The role of biomass and biofuels in the energy transition – a holistic interdisciplinary approach to sustainable anaerobic digestion

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ULOGA BIOMASE I BIOGORIVA U ENERGETSKOJ TRANZICIJI – INTERDISCIPLINARNI I CJELOVITI PRISTUP ODRŽIVOJ ANAEROBNOJ RAZGRADNJI

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DOCTORAL DISSERTATION

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Preface

Non scholae, sed vitae discimus.

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Summary

This doctoral dissertation evaluated the use of sustainable biomass sources (agri-food waste and residues, and industry streams) in anaerobic digestion with the goal of replacing maize silage in a large-scale biogas production and investigated alternative pathways of biogas utilisation incorporated in energy systems operating with high share of renewable energy sources. The methods applied in the research included elements of chemical and mechanical engineering in order to create a holistic approach that could be applicable to various biogas plant cases. Experimental investigations showed the biogas yield of residue lignocellulosic biomass of 0.192-0.275 Nm^3/kgTS, and bulk food waste of 0.252-0.566 Nm^3/kgTS. Meat and bone meal and wastewater sludge were shown to be co-substrates with antagonistic effect in biogas production, however they increased the reaction rate of overall degradation. Pyrolysis of digestate showed lower energy requirements and higher biochar yield (38%) compared to direct pyrolysis of lignocellulosic biomass (24%). The gate fee business model for receiving biodegradable waste and the implementation of new technologies, namely biogas upgrading, are the most likely options for biogas plants in the future. A robust mathematical model of power-to-gas integration showed that the installation of 18 MW_{el} of wind and 9 MW_{el} of photovoltaics with an additional import of 16 GWh_{el} from the grid could produce 36 GWh of renewable methane which could be economically competitive with natural gas if the feedstock gate fee in the proposed system was -120 €/t. Geospatial availability of an energy potential of biogas production from examined feedstocks, combined with Life Cycle Assessment of the alternative biogas utilisation pathways created the synergistic effects in terms of reduced environmental burdens by 4-36 times compared to the current operation. Based on the applied methods and outcomes of the doctoral thesis, the research hypothesis *"Applying holistic approach on biogas plants, both on the production and utilisation side, can increase economic profitability and environmental benefits over current subsidised operation"* was tested and confirmed. The economic feasibility of biogas plants after exiting subsidy schemes will include the implementation of the gate fee business model for substrates, new investments in biomass pretreatment lines, increase of on-site biogas storage capacity and additional investments in renewable methane production system, primarily biomethane. Environmental burdens of such actions will be reduced through a contribution of biowaste management on urban and rural level, combined with the utilization of biogas for production of biomethane as a replacement to natural gas.

Prošireni sažetak

Biomasa je obnovljiv izvor energije (OIE) te ima važnu ulogu u diverzifikaciji opskrbe energijom u Europskoj Uniji (EU) [1]. Ona doprinosi ravnoteži ugljikovog dioksida (CO_2), stvaranju radnih mjesta, smanjenju emisija stakleničkih plinova (eng. *Greenhouse gas*, GHG) te osiguravanju dostupnosti resursa i njihovom ekonomičnom gospodarenju [2]. U Republici Hrvatskoj biomasa je definirana prema *Zakonu o obnovljivim izvorima energije i visokoučinkovitoj kogeneraciji* kao "biorazgradivi dio proizvoda, otpada i ostataka biološkog podrijetla iz poljoprivrede (uključujući tvari biljnoga i životinjskoga podrijetla), šumarstva i srodnih proizvodnih djelatnosti, uključujući ribarstvo i akvakulturu, kao i biorazgradivi dio industrijskoga i komunalnog otpada" [3]. Biomasa se može direktno koristiti kao gorivo za dobivanje energije (npr. drvna biomasa u kotlovima), ili se može biokemijskim, kemijskim, ili termokemijskim postupcima pretvoriti u materijal dodane vrijednosti – biogorivo, čime se postiže njezina šira primjenjivost u energetske svrhe [4]. Biogoriva prve generacije dobivena iz prehrambenih usjeva kao uzgojene biomase [5] naišla su na neodobravanje znanstvene zajednice i šire javnosti, primarno zbog korištenja obradivih površina za njihov uzgoj. Napredna biogoriva (druge i treće generacije [5]) proizvedena su iz biomase koja nije kompetitivna s proizvodnjom hrane, a u nju spada otpadna biomasa iz kućanstva i industrije, poljoprivredni ostatci, neprehrambeni usjevi te alge. Ova doktorska disertacija stavlja fokus na korištenje biomase u procesu anaerobne razgradnje za dobivanje bioplina. Cilj istraživanja je ostvariti sinergijski učinak između ekonomičnog korištenja otpadne biomase i proizvodnje energije u sustavima s velikim udjelom OIE kako bi se postiglo smanjenje utjecaja na okoliš u usporedbi s trenutnom praksom u bioplinskim postrojenjima koja uključuje korištenje kukuruzne silaže i proizvodnju električne energije uz zajamčenu otkupnu cijenu.

Mjesto nastanka, tip biomase, te njezine količine bitan su faktor za strateško pozicioniranje novih bioplinskih postrojenja, te za planiranje novih lanaca opskrbe sirovinama u postojećim postrojenjima. Geografski informacijski sustav (eng. *Geographic Information System*, GIS) [6] prepoznat je kao vrijedan alat za mapiranje potencijala izvora biomase, kao i određivanje transportnih udaljenosti od mjesta nastanka biomase do postrojenja. GIS analiza na razini EU pokazala je ukupni energetski potencijal za proizvodnju bioplina iz poljoprivrednih ostataka i životinjske gnojovke na godišnjoj razini jednak 0.7 EJ (oko 195 TWh) [7], što je dvostruko više nego proizvodnja bioplina iz tih supstrata ostvarena u 2016 godini u EU. Primjenom GIS alata na lokalnoj razini u Grčkoj, Sjedinjenim Američkim

Državama i Finskoj pokazano je da ekonomski prihvatljive transportne udaljenosti za supstrate mogu varirati između 10 i 40 km [8–10]. Povećanjem radijusa raspoloživosti biomase povećava se i kapacitet postrojenja čime je moguće ostvariti veću proizvodnju obnovljive energije, no istovremeno stvara se dodatan teret na okoliš, kako je još uvijek većina biomase transportirana teretnim vozilima na fosilna goriva [10]. Ono što također treba uzeti u obzir prilikom procjene korištenja biomase u bioplinskom postrojenju je njezina tržišna vrijednost, odnosno plaća li bioplinsko postrojenje za biomasu, ili dobiva naknadu za njezino gospodarenje (eng. *Gate fee, GF*). U postojećim okvirima proizvodnje bioplina, cijena kukuruzne silaže je između 15 i 40 € po toni sirovine [11], dok alternativni izvori biomase (npr. miješani komunalni biootpad i otpadna hrana) postižu *GF* u iznosu od -60 do 0 €/tona [11].

Nakon što biomasa uđe u prostor bioplinskog postrojenja, potrebno ju je adekvatno pripremiti za proces anaerobne razgradnje. U tu svrhu mogu se koristiti metode predobrade koje se služe termičkim, mehaničkim, kemijskim ili biološkim postupcima (ili nekim njihovim kombinacijama) [12]. Metode predobrade služe kako bi potaknule proces razgradnje kompleksnih polimernih molekula prisutnih u organskoj tvari, čime se postiže viša konverzija biomase u bioplin [13]. Uspješnost razgradnje biomase te proizvodnje bioplina, kao i stabilnost u procesu određuju se eksperimentalnim mjerenjima, pri čemu se prate procesne varijable kao što su sadržaj suhe tvari (eng. *Dry Matter, DM,* ili *Total Solids, TS*), proizvodnja i sastav bioplina, *pH*, koncentracija hlapljivih masnih kiselina (eng. *Volatile Fatty Acids, VFA*), ukupni anorganski ugljik (eng. *Total Inorganic Carbon, TIC*), prisutnost amonijakalnog dušika (eng. *Ammonium-nitrogen,* NH_4*-N),* koncentracija soli, teških metala i ostalo [14]. Na temelju vrijednosti navedenih procesnih varijabli operatori bioplinskih postrojenja znaju odvija li se proces unutar dozvoljenih vrijednosti te kako reagirati ukoliko je primijećena nestabilnost u procesu. Eksperimentalni podatci također služe za modeliranje kinetike anaerobne razgradnje [15] pri čemu se ovisnosti o kompleksnosti ulaznih podataka i traženih rezultata mogu primijeniti razni kinetički modeli [16–18]. Složeniji modeli zahtijevaju veći broj ulaznih podataka, ali također daju i detaljniji uvid u mehanizam reakcija i otkrivanju tzv. *uskog grla procesa* koji određuje ukupnu brzinu nastanka bioplina. Osim bioplina, drugi proizvod anaerobne razgradnje je digestat kojeg čine nerazgrađeni ostatci biomase u tekućoj fazi [19]. Tekuća frakcija digestata je obično bogata makronutrijentima – dušikom (N), fosforom (P) i kalijem (K), što ju čini primjenjivom kao gnojivo za tlo [20]. Čvrsta frakcija digestata također sadrži P, ali i zaostali organski ugljik (C) što ga čini prikladnim za poboljšavanje karakteristika tla, kompostiranje [21] ili za neki od oblika energetske oporabe [22]. Prednost korištenja digestata u opisanim načinima leži u činjenici da je njegova tržišna vrijednost mala, tek 2-4 €/t [23].

Proizvedeni bioplin najčešće se koristi kao gorivo u kombiniranoj proizvodnji električne i toplinske energije, kogeneracija (eng. *Combined Heat and Power*, CHP). Proteklih desetljeća na razini EU mehanizmi subvencija za bioplinske kogeneracije u vidu *feed-in-tariffa* i *feed-in-premija* rezultirale su intenzivnom penetracijom bioplina u elektroenergetski sektor [24]. Razina subvencija je definirana na nacionalnoj razini, ali u svim članicama EU nije niža od 80 €/MWh$_{el}$, što je gotovo dvostruko veći iznos od prosječne veleprodajne tržišne cijene električne energije u EU [25]. Također, ono što je važno napomenuti jest da su subvencije izdane na određeni period (12-20 godina od statusa stjecanja povlaštenog proizvođača električne energije [26]) nakon čega će bioplinska postrojenja morati razmotriti neke druge načine iskorištavanja (eng. *Utilisation*) bioplina da bi zadržale ekonomski isplativo poslovanje. Prema podatcima Europske udruge za bioplin (eng. *European Biogas Association*, EBA) u 2020. godini u Europi je bilo instalirano 18,943 bioplinskih postrojenja, od kojih je 18,214 (96%) radilo u kogeneracijskom načinu, a ostalih 4% kao postrojenja za proizvodnju biometana kroz tehnologiju poboljšavanja bioplina (eng. *Biogas upgrading*) odnosno uklanjanje svih ne-CH_4 komponenti bioplina [27]. Ova doktorska disertacija detaljno razlaže inovativnije načine iskorištavanja bioplina u budućim energetskim sustavima, što će uključivati rad kogeneracijskih postrojenja u tržišnim okvirima [28], pretvorbu bioplina u biometan te proizvodnju e-metana kroz implementaciju *power-to-gas* (P2G) koncepta [29] u sustavima s visokim udjelom energije iz varijabilnih OIE.

Primjena procjene životnog ciklusa (eng. *Life Cycle Assessment*, LCA) [30] može otkriti utjecaje promjene politika sirovina u proizvodnji bioplina i njegovog iskorištavanja u sprezi s budućim energetskim sustavima u odnosu na okoliš. Usporedba LCA performansi za bioplinsko postrojenje koje koristi životinjsku gnojovku i energetske usjeve pokazala je da bioplin za proizvodnju električne energije stvara uštede od oko 300 kgCO_2-eq/MWh$_{el}$, dok *upgrading* bioplina u biometan i njegovo ubrizgavanje u plinsku mrežu štedi oko 191 kgCO_2-eq za proizvedeni MWh biometana [31]. Za preglednije tumačenje opisanih rezultata potrebno je izraziti emisije istom jedinicom, ali i prezentirati podatke o sastavu miksa električne energije (eng. *Electricity mix*). Za slučaj Irske, LCA je pokazao da integracija P2G koncepta za *upgrading* bioplina, uz korištenje električnog miksa od 85% OIE, može rezultirati smanjenjem GHG emisija za 70% u odnosu na fosilna goriva [32].

Na temelju pregleda literature (detaljniji prikaz u poglavlju *Introduction*), dosad nije zabilježeno istraživanje u području anaerobne razgradnje koje povezuje mapiranje i korištenje ostatne i otpadne biomase za proizvodnju bioplina sa njegovim iskorištavanjem u budućim energetskim sustavima. Ova doktorska disertacija je ocijenila takav cjeloviti pristup i predstavila rezultate istraživanja iz perspektive jednog, odnosno više bioplinskih postrojenja.

Interdisciplinarni i cjeloviti pristup prema promatranoj temi koristio je elemente kemijskog i strojarskog inženjerstva za ispunjavanje **četiri glavna cilja istraživanja**:

- Kvantificirati proizvodnju bioplina koristeći nove supstrate biomase kao što su lignocelulozni ostatci iz poljoprivredne proizvodnje, otpadna hrana i industrijski nusproizvodi koji nisu konkurentni proizvodnji hrane, kao što je to slučaj s kukuruznom silažom u sadašnjoj proizvodnji bioplina.
- Procijeniti kinetičke parametre anaerobne razgradnje novih supstrata kombinirajući matematičko modeliranje i eksperimentalne podatke kako bi utvrdili utjecaj kemijskog sastava supstrata na stabilnost procesa i eventualna ograničenja u procesu.
- Utvrditi ekonomski isplative načine budućeg rada bioplinskih postrojenja na naprednim energetskim tržištima nakon što bioplinska postrojenja ostanu bez financijskih potpora i zajamčene cijene električne energije.
- Procijeniti utjecaje na okoliš različitih načina korištenja bioplina integriranih u buduće energetske sustave s visokim udjelom obnovljivih izvora energije.

Ostvareni ciljevi istraživanja te rezultati prezentirani su široj znanstvenoj zajednici kroz sedam objavljenih znanstvenih radova (šest radova u kvartilu Q1 te jedan rad u Q2).

Znanstveni članak 1 (*ARTICLE 1*) [33] prikazuje detaljnu analizu lanaca vrijednosti biomase iz različitih poljoprivrednih ostatka, nusproizvoda i otpada (eng. *Agricultural wastes, co-products and by-products*, AWCB). Rad opisuje faze u kojima i kako nastaje otpad kroz tri specifična koraka u lancu vrijednosti: proizvodnja/uzgoj, obrada u industriji te potrošnja/konzumacija. Analiza uključuje razdoblje od 7 godina, od 2010. do 2016. u 28 zemalja članica Europske unije (EU28) te uključuje četiri različita sektora sa 26 analiziranih dobara (eng. *Commodity*) i prikladnim vrstama otpada koji se pojavljuju u tim sektorima. Za izračun tehničkog potencijala AWCB korišteni su javno dostupni podaci iz EUROSTAT i FAOSTAT baze, a metoda proračuna uključivala je upotrebu specifične količine AWCB po analiziranim dobrima i sektoru. Rezultati su pokazali da je u analiziranom periodu u EU28 procijenjena količina AWCB iznosila oko 18,4 milijarde tona, a prema udjelima: animalni sektor ~ 31%, sektor povrća ~ 44%, sektor žitarica ~ 22% te sektor voća ~ 2%. Analizirajući pojedine sektore i količine nastalog AWCB, daljnje istraživanje bilo je usmjereno na evaluaciju korištenja određenih AWCB iz lanca vrijednosti biomase u procesu anaerobne razgradnje s ciljem proizvodnje bioplina. Znanstveni članci *2*, *3* i *4* pokazuju rezultate takvog pristupa uz primjenu istraživačkih metoda kemijskog inženjerstva.

ARTICLE 2 [34] istražuje upotrebu lignoceluloznih ostataka trave kao zamjene za silažu kukuruza u anaerobnoj razgradnji. Uzorci trave prikupljeni su s područja koja nisu kompetitivna s proizvodnjom hrane: neobrađeno zemljište, obala rijeke Save u gradu Zagrebu te bankina autoceste. U istraživanju je određen svježi i suhi prinos biomase, njezin kemijski sastav, prinos te sastav proizvedenog bioplina, a primjenom *Anaerobic Digestion Model No. 1* (ADM1) modela određeni su kinetički parametri razgradnje trave. Ujedno, na kraju je dana usporedba okolišnijih učinaka zamjene kukuruzne silaže ostatnom travom u proizvodnji električne i toplinske energije. Rezultati istraživanja su pokazali da je najveći prinos ostatne trave utvrđen za obalu rijeke, sa prosječnom vrijednošću od 19 t/ha svježe mase i 2.6 t/ha suhe mase. Svi uzorci trave pokazali su zadovoljavajuće parametre za primjenu u anaerobnoj razgradnji − omjer C/N između 16.6: 1 do 22.8: 1. Ostvareni biokemijski potencijal metana u monorazgradnji (monodigestiji) ostataka trave su: 0.275 Nm^3/kgTS za travu s neobrađenog zemljišta, 0.192 Nm^3/kgTS za travu s obale rijeke i 0.255 Nm^3/kgTS za travu s bankine autoceste. Procijenjeni kinetički parametri razgradnje trave razlikuju se od do sada objavljenih rezultata, prvenstveno zato što prijašnje analize uključuju specifične tipove travnate biomase, a ne ostatnu (miješanu) travu. Procijenjeni okolišniji utjecaji zamjene kukuruzne silaže travnatom biomasom u proizvodnji električne i toplinske energije pokazali su prednosti u smislu ostvarenog doprinosa kvaliteti ekosustava (eng. *Ecosystem quality*) i ljudskog zdravlja (eng. *Human health*), no također i nešto veće emisije GHG uzrokovane izgaranjem fosilnih goriva u poljoprivrednoj mehanizaciji i povećanim transportom trave zbog nižeg prinosa bioplina u odnosu na silažu. Čvrsta frakcija digestata dobivena u procesu monodigestije trave korištena je u znanstvenom članku 3 (*ARTICLE 3*) kao ulazni materijal za istraživanje procesa pirolize.

