow - Nov pretok«, nato izberite vrsto pretoka »Product (izdelek)«, referenčni vrednost pretoka »Mass« in kliknite »Finish«. Tok se zdaj prikaže v mapi v oknih za krmarjenje in v oknu za urejanje.

Na podoben način bomo stvarili druge tokove v skladu s Preglednico 1.

Preglednica 1: Vnosi za ustvarjanje novih tokov

Ime toka (Name)	Vrsta toka (Flow type)	Lastnosti referenčnega toka (Reference flow property)
polyethylene terephthalate (PET)	Proizvod (product)	Masa
polypropylene (PP)	Proizvod (product)	Masa
polyethylene high density granulate (PEHD)	Proizvod (product)	Masa
polybutadiene (PB)	Proizvod (product)	Masa
polycarbonate (PC)	Proizvod (product)	Masa
polyethylene high density granulate (PEHD)	Proizvod (product)	Masa
Aluminium waste	Odpadki (Waste)	Masa
Aluminum, primary	Proizvod (product)	Masa
Aluminum, secondary	Proizvod (product)	Masa

5.4 Ustvarjanje novega procesa

Če želite ustvariti mapo v mapi elementov »Processes«, z desno miškino tipko kliknite na mapo s procesi »Processes«, izberite »Add new child category« in jo poimenujte npr. »Embalaza s pijačo«. Če želite ustvariti nov proces, z desno tipko miške kliknite zraven »Embalaža s pijačo (PET)« in izberite »New process«.

Znotraj mape bomo ustvarili 3 procese: Embalaža s pijačo (PET), Embalaža s pijačo (PC) in Embalaža s pijačo (ALU). Poimenujte nov proces »Embalaža s pijačo (PET)«, izberite kvantitativno referenco »Embalaža za pijačo« in kliknite "Finish". Proces »Embalaža s pijačo (PET)« naj bi se zdaj pojavil v mapi »Embalaža s pijačo« tako v oknih za naigacijo kot tudi v oknu za urejanje.

Okno urejevalnika procesov je strukturirano v več zavihkov na dnu vsakega okna urejevalnika. V zavihku Vtok / Iztok lahko vidite, da je kvantitativni referenčni tok »Embalaža za pijačo« prikazan kot izhodni tok.

Dodajte vtoke v razdelku Vtoki v zavihku Inputs/ Outputs (vtoki / Iztoki), kot je opisano v Preglednici 1, z uporabo filtra za pretok (flow filter): Pritisnite zeleni gumb "+" v zgornjem desnem kotu ali dvokliknite v stolpec "Flow (Tok)" v razdelku Vtoki.

Preglednica 2: Vtoki za procese proizvodnega sistema »Embalaža s pijačo (PET)«

Flow	Category	Amount	Unit	Provider
drinking water	Materials production/ Water	1.00	kg	Drinking water, production mix, at plant, water purification treatment, from surface water - RER
polyethylene high density granulate (PE-HD)	Materials production/Plastics	0.004	kg	Polyethylene high density granulate (PE-HD), production mix, at plant - RER
polyethylene terephthalate, granulate, bottle grade | polyethylene terephthalate production, granulate, bottle grade - RER	201:Manufacture of basic chemicals, fertilizers and nitrogen compounds, ...	0.06	kg	polyethylene terephthalate production, granulate, bottle grade | polyethylene terephthalate, granulate, bottle grade | APOS, U - RER
polypropylene granulate (PP)	Materials production/Plastics	0.001	kg	Polypropylene granulate (PP), production mix, at plant - RER
transport in t*km	Transport services/Other transport	77.25	kg*km	Articulated lorry transport, Euro 0, 1, 2, 3, 4 mix, 40 t total weight, 27 t max payload - RER

Mogoče je uporabiti tudi funkcijo iskanja v zgornjem desnem kotu, če želite poiskati vse elemente znotraj aktivne baze podatkov. Za iskanje v različnih vrstah elementov baze podatkov uporabite puščico poleg vrstice za iskanje. Prav tako je mogoče iskati tokove v oknu Navigator Window in jih dodati kot vtoke za proces s pomočjo sistema »povleci in spusti«.

Ko najdete tokove, jim lahko prilagodite količine, ki so potrebne za vsak vtok in iztok v skladu s Preglednico 2. Dvokliknite stolpec "Provider - Ponudnik", da povežete vtoke z njihovo ustrezno dobavno verigo in shranite spremembe. Opomba! Številčni format: uporabite piko namesto decimalnih vejic. Ne shranjene spremembe v urejevalniku so označene z *. Shranite spremembe, tako da v glavnem meniju kliknete gumb Save (Shrani) ali uporabite ukaz Ctrl + S. Sedaj ustvarite drugi proces za »Embalaža s pijačo (PC)«.

Preglednica 3: Vtoki za procese proizvodnega sistema »Embalaža s pijačo (PC)«

Flow	Category	Amount	Unit	Provider
drinking water	Materials production/Water	1.00	kg	Drinking water, production mix, at plant, water purification treatment, from surface water - RER
polybutadiene granulate (PB)	Materials production/Plastics	0.004	kg	Polybutadiene granulate (PB), production mix, at plant - RER
polycarbonate | polycarbonate production - RER	201:Manufacture of basic chemicals, fertilizers and nitrogen compounds, ...	0.06	kg	polycarbonate production | polycarbonate | APOS, S - RER
polyethylene high density granulate (PE-HD)	Materials production/Plastics	0.001	kg	Polyethylene high density granulate (PE-HD), production mix, at plant - RER
transport in t*km	Transport services/Other transport	77.25	kg*km	Articulated lorry transport, Euro 0, 1, 2, 3, 4 mix, 40 t total weight, 27 t max payload - RER

Sedaj ustvarite tretji proces za »Embalaža s pijačo (ALU)« v skladu s Preglednico 4.

Preglednica 4: Vtoki za procese proizvodnega sistema »Embalaža s pijačo (ALU)«

Flow	Category	Amount	Unit	Provider
drinking water	Materials production/Water	1.00	kg	Drinking water, production mix, at plant, water purification treatment, from surface water - RER
Aluminum, primary, ingot, at plant - RNA	Product and Waste Flows	0.018 - recycled alu	kg	Aluminum, primary, ingot, at plant - RNA
Aluminum, secondary, rolled - US	Product and Waste Flows	0.018*recycledalu	kg	Aluminum, secondary, rolled - RNA
transport in t*km	Transport services/Other transport	77.25	kg*km	Articulated lorry transport, Euro 0, 1, 2, 3, 4 mix, 40 t total weight, 27 t max payload - RER

5.5 Ustvarite produktni sistem

Sedaj ustvarite produktne sisteme »PET«, »PC« in »ALU«. Ko končate z ustvarjanjem vseh procesov v proizvodni verigi, lahko izdelate produktni sistem izdelkov na podlagi zadnjega procesa kot referenčnega procesa sistema proizvoda.

Pojdite na zavihek »General information - Splošne informacije« v urejevalniku procesov »PET« in pritisnite gumb »Ustvari sistem izdelkov - Create product system« ali v glavnem meniju uporabite »Ustvari ikono produktnega sistema«. Poimenujte produktni sistem »PET«, izberite »Embalaža s pijačo (PET)« kot referenčni proces, omogočite »Auto link processes«, da se vzpostavijo vse povezave med procesi, izberite »Prefer default providers« in izberite »Prefer proces type« ter kliknite" »Finish – Dokončaj«.

Produktni sistem »PET« se odpre v oknu urejevalnika z jezičkom Splošne informacije. Pojdite na zavihek Modelna grafika in si oglejte izdelan izdelek. Če sta izbrani možnost »Auto link processes«, se bodo v zgornjem levem kotu vsakega postopka samodejno upoštevali postopki za vhodni tok, označen z »+«. Dvakrat kliknite na procese, da povečate pogled in videli boste vtoke in iztoke izdelkov, kliknite gumb "+", da razširite pogled in si oglejte ponudnike za vtoke procesnih enot, ki ste jih modelirali.

Podobno kot za »PET« ustvarite produktni sistem še za »PC« in »ALU«.

5.6 Ustvarite projekt

Sedaj ustvarite nov projekt »Primerjava_PET_PC_ALU«. Če želite ustvariti nov projekt, z desno tipko miške kliknite elemente mape »Projekti« in izberite »Nov projekt« in ga poimenujte »Primerjava_PET_PC_ALU«.

Urejevalnik projekta se odpre v razdelku za nastavitev projekta. Izberite metodo LCIA »CML (baseline)«. Za količinsko opredelitev vplivov analiziranega proizvoda na okolje je potrebno metodo ocenjevanja vplivov uvoziti v openLCA. GreenDelta brezplačno ponuja obsežen paket okoljskih metod za uporabo z vsemi zbirkami podatkov, ki so na voljo v spletni trgovini Nexus, in jih je mogoče prenesti s spletne strani openLCA (http://www.openlca.org/downloads).

Dodajte proizvodni sisteme kot možnost 1 in ga poimenujte »PET«. Dodajte »PC« kot možnost 2 in »ALU« kot možnost 3. Shranite spremembe in kliknite »Report - Poročilo«. Prikazalo se bo poročilo o rezultatih projekta z projektnimi variantami, LCIA rezultati, rezultati za posamezne kazalce, procesni prispevki, relativne rezultate ipd. Diagrami prikazujejo posamezne rezultate vsake variante projekta za izbrani kazalnik. Izbiro kazalca lahko spremenite in grafikon se dinamično posodablja.

6 Zaključek

Analiza LCA nam z orodjem openLCA omogoča izbrati proizvod, ki ima iz vidika negativnih vplivov na okolje najmanjši učinek. To informacijo lahko uporabimo pri iskanju okoljevarstvenih rešitev ter iskanju ekonomičnih in kakovostnih proizvodov. OpenLCA je uporaben za podporo pri odločanju in ugotavljanju priložnosti za učinkovitost vzdolž vrednostne verige. Z orodjem je mogoče identificirati tiste operacije znotraj dobavne verige, ki imajo največjo možnost za izboljšanje (žarišča). Analiza LCA daje zagotovilo, da spremembe, narejene za izboljšavo enega dela industrijskega sistema, ne bodo »preusmerile bremena« s prenosom težav ali ustvarjanjem novih problemov v drugem delu verige. Z njo lažje določimo, ali bo investicija v izboljšave v enem delu dobavne verige povzročila kakšno pomembno izboljšanje skozi celotni življenjski cikel.

Ta študija primera je samo za izobraževalne namene in zato ni mišljeno, da bi rezultate obravnavali kot del celovite ocene življenjskega cikla. Kljub temu daje vpogled o pristopu modeliranja in primerjanja različnih modelov izdelkov. Ta študija primera kaže tudi, kako je mogoče modelirati scenarije recikliranja in jih uporabiti za iskanje možnosti recikliranja z najmanjšimi vplivi na okolje.

Reference

Če želite izboljšati to študijo primera in podrobneje preiti v podrobnosti, si lahko ogledate naslednje spletne strani in dokumente:

OpenLCA 1.7.0, Comprehensive User Manual Version 1.1, November 2017. Authors: Claudia Di Noi, Dr. Andreas Ciroth, Michael Srocka.
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Izboljšanje morskega sedimenta v aplikacijah z zemeljskimi deli s procesom flokulacije/koagulacije

LAURA VOVČKO IN STANISLAV LENART

Povzetek Potreba po poglabljanju pristaniškega dna vodi v stisko s prostorom za odlaganje izčrpanega morskega sedimenta. Z omenjeno problematiko se srečujejo tudi v Luki Koper, kjer ga za normalno funkcioniranje vplovnih poti letno izčrpajo približno 450.000 m^3. To nas spodbuja k iskanju rešitev, ki bi omogočile nadaljnjo uporabo večjih količin izčrpanega morskega sedimenta. Slednji se namreč zaradi visoke vsebnosti vode izkaže kot neuporaben v različnih aplikacijah z zemeljskimi deli. Morebitno rešitev pri izpostavljeni problematiki predstavlja proces flokulacije, ki omogoča nastanek poroznejše strukture izčrpanega morskega sedimenta in mu posledično omogoči hitrejše dreniranje vode. Prispevek obravnava primerjavo in vrednotenje učinkovitosti samodejnega izločanja vode iz izčrpanega morskega sedimenta in vpliv uporabe flokulantov na ta postopek. Na osnovi izvedenih laboratorijskih preiskav so bile primerjane tudi osnovne geomehanske lastnosti ob in brez uporabe flokulantov. Testiranja so bila izvedena z različnimi dodatki, ki so privedli do omenjenega procesa.

Ključne besede: • flokulacija • poglabljanje pristaniškega dna • morski sediment • geomehanske lastnosti • glina •

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DOI https://doi.org/10.18690/978-961-286-211-4.2 ISBN 978-961-286-211-4
Dostopno na: http://press.um.si.

Improvement of Marine Sediment for Engineering Applications with the Flocculation/Coagulation Process

LAURA VOVČKO & STANISLAV LENART

Abstract Deepening of the seabed in harbors causes problems with space on the location of marine sediment disposal. Luka Koper, where an amount of dredged marine sediment is approximately 450,000 m^3 annually, is also affected by this problem. This encourages us to find a sustainable solution for reuse of vast amounts of dragged marine sediment. The latter is unusable in most engineering applications due to its high water content. One of the possible solutions to this problem could be the flocculation process, which allows us to obtain a more porous sediment structure with improved drainage. This research presents the comparison and evaluation of natural water drainage efficacy of dragged marine sediment, and the sediment that went through the flocculation process. In addition, we also compared the geomechanical properties of natural and treated dredged sediment. The tests were performed using materials prepared with the process of flocculation with various additives.

Keywords: • Flocculation • Deepening of the seabed • Marine sediment • Geomehanic properties • Clay •

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DOI https://doi.org/10.18690/978-961-286-211-4.2 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Uvod

Z geomehanskega vidika želimo izčrpan morski sediment pretvoriti v nasipni/zasipni material, ki bi bil lahko uporabljen za zemeljska dela v okviru izdelave transportnih in manipulativnih površin v Luki Koper in bi zagotavljal njihovo dolgoročno stabilnost in funkcionalnost. Po začetni analizi stanja in potreb vezanih na izčrpan morski sediment, smo tako za eksperimentalni del določili dva cilja:

1. Analiza procesa koagulacije/flokulacije ter primerjava in vrednotenje učinkovitosti različnih flokulantov/koagulantov, ki omogočajo hitrejše samodejno izločanje vode iz izčrpanega morskega sedimenta, in
2. Analiza karakteristik morskega sedimenta in ocena primernosti za uporabo v aplikacijah z zemeljskimi deli.

Pri eksperimentalnem delu smo uporabili pet različnih flokulantov, dva naravna flokulanta (hitin in celuloza) in tri sintetične polimere. Oba naravna polimera se uvrščata med polisaharide (Takada in sod., 2015). Dandanes se namesto naravnih polimerov pogosteje uporabljajo sintetični polimeri, ki nastanejo s postopkom polimerizacije. Polimerizacija je kemični proces pri katerem se posamezne molekule (monomeri) vežejo v daljšo verigo (makromolekule). Število vključenih monomerov definira stopnjo polimerizacije, ki skupaj z molekulsko maso posameznega monomera določa molekulsko maso nastale makromolekule. Zaradi vsebnosti velikega števila monomerov je za polimere značilna visoka molekulska masa (Umoredn in sod., 2016). Pri analizi smo uporabili tri sintetične polimere z različnimi molekulskimi masami (nizka, srednja in visoka). Polimer z nizko molekulsko maso ima za osnovno verigo amonijev poliakrilat, poleg smo uporabili tudi dodatek kalcijevega karbonata ($CaCO_3$). Polimera s srednjo in visoko molekulsko maso sta imela za osnovno verigo akrilamid.

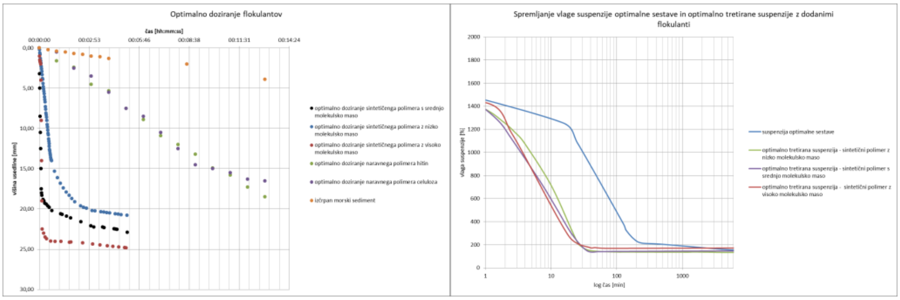
Izvedenih je bilo veliko študij o dejavnikih, ki vplivajo na proces koagulacije/flokulacije. Optimalno doziranje dodatkov na podlagi upoštevanja pH vrednost, doziranje flokulanta in hitrosti mešanja suspenzije so preučevali Saritha in sod. (2017). S preliminarnimi preiskavami smo ugotovili, da je izvedljivost procesa flokulacije povezana z nekaterimi dejavniki (razpoložljiv volumen posode, intenzivnost mešanja suspenzije, količina suhe snovi).

Preiskave smo zato izvedli z nekaj ponastavitvami (uporaba posode konstantnega volumna, uvedba konstantnega mešanja suspenzije) in dodatnim ugotavljanjem ustrezne količine suhe snovi oziroma mase suhe komponente v izčrpanem morskem sedimentu (suspenziji). Slednji dejavnik smo določali eksperimentalno, s spreminjanjem sestave suspenzije in razmerja dodanega flokulanta ter vizualno. V primeru izvajanja flokulacije v drugačnih pogojih (velikost in oblika posode), se pričakuje drugačno optimalno razmerje med sestavo suspenzije in flokulantom.

2 Analiza

2.1 Učinkovitost samodejnega izločanja vode

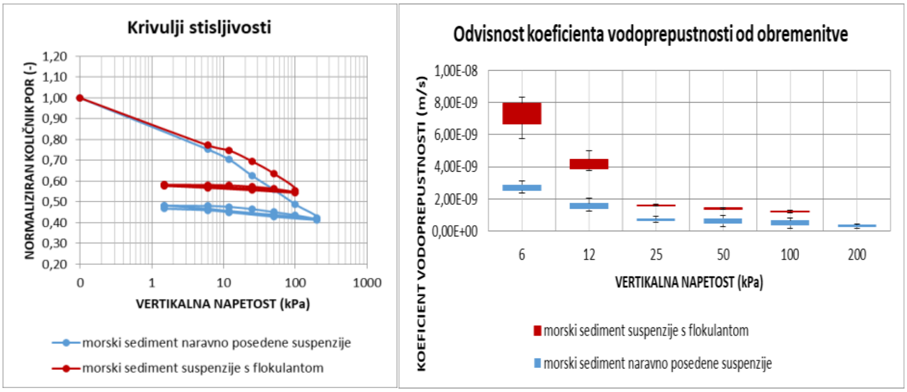
V testiranje smo vpeljali dodatno spremenljivko, suspenzijo z različnimi masnimi razmerji suha snov : morska voda. Štirim različnim sestavam suspenzije smo dodali tri različna razmerja komponente flokulanta in na ta način določili optimalno sestavo suspenzije ter optimalno doziranje posameznega flokulanta. Hitrost posedanja smo privzeli kot merilo za uspešno izveden proces flokulacije (Slika 1). Merili smo jo s tehniko digitalne primerjalne fotografske analize z uporabo steklenih stolpcev. V nadaljevanju smo za določitev učinkovitosti samodejnega izločanja vode iz usedline obdelane suspenzije uporabili geosintetično odcejalno membrano.



Slika 1: Levo: Hitrosti optimalno doziranih flokulantov. Desno: Spremljanje vlage suspenzije optimalne sestave in optimalno tretirane suspenzije z dodanimi flokulanti

2.2 Geomehanske lastnosti

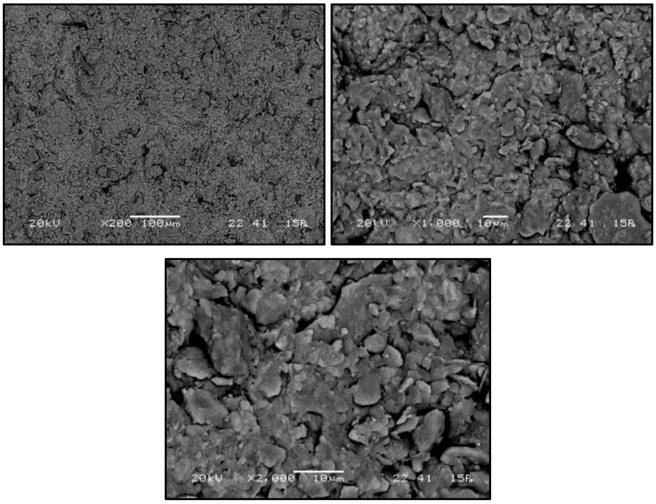
Preiskave geomehanskih lastnosti (naravna vlažnost, stisljivost in vodoprepustnost) smo izvedli na izčrpanem morskem sedimentu in optimalno obdelanem materialu, tj. zmesi suspenzije in flokulanta z ugotovljenim najbolj izločanjem vode (Slika 2).



Slika 2: Prikaz krivulje stisljivosti in koeficientov vodoprepustnosti

3 Ugotovitve

Preiskan material se po USCS klasifikaciji uvršča med mastne gline. Osnovni element strukture plastnatih silikatov (filosilikatov) so plasti, ki so zaradi negativnega naboja med sabo rahlo razmaknjene (Slika 3). Negativni naboj teh plasti se kompenzira s pozitivnimi naboji dodanega flokulanta, kar vodi v proces flokulacije. Nizka hitrost posedanja slabše razvitih flokul je tako opazna ob uporabi naravnih flokulantov (hitin in celuloza). Bistveno višja hitrost posedanja dobro razvitih flokul je opazna ob uporabi sintetičnih polimerov (slika 1). Hitrosti posedanja so neposredno povezane s molsko maso posameznega flokulanta. Mehanizme, ki vodijo v nastanek obravnavanega procesa za različne tipe flokulantov in koagulantov podrobneje opisujejo Lee in sod. (2014).



Slika 3: Prikaz strukture naravno posedenega morskega sedimenta s SEM posnetki pri povečavah 200x, 1000x in 4000x

Vlažnost izčrpanega morskega sedimenta, ki je šel skozi proces flokulacije upade hitreje kot pri izčrpanem morskem sedimentu (slika 1, desno). Določena količina vode se uskladišči v strukturi sedimenta in ni opazne bistvene spremembe v končni vlažnosti. S procesom flokulacije se ustvari rahla struktura, ki sprva omogoča hitro dreniranje vode. S preiskavami stisljivosti smo ugotovili, da se že ob delovanju nizkih obremenitev ta struktura poruši. Nastala struktura torej ni obstojna, še vedno gre za izjemno stisljive zemljine (slika 2, levo). Koeficient vodoprepustnosti se z uporabo flokulantov na račun nastale strukture nekoliko poveča (slika 2, desno), še vedno pa gre za praktično neprepustno zemljino.

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1ST INTERNATIONAL CONFERENCE ON TECHNOLOGIES & BUSINESS
MODELS FOR CIRCULAR ECONOMY: CONFERENCE PROCEEDINGS
M. Bogataj, Z. Kravanja & Z. Novak Pintarič (eds.)

University of Maribor Press

Improvement of Colombian Aquaculture Hydric Sustainability: Application of Phytoremediation Process Under a Circular Economy Scheme

JANET BIBIANA GARCÍA-MARTÍNEZ, CRISÓSTOMO BARAJAS-FERREIRA &
VIATCHESLAV KAFAROV

Abstract World water shortage and difficulty in the management of water resources has generated a global alert, which has led to the declaration of the "water crisis". One of the problems arising from difficulties in the efficient management of water resources is a global shortage of food. Within agricultural activities, aquaculture is known for its high-water requirements, in addition, its post-consumption waters have high levels of nitrogen compounds, phosphates and dissolved organic carbon, which must be treated and disposed. Worldwide, several prototypes using microalgae have been used at the laboratory and pilot level. However, gaps in its implementation and operation, in addition to the final quality of post-harvest water are still latent. Due to the above, in this work we propose the evaluation of microalgal biomass production in aquaculture post-consumption waters and its impact on the improvement of water quality. Also, a method is proposed for the reuse of treated water for use in the aquaculture industry as an alternative for the sustainable use of water resources from a perspective of green economy and circular.

Keywords: • Wastewater • Microalgae • Aquaculture • Circular Economy • Green Economy •

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DOI https://doi.org/10.18690/978-961-286-211-4.3 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

Low efficiency in the management of water resources is one of the critical points for the sustainable development of national and global agriculture. According to FAO, in 2050 agriculture will need to produce 60% more food worldwide, which will require high availability of water resources resources (FAO 2014).

Within the agricultural activities, extensive aquaculture is recognized for its ability to solve the food crisis that is looming. However, these processes require high volumes of water.

Wastewater from closed aquaculture systems had high levels of nitrogen and dissolved inorganic phosphorus. The primary responsibility for these high concentrations of nutrients in the food not consumed, since according to Crab et al., (2007). Up to 75% of the food used is maintained in the form of nitrogen and phosphorus in the post-culture water. The latter contributes to the sustained increase in the concentration of organic waste and toxic compounds in aquatic systems (Lananan et al., 2014).

During the last 50 years, significant efforts have been made to remove different nutrients from this wastewater, which prevent the eutrophication of water bodies close to the production systems and allow recirculating the treated water (Crab et al ., 2007). Currently there is a great diversity of biological and chemical methods that have been successfully used in the process of nutrient removal, such as: (1) biological processes for the elimination of nitrogen such as nitrification and denitrification (Boley et al., 2000) and (2) chemical processes as chemical precipitation for the elimination of phosphorus (Ebeling et al., 2003); This last process, although useful, is a less environmentally friendly technique, since it leads to the formation of highly polluting sludge for the environment (Gao et al., 2016).

Although there are conventional treatments for the management of this water, most are high cost and do not generate any added value to the producers. One of the methods that can generate added value is the use of microalgae since they can sequester nutrients and produce biomass enriched with metabolites of industrial interest. The objective of this project is to design and build a recirculation system for aquaculture post-consumption water using microalgae as a phytoremediation system. To achieve the above, we proposed to evaluate the quality of post-consumer water and its viability as a culture medium to be recycled in the process and generate valuable products that are integrated into the production process.

2 Material and methods

2.1 Microorganism and culture conditions

Chlorella vulgaris and *Scenedesmus obliquus* strains were obtained from Microalgae Culture Collection of Universidad Francisco de Paula Santander (Colombia). The strains were mantained in Bold Basal Media (Andersen, 2005) under light cicle 12:12 (light:dark) and 28°C ±2.

2.2 Fisheries wastewater

Wastewater was obtained from the culture of *Oreochromis* sp at the laboratory of fish nutrition from Universidad Francisco de Paula Santander. For the cultivation of microalgae, the effluents were filtered twice with a cloth filter.

2.3 Parameters of algae culture

C. vulgaris and *S. obliquus* were inoculated on three different treatments: (1) Sterile wastewater (by autoclaving at 15 psi, 15 min), (2) Non-Sterile wastewater and (3) Non-Sterile wastewater supplemented with CO_2 (1% or 0,006 vvm). All the experiments had a duration of 20 days.

2.3 Analytical methods

Biomass concentration (dry weight basis or DW), total lipids, total carbohydrates and total proteins were monitored using the methods described by Moheimani and Borowitzka (2013). Orthophosphates (PO_4) and nitrate concentrations in wastewater before and after treatment. PO_4 was determined by Vanadomolybdo phosphoric Acid Colorimetric Method (APHA, 2017) and NO_3 by Horiba LAQUATwin Nitrate sensor. Complementary biochemical and microbiological analyses (BOD, COD, total coliforms and faecal coliforms) were carried out at the beginning and end of the experiments.

3 Results

The concentration of biomass produced after 20 days is presented on figure 1. According to the results both algae were able to grow on Non-Sterile media (NS), with the lowest values for both algae (0,9 g/L for *C. vulgaris* and 0,5 g/L for *S. obliqus*) in comparison with the other two treatments. This lower value can be explained by the possible the competition with other microorganisms present in the wastewater, which can predate algae or consume faster the different nutrients present on the media. One interest feature occurs when the media supplemented with CO_2 ($NS+CO_2$), in this scenario both algae reach its highest biomass concentration (1,5 g/L for *C. vulgaris* and 1,2 g/L for *S. obliqus*). Since CO_2 is the mayor source of carbon for photosynthetic organism, the presence in excess on the wastewater favours the biomass production of algae.

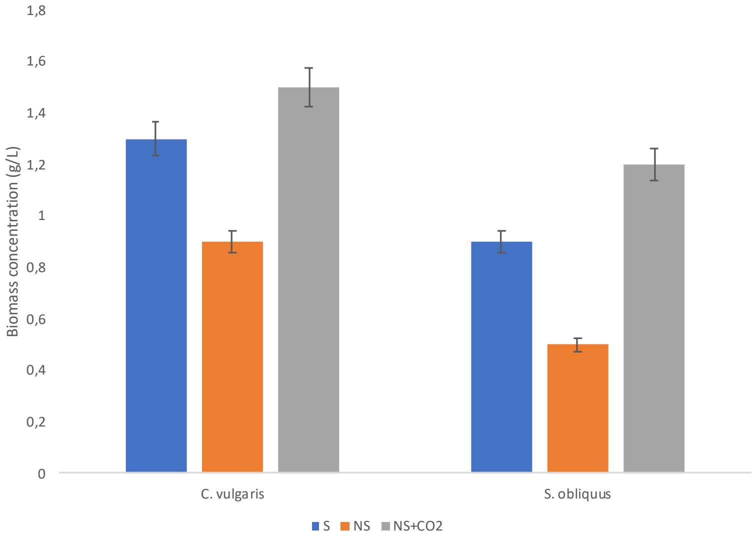

Figure 1: Biomass Concentration for *C. vulgaris* and *S. obliquus*, S: Sterile media; NS: Non-Sterile media. Source: own

On figure 2, the biomass composition for *C. vulgaris* and *S. obliqus* is presented. The results shown that both algae possess a large concentration of proteins (45% w/w), followed by carbohydrates (23-25%) and lipids (12-15%).

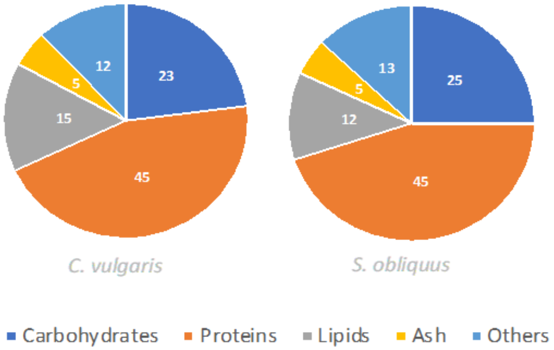

Figure 2: Biomass Composition for *C. vulgaris* and *S. obliquus*, Source: own

The quality of the wastewater after the culture of both algae is shown on figure 3. This results allow to understand that the algae can drastically reduce several parameters such as CDO and BDO_5, while NO_3 and PO_4 (>95%) is almost completely removed from the water.

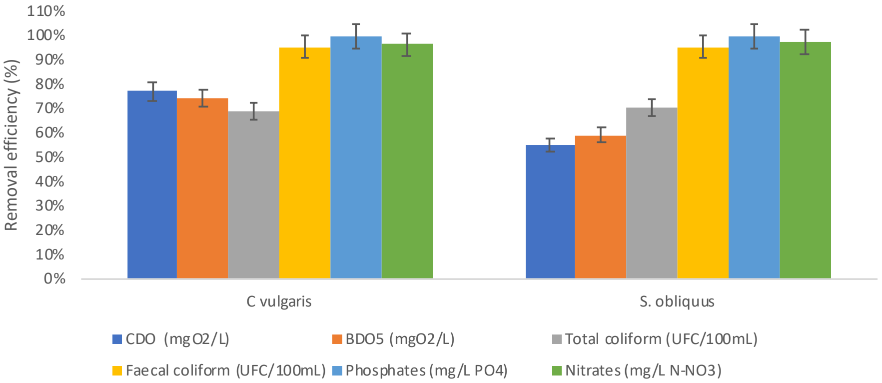

Figure 3: Removal efficiency (%) *C. vulgaris* and *S. obliquus*, source: own.

4 Discussion

Extensive research has shown that algae can be easily produced in wastewater and this allows the production of biomass for high-value products, and the remediation of hazardous nutrients such as nitrogen, phosphates, and others (Ma et al., 2016; Rawat et al., 2011).

In the present study, it was possible to determine high removal rates of COD, BDO_5, nitrates and orthophosphates with efficiencies closer to 100% in the removal of nitrogen compounds. Highlighting the high efficiency in the elimination of nitrates is essential. This high value may point to the fact that culture conditions could be forcing the algae to synthesize nitrogen and phosphate-dependent metabolites (such as proteins and chlorophylls) (Venckus et al., 2017). At a global scale, it is possible to find clear and concrete examples of the use of this type of wastewater for the production of microalgal biomass as a suitable source of food, feed and biofertilizers. Ansari et al., (2017) Guldhe et al., (2017) evaluated at laboratory scale production of *Chlorella sorokiniana*, *Ankistrodesmus falcatus Scenedesmus obliquus* and post-consumption tilapia water in South Africa using heterotrophic and mixotrophic strategies. Milhazes-Cunha and Otero (2017) demonstrated the feasibility of using algae cultures in conjunction with anaerobic systems for the reuse of treated water into the fisheries. The only technology scaled up to a considerable volume (13 m3) is located in Belgium, the MaB-flocSBRs system developed by the researchers of the University of Gent in consortium with the Ecole des Métiers de l'Environnement (EME, France) (Van Den Hende et al., 2011; Van Den Hende et al., 2014).

This system aims to treat Lucioperca waters with microalgae to recirculate the most substantial amount of medium used and use biomass for biogas production. The algal biomass produced on aquaculture water treatment can also be used as live feed for various stages of growth in marine filters (Ferreira et al., 2008), as food for larvae of some gastropods (during their stages of growth), and also as food for some crustaceans and some fish species in their earliest growth stages (Brown and Robert, 2002). Another possible use is as indirect food, especially for the production of zooplankton (i.e., brine shrimp and rotifers) which are essential food for several carnivorous larvae (Welladsen et al., 2014). In recent decades, a large number of microalgae species have been studied as a source of nutrients in aquaculture, with only a small number of species being exploited (Guedes and Malcata, 2012). Other possible uses may be the generation of biofuels and soil conditioners (Alobwede et al., 2019).

5 Conclusions.

It was possible to combine the removal of hazardous nutrients (such as nitrate and orthophosphates) from wastewater and high-valuable algal biomass from the two strains evaluated (C. vulgaris and S. obliquus) with a good concentration of proteins and lipids, which can be used on a further process of valorisation. These two algae were able to adapt rapidly and growth, obtaining a high consumption of both nitrate and phosphate. It is possible to highlight that the cultivation of these two algae in the wastewater significantly reduced the physicochemical and microbiological values. However, C. vulgaris presented the highest rate of COD, BOD_5 and coliforms. Finally, these results allow us to establish a solution focused on the circular economy for wastewater from fish farming, which has the potential to limit the environmental impact generated by the excessive use of fresh water and the disposal of high volumes of effluents. This will substantially reduce the emission of hazardous nutrients to water bodies and will allow the reuse of both water and the recirculation of these nutrients in the same agricultural systems, generating more sustainable and sustainable processes.

Acknowledgments

The Authors thanks to Universidad Industrial de Santander for providing materials and equipment for successfully conclude this research.

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Industrial Symbiosis in the Cement Industry - Exploring the Linkages to Circular Economy

YANA RAMSHEVA & ARNE REMMEN

Abstract Policy makers, industries and academia acknowledge industrial symbiosis (IS) as a strategy for facilitating circular economy (CE) since it evolves around the notion of closed-loop resource circulation. Through IS companies exchange materials, energy, water and by-products, thus promoting cleaner production, improved resource efficiency and lower CO_2 emissions. There exist ample studies analyzing the benefits of IS partnerships for companies. Nevertheless, demonstrative cases on how the link between IS and CE occurs in practice seem to be limited. This study aims at filling that void by examining twelve IS partnerships at a large cement producer in Denmark and linking them to Ellen MacArthur's "Circular economy systems diagram". The study furthermore adds to the discussion of the impacts of CE on businesses, by exploring the influence that the established IS partnerships have on improving resource efficiency.

Keywords: • circular economy • industrial symbiosis • By-products • alternative materials • alternative fuels • case study •

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DOI https://doi.org/10.18690/978-961-286-211-4.4 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

Businesses and policy makers increasingly address the necessity to combat finite resource overuse that negatively impacts the environment (Bocken *et al.*, 2016) and instead to focus on strategies that promote sustainable development and cleaner production (Lieder and Rashid, 2016). At the same time, the engagement of industries is considered critical for sustainable growth (Yang and Feng, 2008). Circular economy (CE) is acknowledged as a key strategy for moving forward in that direction (Korhonen, Honkasalo and Seppälä, 2018a) as it seeks to decouple economic growth from development (Ellen MacArthur Foundation, 2017). CE is an industrial system, which focuses on keeping the embedded value in resources for as long as possible. CE aims at eliminating waste by implementing solutions for prolonging product life, reuse, remanufacturing, recycling.

One way companies have translated open-loop resource circulation in their business activities is through establishing industrial symbiosis (IS) partnerships. IS partnerships enable otherwise diverse industries to set up collaborative activities for exchanging wastes, by-products, energy, water, information, etc. (Chertow, 2004). IS sees the economic system as an integrated ecosystem where residuals from one industry can serve as a resource for another (Wen and Meng, 2015), lowering the initial demand for virgin resources. In the cement industry, for example, currently responsible for about 5 to7 % of the global CO_2 emissions (Benhelal *et al.*, 2013), IS partnerships enable companies to get access to solid wastes as alternative raw materials and fuels, which results in a reduction of global CO_2 impact (Hashimoto *et al.*, 2010). According to (Saavedra *et al.*, 2018), a transition towards a more CE will not be possible without the presence of IS since IS partnerships establish the link between independent businesses for the exchange of by-products, energy, water, and even know-how (Saavedra *et al.*, 2018).

Despite the identified relation between the two concepts of CE and IS, the majority of the existing publications are in the form of literature reviews and conceptual studies (Wen and Meng, 2015; Lieder and Rashid, 2016; Sauvé, Bernard and Sloan, 2016; Mulrow *et al.*, 2017; Homrich *et al.*, 2018). Few studies explore the CE performance of IS schemes (Wen and Meng, 2015), but to our knowledge, little research appears to demonstrate how the link between IS and CE occurs in practice. Additionally, based on the extensive literature review of

Lieder and Rashid (2016) we can deduct that at large, present CE studies focus on how limited resources and the environment are impacted. Apart from a few examples (Lieder *et al.*, no date; Yu, Han and Cui, 2015), studies are not too specific on underlying what the benefits of CE for individual businesses are. That trend does not seem to correspond to the mindset CE theory supports, i.e. for having a focus on the whole product value chain, implementing new business models for takeback and design for easy disassembly, etc. Such business activities must have as much an economic drive as they are motivated by resource efficiency benefits (Korhonen, Honkasalo and Seppälä, 2018b). Our study elaborates on the link between CE and IS, through a demonstrative case study on a large cement producer in Denmark. Data was collected by semi-structured face-to-face interviews and the identified IS partnerships were linked to Ellen MacArthur's "Circular economy system diagram". Furthermore, in this paper we aim at filling the existing gap of the impacts of CE on businesses, by exploring how our company case benefits from the established IS partnerships.

This paper is structured as follows. Section 2 sets the stage with a brief introduction of IS, CE and the link between the two concepts. This section also includes a description of Ellen MacArthur's "Circular economy system diagram", also used as a framework for this study. Section 3 gives an introduction to the company case and the methods of data collection and analysis. Section 4 presents the results of the study and includes a discussion of our findings. Conclusions and limitations of this study are presented in the fifth section.

2 Background

2.1 Industrial Symbiosis (IS)

IS is a relatively new research field which emerges from the sphere of industrial ecology – a concept concerned with the flow of resources and aims at achieving economic, environmental and social benefits (Mirata, 2004). Industrial ecology operates on the levels of firm, inter-firm and regional/global (Chertow, 2000), while IS focuses on the resource flows from an inter-firm perspective (Chertow and Ehrenfeld, 2012). Resource flows include materials, by-products, energy, water, and information (Chertow, 2004).

In this study we use a broader definition of IS by (Jensen *et al.*, 2011) stating that IS are business relations (or synergies) with otherwise unrelated companies for the purpose of exchange and reuse of excess resources, i.e. raw materials, energy, water, steam, etc. Yet, in the results and discussion section of this paper we point at the benefits that geographical proximity offers in the case of sourcing alternative raw materials and fuels for the cement industry.

Academics appear to agree that IS is a tool that can help businesses reduce their dependency on virgin resources (Bocken *et al.*, 2016) and thus act as an enabler for CE (Nakajima, 2000; Wen and Meng, 2015; Sauvé, Bernard and Sloan, 2016). It is considered that companies enter into IS partnerships primary driven by economic motivations, i.e. reduction of raw material costs, lower waste disposal taxes, etc. (Desrochers, 2001; Lehtoranta *et al.*, 2011). Yet, positive environmental impacts have proven to go hand in hand with those partnerships (Ashton and Bain, 2012). In the cement industry for example, IS practices have brought vast reductions of greenhouse gas emissions due to the utilization of various wastes as alternative fuels and raw materials. In the Xinfeng Cement Industrial Park in China, for example, utilizing local municipal solid wastes for the cement production is proven to have the potential of generating reduction of about 3,000 kt CO_2/year combined with energy consumption savings, and bringing also economic and social benefits (Cao *et al.*, 2017).

2.2 Circular Economy (CE)

CE is a relatively new term, but the idea of an economic system, based on renewable energy where materials are circulating in loops and where waste is minimized or eliminated (Yuan, Jun and Moriguich, 2006), has been gaining importance for businesses, politicians and academics ever since 1970s (Geissdoerfer *et al.*, 2017). Compared to the traditional linear (extract-use-dispose) economy, which does not take into account the impacts on finite resource overuse or social capital, CE has a specific focus on minimizing resource overconsumption and identifying approaches for waste reduction and waste avoidance (Govindan and Hasanagic, 2018) by keeping products, materials and components at their highest value.

As it was the case with IS, CE also finds its origins in the fields of industrial ecology. CE considers the industrial system as an ecosystem where elements interact and have the ability to reproduce (Korhonen, Honkasalo and Seppälä, 2018a). CE is inspired by biological ecosystems, where resources circulate in loops (Blomsma and Brennan, 2017). In the CE, the lifetime of components and products is either extended through repair, refurbishment and remanufacturing, or end-of-life products are recycled (Bocken *et al.*, 2017; Overgaard, Mosgaard and Riisgaard, 2018). The closer the loops are to direct reuse, the lower the environmental externalities and the larger the social and economic savings (Wieser and Tröger, 2018).

CE is gaining importance for policy-makers on national, regional and international level. In 2015, for example, the European Commission issued a Circular Economy Action Plan, which has the ambition to move EU towards a more sustainable economy (European Commission, 2015). In Denmark, the government has identified the importance of the CE agenda for both the state and the business, thus implementing strategies for increasing resource efficiency and supporting companies in sustainable innovation (Ministry of Environment and Food in Denmark, 2018). China also translated CE into national law, i.e. "Circular Economy promotion law of the People's Republic of China" (Lieder and Rashid, 2016).

There exist numerous literature studies on CE and related circular business models in the form of literature review studies, some examples are (Lieder and Rashid, 2016; Blomsma and Brennan, 2017; Geissdoerfer *et al.*, 2017; Homrich *et al.*, 2018). Central in the field is the Ellen MacArthur Foundation, a CE think tank promoting CE across businesses, governments and academia (Ellen MacArthur Foundation, 2017). Ellen MacArthur Foundation has various publications on the topic of CE, involving diverse company cases and recommendations to policy-makers on how make the transition from the current liner economic model to a regenerative one (Webster, 2015).

2.3 CE visualization

Ellen MacArthur's "Circular economy system diagram" is a conceptual model, illustrating an ideal vision on how companies can minimize their waste by taking advantage of the reusability of products and materials (Govindan and Hasanagic, 2018). Figure 1 shows a remodified "Circular economy system diagram". The emphasis is only on the technical materials and excludes the biological ones since the focus of this study is only on the life cycle of technical materials, more particularly on cement. Each loop in the figure presents a different strategy for enabling the circulation of products and materials in the economic system. “Maintaining” is a strategy for keeping a product for as long as possible and prolonging its life through repair. “Reusing” refers to reselling or redistributing the product to different markers. “Maintaining” and “reusing” products are considered the most effective cycles, as the value of the product is preserved. If a product cannot be reused, most of its value can be conserved through “remanufacturing” it, i.e. replacing, rebuilding the no-longer usable parts of a product and thus giving the end product a new life. When the product cannot be reused, refurbished or remanufactured, the materials a product consists of can be “recycled”. In that way the value of the product might be lost, but the value of the materials can be conserved.

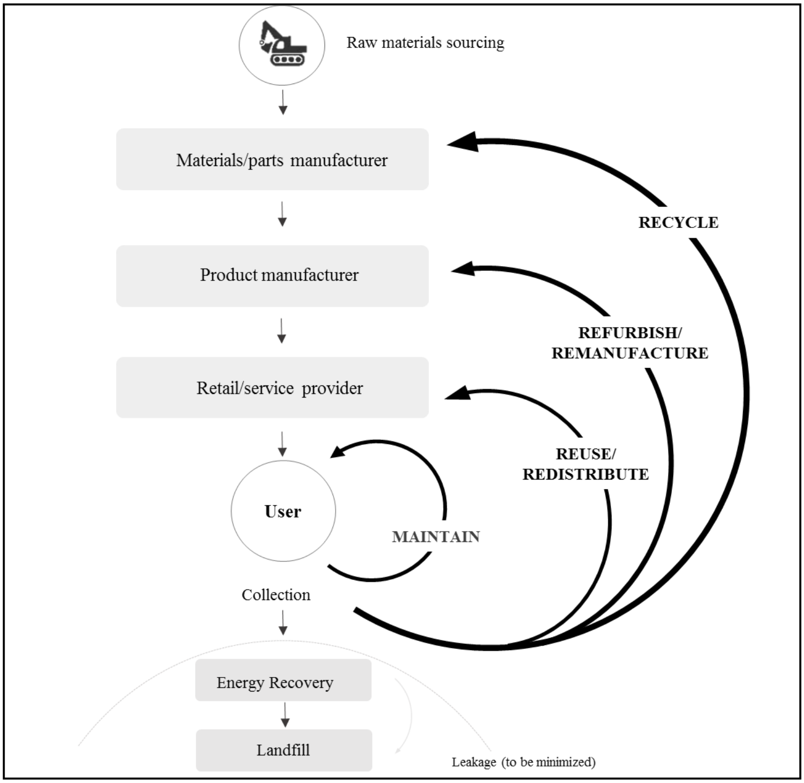


Figure 1: A remodified “Circular economy system diagram” (Ellen MacArthur Foundation, 2017) – edited.

3 Methods

This research aims at elaborating how IS links to CE. Due to the exploratory nature of the topic, a case study approach is selected (Eisenhardt, 1989) and twelve IS partnerships at a large cement producer were explored. Case studies provide us with the possibility to combine evidence from the 'real world' context in order to gain a general overview of company processes (Yin, 2013).

3.1 Case introduction

We carried out an in-depth case study of Aalborg Portland, a Danish cement company situated in Aalborg, Nord Jutland. Aalborg Portland is the world's largest producer of white cement. The cement industry was selected for this study for the following reasons. Firstly, sourcing the raw materials and fuels for the production of cement requires extraction of virgin resources and leads to air emissions (e.g. CO_2, SO_x, NO_x). Aalborg Portland it is considered a crucial source of IS examples, i.e. fossil fuels substitutes with industry wastes and by-products (Tsiliyannis, 2017), which are now recognized as opportunities for lowering those GHG emissions. In respond to the increasing focus on resource efficiency and emission control from the European Commission, our case company has publically communicated its deliberate strategy of using IS as a means of lowering environmental impacts from the production of cement and is continuously monitoring its environmental performance. Secondly, the company has recognized the importance of establishing synergies with both public and private organizations, as a mean for lowering resource input costs and improving resource efficiency (Mirata and Emtairah, 2005). Thirdly, the company is situated strategically with direct link to Aalborg harbour, making it an ideal case for establishing IS with both close and distant partners. Lastly, the company is situated close to the center of Aalborg, a city with an ambitious sustainability strategy and goals for implementing CE as a way to keep resources within the local borders. That gives the company an additional incentive to look for local partners when possible, improve its performance and be a key contributor for achieving the ambitious city vision for sustainable development.

Stages of cement production

In order to get a more clear understanding of the underlying potentials for improving cement via IS partnerships we briefly present the stages of its production. Figure 2 is a simplified illustration of the production stages at Aalborg Portland, and can be linked to cement production in general. The limestone extracted from a closely located quarry, while the rest of the raw materials are sourced externally. In our case company the limestone is partly located under the ground water table and is therefore wet when extracted, making the cement production a semi-dry process. At the next step, the raw materials are grounded and processed. The kiln process, being rather energy-intensive, requires heating the raw materials to 1500°C in order to form cement clinker, which is then further grounded and mixed with gypsum or mineral additivesm such as limestone, to produce cement. The cement is then packaged and transported. ('CEMBUREAU', 2017)

Even though we acknowledge that cement is not an end product, but an ingredient in the production of concrete, which in turn becomes part of a long-lasting construction, the boundaries of this study are within the cement industry.

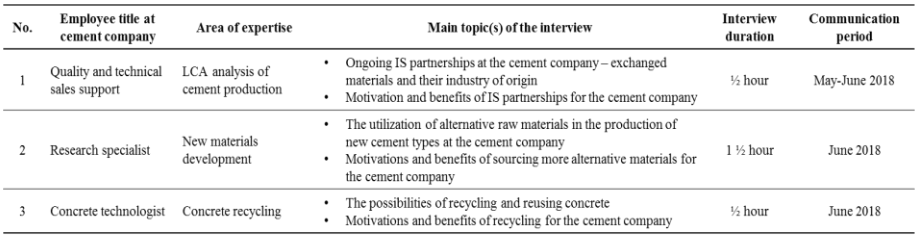
Figure 2: A simplified illustration of the stages of cement production

3.2 Data collection and analysis

This study is inductive by nature, and involves the collection and analysis of both qualitative and quantitative data, giving us the chance to get detailed understanding of the IS partnerships at our case company (Maxwell, 2005). To avoid biases, data on the IS partnerships were collected by triangulation (Yin, 2011), i.e. three individual semi-structured face-to-face interviews with employees were conducted, written communication was analysed and data was verified by external experts.

The order of conducting the interviews and the main topics under discussion with the selected interviewees is described in Table 1. The interviewees were selected based on their professional experience and in-depth technical knowledge on cement properties and impacts of changing the raw material and fuel mix of cement. The interviews were recorded or detailed notes were taken in the dialogue process. To increase the validity of the responds, the information collected during the interviews was subsequently confirmed by the interviewees and additional clarifying questions were raised.

Table 1: Interviews overview.



No.	Employee title at cement company	Area of expertise	Main topic(s) of the interview	Interview duration	Communication period
1	Quality and technical sales support	LCA analysis of cement production	• Ongoing IS partnerships at the cement company – exchanged materials and their industry of origin • Motivation and benefits of IS partnerships for the cement company	½ hour	May-June 2018
2	Research specialist	New materials development	• The utilization of alternative raw materials in the production of new cement types at the cement company • Motivations and benefits of sourcing more alternative materials for the cement company	1 ½ hour	June 2018
3	Concrete technologist	Concrete recycling	• The possibilities of recycling and reusing concrete • Motivations and benefits of recycling for the cement company	½ hour	June 2018

Based on the interviews, additional internal company data was collected and analysed. That gave us a more complete overview of the effects of including alternative raw materials and fuels in the cement production process. Such internal data involved environmental reports, input-output analysis, chemical test results, material R&D projects, etc. To further increase the details and legitimacy of our findings (Yin, 2013), over the course of 2018, we verified the local role of the IS partnerships established by the cement company through informal communication with local municipal planners, environmental authorities and the local heat utility company.

We analysed the collected data through the following steps. Firstly, we identified which product life cycle stage of the IS partnering company the exchanged resource derive from and which life cycle stage of cement it influences. Secondly, we looked into what virgin resource is substituted/complemented through each of the IS partnerships. Thirdly, we grouped the exchanged resources according to their application at our company case, i.e. alternative raw materials, alternative fuels, energy, water. Fourthly, we identified whether the resource exchanged occurs on a local, national and international level, depending on the geographical proximity of the IS partner. Lastly, based on the preceding steps, each IS partnership was then linked to the loop of Ellen MacArthur's "Circular economy system diagram".

4 Results and Discussion

Section 4.1 will present the identified IS partnerships, where the exchanged resources derive from and what they act as a substitute for. Section 4.2 places the IS partnerships according to the loops of Ellen MacArthur's "Circular economy system diagram" they influence. Section 4.3 provides a discussion on how IS partnerships can improve resource efficiency and as a result bring benefits for the company.

4.1 IS partnerships at case company

Based on the conducted interviews and additional data analysis, we identified twelve IS partnerships between the cement company and diverse industries. Three of those supply alternative fuels to the cement producer. Seven of the IS partnerships provide alternative raw materials. The last two focus on energy and water IS exchanges. The cement company sends excess heat from the cement production process for district heating in the area and is expected to send cold water from its own quarry for district cooling to a new regional hospital. Table 2 summarizes our findings.

Table 2: Identified IS partnerships at Aalborg Portland

Resources exchanged through IS		Source	Acts as a substitute/complement of	Proximity of partner
Alternative Fuels	1. Dried sewage sludge	Wastewater treatment plant	Conventional fuel (either bituminous coal or petroleum coke)	Local
	2. Meat and bone meal	Animal fodder producer		National
	3. Waste from industry (RDF - refused derived fuel)	Diverse waste collection schemes		Local/International
Waste Materials	4. Desulphurization gypsum	Power station	Natural gypsum	Local
	5. Fly ash		Alumina-containing materials (e.g. clinker, cement)	Local/International
	6. Sand	Dredged from fjord	Excavated sand	Local
	7. Iron oxide	Sulphiric acid factory	Pyrite ash (source of iron)	International
	8. Paper sludge	Paper recycling factory	Conventional fuel, chalk and fly ash	National
	9. Aluminium by-products	Auminium recycling factory	Aluminium, fly ash	International
	10. Bottom ash	Biomass-fired power plants	Conventional fuel, fly ash	Local
Energy	11. Excess heat	City district heating grid	District heating from non-renewable sources	Local
Water	12. Excess cold water	Newly built regional hospital (planned)	The need to operate electrical AC-units	Local

As seen in Table 2, the largest number of ongoing IS partnerships are established with local partners. Several definitions of IS point at the necessity that IS partnerships should occur in a relatively close geographical proximity (Chertow, 2000), while geographical proximity is also proven by plentiful examples not to be a critical prerequisite (Lombardi *et al.*, 2012). Even though not a precondition for IS partnerships (Lombardi and Laybourn, 2012), geographical proximity has been identified in IS literature as beneficial for the exchange of tacit knowledge (Velenturf and Jensen, 2016). Combined geographically proximate and distant IS partnerships, though, have shown to sparkle innovation (Mirata, 2004).

Aalborg Portland has selected those IS partners situated in the surrounding area based on various motives. Firstly, due to the quantities of exchanged materials and fuels (approx. 600,000 tons), long distance transportation is considered neither cost efficient nor environmentally preferred. Waste from industry and aluminum by-products are sourced non-locally since no material of high enough quality can be obtained from the surrounding industries.

Secondly, Aalborg Portland has the ambition to promote local sustainable development and thus bases a considerable part of its production on recycling material flows from the surrounding society. The IS partnerships result in lower environmental impact from transportation, as the virgin materials otherwise used would have been sourced from significantly longer distance. Lastly, the cement producer acknowledges the importance of interaction with regional external partners, as that can lead to innovating through development of greener production methods and expanding their product portfolio. More specifically, the company is currently developing a new "greener" product in collaboration with research institutes and industry, which will include alternative cementitious materials, require less energy and emit less CO_2.

4.2 Linking the IS partnerships to CE

The conceptual model of CE, presented through Ellen MacArthur's "Circular economy system diagram", is used to identify which product life cycle stage the exchanged wastes and by-products derive from and which loop they influence. Figure 3 illustrates how the IS partnerships link to CE.

Five of the IS partnerships of our company case were found to enable CE through recycling of wastes and by-products, linking to the most outer loop of the "Circular economy system diagram", namely 'recycling'. This is the case with dried sewage sludge, waste from industry, sand, paper sludge and aluminium by-products, all wastes and by-products of diverse 'end-of-life' products.