Cilj istraživanja u *ARTICLE 3* [35] bio je odrediti utjecaj anaerobne razgradnje na sastav lignocelulozne biomase korištenjem termogravimetrijske analize (eng. *Thermogravimetric analysis*, TGA). Također, procijenjeni su iznosi energije aktivacije i modificiranog predeksponencijalnog faktora za travu i njezine digestate, kao i prinos konačnog ostatka pirolize (eng. *Biochar*). Rezultati su pokazali da je procijenjena količina razgrađene celuloze i hemiceluloze u istraživanim uzrocima trave oko 44–50%. Nadalje, digestati trave pokazali su veći prinos *biochar-a* (oko 38%) u odnosu na uzorke trave (oko 24%). Kombinirani proces anaerobne razgradnje trave i pirolize njezinih digestata pokazao je manje vrijednosti procijenjenih kinetičkih parametra što upućuje na niže energetske potrebe takvog procesa u odnosu na direktnu pirolizu trave.

ARTICLE 4 [36] bio je izrađen u suradnji sa industrijom biomase i bioplina. U radu je eksperimentalno istražena razgradnja otpadne hrane (eng. *Food waste*, FW) iz bioplinskog postrojenja zajedno s nusproizvodnima iz kafilerije (eng. *Rendering plant*): mesno-koštano brašno (eng. *Meat and bone meal*, MBM) i mulj sa otpadnih voda (eng. *Wastewater sludge*, WWS). Prvo je provedena termička predobrada uzoraka FW (FW1 i FW2) pri temperaturi od 35 °C i trajanju 5 dana u koju su bili dodani MBM i WWS u udjelima od 5, 10 i 15% TS. Nakon toga slijedila je anaerobna razgradnja pri 40.5 °C u trajanju od 40 dana. Uvjeti termičke predobrade i proizvodnje bioplina u laboratorijskom mjerilu replicirani su iz rada samog bioplinskog postrojenja. Također, za vrijeme procesa u laboratoriju bile su praćene sve procesne varijable kao i u radu digestora na postrojenju. Kao rezultat predobrade kemijska potrošnja kisika (eng. *Chemical Oxygen Demand*, *COD*) ispitivanih uzoraka povećala se za 7 – 26%. Dodavanjem MBM u FW1 došlo je do povećanja vrijednosti *COD* kao i NH_4-N, dok se u slučaju dodatka WWS u FW2 postiglo smanjenje, što je i bilo očekivano, budući da je WWS materijal s niskim udjelom organske tvari. Kao rezultat testa anaerobne razgradnje dobiveni su sljedeći prinosi bioplina: za FW1 – 0.566 Nm^3/kg TS, za FW1-MBM – 0.499 Nm^3/kg TS, za FW2 – 0.252 Nm^3/kg TS i 0.195 Nm^3/kg TS za FW2-WWS. Tako širok raspon vrijednosti rezultat je heterogenosti FW (FW1 i FW 2 uzete su s vremenskim razmakom od dva mjeseca na istom postrojenju). Prema sastavu proizvedenog bioplina, kao i ostalim procesnim varijablama može se zaključiti da su FW1 i FW2 vrlo slični po sastavu, ali da je istovremeno postojao neki uzročnik inhibicije u proizvodnji bioplina za uzorak FW2, koji se nije mogao procijeniti na temelju dostupne opreme i provedenih mjerenja. Tek su mjerenja električne vodljivosti ukazala na to da uzorak FW2 sadrži nešto veću koncentraciju soli koja bi mogla biti uzročnik smanjenog prinosa bioplina. Nusproizvodi kafilerije dodani u 5%-tnom udjelu uzrocima FW rezultirali su smanjenjem proizvodnje bioplina za 12% u slučaju MBM i 23% u slučaju WWS, ali nisu utjecali na stabilnost proizvodnje. Štoviše, analizom kinetike razgradnje ustanovljeno je da MBM i WWS ubrzavaju proces razgradnje FW što se vidi iz višeg iznosa reakcijske konstante. Također, pokazano je da ispitivani uzorci najbolje koreliraju sa kinetikom prvog reda što je vidljivo iz najniže ostvarene vrijednosti *RMSE* (eng. *Root mean square error*) koja je iznosila 0.015 Nm^3/kg TS.

U znanstvenom članku 5 (*ARTICLE 5*) [37] provedena je tehno-ekonomska i scenarijska analiza rada bioplinskog postrojenja nakon isteka subvencija za proizvodnju električne energije. Vođenje takvog sustava temeljilo se na iznosu cijena električne energije i biometana (eng. *Unit commitment with economic dispatch*) koje su određivale koja od jedinica za prihvat bioplina: CHP, *upgrading* ili spremnik ima najveću ekonomsku isplativost u danom trenutku. Za opis dinamike korišten je program MATLAB/Simulink, a za ekonomsku analizu MS Excel. U prvom scenariju prikazan je utjecaj cijene proizvodnje električne energije u bioplinskom postrojenju (eng. *Break-even point of electricity production*, $BECP_{el}$) na broj radnih sati kada ono može ostvariti svojevrstan profit na dan-unaprijed tržištu (eng. *Day-ahead market*) električne energije. Rezultati su pokazali da kada vrijednost $BECP_{el}$ postane 40 €/MWh_{el}, bioplinsko postrojenje može ostvariti (neki) profit radeći samo 4,000 sati godišnje, kako je ostalo vrijeme cijena električne energije na tržištu niža od cijene proizvodnje. Kada $BECP_{el}$ postane 100 €/MWh_{el} bioplinsko postrojenje ne može ostvariti nikakav profit radeći na dan-unaprijed tržištu. Kao jedno od rješenja koje se nameće za smanjenje vrijednosti $BECP_{el}$ je korištenje supstrata s negativnom cijenom (*GF* model) koja je detaljnije prikazana u članku 6 (*ARTICLE 6*). Drugi scenarij uključivao je instaliranje *upgrading* jedinice i proizvodnju biometana, a proizvodnja električne energije ovisila je o cijenama na tržištu uravnoteženja (eng. *Balancing market*). Takav pristup je pokazao da bioplinsko postrojenje i uz relativno visoku cijenu biometana od 80 €/MWh, može u određenim trenutcima ostvariti i veći profit ako radi na *balancing* tržištu. Treći scenarij za bioplinsko postrojenje uključivao je integraciju industrijskog otpada iz proizvodnje šećera za proizvodnju bioplina i njegovo korištenje za proizvodnju procesne topline u vrijeme šećerne kampanje. Takav pristup pokazao se relativno neisplativim za bioplinsko postrojenje kako je cijena prirodnog plina na veleprodajnom tržištu još uvijek dosta niska i bioplin joj ne može u tom smislu biti konkurentan.

ARTICLE 6 [38] predstavlja rezultate integracije P2G koncepta u rad bioplinskog postrojenja koje se nalazi u *GF* poslovnom modelu, odnosno prima naknadu za ulazni supstrat pri proizvodnji bioplina. Cilj istraživanja bio je razviti robustan matematički model na satnoj razini za procjenu optimalnih kapaciteta vjetroelektrane i solarne elektrane, veličine spremnika za bioplin te kapacitete elektrolizera, *upgrading* jedinice i metanatora (eng. *Methanation unit*) koristeći linearno programiranje i besplatni (eng. *Open source*) programski jezik Julia. Kao funkcija cilja korištena je minimizacija ukupnih troškova. Matematički model testiran je na postojećoj bioplinskoj elektrani instalirane snage 1 MW_{el}. Utvrđeno je da P2G koncept zahtijeva integraciju 18 MW_{el} vjetra i 9 MW_{el} solara na lokaciji, uz dodatan uvoz električne energije iz mreže u iznosu 16 GWh_{el} kako bi se na godišnjoj razini proizvelo 36 GWh obnovljivog metana. Analiza je pokazala da *GF* (u promatranom slučaju za otpadnu hranu) značajno doprinosi ekonomskoj održivosti obnovljivog metana: promjena *GF* za 100 €/toni rezultira smanjenjem troškova njegove proizvodnje za 20-60%. Ustanovljeno je da za vrijednost *GF*=-120 €/tona obnovljivi metan iz prikazanog koncepta postaje cjenovno konkurentan prirodnom plinu. Robusna priroda modela pokazala je da nesigurnosti povezane s proizvodnjom električne energije iz vjetra i solara na lokaciji mogu povećati troškove proizvodnje obnovljivog metana za 10-30%.

ARTICLE 7 [39] integralno obuhvaća rezultate svih dotad objavljenih radova u sklopu izrade doktorske disertacije i smješta ih u kontekst testiranja hipoteze. U njemu je provedena geoprostorna analiza (eng. *Geospatial analysis*) bioplinskog sektora korištenjem javno dostupnog programa QGIS te procjena okolišnijih utjecaja pomoću programa SimaPro. Cilj rada bio je mapirati energetski potencijal otpadne trave, industrijskih nusproizvoda i otpada, te komunalnog biootpada (otpadne hrane) za zamjenu kukuruzne silaže u postojećoj proizvodnji bioplina te planiranje proširenja bioplinskog sektora. Kao studija slučaja (eng. *Case study*) korištena je Sjeverna Hrvatska (eng. *Northern Croatia*), područje s intenzivnim bioplinskim sektorom te snažnom industrijom, poljoprivredom i velikom gustoćom stanovništva. Rezultati su pokazali da bi navedene sirovine mogle zamijeniti 212 GWh bioplina iz kukuruzne silaže u postojećim bioplinskim postrojenjima te stvoriti dodatnih 191 GWh biometana u novim postrojenjima. Također, geoprostorna analiza je pokazala da su neka bioplinska postrojenja izgrađena u neposrednoj blizini plinske transportne mreže (<2km udaljenosti) i da imaju potencijal za utiskivanje biometana u plinsku mrežu. Cjelokupna analiza utjecaja na okoliš postojećih bioplinskih postrojenja pokazala je da integralni pristup proizvodnji i korištenju bioplina stvara sinergijske učinke u smislu smanjenja opterećenja na okoliš, što izravno dokazuje hipotezu studije. Kompleksnost P2G koncepta i njegovi intenzivni energetski zahtjevi čine ga trenutno nepovoljnijim u usporedbi sa klasičnim *upgradingom* bioplina, no isti dolazi do izražaja kada se u razmatranje uzmu budući energetski sustavi s visokim udjelom OIE.

Znanstveni doprinosi ovog rada ostvareni su kroz provedena istraživanja te prikazani kroz objavljene rezultate u radovima kako slijedi:

- Eksperimentalnim istraživanjem anaerobne razgradnje novih supstrata biomase odredit će se potencijalne prepreke u proizvodnji bioplina, poput pojave inhibicije ili utjecaja tipa biomase na stabilnost procesa:

ARTICLE 2: Ustanovljeno je da lignocelulozna biomasa u obliku ostatne trave ne sadrži fizikalno-kemijske karakteristike koje bi ograničile njezinu upotrebu za proizvodnju bioplina. Štoviše, pokazalo se da ista uzrokuje poboljšanu kontrolu pH što doprinosi stabilnosti proizvodnje bioplina. Nedostatak njezinog korištenja je taj što je za ostvarivanje većih prinosa potrebno primijeniti neki oblik predobrade.

ARTICLE 4: Heterogenost otpadne hrane utječe na vođenje procesa za što je potrebno ustanoviti robusnu kontrolu procesnih varijabli. Pokazalo se da i na razini bioplinskog postrojenja postoje neke varijable koje se ne prate na dnevnoj razini (prisutnost soli i metala), a koje mogu uzurpirati proizvodnju bioplina. Ustanovljeno je da kafilerijski nusprodukti i otpad u manjim količinama mogu doprinijeti povećanju brzine razgradnje otpadne hrane.

- Predložiti alternativne mjere za trenutni sektor bioplina uzimajući u obzir tržišne cijene i analizu utjecaja na okoliš koristeći pristup procjene životnog ciklusa.

ARTICLE 5: Alternativne mjere za bioplinski sektor u vidu proizvodnje biometana i rada bioplinskih postrojenja na *day-ahead* i *balancing* tržištu električnom energijom pokazala se kao najvjerojatnija opcija nakon napuštanja poticajnih sustava za proizvodnju električne energije. U takvim okvirima tranzicija s kukuruzne silaže na supstrate alternativne supstrate postati će prihvatljiva operativna odluka uz dodatne investicije u novu opremu.

ARTICLE 6: Integracija varijabilnih OIE u rad bioplinskih postrojenja pokazala je da će se u budućnosti paradigma bioplinskih postrojenja kao takvih promijeniti – više neće biti samo pasivni proizvođači struje, nego će postati aktivni sudionici na tržištima energijom.

ARTICLE 2: Pokazano je da otpadana trava više doprinosi kvaliteti ekosustava i ljudskom zdravlju nego kukuruzna silaža, iako uzrokuje veće emisije stakleničkih plinova, prvenstveno zbog intenzivnijih potreba za transportom na fosilna goriva.

ARTICLE 7: LCA predloženih mjera za sektor bioplina koje uključuju zamjenu kukuruzne silaže alternativnih oblicima biomase te iskorištavanje bioplina u sustavima s visokim udjelom OIE pokazala je sinergistički efekt u smislu smanjenja cjelokupnog tereta na okoliš. Analiza je također pokazala da je integracija P2G u promatranim okvirima još uvijek neatraktivna zbog kompleksnosti sustava i energetski intenzivnih procesa.

- Napredni model geografskog informacijskog sustava mapiranja novih izvora biomase koji će u kombinaciji s različitim načinima korištenja bioplina integriranim u sustave visokih obnovljivih izvora energije u naprednim energetskim tržištima rezultirati robusnim matematičkim modelima primjenjivim na različite slučajeve bioplinskih postrojenja.

ARTICLE 6: Razvijeni robusni model integracije P2G koncepta u rad bioplinskog postrojenja pokazao je sinergiju između *GF* poslovnog modela te integracije obnovljive električne energije i topline koji su objedinjeni u postavljenoj matematičkoj formulaciji nivelirane cijene obnovljivog metana (eng. *Levelized cost of renewable methane, LCORM*).

ARTICLE 7: Razvijeni GIS model obuhvaća analizu postojećih bioplinskih postrojenja i pozicioniranje budućih biometanskih postrojenja na temelju geoprostorne analize dostupnih alternativnih supstrata i položaja plinske mreže.

Hipoteza ovog istraživanja je da je primjenom cjelovitog pristupa u radu bioplinskih postrojenja, i na strani proizvodnje i iskorištavanja bioplina, moguće povećati ekonomsku profitabilnost i doprinos zaštiti okoliša u usporedbi s trenutnim subvencioniranim radom. Kroz provedena istraživanja hipoteza je testirana i potvrđena uzevši u obzir sljedeće:

- Ekonomska profitabilnost bioplinskih postrojenja nakon napuštanja subvencija i ograničenja u korištenju kukuruzne silaže bit će teže ostvariva. Uključivat će implementaciju *GF* poslovnog modela za supstrate za što će biti potrebne nove investicije po pitanju linije za predobradu, povećanje kapaciteta za spremanje bioplina na lokaciji kako bi postrojenje bilo fleksibilnije na tržištu električne energije te dodatne investicije u sustav za proizvodnju obnovljivog metana, prvenstveno biometana.
- Cjeloviti pristup pokazao je da će doprinos budućeg bioplinskog sektora smanjenju okolišnih tereta ići kroz dvostruki doprinos: iz gospodarenja otpadom za proizvodnju bioplina koji će uključivati prvenstveno komunalni i industrijski biootpad u urbanim bioplinskim postrojenjima, a poljoprivredne ostatke u ruralnim bioplinskim postrojenjima, te iskorištavanja bioplina za proizvodnju obnovljive energije u vidu biometana.

Keywords: Biomass, biofuels, anaerobic digestion, renewable energy sources, chemical kinetics, geospatial availability, environmental impacts.

Ključne riječi: Biomasa, biogoriva, anaerobna razgradnja, obnovljivi izvori energije, kemijska kinetika, geoprostorna dostupnost, utjecaji na okoliš.

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List of abbreviations

Ac	Acetate
AD	Anaerobic digestion
ADM1	Anaerobic Digestion Model No. 1
AWCB	Agricultural wastes, co-products and by-products
Ch	Carbohydrates
CHP	Combined heat and power
DM	Dry matter
EBA	European Biogas Association
EU/EU28	European Union
FIP	Feed-in-premium
FIT	Feed-in-tariff
FM	Fresh matter
FR	Friedman
FW	Food waste
GHG	Greenhouse gas
GIS	Geographic information system
IEA	International Energy Agency
IN	Inoculum
KAS	Kissinger-Akahira-Sunose
LCA	Life Cycle Assessment
LCFAs	Long chain fatty acids
Li	Lipids
MBM	Meat and bone meal
MMS	Monodigestion of maize silage
MRG	Monodigestion of residue grass
MS	Maize silage
NUTS	Nomenclature of Territorial Units for Statistics
P2G	Power-to-gas
Pr	Proteins
PV	Photovoltaic
RES	Renewable energy sources
RG	Residue grass
RGD	Residue grass digestate

RG-H	Residue grass near highway
RG-MR	Residue grass near minor road
SNG	Synthetic natural gas
TGA	Thermogravimetric analysis
TS	Total solids
VFAs	Volatile fatty acids
VS	Volatile solids
WWS	Wastewater sludge

Nomenclature

$BECP_{el}$	*Break-even point of electricity production* [€/MWh_{el}]
BGP	*Biochemical biogas potential* [Nm^3/kgTS]
BMP	*Biochemical biomethane potential* [Nm^3/kgTS]
COD	*Chemical oxygen demand* [gO_2/L]
E_α	*Activation energy* [kJ/mol]
GF	*Gate fee* [€/tonne]
GWP	*Global warming potential* [$kgCO_2$-eq]
IRR	*Internal rate of return* [−, %]
k	*Reaction rate constant* [d^{-1}]
k_{dis}	*Disintegration constant* [d^{-1}]
k_{hyd}	*Hydrolysis constant* [d^{-1}]
k_m	*Monod maximum specific uptake rate constant* [kgO_2/m^3]
K_S	*Half-saturation constant* [$kgO_2/(kgO_2 \cdot d)$]
LCOE	*Levelized cost of electricity* [€/MWh_{el}]
LCORM	*Levelized cost of renewable methane* [€/MWh]
LHV	*Lower heating value* [MJ/kg]
m	*Mass* [g, kg, t]
n	*Shape factor* [−]
NH_4-N	*Ammonium nitrogen* [g/L]
P	*Power (electrical)* [kW_{el}, MW_{el}, GW_{el}]
pH	*Power of hydrogen* [−]
R	*Biogas production rate* [$Nm^3/(kg\ TS \cdot d)$]
R_m	*Maximum Monod uptake* [$Nm^3/(kg\ TS \cdot d)$]
RMSE	*Root mean square error* [Nm^3/kg]
S	*Biogas yield* [Nm^3/kg]

t	*Time* [h, d]
TIC	*Total inorganic carbon* [g $CaCO_3$/L]
UHV	*Upper heating value* [MJ/kg]
V	*Volume of gas* [Nm^3]
VFAs	*Volatile fatty acids* [g CH_3COOH/L]

Subscripts

dem	*demand*
el	*electric*
exp	*experimental*
imp	*imported*
mod	*model*

Greek Symbols

α	*Degree of conversion* [−]
λ	*Lag phase* [d]

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1 Introduction

1.1 Background

Sustainable biomass, and its important role in a net-zero GHG emissions economy, is recognized in the ″Clean Planet for all″, European strategic long-term vision for a prosperous, modern, competitive and climate neutral economy [40]. Biomass can be used as biofuel or transformed into them, replacing the fossil fuels in energy sectors and in the production of value-added products. Conventional approaches for biofuel production are divided in two groups based on the feedstocks used and conversion methods. Thermochemical methods consider pyrolysis, gasification and liquefaction of biomass, while biological and biochemical pathways are represented by aerobic fermentation and anaerobic fermentation (more commonly known as anaerobic digestion) and biocatalyst [41]. Lignocellulosic biomass is usually utilised in thermochemical processes to produce hydrocarbons, bio-oil and synthetic gas [42]. Oil crops and algae are common in transesterification where the target product is biodiesel [42]. Biomass rich in starch and sugars is usually utilised in aerobic fermentation to produce bioethanol and biobutanol [42]. In the end, wet biomass (in general from all sources) is applicable in anaerobic digestion (AD) to produce biogas [42].

Total energy from biomass (bioenergy) accounts for about 10% of the total European energy consumption [43], and further expansion is expected in the future as most technologies are mature and available on the market. However, in the coming decade the sector of bioenergy and biofuels will certainly need to adopt some new measures and policies in order to avoid sub-optimal use of biomass and the long-term lock-in effect caused by subsidy mechanisms [44]. Such measures were already recognized in a revised version of the Renewable Energy Directive (RED II) from 2018 [45], in which it was stated that when planning future renewable sources of energy (RES), Member States should consider the available supply of biomass and take into account the principles of the circular economy and waste hierarchy, the promotion of waste recycling and waste prevention, all that in order to avoid unnecessary distortion of raw materials markets. Among all mentioned biomass conversion technologies, only AD is considered as a recycling technology for waste, as it recovers both energy (in the form of biogas) and materials (in the form of digestate applicable as a fertiliser on land) [46].

In the European bio-based economy, biogas is positioned as a flexible and multifunctional RES that has an important role in reducing non-CO_2 emissions and store carbon through sustainable biomass management. In comparison to other biofuels such as biodiesel, bioethanol, biobutanol, etc., biogas is the only biofuel type which can be produced using a wide range of biomass sources like animal waste and residues, agro-industrial waste, sewage sludge, biowaste and energy crops [47]. Another advantage of biogas over other biofuels is its chemical composition which accounts for ca. 60% CH_4 and ca. 40% of biogenic CO_2 [48]. In that form biogas has favourable properties (heating value of ca. 6 kWh/m^3) to be directly utilised as a fuel in internal combustion engines and boilers [49] to generate power and heat on a large scale, or to be utilised as a transport fuel.

Over the years biogas took significant portion in generating electricity and heat, while recently more stress was given on using biogas as an alternative fuel to natural gas, and in the production of value added products [50]. EU is a world leader in the biogas production and utilization with almost 19,000 operating plants as shown in Figure 1, which produce ca. 15.8 · 10^9 m^3 of biogas per year [27].

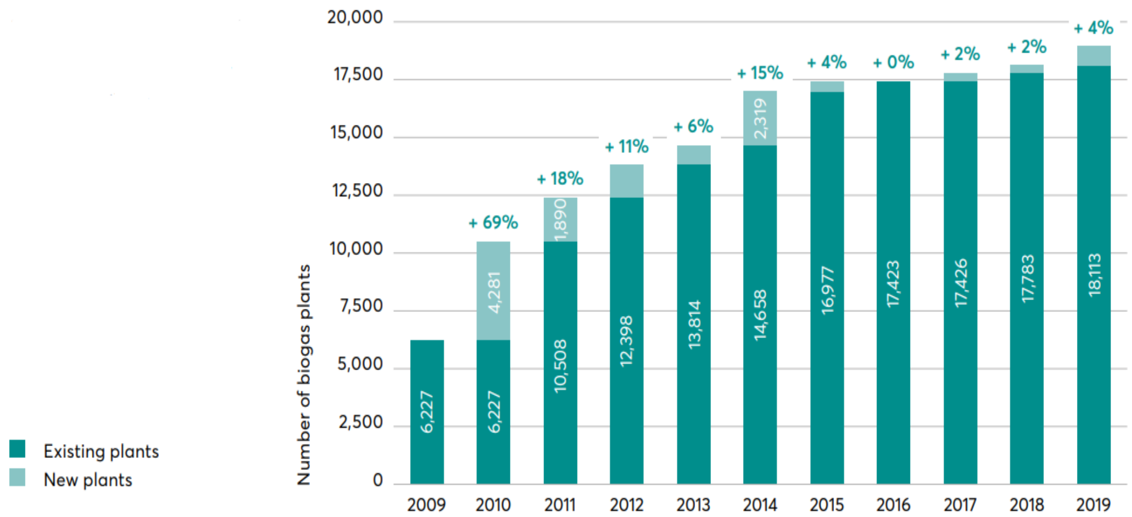


Figure 1 European Biogas Association (EBA): Development of the number of biogas plants in Europe, 2009-2019 [27]

The intensive expansion of the European biogas sector was recorded between 2010 and 2012. This was a result of strong subsidy mechanisms and tariffs which opened biogas technologies a pathway to enter the production of electricity [26]. In 2017, the total installed capacity of biogas CHP units in the EU was 10,532 MW_{el} which produced in total 65,179 GWh_{el} [51]. An overview of subsidy mechanisms in form of feed-in tariffs (FIT) and feed-in-premiums (FIP) for biogas electricity in EU countries [52] showed that the level of initiatives, as well as the granted operation under subsidy models are country specific, but in general they are quite similar. In more details, Table 1 presents the extracted levels of subsidies for biogas plants producing electricity and duration of granted operations [52].

Table 1 An overview of subsidy mechanisms and granted durations for biogas electricity in EU28 [52]

EU Country	Subsidy mechanism	Level of subsidies [€/MWh_{el}]	Granted duration [y]
Austria	FIT	125.1 – 186.7	15
Bulgaria	FIT	173.9 – 207.6	15
Croatia	FIT	150.0 – 190.0	14
Denmark	FIP	Max. 110.0	Several terms and Deadlines
Finland	FIP	83.5 + 50.0 heat bonus	12
France	FIT	81.2 – 97.5	15
Germany	FIT/FIP	56.3 – 277.3	20/20
Greece	FIT	94.0 – 230.0	20
Hungary	FIT	75.0 – 121.0	At most the duration of amortization of the plant
Italy	FIP	140.0 – 236.0	20
Ireland	FIT	136.6 – 157.0	15
Lithuania	FIT	111.0 – 134.0	10
Luxemburg	FIT	117.0 – 147.0	15
Netherlands	FIP	70.0 – 113.0	12
Portugal	FIT	102.0 – 117.0	15
Slovakia	FIT	102.3 – 120.5	15
Slovenia	FIT/FIP	161.8 – 165.6	15/12
United Kingdom	FIT	81.5 – 84.0	20

In all country states the level of subsidies depends on the installed capacity of biogas power plant − the higher the capacity, the lower the subsidy. Also, in some countries the level of subsidies complies with the origin of biogas (higher subsidy for waste feedstocks utilised), and for higher energy performances. Belgium, Cyprus, Czech Republic, Estonia, Latvia, Romania, Poland, Malta, Spain, and Sweden were not included in the analysed study. Table 1 indicates that subsidies for biogas electricity are significantly higher than the average wholesale baseload electricity prices in Europe, which were in 2020 in the range of 24.5 €/MWh$_{el}$ in Sweden to 44.6 €/MWh$_{el}$ in Greece [53]. It is important to remark that average wholesale market prices were introduced in the discussion only for the rough comparison. Namely, the price of electricity changes from hour to hour and it is impacted by numerous factors such as the energy mix, distribution/transmission costs, energy taxes, and other factors.

By looking at the data presented in Figure 1 and Table 1 it can be concluded that some biogas plants in EU are near the end of operation under subsidy models, which could mean that they will continue operation on liberal electricity markets. For biogas plant owners that utilise high-cost substrates (e.g., maize silage) in biogas production this would mean significant reductions of profit, facing a non-feasible operation and closing the businesses. An overview of the feedstocks used in European countries to produce biogas is shown in Figure 2.

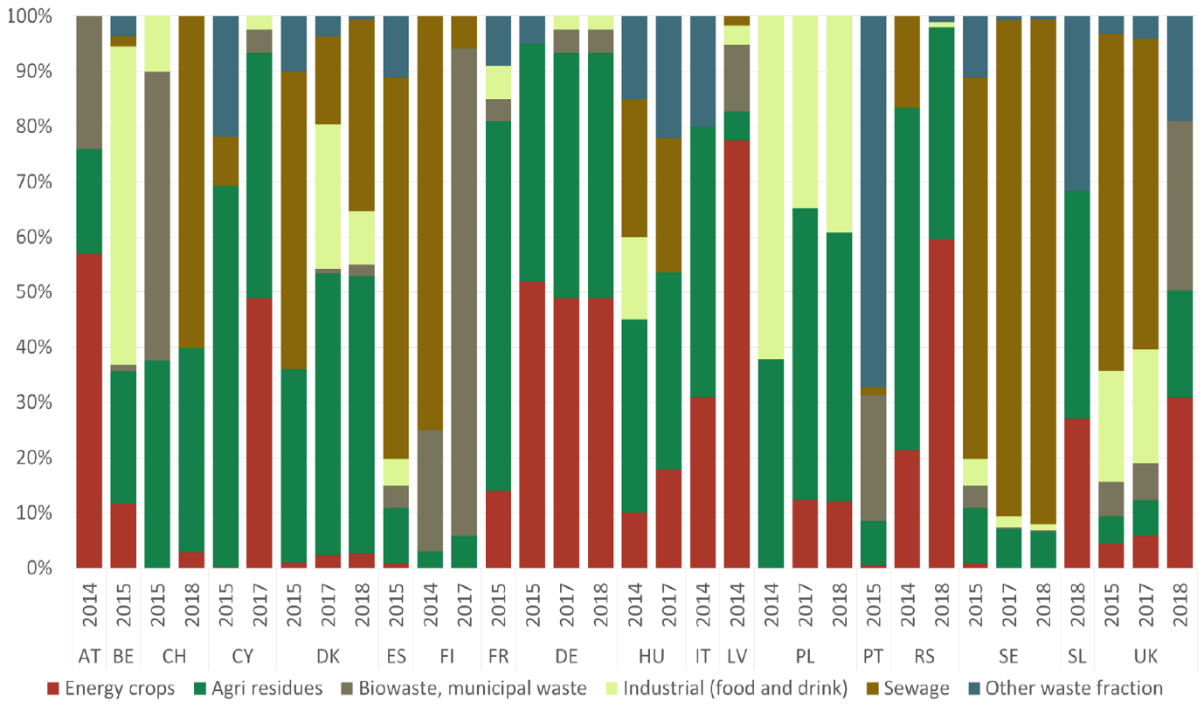


Figure 2 Feedstock use (excluding landfill) for biogas production in European countries, expressed as mass percentage [54]

As it can be seen in Figure 2, agricultural feedstocks composed of livestock manure, farm residues, plant residues and energy crops are the driving force of biogas production in Europe. In the highly developed biogas sectors (like in Switzerland, Denmark, Finland, and Sweden) more than 50% of feedstocks come from biowaste, sewage and industrial waste. Energy crops were intensively utilised in Austria and Germany, however their tendency decreased in the total feedstock composition over the years. Utilising energy crops for biogas production is not in line with the principles of sustainable development and the production of biofuels of second and third generation [5]. Therefore, several biogas sectors among the European countries limited the utilization of maize silage and corn, to a share of 30-50% of the total input feedstock [55,56], and a further decrease in the use of maize silage is expected. Less developed biogas sectors which were not presented in Figure 2 originate mostly from countries of East and Southeast Europe, where biogas technology is not yet extensively deployed [57]. Biogas sector in those countries has the potential to start implementing more sustainable approaches from the start, avoiding recognized operational issues in more mature sectors, and create additional benefits.

The main strengths related with adaptation of biogas technology are reflected in the local accessibility of biomass and application of various waste types, reduction of carbon footprint in energy production, and contribution to the protection of environment and climate [58]. From the economic aspect, biogas was recognized as an investment-intensive technology, which requires a certain level of subsidies in order to maintain a stable and feasible business operation [58]. Also, biogas plants depend on the raw materials market which can be highly different from region to region. In the end, the social barriers coming from the local community stopped the development of some biogas projects in the past, mainly caused from the deficiencies in the education regarding processes in biogas plant [58].

As can be concluded from the overview of biogas sector, two major operating issues will be present in the upcoming decade: restrictions in using energy crops and exiting subsidy systems with guaranteed prices of electricity. In such conditions, biogas plant owners and operators will need to look for a broader approach, leading to the change of existing paradigm of biogas plants as passive energy producers [59]. Furthermore, non-technical issues will also be present, pointing mainly to concerns of stakeholders for the further development and expansion of biogas sector [60]. In the following part of this section, a comprehensive analysis of AD technologies is given with an emphasis of applying scientific and engineering research methods.

1.2 Science and engineering of anaerobic digestion

The biogas-related topic falls under the multidisciplinary engineering area. The field of (bio)chemical engineering contributes to studying AD through experimental research, analysis of feedstock composition, and modelling of reaction kinetics. The elements of mechanical engineering are used to examine the utilisation of biogas for various energy purposes, as well as identification of economic and environmental features of biogas. Except for these two dominant engineering approaches, biogas is also studied in other engineering fields like agriculture, civil, electrical, materials, etc. The scientific community recognized AD as an interesting topic that has potential for expanding and presenting new trends in research and development. By entering the keyword “biogas” in the Web of Science search engine [61], the cumulative number of publications in the period 2000-2020 was equal to 9,709, out of which the dominant category was articles in journals (ca. 80 %). The same approach was repeated using keyword “natural gas”. The distribution of counted publications (shown in bars) and cumulative publication (lines) for both keywords is given in Figure 3.