We identified the presence of two additional loops in the "Circular economy system diagram", linking back resources from product manufacturer to material/parts manufacturer through 'recycling' and 'reuse'. Meat and bone meal, desulphurization gypsum, fly ash, iron oxide and bottom ash are five wastes and by-products generated during the production phase of respectively animal fodder and energy. They are recycled by re-introducing them as alternative fuels or raw materials in the cement production and belong to the 'recycle' loop between product manufacturer and materials/parts manufacturer. Excess heat is considered a secondary output from the kiln process of cement production, utilized by the local district heating system. Thus, the excess heat from the cement manufacturer is reused at input for other processes and results in a new 'reuse' loop. Excess cold water, though, is not considered part of this 'reuse' loop as it derives already at the raw material sourcing stage. When limestone is extracted from the nearby quarry, groundwater rises to the surface and can be utilized directly for district cooling without much further treatment.

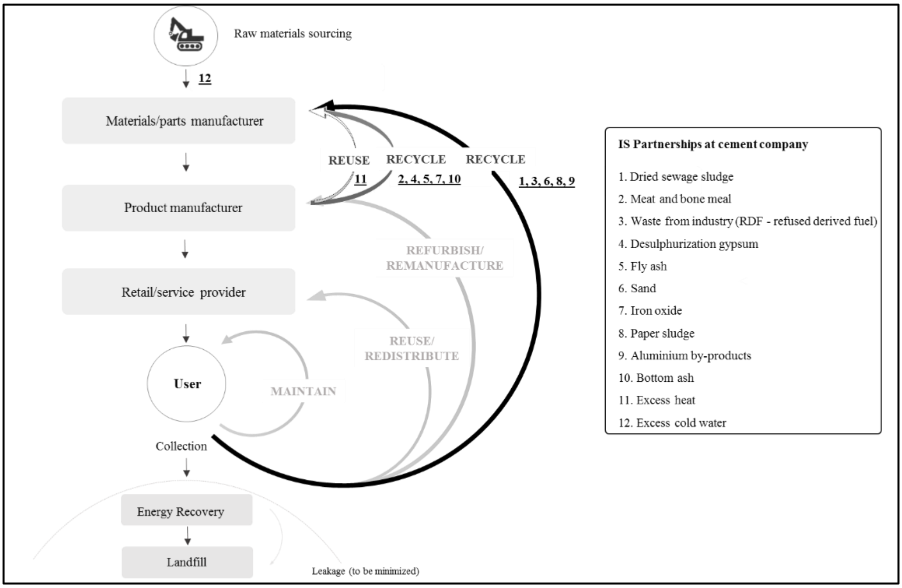


Figure 3: The IS partnerships at the cement company and how they are linked to CE

4.3 Improving resource efficiency through IS partnerships

As evident from this study, IS partnerships in the case of cement currently enable mainly the 'recycling' loops, which brings less value than the inner loops, such as 'reuse' or 'remanufacturing'. Nevertheless, we acknowledge that especially in energy-intensive industries, such as the cement, even a small step in modifying the material and fuel mix with wastes and by-products can lead to significant environmental, economic and social benefits – a cornerstone in the notion of CE.

The global CO_2 emissions associated to cement production have a potential to significantly decrease due to the utilization of waste and by-products by the industry (Miller *et al.*, 2017). The IS partnerships of the case company were found to lower the overall environmental impact of cement production. The cement company utilizes about 2,600 TJ from alternative fuels, sends about 1,200 TJ of excess heat and uses 450,000 tons of alternative raw materials, translating savings of about 430,000 tons CO_2-eq/year (Sacchi, 2018). According to the collected data from our company case, one of the reason is that a large number of the alternative resources are considered carbon-neutral, since the emissions associated to them are linked to the primary purpose they serve. Nonetheless, the impacts of the alternative resources are proven to be lower compared to traditional raw materials and fuels (Habert *et al.*, no date). Additionally, an earlier study on the district heating sources in the area points at potential for the cement company to double its excess heat delivery to the district heating grid, which would lead to more than 90% reduction in the carbon footprint of the heat in the heating system (Sacchi and Ramsheva, 2017).

Alternative raw materials and fuels has already been used by a large number of cement plants especially in Europe, however (Aranda U*són et al*, 2013) points at the still untapped potential for cement companies. From an economic perspective, additional infrastructure for storing and processing the received alternative resources is required, also reflected by our company case. For example, the cement company had to invest in two silos and a feeding system to the kiln, in order to utilize meat and bone meal as alternative fuel. Nevertheless, both our interviewees and studies on cement production point out that possibilities for reducing costs of fuels and materials can bring the highest savings for cement companies (Aranda Usó*n et al*, 2013).

4 Conclusion and limitations

This study demonstrates the link between IS and CE by examining twelve IS partnerships of Aalborg Portland, a large cement producer in Denmark and discussing how they relate to the loops of Ellen MacArthur's "Circular economy system diagram". IS plays a role in closing the CE loops, but there exists no one-size-fits-all approach for industries. In the case of cement, it is currently hard to trace the end-product back to the producer since cement is an ingredient of concrete. IS partnerships of our case company enable mainly the recycling loop of other materials. Recycling of end-products and materials represents the most outer circular loop and does not offer the most resource efficient solution in a circular context. That is partially due to the fact that as part of the energy-intensive sector, cement requires a vast amount of energy and resources in the production process, and utilizing alternative fuels and materials is a way to lower CO_2 emissions from production. The direct reuse of resources in the context of cement production is also possible and exemplified by the "excess heat" IS partnership between the cement producer and the local district heating system. Nevertheless, we highlight the importance of the cement industry to direct its attention towards the more inner circles of the CE where more resource value can be captured. Such a focus may require going beyond the borders of the cement production plant, following the product life cycle of cement towards concrete production facilities and construction companies responsible for infrastructure projects. Though technically difficult and currently not economically feasible, in principle, it is possible to recycle concrete and reuse concrete elements. Today most concrete demolition waste is recycled as aggregate for new concrete or backfill for road construction, replacing virgin aggregate. However, there is need for further research to analyse this topic in more detail.

Furthermore, the current trend of utilizing wastes and by-products from certain processes, for example energy production from coal power plants, could be considered a potential future concern. The reason is that in Denmark, and in other countries, energy sourced from coal is being slowly, but gradually phased out. That brings future uncertainty of alternative raw materials supply for the cement industry, but also gives stimuli to continuously look for alternatives in terms of the materials and fuels the cement industry can source and utilize in its production. We suggest a further investigation of that trend, looking more specifically for future availability of certain waste and by-products.

On a broader context, this study opens up for a wider discussion on the development of inter-company networks for the exchange of resources, i.e. materials, by-products, even knowledge. In an economy with limitless industrial activities and by-products generated, there is a need to either establish more structured IS programs, such as the well-known the National Industrial Symbiosis Program (NISP) in UK, or encourage self-driven eco-industrial initiatives, the case of Kalundborg symbiosis (Boons, Spekkink and Mouzakitis, 2011). In either case, such IS initiatives should encourage companies to connect and work as an ecosystem, identify possibilities for resource exchange and innovation, and thus enable CE. Both public and private industrial partners should be involved in such IS partnerships, the exchanges should not be limited by physical materials and by-products, but also include information and knowledge. Inter-company collaboration through establishing IS partnerships has been identified as way towards innovation and creating a positive impact for both economy, society and environment (Mirata and Emtairah, 2005). Still, we recognise the need for further research to explore what the effect of those IS networks is from a regional and local perspective.

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Life Cycle Assessment (LCA) in Combustion Processes of Agricultural Biomass Pellets

VIATCHESLAV KAFAROV & YURLEY PAOLA VILLABONA DURÁN

Abstract The objective of this work is to evaluate the environmental impact associated with the emissions and uses of natural sources through life cycle assessment with the purpose of suggesting an efficient and sustainable solution to the energy problem of non-interconnected zones in Colombia. The work represents an environmental evaluation of the rice husks pellets combustion process. The process is divided into six stages: transport, drying, crushing, compaction and biomass combustion. The cradle to grave Life Cycle Assessment was enabled by integrating them into a single process. The environmental profile obtained reflects that the stage of biomass combustion exerts an influence on both, the entry and exit impact categories.

Keywords: • Life Cycle Assessment (LCA) • Combustion • Biomass • Pellets • Environmental impact •

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DOI https://doi.org/10.18690/978-961-286-211-4.5 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

Every process is affected by the inevitable wear and tear over time, which decreases its efficiency and increases its environmental impact. The Life Cycle Assessment (LCA) is an engineering tool that enables us to classify, quantify and monitor these impacts throughout the life cycle of a product or activity - from the extraction of raw materials until they become waste (Hsiao and Surendra, 2011). This approach is known as the "cradle to grave" analysis (Benveniste et al., 2011).

Because of the environmental impacts that the exercise of progress has caused in the habitat, the industry has focused efforts in conjunction with the scientific community in finding energy alternatives that mitigate environmental damage and in turn combat other forms of pollution through reuse of waste. Biomass, e.g. waste of the agricultural industry, can be used as fuel to generate electrical energy. However, it can still be questioned, if biomass-based energy generation is a good environmental choice with regards to the impact on greenhouse gas emissions (Kimming, et al., 2011). Even though, the LCA methodology is well established, the literature is not very specific on the LCA of combustion processes or cogeneration of energy from biomass. For this reason, a research work was conducted aiming to propose a more detailed methodology that is tailored to this type of processes.

2 Methodology

We propose an LCA methodology for evaluation of rice husk pellets combustion process. The methodology is based on the ISO 14040 (1999) standard and comprised of four elements. The elements that structures the LCA are not only sequential, but they are also iterative with each other, as shown in Figure 1.

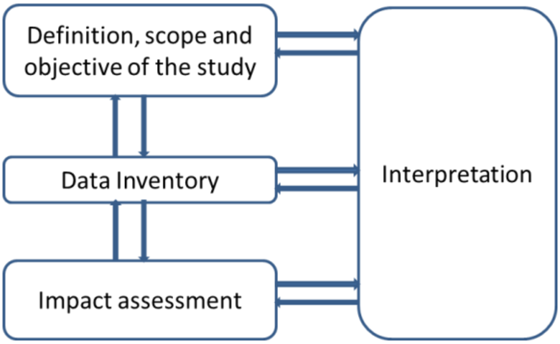

Figure 1: The four elements that structures the LCA, source: Amaya et al, 2008.

2.1 Definition of objectives and scope of the study

The definition of scope and the objectives is the first stage of the LCA. The goal of this study was to examine environmental sustainability of the agricultural type biomass combustion system through the technique of LCA.

The systems involved in the LCA analysis of the biomass combustion were: agricultural activity, crushing, drying, compaction and combustion of biomass (see Figure 2). The hierarchy proposed by ISO 14040 was followed regarding the allocation rules. For the phases of process for which no primary data found we resorted to the use of data in published literature. For the resulting emissions, the energy consumed in the combustion process, electricity and steam the data was collected from sources such as Knospe and Walleser (2010); Gutierrez and San Miguel, (2015); John Carroll, J. F. (2013).

We have to note that the construction stage or the maintenance of the infrastructure of the plant, economic factors, social factors, and catastrophic natural phenomena were not considered in the study. In addition, certain environmental impacts were not covered in full, due to the difficulty in collecting the data for local conditions.

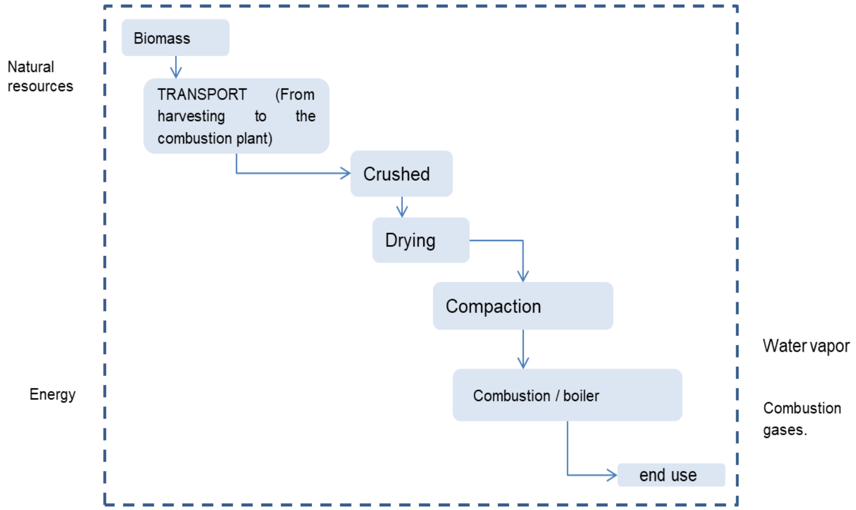

Figure 2: The systems involved in the LCA of biomass combustion.

2.2 Inventory analysis

This LCA stage has taken into account the environmental and energy flows of the raw materials and processes that have been included in the life cycle of the combustion process of the rice husk pellets.

At the first stage of agricultural activity, the identification and accounting of environmental flows were done. The production of rice husks, associated with energy, was accounted. All related work with the agricultural part, as well as all the production processes and transportation of supplies was accounted (Nishihara, et al., 2015). It was considered that the land was savannah type and did not have high vegetation. In addition, rotation was not performed with another crop.

LCA study assumed that the land is productive for at least five years. This cycle was repeated until the completion of the LCA. Additionally, no effects were considered for the use of agrochemicals (herbicides, pesticides, insecticides) because the lack of the data and minimal contribution to overall results.

The integration of the carbon and nitrogen cycle was considered at the stage of rice cultivation. During the rice cultivation, a quantity of CO2 from the atmosphere is captured to several destinations: a part is fixed in the biomass that is harvested, another part in the biomass that remains in the ground and another part returns to the atmosphere by the mechanism of respiration of the plant (Pechón, et al., 2006). For atmospheric decay of CO2 emissions from combustion of biomass pellets be should consider the basic principles remain unchanged: if biomass is replanted, emissions from combustion are neutralized by CO2 removal during regrowth; if biomass is not replanted, bio CO2 emissions become anthropogenic CO2 (Cherubini et al., 2011). Also, it was only considered that there is a net fixation of C on the ground represented as a percentage of CO2 incorporated by the plant (Figure 3). However, a sensitivity analysis was carried out for this percentage taking as initial value 56.8% (average obtained from studies for other crops). It should be noted that the percentage of CO2 fixation for stubble was considered 56.8% (Da Costa, 2005). Regarding nitrogen, it is found mainly in the plant, in plant residues, in mineral nitrogen and in humified organic matter. There are nitrogen fluxes between these components and with the medium outside them. The most important inputs were: biological nitrogen fixation, fertilization and larger outflows are volatilization. On the other hand, it was considered that there is a net fixation of N on the ground due to the presence of non-symbiotic bacteria that do not exceed 15 kg / ha year (Amaya, et al., 2008).

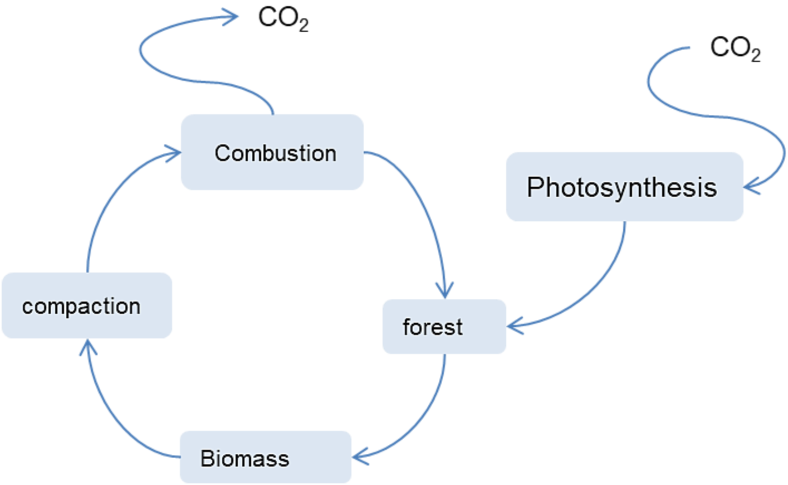

Figure 3: Biomass combustion process cycle, source: own.

3 Results

The inventory of impact categories, taking into account the activities in each stage of the process, is presented in Table 1. The inputs and outputs of the system are shown in Table 2.

Table1: Inventory of impact categories

Phase	Activity
Agricultural	1. Preparation and attention of the soil, agronomic techniques and fertility. 2. Maintenance and planting 3. Fertilization 4. Collection of biomass 5. Fruit transport
Drying and crushing	6. Biomass drying 7. Crushing of biomass
Compaction	8. Pressing biomass in the form of pellets
Biomass combustion	9. Rice husk combustion
End of life	10. Waste management 11.Emissions management

source: own

The inputs and outputs of the system were defined as seen in table 2

Table 2: The inputs and outputs of the system

PROCESS	CONSUMPTION					
	Means Materials	Quantity (kg)	Electric power	Quantity (kWh)	Waste Generated	Quantity (kg)
Agricultural	Gasoline	0,0009				
Drying			Dryer	2,6404		
Crushed			shredder	0,1932		
Compaction	Rice husk	1,2				
Biomass combustion	Biomass pellets	3			Combustion gases	1

source: own

Figures 4 and 5 show impacts of the agriculture stage against each of the categories carried out by SimaPro 8.5. The energy use for field work has the highest score (145 µPt) in the Fossil depletion category. The highest percentage of participation impacts belong to human health, environment and resources.

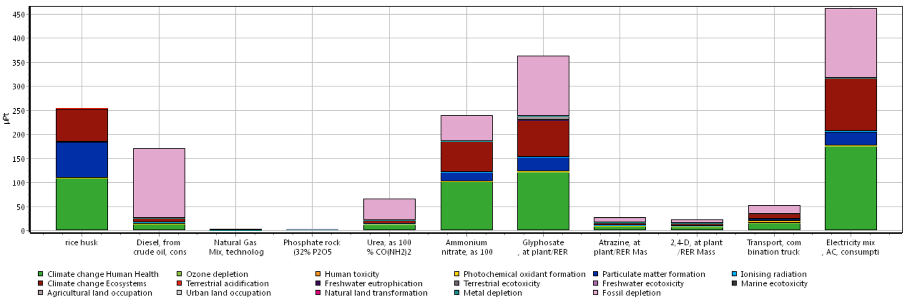

Figure 4: Analysis of the impact of the stage agriculture in each category.

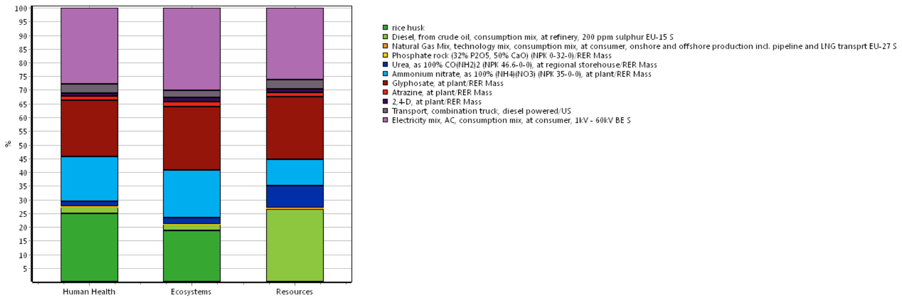

Figure 5: Evaluation of the damage of the steppe agriculture in human health, environment and resources.

Figures 6 and 7 show the impact analysis of the drying stage for each of the categories. The use of energy is the one that has the greatest impact. The reason was necessity to perform a forced drying in order to have the desired percentage of humidity. This is reflected in the same way in the evaluation of impacts on human health, environment and resources.

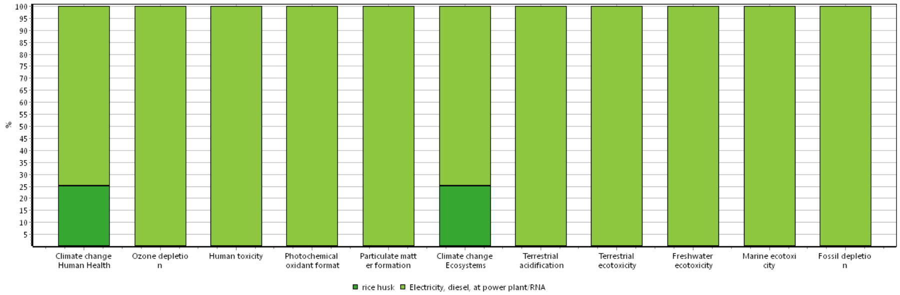

Figure 6: Analysis of the impact of the drying stage in each category.

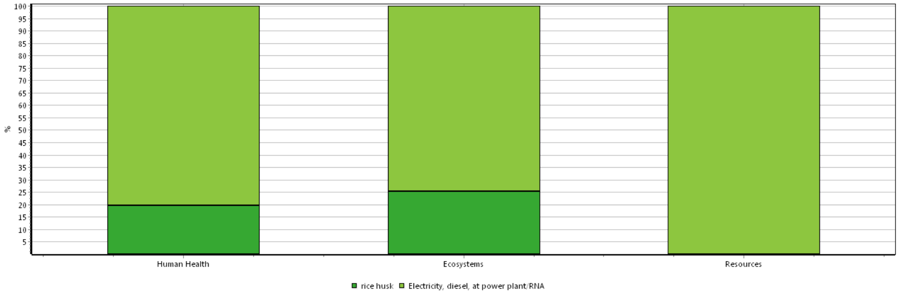

Figure 7: Evaluation of the damage of the drying stage in human health, environment and resources.

Figures 8 and 9 show the impact analysis of the grinding stage in relation to each of the categories where the use of energy is the one that has the greatest impact. The reason was the need to obtain particle sizes specific to the biomass. This is reflected in impacts on human health, environment and resources.

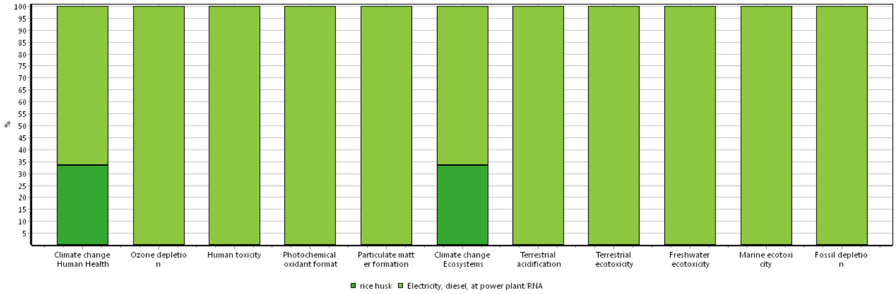

Figure 8: Analysis of the impact of the grinding stage in each category.

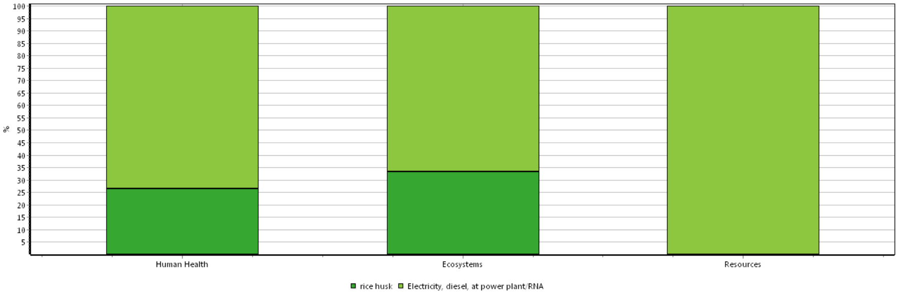

Figure 9: Evaluation of the damage of the milling stage in human health, environment and resources.

Figures 10 and 11 show the impact analysis of the compaction stage against each of the categories. The use of energy has the greatest impact due to the need of the pelletizer to heat and compress the biomass. This is reflected equally in the evaluation of impacts on human health, environment and resources.

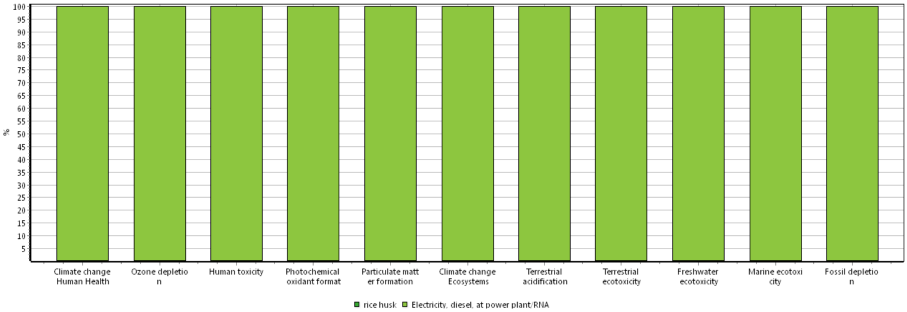

Figure 10: Impact analysis of the compaction stage in each category.

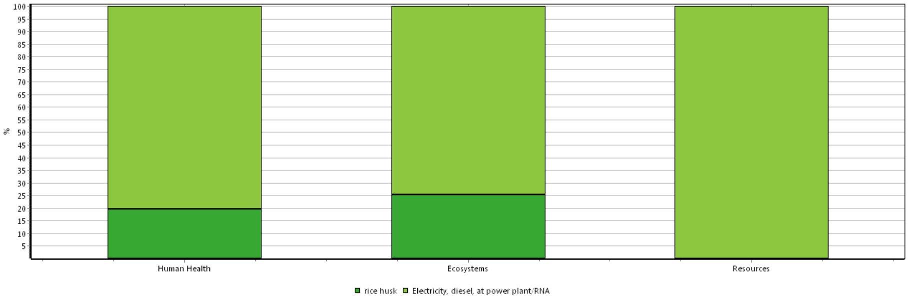

Figure 11: Evaluation of the damage of the compaction stage in human health, environment and resources.

Figures 12 and 13 show the analysis of the impact of the combustion stage against each of the categories. The use of energy is the one that has the greatest impact due to the energy needed to operate the boiler. This is reflected equally in the evaluation of impacts on human health, environment and resources.

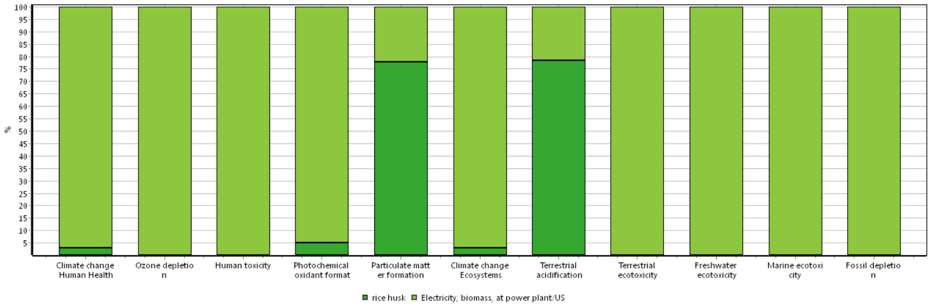

Figure 12: Analysis of the impact of the combustion stage in each category.

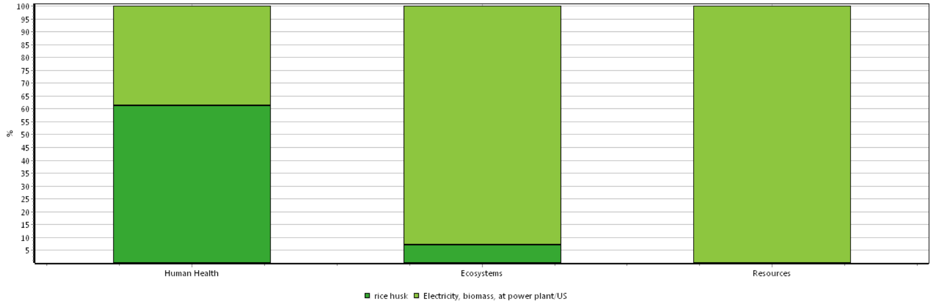

Figure 13: Evaluation of the damage of the combustion stage in human health, environment and resources.

The percentages of participation of each of the stages contemplated for the environmental analysis are shown in Figure 14. To interpret the data obtained from the inventory analysis, it was necessary to evaluate the environmental impact associated with the emissions and uses of natural sources through the analysis of the carbon footprint (Figure 15).

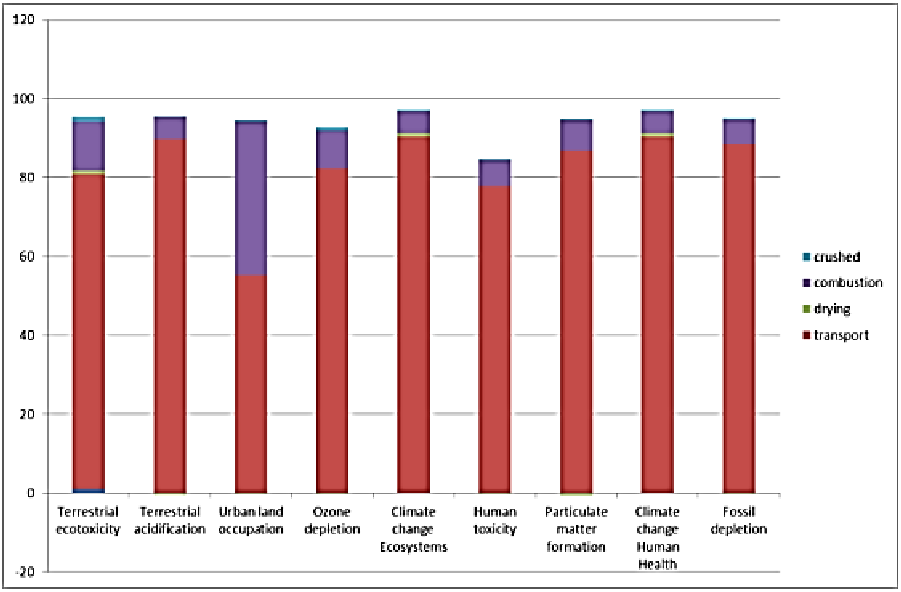

Figure 14: The data obtained from the inventory analysis, source: own.

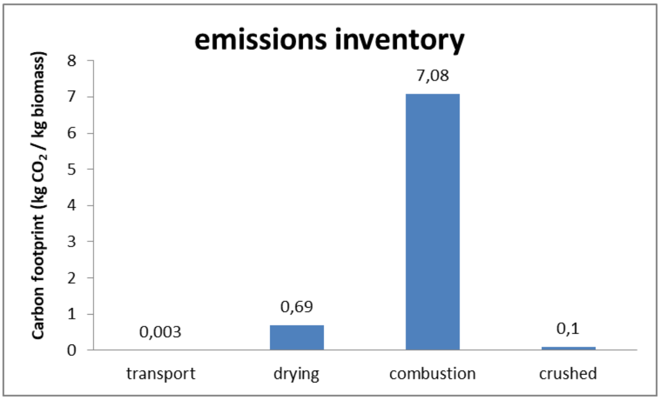

Figure 15: The analysis of the carbon footprint, source: own.

To interpret the obtained data of the inventory analysis, it was necessary to evaluate the environmental impact associated with emissions and uses of natural sources. Each impact category was represented by means of the impact category indicator (I_IC), which is a sum of different environmental interventions caused by the different substances that make it up. In the classification of emissions, each environmental intervention was associated with the impact categories in which it has an effect. For example, CO2 is associated with climate change. Once the data is classified, the addition of these was made for each of the categories using the equivalence factors (f_Ei) and the following equation:

$$I_{\mathrm{IC}} = \sum_i m_i * f_{\mathrm{E}i} \tag{1}$$

Where mi is the emission of the resource i used and f_Ei is the corresponding equivalence factor. With the results obtained the participation percentage was calculated which each of the stages has considered for the process of combustion of rice husk pellets in the different impact categories.

The environmental profile reflects the combustion stage as one with the greatest impacts in the emission of CO2 in all categories. The other stages contribute to a smaller proportion, as can be seen in Figure 15. It is important to clarify that emission of sulphur dioxide (SO2) and nitrogen oxides (NOx) are generated among other gases at this stage.

4 Conclusions

The work constitutes an environmental evaluation of the process of combustion of biomass pellets. The process was divided into different stages: transport, drying, crushing, compaction and biomass combustion

Through the quantification of the inflows and outflows in the different stages of the process, it was possible to determine the emissions most relevant in each of them together with their associated energy consumption.

The environmental profile elaborated reflects that the stage of biomass combustion exerts the greatest influence on both, the entry and exit impact categories.

Acknowledgments

The authors of this paper express their acknowledgments to the Administrative Department of Science, Technology and Innovation of Colombia (COLCIENCIAS) for economic support of this work that is part of the project "Study and characterization of the combustion of biofuels produced with autochthonous biomass with the purpose of increase eco efficiency in energy systems in residential sectors, with Code of COLCIENCIAS: 1101-543-32153.

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1. MEDNARODNA KONFERENCA TEHNOLOGIJE IN POSLOVNI MODELI ZA KROŽNO GOSPODARSTVO, KONFERENČNI ZBORNIK
M. Bogataj, Z. Kravanja in Z. Novak Pintarič (ur.)

Univerzitetna založba
Univerze v Mariboru

Krožni poslovni modeli na osnovi novih produktov iz odpadkov

ZORKA NOVAK PINTARIČ, LIDIJA FRAS ZEMLJIČ, OLIVIJA PLOHL,
RIKO ŠAFARIČ, BOŽIDAR BRATINA IN SLAVKO DVORŠAK

Povzetek V prispevku je prikazana preliminarna zasnova krožnega poslovnega modela za pretvorbo odpadnih procesnih tokov v sekundarne surovine, nove produkte in vire energije. Pri tem je cilj definirati nove vire prihodkov za podjetja, kar vključuje izbor ustreznih tehnologij za predelavo odpadkov, izbor novih produktov in storitev, njihovih uporabnikov in dobavnih mrež, s čemer se vzpostavljajo nove krožne verige vrednosti. Optimalni izbor tehnologij, produktov in storitev izvedemo z uporabo večkriterijskega optimiranja, tako da upoštevamo ekonomske, okoljske in socialne vidike obravnavanih alternativ. Pristop za razvoj krožnega poslovnega modela je prikazan na primeru zbiranja, sortiranja in predelave nenevarnih odpadkov, pri čemer smo se osredotočili na i) izdelavo visokokvalitetnega trdnega goriva iz odpadne embalaže, ki je ni mogoče reciklirati in ii) predelavo muljev komunalnih čistilnih naprav v koristne produkte. Izdelali smo shematski prikaz krožnega modela, v katerega smo k obstoječim tehnologijam dodali predloge novih tehnologij za predelavo odpadkov v nove produkte in povečanje dodane vrednosti podjetja na trajnostni način. Predlagane alternative smo ekonomsko ovrednotili, v nadaljnjem delu bodo ovrednoteni še okoljski in socialni vplivi ter izveden večkriterijski izbor optimalnih tehnologij in produktov.

Ključne besede: • krožno gospodarstvo • trdno gorivo iz odpadkov • poslovni model • ravnanje z odpadki • večkriterijska optimizacija •

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DOI https://doi.org/10.18690/978-961-286-211-4.6 ISBN 978-961-286-211-4
Dostopno na: http://press.um.si.

1ST INTERNATIONAL CONFERENCE ON TECHNOLOGIES & BUSINESS
MODELS FOR CIRCULAR ECONOMY: CONFERENCE PROCEEDINGS
M. Bogataj, Z. Kravanja & Z. Novak Pintarič (eds.)

University of Maribor Press

Circular Business Models Based on New Products from Wastes

ZORKA NOVAK PINTARIČ, LIDIJA FRAS ZEMLJIČ, OLIVIJA PLOHL, RIKO ŠAFARIČ, BOŽIDAR BRATINA & SLAVKO DVORŠAK

Abstract This contribution presents a preliminary development of a conceptual circular business model based on processing waste streams into secondary raw materials, new products and energy sources. The main goal is to identify new alternatives for generating revenues and profits. This includes the selection of appropriate technologies for waste processing, new products and services derived from wastes, supply networks for products and services, thus creating new circular value chains. A portfolio of optimal technologies, products and services should be selected by using multi-objective optimization while taking into account the economic, environmental and social aspects of possible alternatives. The methodology for developing circular business models is illustrated on a case study of collecting, sorting and treating non-hazardous wastes. The focus was on i) producing high quality solid recovery fuel from non-recyclable packaging waste, and ii) converting sludge from waste-water treatment plants into valuable products. A schematic concept of circular business model was developed in which alternative technologies and products from wastes were added to the existing ones in order to increase value added in a sustainable manner. Preliminary economic analyses were performed for proposed alternatives. In subsequent work, environmental and social aspects will be evaluated following by multi-objective selection of optimal technologies.

Keywords: • Circular economy • Solid recovery fuel • Business model • Waste management • Multi objective optimization •

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DOI https://doi.org/10.18690/978-961-286-211-4.6 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Uvod

Ravnanje z odpadki je eno izmed ključnih področij pri napredku družbe v krožno gospodarstvo. Posebej pomembni so odpadki, ki jih ni mogoče ponovno uporabiti ali reciklirati, zato je zanje glede na hierarhijo ravnanja z odpadki [1] ključno poiskati možnosti za ustrezno snovno in energetsko predelavo, s čemer se zmanjša količina odpadkov za odlaganje.

Sistemi zbiranja in ločevanja odpadkov so v številnih državah dobro razviti, vendar se veliko zbranih in sortiranih odpadkov prevaža na snovno in energetsko predelavo čez mejo, kar velja tudi za Slovenijo. Razlog je praviloma ta, da se predelava v manjših skupnostih ne splača zaradi premajhnih količin [2], problem predstavljajo tudi spremenljive vrste in sestave odpadkov, vsebnost klora in težkih kovin [3].

Zato izziv na področju odpadkov predstavlja razvoj tehnologij, s katerimi bi odpadke predelali v nove izdelke, toploto in elektriko [4], pridobili dodaten vir prihodkov in tako prilagodili poslovne modele v smeri krožnega gospodarstva. V prispevku prikazujemo možnosti za izdelavo novih izdelkov iz dveh vrst nenevarnih odpadkov: a) odpadne embalaže, ki je ni mogoče reciklirati in b) muljev čistilnih naprav.

V prvem primeru smo prikazali študijo možnosti za izdelavo visokokvalitetnih goriv iz predhodno sortirane odpadne embalaže. Cilj je predlagati preliminarni načrt postrojenja za izdelavo goriva prve kvalitete z nadzorovano sestavo in kalorično vrednostjo, ki se lahko uporabi kot nadomestek ali dodatek fosilnim gorivom (ang. Solid Recovery Fuel, SRF). V drugem primeru smo izvedli odstranitev težkih kovin z oplaščenimi magnetnimi nanodelci in vakuumsko sušenje mulja ter predlagali alternativne izdelke, ki bi jih lahko proizvedli iz mulja.

Za predlagane alternative smo izvedli približne ekonomske ocene, kar predstavlja osnovo za izbor tehnologij predelave odpadkov v koristne produkte in s tem temelj novega, optimalnega, krožnega poslovnega modela.

2 Sistematična izvedba projektov krožnega gospodarstva

Projekti na področju krožnega gospodarstva se razlikujejo od konvencionalnih razvojnih projektov v več ozirih: tehnologije so malo raziskane, zato so praviloma potrebne zahtevne raziskave in razvoj novih tehnoloških postopkov in produktov, investicije so praviloma visoke, medtem ko dobljeni rezultati niso visoko dobičkonosni, zato so klasični ekonomski kazalci pogosto neugodni. Gre za dolgoročne projekte z nizko dodano vrednostjo, ki zahtevajo vlagatelje dolgoročnega, t. i. 'potrpežljivega' kapitala, tj. vlagatelje, ki ne pričakujejo hitrih dobičkov, ampak so pripravljeni počakati na koristi v daljšem obdobju. Pomembno vlogo pri spodbujanju projektov krožnega gospodarstva ima tudi zakonodaja, ki z določenimi normativi spodbuja podjetja in družbo k odgovornejšemu ravnanju z viri.

Pri razvojnih projektih v gospodarstvu so glavni odločitveni kriteriji ekonomski kazalci, npr. doba vračanja, donosnost, neto sedanja vrednost, interna stopnja donosnosti itd. Za presojo projektov na področju krožnega gospodarstva pa je potrebno vpeljati večkriterijsko odločanje, kjer poleg ekonomskih kriterijev upoštevamo tudi okoljske in socialne vplive. Izvedba 'krožnih' projektov ima zato določene značilnosti, ki jih lahko opišemo z naslednjimi aktivnostmi:

a) Pregled vseh tokov, ki prehajajo med sistemom in okolico. Določiti je potrebno količine in sestave vseh tokov, ki prihajajo v proces in iz njega izhajajo. Prav tako je pomembna vrsta toka, npr. ali gre za produkt, stranski produkt, odpadek, primarno surovino, sekundarno surovino ipd. Za vse tokove je potrebno raziskati, kaj se z njimi dogaja, preden vstopijo v podjetje oz. potem, ko ga zapustijo, kolikšen prihodek ali strošek predstavljajo za podjetje in kateri predpisi regulirajo ravnanje s takšnimi tokovi.
b) Predlogi alternativ. Za tokove, ki izhajajo iz sistema, iščemo možnosti, kako jih predelati v oblike, ki bi podjetju prinesle višji prihodek ali celo prihodek namesto stroškov, npr. predelava v produkte višje kakovosti, sekundarne surovine ali različne funkcionalne materiale. Za tokove, ki prihajajo v sistem, iščemo možnosti za zamenjavo z manj škodljivimi, okolju prijaznejšimi, recikliranimi, sekundarnimi ipd. Vir informacij so najboljše razpoložljive tehnologije (BAT, ang. Best Available Technologies), pregled stanja tehnike (SOTA, ang. State-Of-The-Art) in lastne inovativne ideje za preseganje obstoječih tehnik ter predlogi novih produktov z višjo dodano vrednostjo.

c) Pridobivanje podatkov. Za predlagane nove tehnologije in produkte pridobimo podatke v literaturi, kot so patenti, članki in referenčni dokumenti o najboljših razpoložljivih tehnologijah (BREF), nekatere podatke pa je potrebno pridobiti tudi z laboratorijskimi eksperimenti in preliminarnim načrtovanjem, ki vključuje računalniška orodja za različne izračune, simulacije in optimizacije procesov. Posebna dodana vrednost je, če v raziskavi smiselno uporabimo in povežemo laboratorijske in inženirske metode.

d) Ekonomske analize. Za predlagane alternativne tehnologije in produkte pridobimo podatke o investicijah za opremo ter prihodkih, stroških, prihrankih, okoljskih dajatvah ipd. Na osnovi tega lahko izračunamo ekonomske kazalce.

e) Analize okoljskih vplivov. Okoljske vplive ocenimo za celotni življenjski cikel z uporabo pristopa LCA (ang. Life Cycle Analysis) v obliki različnih odtisov in potencialov globalnega segrevanja, tanjšanja ozonske plasti, acidifikacije, evtrofikacije itd.

f) Analize socialnih vplivov. Družbene vplive projektov na področju krožnega gospodarstva ovrednotimo z različnimi dejavniki, kot so npr. nova delovna mesta, višja kvaliteta življenja, zmanjšani izdatki za brezposelne, socialni transferji za novo zaposlene, olajšave, subvencionirano varstvo otrok, štipendiranje, podpora lokalnim skupnostim ipd.

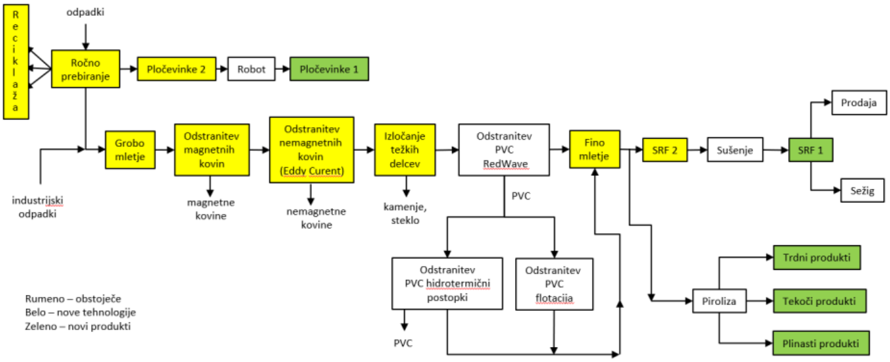
g) Večkriterijsko odločanje. Med alternativnimi možnostmi izberemo tisto, ki predstavlja uravnotežen kompromis med vsemi tremi dejavniki, tj. ekonomskim, okoljskim in družbenim. Za to uporabimo metode večkriterijskega optimiranja, kot je npr. metoda Pareto, ali sestavljene trajnostne kazalce, ki združujejo monetarizirane, tj. v denarju izražene ekonomske, okoljske in socialne vplive [5].

3 Eksperimentalni del – razvoj krožnega poslovnega modela

Razvoj krožnega poslovnega modela prikazujemo na primeru zbiranja, sortiranja in predelave nenevarnih odpadkov. Posebej smo se osredotočili na izdelavo visokokvalitetnih goriv iz predhodno sortirane odpadne embalaže in predelavo muljev komunalnih čistilnih naprav v produkte z dodano vrednostjo.

3.1 Izdelava visokokvalitetnih goriv iz odpadkov

V sistemu poteka zbiranje nenevarnih industrijskih odpadkov in njihovo sortiranje na različne vrste plastike, papirja, kovin, sestavne dele odpadne elektronske opreme ipd. Večina sortiranega materiala je primerna za reciklažo, preostanek prehaja v obrat za izdelavo trdnih goriv iz odpadkov (slika 1). Med recikliranimi materiali je tudi tok pločevink, ki vsebuje nekaj nečistoč, zato smo preučili možnost namestitve robotske roke, s katero bi vsebnost nečistoč znižali in dosegli višjo ceno recikliranih pločevink. Nereciklirani del odpadkov se združi s tokom industrijskih odpadkov in grobo zmelje, sledi odstranitev magnetnih in nemagnetnih kovin ter težkih delcev, kot so kamenje in steklo. Dobljeni material gre na fino mletje, katerega rezultat je trdo gorivo (SRF, ang. Solid Recovery Fuel) z letno kapaciteto okoli 50 000 t/a. Da bi gorivo ustrezalo prvemu razredu kvalitete, mora vsebovati manj kot 0,2 % klora in imeti kurilno vrednost večjo kot 25 MJ/kg [6]. Zato smo preučili možnost za odstranjevanje plastike, ki vsebuje klor in za sušenje trdnega goriva za zmanjšanje vsebnosti vlage, s čemer bi dosegli višjo kurilno vrednost. Tako dobljen produkt bi ustrezal kvaliteti prvega razreda in bi ga lahko prodali ali sežgali v sežigalnici in s tem pridobili toploto za sušenje. Obdelali smo tudi možnost pirolize trdnega odpadka, s čemer bi pridobili tekoča in plinasta goriva ter trdni ostanek, ki ima prav tako možnosti uporabe kot gorivo (oglje) ali za nadaljnje uplinjanje v plinaste in tekoče produkte [7].



Slika 1: Shema procesa izdelave trdnega goriva iz odpadkov

3.1.1 Robot za zmanjšanje deleža primesi v aluminijastih pločevinkah

V sistemu poteka ročno prebiranje aluminijastih pločevink v obsegu 2000 t letno, pri čemer v pločevinkah ostane okoli 2 % nealuminijskih primesi. Zmanjšanje deleža primesi bi bilo možno z robotsko napravo, ki sestoji iz robotske roke, kamere, varovalne kletke okoli robota in programske opreme. S to napravo bi zmanjšali vsebnost primesi z 2 % na 1 % in s tako prebranimi pločevinkami dosegli tudi do 50 % višjo ceno na trgu sekundarnega aluminija, kot jo dosegajo pločevinke z 2 % primesi. Načrtovana naprava bi imela kapaciteto 3 kg pločevink na minuto, ocenjena investicija je 150 000 EUR, življenjska doba 6 let ob dvoizmenskem obratovanju 6 dni na teden. Obratovalni stroški vključujejo stroške vzdrževanja (okoli 15 000 EUR/a), stroške elektrike (okoli 8 kWh na uro delovanja) in stroške operaterja, pri čemer lahko ena oseba upravlja in nadzoruje do 10 robotov. Če predpostavimo obratovalni čas 5500 ur letno, bi z eno napravo lahko obdelali 1000 t pločevink letno, za letno kapaciteto 2000 t bi potrebovali dve napravi. Skupni strošek električne energije bi znašal okoli 5300 EUR/a. Če predpostavimo, da je cena recikliranih pločevink z 2 % primesi 400 EUR/t in cena pločevink z 1 % primesi 600 EUR/t, bi s tako prečiščenimi pločevinkami v obsegu 2000 t letno dosegli za okoli 400 000 EUR/a višji prihodek. Doba vračanja investicije za dve napravi bi bila okoli enega leta.

3.1.2 Izdelava goriv z nizko vsebnostjo klora iz odpadkov

V odpadkih je pogosto prisoten klor, ki izvira iz impregnirane plastike, še zlasti polivinilklorida (PVC). Klor v gorivih, izdelanih iz odpadkov, je nezaželen, ker povzroča nalaganje oblog v kurilnih napravah, korozijo in tvorbo dioksinov, ki so v okolju izredno obstojni, se v vodi slabo topijo in so zelo strupeni. Pri sežigu odpadkov, ki vsebujejo klor, se lahko poleg tipičnih produktov zgorevanja sproščajo tudi škodljive snovi, kot so anorganske klorove spojine, npr. HCl, ki povzročajo onesnaženost ozračja in zemlje. Zato je za proizvodnjo visokokvalitetnih goriv potrebno zmanjšati vsebnost klora. Za to obstaja več tehnologij, od katerih so nekatere še v fazi razvoja.

a) Uporaba infrardeče tehnologije

Za ločevanje različnih vrst plastike obstaja dobro razvita tehnologija z uporabo bližnje infrardeče spektroskopije (Near Infrared Spectroscopy, NIR) [8]. Material na tekočem traku se obseva z infrardečo svetlobo. Različne vrste plastike absorbirajo svetlobo različnih valovnih dolžin in oddajajo specifične spektre, ki jih prepozna kamera. Prepoznani materiali se ločijo s pnevmatskim sistemom hitrih ventilov in zračnih curkov. Pridobljen podatek s strani podjetja Meyer Recycling (www.shmeyer.com) je, da stane naprava s kapaciteto 2 t/h okoli 90 000 USD (cca. 80 000 EUR), kar pomeni, da bi za letno kapaciteto 50 000 t ob predpostavljenem obratovalnem času 5000 h/a potrebovali pet takšnih naprav in investicija bi znašala okoli 400 000 EUR. Glavnino obratovalnih stroškov bi predstavljala električna energija za napravo, ki je moči 3,5 kW, kar pomeni strošek okoli 6000 EUR/a.

Učinkovitost ločevanja, kot navaja proizvajalec, je med 90 % in 96 %. Ob predpostavki, da je v celotnem toku odpadkov (50 000 t/a) 2 % PVC, bi znašal tok odstranjenega PVC 900 t/a, preostalih 49 100 t/a bi vsebovalo še 100 t PVC oz. 57 t klora, kar pomeni masni delež 57/49100 = 0,1 %, kar bi ustrezalo kvaliteti goriva 1. razreda, kjer je normativ za klor pod 0,2 %.

b) Flotacija

Flotacija je novejši postopek za ločevanje različnih vrst plastike, ki temelji na principu, da se lahko površinske lastnosti različnih materialov ob stiku s površinsko aktivnimi snovmi selektivno spremenijo, tako da postane površina enega materiala bolj hidrofilna, druga pa ostane v hidrofobnem stanju. V flotacijski koloni so v stiku tekoča, trdna in plinasta faza. Trdni material, npr. zmes plastike, se pomeša z vodo v kašo in prepihuje z zrakom v flotacijski koloni ob dodatku površinsko aktivnih snovi in penilcev. Ob tem zračni mehurčki obdajo hidrofobne materiale, ki prehajajo v penasto fazo praviloma pri vrhu kolone, od koder se odstranijo. Hidrofilni delci ostanejo v flotacijski raztopini. Literatura [9] poroča o uspešni ločitvi zmesi polivinilklorida (PVC) in polietilen tereftalata (PET) v alkalni raztopini z uporabo kalcijevega lignosulfonata kot površinsko aktivne snovi in borovega olja kot penilca. Za različne sestave modelnih raztopin so v laboratorijski flotacijski napravi dosegli 100 % ločitev in čistočo PVC.

V sklopu te raziskave smo preizkusili laboratorijsko flotacijsko napravo. Pripravili smo realni vzorec goriva SRF, mu dodali vodo in kemikalije ter ga prelili v flotacijsko kolono, v kateri je bilo okoli 5 l vode, in ga prepihovali z zrakom 4 min. Vzorce smo odvzeli na treh višinah kolone, PVC je pričakovan v zgornji frakciji, a prisotni so bili tudi drugi odpadki, npr. papir in cigaretni ogorki. Preliminarni poskusi nakazujejo, da je postopek flotacije sicer možen za ločevanje plastike, a predvidevamo, da pri zelo heterogenih vzorcih z nizko vsebnostjo PVC verjetno ne bo ekonomsko učinkovit zaradi velike porabe vode, kemikalij in električne energije. V nadaljevanju raziskave so načrtovane podrobnejše analize posameznih frakcij na različnih višinah flotacijske kolone.

c) Hidrotermični postopki

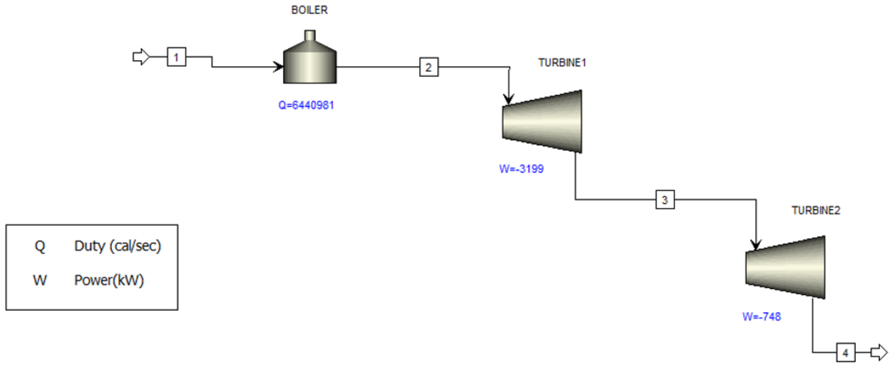
Novejše raziskave poročajo o izdelavi goriv z nizko vsebnostjo klora iz komunalnih odpadkov z uporabo hidrotermičnih postopkov. Material je določen čas izpostavljen nasičeni pari pri določenem tlaku, pri čemer se organski klor pretvori v vodotopno anorgansko obliko, ki jo odstranijo z izpiranjem z vodo. Literatura [10] poroča o komercialnem obratu na Japonskem z reaktorjem prostornine 3 m^3 in kapaciteto 1 t materiala na šaržo. Material je določen čas v stiku z nasičeno paro pri 20 bar in 200 °C ob mešanju z mešalom moči 30 kW. Produkt se nato izpira z vodo ter s filtriranjem loči na trdni produkt in raztopino, ki vsebuje klorove ione. Uporabljeno vodo je po regeneraciji mogoče reciklirati. Ocenjeno je, da poraba vode za paro in izpiranje znaša trikrat toliko, kot je masa odpadkov v šarži. Z izpiranjem se odstrani 96 % anorganskega klora.

Laboratorijski poskusi potekajo tudi za pridobivanje goriva iz odpadkov s superkritično vodo [11], pri čemer poročajo, da je imel dobljen produkt kurilno vrednost primerljivo z rjavim premogom ali lignitom. Večina PVC se je razgradila v topne klorove spojine, ki se odstranijo z izpiranjem.

Hidrotermični postopki izdelave goriv iz odpadkov so zahtevni in dragi zaradi visokih temperatur in tlakov. Primerni so eventuelno za obdelavo odpadkov z zelo visoko vsebnostjo vode, npr. muljev in zelo heterogenih odpadkov, kot so komunalni [12]. Za razmeroma suhe in homogene odpadke je cenejša uporaba optične NIR tehnologije.

3.1.3 Sežig goriva SRF

Manj kvalitetna goriva iz odpadkov, npr. RDF (ang. Refused Derived Fuel) in SRF 2. razreda, prevzemajo toplarne in sežigalnice v okolici oz. v sosednjih državah, za kar je potrebno plačati določeno odjemno ceno (t. i. Gate Fee) in stroške prevoza, kar znaša skupaj od 40 do 90 EUR/t goriva. Za gorivo SRF 1. razreda je vstopna cena 0, ostanejo pa še vedno stroški prevoza (okoli 27 EUR/t). Zato smo preučili možnost postavitve lastne sežigalnice visokokvalitetnega goriva SRF. Simulacijo procesa smo izvedli s programom Aspen Plus. Postrojenje sestavljajo peč s kotlom za proizvodnjo visokotlačne pare s sežigom goriva SRF in dve zaporedni parni turbini za proizvodnjo električne energije (slika 2). Predvidena količina SRF je 45 000 t/a, poraba vode za proizvodnjo pare je 34 t/h. Ocenjena investicija za peč s kotlom in obe turbini s skupno močjo okoli 4 MW znaša 3,8 milijona EUR. Predvideni stroški za vodo znašajo 210 000 EUR/a. Nov vir prihodka predstavlja proizvedena električna energija, glede na obstoječe stanje pa imamo tudi prihranek pri oddaji in transportu SRF zunanjemu odjemalcu. Prav tako v procesu ostaja para s temperaturo 155 °C, ki jo lahko uporabimo za proces sušenja goriva SRF pred sežigom. Skupaj je groba ocena prihodkov okoli 3 milijone EUR/a in ocena dobe vračanja investicije med 1 in 2 letoma.