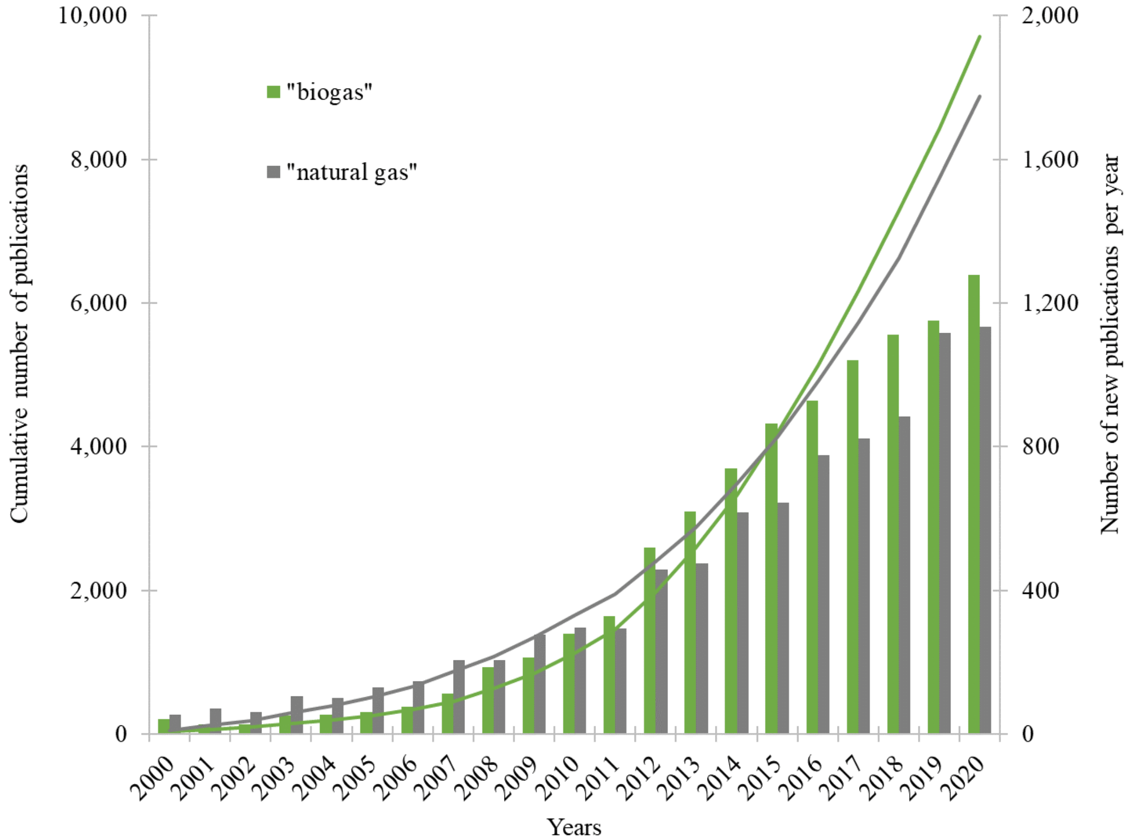


Figure 3 Number of biogas-related and natural gas-related publications in the period 2000-2020, according to the Web of Science [61]

The analysis of data in Figure 3 showed that at the start of this century the natural gas was more favourable in scientific publications than biogas. However, such trend changed over the time, and in 2015 the number of biogas-related publications prevailed. At the end of 2020, the number of biogas publications was by 10% higher than for natural gas, and it is projected that the difference will be more significant in the current decade. In the further elaboration of this doctoral dissertation, a review of AD in terms of biomass availability and conversion and biogas utilization will be given.

1.2.1 Degradation and availability of biomass

For many years, animal manure has been efficiently used as a feedstock in AD, reducing its negative impacts on the environment like the contamination of ground waters and soil [62]; emissions of carbon dioxide, methane and nitrous oxide [63]; reduction of waste, odour and the destruction of pathogens [64] and showing its better fertilisation effect [65]. Cattle manure appears to be a major substrate for biogas plants, especially in the intensive-farming countries [66]. Using only animal manure has some disadvantages, and one of the major is low carbon to nitrogen ratio (C/N) [64] and low biogas yield (10÷20 m^3/t of fresh matter, FM) [67]. To overcome such issues on the large scale biogas production, animal manure is usually co-digested with maize silage, usually under mesophilic conditions, 35-40 °C [68,69]. Benefits of using maize silage in AD is its high yield (10-30 tons of TS per hectare), high specific methane production (0.206–0.283 Nm^3/kg of the volatile solids—VS) and stability in operation [69]. However, the cultivation of maize silage involves environmental burdens related to the consumption of energy and fertilizers, fluctuation of its price on the market of goods, as well as changes in indirect land use [70]. As an alternative to cultivated energy crops, other biomass sources have shown potential to produce biogas, such as residues from agriculture and industry [71], municipal organic waste and various sludge types [72].

Agricultural residues in the form of lignocellulosic biomass showed respective biochemical methane potential (*BMP*) from biomass biodegradation, thus they are promising feedstocks to produce energy-rich methane gas. It has been calculated that the annual global production of dry biomass exceeds $2.00 \cdot 10^{11}$ t [73] and thus there is a significant potential for lignocellulosic biomass to be investigated in the AD and sequentially used in biogas production. Biodegradation of different types of lignocellulosic biomass depends on the chemical structure, primarily on the cellulose, hemicellulose and lignin content and C/N ratio, as it has been presented for rice straw, smooth cordgrass, wheat straw, barley straw and corn stover [74]. Husks, bran and pastry residues showed a biogas potential of 138.4 ± 16.0 $m^3(CH_4)$/tFM [75]. Average production of 500 − 600 m^3 of biogas per t of volatile solids (VS) could be achieved from the AD of residue grass [76]. Also, methane content of the generated biogas ranges between 52 % and 56 %, similar to maize silage [77]. Among the promising type of residue grass in the AD supply chain is the riverbank grass [78]. Fieldwork has shown that the average yield of green biomass on the riverbank was around 13 t/ha. The average dry matter (DM) content in the riverbank grass was 37 % which gives the dry mass yield of around 4.8 t/ha. The overall results pointed to the conclusion that the energy recovery of grass biomass could decrease the dependency of the AD supply chain on the energy crops while obtaining a positive energy return [79]. Antagonistic and synergistic effects on biogas and methane production from batch anaerobic co-digestion of cattle and pig slurries with grass silage have shown that the replacement of cattle slurry with grass silage increased the biogas and methane yields [80].

Waste from the dairy processing industry has shown high energy potential to serve as a feedstock for biogas production [81]. Dairy whey produces about 0.86 Nm^3 of biogas per kg VS, dairy sludge yields biogas production of about 0.48 Nm^3/kg VS, while fatty sludge produces about 1.2 Nm^3 biogas/kg VS. Grease trap sludge has shown synergistic effects in increasing the methane yield of sewage sludge from 0.18 to 0.35 Nm^3/kg VS [82]. The methane yield of sludge from wastewater treatment plants was between 20.6 ± 5.4 and 69.3 ± 22.3 $m^3(CH_4)$/tFM [83–86]. It is known that sewage sludge and sludge from industrial processes are usually poor in VS content, having a long retention time, which gives them low methane (biogas) potential [82]. Mixed industry biowaste mainly composed of whey, fruit and vegetable waste, pomace, yeasts, etc., showed a yield of 22.0 ± 5.0 $m^3(CH_4)$/tFM [87–89]. Since such material is not rich in TS and VS, the low methane yield was expected [87]. For coffee pulp and brewery spent grains, the methane yield was 59.2 ± 12.4 and 66.4 ± 23.3 $m^3(CH_4)$/tFM [90–95]. Fat, oil, and grease waste showed a relatively high range of methane potential, 138.0 ± 43.8 $m^3(CH_4)$/tFM [96–98].

Food waste (FW) [99] and the organic fraction of municipal solid waste [100] have also attracted attention as sustainable substrates for biogas production. The composition of FW is significantly affected by seasonal changes, geographical position, cooking procedures and consumption patterns [101]. Canteen FW and parthenium weed were studied for biogas production using microwave irradiation and steam pretreatment on a laboratory scale [102], where by adding pretreated parthenium weed to FW, pH control was improved as compared to untreated weed. Canteen FW in co-digestion with rice straw showed an approximately 70% higher biogas yield compared to mono-digestion of FW [103]. Thermally pretreated canteen FW and waste activated sludge were studied for biogas production, where the results showed that 24 h pretreatment using fungal mash resulted in a 6% increase in soluble chemical oxygen demand (SCOD), and the SCOD removal during biogas production was estimated to be between 70 and 90% [104]. The co-digestion of pretreated FW and yard waste gave a biogas yield of 431 NmL/g VS, while untreated FW and yard waste had a biogas yield of 335 NmL/g VS [105]. Adding sewage sludge and yard waste to cafeteria FW showed synergistic effects in terms of biogas production compared to mono-digestion of FW [106]. Co-digestion of FW composed of bread, rice, spaghetti, vegetables, fruits and meat gave a 1.4-fold higher methane yield compared to sludge mono-digestion. Adding organic FW to sludge increases the organic content in the mixture and improves the digestibility of the mixture [107]. Anaerobic co-digestion of restaurant FW and sewage sludge showed that, when adding 10% of sludge to FW, biogas production is stable [108].

The second product of AD is a digestate − nondegraded solid biomass residues in liquid phase [19]. Solid fraction is usually rich in macronutrients, nitrogen, phosphorus and potassium, which makes it applicable as a fertiliser [20]. Solid fraction of digestate contains also phosphorus and residual organic carbon which makes it also suitable as a soil conditioner, as a feedstock for compositing [21] or in energy recovery [22]. Of all, the process of pyrolysis showed several advantages to be integrated with digestate management [109]. Biochar from pyrolysis of digestate can effectively be used for various applications, and therefore combined anaerobic digestion – pyrolysis process might be beneficial due to the low economic value of digestate [23] and thus subsequent pyrolysis of digestate offers an opportunity to improve profitability of biogas production processes [110]. Among the applications of biochar from digestate are: it could be used as a sorbent for heavy metal [111] and phosphate removal [112], for carbon biosequestration, as a soil improver and for biofuel production [113].

Usually, pyrolysis of biomass and waste is widely examined with thermogravimetric analysis (TGA) together with kinetic studies [114]. Digestates from various biomass and waste sources have been analysed for better understanding of the pyrolysis, such as from different organic solid wastes (sewage sludge, food waste, vinasse and cow manure) [115], waste sludge from a pharmaceutical industry, cattle manure and a mixture of primary sludge and organic fraction of municipal solid waste [116], cattle manure digested at mesophilic and thermophilic conditions [117], digestate from anaerobic treatment unit [118], rice straw [119], algae [120] and other. The main advantage of using digestate is it low economic value, estimated to only 2-4 €/t [23].

Kinetic analysis and estimation of the kinetic parameters of AD are important in predicting the behaviour of an anaerobic system and in optimizing biogas production [121]. Results of the kinetic analysis quantify the impact of changing process variables like pH, total solids, added co-substrate and others on the rate of biogas production and biogas yield [122]. Some of the most common kinetic models for AD of organic biomass are ADM1, Modified Gompertz, Monod [123], the First-order model and the Cone model [124]. Recent studies on modelling of the AD using ADM1 have been applied to several substrates: blackwater and rotten vegetable [125]; grass silage [126]; a mixture of municipal waste and grease [127]; microalgae [128] and many others. Estimated kinetic parameters for AD of FW performed in a batch mode [124] yielded a value of the first-order kinetic parameter equal to 0.099 d^{-1}, while the Modified Gompertz kinetic parameter was equal to 0.126 d^{-1}. Changing the FW composition and finding its impact on the value of kinetic parameters constituted an attractive method in studying FW capacity for AD [129]. It was established that using an exponential model (First-order model) resulted in a wide range of rate constant values for VS reduction, between 0.55 and 3.63 d^{-1}.

Except for analysing biodegradable properties of biomass for biogas production, it is important to know where and in which amounts is biomass generated. In that sense, the Geographical information system (GIS) was recognized as a valuable tool for a detailed mapping of physico-chemical properties of biomass [130]. The geospatial assessment of the energy potential of crop residues and manure for biogas production in the EU showed the availability of 0.7 EJ (ca. 195 TWh) on a yearly level [7], which was ca. double than the EU production of biogas from agricultural feedstocks in 2016. The Bottom-up GIS model applied in the assessment of biomass potential from grasslands in Northwest Europe showed that ca. 45% of the sustainable grass could be utilised for energy production purposes in the model region [131]. Another Bottom-up analysis of using animal manure from various husbandry operations in East Croatia showed the potential of feedstock to produce 6.5 GWh of biogas, which could generate double the yearly electricity consumption of that municipality [132]. The Top-down mapping of agricultural residues in Croatia using Quantum GIS (QGIS) software [133] showed that stover, straw and stalk could generate biogas potential up to 3,000 $MWh/(km^2 \cdot y)$ in the extensive agricultural regions of Croatia. ArcGIS software was applied in revealing the potential of renewable electricity generation from municipal solid waste, including organic and dry material in Iran [134]. Results showed that the studied region could produce ca. 2% of the total household electricity consumption, while achieving avoidance of $6.7 \cdot 10^3$ t of CO_2-eq/y due to the proposed measures. Integrated tools in GIS softwares allows users to determine important factors in assessing the availability of feedstocks for biogas production, such as the length of transportation routes from the biomass harvesting location to the biogas plant, the optimum location for setting up a new biogas plant, etc. [135]. In that sense, QGIS was successfully applied in determining the optimum area for establishing the biogas hub in Karditsa, Greece [8]. Results showed that the optimum distance between the available biomass sources and the planned hub was ca. 20 km in order to maintain a feasible hub operation. ArcGIS was applied in finding an optimum biogas plant sited on the territory of Ohio in the US, for the case of corn stover and wheat straw [9]. It was found that the average biomass availability radius for that case ranged between 22 and 34 km in the case of 10 newly examined biogas plants. The same software was applied to the case of Southern Finland, with the goal of quantifying the relation between the length of transportation distances to deliver feedstocks to existing biogas plants and an increase in their production capacity [10]. Increasing the radius of biomass collection from 10 km to 40 km could increase biogas plant production capacity by ca. 10-127%. However, the study did not reveal the impact of capacity extension on the environmental performance of plants.

1.2.2 Utilisation of biogas

The International Energy Agency (IEA) has recognized the energy from biomass as a stabilizing element in balancing the electricity grid and providing options for energy storage in the EU [136]. The flexible operation of biogas-driven CHP units in terms of load and frequent starts and stops is growing in importance, owing to the increasing share of variable RES in energy systems [137]. The potential of biogas plants to balance the power supply from wind power plants was examined in the case of Latvia [138]. Results showed that the surplus of wind power capacity could be balanced using currently installed biogas CHP plants. In the case of Germany's power system [139], it has been shown that the flexible power generation of biogas plants, integrated with the substitution of fossil fuels in the heating sector, could contribute to economic benefits, compared to subsidised electricity production. Dynamic analysis of the operation of biogas plants in the peak power reserve market in Germany [140] has shown that biogas plants with excess capacity can profitably exploit peak power prices. Results of the study have also shown that a single oversized CHP unit (2 MW_{el}) is economically more feasible than two smaller CHP units (2 x 1 MW_{el}). The market-based optimisation model for biogas plants operating on the spot market [141] showed that biogas facilities can control electricity production through their storage capability and flexible operation in time, duration and amount. For flexible operation of a biogas plant using a CHP of 1.36 MW_{el} and an upgrading unit of 600 Nm^3/h capacity, the size of installed gas storage of 4,800 m^3 proved to be sufficient to provide control reserves and biomethane simultaneously [142].

In the transition by the biogas sector towards low-cost sustainable feedstocks and feasible operation on energy markets, the integration of variable renewable energy sources (RES) [143], primarily wind and photovoltaics (PV), seems an attractive option, since their capacity is continuously on the increase globally, providing low-cost electricity [144]. In Germany, utilisation of excess electricity from wind farms for biogas upgrading has shown potential for converting and storing of surplus electricity without long transport routes [145]. Utilising 0.70 TWh_{el} of excess electricity to 480 biogas plants could produce $100 \cdot 10^6$ Nm^3/y of upgraded CH_4. Apart from covering the electricity demand in a certain process, excess electricity from variable RES is also utilised to produce hydrogen (H_2) through the process of water electrolysis [146]. The integration of renewable H_2 in fuel production can reduce the demand for biomass, while simultaneously increasing the flexibility of the energy system by enabling higher penetration of variable RES in energy systems [147]. The surplus energy generated by wind turbines or PV modules can also be used in a technology called power-to-gas (P2G), where the carbon dioxide (CO_2) and H_2 produced in electrolyser are converted to synthetic natural gas (synthetic methane/e-methane, e-CH_4) in the methanation process [148]. Since both biogas CHP and biogas upgrading act as sources of CO_2, the integration of the P2G concept together with sustainable biomass management offers a high gain perspective [149]. Installing a P2G unit near the biogas CHP unit ensures that both units can operate independently: when there is demand for P2G operations, biogas is used for methanation, and when it is not required, biogas is used in the CHP unit [150]. Moreover, electrolysers and methanators are sources of heat, where electrolysers usually provide low-grade heat [151], while methanators produce high-grade heat that can be used in local district heating appliances or in industrial processes [152].

The examples of integrating variable RES in renewable gas production are the *WindGas Falkenhagen* methanation plant [153] and the *Audi e-gas* plant [154], both located in Germany, where wind supplies electricity to run the P2G facilities. In Denmark, the *BioCat* plant uses CO_2 from biogas upgrading and renewable H_2 to produce synthetic CH_4, which is fed to the national gas grid [155]. Compared to biogas upgrading and separate CO_2 utilisation in P2G, the direct methanation of biogas [156] has proven the more efficient and less energy demanding process [157], enabling full carbon utilisation from biomass [158]. Synthetic natural gas produced in the direct methanation of biogas from the wastewater treatment plant has a CH_4 share of ca. 90%, with ca. 5% of H_2 [159]. The second P2G project by the *Audi e-gas* company in Germany, with direct methanation of raw biogas using renewable H_2, produces renewable methane with a 98% share of CH_4 [154]. Previous economic analyses have shown that the renewable gas produced by integrating P2G into biogas plants cannot be competitive in price with natural gas, unless there are subsidies [160]. However, the integration of alternative substrates, namely in the form of biowaste, could make the operation of such plants feasible without subsidies. The reason lies in the “gate fee − *GF*” business model in which biogas plants receive a fee (negative value) from the waste producers to handle their biodegradable waste [161]. Usually, the purchase price for food waste and other bio-waste types is between -60 and 0 €/t [11]. Also, the amount of the *GF* depends on the origin and complexity of the waste [162], and in some cases it can be as high as -100 $/t [161].