Slika 2: Shema procesa sežiga goriva ter proizvodnje pare in električne energije

3.1.4 Piroliza odpadkov

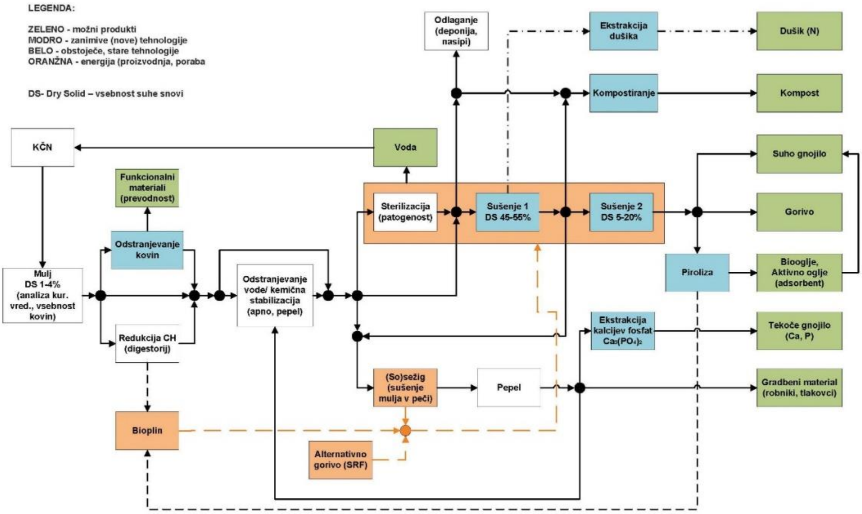
V laboratorijskem merilu smo izvedli pirolizo vzorcev čistega polietilena, goriva SRF, delno posušenega SRF in popolnoma posušenega SRF ter goriva SRF obogatenega s humusom in plastiko. Laboratorijska naprava je dopuščala najvišjo temperaturo okoli 350 °C. Predpostavljene komponente plinastega produkta so alkani C1 do C4 ter vodna para, v nadaljevanju raziskave so načrtovane podrobnejše analize plina s plinsko kromatografijo. Tekočo frakcijo smo zbirali v bučki in jo analizirali s plinsko kromatografijo in masno spektrometrijo (GC MS in GC FID). V primeru čistega PE so spektri pokazali pričakovane komponente, tj. alkane C6 do C12. V primeru vzorcev SRF smo dobili dve frakciji, vodno in organsko. V organski frakciji smo določili aromatske spojine in različne kisikove spojine, kot so etri, ketoni, aromatske spojine s kisikom, acikličnih ogljikovodikov je bilo malo. Preizkus gorenja je pokazal, da so produkti sicer gorljivi, vendar niso primerni za takojšnjo uporabo kot gorivo. Gorivo bi bilo potrebno pred pirolizo posušiti. Trdni ostanek je zoglenel produkt (ostanki tekstila in papirja), ki gori in bi bil potencialno uporaben kot gorivo. Preliminarne masne bilance kažejo, da je delež trdnega ostanka okoli 40 %, tekočih in plinastih produktov pa po 30 %. Nekoliko več tekočega in plinastega produkta smo dobili, če je vzorec SRF vseboval višji delež plastike glede na tekstil in papir, zato se nakazuje varianta, da bi pirolizirali v glavnem del plastike in manjši del tekstila, preostali odpad (tekstil in papir) bi sežgali in toploto uporabili za pirolizo. V nadaljevanju raziskave je načrtovana piroliza goriva SRF v pilotnem pirolizatorju pri temperaturi okoli 600 °C, kjer predvidevamo, da bodo imeli dobljeni produkti primernejšo sestavo za uporabo kot gorivo.

Postopek pirolize bi bilo mogoče učinkovito toplotno integrirati z drugimi procesi v predlaganem sistemu. Za kondenzacijo produktov se namreč uporablja hladilna voda, ki se pri tem segreje in bi jo lahko uporabili za vakuumsko sušenje muljev in vhodne surovine SRF ter nato ponovno uporabili v hladilniku pirolize. Trdne in plinaste produkte pirolize lahko uporabimo kot energent za dovajanje toplote v pirolizni kotel.

3.2 Predelava muljev v koristne produkte

Mulji iz komunalnih čistilnih naprav vsebujejo hranilne snovi, kot sta dušik in fosfor, velik odstotek vlage (več kot 85 %), možna je tudi prisotnost težkih kovin. Največji delež ravnanja z blati čistilnih naprav predstavlja sežig, sledijo predelava v bioplin in kompost, odlaganje neobdelanega mulja ni več dovoljeno. V prihodnosti se predvideva dolgoročno skladiščenje ostankov po sežigu za kasnejše pridobivanje fosforja, ki še ni ekonomsko učinkovito in se v Sloveniji še ne izvaja.

Slika 3 prikazuje nabor tehnologij za predelavo muljev v različne produkte. Predelava muljev v bioplin je dobro poznana, prav tako stabilizacija mulja z apnom, s čemer se zmanjša aktivnost mikroorganizmov v mulju. Stabiliziran mulj je možno odlagati na deponije, ga uporabiti pri gradnji, npr. nasipov, ali ga pretvoriti v kompost. Med nove tehnologije uvrščamo sušenje mulja v vakuumski sušilni napravi, kjer z doseganjem vsebnosti suhe snovi med 45 % in 55 % pridobimo gnojilo, bogato z dušikom, medtem ko sušenje na okoli 10 % suhe snovi daje suho gnojilo ali gorivo. V fazi raziskav je možnost odstranjevanja težkih kovin z magnetnimi nanodelci, oplaščenimi z amino-biopolimeri, ki so kelatorji kovin, kot npr. hitozan. Možna je tudi piroliza posušenega mulja, s čemer pridobimo biooglje oz. aktivno oglje z dobrimi adsorpcijskimi lastnostmi, ki ga lahko dodajamo gnojilu za izboljšanje učinka. Plinasti produkti pirolize se lahko uporabijo kot vir toplote za sušenje. Naslednja možnost je (so)sežig mulja v peči, pri čemer nastane pepel, bogat s fosfati, ki ga lahko pretvorimo v gnojilo, uporabimo kot gradbeni material (robniki, tlakovci) ali kot sredstvo za kemično stabilizacijo mulja. Toploto, nastalo pri (so)sežigu, uporabimo za sušenje. Podrobneje smo obdelali odstranjevanje težkih kovin z magnetnimi nanodelci in vakuumsko sušenje muljev.



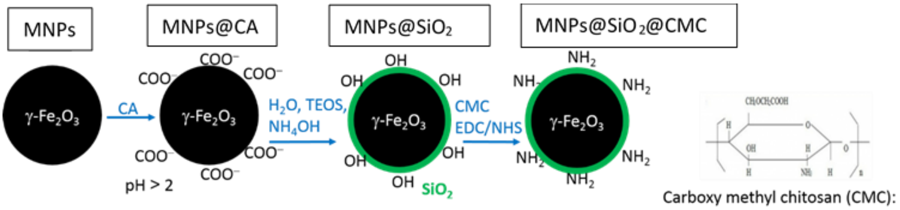
Slika 3: Shema predelave muljev v koristne produkte

3.2.1 Odstranjevanje težkih kovin iz muljev

Mulji čistilnih naprav lahko vsebujejo težke kovine, kot so cink, baker, svinec, nikelj in drugi. Znižanje vsebnosti težkih kovin je možno z adsorpcijo na magnetne nanodelce, oplaščene z amino-biopolimeri, kot sta lizin in hitozan, ki prispevajo razpoložljive amino skupine za adsorpcijo težkih kovin. Raziskave kažejo, da je možno adsorbirati preko 100 mg težkih kovin na 1 g oplaščenih nanodelcev [13]. Nanodelce odstranimo iz raztopine mulja z magnetom, jih regeneriramo in ponovno uporabimo. Izvedli smo laboratorijske poskuse in preliminarno načrtovanje postrojenja za industrijsko izvedbo.

a) Laboratorijski eksperimenti sinteze oplaščenih magnetnih nanodelcev

Sinteza magnetnih nanodelcev je bila izvedena iz železovih sulfatov s koprecipitacijo z uporabo amoniakalne vodne raztopine pod zračno atmosfero ter nadaljnjo stabilizacijo s citronsko kislino (MNPs@CA), kot je podrobneje opisano v literaturi [14]. Sintezni postopki so shematsko prikazani na sliki 4. Za nadaljnjo funkcionalizacijo z amino-biopolimeri smo sintetizirane magnetne nanodelce prevlekli z amorfno plastjo silicijevega dioksida (SiO_2). S tem je dosežena večja specifična površina oblečenih nanodelcev zaradi poroznosti in dostopa več aktivnih mest za poznejšo funkcionalizacijo ter posledično boljšo vezavo težkih kovin. Elektrokinetične meritve zeta potenciala z elektroforezo kot tudi infrardeča spektroskopija so pokazale uspešno oplaščenje magnetnih nanodelcev s plastjo silicijevega dioksida. Po oblačenju nanodelcev (MNP) z SiO_2 (MNPs@SiO_2 na sliki 4) pade nasičena magnetizacija z 68 emu/g na 17 emu/g zaradi razredčitve magnetne faze oz. zaradi prisotnosti nemagnetnega materiala. Nadalje smo magnetne nanodelce, oplaščene s prevleko silicijevega dioksida, funkcionalizirali z biopolimerom karboksimetil hitozanom (CMC), vzorec MNPs@SiO_2@CMC na sliki 4. Slednjega smo vezali s kovalentno vezjo na MNPs@SiO_2 z uporabo EDC kemije, da bi preprečili desorpcijo biopolimera CMC z nanokompozita ter posledično povečali učinkovitost odstranjevanja kovin.



Slika 4: Prikazana metodologija dela za funkcionalizacijo s karboksimetil-hitozanom (CMC) [14]

Elektrokinetične meritve zeta potenciala za vzorec MNPs@SiO_2@CMC pokažejo premik izoelektrične točke IEP k višjim vrednostim pH, tj. od pH 1-2 do pH 5-6, kar nakazuje na uspešno vezavo CMC na MNPs@SiO_2, saj protonirane aminske skupine vezanega biopolimera CMC prispevajo k pozitivnejšemu zeta potencialu. Spektri infrardeče spektroskopije (FTIR) pokažejo po oplaščanju s CMC tipične vrhove pri 3455–3445 cm^{-1}, ki jih pripišemo N-H vezem, hkrati pa je vrh pri 1404 cm^{-1} po funkcionalizaciji s CMC izginil, kar nakazuje na uspešen nastanek kovalentne estrske vezi med CMC in OH skupino z MNPs@SiO_2 (slika 4). Po funkcionalizaciji MNPs@SiO_2 s CMC je nasičena magnetizacija padla s 17 emu/g na 15,7 emu/g. kot posledica prisotnosti biopolimera CMC. To je dodatna potrditev prisotnosti CMC na MNPs@SiO_2@CMC. Za uporabo v realnih sistemih magnetizacija oplaščenih in funkcionaliziranih magnetnih nanodelcev predstavlja dovolj veliko magnetno silo za njihovo odstranitev iz npr. mulja po procesu adsorpcije, kar smo dokazali z realnimi poskusi odstranjevanja Cu^{2+} ionov iz modelne raztopine bakrovega klorida [14]. Ugotovili smo, da se z masno koncentracijo adsorbenta, tj.

$MNPs@SiO_2@CMC$ povečuje učinkovitost adsorpcije. To lahko pripišemo večjemu številu aktivnih mest za adsorpcijo, kar v našem primeru predstavljajo aminske skupine na $MNPs@SiO_2@CMC$. Pri vrednostih pH večjih od 5 je moč zaznati največjo kapaciteto odstranitve bakrovih ionov. Pri slednjem pH prevladuje disperziji nanodelcev celokupni negativni zeta potencial, kar lahko povzroči elektrostatski privlak med pozitivnimi bakrovimi hidroksidi in tako dodatno prispeva k večji učinkovitosti odstranjevanja le-tega zraven kelacije kovin s prostimi aminskimi skupinami, prisotnimi na MNPs@SiO2@CMC. Tovrstni rezultati kažejo, da sintetizirani nano-adsorbent predstavlja obetajočo možnost za odstranjevanje težkih kovin v realnih vzorcih, kot je gošča mulja.

b) Preliminarno načrtovanje industrijskega postrojenja

Industrijsko postrojenje za odstranjevanje težkih kovin iz muljev smo načrtovali za letno kapaciteto 30 000 t mulja ob predpostavki, da ves mulj vsebuje težke kovine in ga obdelamo z oplaščenimi magnetnimi nanodelci. Proces bi potekal šaržno, predpostavljen kontaktni čas mulja in nanodelcev je 2 uri, izvedemo 6 šarž dnevno oz. 2000 šarž letno po 15 t mulja na šaržo. V postrojenju smo predpostavili kontaktni rezervoar s prostornino 20 m^3 in mešalom moči 37 kW, za kar je ocenjena investicija s programom Aspen Process Economic Analyzer 285 000 EUR. Ceno magneta za ločitev nanodelcev od mulja smo ocenili na 15 000 EUR. Groba ocena investicije je tako okoli 300 000 EUR.

Strošek sinteze nanodelcev smo ocenili ob predpostavki, da mulj vsebuje 2 % suhe snovi in da je vsebnost težkih kovin 600 mg/kg suhe snovi [15], kar pomeni, da je potrebno pri 15 t šarži mulja (300 kg suhe snovi) odstraniti 180 g težkih kovin. Ocenjujemo, da 1 g nanodelcev veže 160 mg težkih kovin, zato potrebujemo 1,125 kg nanodelcev na šaržo. Ob predpostavki, da je strošek izdelave nanodelcev reda velikosti 750 EUR na 1 kg, bi znašal strošek sinteze nanodelcev za eno šaržo 845 EUR. Ob predpostavki, da bi lahko iste nanodelce uporabili 6 krat, bi znašal letni strošek nanodelcev okoli 281 000 EUR/a. Temu je potrebno dodati še strošek elektrike za mešalo, ki je ocenjen na 9000 EUR/a, tako da bi znašali skupni stroški 290 000 EUR/a.

Glede na preliminarne izračune je možno sklepati, da na ekonomiko odstranjevanja zelo vpliva potreben kontaktni čas mulja z nanodelci, ki določa velikost rezervoarja in s tem investicijo, ter sposobnost nanodelcev za večkratno uporabo, saj se s tem zmanjšajo stroški sinteze nanodelcev.

3.2.2 Vakuumsko sušenje mulja

Velika vlažnost muljev čistilnih naprav onemogoča direktno predelavo le-tega v koristne produkte z izjemo odvoza v kompostiranje ali raztros. Na sliki 3 je razvidno, da je odpadni mulj mogoče predelati v različne (pol)produkte, za kar pa morajo biti zagotovljeni ustrezni pogoji (pravni, okoljski, ekonomski, socialni, tehnološki). Zaradi visoke vsebnosti vode v mulju (več kot 95 %) ga je pred nadaljnjo obdelavo potrebno dehidrirati in posušiti. Klasični in cenejši postopki s sušenjem na prostem, s sončno energijo niso najbolj okoljsko in socialno primerni, ostali postopki pa lahko hitro postanejo ekonomsko nevzdržni zaradi velike porabe toplote za sušenje. V sklopu krožnih modelov je v segmentu odpadnih muljev poleg energijskega pomemben tudi snovni vidik, kjer se primarno surovine vrnejo nazaj v okolje pred sekundarnim (so)sežigom. Zato se za sušenje mulja razvija nove tehnologije, ki so učinkovite in ekonomsko zanimive ter omogočajo različne nadaljnje predelave mulja v (pol)produkte, kot so gorivo ali gnojilo, ali so del postopka pirolize itd.

Vakuumsko sušenje mulja je ekonomsko zanimiva tehnologija, ki poteka pri znižanem tlaku v zaprti posodi. Pri teh pogojih vlaga iz mulja izhlapeva pri nižjih temperaturah, kar pomeni nižje stroške sušenja. Ocenjena vrednost vložene toplotne energije za izhlapevanje vode iz mulja znaša 1 kWh/L vode. Biološko stabiliziran mulj se da hitro posušiti, postopek je tehnološko enostaven in poteka stabilno zaradi neaktivnih mikroorganizmov v mulju, ki sicer vplivajo na pogoje in postopek sušenja. Seveda pa znaten dodatek stabilizatorjev, kot sta apno in pepel, spremeni strukturo mulja in omeji njegovo uporabnost. Biološko nestabilizirani mulji, ki se tudi razlikujejo glede na sestavo in delež vlage, so tehnološko in okoljsko zahtevnejši za sušenje. Obvladovanje nastanka toplogrednih plinov, procesnih nelinearnosti, prehodov med fazami procesa sušenja mulja iz pastoznega v praškasto, omejitve procesnih veličin itd. smo strnili v napreden sistem vodenja, ki se je sposoben med postopkom sušenja prilagajati različnim tipom mulja in ustrezno prilagajati parametre. Pri razvoju sistema vodenja smo uvodoma modelirali postopke sušenja na obstoječih podatkih eksperimentov sušenja muljev ter zgradili ustrezne matematične oz. nevronske modele. Ti modeli, ki opisujejo delovanje procesa sušenja, nam služijo za simulacije, učenje in optimizacijo, s katerimi lahko razvijemo zadovoljiv regulator oz. sistem vodenja. Pri tem je bilo potrebno določiti glavne procesne veličine, filtrirati meritve, rekonstruirati nemerljive ali manjkajoče signale itd. Končni nevronski model procesa sušenja sestavlja pet parcialnih modelov, vsak s svojimi specifikami. Razvit mehki regulator ima na podlagi merjenih vrednosti tlaka, temperature, faze procesa, vlažnosti, nalogo prilagajanja hitrosti in smeri mešala, ter intenziteto vzdrževanja podtlaka v sistemu. Vstopni podatki o vlažnosti in masi mulja služijo za določitev konca postopka sušenja (suhost) in končne granulacije izstopnega mulja. Predstavljen mehki sistem vodenja s pomočjo nevronskih modelov omogoča načrtovanje optimalne regulacije procesa sušenja, kar s skrajšanjem časovne komponente vpliva na boljše ekonomske rezultate sheme krožnega gospodarjenja z muljem.

Investicija v napravo s kapaciteto sušenja 100 t mulja dnevno oz. 30 000 t/a je okoli 3 milijone EUR, obratovalni stroški sušenja so ocenjeni na 315 EUR/t suhe snovi [13] in vključujejo elektriko, plače zaposlenih, režijo, transport, plačila okoljskih dajatev, kanalščin. Ob predpostavki, da sušimo 30 000 t mulja letno s 25 % oz. 7500 t/a suhe snovi, bi znašal strošek sušenja 2,36 milijona EUR/a. Vir prihodkov predstavljata prevzemna cena mulja, ki znaša okoli 80 EUR/t mokrega mulja oz. 320 €/t suhe snovi, in prodaja posušenega mulja, ki ga lahko prodamo kot gnojilo in/ali gorivo (okvirna cena 275 oz. 153 €/t). Pri kapaciteti suhe snovi 7500 t/a in prodaji celotnega posušenega mulja za gorivo, bi znašal prihodek 3,55 milijona EUR/a. Kot vir toplotne energije lahko vzamemo sežig SRF ali toploto kondenzacije pri pirolizi. Za hlajenje uporabimo naravne vodne vire v bližini. Vračilni rok investicije je po tej približni analizi ocenjen na 2 do 3 leti. Omeniti velja, da se cene, ki smo jih uporabili v izračunu, na trgu precej spreminjajo. Poleg tega tudi zakonodaja še ne dovoljuje prodaje posušenega mulja kot gnojilo, zato so na tem področju potrebne nove zakonodajne rešitve.

4 Zaključek

V prispevku smo prikazali zasnovo krožnega poslovnega modela na primeru zbiranja in predelave nenevarnih industrijskih odpadkov. Osredotočili smo se na izboljšanje predelave odpadkov v trdna goriva in na predelavo muljev čistilnih naprav v koristne produkte. Med obstoječe tehnologije smo dodali nove postopke in definirali potencialne nove produkte. Za nekatere od njih smo izvedli laboratorijske eksperimente in izračunali okvirne ekonomske analize.

V laboratorijskem delu raziskav smo izvedli pirolizo trdnega goriva v laboratorijskem merilu in pokazali, da vsi trije produkti, plinasti, tekoči in trdni, izkazujejo potencial za nadaljnjo uporabo. Zastavili smo poskus ločevanja PVC iz goriva s flotacijo, podrobnejše analize bodo predmet bodočih raziskav.

Sintetizirali smo magnetne nanodelce, jih oblekli s plastjo silicijevega dioksida in funkcionalizirali s hitozanom, ki je amino-biopolimer in ima zaradi aminskih skupin v svoji strukturi sposobnost keliranja kovin. Ugotovili smo, da lahko s temi delci odstranimo do 160 mg težkih kovin na g nanodelcev. Izdelali smo preliminarni načrt industrijskega postrojenja in ga okvirno ekonomsko ovrednotili.

Pri vakuumskem sušenju mulja smo razvijali regulacijski sistem, s katerim bi učinkovito nadzirali proces sušenja za različne vrste muljev. Razvili smo nevronske modele, ki opisujejo delovanje procesa sušenja in služijo za simulacijo, učenje in optimizacijo, s katerimi lahko razvijemo zadovoljiv regulator oz. sistem vodenja. Razviti mehki regulator na podlagi merjenih vrednosti tlaka, temperature, faze procesa in vlažnosti mulja prilagaja hitrost in smer mešala ter vzdržuje ustrezen podtlak v sistemu. Tako bi pridobili ustrezne produkte sušenja ne glede na vrsto vhodnega mulja.

Zastavljen krožni poslovni model nakazuje veliko možnosti za predelavo odpadnih snovi v koristne produkte, z uvedbo novih tehnologij se odpirajo tudi nova delovna mesta. Prihodnji cilj je, da z večkriterijsko optimizacijo, ki bo poleg ekonomskih kazalcev upoštevala tudi okoljske in družbene vplive, izberemo optimalni nabor tehnologij in produktov za trajnostno povečanje dodane vrednosti, zapiranje snovnih in energijskih tokov ter ustvarjanje novih verig vrednosti na področju ravnanja z odpadki.

Zahvala

Avtorji se zahvaljujejo Ministrstvu za izobraževanje, znanost in šport Republike Slovenije in Evropskemu socialnemu skladu za sofinanciranje projekta KRONOD v okviru razpisa Po kreativni poti do znanja 2017-2020. Prav tako se zahvaljujejo za sodelovanje v projektu gospe Vilijani Brumec in g. Davorinu Mejalu iz podjetja Gorenje Surovina, g. Andreju Cenčiču iz podjetja Alp-Lab in študentom Matevžu Roškariču, Aljažu Marinu, Mateju Fureku, Kristini Kranjčec, Kristini Olovec, Kenu Kolarju, Jožetu Vovku in Klemnu Zaponšku.

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University of Maribor Press

TERMIT's Circular Economy

ALENKA PAVLIN, BARBARA HORVAT & VILMA DUCMAN

Abstract TERMIT d.d. is a mining company for the production and processing of silica sands and the production of auxiliary casting materials. In 2004 Termit decided to rehabilitate open pits with non-dangerous and inert waste, and started with processing this waste into artificial soil Tersan. At the moment 10 different construction composites are produced from 24 different wastes of various suppliers. Majority of the waste used for rehabilitation presents used Termit's silica sand sold to foundries. Returning used sand to Termit lowers foundries' expenses for their waste disposal, lowers burden on municipal waste dumps, and stores silica sand on known place that might be useful for future generations. In 2017 Termit started project with ZAG where various waste materials containing enough SiO_2 and Al_2O_3 will be up-cycled into porous lightweight insulating alkali activated materials/foams. Therefore several waste materials from Termit, which are in abundance, were tested. Results of chemical analysis are presented in this article.

Keywords: • circular economy • rehabilitation materials • construction composites • alkali activated materials • lightweight porous insulating material •

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DOI https://doi.org/10.18690/978-961-286-211-4.7 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

TERMIT d.d. is a mining company established in 1960 for the production and processing of silica sands and the production of auxiliary casting materials. Termit's silica sands are used in civil engineering and for sports facilities. At the moment Termit is the largest European manufacturer of coated silica sands, producing cores and forms for casting using Croning, cold box, and inorganic methods from its own sands. Termit covers the majority of the casting market in Central and South-East European countries.

Termit produces sands in opencast mines located in the Moravče tertiary basin. Approximately 200,000 tons of silica sands are produced per year. According to the Slovene law all pits have to be rehabilitated after excavation ends[1] which can be done using natural material obtained on the market, or by alternative solution using waste material. To rehabilitate opencast mines, enormous amount of materials to replace the excavated sands are required.

Termit decided to try the alternative in 2004, i.e. by contacting industries generating large quantities of non-dangerous and inert waste, Termit started to process this waste and use it to produce appropriate rehabilitation materials. Majority of the waste used for rehabilitation presents used Termit's silica sand sold to foundries. Returning used sand to Termit lowers foundries' expenses for their waste disposal, lowers burden on municipal waste dumps, and stores silica sand on known place that might be useful for future generations. Since 2004 Termit was granted the permit for processing waste into artificial soil, which got name Tersan. At the moment 10 different construction composites are produced from 24 different wastes of various suppliers.

In 2017 Termit started another circular economy project, where various waste materials were tested for the suitability for up-cycling into porous lightweight insulating alkali activated materials/foams that could be used in the building industry. Aim is not just to lower the amount of different wastes, but to produce useful functional product with added value.

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[1] Zakon o rudarstvu (ZRud-1), Uradni list RS, št. 14/14.

2 Rehabilitation of open pits

2.1 Problem of rehabilitation

At the beginning of 2004, Termit was faced with a great challenge how to rehabilitate a 2 million-m^3 mine that increased due to Termit's operations by 150,000 m^3 every year. There were two options: purchase natural materials on the market, transport them across the whole country and open a new wound in the nature elsewhere, or alternatively, contact industries generating large quantities of non-dangerous and inert waste, process this waste and use it to produce appropriate rehabilitation materials. According to expenses and effect on nature, second option was chosen and casting industry, where Termit's sands are used to make moulds and cores for casting metals, was contacted.

Sands that are used in casting can not be re-used in the process because along the casting procedure they lose needed properties. Therefore used sands present waste, financial burden for foundries and ecological burden for nature due to dispose of the used sands at waste dumps, while Termit could primarily use these sands for rehabilitation as the most appropriate material.

Due to win-win situation on both ends, i.e. Termit and casting industry, Termit implemented a closed loop for castings sands already in 2005 and won an environment-friendly award for the process of rehabilitation using the artificial material the same year.

2.2 Industrial symbiosis

In 2004 Termit was the second in Slovenia to have been granted a permit for processing waste into the artificial soil for rehabilitation of opencast mines with silica sands. The rehabilitation materials production was certified and production of construction composites started with all Slovenian technical approvals. In the beginning 742 tonnes of waste material was recovered, but now already over 70000 tonnes, which for some years represents over 1 % of all recovered waste in Slovenia.

Termit currently produces 10 different construction composites made from 24 different wastes of various suppliers. The Slovenian National Building and Civil Engineering Institute, who issued the Slovenian technical approval for Termit's manufactured construction composites, oversees production of construction materials.

Termit established an efficient and effective example of industrial symbiosis, successfully attracting large industries – casting, civil engineering, paper, glass, municipal waste, etc. From industrial waste, Termit manufactures custom-made geotechnical composites that match the natural geological soil structure.

Recovery of waste and manufacture of construction composites is done in several steps:

- all waste and accompanying documentation is checked and waste weighted;
- structure and composition of waste is examined;
- waste is sieved, larger pieces grinded, and impurities removed to special containers;
- moisture of waste is measured and dry weight calculated;
- in accordance with the formula specific wastes are mixed with autochthonous materials and other components in order to obtain a homogenous material;
- moisture content is measured once again and if the moisture level is appropriate, such construction composite can be used on the site.

When using the material, geotechnical rules are considered:

- materials are used in layers;
- each layer is compacted to at least 96% using heavy construction machinery.

With the right ratio of materials, moisture, and compaction, all potentially hazardous substances in waste become permanently immobilised to not to present problem for environment.

By manufacturing construction composites from waste generated in various industries, Termit contributes to the sustainable development in the field of environment at least in 3 ways:

- use of construction composites enables a quick and quality rehabilitation under controlled conditions, thus nearing the original state or mostly exceeding it;
- manufacture of construction composites from waste helps industries that are generating large quantities of waste, e.g. casting, paper, timber, and stone industry, to lower large financial burden with returning the used material to Termit instead of disposing it on dumping sites;
- by recovering construction composites from large quantities of waste, Termit extends the lifespan of municipal waste dumps, thus reducing the costs of waste collection for everyone and following the development strategy of the Republic of Slovenia and the requirements of the European Union, which state that as much waste as possible should be recovered.

At the same time, Termit helps the environment and restores nature to its original state for everyone (**Figure 1**).

Figure 1: Opencast mines before (left) and after (right) rehabilitation, foto: Termit.

3 Up-cycling with alkali activation technology (AAT)

3.1 Waste material as a burden or as a material of the future

Consumption of raw materials for modern style of life is an unavoidable fact leaving behind large quantities of waste. Due to limited quantities of existing raw materials there is serious concern about nowadays technologies and products used. At the same time quantities of wastes are getting bigger and bigger. Therefore it is necessary to start using waste material as the source material for alternative products with similar properties to the current products available on the market.

With this bearing in mind Termit started in 2017 project with ZAG, where the focus is to use Termit's abundant waste material as the main source material that would be used as precursor for synthesis of alkali activated materials (hereinafter: AAM), often also called geopolymers.

3.2 Introduction into AAM

AAM are produced from precursors that contain sufficient amount of amorphous SiO_2 and Al_2O_3, that are activated with alkalis and alkali glasses or even with their waste material alternatives. After dissolution of ingredients in the waste material precursor, potential additional secondary reactions along with mechanics of continuum hindered by viscosity take place. In few hours of process the alumina-silicate 3-dimensional O-Si-O-Al-O network forms. This process is followed by curing at different temperatures which can affect the final mechanical properties of synthesized AAM.

AAM have potential to replace several construction products used nowadays (Provis, 2010, Zhang, 2014). So far there are several products already available on the market and few structures that are made completely from geopolymers:

- geopolymer concrete, sprayed geopolymer fire-resistant foam, low temperature geopolymer bricks, (www.renca.org)
- geopolymer concrete, (http://www.geocement.in/geo_home.php)
- fire resistant in- and out-door paint, (https://www.inomat.de/)

- geopolymer fiber-reinforced mortar for structural rehabilitation, for corrosion prevention, water-activated geopolymer mortar for surface reinforcement, (http://infrastructure.milliken.com/geopolymer/)
- in 2013 1st building with geopolymer concrete used for structural purposes was built in Australia, i.e. University of Queensland's Global Change Institute, (www.geopolymer.org, 2013)
- in 2014 geopolymer concrete aircraft pavements were built in Australia, i.e. Brisbane West Wellcamp Airport, (Glasby, 2015)

With using AAM instead of traditional products, CO_2 footprint is significantly reduced, which makes AAM nature-friendlier product.

3.3 Experimental

In Termit d.o.o. up to 2 kg of different waste materials were taken in their open waste dumps for preliminary research of materials' potential for alkali activation. Materials are presented in **Table 1** (with laboratory sample name, description of the sample and waste label from the Classification list of waste from Official Gazette of the Republic of Slovenia, no. 20/01 Annex 1).

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

Laboratory sample label	Sample	Waste label
Wastes from MFSU of adhesives and sealants (including waterproofing products)		08 01
V-160/17	Wastes from MFSU and removal of paint and varnish	08 01 99
Wastes from power stations and other combustion plants (except 19)		10 01
V-161/17	Bottom ash, slag and boiler dust	10 01 01
Wastes from casting of ferrous pieces		10 09
V-175/17	Furnace slag	10 09 03
V-162/17	Casting cores and moulds which have not undergone pouring other than those mentioned in 10 09 05	10 09 06
V-174/17	Casting cores and moulds which have undergone pouring other than those mentioned in 10 09 07	10 09 08
V-165/17	Flue-gas dust other than those mentioned in 10 09 09	10 09 10
Wastes from manufacture of glass and glass products		10 11
V-166/17	Solid wastes from on-site effluent treatment other than those mentioned in 10 11 19 (gypsum)	10 11 20
Wastes from manufacture of ceramic goods, bricks, tiles and construction products		10 12
V-167/17	Waste preparation mixture before thermal processing	10 12 01
V-168/17	Waste ceramics, bricks, tiles and construction products (after thermal processing)	10 12 08
Wastes from shaping and physical and mechanical surface treatment of metals and plastics		12 01
V-169/17	Wastes not otherwise specified	12 01 99
Waste linings and refractories		16 11
V-170/17	Refractory materials	16 11 06
Construction and demolition wastes		17 09
V-171/17	Glass wool	17 09 04
V-222/17	Rock wool	17 09 04
V-264/17	Rock wool	17 09 04
Not waste		
V-162/17 Q	Quartz sand MAP-1	Not waste
V-163/17	EKOSANDS aggregates made from used casting cores	Not waste
V-164/17	AGREGAT S aggregates made from used casting cores	Not waste
V-173/17	Green clay	Not waste
V-172/17	Phenol sludge - hydrophobic	Not waste
V-172/17 SI	Phenol sludge - sandy (inside)	Not waste
V-172/17 SO	Phenol sludge - sandy (outside)	Not waste
V-295/17	Red clay	Not waste
V-296/17	Sludge after separation in silica quarry	Not waste
V-161/17 C	Coal	Not waste

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

On collected samples first dried on 70 °C for 24 h in WTB Binder dryer and then with IR dryer at 105 °C to constant mass, grinded in vibrating disk mill (Siebtechnik) and sieved below 90 μm, X-ray fluorescence (XRF, Thermo Scientific ARL Perform'X Sequential XRF) was performed to classify waste materials' potential for alkali activation.

3.4 Results and discussion

Waste V-169/17 was the only material that was excluded from all further investigations because sample included plastic which is not the material used in our project. Results of chemical analysis performed on the remaining samples with XRF where mass percent of oxides is close or above 0,1 % are presented in **Table 2**.

Table 2: Mass percentage of oxides measured with XRF. Oxides presenting majority in each individual sample are in grey boxes.

Laboratory sample label	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3	ZnO	ZrO_2	BaO	PbO
V-160/17	0,5	1,9	0,9	4,7	0,3	0,09	0,08	88,3	0,8			0,2				
V-161/17	0,3	9,4	10,5	26,9	1,0	2,7	4,1	25,3	0,6		0,4	16,8				
V-161/17 C		2,0		8,9		2,0	0,3	13,9	0,4		0,3	21,7		0,2	0,3	
V-162/17			2,5	95,6			0,1	0,1	0,08			0,5				
V-162/17 Q			0,2	98,2			0,05	0,2	0,1			0,4				
V-163/17	0,6	0,6	3,9	90,7			0,3	0,9	0,2			1,2				
V-164/17	1,5		0,6	94,0			0,1	0,2	0,08			0,8				
V-165/17	0,9	0,8	8,2	83,1			0,3	1,3	0,8			2,3				
V-166/17	0,6	1,6	0,4	6,2		31,9	0,4	46,9				0,2				3,4
V-167/17	0,3	1,4	23,1	61,6			4,4	3,4	0,2	0,8	1,5	1,5			0,4	
V-168/17	0,6	0,3	49,3	42,9			3,2	0,6	0,2	0,2	0,3	1,2			0,1	
V-170/17	0,3	0,7	44,1	43,1	0,3		0,3	4,3	0,8	0,5		3,5		0,5	0,2	
V-171/17	16,5	3,7	2,5	65,9			0,3	7,1	0,1			0,6				
V-172/17		0,1	3,8	87,6		0,1	0,4	4,9	0,2			0,6				
V-172/17 SI		0,1	0,1	98,0			0,09	0,2	0,2			0,5				
V-172/17 SO		0,1	1,3	92,7			0,2	0,3	0,5	0,08		1,1				
V-173/17	0,5	3,6	17,6	62,8	0,2		2,7	5,1	0,7			5,8			0,08	
V-174/17	0,2	0,3	3,6	87,7			0,2	0,5	1,0		0,3	5,0	0,09			
V-175/17	0,3	3,4	6,2	56,1		0,4	0,3	24,1	0,4	0,1		2,7	4,6		0,09	
V-222/17	2,1	9,8	17,3	43,5	0,3		0,8	16,8	1,3		0,3	6,7			0,07	
V-264/17	2,1	10,1	16,3	40,6	0,1		0,3	16,2	1,5		0,2	10,9				
V-295/17		0,5	8,9	83,8			0,8	0,3	0,3			3,6				
V-296/17		0,2	8,7	87,3			0,8	0,2	0,3			1,5				

All analysed samples contained SiO2, just 3 of them, i.e. wall paint (V-160/17), coal (not waste, V-161/17 C), gypsum (V-166/17) below 10 %. Due to the lack of most important ingredient in alkali activation, all 3 samples (V-160/17, V-161/17 C, V-166/17) were excluded from further analysis. The rest of the samples contain sufficient amount of Si and Al to be further processed, only X-Ray Diffraction (XRD) analysis will have to be performed to determine the amount of amorphous and crystalline phase to estimate the amount of amorphous SiO2 and Al2O3 whose content play crucial role in alkali activation technology.

4 Conclusion

Beside its core business (manufacturer of coated silica sands, and of casting cores), company Termit is an important manufacturer and seller of construction composites that are technically, ecologically, and economically suitable for rehabilitating degraded surfaces.
Recovery of waste materials into rehabilitation materials and their use is a sustainable alternative to rehabilitation using natural materials, without creating new wounds in the nature and with returning material where it was excavated for future generations.

Majority of Termit's wastes shows potential to be used as precursors in alkali activation process with which waste material will become source material and the product will have added value. In this manner the amount of waste will be lowered, raw materials will be saved, contribution of CO_2 will decrease, and economy will become circular.

Acknowledgments

Project No. C3330-17-529032 "Raziskovalci-2.0-ZAG-529032" was granted by Ministry of Education, Science and Sport of 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.

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Circular Economy Model of Cathode Waste Processing

BLAŽ TROPENAUER, DUŠAN KLINAR, NIKO SAMEC & JANVIT GOLOB

Abstract The production of aluminium achieved significant step regarding energy efficiency while one of important waste stream remains untreated. Namely, waste, known as Spent Pot Lining (SPL) derives from each individual electrolytic cell, or more precisely from the material of the cathode electrode bath. The SPL stream contributes to about million tons per year of hazardous waste in the world's smelters production. The carbonaceous content represents 60 % of the whole SPL mass and consists of a great part of graphite. This part of waste represents a great opportunity to harvest its usable material flows. Laboratory tests confirmed the inefficiency of one-step treatment separation of different impurities as needed. With the help of laboratory investigations, the possibilities of material utilization of SPL have been studied. Comprehensive aspects of preliminary inquiry allow placing a new model for the preparation of products that satisfy customer's needs. This approach improves process economics and effectively close the loop of mass flow.

Keywords: • spent pot lining • carbon • waste treatment • cryolite • circular economy •

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DOI https://doi.org/10.18690/978-961-286-211-4.8 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

The origins of SPL formation lie in the electrolysis cells entire life of the operation. During start-up, melts of cryolite and alumina salts penetrate and fully impregnate the carbon cathodes. On the overall, the rate of sodium and bath penetration into the cathode is a function of its graphitization rate, current density, cryolite ratio (CR) and time of electrolysis (Soerlie, 1994).

Disposal or landfilling will soon not be an option in the future. The important starting point of research activities is based on possible applications of products in the regional economy. Namely, different applications direct the criteria for the product and consequently determinates the more precise concept of processing SPL.

The target of the research is to elaborate the concept and define the conditions for setting up efficient technologies for SPL treatment for already separated carbon and brick parts. A special emphasis is put on the local solution to these environmental problems.

Following modern trends, the effort directs to prepare SPL material for the full reuse, what means, establishing a circular economy, connected to several industries like metallurgy, cement production, construction and mineral wool production. Regarding self-usage of the processed waste (back to the electrolysis process or/and anode production) the preliminary investigations show that such a treatment can cause some quality problems regarding increasing sodium content despite positive economic effect.

2 Materials and Methods

A circular model to solve the environmental problem is difficult to conceive. This is partly the result of the wrong starting points, which put the existing methods and techniques in the forefront, and partly because of the many factors that influence the definition of the appropriate concept. The fact is that the development cycle started, which the stakeholders generally do not realize, but they are forced to initiate certain actions with which they have not met before. Therefore, a systematic approach is needed, which leads through the model of problem-solving.

2.1 The approach

In the beginning, it is necessary to be acquainted with the problems and existing solutions while further decisions are made upon these basics. Research strategies and actions follow, depend on developed technology concept. Therefore, a research and development phase necessary thoroughly examine the information about the origin of an environmental challenge, the problems caused by and recognize consequences. As enough knowledge is gathered about the environmental problem, the solution investigations begin. They can vary in different economic models and can offer outsourcing turnkey solutions or solutions that require own knowledge and efforts. In any case, an in-depth analysis of economic as well as technological solutions is required. Especially if the waste collection service express difficulties in running this activities or prices rise constantly, another model for an environmental solution should be pursued. This model extends the research phase to the technical level. Environmental problem owners must gather not only local but also professional and scientific knowledge to evaluate the existing state of the art technical solutions to choose the right technology provider. As Raymond (Raymond, 2010) exposes, this interdisciplinary knowledge integration is very demanding and linked with a significant degree of confusion. Problem owner can carry out laboratory tests or try to find on a market convincing information upon given technical solutions. The analytic results present strong support for the decision upon selected technology that would most likely solve the specific environmental problem of the company.

2.2 Standard and innovative models

Because the aluminium production industry, besides electrolysis aluminium, produces castings and foundry alloys, the technical knowledge is merely based on pyrometallurgical processes. Therefore, processes linked with this kind of technology is the first to be pursued by the techno-developing teams.

Company Talum has many foundries and produces cast alloys, billets, castings, and slugs out of its own produced primary or electrolysis aluminium. Company's experts decided to follow trends in the thermal waste decomposition of SPL waste as their expertise and education originated mostly in this engineering field.

The standard model

A classic path to decide appropriate technology was chosen. Only thermal review of SPL waste treatment was performed. Classical thermal treatment technologies reported troubles processing SPL as difficult grinding, clogging of feeding equipment, material adhesion, 30 % of inorganic residues and incomplete destruction of fluorides. Therefore, a new, innovative thermal technology was chosen for investigations, namely plasma technology. Pro and contras were investigated. This technology is believed to have many advantages like only 5 to 10 % glazed and inert residues, complete destruction of toxic waste components, high throughput, modularity, small-scale economics, production of calorific and combustible gas and no environmental impact.

To proof of these benefits, it is important to contact few technology providers and test their equipment for SPL processing. Detailed specifications of the waste must be carried out to submit as much as possible information to the provider. The goal is to convince the provider for laboratory and pilot test examination and receive feedback information. The provider can submit a bid, namely for simulation of the solution, laboratory tests or to continue with more tests.

Thermal tests on existing pilot devices offered by the equipment provider usually become very expensive. This turns out as a crucial hindrance to proceed with investigations as technology provider requests substantial cost refund to perform tests on a larger amount of waste sample. The customer is subjected to two choices. First, it can rely on the provider's simulation results and then it can secure the purchase of new technology with specific guarantees in the contract. However, there is no guarantee that with a new technology and special waste the economic outcomes will be the same as described in the business plan. In addition, the risk of the provider’s business failure is always present. Therefore, very little customers are willing to take the risks by installing new environmental technologies that are not proven in practice.

The innovative model

Environmental solutions are usually technologically demanding and innovative. Because the standard approach does not give a solution to this environmental problem, some new, innovative approaches are many times considered. Such an approach can secure customers' investments in new technology to a far better extent than a standard approach does. It extends the design phase and allows the customer to convince himself upon the suitability of technological solutions.

The first difference is integrity. Namely, all the existing technological solutions should be considered and not just the staff's expertise. Therefore, a complete review of existing technologies is essential. An interdisciplinary approach to management is the next step. Combining interdisciplinary knowledge reduces the degree of complexity. Interdisciplinary knowledge is necessary to include understanding the state-of-the-art solutions. With a team of experts with diverse knowledge, the problem is covered comprehensively to gain an overview of the current state of managerial solutions and current technologies. External experts are usually part of such teams, as companies do not possess enough expertise in knowledge. Prior to checking the selected technological solution at the experimental level, it is necessary to familiarize with the complexity of the technological solution and the processing of the resulting products. Insofar, as the technological solution is based on laboratory tests, it is appropriate to check the results with different types of knowledge that can be either within the company itself or outside. The results stimulate new thinking and form the basis for the development of tacit knowledge and the delivery of this knowledge. New conceptual solutions and a combination of interdisciplinary knowledge renew the concept of the solution itself. From the many times discussed ideas and new concepts, requirements are defined that determine the quantitative scope, location, and user of the technology. It seems the solution lies in the local economy where derived products can circulate. New innovative technology needs to provide SPL detoxification and deactivation and consequently decomplex waste to the final inert material.

To be able to provide the appropriate technological solution and the products obtained, it is necessary to switch from the laboratory level to the pilot technology tests. Users of waste-derived products require an appropriate quantity to check the quality of products themselves. Positive results from the pilot plant confirm technological relevance and minimize risks associated with up-scaling technology and investment on a real scale.

If the technological solution and derived products can be confirmed, the environmental approval is close to being obtained. The priority of the solution lies not in the economies of scale of the investment, while local relevance and integration into the ecological circle of the local economy are quite more important. Also, the possibility to obtain relevant approvals for the issuance of an environmental permit given by the state. In this process, the team of experts also acquire local, tacit knowledge to finalize the solution. Tacit knowledge is personal and gained from direct interaction with suppliers, customers and people within the company (Nonaka, 1998).

If there is a suitable technology provider on the market, it is possible to negotiate for the delivery of most of the equipment. Because the basic engineering skills for this type of technology has been mastered, the provider's suitability can easily be checked. However, the equipment can also be bought, as a component on a market and finally assembled with own engineering knowledge to whole technology.

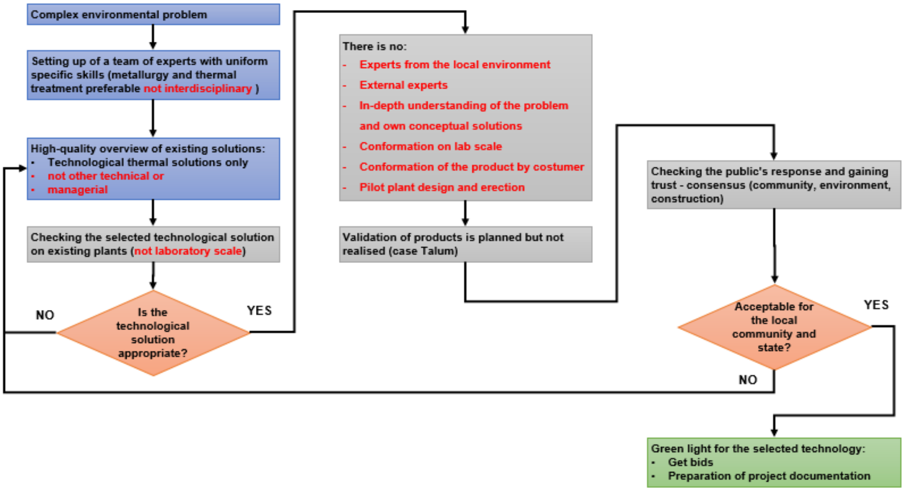


Figure 1: The shortcomings of the standard model (exposed with red text).

Important differences are notable between standard and innovative model. There are highlighted in the standard model shortcomings (Fig. 2). The standard model does not propose the interdisciplinarity of environmental issues and not incorporate needed experts. Therefore, the problem cannot be discussed comprehensively. The main disadvantage of the standard model is, however, the lack of laboratory scale experiments. This phase gives low budget solutions of the studied technology with costumer conformation of the gained products. In a next step, a pilot plant can be built to test technological solutions, type of the equipment and gain product samples for tests.

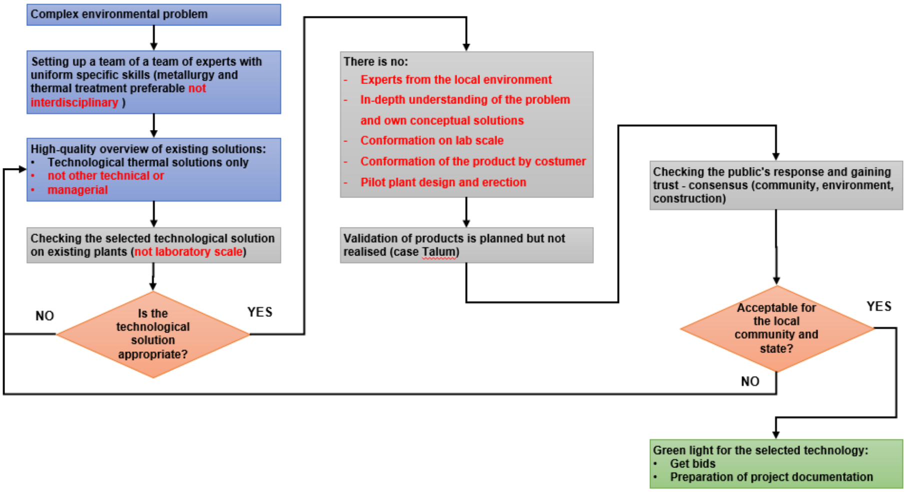


Figure 2: The shortcomings of the standard model (exposed with red text)

3 Results and Discussion

With the pursuing of the given innovative development model (Fig. 1), a new approach for the special environmental problem of the cathode SPL waste is addressed more adequately.

3.1 Environmental issues

SPL waste generating companies have constant environmental challenge linked with material handling, processing, and delivery. Dismantling process of an electrolysis cell starts with the mechanical demolition of various material layers. First, the cryolite layer is removed as it can be easily used again for the start of the electrolytic process. In next phase, the carbon part or the cathode is crushed and the firebrick layer separated. The carbon part is called the First cut, as it is cut off firstly, analogous to the Second cut represent the firebrick part.

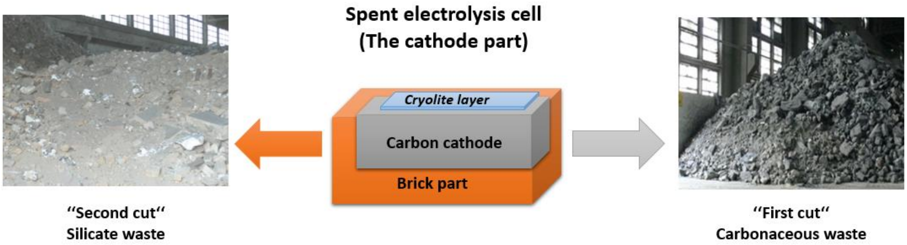


Figure 3: The spent cathode waste parts generation: first and second cuts.

3.1.1 Waste problematics

Above discussed "first and second cuts" contain cyanides and fluorides and are therefore toxic. An additional dangerous feature is fire hazard and explosiveness. The first cut contains a large amount of carbon with a relatively high calorific value. In the event of contact with moisture and water, some amounts of inflammable, toxic and explosive gases are generated as well (methane, ammonia, hydrogen). Also, by the dismantling process lot of toxic dust particles become airborne. Consequently, the process needs to be maintained in a closed storage hall.

The upon described properties make SPL a very dangerous and hard to process waste. Usually, an electrolysis plant has a dismantling team which is an everyday challenge to handle, process and deliver this waste to a waste disposal company. Such companies deliver waste to cement plants and incinerators which need fine material of rather small particles (approx. 200 micro m). The bulky waste is still toxic, flammable, and explosive. Grinding is very difficult due to graphite and sodium content, which cause the material to be sticky and slippery at the same time (Li, 2007). Besides, if grinding is proposed it must be processed by the support of water spray action to prevent over dusting. In short, the waste disposal companies also have a huge challenge and therefore the prices for SPL destruction rises.

3.1.2 Waste properties

The SPL waste is impregnated with soluble salts like NaF and insoluble cryolite and further with approx. 2 % of different types of cyanides. The silicate brick part can be used in construction, brick, cement works and glass wool production. The carbonaceous part of SPL is of special interest as it has energetic and material potential. The carbon can be utilized as an energy source to produce heat in various melting, combustion and incinerator applications. The carbon is partly graphitized and can, therefore, be a rich source of graphite products.

The silicate or brick part of the waste contains besides impurities like NaF merely possesses Quartz (SiO_2) and Mullite ($Al_4Si_6O_{10}$). Carbon content in the first cut reaches on average approx. 60 % of the whole sample, the NaF part covers about 20 to 30 % and the cryolite about 15 %.

3.2 Overview of existing technical solutions

Peer review of possible approaches and technologies for the processing of SPL provides comprehensive information disseminated in recent decades. This information spreads from individual research efforts to existing technological solutions.

Generally, two basic processes are in progress. Those are chemical and pyrometallurgical (or thermal) approaches with important weaknesses and advantages. The standard waste processing starts with waste mechanical preparation and later treatment process used, gives some intermediate products in form of energy and material. The products are for economic reasons subjected to further conversion to reach commercial products. Usually, there is always some waste present at the end of the process.

Mentioned processes have the same basic approach technique but differ in the flow of intermediate and final products. It is common to produce useful products out by the treatment process. Aluminium fluoride is a chemical product used in the production of electrolysis of the alumina and represents a high value and desirable product.

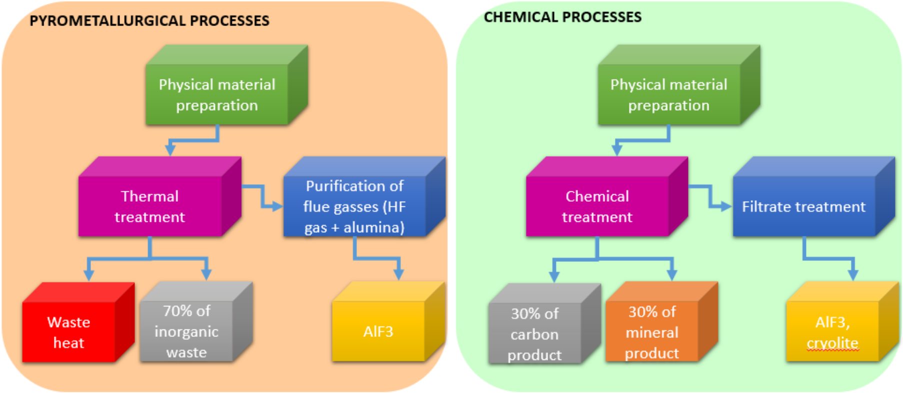


Figure 4: Two different processes with the same approach.

Chemical processes take place in several stages, and quite, different equipment is required. In thermal processes, one, the main phase, is predominant, and this is the thermal decomposition of the material. This phase, however, is very energy intensive and demands extensive maintenance. Although chemical processes seem to be more complex, they can offer a complete sustainable solution at normal environmental conditions (temperature, pressure). Finally resulted in commercial products with low CAPEX and OPEX with significant possibilities of material utilization.

3.2.1 The review of existing technical solutions

Thermal processes reduce the amount of SPL waste to the level of only mineral remains and brick parts. The carbon part burns, cyanides decompose at high temperatures, and fluorides are partially discharged in the form of gaseous HF. Afterwards, they are adsorbed using an alumina, where the product of aluminium trifluoride (AlF_3) is formed. This is the desired input compound in the chemical composition of electrolyte in the electrolysis cell. There are also cases of SPL use in cement plants and ironworks, but due to increasingly stringent legislation, these plants demand sorted and pre-processed input flow. The challenges are high levels of Sodium, Fluorine and toxic Cyanides and a high proportion of water-soluble part (like NaF) respectively (Holywell, 2013).

Best available technologies for non-ferrous metals describe many options to treat SPL: re-use of SPL in cement production, as a carbonaceous substance in the ironworks, as a secondary raw material (glass wool, salt slag) and as a substitute of fuel (BREF, 2014). Oye describes both thermal and chemical methods of SPL processing, emphasizing the challenges of salt separation, which account for as much as 30 % of the total SPL content. Another technology considers solutions to produce graphite and the inclusion in the mass fraction of the cathode as well as the anodes (Hop, 2004).

In cement plants, the carbon part is used as a substitute for fuel, while the brick part becomes a part of clinker (Pawlek, 2012). Consequently, there is a noticeable decrease in the process temperature in the clinker production mass, which in turn reduces the consumption of heat per kilogram of clinker produced (Renó, 2013).