From an environmental point of view, the penetration of bioenergy into energy production systems (especially the ones based on fossil fuels) could bring multiple contributions and benefits [163]. In that context, the application of Life Cycle Assessment (LCA) can reveal the actual environmental impact of feedstock changing policies in biogas production and utilization related to future energy systems [30]. It was shown that sugar beet generates ecological effects similar to those of maize crops in bioenergy production [164], while intercropping of forage sorghum with maize contributes to lower environmental impact than maize monoculture [164]. Examining the environmental impact assessment of replacing maize silage by marine macroalgal biomass using SimaPro (an LCA software) showed a reduction of environmental burden in almost all the impact categories being examined. However, the significantly longer transport route for algae (150 km) compared to maize silage (12 km) resulted in higher values in the global warming potential (GWP) category, from 140 g CO_2-eq/kg(energy crops), to 160 g CO_2-eq/kg(macroalgae). A similar observation was also found by the authors of the present study in the case of applying residue grass from landscape management as a replacement for maize silage in existing biogas production [34]. Biogas plants fed with agro-industry by-products and waste like distiller’s waste, rapeseed cake, cheese whey, pulp, seeds, peel, fruit and vegetable residues, etc. yielded better environmental performances than those fed with cereal silage [165]. Nevertheless, the overall environmental performance also depends on the variability in terms of total solids/volatile solids (TS/VS) content, specific biogas yield, origins, and other factors [165]. A comparison of LCA performance for a biogas plant fed with animal manure and energy crops for various biogas utilisation pathways [31] showed that biogas for electricity generation saves around 300 kg CO_2/MWh(electricity), while upgrading of biogas to biomethane and its injection into the gas grid saves 191 kg CO_2-eq/MWh(biomethane). Another study of LCA claimed that using biogas in cogeneration achieved better overall environmental results compared to biogas upgrading [166]. In both studies the details about the considered electricity mix in the study were not provided, and the results were not presented using the same reference point. Projections from the Joint Research Centre (JRC) of the European Commission (EC) showed that by 2030 the further penetration of renewable energy sources (primarily wind and solar photovoltaic) will decrease the overall GHG emissions of the electricity generation sector [167]. The integration of P2G and methanation in a biogas plant to fully exploit biogenic CO_2 potential yielded better environmental performance, with a projected European electricity mix for 2030 compared to 2016 [168]. In the case of Ireland, LCA of biogas upgrading with P2G integration showed that using an electricity mix with an 85% share of renewables could satisfy the GHG savings of 70% compared to fossil fuels [32]. Future development of P2G efficiency and integration of renewable credits from CO_2 valorisation could increase the competitiveness of the biogas sector in future energy systems [169].

1.3 Motivation for work

Based on the comprehensive literature review with an emphasis on the biogas production and biogas utilisation methods, this doctoral research was inspired to give a contribution to the biogas sector by applying a holistic and interdisciplinary approach in discovering key elements to increase the competitiveness of biogas technologies over other energy sources and catalyse the transition towards sustainable energy and environmental systems.

In that sense, the doctoral research integrally analysed the geospatial availability of novel feedstocks in the replacement of maize silage in biogas production; the evaluation of their biodegradable properties using experimental research and modelling of reaction kinetics; optimisation of biogas plant operation on liberal electricity markets by integrating variable RES; and finally, the evaluation of economic feasibility, environmental benefits, and burdens of the proposed measures.

The author of the dissertation believes that the role of biogas technologies in the future will be even more emphasised with the integration of waste management systems and energy systems that operate with a high share of RES. Therefore, this dissertation demonstrated pathways on how to achieve such operation, using actual biogas plants as testing cases, as well as proposing the expansion of biogas sector. Furthermore, the work carried out in this dissertation summarizes operational decisions for biogas plant owners and operators with goal to maintain the long-term prosperity of biogas sector, while generating outcomes which are in line with the principles of sustainable development.

The motivation for the research was transferred into the research objectives, proposed scientific contributions and the defined hypothesis of the research, which are described in more detail below. After, a brief description of the applied materials and methods is given, and the presentation of innovative elements of work.

1.4 Objectives and hypothesis of the research

Objectives of this research are:

- To quantify the biogas production using novel biomass substrates like lignocellulosic agriculture residues, food waste and industry by-products that are not competitive with production of food, as is the case for a maize silage in the present biogas production.
- To estimate kinetic parameters of anaerobic digestion of novel biomass substrates in order to determine impacts of substrate's chemical composition on process performance using mathematical modelling and experimentally obtained data.
- To reveal economically feasible pathways for future biogas operation in advanced energy markets when biogas plants run out support schemes and guaranteed price of electricity.
- To evaluate environmental impacts of the biogas utilisation pathways incorporated in the future energy systems operating with high share of renewable energy sources.

The **hypothesis** of the research is that applying holistic approach on biogas plants, both on the production and utilisation side, can increase economic profitability and environmental benefits over current subsidised operation.

1.5 Scientific contributions of the research

The proposed research has following contributions:

- By an experimental research of anaerobic digestion using novel biomass substrates the potential obstacles in biogas production like as the occurrence of an inhibition and the process stability will be identified.
- Alternative measures for the current biogas sector will be proposed considering market prices and environmental impact analysis using Life Cycle Assessment approach.
- Advanced Geographical Information System model for mapping of novel biomass sources, combined with various biogas utilisation pathways integrated in energy systems with high shares of renewables under advanced energy markets, will result in robust mathematical models applicable to various biogas plant cases.

1.6 Applied methods and used materials

This research combines elements of chemical and mechanical engineering to evaluate a holistic approach to advanced anaerobic digestion technology. Applied methods were integrated together in order to create an added value and greater applicability compared to individual approach.

1.6.1 Chemical engineering approach

Methods used in this part of the research relied on the physico-chemical evaluation of substrates collected at several locations, and laboratory investigation and reaction modelling of the process. In brief, the main applied methods included:

- Collection of residue grass, food waste and industry by-products, and analysis of their composition and properties.
- Set-up of a laboratory equipment to perform batch assay tests, monitor the process performance and evaluate product yield and composition.
- Assessment of kinetic parameters of the biomass degradation due to anaerobic digestion and pyrolysis by applying predefined mathematical models.

More details on applied chemical engineering methods and materials can be found in *ARTICLES 2*, *3* and *4* of this doctoral dissertation.

1.6.2 Mechanical engineering approach

Methods applied in this step refer to processes which occur before the actual anaerobic digestion, and on processes of utilisation of the produced biogas. In a nutshell, the applied mechanical engineering methods composed of:

- Assessment of a technical potential of available biomass sources from the agricultural wastes, co-products, and by-products value chain.
- Hourly-based economic optimisation and unit commitment dispatch of a biogas plant operation in the post-subsidy era by using alternative substrates and integrating variable RES.
- Geospatial analysis of biogas potential from alternative substrates to replace maize silage in existing plants and to set-up new renewable gas producing plants.
- Life Cycle Assessment of applied measures to biogas sector operating in energy systems with high share of RES.

More details on applied mechanical engineering methods and materials can be found in *ARTICLES 1, 5, 6* and *7* of this dissertation.

1.7 Innovative elements of the work

Innovative elements of the work are seen in:

- Determined thresholds of process parameters for the stable and efficient anaerobic digestion of alternative substrates.
- Geospatial availability of low-cost and gate-fee substrates for biogas production in existing and new facilities which would generate additional income to biogas plants compared to present operation.
- Synergy between the optimised RES integration and *gate fee* business model in biogas plants with goal to produce renewable gas economically competitive to natural gas.
- Environmental impact assessment of the holistic and interdisciplinary measures applied in the biogas sector.

Except for having the international character, this doctoral dissertation was accomplished in a close collaboration with the biomass and biogas industry, which gives added value to research outcomes and creates a high potential for an actual implementation of proposed measures outside the scientific area.

2 Selected results and discussion

In this section, the detailed discussion of applied methods and achieved key results obtained by the studies is given. Figure 4 presents the structure of the created doctoral dissertation based on the Scandinavian model.

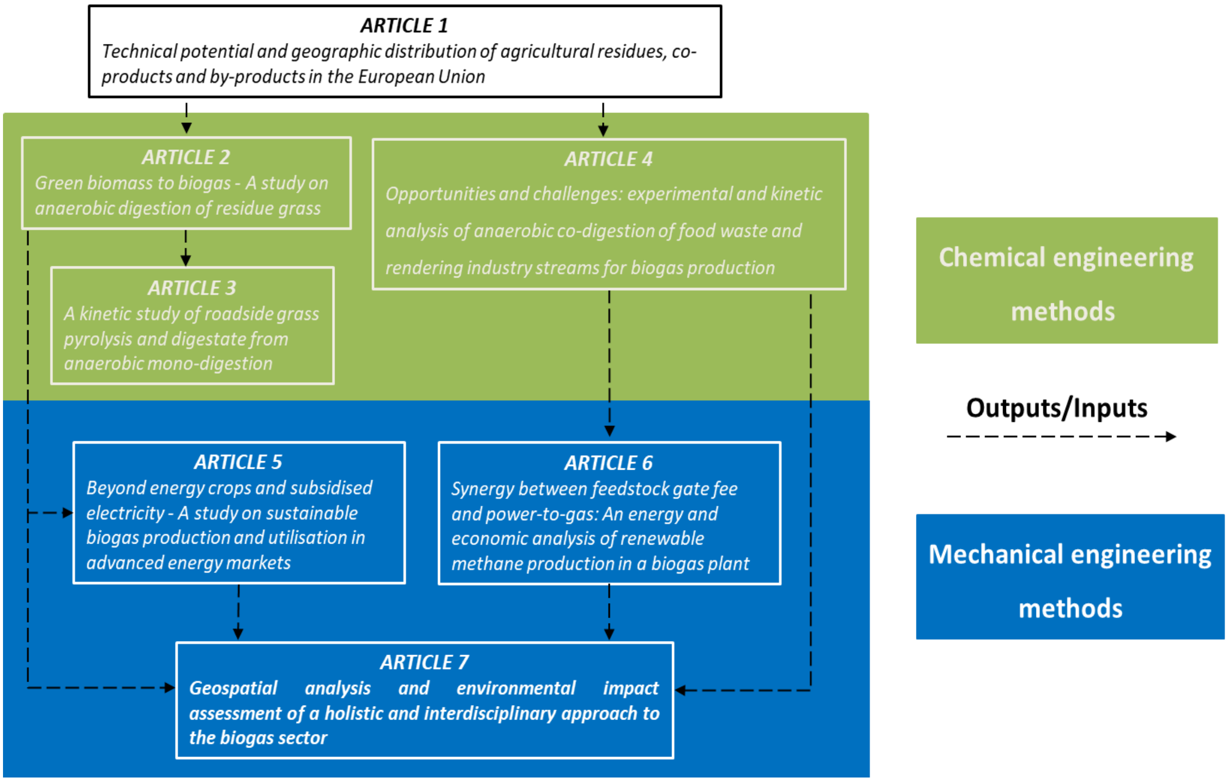


Figure 4 The Scandinavian structure of doctoral dissertation

As shown in Figure 4, the starting point for the research was a comprehensive analysis of biomass value chain from agricultural residues, industry co-products, by-products, and waste streams in the European context. Based on the conducted overview and analyzed potential, several biomass types were selected for further examination as alternative substrates to maize silage in biogas production. In that sense, chemical engineering methods were used to determine operational thresholds for the stable and efficient anaerobic digestion of selected biomass types, as well to determine reaction kinetics and biogas production rate. Continued to outcomes of the chemical engineering approach, elements of mechanical engineering were applied with goal to create robust models applicable for the evaluation of economic feasibility of various biogas utilisation pathways, and to quantify environmental benefits of the integrated approach. As a whole, published *ARTICLES* were mutually linked, demonstrating the connection between two approaches, and achieving the added values of the overall concept.

In section 2.1, the analysis of potential of AWCB was given considering in-depth analysis of biomass value chain. Section 2.2 presents the discussion of selected results obtained by the applied methods of chemical engineering, related to the evaluation of alternative substrates in biogas production. Section 2.3 presents the discussion of selected results obtained by applied methods of mechanical engineering, focusing on various biogas utilisation pathways, mapping of biogas potential and assessment of environmental impacts. In the end, section 2.4 gives the evaluation of an overall concept carried out, discussion of achieved scientific contributions and testing of the hypothesis of the doctoral research.

2.1 Biomass value chain – *ARTICLE 1*

The overall aim of *ARTICLE 1* was to perform in-depth analysis of residue and waste appearance within the biomass value chain as shown in Figure 5. In the first stage the quantities of residue materials originated from harvesting and cultivation of crops, vegetables and fruits, and farming of animals were examined. The second stage included co-products and by-products which appear during the processing of selected commodities in industry facilities. The last stage presented the food waste losses due to consumption of commodities.

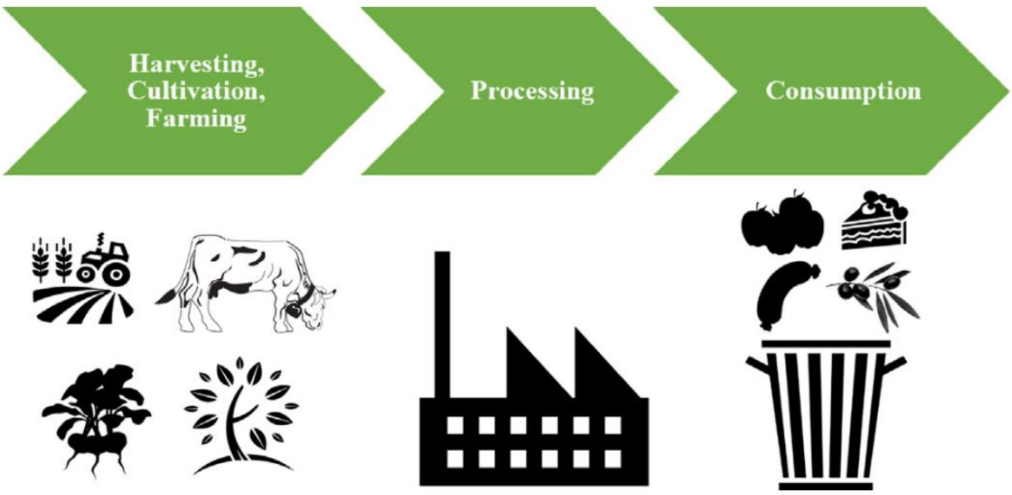


Figure 5 Biomass value chain analysis [33]

By using a specific waste to commodity ratio and publicly available data for yearly commodity production, the technical potential of commodities was assessed on the European Nomenclature of Territorial Units for Statistics (NUTS) 1 level. Results showed that the dispersion of technical potential is impacted by land activities, climate conditions and human eating habits (consumption of goods). Western European countries having less available land areas, a significant number of industrial zones and high population density showed the highest potential of residues from animal farming (the Netherlands – 2,200 t/km^2; Belgium – 1,500 t/km^2; Denmark – 1,000 t/km^2) and vegetable cultivation (the Netherlands - 2,600 t/km^2; Belgium - 2,525 t/km^2; the UK, Germany, and Denmark > 300 t/km^2). South European countries, with lots of land areas and mild weather conditions were shown to be more dominant in the quantities of the generated fruit residues (Greece - 50 t/km^2, Italy – 40 t/km^2). Residues from cereals production had the highest potential in the countries of Central and Eastern Europe (Hungary - 360 t/km^2; Germany - 220 t/km^2, Romania and Bulgaria > 200 t/km^2).

Based on the biodegradability of residues originated from biomass value chain and their assessed potential, a decision was made which of biomass types would be applicable for further studies on AD process.

From the first stage, the most abundant residue was animal manure. However, it is efficiently utilised for biogas production for many years already. After animal manure, the post-harvesting residues such as pruning residues, leaves, stalks, straw, husks, etc were considered. These residues belong to a type of lignocellulosic biomass, which can be applicable in AD, but also having some limitations. The utilisation of pruning residues and leaves for biogas showed to be limited due to higher lignin content which requires intensive pretreatment prior to AD [170]. Straw is used as a bedding material in stables, while stalks and husks had a very low technical potential to be examined in the replacement of maize silage in biogas plants. The idea of using lignocellulosic biomass as a possible feedstock for biogas production was taken into consideration for biogas production using the residue grass from the landscape management (uncultivated land, riverbanks, and highway verges) as demonstrated in *ARTICLE 2*. Co-products, by-products and wastes from the second stage were mainly considered to be animal processing and slaughterhouse waste. Since such wastes gain high potential for creating environmental damage and a spread of hazard [171], and they come in various forms having very different properties [172], it was decided that these wastes will not be studied directly in AD, but as materials that appear after animal residue processing in a rendering plant [173]. For that purpose, meat and bone meal (MBM) and wastewater sludge (WWS) were considered for experiments. Finally, food waste originated from the last stage was studied as a bulk substrate – a mixture of food waste from human consumption in restaurants, canteens and kitchenets [174]. Rendering industry streams and food waste were studied together in AD as demonstrated in *ARTICLE 4*.

2.2 Alternative substrates for biogas production and valorization of digestate

This part of the dissertation presents selected results obtained by the chemical engineering approach to biogas production from alternative substrates. Obtained process performances were presented and discussed regarding set research objectives and proposed scientific contributions. The section 2.2 is divided into three subsections, each one for the published article.

2.2.1 Residue lignocellulosic biomass – ARTICLE 2

The focus of this study was on the use of residue grass (RG) as a replacement for maize silage (MS) in the AD. The grass samples have been collected from the areas that do not compete with the food production: uncultivated land (RG1), the Sava riverbank in the city of Zagreb (RG2) and highway verge (RG3). The study includes determination of the fresh and dry yield of residue grass biomass, chemical characterisation of residue grass, determination of biogas yield and biogas composition from the residue grass, the application of ADM1 model to describe the AD and compare the modelling results with the experimental results. In the end, LCA has been used to determine the environmental effects of biogas production from residue grass in the production of heat and electricity.

The results of the grass yield determination, the length of stems and the chemical composition of the examined fresh and dry grass are shown in Table 2. Field measurements have shown that the greatest yield of fresh grass is present for the riverbank grass RG2. Other two samples have shown similar fresh grass yield, where the yield for RG3 appeared to be a bit higher compared to RG1. At the same time, by using the moisture content in grass samples, the yield of dry matter on grasslands is similar for RG2 and RG3. The higher moisture content of grass sample RG2 compared to samples RG1 and RG3 can be explained by the fact that the riverbank area is occasionally flooded.

Table 2 Results from field measurements, proximate and ultimate analysis and heavy metal presence analysis of residue grass, fresh (dry) matter basis [34]

Characterisation	Parameter	RG1	RG2	RG3
Field measurements	Average yield [kg/m^2]	0.74 (0.14)	1.90 (0.26)	1.01 (0.23)
	Average stems length [m]	0.28	0.68	0.49
Proximate analysis	Moisture [%]	80.9 (/)	86.3 (/)	77.5 (/)
	Ash [%]	2.0 (10.4)	1.6 (11.2)	1.9 (8.4)
	LHV [MJ/kg]	1.48 (18.08)	0.25 (17.23)	2.07 (17.61)
	UHV [MJ/kg]	3.69 (19.34)	2.53 (18.45)	4.24 (18.85)
Ultimate analysis [%]	Carbon	8.9 (47.1)	6.3 (44.7)	10.4 (46.2)
	Hydrogen	1.1 (5.8)	0.8 (5.6)	1.3 (5.7)
	Nitrogen	0.54 (2.84)	0.31 (2.18)	0.46 (2.03)
	Oxygen	8.5 (44.2)	6.3 (47.2)	10.3 (45.9)
	Sulphur	0.017 (0.089)	0.039 (0.278)	0.033 (0.146)
Metal presence analysis [mg/kg]	Lead	0.019 (0.10)	0.010 (0.07)	0.081 (0.36)
	Cadmium	0.002 (0.01)	0.001 (0.01)	0.002 (0.01)
	Mercury	0.004 (0.02)	0.003 (0.02)	0.005 (0.02)
	Chromium	0.124 (0.65)	0.064 (0.47)	0.173 (0.77)
	Nickel	0.145 (0.76)	0.095 (0.69)	0.196 (0.87)
	Manganese	1.459 (7.64)	0.486 (3.55)	1.928 (8.57)
	Zinc	1.119 (5.86)	0.682 (4.98)	2.520 (11.20)
	Iron	10.390 (54.40)	2.617 (19.10)	21.060 (93.60)
	Copper	0.711 (3.72)	0.393 (2.87)	1.024 (4.55)

The results from the ultimate analysis of grass samples for all elements except sulphur showed to be very similar for all the examined grass samples. Deviations in the term of sulphur content could be due to different positions of grasslands and the soil type on which the examined grass grows. Higher sulphur contents in residue grasses from the riverbank and highway verge are due to the sulphur presence in the Sava River [175] and the uptake of sulphur dioxide emissions from vehicles by plants [176].

The results of the metal presence analysis have shown that metal presence is the highest for the grass collected on the highway verges (RG3). Large traffic volumes and consequently high vehicle pollutant emissions are the probable cause. The grass from the uncultivated land has also shown the relatively high presence of heavy metals. The reason for such a trend could be found in the fact that the uncultivated land is located near the state road with a relatively high traffic concentration. Studies of the presence of metals in roadside grass have been successfully conducted in Denmark [79], the UK [177], and Northern Germany [178]. The differences in the results of the metal presence of roadside grass indicate that their presence is primarily a function of the traffic density and past activities in that area.

The lowest presence of heavy metals was found in the grass samples collected from the riverbank of the Sava River. Although the riverbank grass has shown the lowest share of heavy metals, the data were not drastically lower compared to the other grass samples, except for the iron presence. As the Sava riverbank is occasionally flooded [179], heavy metals from the river accumulate in the soil and grass. As the Sava River springs in Slovenia where it passes through an area that has been strongly industrialised in the past, the presence of heavy metals in the river is not unexpected. Several mines, car, chemical and pharmaceutical industries, as well as the nuclear plant in Slovenia have contaminated the river in the past [180]. The past activities related to mining have thus caused significant pollution of the Sava River and its banks.

Biochemical biogas and methane potentials for monodigestion of grass and maize silage (MMS) and the co-digestion of RG2 with MS are shown in Table 3 and Table 4.

Table 3 Measured biochemical biogas and biochemical methane potentials of the analysed samples in monodigestion [34]

Parameter	MMS	MRG1	MRG2	MRG3
BGP [$Nm^3/kgTS$]	0.4744	0.4361	0.3482	0.4131
BMP [$Nm^3/kgTS$]	0.2896	0.2750	0.1921	0.2552

All grass samples (MRG1, MRG2 and MRG3) have shown both lower *BGP* and *BMP* compared to the mono-digestion of MMS, which was expected. The riverbank grass (MRG2) has shown the lowest potential for biogas and biomethane production, which could be related to the lowest *COD* value determined [34]. Also, the higher *COD* value-the higher *BGP* and *BMP* trend has been observed for the grass samples RG1 and RG3. Even though the sample RG2 has shown the lowest production of biogas, it has been selected for further analysis in co-digestion tests with maize silage and cattle slurry since it has shown the highest yield on the grasslands (Table 2). Therefore, the potential of replacing the part of maize silage by riverbank grass has been investigated in the samples C1 to C5. RG2 and MS have been added as a co-substrate with the animal slurry in the 1:1 ratio based on a dry mass (C1 and C5). Additionally, RG2 was mixed with MS at different ratios on dry basis (C2 - 0.75:0.25, C3 - 0.5:0.5, C4 - 0.25:0.75) together with animal slurry in the 1:1 ratio. The results point to the expected situation, as the share of maize silage in the feedstock increases, both the *BGP* and *BMP* increase, as shown in Table 4.

Table 4 Measured biochemical biogas and biochemical methane potentials of the analysed samples in codigestion [34]

Parameter	C1	C2	C3	C4	C5
BGP [Nm^3/kgTS]	0.2888	0.3211	0.3268	0.3861	0.4029
BMP [Nm^3/kgTS]	0.1724	0.1965	0.1952	0.2514	0.2521

In general, it can be stated that the riverbank grass gives the lower quantity of the biogas compared to maize silage. At the same time, it is non-competitive with food production, and as a residue material it can be cheaper feedstock compared to maize silage, and thus it could reduce the operating cost of biogas plants.

To estimate the sensitive kinetic parameters of grass degradation, the following recorded data have been used: methane and carbon dioxide content in biogas and the biogas production for grass mono-digestion sample RG2. Results for the assessment of kinetic parameters are shown in Table 5.

Table 5 Estimated kinetic parameters in the grass degradation [34]

Parameter	Initial values (default) [181]	Estimated by MRG2 experimental data	Unit
k_{dis}	0.50	0.17	1/d
k_{hyd_Ch}	10	7.07	1/d
k_{hyd_Li}	10	4.31	1/d
k_{hyd_Pr}	10	6.29	1/d
k_{m_Ac}	8	1.70	$kgO_2/(kgO_2 \cdot d)$
k_{m_H2}	50	70.2	$kgO_2/(kgO_2 \cdot d)$
K_{s_Ac}	0.15	0.12	kgO_2/m^3
K_{s_H2}	$7 \cdot 10^{-6}$	$4.7 \cdot 10^{-4}$	kgO_2/m^3

The results of the parameter estimation procedure showed that both disintegration and hydrolysis steps for lignocellulosic biomass are slower compared to the default values in the model, which was expected. Furthermore, for the degradation of acetate, default and the estimated value of half-saturation constants (K_S) do not differ significantly, but the estimated kinetic parameter for the Monod maximum specific uptake rate constant (k_m) is significantly lower compared to the default value.

For the LCA study it was assumed that the biogas produced is used for generation of 1 kWh of heat and electricity. A single score characterisation expressed in µPt was used to determine contributions of four damage categories; Resources, Climate change, Ecosystem quality and Human health. The results of LCA are shown in Figure 6.

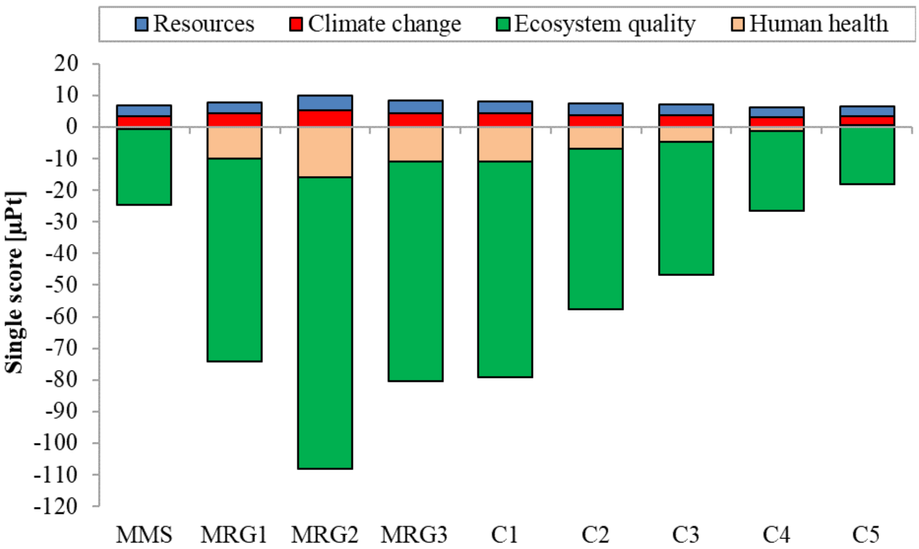


Figure 6 The single score results of the life cycle impact assessment [34]

The results by the single score characterisation identify the ecosystem quality category as a category that makes a significant difference among all studied cases. Negative results should be interpreted as an environmental benefit. Compared to maize silage, the grasses grow naturally without using any agricultural inputs and without cultivating the soil, and therefore, the results in Aquatic ecotoxicity, Terrestrial ecotoxicity and Land occupation (all are part of the Ecosystem quality category) show beneficial effects to the ecosystem quality. Comparing only the results obtained from the processes with co-digestion (C1–C5), it can be noted that the ecosystem quality arising from the process C1 and carried out with the residue grass and cattle slurry is 3.8 times environmentally better than the process C5, carried out with the maize silage and cattle slurry.

GHG emissions obtained by LCA are the result of quite high energy inputs (fossil fuels) for collecting and baling of grass. Compared to the GHG emissions from maize silage, all studied grass types have lower biogas yield potential which increases the emissions for transportation since more grass needs to be transported to the AD plant to produce the same amount of energy. For that reason, the process C1 resulted in 32% higher GHG emissions than the process C5. It should be noted that the benefit of using grass from the uncultivated lands for biogas production instead of its natural decomposition on the field, resulting in avoiding GHG emissions, was not considered in this study. Also, GHG emissions related to land use changes were not considered.

2.2.2 Valorization of digestate – ARTICLE 3

ARTICLE 3 presents the continuation of the previous experimental study on anaerobic digestion of two types of roadside residue grass, residue grass from the uncultivated land (next to minor road, RG-MR) and from the highway verge (RG-H) as shown in Figure 7. The research contains two novel scientific contributions, such as the study on pyrolysis of residue roadside grass and its digestate and the study on determination of degraded organic matter during anaerobic process based on the analysis of thermogravimetric (TGA) curves.

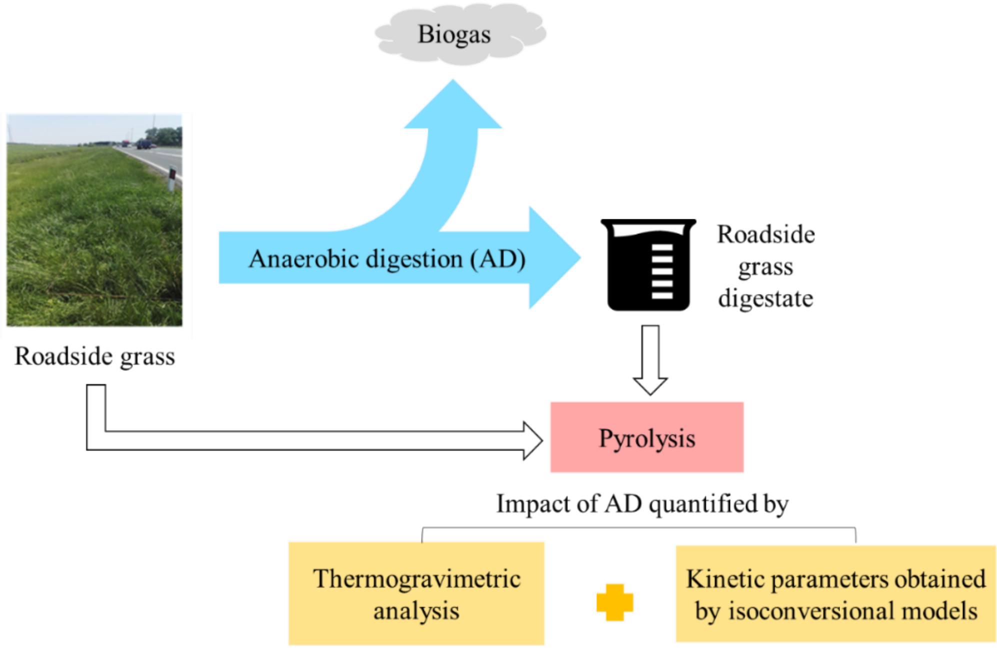
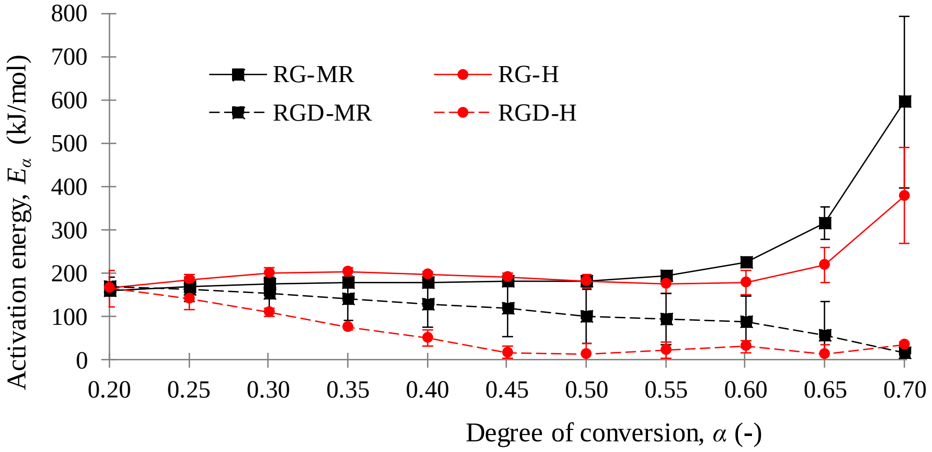


Figure 7 Integration of a pyrolysis in a roadside grass digestate management [35]

The application of TGA is described in more details in *ARTICLE 3* [35]. The results showed that during monodigestion of RG-MR, ca. 50% of cellulose and hemicellulose was converted to biogas, and in the case of RG-H, degradation of cellulose and hemicellulose is estimated at 44.0%. Degradation is similar for both grass types, which is also supported by the fact that for both, similar biochemical biogas potential values (*BGP*) were obtained, 0.436 Nm^3/kgTS for RG-MR and 0.413 Nm^3/kgTS for RG-H [34]. The average final residue yields for RG-MR and RG-H were ca. 25% and 23%. However, RGD (residue grass digestate) samples have shown a higher yield of final residue at the end of the process; for RGD-MR, the yield was ca. 38%, and for RGD-H, ca. 37%. Similar observations were obtained when food waste and its digestate were analysed in pyrolysis [182].