Aluminum Pechiney and Ciment D'Origny from France use a brick part as a substitute for the raw material for cement production in South Africa (CSIR, 2002). Care must be taken when grinding, storing and transporting crushed material and dosing, as there is a risk of gas formation (Rahman, 2015). The problem in cement plants is also caused by the diverse chemical composition of the waste that affects the industrial process. It is therefore important to prepare an appropriate and rather a constant mixture composition of the material used as the input raw material (Black, 2015).

In the ironworks, carbon part is used as a fuel and a reducing agent. Fluorides increase the flow rate of the slag and lower the melting point, but at the same time, they are also harmful to the pot wall (Meirelles, 2014). The metallurgical fluorspar contains between 60 and 85 % CaF2. It is widely used in the manufacture of iron, steel, and other metals. It acts as a flux to remove impurities (S, P) from the melt while improving the slag flow rate. The carbon part of the SPL can successfully replace fluorspar or fluorite (CaF2). Successfully increases the flow rate of the slag and reduces the levels of sulphur and phosphorus. The tests were successfully carried out in Russia (Personnet, 2016).

For special steel alloys with silicon and magnesium manufactured using an arc furnace, only the carbon section (first cut) should be used. It has the most suitable chemical, physical and metallurgical composition and properties as an addition to iron Si-Mg alloys. The brick part has an excessively powdery structure [Krüger, 2011].

Some also suggest other thermal techniques. One of them deals with the heating of the spent bricks above 750 °C to remove volatile impurities (Oliveira, 2000). Some recommend grinding spent cathodes and incineration in the fluid bed (Courbariaux, 2001), while others propose the glazing of this kind of waste by adding ingredients needed for the formation of glass (Balasubramanian, 2000). The problem with the fluid bed is the agglomeration of SPL particles with sand. Several authors (Saxena, 1994, Oye, 1994)] report about this, and it was also observed in our own tests (Mele, 2015).

We have noticed that a high temperature is needed for the decomposition of the spent carbon part (above 950 °C) and that these temperatures begin to liquefy the soluble salts. This leads to the prevention of oxygen access to the carbon structure and consequently greatly complicates thermal decomposition. The spent cathode sample without soluble salts ignites at substantially lower temperatures; also, thermal decomposition of the sample is effective.

According to own tests, it is obvious that soluble salt fraction must be removed before any treatment is proceeding as its negative influence prevail.

Chemical methods allow the separation of components and their purification in order to produce products that could be used either in their own processes or in other local industries. Some methods are based on the neutralization of the filtrate with calcium compounds (e.g. calcite $CaCO_3$) (Turner, 2008). Others focus on reuse and mostly predominate in the full exploitation of the raw material base. They tend to extract cryolite and carbon (Shi, 2012; Cao, 2014) and useful fluoride compounds (Lisbona, 2008, Ntuk, 2015) by dissolving in bases, acids or in solutions of aluminium salts. Some separation techniques use a two-step technique. Other techniques use three-stage separation, namely: water purification, basic and, finally, acidic cleaning (Indurkar, 2014; Shi, 2012, Schönfelder, 2014). Also, flotation is used to physically separate the carbon and brick part (Li, 2010; Holywell 2013; Schönfelder, 2014).

3.3 The results of experimental work

The decision to proof, the technological process on a laboratory scale before further development with different technology providers have been made. Managerial proposal to process the waste in the cement production process was not feasible as cement works experienced a series of operational problems. In addition, this kind of waste has a lower calorific value and is not competitive with some others like preferable wastes tires. The state-of-the-art findings from scientific articles about other treatment technologies were included in the knowledge. Cooperation with people from different departments inside the organization began and, in this way, the exchange of tacit and explicit knowledge followed. Company's experts from the different field of expertise and outsourcing experts were involved.

Firstly, the thermal option was verified, as the goal was to reduce the volume of the waste. Afterwards, chemical testing was performed.

3.3.1 Thermal tests on SPL

Thermal tests on different thermal devices offered by the equipment providers are usually very expensive. To proof some thermal technology solutions that exist on the market, laboratory tests need to follow. These technologies merely base on gasification processes at a temperature of around 900 °C where the products are syngas and inert residues.

Tests were done with a sample of SPL first cut. Preliminary tests were done with a ceramic crucible, which was exposed to a direct gas burner flame. The waste sample did not ignite until 950 °C. One reason is that the material is supposed to withstand high operating temperatures in electrolysis environment. The other is that the inorganic components like NaF melt and prevent oxygen access to the carbon matrix.

Induction heating with direct coil exposure gave no promising results, as there was no increase in temperature of the granulated waste sample. The opposite was the case of an induction coil wrapped around a bulky sample of first cut SPL sample. The temperature raised but only to 250 °C as low power induction apparatus was used for experimenting (1 kWe). By using stronger power equipment (7 kWe) and indirect heating trough stainless steel the temperature raised quickly to 900 °C and the effect was like the mentioned indirect heating with a gas burner. The problem is the stainless-steel crucible which material is at this elevated temperature rapidly degrade.

In addition, some individual providers of the high-temperature technology of waste treatment (more than 3,000 °C) were reviewed and contacted. The so-called plasma gasification technology has some advantages regarding waste volume decomposition but also shortcomings regarding electricity consumption, high capital costs and in some cases unreliable operation and performance. Some tests were also performed with plasma generating equipment on a first cut SPL sample. The first testing was performed exposing the granulated sample to an arched flame at an electrical power of 2 kW. The result was a molten inorganic form and later also crust that again prevented oxidation of carbon. The next test was performed with a powerful plasma cutter equipment (13.7 kWe). A bulky stone of first cut SPL waste was exposed to a plasma flame. The mass of the missing piece of the bulky stone was measured and residence time and used energy calculated. The calculated result of the test gives a throughput of treated first cut SPL in the size of 2 kg/h at operating cost that would double the existing cost of the SPL destruction.

Testing was also performed within a fluid bed pilot plant technology at operating temperatures up to 800 °C. The test result in the reactor gives the SPL waste and the operating sand material lumped together to form stone like products that completely clog the feed equipment. Even if the waste material was subjected to temperatures up to 1,200 °C, the results of the leaching of fluorides from the residual waste exceeded the legally permitted limit values (Mikša., 2003).

a) b) c) d)

e) e) f)

Figure 5: Thermal laboratory testing of SPL waste decomposition:

- Induction heating of waste sample with ceramic (a) and stainless steel crucible (b)
- Gas burner indirect heating of SPL (c)
- Thermal arc plasma of SPL (d) and plasma cutting with resulted bulk SPL piece (e)
- fluid bed reactor pilot plant test (f)

3.3.2 **Conclusion of laboratory thermal testing on** SPL

The laboratory thermal tests imply that this kind of treatment need high temperature and energy demand, uses large quantities of oxygen and requires complex equipment maintenance as the process operates in a corrosive environment. The results of thermal laboratory tests of SPL waste were unsatisfactory even after exposure to very high temperatures. The general problem of the results without adequate mixing is contact with oxygen. Carbon in the SPL does not get enough oxygen because molten inorganic waste fraction, which liquefies at temperatures around 900 °C overflow the SPL particle. To proceed with thermal testing, the inorganic fraction of waste needs to be removed. Namely, as thermal testing on water-washed SPL sample give sample ignition at a substantially lower temperature (750 °C) and burned later independently without disturbance caused by mentioned impurities.

3.3.3 Chemical leaching tests

As the results from thermal tests were negative, the decision to continue with chemical treatment on laboratory tests seems to be logical. To enable the thermal test results some major impurities must be removed first. A review of existing technology solutions was performed, some of them are still at the stage of laboratory development, while others are already close to commercial scale. This kind of technologies differs in process steps and types of products at output like cryolite, carbon and aluminium fluorides.

In the first step, water-soluble salts extraction gives best results also in combination of soluble cyanide degradation. Insoluble salts, like cryolite, can only be extracted by chemical reaction, a combination of reactive extraction offer an optimal solution of the problem. Flotation can be used to separate mixed SPL into silicate (chamotte) part and a carbon one. For all three procedures, water leaching, reactive extraction, and flotation, introductory tests were carried out to test the promise of basic results. The testing procedure was divided into three phases. Reactive extraction of insoluble salts or cryolite represented the 1st phase. Based on 1st phase tests, optimum parameters for the dissolution of the cryolite were obtained and represent an input for the second phase. In a 2nd phase followed in optimized reactive extraction conditions help to purify First Cut samples. Finally, in the 3rd phase flotation is combined to separate carbonaceous parts from Chamotte ones. The carbon part was subsequently subjected to the optimal conditions obtained from the 2nd phase of reactive extraction of the First Cut sample.

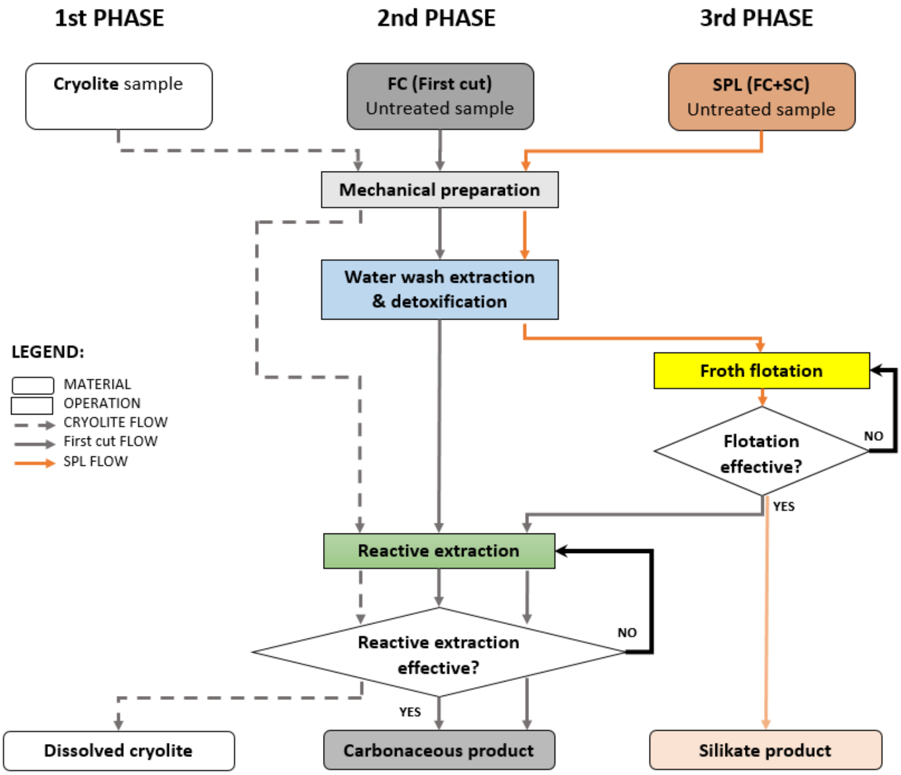


Figure 6: A model of laboratory scale testing of SPL waste recovery.

The first test was intended to separate impurities which are soluble in water. Sodium fluoride dissolves quickly in water and therefore leach quickly. A variety of test was performed to define optimal parameters for dissolution time, liquid-solid (L/S) ratio and the number of water extraction repetitions or equilibrium data at different L/S conditions. Such basic parameters are crucial for further process design.

Review of the flotation was performed with two types of commercially available mixtures of flotation reagents. Promising results give 95 % separation efficiency, enough for most application of the separated material.

Further experiments with the extraction of most water-insoluble inorganic impurities follow some information about basic, acid (Shi, 2012) and Al^{3+} [Lisbona, 2008] reactive leaching. To simplify preparation of samples all experiments were performed with the mechanical separated first material. Initial water leaching tests remove water-soluble components (NaF and Na_2O all around 10 %), dissolve most of the cyanides and rise carbon content to approx. 72 %. Reactive components like small amounts of carbides (less than 0.5 %) react to form methane gas. The inert and insoluble material still contain fluorine, sodium salts (cryolite, calcium fluoride; more than 10 %), sodium silicates and sodium components of alumina (diaoyudaoite and alumina). Further reactive leaching can be directed toward removal of all fluorine and sodium or same sodium alumina components and calcium fluoride can be left. Important results on rising carbon content are achieved by NaOH reactive leaching where no additional ionic species is introduced in the system. Carbon content rises to 83 % what can be, together with useful remaining (mainly CaF_2, and some parts of sodium silicate and alumina components), an acceptable composition for some metallurgical applications. Next level of carbon content close to 90 % is reached only with acid or Al^{3+} leaching but enormous complications with new ionic species (chlorine or sulphate) appear at final recycling of extract. This is not the case in sodium hydroxide extraction where almost complete reuse of chemicals is possible.

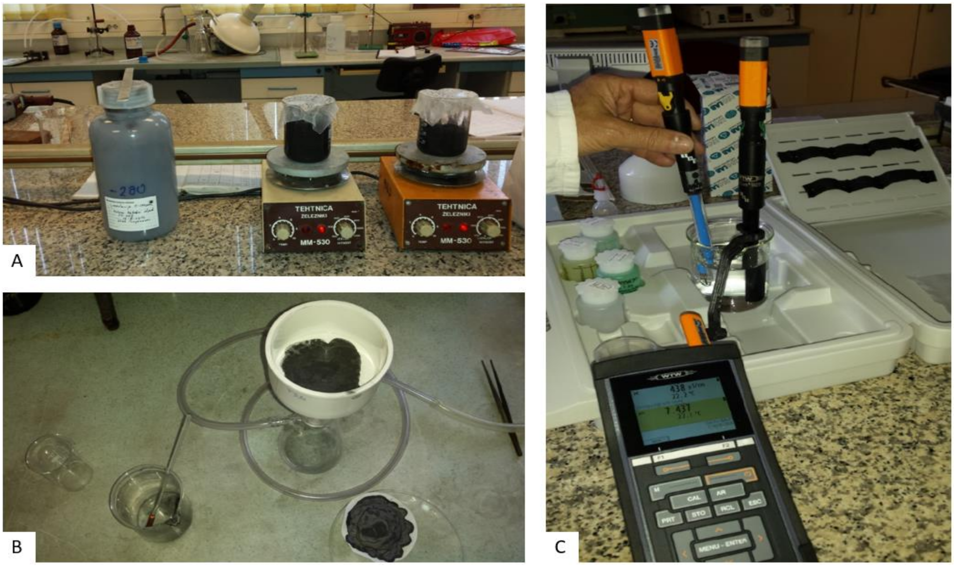


Figure 7: Chemical laboratory testing of SPL waste recovery (A mixing, B vacuum filtration, pH and conductivity measurements)

3.3.4 Conclusion of laboratory chemical tests on SPL

Results of chemical testing, in comparison to thermal techniques, open totally new perspectives in a direction of material recycling and reuse in the local economy. There are several advantages: operating at normal environmental conditions, low maintenance of equipment, low operating costs, promising products and no residues.

Undoubtedly, the direction toward preparation of SPL with reactive extraction seems to be a most permissible path toward reuse and material recycling of still now a toxic waste burden. Such a path of research and development toward acquiring sustainable solutions to remain waste problems in primary aluminium production can lead to sustainable waste-free and low carbon local economy.

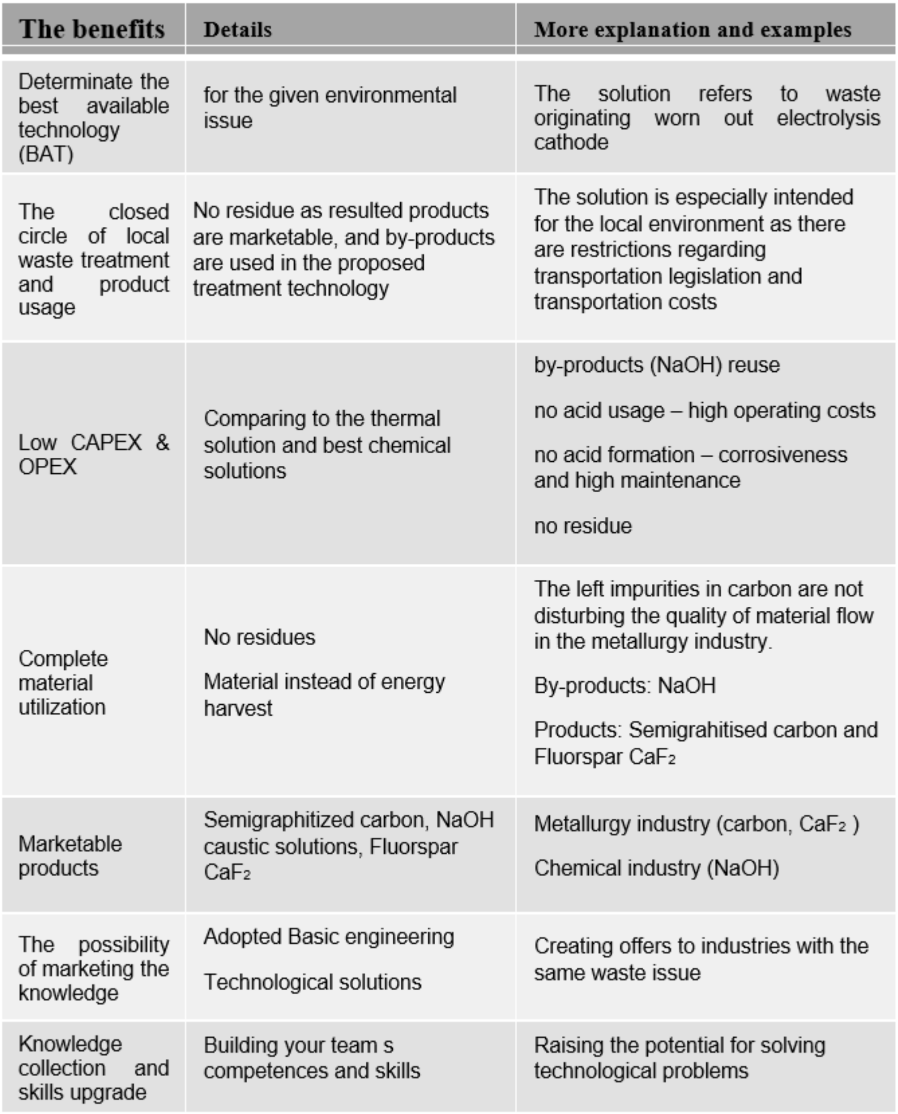
4 Conclusion

Comparison of results/products by the standard approach and by the innovative method are presented in the following tables.

Table 1: New developments achieved with the introduction of the innovative method

What's new?	**Details**	**More explanation and examples**
Comprehensive & interdisciplinary approach	Review of available technology	Mechanical, Physical, Thermal, Chemical BAT treatment techniques; Peer- review
Local tacit knowledge	Experiences with technology, and providers Examples of good practices	Thermal treatment Local Cement works, waste companies
Laboratory verification	of technology advantages of products of by-products	Thermal tests: point of ignition, energy balance, residues after incineration Chemical tests: equilibrium states by the method of multi-stage extraction, dissolving the contained weakly soluble structures (cryolite, CaF2, aluminates) and gaining useful products (AlF2OH, separated cryolite, etc.)
A solution for the local environment	Waste is processed at the location it generates Products are consumed at the treatment plant or/and at local industries	SPL is processed at or near electrolysis plant NaOH is consumed in the waste process, CaF_2 in metallurgy

Table 2: The benefits of the innovative method



The benefits	Details	More explanation and examples
Determinate the best available technology (BAT)	for the given environmental issue	The solution refers to waste originating worn out electrolysis cathode
The closed circle of local waste treatment and product usage	No residue as resulted products are marketable, and by-products are used in the proposed treatment technology	The solution is especially intended for the local environment as there are restrictions regarding transportation legislation and transportation costs
Low CAPEX & OPEX	Comparing to the thermal solution and best chemical solutions	by-products (NaOH) reuse no acid usage – high operating costs no acid formation – corrosiveness and high maintenance no residue
Complete material utilization	No residues Material instead of energy harvest	The left impurities in carbon are not disturbing the quality of material flow in the metallurgy industry. By-products: NaOH Products: Semigrahitised carbon and Fluorspar CaF_2
Marketable products	Semigraphitized carbon, NaOH caustic solutions, Fluorspar CaF_2	Metallurgy industry (carbon, CaF_2) Chemical industry (NaOH)
The possibility of marketing the knowledge	Adopted Basic engineering Technological solutions	Creating offers to industries with the same waste issue
Knowledge collection and skills upgrade	Building your team s competences and skills	Raising the potential for solving technological problems

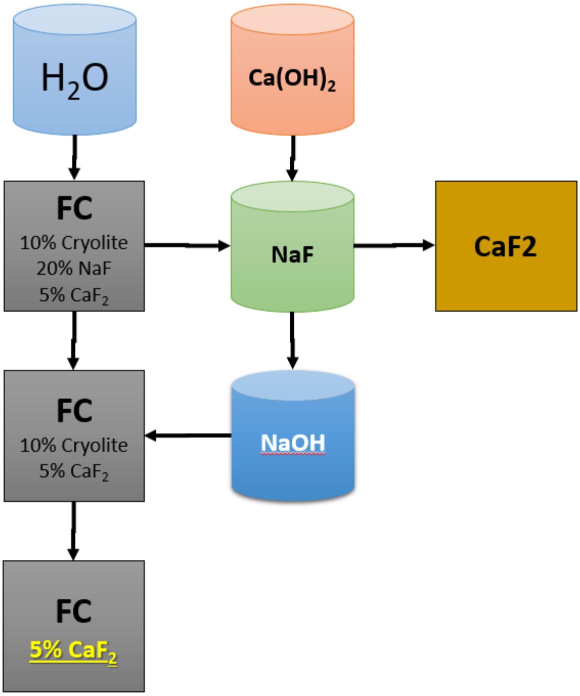


Figure 8: The proposed solution diagram for SPL treatment.

Acknowledgements

The authors gratefully acknowledge support from the University of Maribor, Faculty of mechanical engineering for managing to unite interdisciplinary professions and Talum d.d. (JSC) Kidricevo for providing the SPL samples as also for financial support for analytics and cooperation with a team from program P2-0346 financed by Slovenian Research Agency.

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Collection of Dry Recyclables as an Effective Step in Waste Management?

JIŘÍ GREGOR, JIŘÍ KROPÁČ & MARTIN PAVLAS

Abstract Current trends in European waste management (WM) focus on technologies and methods. Currently, European Commission adopted a new set of measures in Circular Economy Action Plan, the main motivation is according to an economic point of view a minimization of the collection costs. The costs of municipal waste collecting and transporting are a significant part of municipal budgets. Therefore the need for analysis and subsequent evaluation of claims and options of different systems for the collection of municipal waste usable components is motivating. The separate municipal waste is transported by garbage trucks to a sorting line for secondary raw materials production. The author's team develops a complex set of innovative tools in the context of WM. The tools are able to evaluate the current situation, to prepare forecasts and especially to propose optimal and effective solutions for selected territorial units. This paper describes the potential of separate collection dry recyclables (plastics, paper, glass, metals) into one container. The comparison with standard collection system is mentioned (separate containers for individual fractions). The main objective of this article is to compare the costs of material recoverable municipal waste collection, treatment and transport to final processing in conditions of Czech waste management.

Keywords: • Sorting line • Waste management • Dry recyclables • Techno-economic assessment • Collection model • Transport •

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DOI https://doi.org/10.18690/978-961-286-211-4.9 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction and motivation

Current trends in European waste management (WM) focus on technologies and methods that comply with preferred procedures of waste treatment hierarchy. The Member States are encouraged to increase the preparing for re-use and the recycling of waste materials (such as paper, metal, plastic and glass) from households at least (and possibly from other sources as far as these waste streams are similar to waste from households) to a minimum of overall 50 % by weight by 2020 (directive 2008/98/EC). Further, in January 2018 the European Commission adopted a new set of „Circular economy package“ measures, including the Europe-wide EU Strategy for Plastics, options to address the interface between chemical, product and waste legislation and a Report on Critical Raw Materials and the circular economy (Brouwer et al., 2018).

Based on prepared legislation and European targets, the main goal is to increase recycling rate. This key milestone is planned until 2035 when the following recycling targets are forced:

- 70 % recycling of all packing material;
- Plastics 55 %;
- Wood 30 %;
- Metal 80 %;
- Aluminum 60 %;
- Glass 75 %;
- Paper and cardboard 85 %;

According to these goals, it is necessary to obtain the secondary raw material from the producers (inhabitants) in a certain quality and quantity. The very important aspect is China and its market - Chinese market has limited the import of plastics from Europe and is only interested in a high-quality secondary raw material, especially the PET fraction (white or mix). In Europe, a large number of secondary raw materials, especially plastics, are currently being accumulated. There are not relevant capacities in Europe which can handle plastic fractions or other secondary raw materials from the separate collection. At first, it is necessary to build new facilities for recycling paper, plastics, metal, glass, others and find correct utilization for each of interested streams.

The author's team is interested in the development of relevant tools for waste management assessment. The key element is the *NERUDA* tool (Šomplák, 2014), which is based on complex logistic optimization supporting decision-making in waste management. *NERUDA* tool works with various types of facility models e.g. (waste-to-energy plant, transfer station, MBT plant, sorting line and others key elements) – Figure 1. The main principle of *NERUDA* tool is the transportation task, therefore, it is necessary to improve the accuracy of input parameters calculated by transportation models. Gregor et al. (2017) described techno-economic models of transportation systems. Each transportation model has been analyzed according to its specific parameters (transport distance, amount of waste transported) and the main output is transportation cost. Models can calculate the linear or variable cost of transportation. Both types of costs have advantages and disadvantages. The main differences between the approaches are computation times in *NERUDA* tool, where it is more time-consuming for variable cost of transportation. Another key step is the preparation of techno-economic models for various types of facilities, e.g. transfer station for transportation of pressed waste or non-pressed waste (Gregor et al., 2017), sorting line (Gregor et al., 2018), MBT technology (Fei et al., 2018), Waste-to-energy plant (Ferdan et al., 2015).

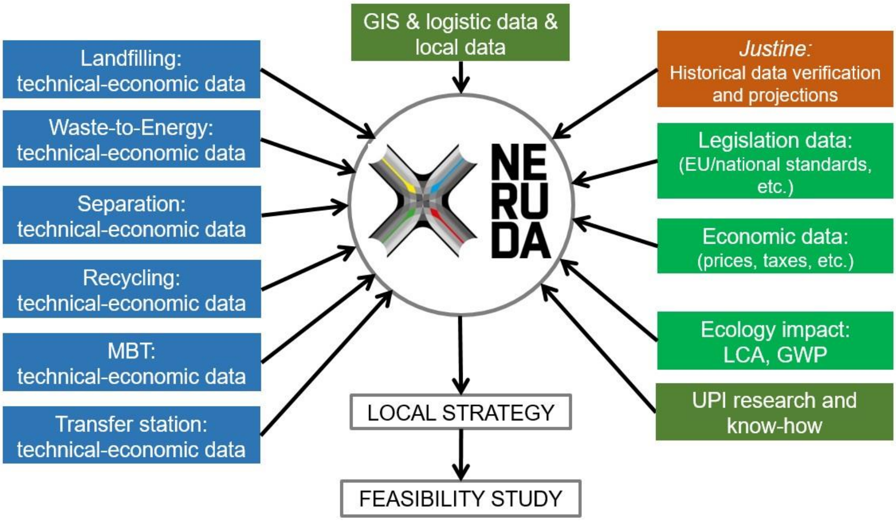

Figure 1: NERUDA tool – modular structure

Forecasting of future amounts of waste is based on *JUSTINE* tool, see (Šomplák et al., 2017). For the purpose of complex modelling in the field of waste management it is necessary to be able to take into account current legislation, economic data and environmental impact. Subsequently, with *NERUDA* tool and other sub-models (mathematical and techno-economic models), it is possible to prepare feasibility study which can be applied within any territory. The case study in a specific region using the main outputs from *NERUDA* tools were presented by Kropáč et al. (2016). Details about the potential of environmental impact are described in (Nevrlý et al., 2018).

2 Waste management in the Czech Republic

In 2016, the Czech Republic produced ca. 34.2 million tons of all waste. A total of 85 % of all wastes were recovered – 82% material recovery and 3 % energy recovery, while 9 % of all waste was transported to the landfill. In the same year – 16 % of the production was the municipal waste, which corresponds to 5.6 million tones in total and 531 kg of municipal waste per year and inhabitant. From the municipal waste point of view, 38 % were material recovery, 12 % energy recovery and 50 % was landfilled.

The support of the CEP concept and increased recycling rates will be facilitated by the introduction of compulsory sorting of metals and bio-waste, and the current ban on landfilling of mixed municipal waste, recyclable and recoverable waste from 2024, which has been in Czech legislation since 2014.

2.1 Waste transportation chains in the Czech Republic

Waste collection and transportation of waste is in the Czech Republic divided according to three systems:

- Garbage trucks + direct transport to the nearest landfill site, transfer station or sorting line;
- Garbage truck + transfer station with press equipment + vehicle with containers + pressed waste;
- Garbage truck + transfer station + handling equipment + vehicle with Walking Floor semitrailer + non-pressed waste;

3 DRY recyclables and comparison with standard systems

The system of DRY recyclables is operating in some regions in England or Germany. Dry recyclables have big potential for a waste management system when they use a returnable package (plastics bottle, glass bottles, tins and others). Inhabitants have a motivation to return package (potential of saving money) and package which are damaged can be thrown away to the bin with DRY recyclables. The main advantage of this system is that biological waste is not collected together with DRY recyclables, because it can decrease the quality of materials, especially paper. Subsequently, it is not difficult to sort the flow of DRY recyclables.

Dry recyclables consists of paper, plastic, metal and glass. Paper and plastic can be divided into more fractions, see (Gregor et al., 2018) for more details about fractions and sorting. For calculation of transport (non-pressed) and sorting, the bulk density 80 kg/m^3 of dry recyclables was considered. Density was determined according to the production of a waste and operating experience from the collection and sorting lines.

4 Case study related to the dataset from the Czech Republic

Authors of this paper have analyzed waste production in 206 Czech municipalities. Datasets describing 206 regional waste productions were prepared on the basis of the data from 2015. Representative waste production of all examined commodities (plastic, paper, glass and metal) were estimated for each municipality. For further analysis, an exemplary municipality was chosen. The calculations were performed with regards to the data of all municipalities (average and median). The expected composition of dry recyclables is stated in Table 1.

Table 1: Waste production of 206 Czech municipalities (year 2015)

Commodities	Median	Average	Production of Czech Republic	
-	t/y	t/y	t/y	-
Metal	916	1 386	285 461	25%
Paper	1 678	1 981	408 102	36%
Plastic	1 402	1 316	271 012	24%
Glass	814	821	169 028	15%
Dry Recyclables	**4 811**	**5 503**	**1 133 603**	**100%**

With respect to values in Table 1, the characteristic transport route was generated with the following parameters:

- The distance of 30 km for one collection route;
- Working hours – 8 hours per day;
- Working days per week – 5 days;
- Collection of separate commodities by garbage trucks with two axles;
- Collection of dry recyclables by garbage trucks with three axles;

The costs for the collection of separated commodities (plastic, paper, glass and metal) and potential of dry recyclables were calculated, see Figure 2. Evaluation of the collection costs was established according to Table 1.

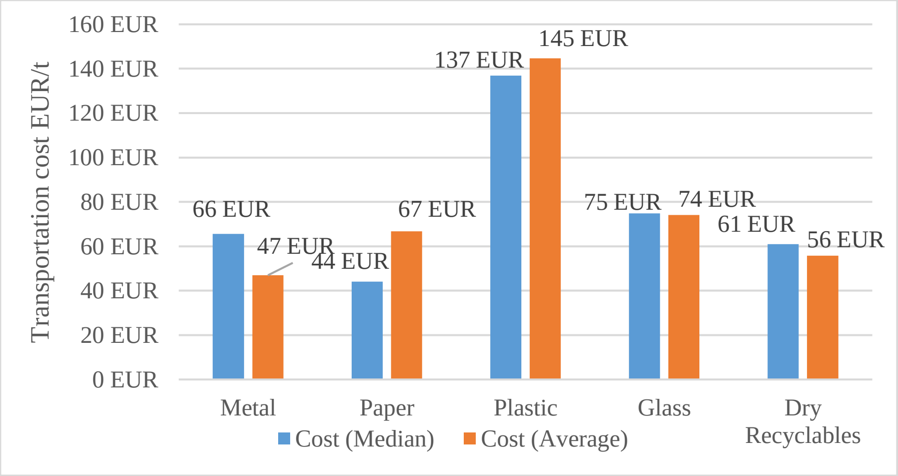

Figure 2: Transportation cost of selected commodities

Figure 3 presents the comparison of annual transportation cost for both collection systems. There are lower annual costs in the context of the considered average and median capacities. The use of dry recyclables evinces savings of up to 30% in the collection costs.

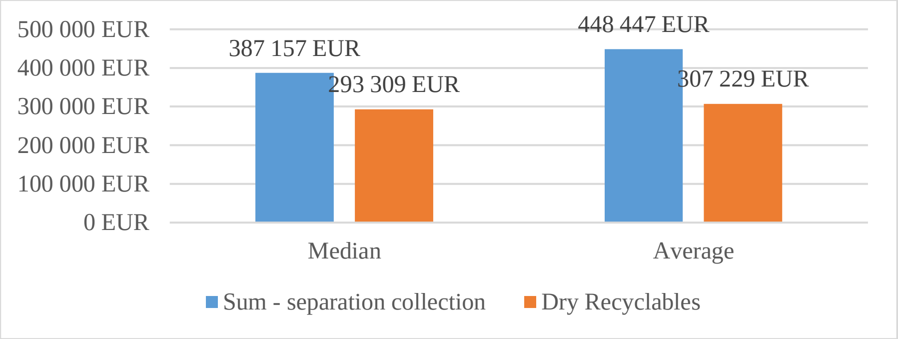

Figure 3: Annual transportation cost of selected commodities

The next analyses assess the operating costs of sorting lines. Due to low capacities, the manual line has been selected and operating costs set. The calculation takes into account operating and wage costs, while construction and technology are not included. The calculation was made with the following assumptions:

- Separated commodities: sorting of the paper and the plastic, in the case of glass and metal it is a temporary warehouse;
- Dry recyclables: sorting of selected fractions;

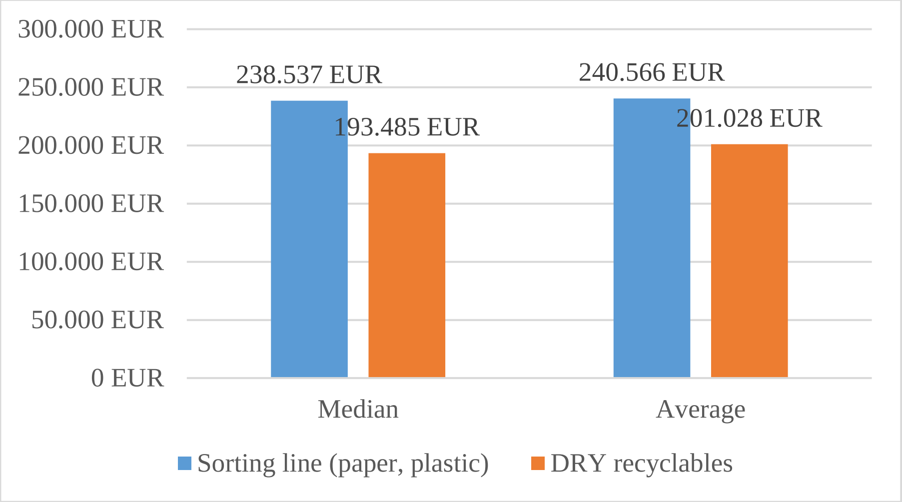

Figure 4: Annual operating cost for sorting line

After processing of separated commodities from MSW, respectively dry recyclables, the pressing into bundles follows. Then the bundles are transported for final treatment which may be:

- Separated waste;
  - Metal – metallurgy;
  - Glass – glassworks;
  - Paper: Secondary raw material – paper mill, residual flow – waste-to-energy plant, landfill;
  - Plastic: secondary raw materials – recycling plant, selling material with profitable cost, residual flow – waste-to-energy plant, landfill, others;
- DRY recyclables;
  - Secondary raw materials – see above;
  - Residual flow – waste-to-energy plant, landfill, others;

The transport from sorting lines to recycling plants or energy recovery is carried out by vehicle with containers. The corresponding cost per ton varies between 10 and 35 EUR depending on the distance and the quantity transported.

In the overall assessment in terms of operating costs, it can be stated that the dry recyclables system is economically more lucrative, see Figure 5. The respective savings are 29 and 38 % related to current system and the savings can be considered as economically significant.

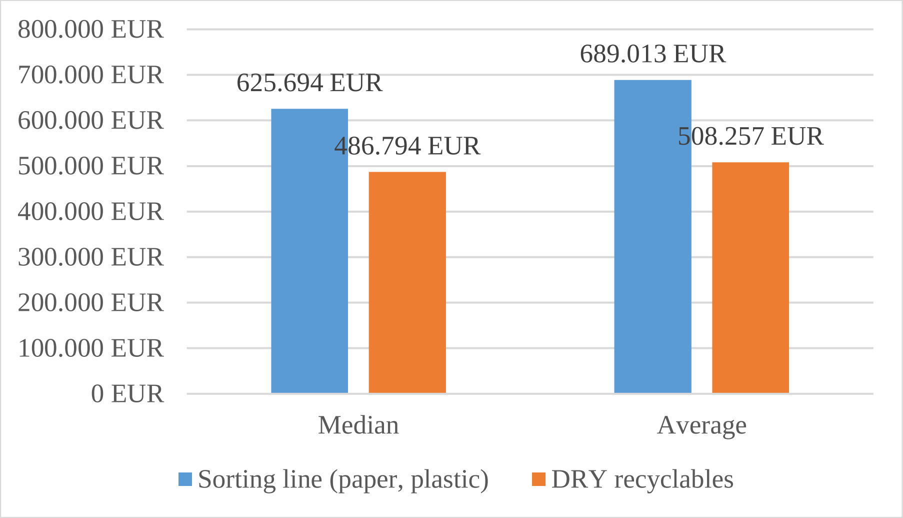

Figure 5: Annual operating cost related to two waste streams (transportation and sorting)

The main disadvantages of DRY recyclables:

- Use of more expensive sorting technology (automated sorting elements);
- Dry recyclables are not economically supported by authorized packaging companies in the Czech Republic;
- Higher residual stream from sorting;
- The lower purchase price of secondary raw material in terms of purity;
- New implementation of infrastructure needed;
- Social acceptability of a completely new system;

The main advantages of DRY recyclables:

- More economical option than the standard collection system from the operational costs point of view;
- Less amount of containers to be serviced;
- The compliance of the European recycling targets;

- Possible interconnection with the system of returnable packages – profit from the secondary raw material of high-quality;
- Financial incentives for inhabitants (returnable packages);

5 Conclusion

The proposed analysis revealed the DRY recyclables system as a great potential for possible further research because it is an economically interesting solution which minimizes the cost of transport and improves the overall waste management system. From one point of view, it is necessary to expect a higher rate of discard which may arise from contamination of the paper fraction. Economic analysis proved that DRY recyclables system is a meaningful system that can be economically viable when properly configured.

The applicability of DRY recyclables depends on local conditions, which must always be properly evaluated. The particular project needs a techno-economic assessment, however, for deeper analysis, it is better to use the complex computational or optimization tools. It is also necessary to correctly identify whether it is economically advantageous to use manual or fully automated lines, which range from EUR 6,000 (technology only). The advantage of automated lines is the component identification with a minimal error rate of selected fractions (Gundupalli et al., 2017). Combining the right system and the returnable packaging represents an interesting solution for high recycling targets proposed by EU legislation.

Acknowledgements

The authors gratefully acknowledge the financial support provided by Technology Agency of the Czech Republic within the research project No. TE02000236 "Waste-to-Energy (WtE) Competence Centre".

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1ST INTERNATIONAL CONFERENCE ON TECHNOLOGIES & BUSINESS
MODELS FOR CIRCULAR ECONOMY: CONFERENCE PROCEEDINGS
M. Bogataj, Z. Kravanja & Z. Novak Pintarič (eds.)

University of Maribor Press

High-Pressure Processing: A Smart Way to Increase Energy Efficiency with Less Toxic Residues

GREGOR KRAVANJA, MAŠA KNEZ HRNČIČ, DARIJA CÖR &
ŽELJKO KNEZ

Abstract High-pressure processes involving sub and supercritical fluids enable the design of products with special physical characteristics, less toxic residues, low energy consumption, and are eco-friendly and sustainable. Supercritical fluids show potential as solvents in boosting green chemistry by replacing environmentally harmful conventional organic solvents. Tunable physical properties of the supercritical fluids enable selective extraction, purification and fractionation of value-added products and by-products. Absorption of compressed gas in polymer matrices results in a wide spectrum of possible applications in the field of sustainable polymer processing, for example, production of fibers, microparticles and foams. As a heat transfer fluid, supercritical CO2 has been reintroduced as an environmentally friendly refrigerant in heat pumps working cycles. There is also great potential in the treatment of sewage wastes with supercritical fluids and production of value compounds from waste streams. Several supercritical fluid applications are presented from the perspective of their environmental and economic benefits.

Keywords: • Supercritical fluids • Energy efficiency • High-pressure • Extraction • Biofuels •

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DOI https://doi.org/10.18690/978-961-286-211-4.10 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

Supercritical fluids (SCFs) were discovered in 1822 by Baron Charles Cagniard de la Tour, who proved the existence of a critical point by conducting an acoustics experiments in a sealed cannon. He noticed that a splashing sound generated by a solid ball in a liquid phase inside the cannon ceased above a certain temperature and pressure. That indicates no liquid-gas phase boundary and surface tension in a supercritical fluid phase [1]. Compared to these pioneering experiments, today's industrial process involving supercritical fluids operate at pressures of several magnitudes higher, ranging from 10 MPa in extraction and formation processes up to 20 000 MPa in the production of artificial diamonds [2]. In nature, SCFs can occur below the Earth's ocean floor, on the planet Venus, and probably on exoplanets such as Super-Earths. They can also considered to be life-sustaining solvents, since some bacteria species have been shown to be tolerant of SFCs [3].

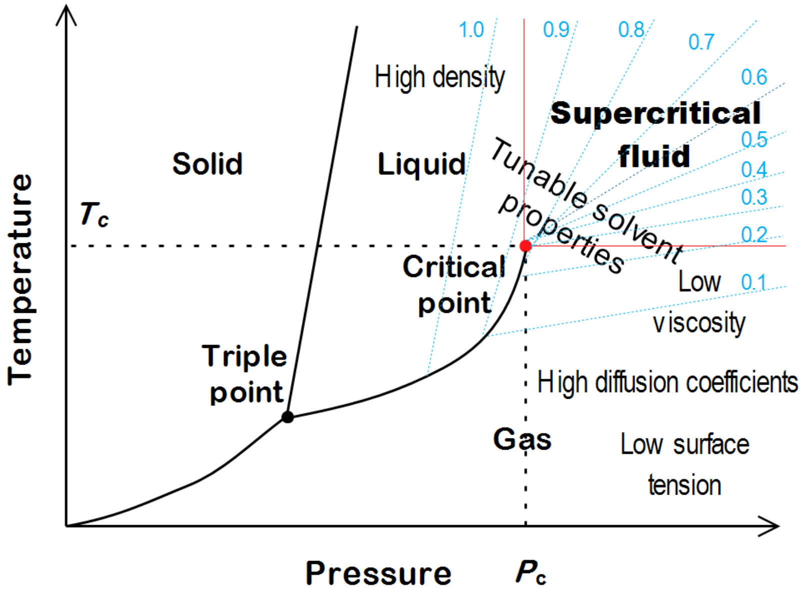

Figure 1: *P-T* diagram for supercritical fluid with the lines of constant density.

SCFs are defined as any substances whose temperature and pressure are above their critical values. The phase behaviour of pure compounds is presented in a P-T diagram (Figure 1). SCFs can be easily removed from a product by depressurization since they are gaseous under atmospheric pressure. That means there are no solvent residues in the final product and consequently lower processing costs. The choice of which supercritical fluid is used for chemical and industrial processes must be determined by a compromise of practical factors. Carbon dioxide (CO_2) is the most commonly used supercritical fluid because of its moderate critical constants (T_c = 31.0°C, P_c = 7.38 MPa), non-flammability, and non-toxic, non-corrosive nature [4]. It's available on the market for low prices and is considered to be the second cheapest solvent after water. Hot compressed water has attracted attention as an excellent green reaction and processing media for the conversion of biomass into biobased chemicals and biofuels. However, water has a relatively high critical point (T_c=374.14°C, P_c=22.12 MPa) and energy requirements are high. A possible solution to reduce the operating temperature and consequently energy requirements of processing biomass with water is to process at higher pressures or by adding supercritical CO_2 to the reaction mixture [5].

2 Applications of Supercritical fluids

High-pressure technology involving SCFs is German in origin, with the first large-scale application in the food industry (decaffeination of coffee or tea and hop extraction) mainly oriented toward the production of natural products. Today, many new SCF applications have been developed worldwide with an extensive potential for increase in capacity as new high-quality products are required.

SCF technology can be used as a new reaction media for chemical reactions, in large-scale operations in petrochemical plants [6], for biochemical reactions in the pharmaceutical industry for production of intermediate and final products [7], for powder coatings [8], for polymer processing including particle formation and encapsulation [9], for jet cutting [10], dry cleaning [11], for sterilization processes, virus inactivation in plasma fractions [12] and bone implants [13], for separation process in supercritical chromatography [14], as an alternative refrigerants in power cycles [15] and for extraction of value added products and by-products [16]. There is also great potential in the treatment of sewage wastes with SCFs and generated value products from waste streams [17]. Several SCF applications will be briefly presented from the perspective of their environmental and economic benefits.

2.1 Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction (SFE) has been successfully introduced in many fields, from decaffeination of coffee beans and black tea leaves, isolation of some flavouring from hops, fatty acid refining, to the production of herbal production [18]. Tuneable physical properties of the most frequently used SCF, CO_2, enables selective extraction purification and fractionation [18]. Lipids and carotenoids can be easily isolated from the natural source (algae, microalgae, dairy production) [19]. Since CO_2 is a non-polar solvent, a small amount of ethanol can be added to extend the range of its solvating strength to extract polar components like phenolic and metal-ligand complexes [20]. Recently, new processes have been developed to recover components from wastes ranging from manure to packing residuals. In the food industry, SFE can be used to extract value products from by-products that are generated during food manufacturing. Another interesting field is the removal of heavy metals from solid matrices and liquids, where using SFEs presents an excellent option [21].

SFE can be carried out in different modes of operation; the most frequently used is extraction from solids, which is carried out in batch and single stage mode since solids are difficult to handle continuously in pressured vessels. The size of vessels used in industry today varies from $1 m^3$ up to $40\ m^3$ volume. The maximum throughput of a single industrial plant for extraction from solids is above 10 000 t/a. [22]. Like many other processes, SFE has to be properly adjusted before every single run. Extraction yield depends on temperature, pressure, amount and type of modifier, amount and particle size of a sample and use of a dispersing agent. One option is experimental design and proper statistical analyses with a small number of trials [23].

Most companies believe that supercritical extraction is too expensive and because of high investment costs in comparison with classical methods, should be restricted only to high-quality products. Hoverer, that is far from true when a very large amount of material is treated, as in the case of coffee and hops processing and waste treatment [24]. Reported costs for production of solid feed with a capacity around 1000 t/a are around 3 EUR/kg. The economy of scale may bring the cost down to less than 0.5 EUR/kg for batch operation. In the case of continuous operation, the cost can be reduced even more [22]. Figure 2 presents an economy of a scale for SCE of solids using CO_2 as a solvent. The lower line represents continuous operation where an increase in productivity is proportional to throughput feed.

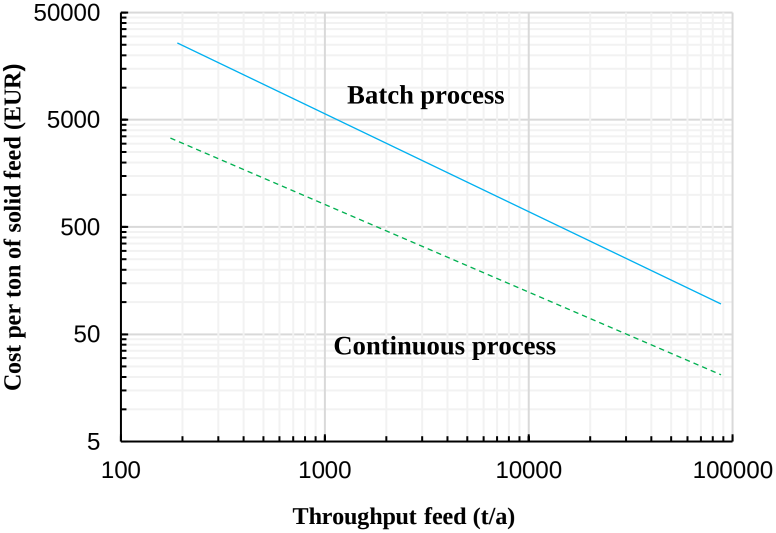

Figure 4: Economy of scale for SCE of solid using CO_2.

2.2 Polymer processing

Supercritical fluids (SCFs) are well established for use as a green processing solvent in polymer applications such as polymer modification, the formation of polymer composites, polymer blending, microcellular foaming, polymerization and particle production [25].

In the field of polymeric foams, supercritical CO_2 is used as blowing agent. To obtain polymer or composite foams, the substrate is saturated with SC CO_2, followed by rapid depressurization at a constant temperature (pressure quench) [26]. This method takes advantage of the large depression of the glass transition temperature (T_g) observed for many polymers in the presence of dense CO_2 [27]. In the polymer industry, polyurethane (PU) foams comprise the largest segment of the foams market in many products, followed by polystyrene (PS) foams. The replacement of ozone-depleting foaming agents like R12 and R22 by CO_2 has the potential to create a great impact in the foam industry [28]. Nucleation growth can be optimized by changing the saturation pressure, temperature and the rate of release gas. At higher temperature, less gas is dissolved in the polymer matrix;

therefore, low growth of pores is expected. When pressure is increased, CO_2 solubility in polymer matrices increases, creating more small size nuclei available for the formation and growth of pores. Rate of gas release also significantly influences the size of porous structures. At higher rates, more nuclei are generated with a smaller size compared to lower rates [29].

Special attention is dedicated to using biodegradable polymers in particle size reduction processes that are related to pharmaceutical applications for controlled drug release [30]. Particles have been obtained with rapid expansion of supercritical solutions (RESS) [31], the gas antisolvent process (GAS) [32], supercritical antisolvents (SAS) [33], solution enhanced supercritical dispersion processes (SEDS) [34], aerosol solvent extraction systems (ASES) [35], supercritical fluid extraction of emulsions (SFEE) [36] and particles from gas-saturated solutions (PGSS™) [37]. Weidner [38] has considered an economic evaluation of a PGSS™ plant with a capacity of 1.5 t/h. The process with low energy consumption features low operating costs, as low as 0.20 €, including investment, consumables maintenance, interest and personal. Additionally, the feasibility of a plant of that size can be increased by installing a CO_2 recovery capability.

Table 1: High-pressure technologies for producing powder particles [39].

	RESS	GAS/PCA/SAS/ASES/SEDS/SA	PGSS™
SCF used as	Solvent	Antisolvent	Dissolved
Gas quantity	High	Medium	Low
Organic solvent	Absent	Present	Absent
Pressure	High	Medium	Medium
Separation of gas	Easy	Easy	Easy

2.3 Supercritical fluids in the energy domain

SCF was first introduced in the energy domain in steam cycles in order to increase the thermal efficiency of fossil-fired power plants. Steam at supercritical conditions was used for recovering heat from flue gases and transforming the energy into kinetic and electrical energy [40]. Recently, SCFs have been studied as heat transfer fluids (HTF) in refrigeration systems, advanced power cycles, solar collectors, as a processing media in fuel cell applications, in carbon capture and storage (CCS) processes and as reactants in biofuel production.

The Supercritical Rankine Cycle (SRC) has been widely studied in terms of efficiency and conversion of energy at lower temperatures. Compared to the organic Rankine cycle, there is a better thermal match between the working fluid and the heat source at the pinch point. In SRC, fluid is heated directly from the liquid phase into the supercritical region, bypassing the two-phase region, which results in less energy loss [41]. As an HTF, supercritical CO_2 can also be integrated with solar energy in power cycles. Over the past several years, there has been a significant amount of research done on supercritical Brayton cycles. Thermal efficiency above 50% can easily be achieved. The main advantages lie in significantly reduced compressor work. Supercritical CO_2 Brayton is present in many applications, ranging from nuclear, geothermal to solar-thermal [42]. There are many opportunities in the development of turbomachines for supercritical power cycles, in research for heat transfer near the critical condensation and evaporation points, and also in recovery processes for hydrocarbons, and in enhanced oil recovery processes at great depths [40].

Global warming and air pollution resulting from the use of enormous quantities of fossil fuels can be significantly reduced with the usege of carbon sequestration processes. One way of making CCS more economically attractive, while at the same time contributing to energy security, is to use captured CO_2 to maximize production from declining oil fields with a process known as enhanced oil recovery (EOR) [43]. Globally, CO_2-EOR has the potential to produce 470 billion barrels of additional oil and to store 140 billion metric tons of CO_2, which are equivalent to the greenhouse gas emissions from 750 large one GW size coal power plants over 30 years

2.3.1 Hydrothermal reactions

Hydrothermal (HT) processes are technologies for the conversion of biomass into biobased chemicals and biofuels, using pressurized water (343 °C, 22.1 MPa) as processing media. Hydrothermal processes are divided into four main processes:

- hydrothermal carbonization (HTC),
- aqueous phase reforming (APR),
- hydrothermal liquefaction (HTL),
- hydrothermal gasification (HTG).

HT carbonization is carried out at mild temperatures, typically below 250 °C. Solid products have a high content of carbon and are suitable for different applications. Hydrothermal liquefaction is demonstrated as a process that is typically carried out at temperatures between 250 °C K and 375 °C and is ideal process for production of biofuel form algae biomass. At higher temperatures, above 380 °C, hydrothermal gasification is performed.

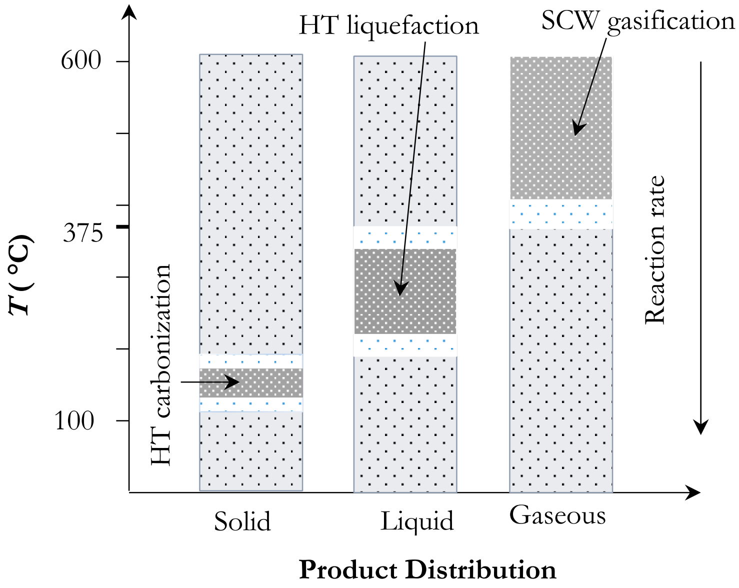

Figure 3: Hydrothermal treatment processes depending on temerature; (*T*c - critical temperature, *P*c - critical pressure).

A topic that has been enjoying increasing attention in recent years is the hydrothermal carbonization. The first step in this process is hydrolysis of cellulose chains to different oligomers and glucose, which can isomerize to fructose. Next products are organic acids, which decrease the pH value close to 3. The oligomers also hydrolyze into their monomers, which further pass through dehydration and fragmentation reactions leading to formation of different soluble products. Acid/aldehydes and phenols are obtained by decomposition of the furfural-like compounds. Polymerization or condensation reactions of the monomers and/or their decomposition products lead to the formation of soluble polymers.

3 Environmental impacts

In order to make a good comparison between the environmental impacts of different CO_2 utilization processes (CCU), global warming potential (GWP), with units defined as the mass of CO_2 produced divided with 1 ton of CO_2 removed, is presented. Utilization of CO_2 at high pressure through enhanced oil recovery (EOR) is the best option (average value around 500 kg CO_2 eq./t CO_2). Direct utilization of CO_2 for supercritical extraction of coffee beans is the second best option and has an GWP close to 1.20 kg CO_2 eq./t CO_2. [16]. Carbon utilization for production diethanolamine (DME) is the worst option, with a GWP near 600 t CO_2/t CO_2, which is 100 times higher than supercritical extraction process [44].

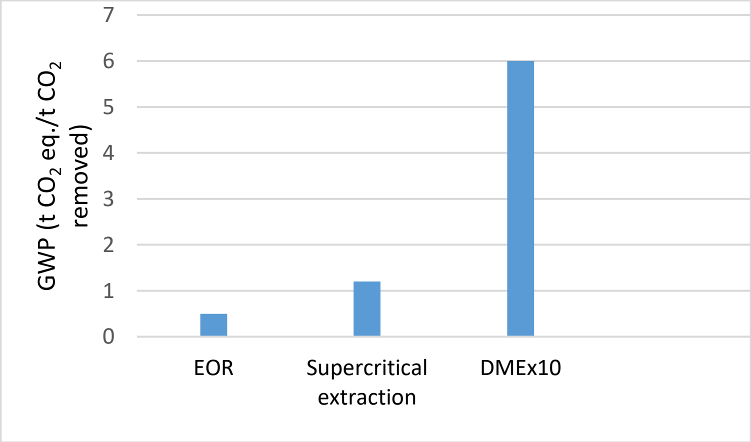

Figure 5: Average GWP (global warming potential) for enhanced oil recovery (EOR), supercritical extraction of coffee and direct production of diethanolamine (DME).

4 Conclusion

SCFs have a great potential in many areas and new applications are developing daily. Several high-pressure applications involving SCFs have already found a way to industrial scale production. They offer ways to develop new products with special physical characteristics, less toxic residues, low energy consumption, and which are eco-friendly and sustainable. SCFs can be easily removed from a product by depressurization since they are gaseous under atmospheric pressure. Additionally, the economy of scale may bring the cost down to be economical competitive with conventional processes.

Acknowledgments

The authors would like to acknowledge Slovenian Research Agency (ARRS) for financing research in frame of Programme P2-0046 (Separation processes and production design).

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MINLP Optimization of the Underground Lined Rock Cavern

STOJAN KRAVANJA & TOMAŽ ŽULA

Abstract The paper presents the cost optimization of a lined rock cavern (LRC), designed for an underground gas storage (UGS). The optimization was performed by the mixed-integer non-linear programming (MINLP) approach. GAMS/DICOPT was used. For this purpose, the MINLP optimization model was developed. The model comprised the cost objective function, which was subjected to geomechanical and design constraints. The rock mass strength stability and safety of the system were assured by these constraints. In the near past, the non-linear programming (NLP) optimization of a single gas cavern, of a whole underground gas storage and of a UGS in different rock environments was performed. Contrary to the mentioned NLP optimizations, where only the theoretical optimal results with continuous variables were obtained, in this paper the MINLP optimization of the LRC is proposed in order to handle the discrete alternatives explicitly. In this way, the solution obtained is a real optimal engineering solution with the calculated discrete values of different design parameters like cavern depth, diameter, height, wall thickness and inner gas pressure. A numerical example at the end of the paper shows the MINLP optimization of the investment costs of the lined rock cavern for the UGS in Senovo, Slovenia.

Keywords: • Lined rock cavern • Underground gas storage • Cost optimization • Mixed-integer non-linear programming • MINLP •

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DOI https://doi.org/10.18690/978-961-286-211-4.11 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

The paper deals with the cost optimization of a lined rock cavern (LRC), designed to be used for an underground gas storage (UGS). While the LRC is a high pressure gas reservoir, the UGS is normally planned with one to four LRCs. The LRC is typically designed in a cylindrical shape with a concrete wall and a steel lining. The concrete wall transports the gas pressure onto the neighbor rock, while the steel lining enables the impermeability, see also Stille and Sturk (1994), Sofregaz US Inc. (1999), Brandshaug et al. (2001), Chung et al. (2003) and Glamheden and Curtis (2006).

In the near past, the non-linear programming (NLP) optimization of a single gas cavern was performed by Kravanja and Žlender (2010), the optimization of a whole UGS was carried out by Žlender and Kravanja (2011), whilst the optimization of the UGS in different rock environments was calculated by Kravanja and Žlender (2012). In addition, analyses of UGS caverns with the adaptive network based fuzzy inference system (ANFIS) were done and reported by Žlender et al. (2012, 2013). In the mentioned NLP calculations, a simple economical objective function was defined to be subjected to geomechanical and design constraints. While the rock mass strength stability and safety of the system were assured by the geomechanical constraints, the relations between cavern dimensions, rock mass and gas pressure were defined by the design constraints. The geomechanical constraints assure that the strength of the rock mass is sufficient, the uplift of the rock above the cavern is prevented, the collapse of the rock between the caverns is prevented and that deformations of the concrete wall and steel lining is limited (large deformation or destruction of the steel lining is prevented). These constraints were derived from a series of the finite element method (FEM) analyses for the combinations between different alternatives of parameters: different gas pressures, cavern depths, cavern diameters, wall thicknesses and different load cases. While the FEM analyses were performed with the computer code Plaxis Version 3D, see Brinkgreve and Broere editors (2008), and Hoek et al. (2002); the NLP optimizations were carried out with the computer program GAMS/CONOPT2 (the general reduced gradient method), Drudd (1994).

Contrary to the above mentioned NLP optimizations, where only the theoretical optimal results with continuous variables (dimensions) were obtained, the mixed-integer non-linear programming (MINLP) optimization of the LRC is proposed in this paper in order to handle the discrete alternatives explicitly. In this way, the solution obtained is a real optimal engineering solution with the calculated discrete values of different design parameters like the depth, diameter, height and the wall thickness of the cavern, and the inner gas pressure.

2 MINLP model formulation

The problem of the lined rock cavern is the non-linear, continuous and discrete optimization problem. For this reason, the MINLP is applied. The general MINLP optimization problem can be formulated as follows:

$$\begin{aligned} &\min \ z = f(\mathbf{x},\mathbf{y}) \\ &\text{subjected to: } g_k(\mathbf{x},\mathbf{y}) \leq 0 \quad k \in K \\ &\mathbf{x} \in X = \{\mathbf{x} \in R^n\text{: } \mathbf{x}^{\mathrm{LO}} \leq \mathbf{x} \leq \mathbf{x}^{\mathrm{UP}}\} \\ &\mathbf{y} \in Y = \{0,1\}^m \end{aligned} \qquad \text{(MINLP)}$$

where **x** are the continuous variables and **y** are the discrete (0, 1) variables. Non-linear function $f(\mathbf{x}, \mathbf{y})$ is the objective function, which is subjected to non-linear (and linear) equality and inequality constraints $g_k(\mathbf{x},\mathbf{y})$.

3 Handling discrete alternatives

The MINLP optimization model of the LRC is developed according to the above MINLP formulation. The optimization problem defined is simple, because the optimization of the LRC is proposed to be performed only for the draft phase. In the model, the following design variables (**x**) are defined: inner diameter of the cavern *DCAV* [m], depth of the cavern *DEPTH* [m], height of the cavern tube *HCAV* [m], thickness of the concrete cavern wall *TWALL* [m] and gas pressure *PGAS* [MPa], see Fig. 1.

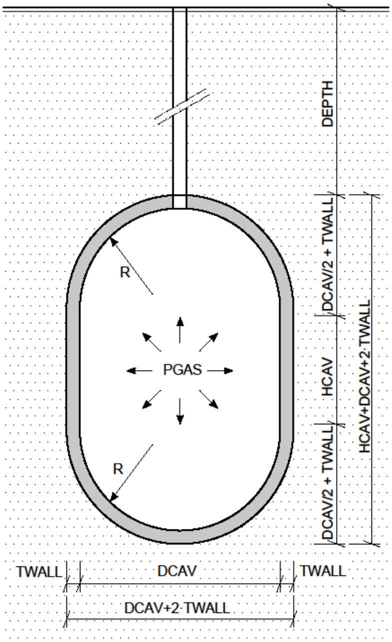

Figure 1: The vertical cross-section of the lined rock cavern

In order that the optimal solution will be a real one, all the above variables have to be rounded on whole discrete values. While the dimensions are proposed to be rounded on whole decimeters (dm), the gas pressure is rounded on one tenth of megapascal (0.1 MPa). For this purpose, a set of discrete value alternatives is defined to each variable, which is then rounded (calculated to be equal) to one of the discrete alternative during the optimization process. This calculation procedure leads to the simultaneous cost and rounded dimension type of the optimization.

The variables are bounded by their lower and upper bounds, see Eqs. (1), (4), (7), (10) and (13). Each variable is calculated as a scalar product between a vector of discrete value alternatives (q_{DCAVi}, q_{DEPTHj}, q_{HCAVk}, q_{TWALLl}, q_{PGASm}) and a vector of binary variables (y_{DCAVi}, y_{DEPTHj}, y_{HCAVk}, y_{TWALLl}, y_{PGASm}), see Eqs. (2), (5), (8), (11) and (14). One discrete value is then selected to each variable, because the sum of its binary variables is equal one, see Eqs. (3), (6), (9), (12) and (15).

Inner diameter of the cavern *DCAV* [m]:

$$\mathrm{DCAV}^{\mathrm{LO}} \leq DCAV \leq \mathrm{DCAV}^{\mathrm{UP}} \tag{1}$$

$$DCAV = \sum_{i \in I} q_{DCAV_i} \cdot y_{DCAV_i} \tag{2}$$

$$\sum_{i \in I} y_{DCAV_i} = 1 \tag{3}$$

Depth of the cavern *DEPTH* [m]:

$$\mathrm{DEPTH}^{\mathrm{LO}} \leq DEPTH \leq \mathrm{DEPTH}^{\mathrm{UP}} \tag{4}$$

$$DEPTH = \sum_{j \in J} q_{DEPTH_j} \cdot y_{DEPTH_j} \tag{5}$$

$$\sum_{j \in J} y_{DEPTH_j} = 1 \tag{6}$$

Height of the cavern tube *HCAV* [m]:

$$\mathrm{HCAV}^{\mathrm{LO}} \leq HCAV \leq \mathrm{HCAV}^{\mathrm{UP}} \tag{7}$$

$$HCAV = \sum_{k \in K} q_{HCAV_k} \cdot y_{HCAV_k} \tag{8}$$

$$\sum_{k \in K} y_{HCAV_k} = 1 \tag{9}$$

Thickness of the concrete cavern wall *TWALL* [m]:

$$\mathrm{TWALL}^{\mathrm{LO}} \leq TWALL \leq \mathrm{TWALL}^{\mathrm{UP}} \tag{10}$$

$$TWALL = \sum_{l \in L} q_{TWALL_l} \cdot y_{TWALL_l} \tag{11}$$

$$\sum_{l \in L} y_{TWALL_l} = 1 \tag{12}$$

Inner gas pressure *PGAS* [MPa]:

$$\mathrm{PGAS}^{\mathrm{LO}} \leq PGAS \leq \mathrm{PGAS}^{\mathrm{UP}} \tag{13}$$

$$PGAS = \sum_{m \in M} q_{PGAS_m} \cdot y_{PGAS_m} \tag{14}$$

$$\sum_{m \in M} y_{PGAS_m} = 1 \tag{15}$$

4 Numerical example

The example shows the MINLP optimization of the investment costs of the lined rock cavern, designed for the UGS in Senovo, Slovenia. The project of the UGS in Senovo comprises four equal LRCs in order to store 5.56 million m^3 of natural gas each, see Žlender and Kravanja (2011).

Table 1: Cost items and prices

Cost item	Price	
Upper ground works	2 982 500	EUR
Underground works	2 798 025	EUR
Price of the tunnel excavation	2 440	EUR/m^1
Price of the tunnel protection	1 340	EUR/m^1
Price of the cavern excavation	100	EUR/m^3
Price of the cavern protection	90	EUR/m^2
Price of the cavern drainage	60	EUR/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

The optimization model is developed. Cost items and prices, defined in the objective function, are the same as they were used in the project and our mentioned previous research works (NLP optimizations), see Table 1. The optimization model includes the same constraints as in Kravanja and Žlender (2010). In order to handle discrete alternatives for variables, the model is extended with Eqs. (2), (3), (5), (6), (8), (9), (11), (12), (14) and (15). The model is modelled in GAMS (General Algebraic Modelling System) by Brooke et al. (1988).

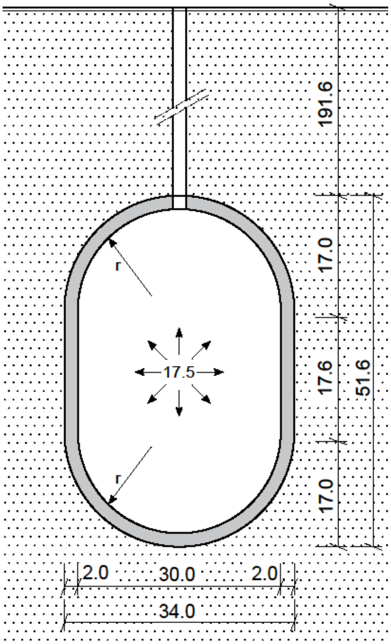

Figure 2: The optimized lined rock cavern

The LRC superstructure comprises 201 different rounded dimension alternatives for the inner diameter of the cavern, 2001 alternatives for the depth of the cavern, 301 alternatives for the height of the cavern tube, 31 alternatives for the thickness of the concrete cavern wall and 201 discrete alternatives for the inner gas pressure. 2735 binary variables are defined. In this way, the combination between the given dimension and gas pressure discrete alternatives gives $7.54 \cdot 10^{11}$ different LRC structure alternatives. One of them is the optimal one.

For the solution of comprehensive MINLP optimizations of structures, we usually use computer program MIPSYN by Kravanja (2010). Because the non-linear and discrete MINLP problem in the paper is simple, i.e. it discusses the cost and rounded dimension optimization only, GAMS/DICOPT (Grossmann and Viswanathan, 2002) was selected for application.

The optimal result represents the obtained minimal investment costs of 18.22 million EUR per the lined rock cavern. All four LRCs of the UGS in Senovo thus reach 72.88 million EUR. Fig. 2 shows the vertical cross-section of the optimized lined rock cavern. In the figure, the calculated "optimal" variables (dimensions and the inner gas pressure) are shown. The optimal result exhibits

47.7 % of savings when compared to the design, obtained by the classical method (FEM).

5 Conclusions

The paper presents the cost optimization of a lined rock cavern (LRC), designed for an underground gas storage (UGS). The optimization was performed by the mixed-integer non-linear programming (MINLP) approach in order to handle discrete alternatives of dimensions and inner gas pressure explicitly. The MINLP optimization model of the structure was modelled and the computer program GAMS/DICOPT was used for the optimization. Advantages of the MINLP optimization approach are noticed. The calculated optimal result exhibits 47.7 % of net savings in investment costs when compared to the design, obtained by the classical method.

Acknowledgments

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

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MODELS FOR CIRCULAR ECONOMY: CONFERENCE PROCEEDINGS
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Optimization of the sustainability profit generated by the production of beams

TOMAŽ ŽULA & STOJAN KRAVANJA

Abstract The paper presents the optimization of the sustainability profit generated by the production of simply supported beams in the area of civil engineering. A number of beams are proposed to be designed from three different material alternatives: from the structural steel, from the reinforced concrete and from the laminated timber. For this reason, three optimization models of beams are developed for the three materials. In addition, two different objectives are defined for each different material alternative: for the economic profit and for the sustainability profit (which includes eco costs of the global warming). The proposed objective functions are subjected to the design, resistance and deflection constraints of the beams, determined in accordance with Eurocode 2, 3 and 5 specifications. The optimizations of the beam alternatives are performed by the mixed-integer non-linear programming (MINLP) approach. GAMS/Dicopt is used. The task of the optimization is to find the most advantageous material alternative for the beams. The numerical example, presented at the end of the paper, clearly shows that the reinforced concrete beams exhibit the highest economic profit, but the timber beams give the highest sustainability profit.

Keywords: • Sustainability profit • GHG emissions • Structures • Mixed-integer non-linear programming • MINLP •

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DOI https://doi.org/10.18690/978-961-286-211-4.12 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

The paper handles with the optimization of the sustainability profit generated by the production of simply supported beams in the area of civil engineering. In this case sustainability profit is a summation of the economic profit and eco costs of the global warming. A number of beams are considered to be designed from three different material alternatives: from the laminated timber, from the structural steel and from the reinforced concrete. The objective of this paper is to find the optimal design of the simply supported beam subjected to the highest economic profit and to the sustainability profit, performed by mixed-integer non-linear programing approach.

In the fields of optimization and sustainability, different optimization techniques and objectives have been proposed. Zaforteza et al. (2009) used simulated annealing algorithm (SA) applied to two objective functions, namely the embedded CO_2 emissions and the economic cost of reinforced concrete structures. Camp and Huq (2013) have proposed a hybrid big bang-big crunch algorithm (BB-BC) for the optimal design of reinforced concrete frames. The objective was to minimize the total cost or the CO_2 emissions. Alonso and Berdasco (2015) presented the carbon footprint of sawn timber products. Li et al. (2017) have introduce a topology optimizer to get the best-possible welded box-beam structures that emit less greenhouse gases by using improved ground structure method (IGSM).

2 MINLP model formulation

Since the problem of simply supported beam is the non-linear discrete-continuous optimization problem, the MINLP is applied for the solution. The general MINLP optimization problem can be formulated as follows:

$$\begin{gathered} \min \ z = f(\mathbf{x},\mathbf{y}) \\ \text{subjected to: } g_k(\mathbf{x},\mathbf{y}) \le 0 \quad k \in K \\ \mathbf{x} \in X = \{\mathbf{x} \in R^n: \ \mathbf{x}^{\mathrm{LO}} \le \mathbf{x} \le \mathbf{x}^{\mathrm{UP}}\} \\ \mathbf{y} \in Y = \{0,1\}^m \end{gathered}$$

where **x** are the continuous variables and **y** are the discrete (0, 1) variables. Function $f(\mathbf{x}, \mathbf{y})$ is the objective function for the economic profit and for the sustainability profit (which includes eco costs of the global warming). g_k (**x**,**y**) stands for the design, resistance and deflection constraints.

3 Numerical example

The example shows the optimization of 500 equal simply supported beams. Each beam is 9.0 meters long, subjected to the combined effect of the dead-weight, the permanent continuous load of 9.0 kN/m (g) and the imposed variable continuous load of 9.0 kN/m (q), see Fig. 1.

Each simply supported beam is proposed to be made from three different material alternatives: from the laminated timber, from the structural steel and from the reinforced concrete. At this point the comparison and the competitiveness between these three materials of the beams was investigated for various material and dimension alternatives, and for two different objectives i.e. for the optimization of the economic profit and of the sustainability profit.

For comprehensive topology optimization problem, we usually use program MipSyn (Kravanja, 2010). As the optimization problem of the beam a simple discrete and non-linear problem, Dicopt (Grossmann, 2002) was selected for application. Six optimization models for the simply supported beam (SIMSBOPT) were developed as a combination between three different materials (timber, steel and concrete) and two different objective functions. For mathematical modelling GAMS (General Algebraic Modelling System), (Brooke et al., 1988), was used. The models consist of the objective functions, subjected to the 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 3 (2005) for steel and Eurocode 2 (2004) for the reinforced concrete. The beams were checked for the shear, bending moment and lateral torsional buckling resistances as well as for the vertical deflections.

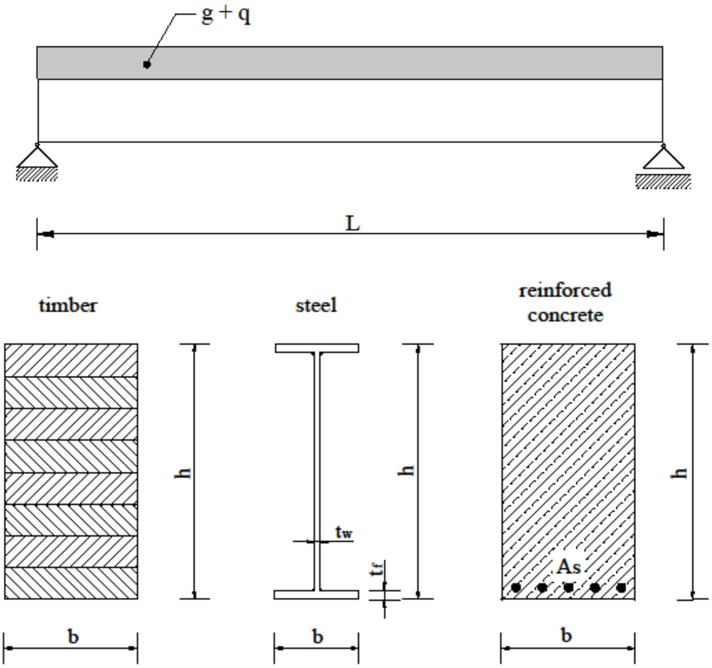

Figure 1: Simply supported beam

The simply supported beam superstructure comprises three different materials. The laminated timber beam superstructure comprises 101 different rounded dimension alternatives for the cross-section width and 131 rounded dimension alternatives for the cross-section height. The steel beam superstructure includes 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 dimensions alternatives for the height of the web. In addition, 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 on whole centimeters) are involved in the reinforced concrete beam superstructure.

The given material and dimension alternatives (binary variables) gives 13231 structure alternatives for the timber beam, 262 531 392 different structure alternatives for the steel beam, and 1204021 different structure alternatives for the reinforced concrete beam.

Two different objective functions were proposed for two different defined criteria. The first criterion of the optimization includes the maximization of the economic profit (P_{E} [€]) of 500 equal beam structures. The economic profit is determinate as a sum of the selling price, the self-manufacturing material and labor costs, and overheads. The objective function was defined for three different materials separately, see Eq. (1). N is a number of simply supported beams (N = 500), C_{S} [€] is a selling price of a single simply supported beam, $C_{\mathrm{M}i}$ [€/kg] represents the material unit prices of ($i \in I$: laminated timber, impregnation and protection paint for the timber beam; structural steel, electrodes, gas consumption and anticorrosion-resistant paint for the steel beam; and concrete, reinforcing steel bars and formwork slab-panels for the concrete beam). ϱ_i [kg/m^3] is the corresponding unit mass and V_i [m^3] is volume. While $C_{\mathrm{L}j}$ stands for the hourly labor costs [€/h], t_j [h] are times required for ($j \in J$: impregnating and painting the timber beam; cutting, welding and painting the steel beam; and placing, curing and vibrating the concrete, cutting and placing the reinforcement, and paneling the concrete beam), and f_{O} is an indirect cost factor for overheads (f_{O} = 2). More detail about cost items used in the economic objective function see (Jelušič, 2017) and (Kravanja, 2017).

$$\max P_{\mathrm{E}} = N \cdot \left(C_{\mathrm{S}} - C_{\mathrm{M}i} \cdot \varrho_i \cdot V_i - C_{\mathrm{L}j} \cdot t_j \cdot f_{\mathrm{O}} \right) \tag{1}$$

The second criterion is the maximization of the sustainability profit (P_{SUS} [€]), calculated for 500 beams as a summation of the economic profit and eco costs of the global warming (EVR, 2018) caused by the beam production. The objective function was defined for three materials separately, see Eq. (2). C_{GW} (€/kg CO_2 eq.) is a price of global warming, 0.116 €/kg CO_2 eq. (EVR, 2018), ϱ_k [kg/m^3] and V_k [m^3] are the corresponding unit masses and volumes, respectively and $f_{\mathrm{CFEF}k}$ is carbon footprint emission factor ($k \in K$; for the timber beam, steel beam and for the reinforced concrete beam). The carbon footprint emission factor used in the study are 0.69 kg CO_2 eq./kg for timber, 1.72 kg CO_2 eq./kg for steel, 0.11–0.16 kg CO_2 eq./kg for concrete and 2.43 kg CO_2 eq./kg for the reinforcing steel bars.

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

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

Table 1: Results of the simply supported beam optimizations

Criterion		Timber GL24h	Steel S 235	Reinforced Concrete C 50/60
1.	**Economic profit (€)**	**123 890**	**-192 801**	**161 939**
	b (cm)	21.0	32.9	29.0
	h (cm)	77.0	50.0	59.0
2.	**Sustainability profit (€)**	**97 179**	**-257 776**	**93 745**
	b (cm)	21.0	32.9	29.0
	h (cm)	77.0	50.0	59.0

1. Economic profit; 2. Sustainability profit

4 Conclusion

The paper presents the optimization of the sustainability profit generated by the production of simply supported beams in the area of civil engineering. The optimal solutions are calculated using two different objective functions, i.e. economic profit and sustainability profit. The optimizations of the beam alternatives are performed by the mixed-integer non-linear programming (MINLP) approach. The numerical example clearly shows that the reinforced concrete beams exhibit the highest economic profit, but the timber beams give the highest sustainability profit.

Acknowledgments

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

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University of Maribor Press

Conversion of CO_2 Within Sustainable Process Industry Through Resource and Energy Efficiency

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Abstract The Laboratory of Catalysis and Chemical Reaction Engineering (LCCRE) within the National Institute of Chemistry, Slovenia, is alongside several European academic and industrial partners involved in the development of innovative green chemical production technologies in an industrially-relevant environment by increasing the overall resource efficiency and energy intensity, and by decreasing the greenhouse gas emissions into the environment. The mentioned research and innovation efforts are joined under the SPIRE initiative within the Horizon 2020 Framework Programme.

Keywords: • CO_2 Conversion • DFT • KMC • CFD • multiscale modelling •

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DOI https://doi.org/10.18690/978-961-286-211-4.13 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

The MefCO$_2$ (Synthesis of Methanol from Captured Carbon Dioxide Using Surplus Electricity) and FReSMe (From Residual Steel Gases to Methanol) projects are aimed at an increase of renewable energy usage and a decrease of CO2 emissions, which are important European strategic objectives. Carbon dioxide, a greenhouse gas, which would normally be emitted into the atmosphere, is captured and converted to methanol with hydrogen, which is produced by water electrolysis. The electricity, used for electrolysis, is obtained from the surplus electricity at the peaks of its generation from renewable resources (wind, solar, etc.), simultaneously stabilizing the electrical grid. The product, methanol, is a widely-useable platform chemical and a precursor for further synthesis.

A comprehensive list of theoretical calculations for methanol synthesis was carried out to better understand the kinetics and mechanism of the reaction on a complex catalyst. To study kinetics of the catalysed reaction, a crystal structure was constructed that mirrored the actual catalyst structure, based on existing literature data and our experimental techniques. We studied detailed kinetics on four catalyst combinations (Zn_3O_3/Cu, Cr_3O_3/Cu, Fe_3O_3/Cu, and Mg_3O_3/Cu), which had not been done in such detail before. A thorough reaction pathway network was put together and investigated using density functional theory (DFT), including less frequently encountered intermediates and reactions on side pathways. We calculated reaction rates at different temperatures and pressures. All possible elementary reaction steps were considered.

2 Operational laboratory-scale reaction models

2.1 Density functional theory modelling

Density functional theory (DFT) calculations were carried out with the program suite Quantum Espresso 5.4 [1], which uses PWscf code to calculate the electronic structure of periodic atomic structure. For visualization of structures, an open-source tool XCrysDen was used [2]. As the best compromise between accuracy and computational cost, Perdew-Burke-Ernzerhof (PBE) functional was selected [3,4]. Ultrasoft pseudopotentials from scalar-relativistic calculations were used. To account for insufficient description of van der Waals interactions by DFT methods, a modified semi-empirical Grimme dispersion correction was included [5]. Convergence testing showed that the kinetic energy cut-off of 300 eV and wavefunction cutoff of 2400 eV sufficed to obtain well converged results. Metallic nature of the catalyst was taken into account by using Gaussian spreading of width 0.1 Ry for Brillouin zone integration. It was sampled on a Monkhorst-Pack mesh with 8 x 8 x 1 points [6]. Convergence threshold of 10^{-8} Ry for self-consisted cycles was selected. For geometric optimisation of adsorbates, residual forces were required to drop below 10^{-3} Ry/au and energy change per step below 10^{-4} Ry. For gaseous species calculations, a large (25 × 25 × 25 Å) cubic cell was used. As there is no periodicity to account for, Brillouin zone was sampled at a single point (Γ) and no dipole correction was used. To seek for the transition states, nudge elastic band (NEB) method was used. After preliminary identification of the transition state structure, it was determined with climbing image approach until forces orthogonal to the reaction path dropped below 0.05 eV/Å [7,8]. Vibrational analysis was carried out to ensure that each transition state structure had exactly one imaginary frequency, corresponding to the movement along the reaction coordinate. For adsorbed species, zero-point energy (ZPE) correction was calculated from the vibrational component only, perturbing only adsorbate atoms

$$\Delta E_{ZPE} = \sum_i^{3N} \frac{h\upsilon_i}{2}. \tag{1}$$

Adsorption energies of reactants, intermediates and products were calculated as

$$\Delta E_{ads} = E_{species+catalyst} - E_{catalyst} - E_{species} + \Delta E_{ZPE}. \tag{2}$$

Reaction barrier (E_A, activation energy) and reaction energy (ΔE) for each elementary step were calculated in a standard fashion as

$$E_{\mathrm{A}} = E_{\mathrm{TS}} - E_{\mathrm{reactant}} \tag{3}$$

and

$$\Delta E = E_{\mathrm{product}} - E_{\mathrm{reactant}}. \tag{4}$$

This allowed us to obtain reaction rates as

$$k_{fwd} = \frac{k_B T}{h} \frac{q_{vib,TS}}{qvib_{,IS}} e^{-\frac{E_A}{k_B T}} \tag{5}$$

where k_B denotes Boltzmann constant, T absolute temperature, h Planck constant and q_{vib} vibrational partition function, which is in turn estimated from the real vibrational contributions only (as the imaginary mode along the reaction coordinate is factored out in transition state theory) as

$$q = \prod_i^{3N} \frac{1}{1 - e^{-\frac{h v_i}{k_B T}}}, \tag{6}$$

Equilibrium constants are obtained from

$$K = \frac{k_{fwd}}{k_{bwd}} = e^{-\frac{\Delta E}{k_B T}}. \tag{7}$$

and allow us to determine the rates for the reverse reactions

$$K = \frac{k_{fwd}}{k_{bwd}} = \frac{q_{vib*}}{q_{vib} q_{rot} q_{trans,g}} = e^{-\frac{\Delta E_{ads}}{k_B T}}, \tag{8}$$

For adsorbed hydrogen atoms, surface diffusion was explicitly taken into account as an elementary reaction, when hydrogen migrates from one fcc site on Cu to the adjacent one.

Kinetic constants for adsorption and desorption are obtained from the collision theory. Rate of adsorption can be evaluated if we assume that the sticking probability equals unity as

$$k_{ads} = \frac{1}{N_0 \sqrt{2 \pi m k_B T}} \tag{9}$$

where N_0 denotes the number of reaction sites per catalyst as $1.9 \cdot 10^{17}$ m^{-2} and m the mass of a molecule. For desorption rate, one calculates the equilibrium constant and by taking into account vibrational, rotational and translational components of the partition function for gaseous species.

$$K = \frac{k_{ads}}{k_{des}} = \frac{q_{vib,ads}}{q_{vib,g} q_{rot} q_{trans}} exp\left(-\frac{E_{ads}}{k_B T}\right) \tag{10}$$

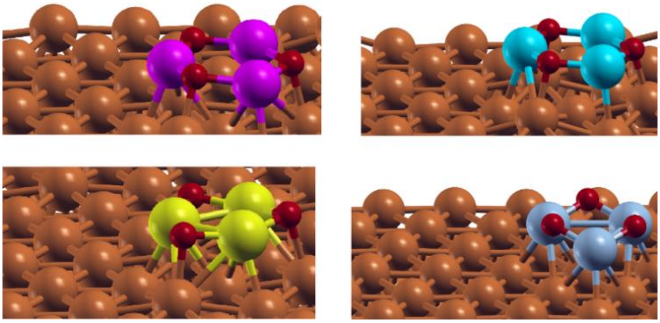

Figure 2: Modelled active site of the M_3O_3/Cu catalyst (from top left clockwise M: Zn, Mg, Cr, Fe) consists of a M_3O_3 deposited atop of Cu(111) plane. Reactions proceed at the interphase boundary.

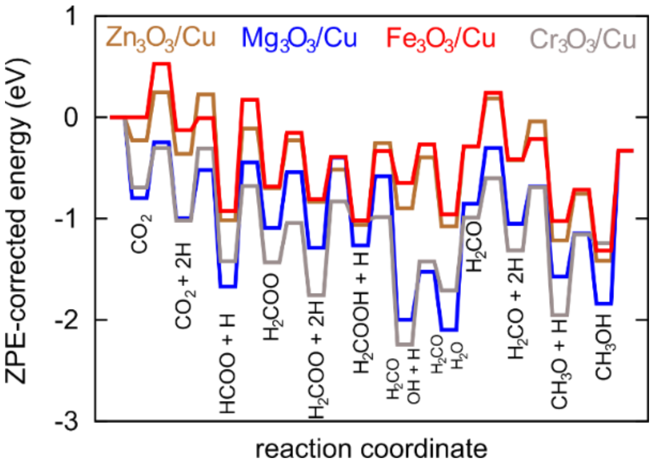

Figure 2: Potential energy surface for the most probable reaction route on all four studied catalysts. Note that CO_2 does not bind to Fe_3O_3/Cu catalyst, effectively making the reaction follow the Eley-Rideal mechanism.

2.2 Kinetic Monte Carlo (KMC) simulations

Using the graph-theoretical KMC software package Zacros, we simulate methanol (CH_3OH) synthesis from CO_2 hydrogenation. We focus on theoretically modelled catalysts, in particular the Cu(111) and the commercial-like Cu/metal oxide catalysts $(Zn,Cr,Fe,Mg)_3O_3$/Cu. We study methanol synthesis via formate (HCOO) and hydrocarboxyl (COOH) reaction path, but also include H_2O effects and reverse water-gas shift (RWGS) reaction path. The dependence of conversion, selectivity, and the rate of desorbed bulk CH_3OH production upon operating process conditions, primarily temperature and pressure, was examined. Furthermore, KMC simulations provide the detailed surface coverage and elementary steps' event frequency, to study the catalytic performance in temporal domain [9]. The results are qualitatively well comparable with the available experimental data for heterogeneous copper-based materials. This demonstrates that an accurate evaluation of ab initio theoretical research is crucial, especially upon paralleling them to experimental reactor concentrations.

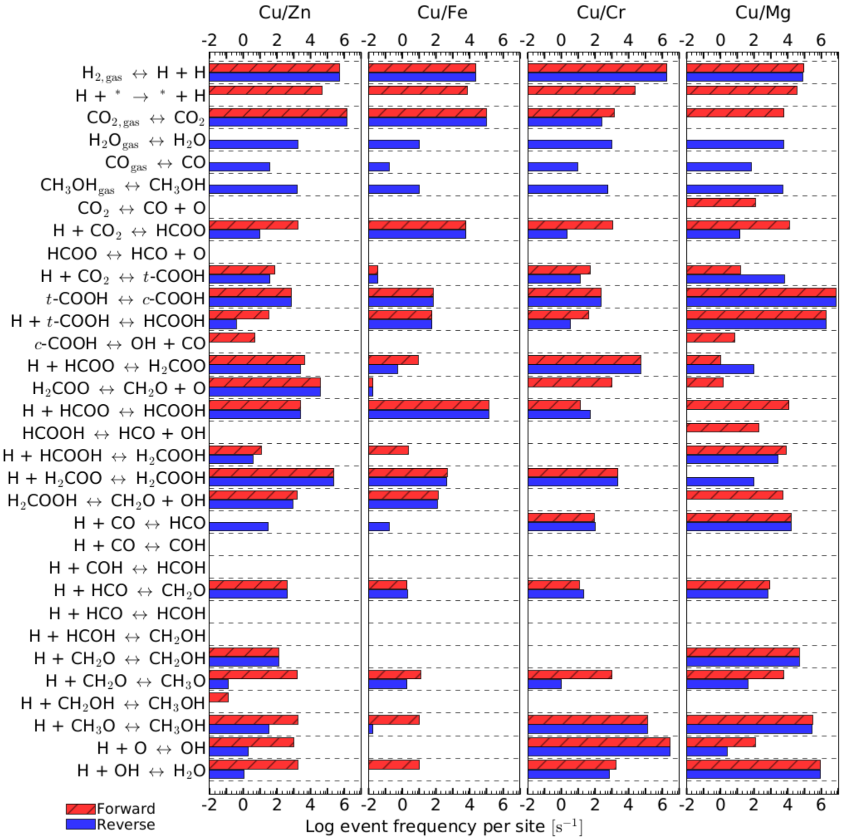

Figure 2: Elementary step frequency for the case of T = 500 K and P = 40 bar, for all 4 investigated catalysts (M_3O_3/Cu catalysts, M being Zn, Cr, Fe, or Mg). Red steps indicate forward reactions, while blue ones indicate reverse reactions. From [10].

2.3 Fluid dynamics and transport phenomena (computational fluid dynamics – CFD)

In contrast to empirical correlation (EC), computational fluid dynamics (CFD) acknowledges specific vessel geometry, where local physical and chemical phenomena, contributing to apparent catalytic turnover, prevail. Presently, EC and CFD were compared considering the pressure drop predictions within the packed bed columns for spherical, cylindrical, trilobe and quadrilobe particle packing. 52 configurations were simulated and the estimations within EC validity range margins were in agreement with CFD (< 15%), while in extremes (non-negligible entrance and exit patterns), a 70% deviation could be exceeded. Furthermore, boundary wall effects were found to be dependent on the stacked pellet shape and orientation, and did not necessarily lead to an increase of viscous friction loss, relative to the infinitely wide systems, for the column-to-particle diameter ratios, lower than 10, which is contradictory to non-mechanistic relationship models. While the induced pressure difference within realistic fixed beds is elevated due to gas or liquid surface interaction and back-mixing, it can also be decreased by channelling/tunnelling, which is why the effective net influence should be analysed with CFD simulations, particularly in novel intensified and micronized processes, in which momentum, mass and heat transfer resistances are far from bulk medium continuity. Finally, new solver was developed which included surface catalytic reactions. On the bases of the Open Source Computational Fluid Dynamics (CFD) Toolbox OpenFoam we manipulate the reactingFoam solver which was developed for homogeneous reacting flows. To include heterogeneous catalytic reaction new dynamic boundary condition was written which was applied in the new solver called surfaceReactingFoam.

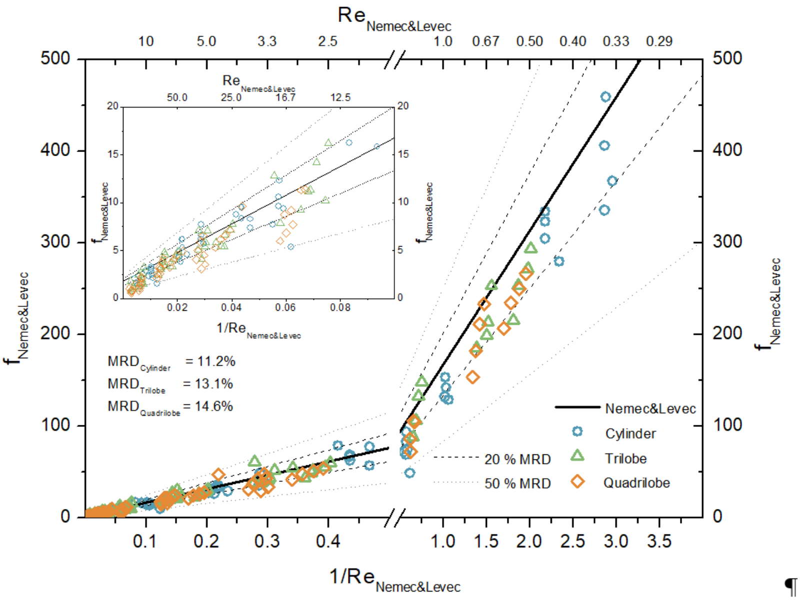

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Figure 2: Modified friction factor predicted by CFD and Ergun correlation [11]**.**

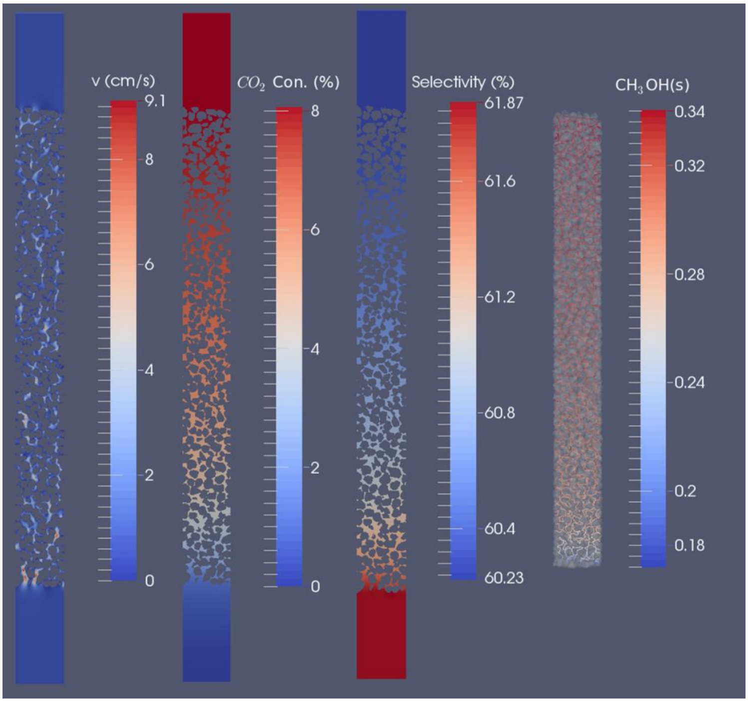

Figure 2: CO$_2$ hydrogenation to methanol at 220 ^{o}C – (left-right) – velocity field, CO$_2$ conversion, methanol selectivity and methanol coverage .

Acknowledgments

The authors gratefully acknowledge the European Commission, as the herein-presented research work was established within the $MefCO_2$ and FReSMe projects. $MefCO_2$ and FReSMe have received funding from Programme for Research and Innovation Horizon 2020 under grant agreement n° 637016 and n° 727504, respectively. The authors also gratefully acknowledge the Slovenian Research Agency (ARRS) for funding the program P2–0152 and project J2–7319.

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MODELS FOR CIRCULAR ECONOMY: CONFERENCE PROCEEDINGS
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A Study on Mono- and Co-digestion of Riverbank Grass Under Anaerobic Conditions for Production of Biogas

ROBERT BEDOIĆ, LIDIJA ČUČEK, DAMJAN KRAJNC, BORIS ĆOSIĆ,
ZDRAVKO KRAVANJA, TOMISLAV PUKŠEC & NEVEN DUIĆ

Abstract This paper investigates the application of riverbank grass as a potential alternative energy crop for maize silage in the production of biogas. Grass samples have been mowed on the embankments of the Sava River in the city of Zagreb, Croatia. Carbon and nitrogen content and C/N ratio have been determined in the grass samples. Further, laboratory investigations on the anaerobic mono- and co-digestion of the collected riverbank grasses with different ratios with maize silage and animal manure have been conducted. The laboratory reactors have operated under the mesophilic conditions (39 °C) with the dry matter contents of 6 %. During the anaerobic digestion process, the biogas production and composition and pH value of the reaction mixture have been monitored. Results show that the riverbank grass could serve as a (co)-substrate in the anaerobic mono- and co-digestion.

Keywords: • Anaerobic digestion • Mono- and co-digestion • Riverbank grass • Biogas production • laboratory experiment •

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DOI https://doi.org/10.18690/978-961-286-211-4.14 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

Anaerobic digestion is a technology of conversion of organic compounds into a sustainable source of energy, biogas and digestate (Siddique & Wahid, 2018). Any biodegradable material can be used as a substrate in anaerobic digestion. However, the focus should be put on substrates that ensure sustainable management and development, with prior characteristics like abundant quantities and non-competitiveness with the food production. As authors in the article (Meyer et al., 2016) have stated, the biogas production in Europe should be based on the use of animal manure, straw and grass as main substrates. Riverbank grass comes in abundant quantities and does not compete with production of food, and therefore it is suitable feedstock for biogas production.

The quality of grass for biogas production depends on the composition, time of harvest and particles size (Elsäßer et al., 2012). Current investigations have shown that different types of grass give different cumulative biogas and methane yields. For instance, canary grass has shown biogas yield of 406 Ndm^3/kg of volatile solids, while wild grass only 120 Ndm^3/kg of volatile solids (Oleszek et al., 2014). Such variety of results indicate that not all the grass types are equally suitable for biogas production.

The aim of this study is to investigate the possible application of fresh riverbank grass as a mono-substrate in the anaerobic digestion, and as a co-substrate together with animal slurry in the ratio 1:1 based on dry mass. Additionally, grass was mixed with maize silage at different ratios on dry basis (0.75:0.25, 0.5:0.5, 0.25:0.75) to investigate if grass could be an alternative substrate for food-competitive maize silage in the actual biogas plants. Anaerobic digestion was performed under mesophilic conditions (39 °C) and wet fermentation (6 % of dry matter content).

2 Materials and methods

Grass samples were collected on the southern embankment of the Sava River in the city of Zagreb at the end of April in 2018 (Figure 1). By the visual inspection of the riverbank grass, it has been envisaged that it belongs to a ryegrass type (*Lolium*). After the grass samples were collected, they were put in bags and stored in the fridge at low temperatures. For the purposes of the investigation, the riverbank grass stems have been cut into smaller pieces as it is shown in Figure 1.

The inoculum and maize silage were obtained from a biogas plant treating poultry manure and maize silage and operating under mesophilic conditions. Fresh cattle slurry has been collected from a small farm in a municipality of Šentilj. Before the analyses, inoculum and slurry were filtered through a coarse filter to remove large particles and to improve homogeneity. Before feeding the substrates to reactors, the substrates have been dried in triplicates to determine dry matter content of substrates.

Anaerobic digestion has been performed in 250 mL batch digesters for 42 days in a heating bath at 39 °C. All the samples have been prepared based on the average dry matter (DM) content of samples in triplicates as it is shown in Table 1. The basic medium containing salts (Angelidaki et al., 2009) has further been added to substrate mixtures to reduce the DM concentration in reactors to 6 %.

Figure 1: Collection and preparation of grass stems for analysis

Table 1: Batch assay setup of samples on dry basis (g)

	Inoculum	Grass	Maize silage	Cattle slurry
Grass	4.5	4.5	/	/
Grass-Slurry (Co1)	4.5	2.25	/	2.25
Grass-Silage-Slurry 0.75:0.25 (Co2)	4.5	1.6875	0.5625	2.25
Grass-Silage-Slurry 0.5:0.5 (Co3)	4.5	1.125	1.125	2.25
Grass-Silage-Slurry 0.25:0.75 (Co4)	4.5	0.5625	1.6875	2.25
Silage-Slurry (Co5)	4.5	/	2.25	2.25
Inoculum	4.5	/	/	/

During anaerobic digestion biogas production was measured daily, methane composition in biogas was measured five times during the process (once a week) and twice a week pH was analyzed.

3 Results and discussions

For grass samples the carbon and nitrogen contents have been determined and thus C/N ratio is calculated. C/N ratio of grass (Table 2) shows that it is suitable for biogas production in anaerobic digestion process.

Table 2: Share of carbon and nitrogen in riverbank grass expressed on dry basis

Parameters	Composition
Carbon (C)	44.7 %
Nitrogen (N)	2.18 %
C/N	20.5

Results on biogas yield and biochemical methane potential (BMP) of conducted co-digestion experiments are shown in Figures 2 and 3 where x-axis in Figure 3 represents the share riverbank grass : maize silage.

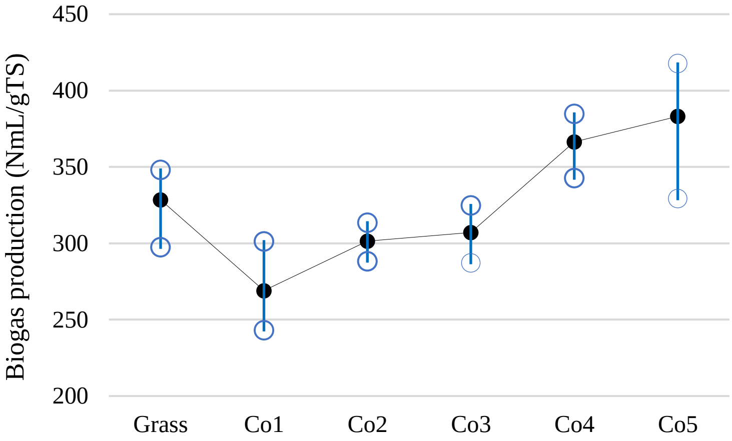

Figure 3: Cumulative biogas yield and the range of biogas production between the parallels

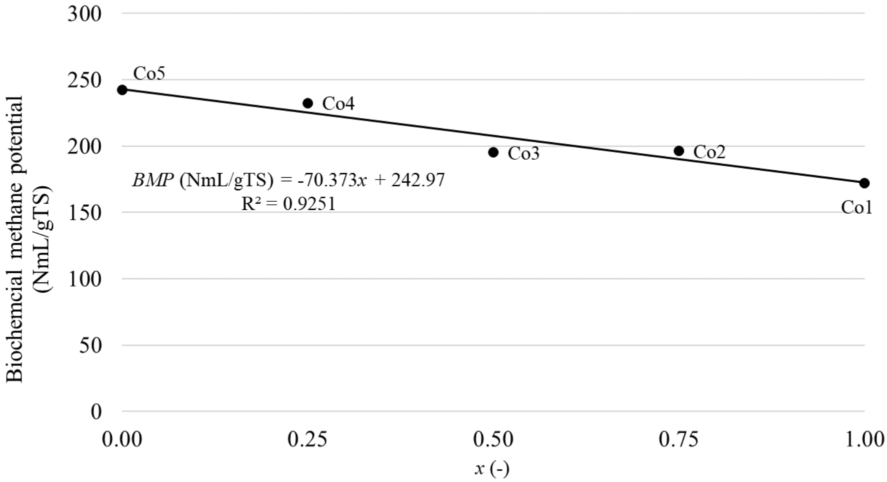

Figure 4: Impact of riverbank grass share in silage mixture on the biochemical methane potential

The highest biogas production has been obtained for co-digestion of maize silage and cattle slurry, 383.1 NmL/gTS on average, and the lowest for co-digestion of grass and cattle slurry, 269 NmL/gTS on average, see Figure 2. Monodigestion of riverbank grass has shown in total 328.5 NmL/gTS of biochemical biogas potential with methane share in biogas of ca. 59 %.

By comparing the results on biogas yield and *BMP* of co-digestions of maize silage and animal slurry (Co5), riverbank grass with maize silage and animal slurry

(Co5, Co4, Co3, Co2) and riverbank grass with animal slurry (Co1), it could be seen that adding the slurry to grass decreases the yield and *BMP*. Results show that as the share of riverbank grass in silage mixture increases, the biogas production and *BMP* decrease almost linearly. Therefore, it can be stated that more riverbank grass is required (on TS basis) compared to maize silage to maintain the same methane production in reactor under mesophilic conditions. pH values in reactors were in the range between 7.14 and 8.2. Initially, the pH was between 7.8 and 8. In the first four days of operation the pH value has significantly decreased due to hydrolysis and generation of volatile fatty acids. After, the pH has increased and after 15th day of operation it remained almost constant (in the range of 8.08 and 8.18) until the process has stopped.

4 Conclusions

Mono- and co- digestion of riverbank grass under mesophilic conditions in a batch mode has successfully been carried out. The results obtained in this investigation point lead to the conclusion that riverbank grass has potential to serve as a co-substrate in the anaerobic digestion. Even though riverbank grass has shown lower production of biogas compared to maize silage in co-digestion with animal slurry, it is available in abundant quantities and does not compete with food and feed chains and thus could be used in biogas plants. However, in order to apply the riverbank grass at the larger scale in biogas plants, the fed-batch or semi-continuous process should be derived.

Acknowledgments

The authors acknowledge the financial support from the Slovenia-Croatia bilateral project Integration of renewable energy within energy systems (INTEGRES), from the Slovenian Research Agency (programs P2-0032 and P2-0377, project L2-7633). Also, this work has been financially supported by the European Union's Horizon 2020 research and innovation programme under grant agreement No: 690142-2 (AgroCycle project).

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1. MEDNARODNA KONFERENCA TEHNOLOGIJE IN POSLOVNI MODELI ZA
KROŽNO GOSPODARSTVO, KONFERENČNI ZBORNIK
M. Bogataj, Z. Kravanja in Z. Novak Pintarič (ur.)

Univerzitetna založba
Univerze v Mariboru

Kinetika nastajanja CH_4 med anaerobno fermentacijo piščančjega gnoja z žagovino in z glivami predobdelane pšenične slame

DARJA PEČAR, ANA VOZLIČ, JANEZ SMERKOLJ, FRANC POHLEVEN IN ANDREJA GORŠEK

Povzetek V tej študiji smo izvedli predobdelavo pšenične slame z glivama Pleurotus ostreatus in Trametes versicolor. Kot substrat pri anaerobni fermentaciji smo uporabili mešanice piščančjega gnoja z žagovino in z glivama preraščeno pšenično slamo v različnih razmerjih (50:50, 60:40 in 80:20). Za kontrolo smo uporabili nepreraščeno pšenično slamo. Anaerobne fermentacije smo izvajali pri (35, 40 in 45) °C. Posamezni proces anaerobne fermentacije smo pri konstantni temperaturi vzdrževali 21 d. Med reakcijo smo spremljali prostornino in koncentracijo nastalega bioplina. Iz dobljenih podatkov smo izračunali kinetične parametre nastajanja CH_4. Največ proizvedenega bioplina smo zabeležili pri slami, ki je bila preraščena z glivo Pleurotus ostreatus (razmerje 50:50) pri 45 °C, najmanj pri slami, preraščeni z glivo Trametes versicolor (razmerje 80:20) pri 35 °C. Koncentracija CH_4 je v začetnih dneh anaerobne fermentacije hitreje naraščala pri višji temperaturi, medtem ko smo po 21 d pri vseh temperaturah dosegli koncentracijo CH_4 nekje med 53 do 55 %.

Ključne besede: • Pleurotus ostreatus • Trametes versicolor • bioplin • metan • kinetika •

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DOI https://doi.org/10.18690/978-961-286-211-4.15 ISBN 978-961-286-211-4
Dostopno na: http://press.um.si.

University of Maribor Press

Kinetics of CH_4 Production During Anaerobic Fermentation of Chicken Manure with Saw Dust and Wheat Straw Overgrown with Fungi

DARJA PEČAR, ANA VOZLIČ, JANEZ SMERKOLJ, FRANC POHLEVEN &
ANDREJA GORŠEK

Abstract In this study pre-treatment of wheat straw with Pleurotus ostreatus and Trametes versicolor fungi was carried out. Mixtures of chicken manure with sawdust and fungi overgrown wheat straw at different ratios (50:50, 60:40 and 80:20) were used as a substrate for anaerobic fermentation. For the control ordinary wheat straw was used. Anaerobic fermentations were performed at (35, 40 and 45) ° C. An individual process of anaerobic fermentation was maintained at constant temperature for 21 d. During the reaction, the volume and concentration of produced biogas was monitored. From the obtained data the kinetic parameters of CH_4 production were calculated. The highest quantity of produced biogas was recorded for the straw, overgrown with Pleurotus ostreatus fungi (ratio 50:50) at 45 ° C, and the smallest one in the case of straw, overgrown with Trametes versicolor fungi (ratio 80:20) at 35 °C. At the beginning of anaerobic fermentation the concentration of CH_4 was increasing faster at a higher temperature, while after 21 d, it was between 53 and 55% regardless of temperature.

Keywords: Pleurotus ostreatus • Trametes versicolor • biogas • methane • kinetics •

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DOI https://doi.org/10.18690/978-961-286-211-4.15 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Uvod

Zaradi povečanega povpraševanja po energiji in varstva okolja se vzpodbuja večja proizvodnja bioenergije, ki je alternativen, cenovno ugoden in trajnosten vir energije v primerjavi z neobnovljivimi viri energije, kot so fosilna goriva. (Ali and Sun, 2015; Bharathiraja et al., 2016; Bishir and Ekwenchi, 2012; Divya et al., 2015; Rouches et al., 2016) Anaerobna fermentacija je eden izmed najbolj obnovljivih procesov proizvodnje energije. Gre za štiristopenjski biološki proces (hidroliza, acidogeneza, acetogeneza in metanogeneza) razgradnje biološko razgradljivih organskih snovi z različnimi mikroorganizmi pri pogojih brez prisotnosti kisika, pri čemer se proizvaja bioplin. Druga pozitivna stvar anaerobne fermentacije je zmanjšanje naravnih emisij CH_4 pri samorazgradnji biomase v okolju, kjer se CH_4 prosto sprošča v ozračje in s tem prispeva k globalnemu segrevanju. Po drugi strani se bioplin, proizveden med anaerobno fermentacijo, uporablja kot vir energije za proizvodnjo električne energije, toplote in tudi kot avtomobilsko gorivo. (Divya et al., 2015; Taherzadeh and Karimi, 2008; Zheng et al., 2014) Učinkovitost anaerobne fermentacije je odvisna od značilnosti substrata, pogojev obratovanja in izbire fermentorjev. (Khalid et al., 2011)

V tej študiji smo kot substrat pri anaerobnih fermentacijah uporabili piščančji gnoj z žagovino (PGŽ) in pred-obdelano in navadno pšenično slamo v različnih razmerjih. Pred-obdelavo smo izvedli z glivama bele trohnobe *Pleurotus ostreatus* (P.o.) in *Trametes versicolor* (T.v.). Tekom fermentacije smo merili količino proizvedenega bioplina in koncentracijo CH_4. Glavni cilj naše študije je bil določiti kinetične parametre proizvodnje CH_4 med anaerobno fermentacijo, vključno z izvedbo primerjave med eksperimentalnimi podatki in podatki, izračunanimi s kinetičnim modelom 1. reda in modificiranim Gompertzovim kinetičnim modelom.