The distribution of activation energy (E_α) for RG and RGD samples has been determined based on the performed thermogravimetric analysis data for conversions between 20 and 70% in step sizes of 5%, as shown in Figure 8. Degrees of conversion lower than 20% and higher than 70% are not shown because of significant fluctuations observed (especially for digestate samples), which were probably associated with the thermal behaviour of lignin [183]. In addition, verification of the applied models was performed, and average values of kinetic parameters obtained by this study were used to verify models with the experimental data.

a)



b)

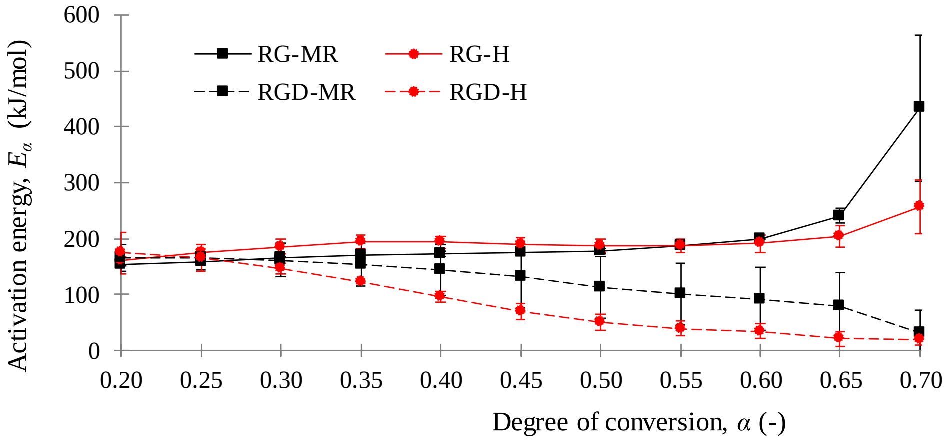


Figure 8 Distribution of Eα with the degree of conversion by means of a) FR model and b) KAS model [35]

Estimated values of E_α in the studied range of conversions vary between 160 and 600 kJ/mol for RG-MR samples, and between 170 and 380 kJ/mol for RG-H samples, when Friedmann (FR) model was applied. Both RG samples show a slight increase in the values of E_α from α = 0.20 to 0.30; between α = 0.30 to 0.50, a stagnation/slight decline of E_α is shown, and after α = 0.50, a significant increase in the E_α can be observed. Such a trend in the distribution of E_α using the FR model was also reported for corn stalk pyrolysis [184] and for miscanthus pyrolysis [185]. On the other hand, RGD samples have shown much lower values of E_α in the considered ranges of conversions; for RGD-MR it is between 20 and 170 kJ/mol, while for RGD-H it is between 10 and 170 kJ/mol. RGD samples show the highest E_α at the lowest value of α, and with an increase in the degree of conversion, E_α continuously declines in the case of RGD-MR, while RGD-H declines up to α = 0.45, and then stagnation appears.

E_α estimated by the Kissinger-Akahira-Sunose (KAS) model for RG samples in the studied range of conversions vary between 150 and 430 kJ/mol for RG-MR, and between 160 and 260 kJ/mol for RG-H samples. Similar results were obtained for the pyrolysis of Para grass (between 180 and 230 kJ/mol, [186]) and Camel grass with the KAS model (between 150 and 190 kJ/mol, [187]). The results obtained in this study and by analyses of specific grass types show a narrower range of activation energies for specific grass types than for unclassified species of grass. On the other hand, RGD samples again show lower values of E_α compared to RG samples; for RGD-MR the range is between 30 and 170 kJ/mol, while for RGD-H it is between 20 and 175 kJ/mol. Again, RGD samples show the highest E_α at the lowest value of α. KAS modeling shows that with an increase of the degree of conversion, E_α continuously declines in the case of both RGD samples.

2.2.3 Food waste and industry streams – ARTICLE 4

The substrates were collected from two companies located near the city of Zagreb, Croatia. Food waste (FW) and inoculum (IN) were sourced from biogas plant, and meat and bone meal (MBM) and wastewater sludge (WWS) from waste of categories 2 and 3 were collected from rendering plant. The IN was sampled in an anaerobic digester of the biogas plant. Two sets of experiments were carried out. For the first set of experiments, FW1, the co-substrate MBM and the inoculum (IN1), were sampled on February 15, 2019, while for the second set of experiments, FW2, the co-substrate WWS and the inoculum (IN2) were sampled on April 15, 2019. Table 6 shows the TS content of the substrates and inoculum that were used for two-stage hydrolysis and AD.

Table 6 TS content of substrate and inoculum samples [36]

Substrate/Inoculum	Total solid content [%]
FW1	19.58 ± 2.23
FW2	19.98 ± 0.31
MBM	99.30 ± 0.52
WWS	12.60 ± 0.03
IN1	4.44 ± 0.01
IN2	4.53 ± 0.01

FW has a TS content of approximately 20%, which is in the range of values found in the literature: 7.6-39.5% [104–106,188–190]. The wide span of TS in FW is mainly due to FW composition. In a biogas plant, the TS content of 5% is achieved by adding water or some waste liquid stream such as spoiled milk, juice, waste soup from restaurants, or any liquid waste available for use. MBM showed the share of TS to be almost 100%, while WWS had a much lower TS content, ca. 13%. The moisture content in MBM is usually around 5% [191] or even below 2% [192], as in this study. Such a high TS content makes MBM highly suitable for incineration as a supplement to or replacement for coal [193]. MBM is typically incinerated when it fails to meet the standards for use as animal feed (waste category 1) [171]. WWS shows TS content to be in a range, as reported previously, between 10.8-16.9% [104,106,188]. The inoculum has a TS content slightly less than 5%, which is in the range of the TS content in biogas plants [23], and is a relatively common value for digestion of FW [194].

After analysing the properties of substrates and inoculum, the thermal pretreatment of FW and rendering industry streams, MBM and WWS, was evaluated by monitoring the change in pH, NH_4-N and *COD*. Values of parameters measured before and after pretreatment are shown in Figure 9 left, for the first experiment (co-substrate MBM, inoculum IN1, sampled on February 15, 2019) and in Figure 9 right, for the second experiment (co-substrate WWS, inoculum IN2, sampled on April 15, 2019). The coloured bar in Figure 9 represents the average value of the variable for the given mixture, while range bars delimit the actual range of values measured in the experiments [195].

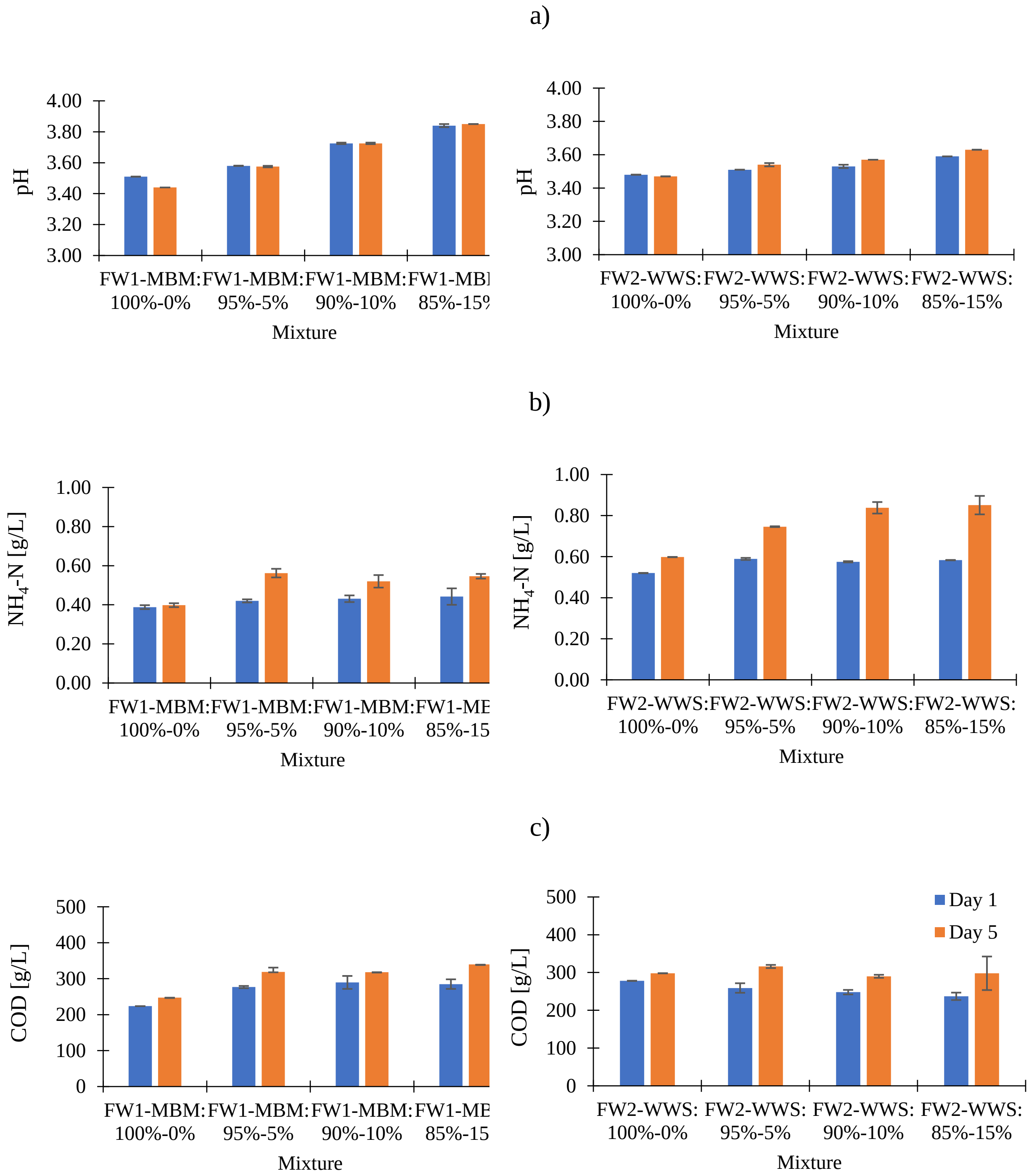


Figure 9 Change in a) pH, b) NH_4-N and c) COD during pretreatment of FW1 and MBM (left) and FW2 and WWS (right) [36]

The presented results show that both FW (FW1 and FW2, collected at different times) show a similar range of pH during the pretreatment, between 3.40 and 3.50. According to the literature, the reported pH range of FW is very wide, between 3.7 and 6.1 [105,188,196,197]. Adding MBM to FW1 slightly increases the pH, from about 3.5 (0% MBM) to about 3.9 (15%

MBM). Such a trend was anticipated, since MBM is the product of alkaline hydrolysis where NaOH is used to dissolve animal industry streams in rendering plants [173]. On the other hand, WWS showed no significant change in pH. The results also show that after pretreatment, the pH values remain similar to those before pretreatment in all the cases analysed.

Figure 9 b) shows the impact of adding rendering industry streams to FW in terms of NH_4-N concentration. The FW2 sample (right) had a greater share of nitrogen-rich material than the FW1 sample (left). Values are slightly higher compared to previously reported values, which are about 0.203 g/L [190]. With more MBM, and especially WWS, in the substrate, NH_4-N concentration increased, since both animal industry streams are rich in proteins [198] that hydrolyse during the pretreatment and increase NH_4-N concentration.

COD values for the samples are shown in Figure 9 c). FW2 has a slightly higher *COD* value (298 g/L) compared to FW1 (224 g/L). Results of the research are in line with results obtained for cafeteria FW with a pH of 4.2 ± 0.3, where *COD* was 197 ± 42 g/L [199]. As a result of the pretreatment, *COD* increased by 7 - 26%, more in the case of FW2-WWS. When adding MBM to FW1, an increasing trend of *COD* occurs, while in the case of FW2-WWS, a decreasing trend is obtained, which is expected, since WWS is a low-organic material [200].

Based on these results, selection criteria were determined to decide which samples to select to reveal their impact in terms of AD. The mixture with the highest relative increase in *COD* and the lowest relative increase in NH_4-N concentration during pretreatment was selected. The first indicator stands for the higher amount of degradable organic matter, which in theory corresponds to higher biogas yield. The second criterion is related to prevention of ammonia inhibition during AD.

Based on the chosen criteria, mixtures FW1-MBM: 95%-5% and FW2-WWS: 95%-5% were selected for the second AD stage and investigation of biogas production. Results for the AD tests for the gas and liquid phases are shown in Figure 10 and Figure 11.

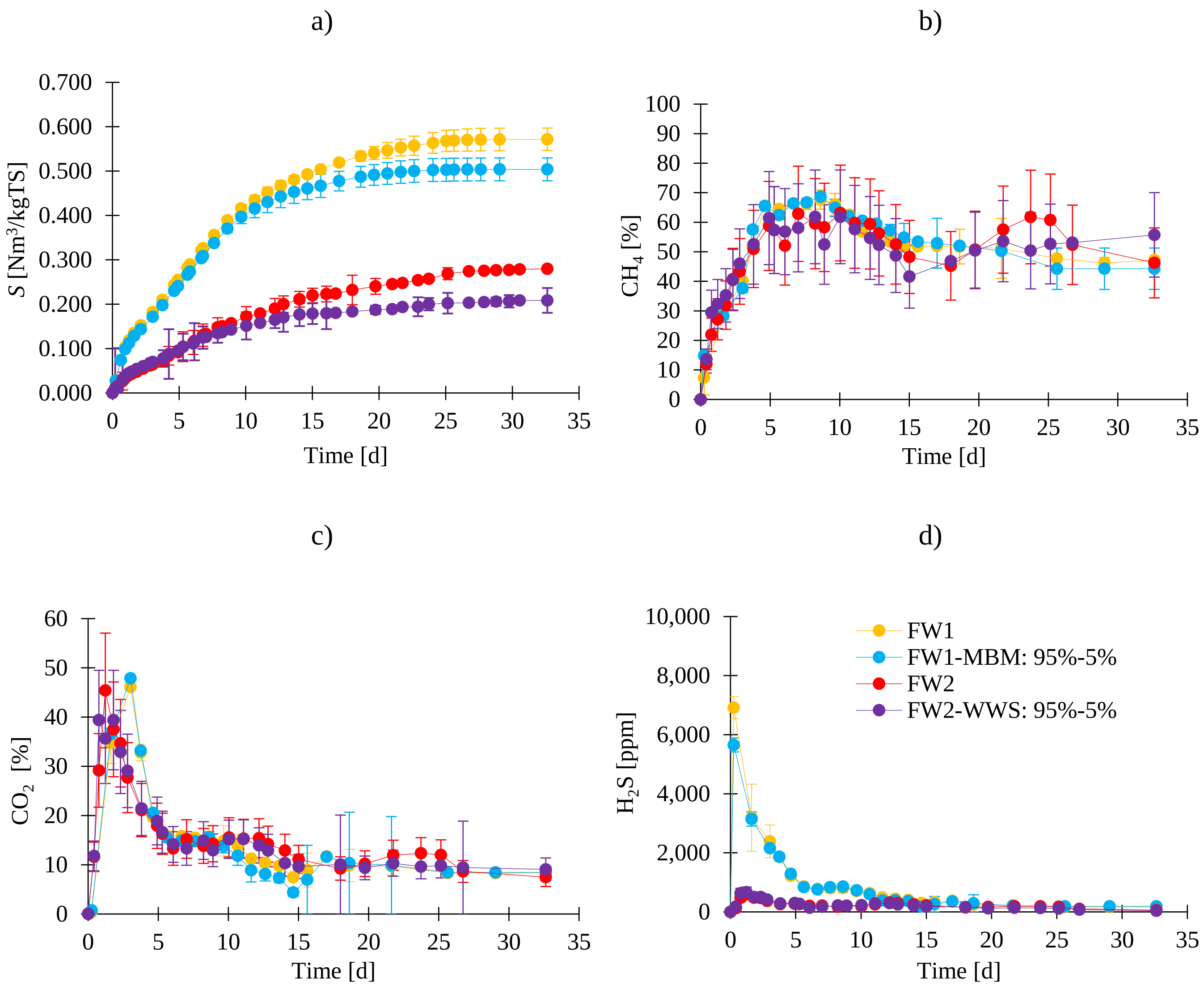


Figure 10 Variables in a gas phase, a) biogas yield, and concentrations of b) CH_4, c) CO_2 and d) H_2S during AD [36]

In this research, it is estimated that sample FW2 is not very different from FW1, since the material that biogas plant receives usually comes from the same sources, and analysis of the liquid phase (see Figure 11) contributes to that statement. Based on the shape of the biogas yield profiles [201] shown in Figure 10a), it can be concluded that inhibition in AD of FW2 occurred, resulting in about 2.25-fold lower biogas yield compared to FW1. More detailed discussion of the causes of inhibition in the process will be provided in the following subsection on analysis of the liquid phase.

This research showed that both rendering industry streams have decreased biogas yield of FW when added in portions of 5% on a TS basis. It has been stated that FW contains fungi and yeast that enhance its biodegradability during AD [202]. MBM and WWS are sterile industry streams of alkaline hydrolysis, and when added to FW in AD, they could possibly decrease the size of the bacterial community of fungi and yeast in FW, which is reflected in a slightly lower biogas yield.

According to the previous report, in the steady state period, the biogas produced from FW reported CH_4 concentrations to be approximately between 53% and 59%, while the CO_2 concentration in biogas was in the range of around 40-47% [189]. In this study, similar concentrations of the main biogas components in the steady state period (after day 20) was observed. By comparing CH_4 and CO_2 profiles in Figures 3b) and 3c), it can be observed that the FW2 and FW2-WWS mixtures showed slightly lower CH_4 and slightly higher CO_2 content in biogas before stabilizing (days 5-20).

The profiles of H_2S concentration in biogas during the AD showed that the FW1 sample had a much higher content of sulphur-rich materials than the FW2 sample. The highest reported H_2S concentration in the experiments was obtained one day from the start of the process and reached approximately 7,000 ppm. According to the literature, raw biogas can have up to 10,000 ppm of H_2S [203]. In both cases, rendering industry streams reduced H_2S generation during AD of FW, which could be a promising topic for further exploration in the future, since high H_2S concentration during combustion produces high amounts of SO_2, which affects biogas engines on account of corrosion [204].

It is also important to note that for both batch experiments, as biogas was produced, it displaced the air which was trapped in the reactor headspace at the start of the process and decreased the share of oxygen in the gas phase. By displacing oxygen and other gases by biogas, anaerobic conditions in reactors were achieved and maintained. Other contaminants such as nitrogen, water vapour and oxygen can be present in raw biogas in amounts up to 15, 3 and 5% [203]. In this research, the maximum oxygen content in produced biogas was 5%, while concentrations of nitrogen and water vapours were not measured.