2 Materiali in metode

2.1 Materiali

Pšenična slama je bila pridelana na lokalnih poljih v Sloveniji. Inokulum, uporabljen v tej študiji, smo dobili iz bioplinarne (Perutnina Ptuj, Draženci, Slovenija). Povprečna skupna trdna snov (TS) inokuluma je bila 12,1 ± 2,0 %.

2.2 Metode

2.2.1 Predobdelava z glivami

Poskuse pred-obdelave z lesnimi glivami smo izvajali v 1L steklenih kozarcih. Slamo smo zmleli na 2 do 3 cm koščke in z njo napolnili kozarce. Na 50 g slame smo dodali 230 mL vode. Kozarce smo zaprli s kovinskim pokrovčkom, ki je imel na sredini okroglo odprtino premera približno 1,5 cm. Odprtino smo zamašili s kosmom vate in pokrovček pokrili s papirjem. Nato smo kozarce dve uri avtoklavirali pri temperaturi 121 °C. Po sterilizaciji smo ohlajen substrat pri sterilnih pogojih (v laminariju) cepili s kulturo micelijev *Pleurotus ostreatus* in *Trametes versicolor*, vzgojenih na PDA gojišču. Za predobdelavo slame smo uporabili dve vrsti lesnih gliv povzročiteljic bele trohnobe in sicer: zimskega ostrigarja (*Pleurotus ostreatus*) – izolat P.o./H35 ter pisano ploskocevko (*Trametes versicolor*) izolat T.v..

Približno tri tedne kasneje smo piščančji gnoj z žagovino zmešali s predhodno obdelano in navadno pšenično slamo v različnih razmerjih (50:50, 60:40 in 80:20). Tako pripravljene zmesi smo nadalje inkubirali 1 teden in nato jih uporabili kot substrat pri anaerobnih fermentacijah.

2.2.2 Anaerobna fermentacija

Vsi eksperimenti so bili izvedeni v termostatiranih šaržnih fermentorjih z delovno prostornino 250 mL pri različnih temperaturah, ϑ = (35, 40 in 45) °C. V posamezen fermentor smo dali 5 g predhodno obdelanega substrata in 5 g inokuluma (suha masa). Nato smo fermentorje 2 min prepihovali z argonom, da smo odstranili ves zrak in ustvarili anaerobne pogoje. Fermentorje smo termostatirali pri želeni temperaturi 21 d. Med fermentacijo smo z metodo izpodrivanja vode merili količino proizvedenega bioplina. Določali smo tudi koncentracijo metana v nastalem bioplinu. Po končanih fermentacijah smo preverjali še vsebnost suhe snovi (total solids – TS) za vsak fermentor.

2.2.3 Analiza

Količino proizvedenega bioplina smo določali z metodo izpodrivanja tekočine. Za meritve koncentracije metana smo uporabljali plinski kromatograf Shimadzu

GC-2010, ki je bil povezan z detektorjem toplotne prevodnosti (thermal conductivity detector – TCD). Ločevanje komponent smo izvedli s kolono HP-PLOT/Q (30 m x 0,32 mm x 20 mm) iz podjetja Agilent. Temperature injektorja, kolone in detektorja so bile 80, 40 in 150 ° C. Razmerje deljenja je bilo 15. Helij smo uporabili kot nosilni plin s celotnim pretokom 19 mL min-1 in tudi kot make-up plin s pretokom 8 mL min-1. Detekcijo smo izvedli pri 50 mA in pozitivni polarnosti. Koncentracijo metana v vzorcih smo določali s primerjavo površin pod pikom metana v vzorcu in v standardni mešanici plinov, ki je vsebovala 10 % metana. Za določanje TS smo material sušili 24 h pri 105 °C.

2.2.4 Kinetični model

Za določitev kinetičnih parametrov proizvodnje CH_4 med anaerobno fermentacijo piščančjega gnoja z žagovino in pred-obdelane in navadne pšenične slame smo uporabili dva različna kinetična modela, tj. kinetični model 1. reda in modificiran Gompertzov kinetični model. Kinetika hidrolize, ki običajno predstavlja najpočasnejšo stopnjo in najbolj vpliva na hitrost anaerobne fermentacije (Kafle and Chen, 2016; Li et al., 2017; Vavilin et al., 2008), naj bi sledila kinetiki 1. reda:

$$-\frac{dc_S}{dt}=k\,c_S \tag{1}$$

kjer je: c_S koncentracija substrata, k konstantna proizvodnosti in t čas. Po preureditvi in integriranju dobimo:

$$\frac{c_S}{c_0}=\exp(-k\,t) \tag{2}$$

kjer je: c_0 začetna koncentracija substrata. Eksperimentalno lažje določimo koncentracijo proizvedenega CH_4 kot koncentracijo substrata. Razmerje med koncentracijo substrata in CH_4 opišemo kot:

$$\frac{c_S}{c_0}=\frac{c_{CH_4max}-c_{CH_4}}{c_{CH_4max}} \tag{3}$$

kjer je: c_{CH_4max} maksimalna koncentracija CH_4. Če združimo enačbi 2 in 3 dobimo:

$$c_{\mathrm{CH_4}} = c_{\mathrm{CH_4max}} \left(1 - \exp(-k\,t)\right) \tag{4}$$

Za določitev kinetike proizvodnje CH_4 je bil uporabljen tudi modificiran Gompertzov kinetični model, ki predvideva, da je kumulativna proizvodnja bioplina v šaržnih fermentorjih posledica hitrosti rasti metanogenih mikroorganizmov (Fu et al., 2018; Kafle and Chen, 2016; Kucharska et al., 2018; Maamri and Amrani, 2014):

$$c_{\mathrm{CH_4}} = c_{\mathrm{CH_4max}} \exp\left(-\exp\left(\frac{r_{\mathrm{CH_4max}} \exp(1)}{c_{\mathrm{CH_4max}}} (t_{\mathrm{L}} - t) + 1\right)\right) \tag{5}$$

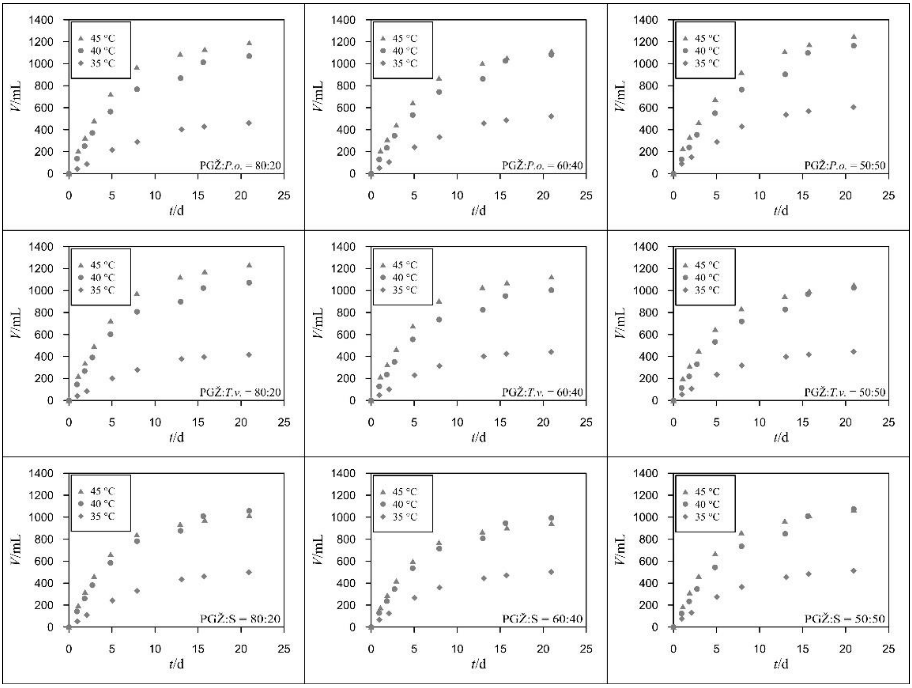
kjer je: c_{CH_4} koncentracija CH_4, c_{CH_4max} maksimalna koncentracija CH_4, r_{CH_4max} maksimalna proizvodnost CH_4, t_L čas lag faze in t čas.

Parametre obeh kinetičnih modelov smo določili z uporabo programske opreme Mathlab.

3 Rezultati

3.1 Prostornina proizvedenega bioplina

Količino proizvedenega bioplina smo merili med anaerobno fermentacijo piščančjega gnoja z žagovino in pred-obdelano ali navadno pšenično slamo. Rezultati pri različnih pogojih so predstavljeni na sliki 1.



Slika 1: Prostornina proizvedenega biolina med anaerobno fermentacijo piščančjega gnoja z žagovino in prehodno obdelano in neobdelano slamo v razčićnih razmerjih.

Na sliki 1 vidimo prostornino proizvedenega bioplina med 21 dnevno anaerobno fermentacijo pri različnih temperaturah, substratih in različnih razmerjih piščančjega gnoja z žagovino in predhodno obdelano ali navadno pšenično slamo. Več kot 1200 mL bioplina se je proizvedlo le pri dveh mešanicah substratov, PGŽ:*P.o.* = 50:50 in PGŽ:*T.v.* = 80:20 pri 45 °C in sicer 1250 mL ter 1234 mL. Pri temperaturi 35 °C se je po 21 d ne glede na substrat proizvedlo več kot 400 mL bioplina. Pri mešanici PGŽ:*T.v.* = 80:20 in 35 ° C se je proizvedlo najmanj bioplina, 417 mL. Na količino proizvedenega bioplina najbolj vpliva temperatura. Vidimo lahko, da je bila količina proizvedenega bioplina najmanjša pri 35 ° C, ne glede na uporabljeni substrat ali razmerje PGŽ in pred-obdelano ali navadno pšenično slamo. Ko smo povišali temperaturo na 40 °C, se je količina bioplina povečala za 2-3 krat, z nadaljnjim povišanjem temperature na 45 °C, se je količina proizvedenega bioplina le rahlo povečala. Če želimo proizvesti veliko bioplina, je učinkovitost višja pri 40 °C kot pri 45 ° C, še posebej, če upoštevamo energijo, ki je potrebna za ogrevanje fermentorjev.

Na začetku poskusa smo posamezni fermentor napolnili z 10 g (suha masa) vsake zmesi in po 21 d smo določili vsebnost suhe snovi (TS) v vsakem fermentorju. Povprečne vrednosti TS pri 35 °C, 40 °C in 45 °C vseh zmesi so bile 8,1 ± 0,8 g, 7,2 ± 0,6 g in 7,2 ± 0,5 g. Rezultati so v skladu s količino proizvedenega bioplina v odvisnosti od temperature. Pri nižji temperaturi je bilo proizvedenega manj bioplina, tako da je ostalo več TS, medtem ko je pri višjih temperaturah nastalo več bioplina. Razlika v TS pred in po fermentaciji je delno posledica nastajanja produktov fermentacije (CH_4, CO_2, drugih plinov, sladkorjev, aminokislin, maščobnih kislin in ocetne kisline) (Zheng et al., 2014), delno pa tudi zaradi eksperimentalne napake, ki izhaja iz nehomogenosti inokuluma in substratov.

3.2 Kinetični model 1. reda

Med anaerobno fermentacijo smo merili koncentracijo CH4. Iz koncentracijskih profilov smo določili kinetične parametre, kar je prikazano v tabeli 1. Kinetični model 1. reda smo uporabili za simuliranje anaerobne fermentacije piščančjega gnoja z žagovino in predhodno obdelano in navadno pšenično slamo pri različnih razmerjih uporabljenih ko-substratov.

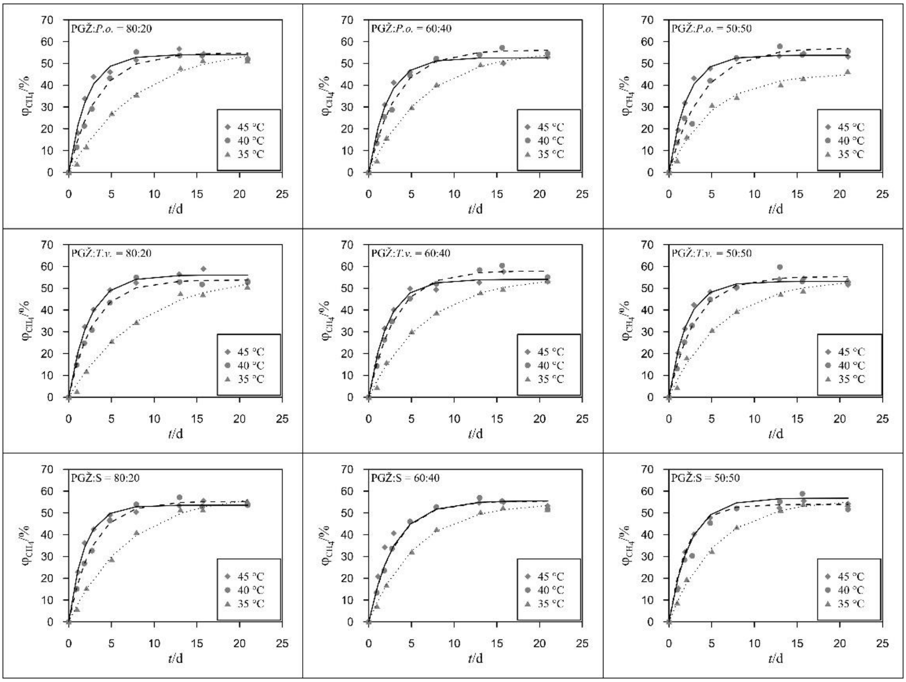
Tabela 1: Parametri kinetičnega modela 1. reda

SUBSTRAT	RAZMERJE	$c_{\mathrm{CH_4}\mathrm{max}}$ %	*k* d^{-1}	SSE	R^2	Adj R^2	RMSE
35 °C							
PGŽ:*P.o.*	80:20	58,09	0,1222	20,74	0,9935	0,9924	1,859
	60:40	56,12	0,1536	8,41	0,9973	0,9969	1,184
	50:50	45,47	0,1966	20,40	0,9907	0,9891	1,844
PGŽ:*T.v.*	80:20	56,58	0,1193	22,84	0,9924	0,9911	1,951
	60:40	55,54	0,1508	10,89	0,9965	0,9959	1,347
	50:50	54,37	0,1625	22,00	0,9927	0,9915	1,915
PGŽ:S	80:20	58,95	0,1417	11,34	0,9966	0,9961	1,375
	60:40	54,62	0,1812	8,28	0,9973	0,9969	1,175
	50:50	56,07	0,1846	7,40	0,9977	0,9973	1,111
40 °C							
PGŽ:*P.o.*	80:20	54,89	0,3001	50,30	0,9854	0,9834	2,681
	60:40	56,13	0,3043	20,29	0,9941	0,9932	1,702
	50:50	57,17	0,2607	79,29	0,9780	0,9748	3,366
PGŽ:*T.v.*	80:20	53,81	0,3432	30,05	0,9904	0,9890	2,072
	60:40	58,00	0,3227	21,02	0,9942	0,9933	1,733
	50:50	55,36	0,3301	40,86	0,9878	0,9861	2,416
PGŽ:S	80:20	55,27	0,3584	21,93	0,9933	0,9923	1,770
	60:40	55,44	0,3353	28,32	0,9917	0,9905	2,011
	50:50	55,55	0,3390	46,80	0,9858	0,9838	2,586
45 °C							
PGŽ:*P.o.*	80:20	54,07	0,4755	46,00	0,9844	0,9822	2,564
	60:40	52,62	0,4538	29,95	0,9894	0,9879	2,069
	50:50	53,76	0,4776	15,18	0,9947	0,9940	1,473
PGŽ:*T.v.*	80:20	56,05	0,4249	23,83	0,9925	0,9914	1,845
	60:40	54,05	0,4477	35,43	0,9880	0,9863	2,250
	50:50	53,10	0,4878	15,57	0,9944	0,9936	1,491
PGŽ:S	80:20	53,54	0,5454	16,08	0,9941	0,9933	1,515
	60:40	53,90	0,4774	15,59	0,9945	0,9937	1,492
	50:50	56,78	0,4132	161,80	0,9430	0,9478	4,808

Kot je razvidno iz tabele 1 in slike 2, se kinetični model 1. reda zelo dobro ujema z eksperimentalnimi podatki.

Konstante proizvodnosti so višje pri višjih temperaturah. Konstanta proizvodnosti pri 35 °C je višja pri višji vsebnosti pred-obdelane ali navadne slame, medtem ko je pri višjih temperaturah neodvisna od vsebnosti slame.

Največja koncentracija CH_4 je bila dosežena med 54,37 % in 58,95 %, razen pri zmesi PGŽ:P.o. = 50:50, kjer je bila samo 45,47 %.



Slika 2: Primerjava med eksperimentalno določenimi koncentracijami CH_4 (točke) in izračunanimi po kinetičnem modelu 1. reda (črte).

Iz dobljenih konstant proizvodnosti pri različnih temperaturah smo določili aktivacijske energije in pred-eksponentne faktorje (tabela 2).

Tabela 2: Aktivacijske energije in pred-eksponentni faktorji za fermentacije pri različnih pogojih

SUBSTRAT	RAZMERJE	E_a / kJ mol^{-1}	k_0 / d^{-1}
PGŽ:*P.o.*	80:20	110,8 ± 19,6	$(8,2 \pm 1,5) \cdot 10^{17}$
	60:40	88,3 ± 12,5	$(1,5 \pm 0,2) \cdot 10^{14}$
	50:50	72,1 ± 15,9	$(3,2 \pm 0,7) \cdot 10^{11}$
PGŽ:*T.v.*	80:20	103,8 ± 38,7	$(5,5 \pm 2,1) \cdot 10^{16}$
	60:40	88,8 ± 19,6	$(1,9 \pm 0,4) \cdot 10^{14}$
	50:50	89,6 ± 14,1	$(2,7 \pm 0,4) \cdot 10^{14}$
PGŽ:S	80:20	109,9 ± 22,9	$(6,9 \pm 1,5) \cdot 10^{17}$
	60:40	79,0 ± 11,6	$(4,7 \pm 0,7) \cdot 10^{12}$
	50:50	65,8 ± 18,7	$(2,8 \pm 0,8) \cdot 10^{10}$

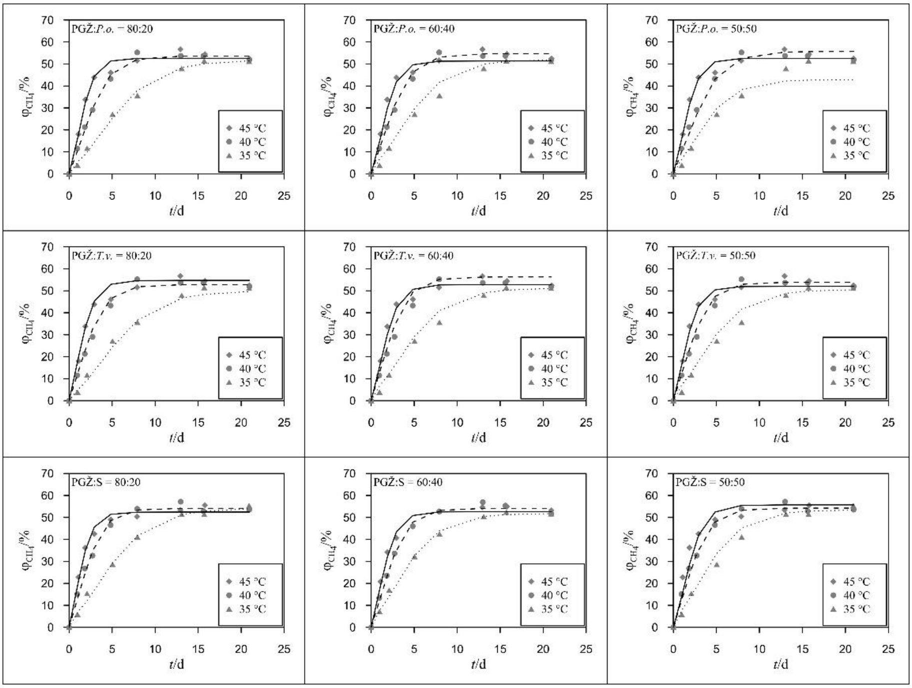
Vrednosti aktivacijskih energij in pred-eksponentni faktorji za različne substrate so zbrani v tabeli 2. Vidimo lahko, da so aktivacijske energije višje pri višji vsebnosti PGŽ substrata, razen za PGŽ:T.v. 60:40 in 50:50, kjer so vrednosti skoraj enake. Predvidevamo, da je to verjetno posledica lažje razgradljivosti slame v primerjavi s PGŽ. Če primerjamo vrednosti, določene za pred-obdelano in navadno pšenično slamo, vidimo, da so pri pred-obdelani slami nekoliko višje vrednosti kot pri navadni pšenični slami.

3.3 Gompertzov kinetični model

Za simuliranje anaerobne fermentacije piščančjega gnoja z žagovino in pred-obdelano ter navadno pšenično slamo v različnih razmerjih PGŽ in predhodno obdelane ali navadne pšenične slame smo uporabili tudi Gompertzov kinetični model. Kinetične parametre smo prikazali v tabeli 3.

Tabela 3: Parametri Gompertzovega kinetičnega modela

SUBSTRAT	RAZMERJE	t_L d	$r_{CH_4 max}$ d^{-1}	$c_{CH_4 max}$ %	SSE	R^2	Adj R^2	RMSE
35 °C								
PGŽ:*P.o.*	80:20	$3,8 \cdot 10^{-1}$	5,49	51,78	21,75	0,9931	0,9904	2,086
	60:40	$7,7 \cdot 10^{-2}$	6,10	52,09	28,78	0,9909	0,9873	2,397
	50:50	$3,1 \cdot 10^{-8}$	6,31	42,85	52,03	0,9762	0,9667	3,226
PGŽ:*T.v.*	80:20	$4,3 \cdot 10^{-1}$	5,31	50,00	27,15	0,9909	0,9873	2,330
	60:40	$5,1 \cdot 10^{-2}$	5,96	51,27	41,39	0,9866	0,9812	2,877
	50:50	$8,2 \cdot 10^{-9}$	6,18	50,62	64,79	0,9784	0,9749	3,286
PGŽ:S	80:20	$8,3 \cdot 10^{-2}$	5,94	54,23	27,40	0,9919	0,9886	2,341
	60:40	$4,3 \cdot 10^{-7}$	6,70	51,85	23,38	0,9925	0,9895	2,162
	50:50	$4,3 \cdot 10^{-11}$	6,91	53,44	47,06	0,9852	0,9827	2,800
40 °C								
PGŽ:*P.o.*	80:20	$9,3 \cdot 10^{-2}$	11,51	53,62	30,23	0,9913	0,9883	2,245
	60:40	$5,6 \cdot 10^{-10}$	11,64	54,65	52,96	0,9845	0,9823	2,751
	50:50	$1,2 \cdot 10^{-10}$	9,99	55,68	103,30	0,9713	0,9672	3,842
PGŽ:*T.v.*	80:20	$5,9 \cdot 10^{-11}$	12,30	52,77	49,96	0,9840	0,9817	2,672
	60:40	$2,7 \cdot 10^{-9}$	12,97	56,28	73,48	0,9797	0,9667	3,240
	50:50	$2,9 \cdot 10^{-10}$	12,54	53,91	69,72	0,9793	0,9763	3,156
PGŽ:S	80:20	$1,1 \cdot 10^{-9}$	13,29	54,14	46,22	0,9859	0,9839	2,570
	60:40	$3,8 \cdot 10^{-2}$	12,85	54,12	33,12	0,9903	0,9870	2,349
	50:50	$2,2 \cdot 10^{-10}$	12,75	54,23	94,88	0,9713	0,9672	3,682
45 °C								
PGŽ:*P.o.*	80:20	$1,7 \cdot 10^{-1}$	19,50	52,60	55,15	0,9813	0,9750	3,032
	60:40	$1,5 \cdot 10^{-1}$	17,64	51,34	31,18	0,9890	0,9853	2,280
	50:50	$9,9 \cdot 10^{-2}$	18,27	52,57	25,09	0,9913	0,9884	2,045
PGŽ:*T.v.*	80:20	$1,0 \cdot 10^{-10}$	16,16	54,74	56,89	0,9820	0,9794	2,851
	60:40	$6,7 \cdot 10^{-2}$	16,95	52,82	50,43	0,9829	0,9772	2,899
	50:50	$5,7 \cdot 10^{-2}$	17,87	52,01	31,67	0,9886	0,9848	2,298
PGŽ:S	80:20	$1,6 \cdot 10^{-2}$	19,71	52,43	50,14	0,9816	0,9755	2,891
	60:40	$2,8 \cdot 10^{-11}$	17,48	52,62	62,45	0,9778	0,9746	2,987
	50:50	$1,3 \cdot 10^{-1}$	16,53	55,73	147,40	0,9584	0,9445	4,957



Slika 3: Primerjava med eksperimentalno določenimi koncentracijami CH_4 (točke) in izračunanimi po kinetičnem modelu 1. reda (črte).

Iz rezultatov statistične analize lahko vidimo, da se oba modela zelo dobro prilegata eksperimentalnim podatkom, vendar je kinetični model 1. reda bolj primeren za opis proizvodnje CH_4 med anaerobno fermentacijo piščančjega gnoja z žagovino in pred-obdelano ali navadno pšenično slamo kot Gompertzov kinetični model. Najnižja vrednost R^2 za kinetični model 1. reda je bila 0,9780, za Gompertzov model pa 0,9713. Slabše prileganje Gompertzovega kinetičnega modela v primerjavi s kinetičnim modelom 1. reda lahko pojasnimo s takojšnjim povečevanjem koncentracije CH_4 na samem začetku fermentacije. Koncentracijski profili CH_4 namreč niso značilne sigmoidne krivulje, ki jih ponavadi opisujejo Gompertzovi kinetični modeli. Na splošno so največje koncentracije CH_4, določene z Gompertzovim kinetičnim modelom, nižje od tistih določenih s kinetičnim modelom 1. reda.

4 Zaključek

Izvajali smo anaerobne fermentacije piščančjega gnoja z žagovino (PGŽ) in pred-obdelano in navadno pšenično slamo pri različnih razmerjih in treh različnih

temperaturah. Pred-obdelavo smo izvedli z glivama bele trohnobe *Pleurotus ostreatus* in *Trametes versicolor*. Tekom fermentacije smo merili količino proizvedenega bioplina in koncentracijo CH_4. Prostornina proizvedenega bioplina je bila nekoliko manjša pri navadni slami v primerjavi z pred-obdelano slamo. Določili smo kinetične parametre proizvodnje CH_4 med anaerobno fermentacijo, ter izvedli primerjavo med eksperimentalnimi podatki in podatki, izračunanimi s kinetičnim modelom 1. reda in modificiranim Gompertzovim kinetičnim modelom. Oba modela se zelo dobro ujemata z eksperimentalnimi podatki. Kinetični parametri se bistveno ne razlikujejo glede na substrat, le vrednosti aktivacijske energije so pri pred-obdelani slami nekoliko višje, kot pri navadni pšenični slami.

Opombe

Javni agenciji za raziskovalno dejavnost Republike Slovenije se zahvaljujemo za sofinanciranje v okviru projekta Načrtovanje trajnostnih in energijsko samozadostnih procesov na osnovi obnovljivih virov, št. L2-7633.

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Potencialna raba prehranskih dopolnil kot zeleni inhibitorji korozijskih procesov

REGINA FUCHS - GODEC

Povzetek S klasično potenciodinamsko metodo smo proučevali inhibitorski vpliv vitamina C, E in K3 na feritno nerjavno jeklo X4Cr13 ter na čisti baker. Kot korozijski medij smo uporabili HCl, kisel dež, ter vodno raztopino NaCl. V primeru Vitamina E in K3 smo s potopitveno metodo formirali hidrofobni sloj na predhodno jedkano kovinsko površino. Ker sta Vitamina E in K3 topna le v maščobah smo površine kovinskih vzorcev modificirali v etanolni raztopini stearinske kisline z dodatkom Vitamina E in K3. Dosežena inhibicijska učinkovitost nastalih hidrofobnih plasti je bila višja od 95%, ponekod celo več kot 99%. Z ozirom na dosežene visoke vrednosti inhibicijske učinkovitosti, bi bilo smotrno preskusiti oziroma narediti tovrstno študijo s prehranskimi dopolnili z zadostno vsebnostjo vitaminov (po pretečenem roku uporabe) v namene korozijske zaščite kovinskih materialov.

Ključne besede: • zeleni inhibitorji • vitamini • korozija • baker • nerjavno jeklo •

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DOI https://doi.org/10.18690/978-961-286-211-4.16 ISBN 978-961-286-211-4
Dostopno na: http://press.um.si.

University of Maribor Press

Potential Use of Dietary Supplements as Green Inhibitors for Corrosion Processes

REGINA FUCHS - GODEC

Abstract The inhibition behaviour of Vitamins C, E in K3 on the ferritic stainless steel type X4Cr13 and on pure copper was studied using potentiodynamic measurements. The corrosive media was HCl, artificially prepared acid rain and NaCl solution. For fabrication of the hydrophobic surface (in the case of Vitamin E and K3) on the stainless-steel and copper surfaces a simple solution immersion method was used. Vitamins E and K3 are fat -soluble vitamins, therefore after chemical etching the specimens were immersed in the ethanol solution of stearic acid (CH3(CH2)16COOH with and without addition of the chosen fat – soluble Vitamin. The inhibitive effectiveness of the chosen metals reached higher values than 95 % in some cases increased to more than 99%. Regarding to the achieved high levels of the inhibition efficiency, it would be appropriate to test also the dietary supplements with sufficient content of vitamins (after the expiry date) as potential corrosion inhibitors for corrosion protection of metallic materials.

Keywords: • green inhibitors • vitamins • corrosion • copper • stainless steel •

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DOI https://doi.org/10.18690/978-961-286-211-4.16 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Uvod

Prehranska dopolnila vse pogosteje predstavljajo pomemben in potreben segment v prehranjevalnih vzorcih tako mlade kot starejše populacije. Med to široko paleto prehranskih dopolnil spadajo tudi vitamini (Vitamin C, Vitamin E, Vitamin D etc.) Vsako prehransko dopolnilo ima določen rok uporabe, po preteku le-ta iz lekarniških polic roma v uničenje, brez pomisleka ali je to edina možna pot in ali možna raba le-teh v druge koristne namene, npr. kot korozijski inhibitorji brez obremenjevanja okolja.

Kovine in njihove zlitine so izmed vseh vrst tehnoloških materialov najpomembnejše in hkrati tudi najuporabnejše. Vendar, kljub vsem svojim posebnim lastnostim, je njihova uporabna vrednost na nek način omejena. Eno izmed največjih ovir predstavlja korozija in materialna škoda, ki spremlja skoraj vsako korozijsko reakcijo. Različni viri pričajo o tem, da se škoda povzročena zaradi korozije iz leta v leto povečuje. Študije NACE poročajo, da je bila v ZDA v letu 2016 ocenjena škoda v višini 1.1 trilijona dolarjev, v letu 2017 pa že 2.5 trilijona dolarjev, kar predstavlja 3.4 GDP. Ekonomski vidik korozije ni le " poškodovan ali uničen material ", ampak posledično vključuje zaustavitev proizvodnje zaradi nenačrtovanih poškodb na opremi. Poleg tega predstavlja grožnjo, ki pa ni osredotočena le na zdravje ljudi, ampak tudi okolju, saj predstavlja svetovni problem skoraj iz vseh zornih kotov. Kisli dež, ki je padal zaradi onesnaženega ozračja v eni državi, onesnažuje okolje, razjeda ter nadalje uničuje material daleč stran od meja te države. Tudi material, ki se odlušči iz korodirane opreme, lahko pride v stik z vodo ali zrakom in če nosi v sebi še toksične primesi lahko kontaminira območja daleč stran od prvotnega mesta. Korozija nikoli ne preneha delovati, vendar lahko njen učinek močno omejimo. Prav zaradi tega je inhibicija zelo pomembna[1-3]. V zadnjih letih se je zahvaljujoč povečanemu zanimanju za ohranitev zdravega in čistega planeta, ter zaradi škodljivih posledic kemikalij na okolje spremenil pristop k izbiri korozijskih inhibitorjev. Strupene inhibitorje, ki se množično uporabljajo v industrijskih procesih, je potrebno nadomestiti z novimi, okolju prijaznimi. Seveda se je potrebno osredotočiti na 'zelene inhibitorje', ki v svoji strukturi pa vendarle vsebujejo značilne funkcionalne skupine, za katere so že poznane inhibitorske lastnosti, ne vsebujejo pa tistih s toksično karakteristiko [4-5]. V raziskavi smo se osredotočili na skupino tako vodotopnih (Vitamin C) kot tudi vitaminov s hidrofobnimi lastnostmi (a-tokoferol in sintetična oblika K3 vitamina). Narejene raziskave so vključevale dodatke že prej omenjenih vitaminov kot čiste komponente z namenom pridobitve osnovnih informacij inhibitornega delovanja omenjenih učinkovin z ozirom na dodane odmerke leteh. Dobljeni rezultati v splošnem prikazujejo pozitiven odziv v smislu inhibicijske učinkovitosti v primeru bakra in nerjavnega jekla. Kot korozijski medij smo uporabili HCl, kisel dež, ter vodno raztopino NaCl. Kisel dež že kar nekaj desetletij predstavlja resen problem v razvitem svetu, saj povzroča škodo na vseh nivojih urbanega življenja; uničuje kovinske strukture (dele stavb, kipe, mostove, cevovode), povzroča zakisanost rek, jezer, potokov kar nadalje vpliva na življenje v vodah, povzroča zakisanost zemlje, ter s tem spremembe za nekatere kulture in še bi lahko naštevali. Velik del kulturne dediščine predstavljajo kipi, katerih osnovni material je baker ali njegove zlitine. Iz tega razloga smo v primeru bakra kot korozivni medij izbrali 'simulacijo' kislega dežja s pH = 5.

2 Eksperimentalni del

Za polarizacijska merjenja smo izbrali klasičen tri-elektrodni sistem in Tacusselovo polarizacijsko celico tipa CEC/TH s termostatiranim plaščem. Vsi potenciali so bili merjeni proti nasičeni kalomelovi elektrodi NKE. Protielektroda je bila iz platine in delovna elektroda iz čistega bakra oziroma iz feritnega nerjavnega jeka (NJ) tipa X4Cr13. Pred vsako meritvijo smo vzorec obrusili z vodobrusnim papirjem različne granulacije, nakar smo jih očistili v ultrazvočni kopeli. Površina vzorca, na katero je učinkovala testna raztopina, je znašala približno 0.785 cm2. Polarizacijske krivulje smo v primeru bakra posneli v mejah od –0.45 V do maksimalno 0.35 V proti NKE, ter od –0.7 V do maksimalno 0.9 V (proti NKE) v primeru nerjavnega jekla.. Potencial je naraščal zvezno s hitrostjo 1 mVs-1. Polarizacijske krivulje smo posneli 30 min po potopitvi vzorca (stabilizacija vzorca na mirovnem potencialu je potekala 30 min). Vse meritve so bile izmerjene pri temperaturi 25 °C +- 1°C. Za potenciodinamska smo uporabili Gamry-ev Potenciostat/Galvanostat/ZRA Reference 600 s pripadajočo programsko opremo s katero smo analizirali dobljene meritve.

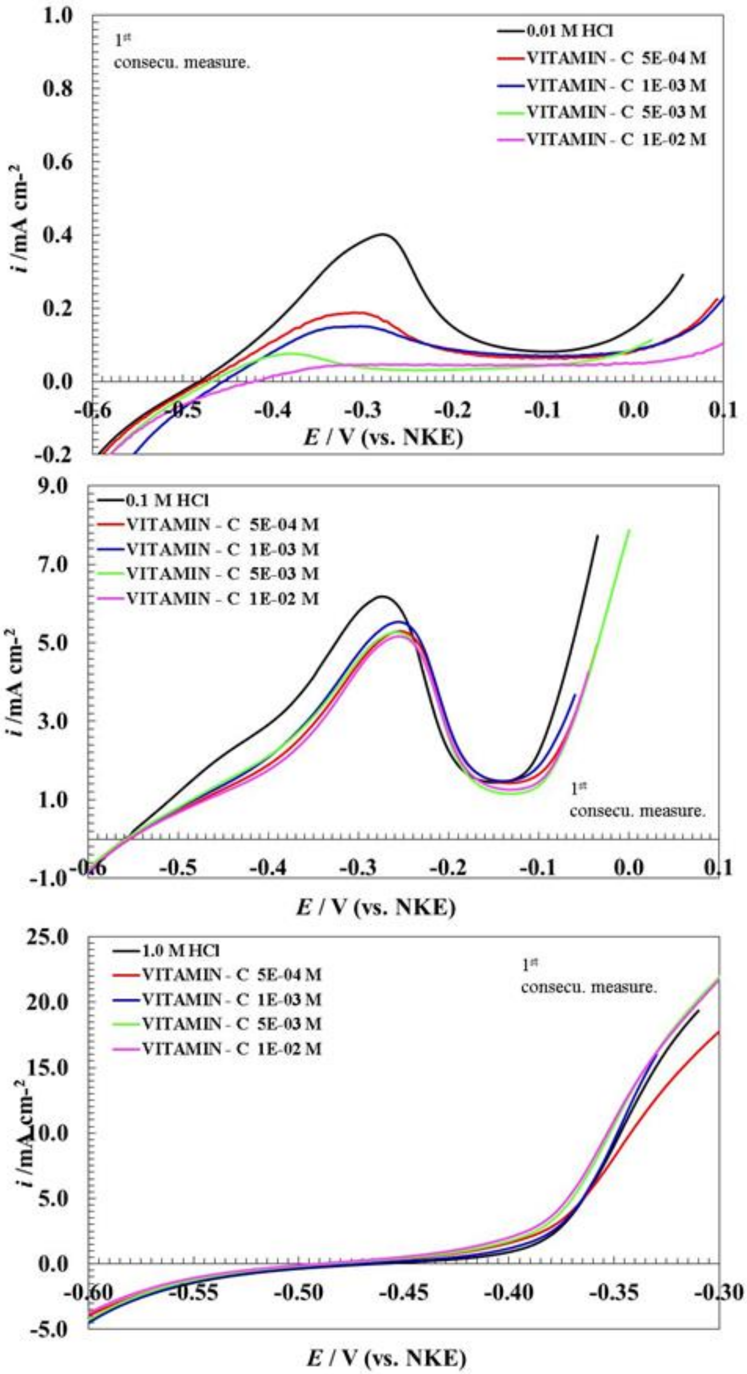
Izbrani korozivni medij je bila 3% raztopina NaCl kisli dež s sestavo; Na_2SO_4, $NaHCO_3$ in $NaNO_3$ z vrednostjo pH= 5, ter klorovodikova kislina. Klorovodikovo kislino smo uporabili kot korodirni medij v primeru proučevanja inhibitorskega vpliva Vitamina C na NJ X4Cr13 in sicer smo izbrali HCl treh različnih koncentracij; c = 0.01, 0.1 in 1.0 mol L-1, medtem ko so bile izbrane koncentracije Vitamina-C naslednje; c = 0.005, 0.001,0.005 in 0.01 mol L-1.

Nadalje smo ta isti material uporabili še kot preizkus obstojnosti v 3% raztopini NaCl (simulacija morske atmosfere), kjer smo proučevali obstojnost hidrofobne prevleke nastale pri potopitveni metodi. V ta namen smo uporabili etanolno raztopino stearinske kisline, ($CH_3(CH_2)_{16}COOH$) s koncentracijo c = 0.05 mol L-1 kateri smo dodali različne koncentracije Vitamina E (a-tokoferol) ; c = 0.5, 1.0 in 2.0 w%. Zaradi izredne inhibicijske učinkovitosti nastale prevleke smo dodatno opravili še teste pri daljši izpostavitvi t.j. po 120 h oz. po 5 dneh.

Kot je bilo omenjeno že poprej so baker in njegove zlitine najpogosteje uporabljeni materiali pri monumentalnih skulpturah bližnje in daljne preteklosti. Kisel dež močno najeda ta del kulturne dediščine. Zato smo v primeru bakra izbrali korodirni medij simulirano obliko kislega dežja s pH = 5. Tudi v tem primeru smo preskušali obstojnost hidrofobnih prevlek nastalih s potopitveno metodo ter enako proceduro kot je bila navedena pri NJ X4Cr13 s to razliko, da smo v primeru bakra naredili hidrofobno prevleko enkrat ob dodatku Vitamina E, ter drugič ob dodatku sintetične oblike Vitamina K3.

3 Rezultati in razprava

Vpliv Vitamina-C za nerjavno jeklo X4Cr13 v raztopini HCl na potek polarizacijske krivulje prikazuje slika 1. Zanimalo nas je tudi, kakšna je stabilnost nastale plasti. Pri vseh krivuljah opazimo, da se z dodajanjem Vitamina C pri koncentraciji HCl c = 0.01 in 0.1 mol L-1 (v nadaljevanju 1M = 1mol L-1) anodni vrh znižuje, s tem pa tudi naboj pod oksidacijskim delom krivulje. Prav tako se znižuje gostota katodnega toka, kar pomeni, da izbrani Vitamin-C spada v skupino inhibitorjev z 'dvojnim delovanjem'. To pomeni, da zavira tako procese raztapljanja, kakor tudi katodno razvijanje vodika. V anodnem delu je moč opaziti manjši plato, ki kaže na pasivacijo površine. Čeprav pa ta vpliv ni tako izrazit, kot je to moč opaziti pri klasičnih inhibitorjih, za katere pa v veliki večini velja, da niso okolju prijazni.



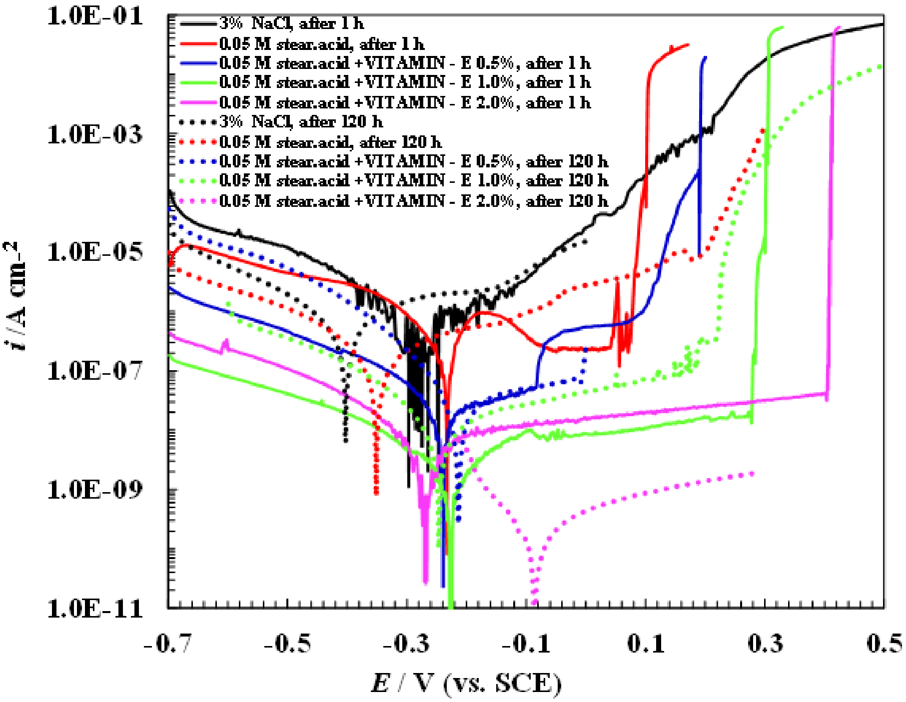
Slika 1: Potenciodinamske polarizacijske krivulje za nerjavno jeklo X4Cr13 v 0.01, 0.1 in 1.0 M HCl pri različnih dodatkih Vitamina C, T = 25 ºC.

Zanimivo je, da se pri koncentraciji kisline c = 1.0 M, anodni vrh ne pojavi več, ampak karakteristični plato, ki obsega potencialno področje□ 100 mV, v katerem lahko pričakujemo stabilnost preskušanega materiala. Če primerjamo korozijski tok icorr dobljen pri c = 0.1M HCl in 1.0M HCl vidimo, da je le-ta nižji pri za red velikosti višji koncentraciji HCl (Tabela 1).

Tabela 1: Karakteristični korozijski parametri za nerjavno jeklo X4Cr13 v HCl; *c* = 0.01, 0.1 in 1.0 mol L^{-1} + x M Vitamin-C.

Corrosive media	E_{corr1} (V vs.SCE)	i_{corr1} ($\mu A\ cm^{-2}$)	R_{p1} ($\Omega\ cm^2$)	r_1 mm y^{-1}
0.01 M HCl + x M	Vitamin C			
0	-0.482	40.13	558.2	0.534
5.0×10^{-4}	-0.468	37.39	717.3	0.511
1.0×10^{-3}	-0.469	31.64	773.2	0.494
5.0×10^{-3}	-0.468	29.28	825.6	0.454
1.0×10^{-2}	-0.468	25.01	1578.1	0.415
0.1 M HCl + x M	Vitamin C			
0	-0.526	456.00	68.14	5.293
5.0×10^{-4}	-0.530	389.83	76.37	4.524
1.0×10^{-3}	-0.534	402.97	66.73	4.676
5.0×10^{-3}	-0.531	489.60	65.15	5.682
1.0×10^{-2}	-0.529	361.14	82.46	4.191
1.0 M HCl + x M	Vitamin C			
0	-0.464	171.43	116.7	1.989
5.0×10^{-4}	-0.482	233.14	85.75	2.703
1.0×10^{-3}	-0.473	226.29	105.2	2.621
5.0×10^{-3}	-0.487	283.09	83.50	3.284
1.0×10^{-2}	-0.492	275.43	80.38	3.190

Polarizacijske krivulje na sliki 2 prikazujejo napetostno tokovni odziv neobdelane in modificirane površino nerjavnega jekla (NJ), X4Cr13 v raztopini 3%NaCl izmerjeno po 60 min (po 1h) stabilizaciji vzorca na mirovnem potencialu, ter v nadaljevanju še po 120 urni izpostavitvi izbranemu korozivnemu mediju. Rezultati meritev po 120 h izpostavitvenem testu kažejo na znatne spremembe tako v katodnem kot v anodnem področju. Zniža se gostota katodnega in anodnega toka. Ta pojav je opazen tudi v primeru neobdelanega vzorca, kar pomeni, da se na površini formira zaščitna pasivna plast. Izračuni inhibicijske učinkovitosti *IE*, ki hkrati kažejo na obstojnost ali ranljivost hidrofobne plasti so prikazani v Tabeli 2. V primeru dodane koncentracije Vitamina E v višini 0.5% se je *IE* po 120 h izpostavitvi znižala le za en odstotek, medtem ko se je v primeru 2% koncentracije dodanega Vitamina E le-ta celo malenkostno povečala. Ne nazadnje se gostota korozijskega toka po 120 h izpostavitvi znižajo za do dva reda velikosti v primerjavi neobdelano površino. Ti rezultati nedvoumno dokazujejo na visoko obstojnost modificirane površine NJ X4Cr13 z izbranim sistemom v 3% raztopini NaCl.

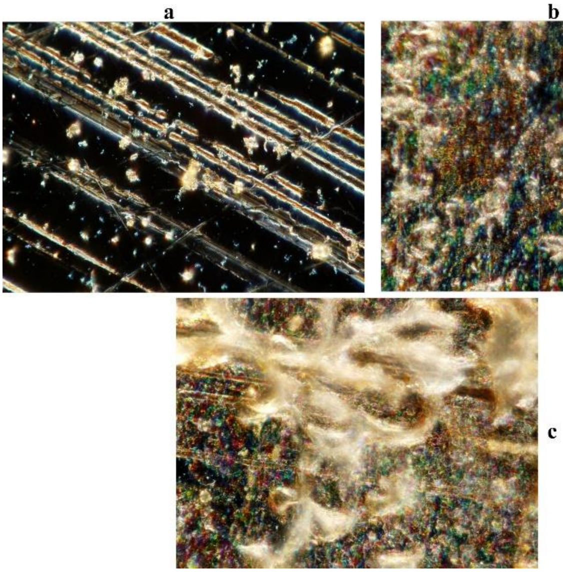


Slika 2: Potenciodinamske polarizacijske krivulje (1mVs-1) za nerjavno jeklo X4Cr13 v 3% NaCl pri 25 °C. Modificirane površine NJ X4Cr13 so bile pripravljene v 0.05M etanolni raztopini $CH3(CH2)16COOH$ z in brez dodatka Vitamina E. (izmerjeno ponovno še po 120 h izpostavitvi 3% NaCl).

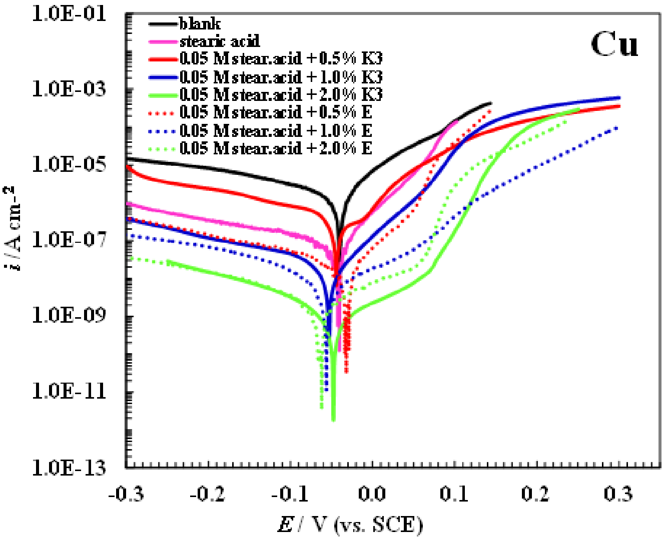
Slika 3 prikazuje mikrostrukturo površine NJ X4Cr13 po enourni potopitvi v korodini medij in sicer, neobdelano, potopljeno v stearinsko kislino, ter potopljeno v stearinsko kislino z dodatkom E-vitamina. V primeru proste, neobdelane površine je moč opaziti prisotnost lokalizirane oblike korozije – točkasta korozija, medtem ko je v primeru modificirane površine opazna precej razgibana struktura, s povečano hrapavostjo, nekateri jo tudi imenujejo struktura 'cvetnih klastrov'. Le-ta s svojo strukturo predstavlja past v katero se lahko 'ujame' večja količina zraka, kar povečuje hidrofobnost površine po eni strani, po drugi pa predstavlja uspešno bariero, ki preprečuje stik kovinskega materiala s korodirnim medijem. Vse to ima odziv v povečanju korozijske inhibicije, *IE* (Tabela 2).

Tabela 2: Karakteristični korozijski parametri za nerjavno jeklo X4Cr13 v 3% NaCl pri 25 °C (izmerjeno po 1 urni izpostavitvi, ter po 120 urni izpostavitvi 3% NaCl). Modificirane površine NJ, X4Cr13 so bile pripravljene v 0.05 M etanolni raztopini $CH_3(CH_2)_{16}COOH$ z in brez dodatka Vitamina E; $c_{\text{Vitamin E}}$ = 0.0, 0.5, 1.0 in 2.0 w%).

Po 1 urni izpostavitvi	i_{corr} ($\mu A cm^{-2}$)	E_{corr} (Vvs.NKE)	R_p ($M\Omega cm^2$)	IE_{corr}	IE_{Ro}
Prosta kovinska površina	0.5935	-0.270	0.022		
Modificirana površina					
0	0.2444	-0.233	0.065	58.82	66.28
0.5	0.0073	-0.238	1.136	98.77	98.01
1.0	0.0017	-0.223	12.44	99.71	99.82
2.0	0.0022	-0.272	6.573	99.63	99.66
Po 120 urni izpostavitvi	i_{corr} ($\mu A cm^{-2}$)	E_{corr} (Vvs.NKE)	R_p ($M\Omega cm^2$)	IE_{corr}	IE_{Ro}
Prosta kovinska površina	0.4760	-0.403	0.054		
Modificirana površina					
0	0.1552	-0.350	0.210	79.00	74.44
0.5	0.0123	-0.213	1.394	98.34	96.14
1.0	0.0086	-0.240	3.032	98.84	98.23
2.0	0.0001	-0.085	132.3	99.98	99.66



Slika 3: Mikrostruktura NJ X4Cr13 po 1 urni izpostavitvi v korozivnem mediju 3%NaCl ob različnih obdelavah (a) neobdelalna površina (b) modificirana površina NJ X4Cr13 po enourni potopitvi v etanolni raztopini stearinske kisline in (c) modificirana površina NJ X4Cr13 po enourni potopitvi v etanolni raztopini stearinske kisline ob dodatku 2% Vitamina E.



Slika 4: Potenciodinamske polarizacijske krivulje (1mVs^{-1}) za baker v raztopini kislega dežja z vrednostjo pH = 5, pri 25 °C. Modificirane površine Cu so bile pripravljene v 0.05

M etanolni raztopini $CH_3(CH_2)_{16}COOH$ z dodatkom sintetične oblike Vitamina K_3 ali z dodatkom α-tokoferola.

Formirana hidrofobna plast na površini čistega bakra prav tako povečuje inhibicijsko učinkovitost kadar je le-ta izpostavljena simulirani obliki kislega dežja (pH=5). Slika 4 prikazuje polarizacijske krivulje t.j. tokovno napetostni odziv v primeru dodanega Vitamina K_3 in Vitamina E (α-tokoferol). Z ozirom na neobdelano, prosto kovinsko površino je v primeru modificirane površine z dodatkom 2.0 w% ali Vitamina K_3 ali Vitamina E padec korozijskega toka za tri velikostne rede, kar daje vrednost inhibicijske učinkovitosti preko 99.0% ali povedano z drugimi besedami, praktično popolno zaščito.

4 Zaključek

Rezultati elektrokemijskih meritev dajejo vpogled v koristno rabo Vitaminov kot zelenih inhibitorjev korozijskih procesov. Poudariti je potrebno, da je v primeru predstavljene preiskave vključena raba več ali manj čistih vitaminov. Z ozirom na dosežene visoke vrednosti inhibicijske učinkovitosti, bi bilo smotrno preskusiti oziroma narediti tovrstno študijo s prehranskimi dopolnili z zadostno vsebnostjo vitaminov po pretečenem roku uporabe v tovrstne namene (protikorozijska zaščita)..

Opombe

Ta raziskava je finančno podprta iz strani ARRS (www.arrs.gov.si) projekt : Fizikalno kemijski pojavi na površinskih plasteh in uporaba nanodelcev (P2-0006.

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University of Maribor Press

Biofuels Production by Torrefaction Process Supplied with Different Biomasses

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Abstract Solid fuel production from different biomass sources become a very challenging area. The paper presents the torrefaction process, mild pyrolysis, where biomass material is converted into solid fuel with higher heating value. The material is processed in inert atmosphere or in the atmosphere with very low oxygen concertation. The study is done for three varied materials, oak wood, mixed wood and dehydrated, granulated sewage sludge. The influence of the temperature is examined, and the optimal temperature is determined. Furthermore, the optimal operation time for each material is evaluated. The experiments were done without flue gases integration. The results show that from energy point of view the optimal operation time for oak and mixed wood is around 1.2 h at 260°C. The torrefaction of sewage sludge is energetically unjustified.

Keywords: • solid fuel • torrefaction • oak and mixed wood • biomass • energetic evaluation •

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DOI https://doi.org/10.18690/978-961-286-211-4.17 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

Biomass is one of the more important sources to produce energy and synthetic fuels, especially in Slovenia being one of the more forested countries in Europe with over 50% of its area covered by forests. Even though biomass is more expensive than coal, the carbon-trading laws are a good motivation for greater usage of biomass. Tenacity of raw biomass is especially challenging, which prevents efficient pulverisation of biomass to use it in higher temperature gasifiers or in boilers of thermal power plants and heating plants. The torrefaction process (mild pyrolysis) is coming to the fore as a possible thermochemical conversion route that enhances the biomass properties obtaining ecologically acceptable energy source, which has similar properties as coal (Correia, Gonçalves, Nobre, & Mendes, 2017; Trop, Anicic, & Goricanec, 2014). Torrefied biomass is hydrophobic, resistant to biodegradation and is suitable for storage. Furthermore, the homogeneity and heating value of torrefied biomass is greater than that of wood. An important advantage of torrefied biomass is also its reduced tenacity. The grind ability of the product is higher and easier milling and application in industrial equipment is achieved(Iroba, Baik, & Tabil, 2017; L. Wang et al., 2017).

Pyrolysis of wood is used mainly for the energetic exploitation, as the product can replace the fossil fuels (van der Stelt, Gerhauser, Kiel, & Ptasinski, 2011). Pyrolysis is a thermal decomposition of organic materials at the inert conditions or at a limited inflow of air. This process leads to a release of volatile substances and the formation of product. Furthermore, waste can be converted to products with high heating value by using the pyrolysis process. It is difficult to achieve an atmosphere totally devoid of oxygen; therefore, oxygen is present in small concertation within every pyrolysis system, causing minor oxidation. The process takes place at a controlled concertation of oxygen, consequently careful reaction control is necessary with options for rapid cooling and heating (Yue, Singh, Singh, & Mani, 2017).

2 Experiment

The comparison between three materials was performed to evaluate the influence of temperature on heating value of the torrefied biomass and to determine optimal operation time according to energy demands.

The first material was oak wood, the second material was dehydrated sewage sludge from waste water treatment plant and the third material was mixed wood. The calorific value and chemical composition for all materials are given in table 1 for raw samples.

Table 1. Properties of raw oak wood

Parameter	Oak wood	Sewage sludge	Mixed wood
GVC/LHV [kJ/kg]	19,074/17,793	15,520/14,421	19,722/18,405
Analytical moisture [%]	10.45	8.5	8.78
Nitrogen [%]	0.34	5.87	0.22
Volatiles [%]	79.12	61.14	49.6
Carbon [%]	48.53	36.59	1.05
Ash [%]	3.24	32.58	6.05
Hydrogen [%]	5.89	5.09	0.02
Sulfur [%]	0.02	0,.8	19,722/18,405

The materials were processed in Bosio electric resistance furnace with nominal power of 2.7 kW. The container was field with the sample and covered with ceramic lid that the inert atmosphere conditions were reached. Ceramic lid was placed in the way that the combustion gasses could discharge.

2.1 The temperature influences

The process started with warm up stage, which took place for 30 minutes, after that stage sample was torrefied for 2 hours at constant temperature. The process continued with cool down stage for 30 minutes when the temperature of the furnace reached 50°C. At the end the sample was cool down to the room temperature. The energy demands were covered by electric power, while the flue gasses were not integrated in the process.

The experiments were done at 220°C, 240°C, 260°C, 280°C, 300°C, 320°C, 340°C and 400°C, according to previous research (Barta-Rajnai et al., 2017; Białowiec, Pulka, Stępień, Manczarski, & Gołaszewski, 2017; Medic, Darr, Shah, Potter, & Zimmerman, 2012; Nanou, Carbo, & Kiel, 2015; Z. Wang, Lim, Grace, Li, & Parise, 2017)]. The analyses of heating value were performed for each sample.

2.2 The optimal operation times

The torrefaction process was performed as it is described in chapter 2.1. The materials were proceeded at 260°C and for different time periods (0.5 h, 1 h, 1.5 h and 2 h) as it is presented on figure 1.

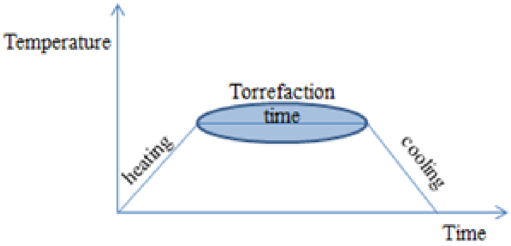

Figure 1: Schematic presentation of the process operation, source: own.

3 Results and discussion

The samples of oak wood, sewage sludge and mixed wood were processed at different condition. The optimal torrefaction temperature was determined at the beginning and in the next step optimal operation time was experimentally specified for each material.

3.1 Temperature

The comparison of higher heating values (GVC) and low heating values (LHV) for torrefied oak wood, sewage sludge and mixed wood at different temperatures are given on figure 2 and figure 3.

Figure 2 presents the values of GVC and LHV for each sample, while on figure 3 the differences between torrefied and raw material are presented.

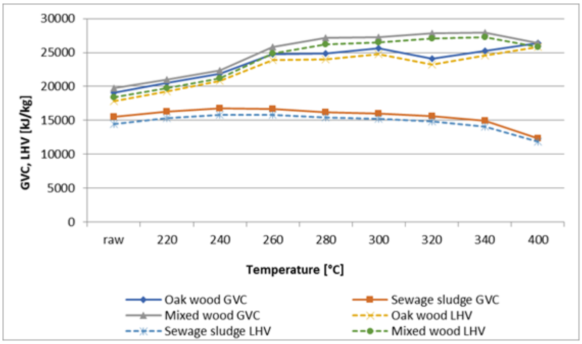

Figure 2. The GVC and LHV for torrefied materials depending on temperature, source: own

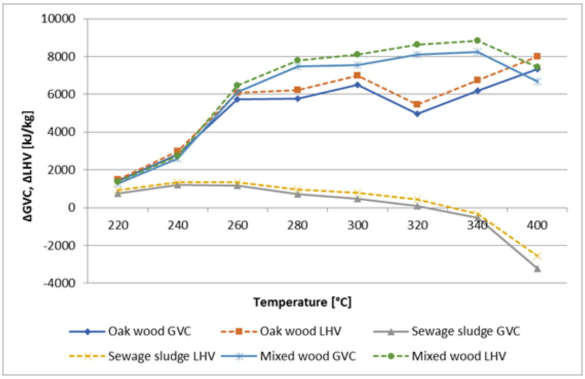

Figure 3. The difference in GVC and LHV depending on temperature, source: own

The heating values increase with raising temperature for both wood samples. The heating values for sewage sludge increases to approximately 320°C, after that temperature are unchangeable or are lower than for raw sample.

Torrefied oak wood samples were more fragile at higher temperatures in comparison to raw or torrefied oak wood samples at lower temperatures. At torrefied sewage sludge samples the changes in fragility could not be detected due to pre-prepared granulates of sludge.

3.2 Operation time

The experiments regarding different operation time of the torrefaction process were proceed at the constant temperature of 260°C according to the results from section 3.1. The temperature was chosen, because of the largest increase of GVC and according to the literature (Barta-Rajnai et al., 2017; Białowiec et al., 2017; Medic et al., 2012; Nanou et al., 2015; Z. Wang et al., 2017). The samples were torrefied for 0.5 h, 1 h, 1.5 h and 2 h at constant conditions and according to literature (Chen, Cao, & Atreya, 2016; Li et al., 2015; Medic et al., 2012; Nanou et al., 2015; Strandberg et al., 2015).

Figure 4 presents GVC and LHV for torrefied materials depending on operation time.

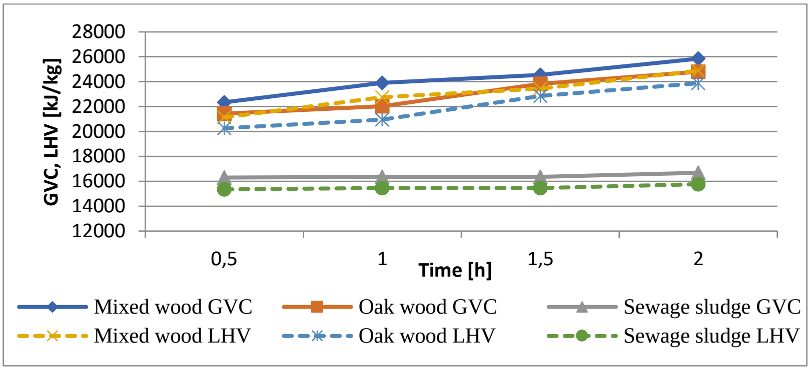

Figure 4. The GVC and LHV for torrefied materials depending on operation time, source: own

The LHV and GVC are increasing with time for oak wood and mixed wood (Figure 4), while the GVC and LHV for sewage sludge is almost the same for different operation time.

Figures 5 present the difference in calorific value between torrefied material and raw material. Also, the invested energy is included, which was evaluated from furnace energy demands, the material mass and operation time.

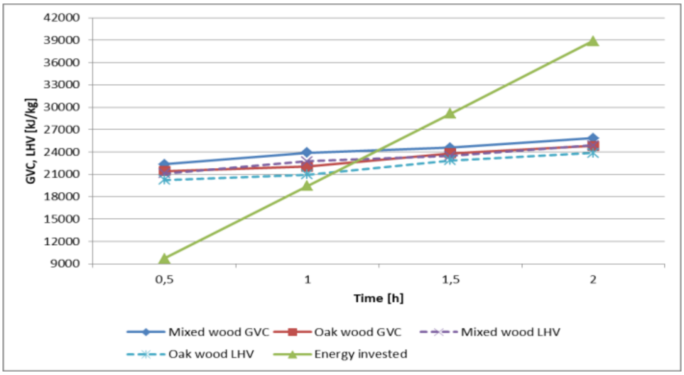

Figure 5: The invested energy, LHV and GVC for mixed and oak wood dependng on operation time, source: own

The results on figure 5 show that the optimal operation time in case of oak and mixed wood is around 1.2 h, because till that time the solid fuel with higher heating value is gained. The operation time could be longer if the flue gases would be integrated for energetic exploitation.

4 Conclusion

The torrefaction of different biomasses was researched and optimal conditions were experimentally determined. Oak wood, dehydrated sewage sludge and mixed wood where processed at different temperatures, but for the same time (2 h) according to torrefaction conditions. The heating value of all materials increases with the temperature. According to the experimental results it was found out that for this material optimal operation temperature is at around 260°C, where the higher increase of heating values is achieved. Similar results are presented in various literature (Chen et al., 2016; Li et al., 2015; Strandberg et al., 2015).

The further research was purposed to determine the optimal operation time of the torrefaction process at previously determined optimal temperature of 260°C. The results show that the torrefaction is favourable for both kinds of wood and it should take place for around 1.2 h, because there is the higher increase of heating values in comparison with invested energy. On the other hand, the results show that from invested energy point of view the sewage sludge torrefaction is not justified in case, if the flue gasses are not integrated in the process.

In a future work, the integration of flue gases in the process will be done and its influence will be evaluated.

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University of Maribor Press

Best Practices for Adopting the Industrial Symbiosis Concept in the Cement Sector

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Abstract The threat of rising energy prices, increased competition for raw materials and the environmental problem of global warming, are major concerns for the European cement industry today. The challenge is to mitigate greenhouse gas emissions and to improve the energy and resource efficiency without reducing competitiveness. In this paper, a review of successful industrial symbiosis case studies in the cement industry was performed with the aim to identify the best industrial symbiosis enabling practices done worldwide. The reviewed sites are assessed based on their current symbiotic exchanges as well as their plans to extend the current industrial symbiosis activities.

Keywords: • circular economy, • industrial symbiosis • cement industry • industrial ecology • by-product synergy •

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DOI https://doi.org/10.18690/978-961-286-211-4.18 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

The long-term goal of the European Union's (EU) 2050 Energy Strategy is to reduce greenhouse gas (GHG) emissions by 80-95%, when compared to 1990 levels, by 2050. The low-carbon transition of the cement industry is vital for achieving this goal, as cement production accounts for 5% of global anthropogenic CO_2 emissions [1]. For instance, the production of 1 ton of Portland cement requires approximately about 1.5 tonnes of raw materials, 920-1200 kWh of thermal energy, and 100-120 kWh of electrical energy; and emits more than 0.9 ton of CO_2 [2].

Over the last decades, cement production has undergone several modifications and improvements to reduce the energy consumption and CO_2 emissions, however further reduction is still required to secure the future sustainability of this vital industry. Among different pathways to achieve CO_2 emission reduction, more and more attention has been paid to industrial symbiosis, a systems approach which aims at a win-win between environmental and economic performances through physical exchanging of waste and by-products and infrastructure sharing among co-located entities.

This paper aims to identify the best industrial symbiosis enabling practices for the cement industry, based on a review of successful industrial symbiosis case studies in the cement sector worldwide.

2 Methodology

A detailed literature search was carried out by initially selecting several keywords. Apart from cement sector related keywords, e.g. cement plant/mill, clinker, Portland cement etc., the following keywords were included: industrial symbiosis, industrial ecology, by-product synergy, eco-industrial park, and circular economy, whereby the Boolean operator "AND" was used to include several keywords in one search. No geographical limitations were applied. Search engines used included databases such as Web of Science and Scopus, as well as publisher-specific search engines such as ScienceDirect, SpringerLink, Wiley Online Library, IEEE Xplore, JSTOR, Emerald, Sage Journals, Oxford Journals etc., and freely accessible search engines, such as ResearchGate and Google Scholar.

2.1 Case study description

In total, 16 cement producer sites involved in IS activities, from 9 different countries and 4 continents, were analysed (Table 1). The majority, i.e. more than 56%, of the considered cement works are located in Asia, of which 7 reside in China as the world's largest cement consumer [3]. Among the rest of the studied cement plants 4 operate in the EU. All cement plants reside in proximity of urban areas, varying in size from 8.5 thousand (Dunbar) to 7.5 million inhabitants (Tangshan). The reviewed cement mills range from 330 thousand to 5 million tons of yearly cement production.

Table 1: Reviewed case studies

Site	Production (kt/a)	No. of IS activities	References
Aalborg (DNK)	3550	10	[4], [5]
Dunbar (UK)	1000	4	[6]
Gladstone (AUS)	1700	3	[7]
Guitang (CHN)	330	3	[8]
IJmuiden (NLD)	1400	1	[9]
Jinan (CHN)	1800	1	[10]
Kawasaki (JPN)	620	7	[11]
Kwinana (AUS)	850	6	[12]
Liuzhou (CHN)	700	1	[10]
Midlothian (USA)	900	3	[13], [14]
Pohang (KOR)	1500	3	[15]
Rizhao (CHN)	1000	3	[16]
Tangshan (CHN)	1400	1	[17]
Taranto (ITA)	900	3	[18]
Wu'an (CHN)	5000	4	[19]
Zaozhuang (CHN)	2200	3	[20]

3 Results and Discussion

3.1 Cross-sectorial synergies

Among the analysed symbiotic activities with the considered cement plants, 14 or 25% (Figure 1) involve the steel sector. In all cases expect one, i.e. in Kwinana where lime kiln dust (LKD) is being sold to the nearby pig iron plant for flue-gas desulfurization, the involved steel mills act as the donor of the shared stream. The most frequently occurring synergetic exchange is the use of blast furnace slag (BFS) and steel slag (STS) as clinker substitute for cement production, as it is present in 9 out the 16 analysed sites (Table 2). The reuse of slags from steel production does not only enhance the properties of cement, i.e. durability due to an increased setting time [21], but also has significant economic and environmental benefits, since up to 80% less energy is required than for the production of ordinary Portland cement [22]. Hence, it is not surprising that the largest documented stream exchange (Tangshan – 4 Mt/a) as well the most substantial economic advantage of 6.74 mio € (Kawasaki) in this review can be attributed to STS and BFS valorisation. BFS and STS are followed by mill scale, which is being used as an alternative iron oxide source in 14% of the IS cases involving the steel sector. There is also one document case of wastewater (WW) sludge utilisation as an alternative cement kiln fuel (Pohang).

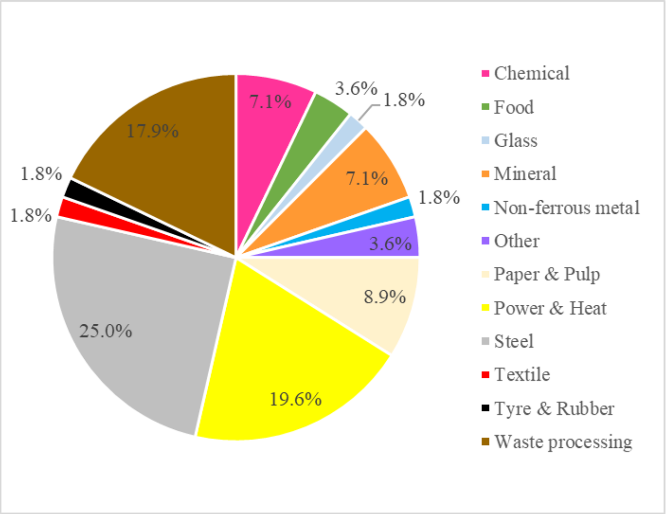

Figure 1: Sectors involved in IS activities with the reviewed cement plants

Table 2: IS activities involving the steel sector

Site	IS activity	Stream	Magnitude	Benefit
IJmuiden	Clinker substitute	BFS	1.4 Mt/a	-
Jinan	Clinker substitute	BFS	1.2 Mt/a	-
Kawasaki	Clinker substitute	BFS	315 kt/a	6.74 mio €/a
Kwinana	Desulphurization	LKD	-	-
Liuzhou	Clinker substitute	STS	1.2 Mt/a	CO_2 reduction 660 kt/a
Midlothian	Clinker substitute	STS	130 kt/a	10% production increase, 11.8 kt/a coal saved
	Alt. raw material	Mill scale	-	-
Pohang	Clinker substitute	BFS	-	-
	Clinker substitute	STS	-	-
	Alternative fuel	WW sludge	-	-
Tangshan	Clinker substitute	STS	4 Mt/a	-
Taranto	Clinker substitute	BFS	0.23 Mt/a	-
	Alt. raw material	Mill scale	5.1 kt/a	-
Wu'an	Clinker substitute	BFS	3870 kt/a	-

The second most common symbiont of the considered cement sites is the power & heat sector (Table 3). In this case, fly & bottom ash recycling of coal fired power and CHP plants is the most conventional activity, i.e. 64% of the document exchanges involving the energy sector, as the reuse of one ton of fly ash (as well as BFS/STS) in cement leads to an equivalent reduction of about 770 kg of CO_2 [7]. Furthermore, fly ash adds strength and durability to concrete, as the concrete is more dense and therefore less prone to decline due to contact with sulphur [21]. An indirect combustion by-product, which is also being utilized as secondary raw material on two sites (Aalborg and Wu'an), is FGD gypsum, a by-product of flue gas desulfurization (FGD). The plant in Aalborg also supplies chalk slurry as a desulfurization agent to the partnering power plant. The same plant is also the only cement work that recovers its waste heat for feeding the local district heating (DH) network (335 GWh/a), which is the only documented energy exchange in this study.

Table 3: IS activities involving the power & heat sector

Site	IS activity	Stream	Magnitude	Benefit
Aalborg	Clinker substitute	Fly ash	200 kt/a	-
	Alt. raw material	FGD gypsum	57 kt/a	-
	Waste heat for DH	Excess Heat	335 GWh/a	-
	Desulphurization	Chalk slurry	10 kt/a	-
Dunbar	Clinker substitute	Fly & bottom ash	500 kt/a	
Gladstone	Clinker substitute	Fly ash	40 kt/a	-
Rizhao	Clinker substitute	Fly ash	66 kt/a	-
Taranto	Clinker substitute	Fly ash	38 kt/a	-
Wu'an	Alt. raw material	FGD gypsum	20 kt/a	-
	Clinker substitute	Fly ash	35 kt/a	-
Zaozhuang	Clinker substitute	Fly & bottom ash	-	-

Cement production is an energy intensive process with fuel accounting for about one-third of the costs for producing clinker [23]. The main energy consumer is the cement (rotary) kiln, which generates thermal energy by burning fossil fuel, primarily coal, for the calcination (900°C) and sintering (1450°C) processes. The rotary kiln used in cement manufacturing is able to burn a wide range of materials due to the long residence time at high temperatures, the intrinsic ability for clinker to absorb and lock contaminants into the clinker and the alkalinity of the kiln environment [24]. Therefore, most of the activities with the waste processing sector, i.e. 80 %, circle around the utilization of collected and processed wastes as an alternative cement kiln fuel (Table 4). This enables the participating cement actors to remain economically competitive and, in case of organic wastes

(Aalborg, Kawasaki), to reduce their CO_2 emissions. Apart from valorising its caloric value, waste is also used as a secondary raw material, such as the reuse of WW sludge for limestone substitution in Kawasaki.

Table 4: IS activities involving the waste processing sector

Site	IS activity	Stream	Magnitude	Benefit
Aalborg	Alternative fuel	Dried WW sludge	4000 t/a	-
	Alternative fuel	Industry waste	-	-
Dunbar	Alternative fuel	Recycled liquid fuel (RLF)	22 kt/a	40 kt/a coal saved
Gladstone	Alternative fuel	Solvent based fuels	2500 m^3/a	-
Kawasaki	Alternative fuel	Waste plastics	6.75 kt/a	9.1 kt/a coal saved
	Alternative fuel	Organic waste	14.86 kt/a	-
	Alternative fuel	Soot, other burned residue	0.7 kt/a	-
	Alt. raw material	Construction soil	-	-
	Limestone substitution	WW sludge	20 kt/a	55 kt/a limestone saved
Midlothian	Alternative fuel	Waste plastics	-	-

The main disadvantage of secondary raw material such as BFS (Table 2) and fly ash (Table 3) is the potential reduction in their availability in enough quantities for cement production, with the expected decline in the use of coal in power & heat generation and steel manufacturing (secondary steelmaking). On the other side, the generation of paper sludge, a by-product of pulping, papermaking, and deinking processes, is expected to increase due to higher paper recycling rates (e.g. 300 kg sludge per ton of recycled paper generated [25]). Since paper sludge consists primarily of cellulose fibres and fillers such as calcium carbonate and kaolinite, it can be used to substitute limestone (Aalborg) and clay (Kawasaki). An additional alternative calcium source for clinker production is also white or lime sludge (Guitang, Rizhao), which is usually utilised in the paper mill on-site in the lime oven. Additionally, in Rizhau (Table 5) fly ash from the coal fired boiler of the pulp and paper plant is being send to the neighbouring cement plant.

Table 5: IS activities involving the paper & pulp sector

Site	IS activity	Stream	Magnitude	Benefit
Aalborg	Alt. raw material	Paper sludge	1700 t/a	-
Guitang	Alt. raw material	White sludge	-	-
Kawasaki	Clay substitution	Paper sludge	16.8 kt/a	263 kt/a clay saved
Rizhao	Clinker substitute	Fly ash	66 kt/a	-
	Alt. raw material	White sludge	70 kt/a	-

Due to the nature of the raw materials used and the manufacturing processes involved in the production of minerals (quarrying, crushing, grinding, drying), only material exchanges, in form of alternative raw materials, are present between the mineral and cement sector (Table 6). Although the sectors share some common raw materials, such as limestone, the shared streams originate primarily from the mineral site, as the latter has significantly higher quality and purity requirements as the cement sector. The only symbiotic activity in which the involved cement plant acts as a donor, is the valorisation of LKD from the cement and lime mill in Kwinana for chlorine removal in the adjacent pigment factory.

Table 6: IS activities involving the mineral sector

Site	IS activity	Stream	Magnitude	Benefit
Kwinana	Alt. raw material	Shale	-	-
	Clinker substitute	BFS	-	-
	Chlorine removal	LKD	-	-
Wu'an	Alt. raw material	Limestone and sandstone fines	1200 kt/a	-

As the chemical industry is more diverse than any other process industry, it comes as no surprise that all of the reviewed IS activates revolving around the chemical sector feature a different shared stream (Table 7). Aalborg Portland, for example, buys iron oxide (pyrite ash) from a sulphuric acid manufacturer and reuses bone mean from a biodiesel plant as alternative cement kiln fuel, while the Kwinana cement plant valorises the spend residue cracking unit (RCU) catalysts from the nearby refinery as a an alternate pozzolan (Si, Al). On the other hand, the cement mill in Zaozhuang receives bottom and fly ash from the coal fired boilers of an ammonia plant.

Table 7: IS activities involving the chemical sector

Site	IS activity	Stream	Magnitude	Benefit
Aalborg	Alt. raw material	Iron oxide	45 kt/a	-
	Alternative fuel	Bone meal	-	-
Kwinana	Alt. raw material	Spend RCU catalysts	-	-
Zaozhuang	Clinker substitute	Bottom & Fly Ash	-	-

More particular IS activities (more than 14%) involve actors from a variety of different sectors, e.g. from food and textile to rubber, glass and non-ferrous metal (Figure 1). A very interesting case is the utilization of sand dredged from the Limfjord fjord in Aalborg (Table 8). Recycled sand and glass from a glass factory is also used in the Dunbar cement mill, which at the same time reuses the scrap tires from a tire plant as an alternative cement kiln fuel. In Gladstone the spent cell linings (SCL) from aluminium smelter are valorised both as alternative fuel and raw material in clinker production. Vice-versa the cement works in Kwinana sells its LKD to various companies for soil conditioning. In contrast to the other analysed sites, a sugar refinery is the main facilitator of IS in Guitang. Namely, it sends both filter sludge and fly ash to the neighbouring cement plant.

Table 8: IS activities involving other sectors

Site	IS activity	Stream	Magnitude	Benefit
Aalborg	Alt. raw material	Sand from dredging	80 kt/a	-
Dunbar	Alt. raw material	Recycled glass/sand	-	
	Alt. fuel	Scrap tires	20 kt/a	41 kt/a of coal saved
Gladstone	Alt. fuel & raw material	SCL	12 kt/a	-
Guitang	Alt. raw material	Filter sludge	-	-
	Clinker substitute	Fly ash	-	-
Kwinana	Soil conditioning	LKD	-	-
Zaozhuang	Clinker substitute	Bottom & Fly Ash	-	-

3.2 Future plans

5 out of the 16 analysed cement sites have future plans to extend their current IS activities (Table 9). As with the already successfully implemented symbiotic exchanges, most cement plants aim to introduce new supplementary cementitious materials (Gladstone, Liuzhou) or alternative raw materials (Kwinana, Liuzhou) in order to reduce their production costs. In Kwinana, for instance, there are proposals to reuse the spent graphite electrodes of a steelmaker's electric arc furnace (EAF) as a secondary raw material. On the other hand, two plants, i.e. IJmuiden and Zaozhuang, intend to lower their GHG emissions by using excess steam from the neighbouring industries as an

alternative energy source. Another interesting idea from the IJmuiden site is the proposed sharing of the residing steel mill's wastewater treatment facility with the adjacent cement works. The cement plant in Kwinana is also thinking about lowering its fresh water consumption by using wastewater from the nearby treatment facility as process and/or washing water.

Table 9: Future plans to extend the IS activities of reviewed cement sites

Site	IS activity	Stream	Symbiont
Gladstone	Clinker substitute	BFS	Steel
IJmuiden	Alt. energy source	Excess steam	Steel
	Facility sharing	WW treatment	Steel
Kwinana	Alt. raw material	Spent graphite electrodes	Steel
	Alt. energy source	Excess steam	Non-ferrous metal
	Alt. raw material	FGD gypsum	Non-ferrous metal
	Alt. water source	WW	Waste processing
Liuzhou	Clinker substitute	Fly ash	Power & Heat
Zaozhuang	Alt. raw material	FGD gypsum	Power & Heat

3 Conclusion

In order to preserve its competitiveness and retain the current number of work places in the European cement industry as well as to meet stricter emission standards (e.g. Paris Agreement) the implementation of industrial symbiosis activities is an unavoidable measure. In this paper, a review of successful industrial symbiosis case studies in the cement industry was performed. In total, 16 cement manufactures, from 9 different countries, were analysed.

While IS activities in 9 of the considered sites were induced though government initiatives, like the Chinese Five-year Development Plan, the Japanese Eco-Town program or the South Korean EIP initiative, the rest of the documented symbiotic connections were formed spontaneously by the motivation of cost reduction. The number of IS exchanges per site varies between 10 in and 1 (Table 1), with an average value of 2.8 for sites with government initiated IS and 4.3 for sites with spontaneously formed IS activities. Hence, there is no obvious correlation between the number of exchanges and the IS driving factor.

In 46 out of the 56 documented IS activities across 16 sites, i.e. in more than 82%, solids are being exchanged between the involved actors. They are followed with a wide margin by liquids and chemicals with 12.5% and 3.6%, respectively. On the other hand, the most rarely exchanged stream type is energy, i.e. only one case. The latter seems like an untapped opportunity with regard to the available excess heat (35% of primary energy use [26], 100-450 °C [27]). However, there are two main factors limiting the expansion of waste heat valorisation. First, since cement manufacturing is an energy intensive process, most waste heat is utilized internally on site, e.g. combustion air preheating, drying, etc. This is also the most cost effective and energy efficient way, since heat and pressure losses limit the proximity and temperature level of potential heat sinks (e.g. maximal distance between a heat source and district heating network about 30 km). One approach to overcome this barrier is to use excess heat to produce electricity, which can not only be transferred over significantly longer distances with minor losses but can also be converted to an arbitrary form of energy at the receiver site. This can be achieved with the application of the organic Rankine cycle (ORC) and the Kalina cycle, which are Rankine based cycles, for converting heat to electricity.

The above-mentioned limitations of energy streams partly explain the widespread exchange of solid streams, since apart from their abundancy (e.g. slag generation approximately 10–15% of crude steel output) they can also be easily transported outside the site of origin or the corresponding industrial park borders due to their easily manageable (stable) characteristics, and lower hazard and risk potential, especially compared to other stream types. The most commonly shared streams include fly ash from coal fired boilers and furnaces, and BFS/STS from the steelmaking industry (11 documented cases each). As both of these by-products can be used to substitute cement clinker, their use cannot only reduce the cost for raw material but, more importantly, significantly decrease the energy consumption and consequently the GHG emissions of a cement plant, i.e. the clinker calcination process represents about 90% of total energy use during cement manufacturing. On the other side, the potential disadvantage of BFS and fly ash is the probable reduction in their availability in sufficient quantities for cement production, with the expected decline in the use of coal in energy generation and steel manufacturing (EAF route). Therefore, paper sludge represents an attractive alternative, as its generation is expected to increase due to higher paper recycling rates.

Another major opportunity to lower the production costs of cement is the use of alternative cement kiln fuels, especially those of biogenic origin, such as WW sludge, that also enable a reduction of GHG emissions. A different approach to lower CO_2 emissions, is to apply carbon capture and storage (CCS) technologies as for example calcium looping [28], which can be used to capture the CO_2 released during the calcination process. The captured CO_2 could then be stored and sold to industries that directly utilize CO_2, e.g. as carbonating agent, preservative, packaging gas etc.

Acknowledgments

The research leading to these results has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement no. 679386, EPOS project. The sole responsibility of this publication lies with the authors. The European Union is not responsible for any use that may be made of the information contained therein.

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University of Maribor Press

Integrated Facility for Power Plant Waste Processing

PAULA MANTECA & MARIANO MARTÍN

Abstract In this work a process has been developed for the transformation of gypsum, a byproduct of the desulfurization within coal based thermal plants, into sodium sulphate. The process consists of the synthesis, the crystallization of sodium sulphate and the possibility of producing the hydrated and/or the anhydrous crystal. This section is integrated within the desulfurization unit by processing the residue and regenerating a fraction of the raw material required, $CaCO_3$. The optimal operating conditions for the evaporation and crystals recovery has been computed using a mathematical programming approach. The economics of the process is attractive to produce the anhydrous crystal, 0.21 €/kg with an investment of 36 M€, as well as for the production of the decahydrated sodium sulpahte, 0.06 €/kg and 26 M€ of investment, processing the gypsum of a 350 MW power plant.

Keywords: • Desulfurization • Gypsum • Solvay • Mathematical optimization • Sodium sulfate •

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DOI https://doi.org/10.18690/978-961-286-211-4.19 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

Power plants are responsible for a fair share of the total power production in any country. The flue gas produced contains a number of pollutants such as SO_2, NOx and a large amount of CO_2. The current regulations limit the emissions of these chemicals. The removal of SO_2 can be performed using various technologies including wet scrubbers, the most used one representing about 85% of all the desulfurizers installed, spray driers, installed in around 12% of the facilities, while 3% use dry injection systems (EPA, 2003) The most common process adds lime and air so that the SO_2 is oxidized and transformed into $CaSO_4$ that precipitates Gypsum from desulfurization could be used in the construction industry. However, the slowdown of the construction industry and the availability of natural product have resulted in an excess of gypsum that represents an environmental challenge due to the large amounts of gypsum that need to be disposed of.

Within the concept of circular economy, gypsum as a waste can be used for the production of sodium sulphate, a product of interest in the pulp and paper industry as well as in the detergents, the glass and the textile industries but also as a raw material for the production of other chemicals such as potassium sulphate, sodium silicate, etc.

In this work, a systematic approach based on mathematical optimization has been performed to design a process that generates sodium sulphate out of gypsum.

2 Process description

The production of sodium sulfate starts with mixing the gypsum and sodium carbonate. While the gypsum is already in the form of fine power, sodium carbonate must be milled for the reaction to take place. The salt particle size is to be reduced to 15 mm (Trendafelov et al., 1995). The reaction takes place at 25°C as follows, obtaining 98% of conversion when using an excess of sodium carbonate.

$$\mathrm{CaSO_4} + \mathrm{Na_2CO_3} \rightarrow \mathrm{CaCO_3} \downarrow + \mathrm{Na_2SO_4}$$

Calcium carbonate precipitates and can be separated using a centrifuge. We can use this precipitate and reuse it to capture SO_2, intensifying the current flue-gas desulfurization process. The presence of residues of sodium carbonate prevent from full recovery of the sodium sulphate. Alternatively, $Ca(OH)_2$ can be used to precipitate the sodium carbonate as calcium carbonate. This alternative is to be evaluated within the design procedure. Next, the solution is sent to a multi-effect evaporator system to concentrate the sulfate and crystallize. The high energy intensity of the process requires integration in the form of a multi-effect evaporation system. Finally, the crystals can be dehydrated in a furnace. Figure 1 shows the flowsheet for the process.

$$Na_2SO_4 \cdot 10H_2O \rightarrow Na_2SO_4 + 10H_2O$$

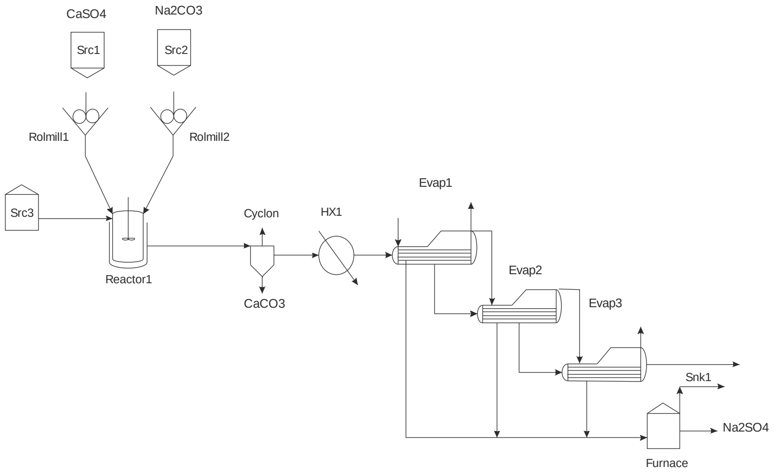

Figure 1: Process flowsheet.

3 Design procedure

The first consideration to comment about is related to the difficulty of crystallizing $Na_2SO_4 \cdot 10H_2O$ in presence of $Na_2CO_3 \cdot 10H_2O$. They both can precipitate together since their solubility is similar. However, note that the presence of the carbonate in the solution is due to the excess provided to reach the 98% conversion reported in the literature. Therefore, the concentration is low. Two alternatives are considered. First, the precipitation of the carbonate in the form of $CaCO_3$ using $Ca(OH)_2$. A preliminary study was carried out comparing the additional profit due to the total recovery of the sulfate. The second alternative consists of recovering the sodium sulphate until both are in the same concentration since the solubility of both, $Na_2SO_4 \cdot 10H_2O$ and $Na_2CO_3 \cdot 10H_2O$ is similar. Two non linear programming (NLP) problems are solvede per alternative. Each one has around 500 variables and 315 eqs. The objective function is a simple profit given as eq. (1)

$$Z=P_{Na2SO4} \cdot fc_{(Na2SO4)} -(P_{GN}) \cdot (Q('Furnace1')+Q('HX1')+Q('Evap1')) -P_{CaOH2} \cdot fc_{(CaOH2)} \quad (1)$$

The second step in the design of the process is related to the number of evaporators. The larger the number of effects, the higher the steam economy. The trade-off is the investment cost. A NLP optimization problem is set up for systems consisting in 1, 2, 3 and 5 evaporator effects. The size of the problem reaches up to around 900 variables and 600 variables when five effects are used using an objective function as given by eq. (1)

4 Results

4.1 Process synthesis

A preliminary study was carried out comparing the additional profit due to the total recovery of the sulfate versus assuming the losses of sodium sulfate in the solution. The high cost of $Ca(OH)_2$, the fact that only an additional 10% recovery of crystals and that gypsum is currently a waste, does not recommend the use of $Ca(OH)_2$.

Next, NLP's optimization problems are set up for systems consisting in 1, 2, 3 and 5 evaporator effects. As expected, the heat load associated decreases with the number of effects while the investment increases but it reaches a plateau which results in the selection of 5 effects.

4.2 Process operation

The design procedure yields a process that consists of the mixing of the reactants, the synthesis, the recovery of calcium carbonate and the crystallization of the sodium sulphate. The first unit only evaporates water and no sulphate is recovered. The second one recovers 7% of the total sulfate and the last three affects almost recover 30% each. The recovery increases as we progress on the number of effects.

The power consumption adds up to 1.2 MW, while the thermal energy corresponds to 40.9 MW with 20% consumed in heating up the solution, 35% in the evaporators system and the rest to dehydrate the sulfate.

4.3 Economic evaluation

The equipment cost is estimated by performing a short-cut sizing of the units involved such as mills, reactor, heat exchanger and multi-effect evaporator system and furnace. The factorial method (Sinnot, 1999) is used to estimate the investment in 36 M€. The raw materials cost account for 2.9M€/yr, utilities add up to 9.7 M€ /yr and labor represents 0.4 M€ /yr. As a result, the production cost results in 0.21 €/kg. Typical costs of sodium sulphate are below 0.2 €/kg (Valmet, 2015). Therefore, renewable sodium sulphate is competitive with regular sodium sulphate.

If hydrated sodium sulphate is sold as such, the price decreases due to savings in water removal at the furnace, around 4.5 M€/yr, and the fact that the product contains water. The facility investment cost without the furnace adds up to 26M€. As a result the production cost decreases down to 0.06€/kg

Acknowledgments

TCUE program for the grant to PM and JCyL grant SA026G18

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LIFE B.R.A.V.E.R. – Povečanje zakonskih prednosti v korist EMAS sistemu

KLAVDIJA RIŽNAR, DUŠAN KLINAR, GREGOR UHAN IN DANILO ČEH

Povzetek Evropska komisija je leta 2015 sprejela akcijski načrt za spodbujanje prehoda Evrope v krožnemu gospodarstvo. Za proizvodne procese je evropski sistem za okoljsko ravnanje in presojo (EMAS) priznan kot pomemben okoljski instrument za izvajanje krožnega gospodarstva. Uporaba EMAS dokazuje njegovo učinkovitost pri izboljšanju okoljske uspešnosti organizacij in podpiranju gospodarskih ciljev. Uredba EMAS navaja, da države članice Evropske unije (EU) brez poseganja v zakonodajo Skupnosti, zlasti zakonodajo o konkurenci, obdavčitvi in državni pomoči, sprejmejo ukrepe, ki EMAS organizacijam omogočijo olajšave in boljšo zakonodajo za večje vključevanje v shemo EMAS. Cilj študije je ovrednotiti politični okvir v državah članicah in regijah EU, ki so razvile vrsto ukrepov za boljšo pravno ureditev v podporo organizacijam, registriranim v sistemu EMAS, v obliki spodbud oprostitve zakonskih določb in fiskalnih/ekonomskih olajšav.

Ključne besede: • krožno gospodarstvo • okoljska uspešnost • EMAS sistem • oprostitev zakonskih določb • LIFE B.R.A.V.E.R. •

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DOI https://doi.org/10.18690/978-961-286-211-4.20 ISBN 978-961-286-211-4
Dostopno na: http://press.um.si.

University of Maribor Press

LIFE B.R.A.V.E.R. – Boosting Regulatory Advantages Vis a vis EMAS Registration

KLAVDIJA RIŽNAR, DUŠAN KLINAR, GREGOR UHAN & DANILO ČEH

Abstract An Action Plan to stimulate Europe's transition towards a circular economy was adopted by the European Commission in 2015. For production processes, the European Eco-Management and Audit Scheme (EMAS) is recognised as important environmental instrument to the circular economy implementation. Application of EMAS demonstrates their effectiveness in improvements of the environmental performance of organisations and support economic objectives. Indeed, the EMAS Regulation states that Member States of the European Union (EU), without prejudice to Community legislation, notably competition, taxation and State aid legislation, shall, where appropriate, take measures facilitating organisations to become or remain EMAS registered such as regulatory relief and better regulation. The aim of this study is to evaluate the policy framework in EU Member States and regions that have developed a set of measures of better regulation for supporting EMAS registered organizations, both in form of regulatory relief initiatives and fiscal/economic incentives.

Keywords: : • Circular Economy • Environmental performance • EMAS system • Regulatory relief • LIFE B.R.A.V.E.R. •

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DOI https://doi.org/10.18690/978-961-286-211-4.20 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Uvod

Sistem za okoljsko ravnanje in presojo (EMAS) je okoljski instrument za prehod v krožno gospodarstvo in hkrati orodje za izvrševanje okoljske zakonodaje. EMAS predstavlja del sistema organizacijskega sistema vodenja, ki podpira javne in zasebne organizacije, da se usklajeno in sistematično lotevajo pomembnih okoljskih vprašanj. EMAS je prostovoljni okoljski sistem Evropske unije in je reguliran z Uredbo EMAS (EK št. 1221/2009). Da bi dosegli večji vpliv okoljskih izboljšav, Evropska unija poziva države članice EU k zagotavljanju širše oprostitve uporabe zakonskih določb in olajšav (Evropska komisija, 2009) za večje vključevanje organizacij v shemo EMAS. Glavne koristi, ki izhajajo iz uporabe sistema EMAS, so njegova učinkovitost za izboljšanje stanja v okolju, zlasti zmanjšanje emisij onesnaževanja, zmanjšanje proizvodnje odpadkov, zmanjšanje porabe energije in učinkovitost rabe virov (Mazzi in drugi, 2017) (Testa in drugi, 2014).

Namen dela je predstavitev preliminarnih rezultatov raziskave o sprejetih ukrepih boljše pravne ureditve v korist EMAS registraciji v državah članicah EU in identifikacija ukrepov za Slovenijo.

2 Material in metode

Metodološki pristop raziskav je bil zasnovan za zbiranje obstoječih ukrepov za boljšo pravno ureditev za EMAS registrirane organizacije v dvanajstih državah članicah EU. Raziskava je bila osredotočena na dve glavni kategoriji ukrepov:

a) oprostitev uporabe zakonskih določb: to pomeni, da so pravni instrumenti oblikovani tako, da se breme EMAS organizacijam odstrani, zmanjša ali poenostavi z namenom spodbujanja učinkovitega delovanja trgov in dviga konkurenčnosti,
b) promocijske spodbude: kar pomeni, da je organizacija v sistemu EMAS nagrajena z davčnimi in/ali ekonomskimi spodbudami.

V okviru projekta LIFE B.R.A.V.E.R. je bilo razvito protokolarno matrično orodje za izvedbo raziskave v sodelovanju z EMAS pristojnimi in regulativnimi organi držav članic EU. Protokol je sestavljen iz šestih delov:

a) spodbujevalne institucije: institucije, ki spodbujajo ukrepe (na primer država, lokalna skupnost, gospodarska zbornica, idr.),
b) vrsta ukrepa: regulativni ukrep ali promocijska spodbuda,
c) referenčna zakonodaja: zakonodajno referenčno besedilo in navedba člena za predviden ukrep,
d) raven uporabe: nacionalna, regionalna ali lokalna raven,
e) status: v veljavi ali se je ukrep iztekel,
f) opis ukrepa: kratek opis ukrepa, vključno z izbiro možnosti: splošno delovanje, navedba sektorja, vključeni akterji (npr. (med)vladne organizacije, organi pregona, idr.).

3 Rezultati in diskusija

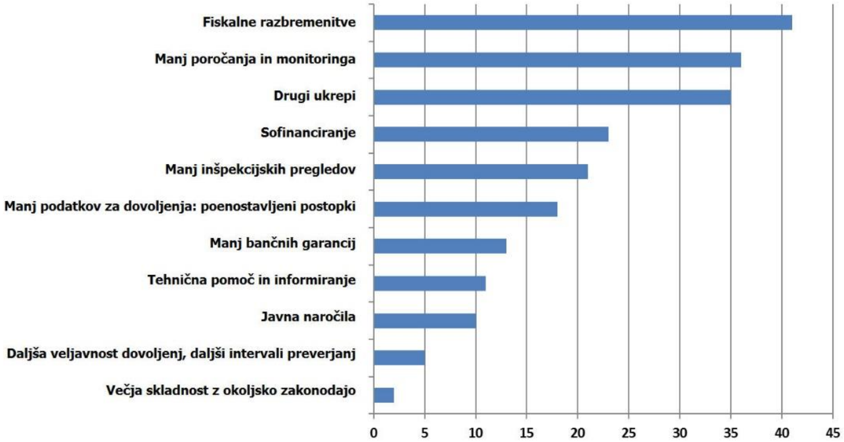
Skupno je bilo identificiranih 318 ukrepov boljše pravne ureditve v korist EMAS. Opredeljeni ukrepi so geografsko porazdeljeni po državah članicah EU kot prikazuje Tabela 1.

Tabela 1: Geografska porazdelitev ukrepov boljše pravne ureditve na območju EU

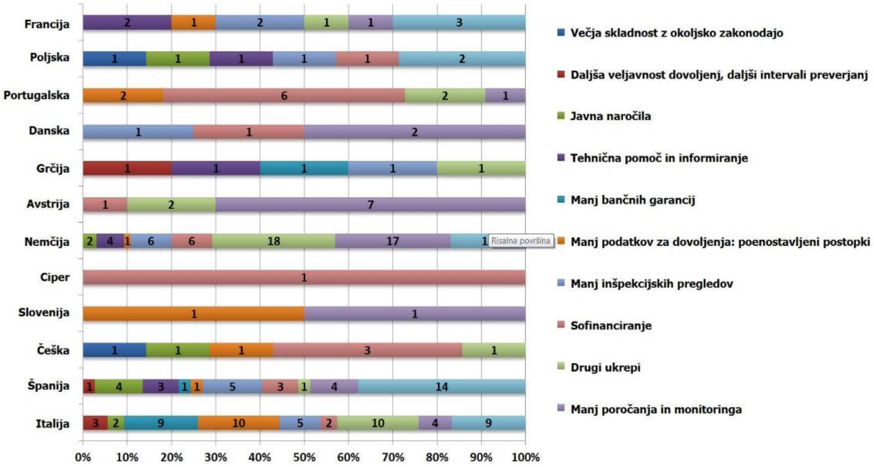
Država članica EU	**Število EMAS organizacij**	**Število identificiranih ukrepov**	**Od tega število regionalnih ukrepov**
Italija	909	57	23 (upoštevana regija: Emilija Romanja)
Španija	861	39	30 (upoštevane regije: Andaluzija, Baskija, Madrid, Katalonija)
Češka Republika	23	7	1
Slovenija	10	2	0
Ciper	3	1	0
Danska	18	4	0
Portugalska	55	11	5
Poljska	69	7	0
Francija	29	12	1
Nemčija	1.171	163	127
Avstrija	291	10	0
Grčija	31	5	0

Glede na število registriranih EMAS organizacij je bilo pričakovati, da je največ ukrepov identificiranih v Nemčiji, kjer Zvezna vlada spodbuja okoljsko certificiranje od leta 1996, tudi z ukrepi za poenostavitve in spodbude. Analiza v Nemčiji je bila izvedena za celotno zvezno raven in vse regije. Italija je na drugem mestu s 57 ukrepi, od tega jih je 23 v regiji Emilija-Romanja. Španija kot tretje uvrščena ima skupno 39 ukrepov, od tega 30 v štirih regijah: Andaluzija, Baskija, Madrid, Katalonija.

Vrste sprejetih ukrepov oprostitve zakonskih določb in olajšav po državah članicah EU je prikazana na Sliki 1 in Sliki 2. Ekonomske in davčne olajšave so najpogosteje sprejeti ukrepi v državah članicah EU, največ v obliki znižanja davkov za poslovanje in opravljanje gospodarske dejavnosti. Zmanjšanje zahtev za poročanje in monitoring je drugi najpogosteje razširjen ukrep oprostitve zakonskih določb za EMAS organizacije. Kategorija "drugi ukrepi" so na tretjem mestu in zajema vrsto različnih spodbud, ki niso opredeljene v drugih kategorijah: splošne spodbude v podporo EMAS registraciji, promocija EMAS za preprečevanje nastajanja odpadkov in zmanjšanje notranjih obveznih presoj. Neposredna finančna podpora za sprejetje EMAS sistema in zmanjšanje inšpekcijskih pregledov se uvršča tudi visoko. Manj razširjena spodbuda so javna naročila, kar potrjuje še vedno težavno stopnjo vključevanja teh instrumentov na ravni držav članic EU.



Slika 6: Vrsta ukrepov oprostitve zakonskih določb in olajšav, sprejetih v izbranih državah članicah EU (prednostna razvrstitev).



Slika 2: Razporeditev ukrepov oprostitve zakonskih določb in olajšav na nacionalni ravni posamezne države.

V okviru sodelovanja Slovenije v projektu LIFE B.R.A.V.E.R. (LIFE 15 ENV/IT/000509) so bili razviti predlogi ukrepov za boljšo pravno ureditev v podporo slovenskim EMAS organizacijam na ravni regulativnih in finančnih spodbud kot sledi:

- poenostavitev administrativnih postopkov pri načrtu gospodarjenja z odpadki,
- zmanjšanje zahtev za poročanje in monitoring emisij snovi v zrak in odpadne vode,
- znižanje finančnih garancij za pošiljke odpadkov,
- prednostni kriterij pri zelenih javnih naročilih,
- finančne spodbude za promocijo EMAS in sofinanciranje stroškov vzpostavitve sistema,
- EMAS Global registracija.

Ukrepi so v fazi testiranja z regulativnimi in pristojnimi organi ter EMAS organizacijami z namenom ovrednotenja njihove regulativne, tehnične in organizacijske izvedljivost ter stroškovne učinkovitosti, ki bo podlaga za sprejem na zakonodajni ravni za njihovo implementacijo v Sloveniji.

Zaključek

Raziskava je pokazala številne prednosti, ki izhajajo iz vzpostavljenih promocijskih, zakonodajnih, finančnih in ekonomskih instrumentov v podporo EMAS registraciji. Preliminarni rezultati o ukrepih oprostitve zakonskih določb in spodbud v korist organizacij, ki so sprejele EMAS sistem, je pokazala, da po več kot desetih letih, odkar je Evropska komisija uradno sprejela poenostavitve regulativnih obveznosti, so številne države članice EU uvedle ukrepe za boljšo pravno ureditev v podporo EMAS registraciji. Ugotovljeno je bilo, da države članice EU dajejo prednost fiskalnim in ekonomskim spodbudam, zmanjšanju poročanj in monitoringov. Poleg kategorij zakonodajnih ukrepov in spodbud za razbremenitve je še vedno veliko rezerv pri širjenju organizacij v shemo EMAS, predvsem se to kaže v tistih državah članicah, kot sta Ciper in Slovenija, kjer je število registracij EMAS precej nizka. Za doseganje večjih učinkov vključevanja v shemo EMAS je potrebna kombinacija pravnih in finančnih instrumentov, ki je podprta z učinkovito promocijsko in komunikacijsko strategijo posamezne države.

Opombe

Raziskava je potekala v okviru projekta LIFE B.R.A.V.E.R. (Boosting Regulatory Advantages Vis a vis EMAS registration - LIFE15 ENV/IT/000509), ki ga sofinancira Evropska komisija v okviru programa LIFE.

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Retrofitting of Industrial Utility Systems Considering Solar Thermal and Periodic Heat Storage

BEN ABIKOYE, LIDIJA ČUČEK, ADENIYI ISAFIADE, ANDREJA NEMET &
ZDRAVKO KRAVANJA

Abstract This paper involves the development of a model that is based on mathematical programming for integrating solar thermal and heat storage with multi-period heat exchanger network (HEN) of industrial operations. The method employed entails discretising the availability of solar thermal on the basis of hourly, daily and monthly time periods using real-life climatic data for hourly solar irradiation and ambient temperature variations. Considering variability in the supply profile, a flowsheet superstructure of closed circuits including direct and indirect solar thermal utilization with periodic heat storage is first developed. Thereafter, the flowsheet is systematically connected with the modified stage-wise superstructure model formulation which allows utility selection at each stage of the HEN. The problem is formulated and solved in GAMS using Slovenia climatic data as a case study, while the objective function maximizes the solar heat output to the heat network. In average 25.9 % (139.6 kW) of hot utilities is saved due to solar thermal. The hourly profile of various climatic features considered within the model will enable more realistic solar heat forecasting for utility retrofit in existing designs and also for new designs.

Keywords: • Solar thermal • Periodic heat storage • Heat integration • Utility retrofit • Mathematical programming • Emission reduction •

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DOI https://doi.org/10.18690/978-961-286-211-4.21 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

Industries and chemical plants are increasingly confronted with the need to urgently respond to the threat of climate change and emission reduction, energy security as well as the continuous exposure to volatile energy costs. While the problems associated with energy security and high cost of energy could to a large extent be addressed through various energy efficiency measures (Worrell et al., 2009), the permanent solution to the carbon emission and climate change problems requires increased usage of various renewable energy sources in industrial utility systems (Klemeš et al., 2010). Among the various renewable energy resources, solar is indisputably a leading type of energy that is fast becoming relevant as a low-carbon source of heat and electricity. Solar is versatile, and it appears naturally at some elevated temperature without any mechanical work or energy input. This has the potential to offset considerable amount of energy costs and carbon emissions if properly integrated with industrial heat network. However, obtainable data in reality is in contrast to the global potential of solar energy as it still remained largely underutilized especially in industrial process heat application (World Energy Council, 2016). This may be due to variability of solar energy supply and technical difficulties in planning and decision making-process for practical applications (Chan et al., 2013). Hence, the inclusion of renewable energy in process heat demand and energy systems requires a systematic approach in order to circumvent the aforementioned supply variations.

In this study the production of heat from solar thermal is optimized on hourly basis according to measured meteorological data obtained from EC-JRC PVGIS (2017). An integrated design of a close circuit, direct and indirect solar thermal system with periodic heat storage is presented for utility retrofit of industrial heat exchange network system (HEN) considering the intermittent changes in supply of solar thermal, as well as the multiperiod changes in the profile of heat supply of the plant.

2 Methodology

The framework for solar heat network design for process utility retrofit (Figure 1) is organized to reflect the flow of harvested solar thermal through the major units and equipment for both direct and indirect utilization in the process plant.

The figure consists of a closed loop flowsheet superstructure of solar thermal incorporated with periodic heat storage, and systematic connection of the flowsheet with the stage-wise superstructure formulation of HEN (Yee & Grossmann, 1990), modified for multi-period operation and utility selection at each stage (Bogataj & Kravanja, 2012), to form a single integrated generic system. The resulting superstructure then comprises of three closed loops (i.e. solar panel – thermal storage – solar panel, solar panel – HEN – solar panel, thermal storage – HEN – thermal storage). The solar panel is connected to a splitter which makes it possible to use the heat captured either directly or channelled to heat storage tank for use at other hours of the day when there is no solar irradiation. Both the direct and indirect solar heat (DSH and ISH) are used to offset as much heat demand as possible that could be satisfied within the plant while it is assumed that high pressure steam (HPS) is also available as backup utility.

The harvested solar thermal is linked with HEN of the process plant via a mixer which makes room for switching between the direct and indirect solar heat connections. A second splitter is placed between the solar thermal-heat storage loop and the HEN to ensure efficient energy use in the integrated system such that the heat transfer fluid can return to the solar panel via the storage tank depending on whether the temperature level of return could be useful to buffer the heat storage fluid in the tank. An integration of solar thermal with the industrial HEN as shown in Figure 1 is implemented using the General Algebraic Modelling Systems (GAMS).

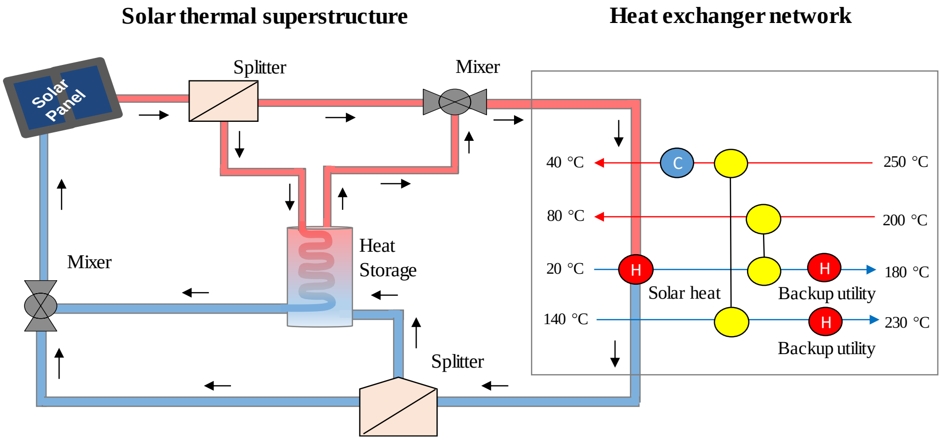

Figure 1: Integration of solar thermal with industrial heat exchanger network

3 Case Study

The model is implemented using Slovenia as case study. The coordinates of the area considered at this location are Latitude 46.552 N, Longitude 15.676 E and the elevation of 267 m. All the metereological data used were obtained from European Commission Joint Research Centre, PVGIS project (EC JRC PVGIS, 2017).

To test the efficacy and practical application of the model, an example of a process with two hot and two cold process streams (Smith, 2005) is adopted and modified for the special case of the solar heat retrofit of HEN presented in this study. The stream data for the modified example is presented in Table 1 and for simplification it is assumed to be fixed over the year.

Table 1: Hot and cold stream data for the modified example

	Supply Temperature °C	**Target Temperature** °C	**Heat Capacity Flowrate** kW/K	**Heat Flow** kW
H1	160	40	2.0	240
H2	180	70	2.0	220
C1	20	170	3.5	525
C2	40	150	4.3	473

ΔT_{min} = 10°C

Source: stream data modified from Smith, (2005)

To account for target design, in the first stage an expanded transshipment model (Papoulias and Grossmann, 1983) with minimal energy consumption as an objective is used. Based on the results obtained, process-to-process heat matches were fixed as: $Q_{\mathrm{H1\text{-}C1}} = 20$ kW, $Q_{\mathrm{H1\text{-}C2}} = 220$ kW and $Q_{\mathrm{H2\text{-}C1}} = 220$ kW, and the cold utility consumption is set to 0. Hot utility consumption in the process is 538 kW.

To reduce computational time, model reduction techniques are applied using the procedure similar to that of Egieya et al. (2018), which is based on an earlier method presented by Lam et al. (2011). Instead of 24 hours a day, 8 periods are used, and instead of 28-31 days a month, 1 period is used. The model is based on mixed-integer non-linear programming (MINLP) with the objective of maximizing the average solar thermal use in the process plant in kWh in a year.

The final model consists of 36,005 single equations, 29,248 single variables and 60 binary variables and was solved using DICOPT solver in GAMS 25.1.1 modeling system (GAMS Development Corp. and GAMS Software GmbH, 2018). Solutions to the model were obtained within 725 s and 2,223,206 iterations by using personal computer with 64 GB of RAM and Intel® Core™ i7-8700 K CPU @ 3.70 GHz 3.70 GHz processor.

Table 2 shows the solar thermal use in HEN for each time-period where the quantities of heat exchanged are shown in kW(h/h). The last column shows the total amount of solar heat used in a specific month where the heat used in a process plant is summed for all time periods in a month (Q1-Q8), and is multiplied by 3 and number of days in a month.

Table 2: Results for solar thermal use in industrial HEN

Periods	**3-6 am**	**6-9 am**	**9-12 am**	**0-3 pm**	**3-6 pm**	**SUM kWh/month**
Month	**Q2 kW**	**Q3 kW**	**Q4 kW**	**Q5 kW**	**Q6 kW**	
January	/	/	302.8	302.8	/	56,320.8
February	/	302.8	302.8	/	295.2	75,667.2
March	302.8	302.8	302.8	302.8	231.8	134,199.0
April	144.5	302.8	302.8	302.8	134.9	106,902.0
May	225.2	302.8	302.8	302.8	159.7	120,276.9
June	253.4	302.8	302.8	302.8	211.5	123,597.0
July	278.0	302.8	302.8	302.8	302.8	138,495.6
August	168.6	302.8	302.8	302.8	157.9	114,845.7
September	244.8	302.8	302.8	302.8	80.7	111,051.0
October	225.1	302.8	302.8	302.8	/	105,415.5
November	302.8	302.8	297.1	/	/	81,243.0
December	/	/	302.8	302.8	/	56,320.8
SUM ($Q_{\text{Solar Exchanged}}$) in kWh/y						**1,224,334.5**

Based on the results, the month with the highest use of solar heat in the industrial HEN is July with a total of 138.5 MWh of heat exchanged. This is approximately 2.5 times higher than the months with the lowest potential for solar which are January and December with each of the months having 56.3 MWh of solar heat exchanged. A total of 1,224.3 MWh of heat is maximally exchanged from solar in a year. The maximum average heat power used in HEN from solar in a year (i.e. the objective value) is 139.62 kW (25.9 % of hot utility requirement in the plant). The optimal area of the panel selected is 3,000 m^2, the volume of fluid in the storage tank is 200 L, and the average amount of heat stored in a storage tank is 17.2 kW. Both area of the panel and volume of the fluid in the tank are selected at their upper and lower bounds. Due to the nonlinearity of the model, the closed loop constraint which is considered on the direct solar utilization (solar panel – HEN – solar panel) was also relaxed in order to obtain feasible solution for the model.

4 Conclusions

A new simultaneous approach for capturing solar thermal, considering the hourly changes in its availability, and the multiperiod profile of process heat supply in HEN has been presented in this paper. The method which is based on MINLP approach is capable of estimating the hourly, monthly and yearly availability of renewable energy for heat generation. Essential features that guarantee efficiency such as heat storage are included in the framework of the model. However, it should be noted that heat losses during heat transport and storage have not been considered. Nonetheless, the results obtained suggest that the model could be used as a decision support tool in the planning, design and operations of renewable energy systems. It should be noted also that the model is highly nonlinear and thus the obtained solutions are only locally optimal.

Acknowledgments

The authors are grateful for the travel supports received from the postgraduate funding office and Engineering and the Built Environment Faculty of the University of Cape Town, National Research Foundation (NRF) of South Africa through the grant number 105780, Slovenian Research Agency (programs P2-0377 and P2-0032 and project L2-7633) and Slovenia-Croatia bilateral project Integration of renewable energy within energy systems - INTEGRES.

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Upcycling with alkali activation technology

BARBARA HORVAT, MARK ČEŠNOVAR, ALENKA PAVLIN &
VILMA DUCMAN

Abstract In 2017 Termit and ZAG started a project where various waste materials containing enough SiO_2 and Al_2O_3 will be up-cycled into porous lightweight insulating alkali activated foams with potential to be used in the building industry. From several tested abundant waste materials from Termit focus in this article is on rock and glass wool. Glass wool had 2-times higher compressive strength from rock wool, which is due to its better dissolution in alkali media. However, both wools were selected for further experimental work.

Keywords: • alkali activated material • mineral wool • compressive strength • upcycling • circular economy •

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DOI https://doi.org/10.18690/978-961-286-211-4.22 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

In 2017 Termit started circular economy project, where various waste materials were tested for the suitability for up-cycling into porous lightweight insulating alkali activated materials/foams that could be used in the building industry.

Focus was on the waste materials that are in abundance and showed high enough compressive strength after alkali activation. Among several tested waste materials from mixture of bottom and fly ash, raw material for ceramics, slag, foundry sand etc. both wools, i.e. rock and glass, were also examined. Both mineral wools represent health hazardous waste material (National Toxicology Program, Headquartered at the National Institute of Environmental Health Sciences NIH-HHS, 2017) in building industry after demolition of buildings. Since now the mineral wool waste material is discarded in municipal waste dumps (Väntsi, 2014) and using it back in the circular economy would not just benefit economy, but also nature with lowering the waste in municipal waste dumps, and animal and human health with complete incorporation of mineral wool fibres in alkali activated materials.

So far there were few researches done on mineral wool used in alkali activated synthesis (Yliniemi, 2016), in combination with fly ash (Kinnunen, 2016), in combination with metakaolin (Elijah, A. D., 2015, Master Theis).

The aim of the present study is thus the assessment of mineral wool for further (re-) use in construction sector.

1.1 Introduction into alkali activation technology (AAT)

Alkali-activated materials (AAM), often called geopolymers, are produced from precursors containing SiO_2 and Al_2O_3 in sufficient quantities and in reactive/glassy form (e.g. ashes, slags, metakaolin...), and alkaline activators, such as NaOH, KOH, Na-water glass, K-water glass). When precursors and activators are mixed, first dissolution and transport of the components (Al, Si) in the alkaline activators takes place, and then through poly-condensation of the Al and Si, an aluminosilicate network is formed. Many products can be obtained by the alkaline activation process which could replace traditional construction products (Provis et al., 2010, Zhang et al., 2014). They range from blocks, slabs, pavingstones, curbs, and partitions to refractory materials and materials for specific industrial applications (e.g. insulation plates).

And if waste material is used for their production, significant contribution to the reduction of the CO_2 footprint can be demonstrated comparing such material to cement, concrete or ceramic.

The technology of alkali-activated materials makes a promising alternative material production for civil engineering purposes because of the advantages such as low processing costs, satisfactory physical properties, high temperature stability, and fire and corrosion resistance in comparison with traditional construction materials. The properties of AAM are strongly affected by the content of reactive SiO_2 and Al_2O_3 in precursor, by the type and amount of alkali activator, and curing regime (Hajimohammadi et al., 2017). To achieve the synthesis of AAM with good mechanical properties, the right precursor to alkaline activator ratio needs to be determined. Different proportions of activator are added to precursor in order to study the alkali reaction products and characteristics such as mechanical properties of AAM. Chemical and mineralogical characterization (XRD, XRF, EDXS…) of precursor and viscosity measurement of mixtures can also be helpful tool for determination of influence of the alkali activator and its optimal amount for alkali activation reaction with precursor material. Properties of AAM are also affected by the curing regime, such as drying at room or elevated temperatures with different period of time.

2 Experimental

Sufficient amounts of rock and glass wool, presented in **Table 1** (with laboratory sample name, description of the sample 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 for research on a laboratory scale.

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

Laboratory sample label	Sample	Waste label
V-171/17	Glass wool	17 09 04
V-222/17	Rock wool	17 09 04

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

Both collected samples were dried on 70 °C for 24 h in WTB Binder dryer. For X-ray fluorescence (XRF) and X-ray powder diffraction (XRD) analysis samples were further dried with measuring the moisture content with IR dryer at 105 °C to constant mass, and were afterwards grinded in vibrating disk mill (Siebtechnik) and sieved below 90 μm.

XRD analysis was performed (Empyrean PANalytical X-Ray Diffractometer, Cu X-Ray source) under same conditions for both samples: measuring in step 0.0263° from 4° to 70° angle, under cleanroom conditions, in powder sample holders with aperture diameter 27 mm. Mineral analysis, Scherrer size of crystallite domains, estimation of amount of amorphous phase and minerals with Rietveld refinement with external standard (pure Al_2O_3 crystal) were performed with X'Pert Highscore plus 4.1 on XRD data.

For XRF analysis (Thermo Scientific ARL Perform'X Sequential XRF) powder samples were first treated for 2 h at 950 °C in furnace (Nabertherm B 150) to remove organic compounds and CO_2, then mixed with Fluxana (FX-X50-2, Lithium tetraborate 50 % / Lithium metaborate 50 %) in ratio 1:10 for Fluxana to lower melting temperature. Mixture of Fluxana and glass wool was melted into discs at 1025 °C for 7 min, while mixture of Fluxana and rock wool was melted at 1075 °C for 9 min, both in furnace Claisse, The Bee Electric Fusion (few drops of LiBr were added to avoid gluing of melt in the platinum vessel). XRF analysis was performed with program OXAS on melted disks, while data were characterized with program UniQuant 5.

Loss of ignition at 950 °C was determined with gravimetric method from 2 parallel measurements and corrected with XRF analytical loss of ignition obtained on the fused basis.

For scanning electron microscopy (SEM; Jeol JSM-5500LV with tungsten filament cathode as electron source) and energy dispersive X-ray spectroscopy (EDXS; Oxford Instruments, Link Pentafet) investigation under low vacuum conditions both samples were dried, grinded and sieved below 90 μm.

On the fibers, dried and sieved below 250 μm (to add additional strength to final product with longer fibres no wool was sieved below 90 μm) mineral wools preliminary alkali activation test was performed. 10 M NaOH (Donau Chemie Ätznatron Schuppen, EINECS 215-785-5) was added to Na-glass (Geosil, 344/7, Woelner) in ratio 1:1, stirred until liquid became clear, poured into the sample under constant mixing. Ratio sample:NaOH:Na-glass was determined with viscometer (Haake PK 100, VT 500, PK2 1.0°), i.e. dry material was added into liquid mixture until viscometer could not measure the viscosity due to overload of torque, to maintain as uniform distribution of synthesized material as possible, and at the same time to have enough liquid phase for solid material to be in contact with alkali activator.

Samples with pre-determined ratio (precursors to activators) were moulded into prisms of 80x20x20 mm^3, and after solidification characterized by XRD (synthesized material was grinded and sieved below 90 μm), SEM and EDXS. Compressive and bending strength were measured with compressive and bending strength testing machine (ToniTechnik ToniNORM) 3 months after synthesis.

3 Results and discussion

Moisture content after drying on 70 °C for 24 h and ignition losses at 950 °C are presented in Table 2.

Table 2: Moisture content after drying on 70 °C for 24 h and loss of ignition determined with gravimetric method and calculated from XRF data.

Laboratory sample label	Moisture [%]	LOI (950 °C)	LOI (XRF)
V-171/17	2,2	8,5	9,4
V-222/17	1,1	4,7	5,5

Ignition loss of rock wool is ca. 80 % higher compared to ignition loss of rock wool saying that glass wool has higher organic and carbonate content comparing to rock wool. (Heiri, 2001)

3.1 Chemical and mineralogical analysis

With XRF analysis amount of different oxides was followed. Results where mass percent of oxides is close or above 0,1 % are presented in **Table 3**.

Table 3: Mass percentage of oxides measured with XRF.

Laboratory sample label	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	MnO	Fe_2O_3	BaO
V-171/17	16,5	3,7	2,5	65,9	0,3	7,1	0,1		0,6	
V-222/17	2,1	9,8	17,3	43,5	0,8	16,8	1,3	0,3	6,7	0,07

Both samples had among detected oxides highest amount of SiO_2, glass wool even 50 % more than rock wool. Glass wool had more than 15 % of Na_2O, and more than 5 % of CaO. Rock wool had more than 15 % of Al_2O_3 and CaO, almost 10 % of MgO, and more than 5 % of Fe_2O_3. All other detected oxides were present in the samples in less than 5 %.

Minerals determined with XRD before and after alkali activation are presented in **Table 4**. Both precursors contained more than 90 % of amorphous phase, rock wool even more than 95 %, according to Rietveld refinement (pt), meaning most of SiO_2 detected with XRF in the initial materials was amorphous and easily available for reaction. Common mineral to both wool precursors is quartz, represented in glass wool in quantity of 5 mass %, and in rock wool in quantity of 3 mass %. Glass wool contains also small amount of calcite and dolomite.

After alkali activation of glass wool calcite dissolves completely, quartz crystallites start to dissolve according to Scherrer equation (crystallite domains shrink from 140 nm to 70 nm), dolomite breaks into smaller crystals or/and new smaller crystals form (there is 10-times more dolomite after alkali activation than before). Beside dolomite formation also thermonatrite forms and amount of amorphous phase lower significantly.

Alkali activation of rock wool leaves quartz intact and forms thermonatrite, almost 3-times bigger crystallites than in case of alkali activated glass wool, but 4-times less amount. Amount of amorphous phase stays high also after alkali activation.

Table 4: Percentage (pt) of minerals and amorphous phase in glass and rock wool and their alkali activated counterparts according to the Rietveld refinement; and size of crystallite domains estimated with Scherrer (S). Extra preparation of precursor is mentioned next to the sample's label.

Mineral	**Quartz**		**Calcite**	**Dolomite**	**Thermonatrite**	**Amorphous phase**
Chemical formula	SiO_2		$CaCO_3$	$CaMg(CO_3)_2$	$Na_2CO_3 \cdot H_2O$	/
Mohs hardness scale [M]	7		3	3,5-4	1-1,5	/
V-171/17 Before AA	pt [%]	5,6	0,6	1,4		92,4
	S [nm]	140	60	90		
V-171/17, dried, milled, 250 µm After AA	pt [%]	4,6		15,5	10,7	69,2
	S [nm]	70		30	30	
V-222/17 Before AA	pt [%]	3,2				96,8
	S [nm]	130				
V-222/17, dried, milled, 250 µm After AA	pt [%]	2,3			2,5	95,2
	S [nm]	130			80	

3.2 Mechanical analysis

Compressive strength as one of the most important properties in building industry is presented in **Table 5**, with bending, shrinkage of width and length of optimally prepared prism, i.e. optimized value of ratio precursor vs. alkali vs. alkali glass according to viscosity measurements was for glass wool 1,5:1:1 and for rock wool 2:1:1.

Table 5: Mechanical properties of alkali activated material prepared from mineral wools.

Laboratory sample label	Ratio P:NaOH:Na-glass	Shrinkage length [%]	Shrinkage width [%]	Bending strength [N/mm]	Compressive strength [N/mm²]
V-171/17	1,5:1:1	0,7	1,4	7,2	18,4
V-222/17	2:1:1	2,3	3,9	1,7	10,1

Glass wool in comparison to rock wool had almost 3-times lower shrinkage, 4-times higher bending strength and almost 2-times higher compressive strength.

3.3 Microstructural analysis

SEM and EDXS of grinded and sieved below 90 µm glass wool is presented on **Figure 2**. It consists of cylindrical rods, fibres, of various diameters.

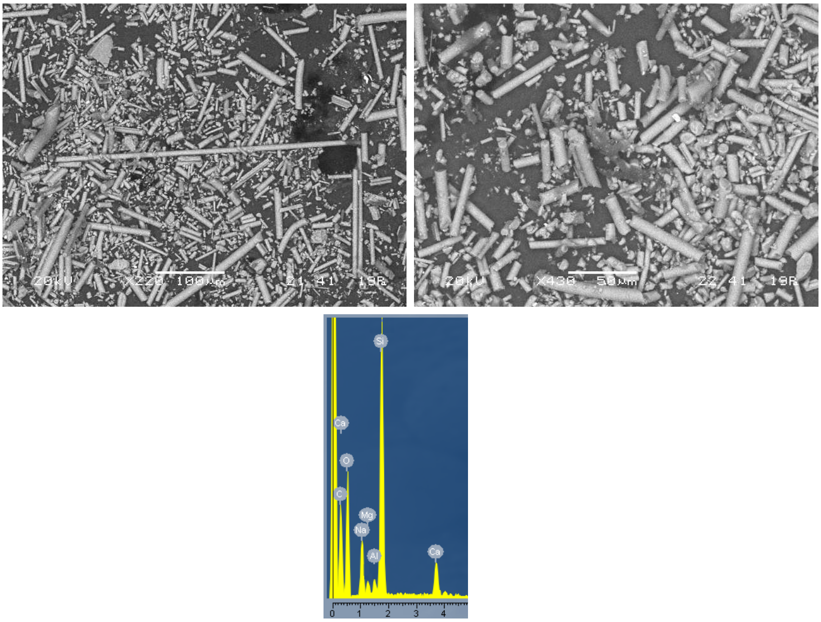

Figure 2: Left and middle: SEM micrographs of grinded and sieved below 90 µm glass wool showing elongated particles. Right: EDXS spectrogram of glass wool.

SEM and EDXS of grinded and sieved below 90 µm rock wool is presented on **Figure 3**. It consists of cylindrical rods, fibres, of various diameters and larger particles of various shapes used in mineral wool synthesis.

Also according to EDXS rock wool contains Fe, while glass wool does not. All other elements are present in both mineral wools. As expected, glass wool contains far more Si comparing to other elements, and very small amount of Al. Sum of Na and Ca is in the sample far greater than amount of Al, meaning that precursor has already enough ions with which inadequate coordination number of Al in the matrix is compensated, and from additional amount of Na crystals can form (thermonatrite).

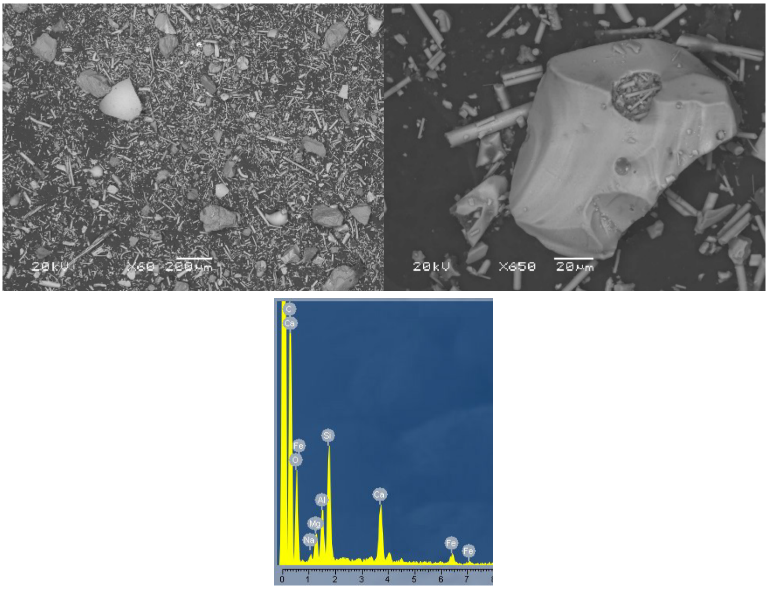

Figure 3: Left and middle: SEM micrographs of grinded and sieved below 90 µm rock wool showing elongated and random-shape particles. Right: EDXS spectrogram of rock wool.

On the other hand rock wool has significant amount of Al, which is far greater than amount of Na, meaning that addition of Na ions in alkali activated synthesis is required for compensation of Al extra bond in the alumo-silicate matrix. When using both mineral wools as precursors, thermonatrite crystals formed, but in case of glass wool the amount of thermonatrite was 4-times greater comparing to rock wool due to amount of initial Na comparing to Al, and due to added amount of Na that was bigger (molarity of alkali was constant) in case of glass wool (estimated surface for glass wool was 10-times higher to rock wool and therefore more liquid was required to wet the surface). Added Na could have been much smaller due to abundance of Na, meaning it is possible to lower molarity of alkali, which is beneficial for environment. The formation of thermonatrite would have been avoided or at least minimized, and it is to be expected that compressive strength due to thermonatrite's low Mohs hardness number would be greater.

SEM of alkali activated glass wool is presented on **Figure 4**. Initial fibres seem to be well incorporated in the matrix, giving it additional strength in all directions due to its random orientation because of low or no mechanics of continuum during alkali activated synthesis.

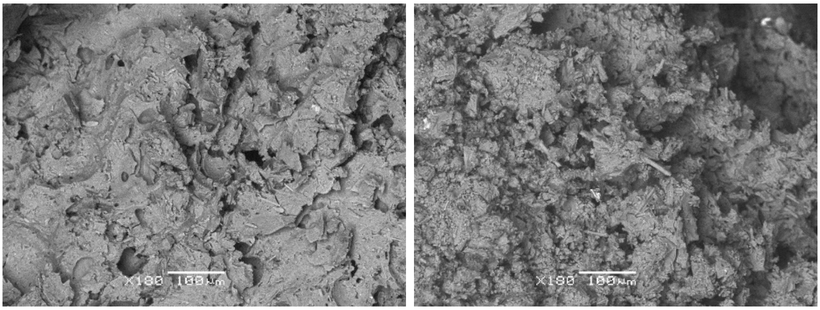

Figure 4: SEM micrographs of matrix from alkali activated glass wool.

SEM of alkali activated rock wool is presented on **Figure 5**. Initial fibres are less incorporated in the matrix when compared to alkali activated glass wool. Throughout the matrix larger particles, presented already in the precursor, did not react with alkali and its surface is not covered with matrix.

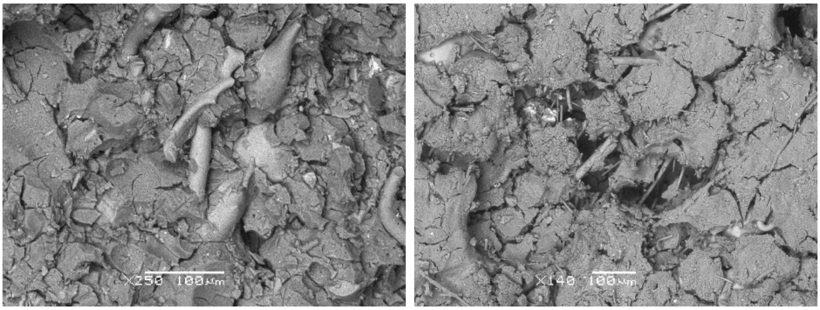

Figure 5: SEM micrographs of matrix from alkali activated rock wool.

4 Conclusion

Alkali activation of both rock and glass wool showed promising results for further research due to high enough compressive strength, i.e. alkali activated glass wool had compressive strength 18 MPa and rock wool 10 MPa (in agreement with (Kinnunen, 2016)) with optimizing only viscosity of alkali activated material at the beginning of reaction. According to (Yliniemi, 2016) glass wool had higher maximal reached compressive and bending strength comparing to rock wool, which is in agreement with our research. Glass wool had approximately 2-times higher compressive strength comparing to the rock wool due to the better dissolution of glass wool's components in alkali media and better embedment of not completely dissolved remainings in the matrix.

With up-cycling waste mineral wools not only that those health dangerous fibres are well incorporated in the matrix, which does not enable inhaling them, but also waste material becomes source material again and gets back into economy circle, which is aim of Termit's research in project with ZAG.

Acknowledgments

Project No. C3330-17-529032 "Raziskovalci-2.0-ZAG-529032" was granted by Ministry of Education, Science and Sport of 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.

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University of Maribor Press

Accessing Risk for Malaysian Palm Oil Biomass Industry with FANP-DEMATEL Mmodel

SUE LIN NGAN, HON LOONG LAM, PUAN YATIM & AH CHOY ER

Abstract The urge for climate change mitigation has created a strong resonance in industrial world on the utilization of renewable resources. As the second-world largest palm oil exporter, Malaysia produces abundant amount of oil palm biomass which can be best utilized for "waste-to-wealth". As the country attempts to transition towards green growth, policy frameworks have been established and implemented to promote and support the industry. However, the overall development of the biomass industry remains under-developed. Lack of understanding of risks associated with the industry is often cited as one of the reasons for the industry's slow growth. Therefore, it is imperative that these risk factors are identified and evaluated in a comprehensive manner so that industry players can address these risks and put in place risk management and mitigation mechanisms. In this study, Fuzzy Analytic Network Process (FANP), and Decision Making Trial and Evaluation Laboratory (DEMATEL) are employed to develop a hybrid model to assess risk factors typically found in biomass industry to determine the top risks in order to put in place effective risk mitigation mechanisms to spur up the growth of the industry in Malaysia.

Keywords: • Oil palm biomass • Risk • Risk mitigation • FANP •. DEMATEL •

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DOI https://doi.org/10.18690/978-961-286-211-4.23 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

Malaysia, as the second world largest exporter of the oil and fat after neighbouring country, Indonesia produce about 20 million tonnes of crude palm oil per annum (MPOB, 2018). The palm oil biomass, such as oil palm trunk, oil palm frond, empty fruit bunches (EFB), palm oil mill effluent (POME), palm kernel shell (PKS), palm pressed fibre (PPF) and decanter cake are expected to reach 100 million dry tonnes by 2020 (AIM, 2013). At current stage, most of the palm oil biomass are still engaging with low utilization value process in downstream activities. For instances, oil palm frond and trunk are mostly left in the field or pre-process (i.e., mulched) and returned to the field as fertilizer. EFB, PKS generated in the palm oil mill and biorefinery are transformed into pellets for power generation. It is estimated by fully capitalise the palm biomass for high value-added downstream activities could contribute additional 30 billion to the country's gross national income (GNI). Recognizing its potential, the government has stepped up its efforts to promote sustainable utilization of oil palm biomass. Biomass Industry Strategic Action Plan is introduced in 2012 as a joint effort of Malaysia with European Union to help small and medium enterprises (SMEs) in Malaysia to exploit biomass resources for high-value utilization (MIGHT, 2013). National Biomass Strategy 2020 that introduce a series of strategy to exploit biomass for commercial opportunities. Furthermore, fiscal incentives such as tax rebate and tax exemptions are also offered to the new entrant to the industry. Financing scheme is also introduced in 2010 to provides financing aid for the user and producer of green technology project, inclusive biomass industry, wherein the government will provide 60 % of guarantee and subsidy 2 % of the total interest rate imposed on the total financing amount. Despite various actions and initiatives have been taken, the growth of the biomass industry in Malaysia is still relatively slow. Literature, anecdotal evidence and businesses have identified that one of the factors contribute to the slow diffusion of the industry is due to the high-risk profile of the industry. Biomass industry is a multidiscipline industry and thus associated with wide range of expertise and stakeholders. Yatim et al. (2017) identify that the industry does not only associated with financial, operation, technology risk as any other industry, it also exposes to five main risk categories, namely technology, financing, supply chain, regulatory, and environmental and social. Risk is generally defined as the product of probability of occurrences of risk event multiple with its impact or consequences. As biomass industry is a relatively new industry, there is still the lack of historical data to aid the estimation of the probability and impacts. Moreover, risk is exerting in both tangible and intangible as well as can be quantitative and qualitative event. Thus, in this work, Fuzzy Analytic Network Process (FANP) and Decision Making Trial and Evaluation Laboratory (DEMATEL) are adopted to develop a hybrid model to assess and prioritize risks to design the most effective solution.

2 Methodology

2.1 Background

Fuzzy Analytics Network Process (ANP) is a combination of fuzzy set theory and Analytics Network Process. Analytic Network Process is the generic form of Analytic Hierarchy Process (AHP) that developed by Saaty in the late 1980s (Saaty and Takizawa, 1986) ANP overcomes the constraint of AHP on unidirectional (i.e., top-to-bottom) problem structure to include feedback dependence and inner dependence in deriving the final composite priority through supermatrix approach. However, there have been increasing argument on the crisp value of the Saaty's traditional 9-point fundamental scale in elicit judgement on pairwise comparison questions. It is claimed that human judgement can be vague and ambiguity in time and not feasible to be fully represented with single crisp value (Promentilla et al., 2008). Thus, fuzzy membership function has often integrating with ANP on better representation of judgement with inclusion of the confidence level of domain in giving judgement. Fuzzy membership function is represented by a vector <l, m, u> wherein l is the lower bound of the judgement, m is the modal value and u is the upper level. The range of upper bound and lower bound (i.e., u-l) indicates the confidence interval of the domain in giving judgement, wherein huge gap signifies the domain is less certain about the judgements given and vice versa. Fuzzy set theory was first introduced by Zadeh (1965) to overcome the constraints of high uncertainty due to incomplete or insufficient information (Zadeh, 1965). Its application is wide extended to multiple field and industry ever since including in multiple criteria decision-making area to include uncertainties in the judgement given by domain. FANP is a powerful for multiple criteria decision making as it offer high flexibility in problem structuring. It enables a clear indication of dominance relationship between clusters, as well as inner relationship of elements in each cluster in fulfilling the overall goal.

On the other hand, Decision Making Trial and Evaluation Laboratory (DEMATEL) is first introduced by the Geneva Research Centre in 1972 (Gabus and Fontela, 1972). The main function of DEMATEL is to analyse the relationship of multiple elements in a complex system to determine the causal and dependency relationship based on expert knowledges. Its ability to analyse and visualize the relationship in matrices or digraph have attracted high attention in recent year in investigating and intertwined complex problems in various field, inclusive but not limited to business arena, research field etc. By recognizing and categorizing the variables into cause and effect factors, it enhances the decision making for optimal selection of the strategy to tackle the issues. The proposed model that integrating FANP and DEMATEL does not offers solution that solely based on the degree of dominance relation of the variables, but also synchronized with the causal and effect relationship in prioritizing risk. The outcome provides a comprehensive picture for the industry players to design the mitigation strategy that is most effective in managing the risk associated with the biomass industry. Meanwhile, policy makers can also utilize the information to put in place supports and mechanisms to reduce the risk barriers more effectively and efficiently to spur up the overall growth of the industry.

2.2 Model formulation

The proposed methodology consists of five main steps with the detailed explanation as follows:

Step 1: Literature review are performed to identify the risks associated biomass industry. Focus group discussion that consists of 8 to 15 participants is conducted to validate the findings from literature review and get extra inputs that are more relevant to Malaysia context. The focus group participants comprised of a good mixed of biomass industry stakeholders, including industry players, researchers, capital providers and policy makers to encourage discussion on the opportunity and challenges faced by different stakeholders in the biomass industry.

Step 2: The information gathered from stakeholders is then structured into a hierarchical model as shown in Figure 1. The hierarchical model consists of 3 levels, with the top level as the goal, to prioritize the risks for debottlenecking, followed by level 2, risk categories and level 3, risk events. The details for the identified risk events are described in Table 1. Arrows are used to represent the relationship of elements and level clusters associated in the model. Downward arrows (i) and (ii) show the direct dependency of the element(s) in the lower level with respect to the element(s) in upper level. Self-looping arrow (iii) indicates the inner dependency of the element with itself and other element(s) within the same level cluster. Self-looping arrow (iv) indicates the interdependency of element(s) with the other element(s) within the same level cluster. Feedback control loop arrows (v) and (vi) connecting all the element(s) back to the controlling element of the model, which is the goal. The purpose of feedback control loop is to ensure that the whole model is strongly connected to avoid judgements that are non-relevance to the purpose of study (Promentilla et al., 2008).

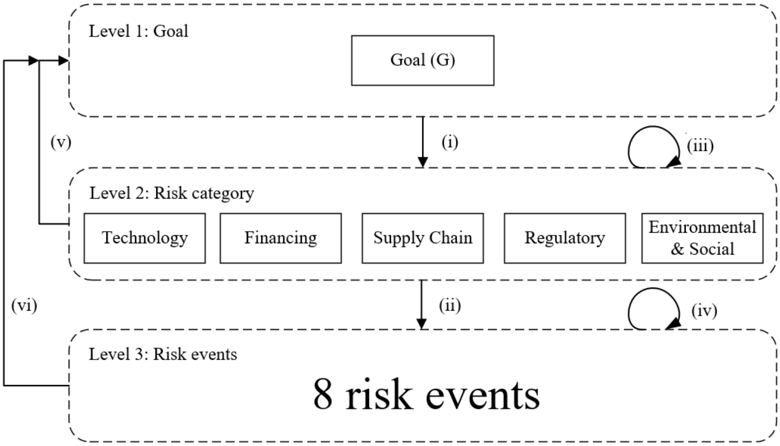

Figure 4: Diagraph of the hierarchical network model

Table 1: The description of the risk events in level 3

Code	Description
R1	Long pay back periods
R2	High upfront capital
R3	Inconsistent feedstock supply
R4	Lack of information to assess the performance of biomass project
R5	High logistics cost
R6	Lack of resources and capability to scale up to industrial level
R7	Lack of technical and safety standards for biomass plant
R8	Unclear regulations and policies related to biomass industry

Step 3: Elicit judgement from experts on the degree of the dominance relationship and intensity of influence power and being influenced through pairwise comparison questionnaires. The questionnaire is divided into two parts. The first section comprises of inputs for FANP to assess: (a) direct dependence of level 2 with respect to level 1; (b) direct dependence of level 3 element(s) with respect level 2 element(s); (c) inner dependence of element(s) in level 2. The second section consists of questions for DEMATEL to determine (d) the interdependence of the element(s) in level 3 and to identify (e) causal and effect factor on the element(s) in level 3. Linguistics scale is adopted in this work to compare the relative dominance relationship of elements and clusters. The description of the linguistics scale with its correspond value for FANP and DEMATEL methods are presented in Table 2 and 3.

Table 2: Fuzzy scale for FANP pairwise comparative judgement

Linguistic scale	Lower bound (l_{ij})	Modal value (m_{ij})	Upper bound (u_{ij})
Equally	1.0	1.0	1.0
Slightly more	1.2	2.0	3.2
Moderately more	1.5	3.0	5.6
Strongly more	3.0	5.0	7.9
Very strongly more	6.0	8.0	9.5

Table 3: Measurement scale for DEMATEL

Linguistic scale	Value
No influence	0
Very low influence	1
Low influence	2
High influence	3
Very high influence	4

Step 4: Derive the priority vectors and matrix to populate the initial supermatrix. The mathematic operation for both FANP and DEMATEL are associated with matrix, with procedures as described in the following. The fuzzy judgements from the first section (i.e. inputs for FANP) of pairwise comparison questionnaire are populated to form reciprocal matrix (i.e., $\hat{A}$) as the following:

$$\hat{A} = \begin{bmatrix} \langle 1,1,1\rangle & \hat{a}_{12} & \cdots & \hat{a}_{1n} \\ \hat{a}_{21} & \langle 1,1,1\rangle & \cdots & \hat{a}_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ \hat{a}_{n1} & \hat{a}_{n1} & \cdots & \langle 1,1,1\rangle \end{bmatrix} \text{where } \hat{a}_{ij} = \langle l_{ij}, m_{ij}, u_{ij}\rangle \quad (1)$$

$$; \hat{a}_{ji} = \langle \frac{1}{u_{ij}}, \frac{1}{m_{ij}}, \frac{1}{l_{ij}} \rangle$$

Geometric mean method is used to aggregate the judgements of multiple experts on the same pairwise comparison judgement prior forming the reciprocal matrix (Orbecido et al., 2016). Every relationship as indicated with arrow (i), (ii) and (iii) consists of its own matrices. The priority vector representing the final priority of the said relationship is derived with the non-linear programming (NLP) calibrated by Promentilla et al. (2015) as follows:

Maximize λ (2a)

s.t.:

$$(m_{ij} - l_{ij})\lambda w_j - w_i + l_{ij} w_j \le 0, \forall i = 1, \dots, n-1; j = i+1, \dots, n \quad (2b)$$

$$(u_{ij} - m_{ij})\lambda w_j - w_i + u_{ij} w_j \le 0, \forall i = 1, \dots, n-1; j = i+1, \dots, n \quad (2c)$$

$$(m_{ij} - l_{ij})\lambda w_i - w_j + l_{ji} w_i \le 0, \forall j = j, \dots, n-1; i = j+1, \dots, n \quad (2d)$$

$$(u_{ji} - m_{ji})\lambda w_i - w_j + u_{ji} w_i \le 0, \forall j = 1, \dots, n-1; j = j+1, \dots, n \quad (2e)$$

$$\sum_{i=1}^{n} w_i = 1 \quad (2f)$$

$$w_i > 1, \forall i = 1, \dots, n \quad (2g)$$

where in λ is the overall degree of satisfaction of the judgements and a measure of consistency. λ value is suggested to be within 0.0 and 1.0, which 1.0 indicates that the judgements achieve perfect consistency while 0.0 indicates that the judgements only satisfy at its boundary. In the event that λ appeared to be negative-value, it is suggested for the respective experts to revisit his/her judgements as some of the judgements are conflicting with each other.

The judgements for DEMATEL questions are populated to form direct relation matrix (D). Varying with the FANP matrices which is reciprocal, D is a square matrix that indicates the intensity of the influence power of the row element i with respect to column elements j. The diagonal value for D (i.e., when i=j) is equal to zero, as it is assumed that an element has no influence upon itself (Si et al., 2018). D is then normalized by divided with the largest value of its row to form direct relation matrix (M). All the possible interacting of the elements in M is then captured to derive total relation matrix as illustrated by following equation:

$$T = M + M^2 + M^3 + \cdots + M^n \approx M(I - M)^{-1}, \quad \text{when } n \to \infty \tag{3}$$

where M is the normalized direct relation matrix and I is an identity matrix.

Next, calculate the sum of row (R_i) and column (C_i) of the T, where R_i indicates the overall influence power of row's element, while (C_i) indicates the intensity of column's element being influenced by other elements. The sum of row and column (i.e., $R_i + C_i$) shows the degree of prominence of the element i in the overall cluster. Meanwhile, (R_i - C_i) indicates the net effects of the element i in the system. Element with a positive value for (r_i - c_i) is classified as cause factor while element with a negative value for (r_i - c_i) is categorized as effect factor. The overall prominence level and cause and effect relationship can be illustrated by plotting a digraph with ($R_i + C_i$) against (R_i - C_i). The total relation matrix is normalized by the largest value of its column prior populated to the supermatrix.

Step 5: The priority vectors derived from FANP method and total relation matrix derived from DEMATEL method (i.e., shaded in grey in Figure 2) are act as entry into the initial supermatrix with the order as illustrated in Figure 2. The supermatrix is multiple by itself until the values are converged. The final priority weightage for the model is presented in the last column of the matrix in Figure 2 (i.e., highlighted in yellow).

$$S = \begin{pmatrix} 1 & e^T \text{ (v)} & e^T \text{ (vi)} \\ w_{21} \text{ (i)} & w_{22} \text{ (iii)} & 0 \\ 0 & w_{32} \text{ (ii)} & T \text{ (iv)} \end{pmatrix}$$

Note:
w_k - FANP priority vectors
T - DEMATEL total relation matrices

	Goal	TC	FN	SP	RG	ES	R1	R2	R3	R4	R5	R6	R7	R8	final value
Goal	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	**1.0000**
TC	0.22	1.00	0.50	0.37	0.29	0.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.2396**
FN	0.32	0.41	1.00	0.34	0.19	0.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.2994**
SP	0.17	0.29	0.28	1.00	0.29	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.1849**
RG	0.14	0.14	0.12	0.14	1.00	0.19	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.1335**
ES	0.15	0.16	0.10	0.15	0.23	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	**0.1425**
R1	0.00	0.03	0.19	0.03	0.12	0.05	0.56	0.70	0.56	0.50	0.53	0.60	0.17	0.20	**0.0930**
R2	0.00	0.14	0.23	0.08	0.17	0.03	1.00	0.65	0.83	0.45	0.77	0.79	0.16	0.22	**0.1157**
R3	0.00	0.07	0.17	0.30	0.09	0.16	0.80	0.47	0.57	0.66	0.98	0.39	0.25	0.45	**0.1105**
R4	0.00	0.14	0.14	0.12	0.11	0.19	0.97	0.79	0.66	0.55	0.58	0.89	0.94	0.78	**0.1555**
R5	0.00	0.08	0.09	0.19	0.05	0.12	0.85	0.48	1.00	0.38	0.53	0.35	0.13	0.19	**0.0913**
R6	0.00	0.27	0.03	0.05	0.13	0.07	0.97	1.00	0.96	0.66	1.00	0.68	0.26	0.50	**0.1442**
R7	0.00	0.18	0.08	0.12	0.17	0.20	0.51	0.45	0.82	0.88	0.60	0.68	0.41	1.00	**0.1391**
R8	0.00	0.09	0.07	0.11	0.16	0.18	0.57	0.64	0.68	1.00	0.49	1.00	1.00	0.43	**0.1507**

Figure 2: The initial supermatrix with the final priority weightages

3 Result and Recommendations

Based on the final priority weightage, financing risk (29.94 %) appeared to be the most prominent risk category in hindering the overall development of the biomass industry, followed by the technology risk (23.96 %), supply chain risk (18.49 %), environmental and social risk (14.25 %) and regulatory risk (13.35 %). Biomass project often associated with high upfront cost, which set a high barrier to enter the industry. It is challenging for the industry players to receive financing or investment from capital providers to start-up the project, particularly for small and medium enterprises (SMEs) that are lack with liquidity and assets to serve as guarantee on the total financing amount. At current stage, the technology associated with high-value added conversion is still extremely expensive and yet to achieve cost reduction with production at economic-of-scale. Lack of the commercialize viable technology and uncertain of long-term performance of the technology intensify the technology risk.

Taking into the causal and effect of risk events in deriving the final priority weightage for the 8 risk events, "R4 Lack of information to assess the performance of biomass project" (15.55 %) ranked the first to be debottlenecked the commercialization of biomass value added products in Malaysia, followed with "R8 Unclear regulations and policies related to biomass industry" (15.07 %) and "R6 Lack of resources and capability to scale up to industrial level" (14.42 %). It is suggested for the government to initiate a centralized data system that congregate all the information related to biomass industry, inclusive but not limited to the price of the supply and demand, technology and process available, supports and incentives offered to the industry stakeholders and rules and regulation associated with the industry. Furthermore, clear, consistent and adequate regulatory framework with supporting policies are also necessary to provide essential information for the industry players to understand the industry as a whole and take advantage on the supports and incentives offered by government to manage the respective risks.

4 Conclusion and Future works

The paper proposed a novel methodology for the assessment and prioritization of the risk associated with Malaysia biomass industry. The hybrid model that integrating FANP and DEMATEL provides a systematic and transparent way to identify, analyse and evaluate the correlation between elements and clusters and pinpoint the causal and effect factors in the model. The results provide a reference for the industry stakeholders to design risk management plan that directly tackle prominence and causal risk, to achieve the maximum output with minimum input. Future work will be focus on extending the model to produce a comprehensive risk profile for the biomass industry in Malaysia. Extra risk events can be added to current model to provides more dimension on the risks associated with the industry. An extra level of mitigation strategy can also be added to select the most effective strategy. Case study will be developed to validate the effectiveness of the risk mitigation strategy on hedge, transfer and reduce risks associated with the biomass industry in Malaysia.

Acknowledgments

The authors would like to thank Long Term Research Grant Scheme (LRGS Code: LRGS/2013/UKM-UKM/PT/06) from Ministry of Higher Education (MOHE), Malaysia and EP-2017-028 under the leadership of Prof. Dr. Er Ah Choy, Universiti Kebangsaan Malaysia for the funding of this research.

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University of Maribor Press

Halophilic Fungi - Alternative Raw Materials for Extremozymes Production

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Abstract *Trimatostroma salinum, Wallemia ichthyophaga, Hortaea werneckii* and *Phaeotheca triangularis* are halophilic fungi, which can thrive in a range of salinity from 0% to 32% NaCl. They present a source of valuable bio-active compounds, enzymes and proteins interesting for food, textile and pharmaceutical industry. Enzymes from these fungi, e.g. α-amylase, cellulase, lipase, and protease, which are thermostable, tolerant to a wide range of pH, less susceptible to denaturation and tolerant to high salt concentrations, present a novel catalytic alternative for biotechnological applications. Different methods (such as homogenization and supercritical treatment) for the separation of enzymes from halophilic fungi cells were used. When SCF is used for enzyme release from fungi cells, additional benefits regarding performance of a biochemical reaction and bioseparation in the same medium leading in integration of all three processes into a single step is offered and presents, from an economic point of view, important advantage in industrial processes. The influence of operation conditions and used separation methods of extremozymes from fungi cells on residual activities of enzymes (protease, α-amylase, β-glucosidase and cellulase) was studied.

Keywords: • Halophilic fungi • Enzymes• Proteins • Enzyme activity • Supercritical treatment •

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DOI https://doi.org/10.18690/978-961-286-211-4.24 ISBN 978-961-286-211-4
Available at: http://press.um.si.

1 Introduction

The great importance of the biotechnology industry is shown in the use of microbial intracellular proteins that possess catalytic or biological activity. For the manufacture of recombinant proteins, the release of catalytic active proteins and enzymes from living cells presents a key unit operation. Any living organism contains biologically active enzymes that can be extracted from them. The importance of microbial cells as a source of commercially useful chemicals, antibiotics and enzymes has been recognized for a very long time. They have several advantages over plant and animal cells with many good physiologic characteristics, such as high growth rate, capability to grow on simple media, no requirements of expensive additives, generation of high yields on the chosen carbon substrate, ability to grow at high cell densities and stable growth in continuous culture [1]. The most common source of industrial enzymes are microbes. The production of microbial enzymes takes place inside their cells (intracellular enzymes), although some may be secreted from outside the cell (extracellular enzymes). Extracellular enzymes are often soluble in water, which facilitates their extraction from the culture medium and purification. Obtaining an intracellular enzyme from microbial cells consists of two steps: harvesting microbial cells (by physical, chemical or enzymatic) from the culture and breaking the microbial cells to release the enzymes [2]. Several intracellular enzymes are produced industrially. The necessity of harvesting the producing cells, in order to subsequently extract an intracellular product, is a major economic disadvantage. Simultaneous isolation of intracellular products following cell disruption could lead to cost reduction [2]. Extremozymes, enzymes derived from extremophilic microorganisms, are an attractive alternative to tuning a given biocatalyst for a specific industrial application, since they can catalyze reactions in non-aqueous environments, water/solvent mixtures, at extremely high pressures, acidic and alkaline pH and also at very high temperatures. These enzymes already contain properties that are usually created in synthetically tailored enzymes by genetic engineering [3]. Extremophilic microorganisms are a rich source of naturally tailored enzymes with great potential for applications at extreme conditions. Especially lignocellulolytic, amylolytic, and other biomass processing extremozymes with unique properties are very interesting as biocatalysts for industrial processes. Extremophiles such as *T. salinum*, *W. ichthyophaga, H. werneckii* and *P. triangularis* present a source of chemically diverse and novel metabolites and proteins (e.g. enzymes such as protease, α-amylase, *β*-

glucosidase and cellulase) which are interesting for food, waste treatment, textile and pharmaceutical industry and offer new catalytic alternatives for industrial applications.

For the disruption of microbial cell walls, different methods can be used. They can be divided into two main groups: mechanical and (such as bead mills, French press, high-pressure homogenizer, ultrasonification etc.) and non-mechanical methods (enzymatic, physical or chemical). Various methods for cell disruption are currently commercially available from small to larger production quantities [4,5]. Nowadays, an interesting alternative to mechanical methods for cell lysis is usage of supercritical technology. Supercritical fluids (SCFs) can also serve as a solvent for the extraction of intracellular components from microbial cells or for isolation of products from the reaction mixture in the production of biomass. When the SCFs (such as supercritical carbon dioxide (SC CO_2)) is used for cell disruption, a sudden release of the pressure resulting in its penetration into cells and after expansion of gas within the cells and decompression of pressure forces the cell walls and causes cell disruption. It is a relatively simple method, can easily be scaled up and it is also comparable from efficiency, as well as economical points of view with a mechanical methods. Additional benefits of using supercritical technology for cell lysis are shown in the possibility of carrying out the release of enzymes from microbial cells, biochemical reaction(s) and bioseparation into a single step. The comparison of using mechanical method – homogenization and non-mechanical method – SC CO_2 treatment for black yeast cell disruption and influence of used method on activity of secreted enzymes was studied.

2 Materials and methods

The halophilic fungi *H. werneckii* EXF- 225, *P. triangularis* EXF-206, *T. salinum* EXF-295 and *W. ichthyophaga* EXF-5676 were kindly donated by the University of Ljubljana, Biotechnical Faculty, Department of Biology (Ljubljana, Slovenia). Carbon dioxide 2.5 (purity 99.5%) was supplied by Messer MG (Ruše, Slovenia). Peptone from meat (pancreatic) granulated, K_2HPO_4 (≥98.0%), Na_2CO_3 (anhydrous, ≥99.5%), $NaHCO_3$ (Ph Eur) and CH_3COOH (p.a.) were supplied by Merck (Darmstadt, Germany). $Na_4P_2O_7 \cdot 10H_2O$ (BioUltra, ≥99.5%), NaH_2PO_4 (≥99.0%), Na_2HPO_4 (BioReagent, suitable for cell culture, ≥99.0%), albumin from bovine serum (BSA) (lyophilized powder, ≥98.0%), malt extract (for microbiology), agar, D-(+)-glucose (BioReagent, suitable for cell culture, ≥99.5%),), CH_3COONa (anhydrous, for molecular biology, ≥99.0%,), Sigmacell, glucose assay reagent, Casein, Hammarsten bovine, CCl_3COOH (TCA), 2-(Hydroxymethyl)phenyl-β-D-glucopyranosid (≥99.0%), starch azure, KH_2PO_4 (for molecular biology, ≥98.0%) and NaCl were purchased from Sigma (Schnelldorf, Germany).

2.1 Cultivation of black yeast and cell disruption

The procedure for black yeast cultivation is documented by Čolnik et al. [6]. Cell lysis was performed using two methods: SC CO_2 treatment [7] and homogenization. The homogenization was performed in sterile centrifuge tube, which was filled with a fresh cell suspension of selected black yeasts, mixed and then placed into a water bath at a fixed temperature of 35 °C. For black yeast cell disruption, a rotor-stator homogenizer (Homogenizer, Polytron Pt1200, Kinematica AG, Switzerland) was used. The cell suspension was homogenized from 10 to 100 min at 25,000 rpm, and at a predetermined time, samples were taken for subsequent analysis. The experiments were repeated three times.

The activities of selected extremozymes from *T. salinum*, *W. ichthyophaga*, *H. werneckii* and *P. triangularis* were defined spectrometric using activity assay for protease [8] at 280 nm, α-amylase [9] at 595 nm, β-glucosidase [10] at 340 nm and cellulase [10] at 340 nm.

3 Results and discussion

An essential first step in the enzyme extraction process from a microbial cell is its rupture. Two different methods were used for black yeast cell wall disruption – SC CO_2 treatment and homogenization.

Some studies of cell wall disintegration and extraction of intracellular components privilege the use of non-mechanical methods but it has been demonstrated that even using mechanical methods such as homogenization, some intracellular enzymes from the halophilic fungal cells can be released while their activity is maintained.

The highest obtained residual activities of cellulase, *α*-amylase, *β*-glucosidase and protease from the studied black yeasts; *T. salinum*, *W. ichthyophaga, H. werneckii* and *P. triangularis*, at defined conditions using homogenizer or SC CO_2 for cell disruption, are presented in table 1.

The initial activity of selected enzymes in the black yeast cell suspensions before homogenization or treatment with SC CO_2 were set to a value of 100 %. Residual activity of enzymes are presented as an increase or decrease in a value after treatment at defined conditions in comparison with initial value.

As can be seen from table 1, the residual activities of enzymes regardless the used method for cell disruption, increase after the treatment. The reason for increase in residual activities is in secretion of intracellular enzymes in cell suspension after damaging or breaking down the cell walls. The highest residual activities for all studied enzymes were detected after the treatment with homogenizer. However, more intracellular enzymes with high residual activities were secreted from the black yeast cells using SC CO_2 treatment.

For release of the high-active enzymes from the black yeast cells, shorter time (from 30 min to 60 min) was needed when the cell suspensions were treated with homogenizer versus SC CO_2 treatment, where the cell suspension were exposed to high pressure from 30 min to 24 h. Each of these methods has its own advantages and disadvantages.

Since it is known, that SCFs can improve enzyme activity and that the release of enzymes from microbial cells, biochemical reaction(s) and bioseparation can be united into a single step (when the SCF is used as reaction medium), the use of SC CO_2 can be an alternative for performance of biochemical reactions in this medium with fungi cells as source of biocatalysts. Anyway, no uniform estimate of the activity of each enzyme after using different method for cell lysis can be given in advance.

Extremophilic microorganisms are a rich source of naturally tailored enzymes with great potential for applications at extreme conditions. Especially lignocellulolytic, amylolytic, and other biomass processing extremozymes with unique properties are very interesting as biocatalysts for industrial processes. Extremophiles such as *T. salinum*, *W. ichthyophaga, H. werneckii* and *P. triangularis* present a source of chemically diverse and novel metabolites and proteins (e.g. enzymes such as protease, α-amylase, *β*-glucosidase and cellulase) which are interesting for food, waste treatment, textile and pharmaceutical industry and offer new catalytic alternatives for industrial applications.

Table 1: Influence of used method and conditions for cell lysis on residual activity of secreted enzymes. Symbol: H – homogenization.

Enzymes	***The maximum residual activity of extremozyme in black yeasts cell suspensions (%)***		***Conditions***		***Black yeasts cell suspensions***	
	SC CO_2	**H**	**SC CO_2**	**H**	**SC CO_2**	**H**
cellulase	300	290	p = 30 MPa t = 24 h T = 35 °C	t = 30 min υ = 25,000 rpm T = 35 °C	*W. ichthyophaga* (intracellular)	*T. salinum* (extracellular)
***α*-amylase**	400	610	p = 30 MPa t = 5 h T = 35 °C	t = 60 min υ = 25,000 rpm T = 35 °C	*T. salinum* (intracellular)	*W. ichthyophaga* (intracellular)
***β*-glucosidase**	370	509	p = 10 MPa t = 30 min T = 35 °C	t = 60 min υ = 25,000 rpm T = 35 °C	*W. ichthyophaga* (extracellular)	*P. triangularis* (extracellular)
protease	230	800	p = 30 MPa t = 2 h T = 35 °C	t = 60 min υ = 25,000 rpm T = 35 °C	*T. salinum* (intracellular)	*H. werneckii* (intracellular)

4 Conclusion

From the biotechnological point of view, the separation of extremozymes (intracellular and extracellular) in the form of cocktail from halophilic fungi is interesting for industrial applications especially for cascade reactions. Different methods can be used to secrete enzymes from fungi cells, and the most appropriate method for a specific microorganism should be determined experimentally. Enzymes from extremophiles possess improved properties and can be used at harsh conditions where non-extremophilic enzymes may deactivate.

Acknowledgments

The authors would like to acknowledge Slovenian Research Agency (ARRS) for financing research in frame of Programme P2-0046 (Separation processes and production design). Special thanks goes to Prof. Dr. Nina Gunde-Cimerman, University of Ljubljana, Biotechnical Faculty, Slovenia for the donation of halophilic fungi.

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SEPTEMBER 5th – 7th, 2018, PORTOROŽ, SLOVENIA