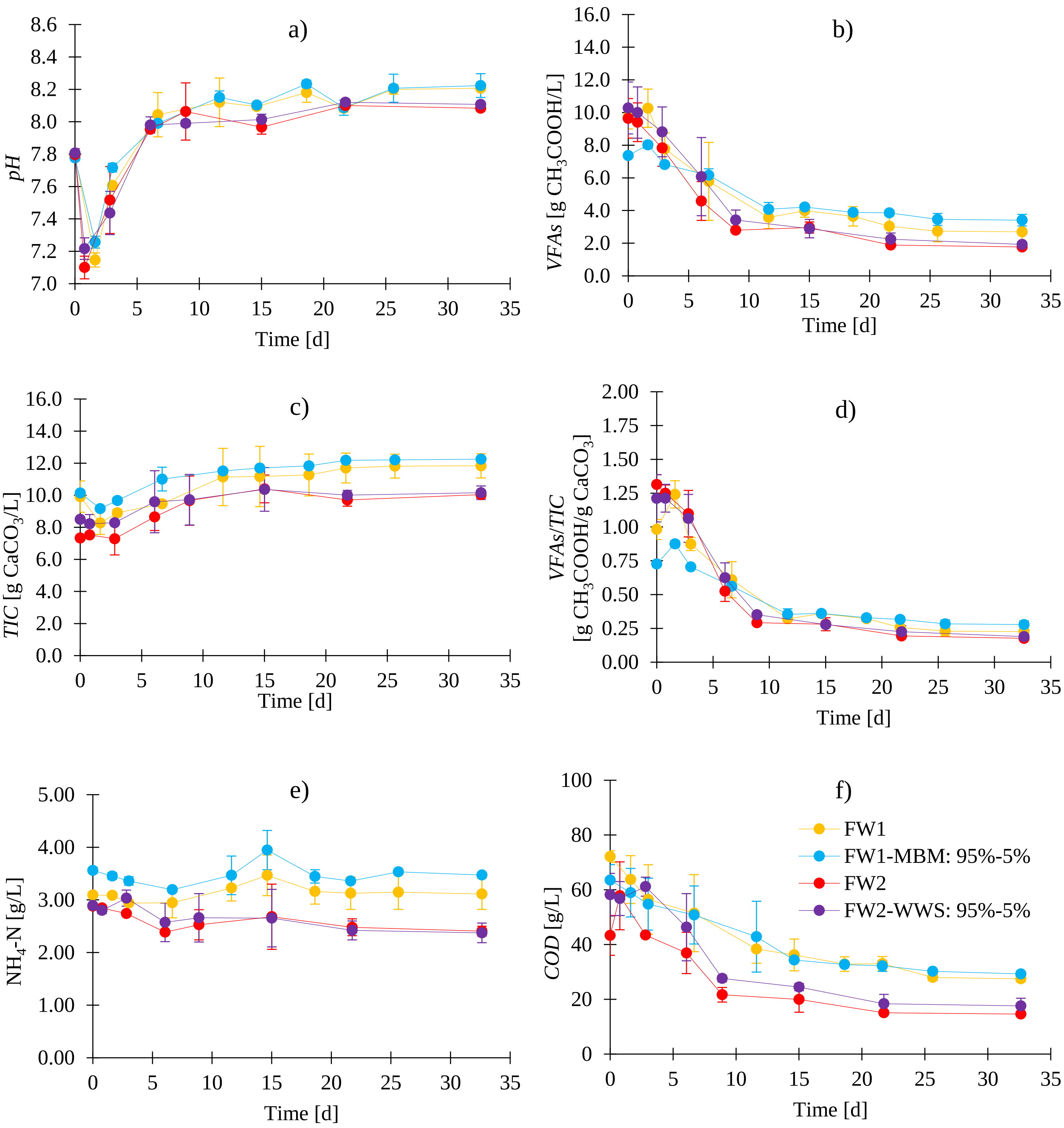


Figure 11 The change in variables in a liquid phase, a) *pH*, b) *VFA*, c) *TIC*, d) *VFAs/TIC*, e) *NH_4-N* and f) *COD* during AD of selected mixtures [36]

The profile of pH values determined in this research follows the theoretical pathway. During the first days of the process, pH value drops because of acidogenesis and acetogenesis, while it subsequently increases as VFAs are consumed to produce CH_4 and CO_2 [205]. As mentioned before, MBM is a product of alkaline hydrolysis of animal industry streams [173], and when added as a co-substrate to FW, it slightly increases pH (see Figure 11a). FW2 showed a similar range of pH values to that of FW1. As with MBM, WWS slightly increased the pH of FW. According to some previous studies, the pH values for AD of FW ranged between 6.0 and 8.5 [102,206]. The pH values obtained in this research showed that there was no indication of inhibition in biogas production caused by poor pH control for FW2 and WWS [207].

Figure 11b) shows the reported profile of VFAs during AD of selected FW mixtures. VFAs are generated during the acidogenesis stage, which causes the drop in pH as shown in Figure 11a). For the AD of FW, it was reported that the concentration of VFAs ranged between ca. 10.0 to 11.0 g/L, while pH ranged between 7.5 and 9.0 [208]. However, another study showed that the maximum value of VFAs concentration during AD of FW was even below 5.0 g/L, while pH was above 8.0 [190]. During the entire process, FW1 achieved a VFA conversion of 81.8%, while FW1-MBM achieved a VFA conversion of 57.5%. Adding MBM to FW causes lower generation of VFAs, which was reflected in lower levels of conversion to biogas and consequently lower biogas yield, as shown in Figure 10a). The VFA conversion was 81.6% for FW2, and 81.2% when WWS was added to FW2. Results show that VFAs in all mixtures under analysis were converted successfully, which is an indication of non-inhibited acidogenesis and acetogenesis steps. Based on that, it can be concluded that inhibition of biogas production for FW2 and FW2-WWS cannot be caused by long chain fatty acids (LCFAs) or VFAs accumulation [209].

The profile of TIC in these mixtures shown in Figure 11c) follows similar trends as the pH profile shown in Figure 11a), since the TIC value represents the buffering capacity of the mixture (ability to change pH by adding acids or alkaline) [194]. The range of TIC values during AD of FW was reported to be between 8.0 and 9.5 g $CaCO_3$/L [210]. Results of this research have proven to be in a slightly broader range: for FW1-MBM, between 8.272 ± 0.715 g $CaCO_3$/L and 11.835 ± 0.933 g $CaCO_3$/L, while for FW2-WWS, the range was between 7.285 ± 1.006 g $CaCO_3$/L and 10.396 ± 1.613 g $CaCO_3$/L. In both cases, the addition of MBM and WWS yielded slightly increased TIC values.

Usually, a high VFAs/TIC ratio (<0.4) is an indicator that the AD reactor is overfed by substrate and that the process is unstable [206]. Such an interpretation is valuable only if AD is studied in continuous operation. In this research, a batch AD was performed, which showed that the VFAs/TIC ratio can go above 1.0 with the process remaining stable. Adding MBM to FW1 decreased the VFAs/TIC ratio, since MBM showed a negative effect in term of VFA production. On the other hand, WWS did not significantly affect the VFAs/TIC ratio for FW2. In the case of batch AD of food-processing industrial waste, the VFAs/TIC ratio at the start of the process was approximately 0.70; after 6 days it increased to around 2.3 and later dropped, reaching the final value of ca. 0.25 after 30 days from the start of the process [211].

Ammonia inhibition of biogas production using FW is a relatively common inhibition type in AD, caused by protein-rich material present in FW [212]. It has been determined that, in the case of AD of FW, there is a wide range in the NH_4-N inhibition threshold concentration, between 2 and 6 g/L [213]. As expected, adding MBM to FW1 increased the release of ammonia during AD, similar to what was observed during the pretreatment stage. However, these higher concentrations of NH_4-N when MBM was added to FW did not affect the stability of AD, since the biogas production was not inhibited, as shown in Figure 10a). It can be seen in Figure 11e) that the highest NH_4-N concentration is achieved when adding MBM to FW1. Among the reasons for stable behaviour (despite a comparably high NH_4-N concentration) is adaptation of the microbial community in a digester over time to operation at higher NH_4-N concentrations (compared to others) without causing a failure in the process [214]. The FW2 and FW2-WWS mixtures had much lower concentrations of NH_4-N than FW1, from which we can conclude that ammonia inhibition cannot be the reason why FW2 gave such a reduced biogas production.

Figure 11f) shows the change in *COD* of these mixtures during the AD. According to the literature, FW shows a wide range of *COD* values at the start of the process, between 69.92 and 181.05 g/L [190,213,215]. The efficiency of *COD* removal during AD was approximately the following: 61.9% for FW1, 53.9% for FW1-MBM, 74.7% for FW2, and 71.2% for FW2-WWS. In the literature, it has been reported that *COD* removal efficiency of two-stage AD of dining hall FW was 78.7% [216], while the *COD* removal efficiency during AD of canteen FW was slightly lower, between 51 and 62% [209].

Based on the results presented in Figure 11, there is no indicative measure in the liquid phase of what caused the inhibition in AD of the FW2 and FW2 mixtures with WWS, since those samples showed almost identical parameter values as FW1 and FW1-MBM.

Finally, to further explore the possible cause of inhibition, electrical conductivity was measured at the end of the process, which could show possible salt inhibition [217]. The explanation of salt-inhibition mechanisms is that a high presence of sodium ions during AD reduces the conversion of acetate to products (inhibition of methanogenesis) and reduces the potential to produce biogas [218]. In this study, it was noticed that the measured biogas composition (Figure 10Figure 11b,c) showed lower methane and higher CO_2 concentrations in the biogas for FW2 and its mixture with WWS. Since the last stage of AD, methanogenesis is related to conversion of acetate and CO_2 to methane, methanogenesis of FW2 is shown to be relatively inefficient.

Measurements of electrical conductivity gave the following results, for FW1 8.99 ± 0.54 mS/cm, for FW1-MBM 9.00 ± 0.39 mS/cm, for FW2 9.96 ± 0.63 mS/cm and for FW2-WWS 9.60 ± 0.44 mS/cm. Results indicate that higher conductivity (higher concentrations of salts [219]) is obtained for FW2. However, the values are still way below the general threshold for salt inhibition of 30 mS/cm [220]. It is possible that a slightly higher concentration of salts in FW2 resulted in the lower biogas yield, but it is highly improbable to expect that an approximately 10% higher electrical conductivity resulted in 2.25-fold lower biogas yield.

The kinetic parameters of AD for the mixtures were estimated using several simple mathematical models. Results of calculated kinetic parameters are shown in Table 7.

Table 7 Estimated kinetic parameters for AD of selected mixtures [36]

Model	Parameters	Mixtures			
		FW1	FW1-MBM 95%-5%	FW2	FW2-WWS 95%-5%
First-order	k [d^{-1}]	0.135	0.150	0.097	0.131
	$RMSE$ [Nm^3/kg TS]	0.0150	0.0153	0.0079	0.0052
Monod	k [d^{-1}]	0.255	0.300	0.168	0.245
	$RMSE$ [Nm^3/kg TS]	0.0512	0.0476	0.0259	0.0146
Modified Gompertz	R_m [Nm^3/(kg TS·d)]	0.0845	0.0950	0.0623	0.0850
	λ [d]	0	0	0	0
	$RMSE$ [Nm^3/kg TS]	0.0218	0.0171	0.0090	0.0112
Cone	k [d^{-1}]	0.200	0.230	0.145	0.210
	n [−]	1.6	1.6	1.6	1.6
	$RMSE$ [Nm^3/kg TS]	0.0305	0.0288	0.0136	0.0106

The best fit of a model to the experimental data for all these mixtures was obtained by the First-order kinetic model, where the estimated reaction rate constant for FW1 was 0.135 d^{-1} and for FW2, 0.097 d^{-1}. As expected, the rate constant for FW2 is lower (by 28%) compared to FW1, owing to the occurrence of inhibition. These results are in line with previous reports.

The first-order reaction rate constant for AD of FW has shown a wide range of values, between 0.027 $d^{-}1$ and 0.49 d^{-1} [121,124,221–223].

In this study, Monod kinetics proved to be the least applicable among the models studied, because of the highest *RMSE* values. Application of the Modified Gompertz model in AD of thermally pretreated FW gave a lag phase (λ) equal to 0 d, which was also reported in some previous studies [121,223,224]. Kinetic analysis using the Cone model showed that FW has a shape factor equal to n=1.6, and a reaction rate constant between 0.145 and 0.200 d^{-1}. A previous report on the application of a Cone model in AD of FW gave a similar shape factor (1.3) and rate constant (0.126 d^{-1}) [124].

2.3 Biogas utilisation in the post-subsidy era

This part of the dissertation presents selected results obtained by the mechanical engineering approach to biogas production from alternative substrates. Recorded process performances were presented and discussed referring to set research objectives and proposed scientific contributions. The section 2.3 is divided into three subsections, each one for the published article.

2.3.1 Operation on liberal electricity markets – ARTICLE 5

The contribution of this investigation was to develop operational methods for existing biogas plants that operate in CHP mode once they lose subsidies for energy production and consequently implement biogas upgrading technology for biomethane production. The system dynamics is determined by the electricity price and biomethane price, where the biogas is supplied to storage, the upgrading unit or the CHP, in order to maximize profit, known as advanced unit commitment with economic dispatch [225]. A similar approach is described in [226], where the combined operation between wind power generation and pumped hydro energy storage was analysed, employing MATLAB/Simulink®.

The study shows how the total operational cost (accounts for harvesting and transport of the feedstock [227], the daily cost of maintenance, salaries and other costs not associated with the purchase of substrates, or their harvesting and transport [228]) impacts the availability of biogas plants to earn profit on day-ahead electricity market. All estimated costs together with the produced electricity and heat in the CHP plant are gathered in the value named as break-even cost of electricity production ($BECP_{el}$). The assumption was made that the owner of biogas plant paid back the initial investment in the period of operation under subsidy mechanisms. Figure 12 presents the impact of $BECP_{el}$ on the CHP operational time using day-ahead electricity prices.

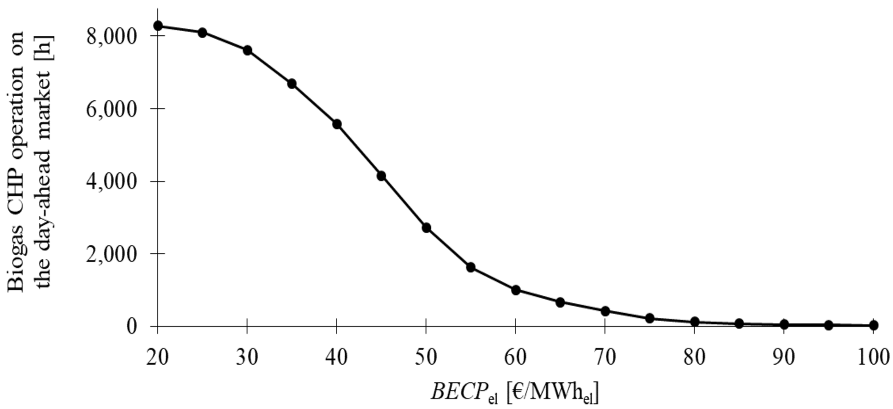


Figure 12 The impact of $BECP_{el}$ value on CHP operational time on the day-ahead electricity market [37]

Beyond the value of 40 €/MWh$_{el}$, the CHP operational time decreases significantly, even below 4,000 h/y. At the price of 100 €/MWh$_{el}$, biogas energy production equals the biogas production costs, and the operation is no longer feasible. In Germany, the $BECP_{el}$ value for maize silage was estimated at ca. 100 €/MWh$_{el}$ [229]. Without subsidies for electricity production, biogas plants could not make a profit while operating using relatively expensive raw materials, such as maize silage. In addition, biogas plants should instead utilise cheaper substrates or even substrates with a negative price, like food waste from canteens, restaurants, etc. [70] to make their operation profitable. The highest gradient in Figure 12 is shown for an approximately 45 €/MWh$_{el}$, which can be attributed to the median electricity price on the day-ahead market. Additionally, in Figure 12 the inflection point is at approximately 45 €/MWh$_{el}$, where the rate of gradient change is maximal, which indicates the $BECP_{el}$ for which the CHP system will experience the most starting up and shutting down of the system.

The feasibility of the implementation of biogas upgrading was studied by changing the selling price of produced biomethane from 40 €/MWh to 80 €/MWh, at intervals of 10 €/MWh, while CHP occasionally operates on electricity balancing markets. The operation of such system is not sensitive to change in the $BECP_{el}$ value, since the primary target is to produce biomethane, and biogas CHP is feasible only when the price of electricity is high. Overall, because the market price of biomethane needs to be high enough to yield profit in continuous operation, biogas storage does not occur. An example of CHP operation on the balancing market is given in Figure 13 for defined prices of biomethane. For the period between 5,500 h and 7,000 h, when the CHP is mainly working, for all biomethane prices in Figure 13, a high electricity price is present. The different dispatching in operation of the scenario is between the biomethane price of 40 €/MWh and 50 €/MWh, which corelate to the largest gradients from Figure 12, and a greater difference in the overall electricity generated. The analysis results show that the most frequent operation of CHP on that balancing market was detected in the last quarter of the year, between hours 6,000 and 8,000. Electricity prices on the DK1 balancing market are significantly influenced by wind penetration, the influence of which is especially marked in the fall period (September, October, November) [230].

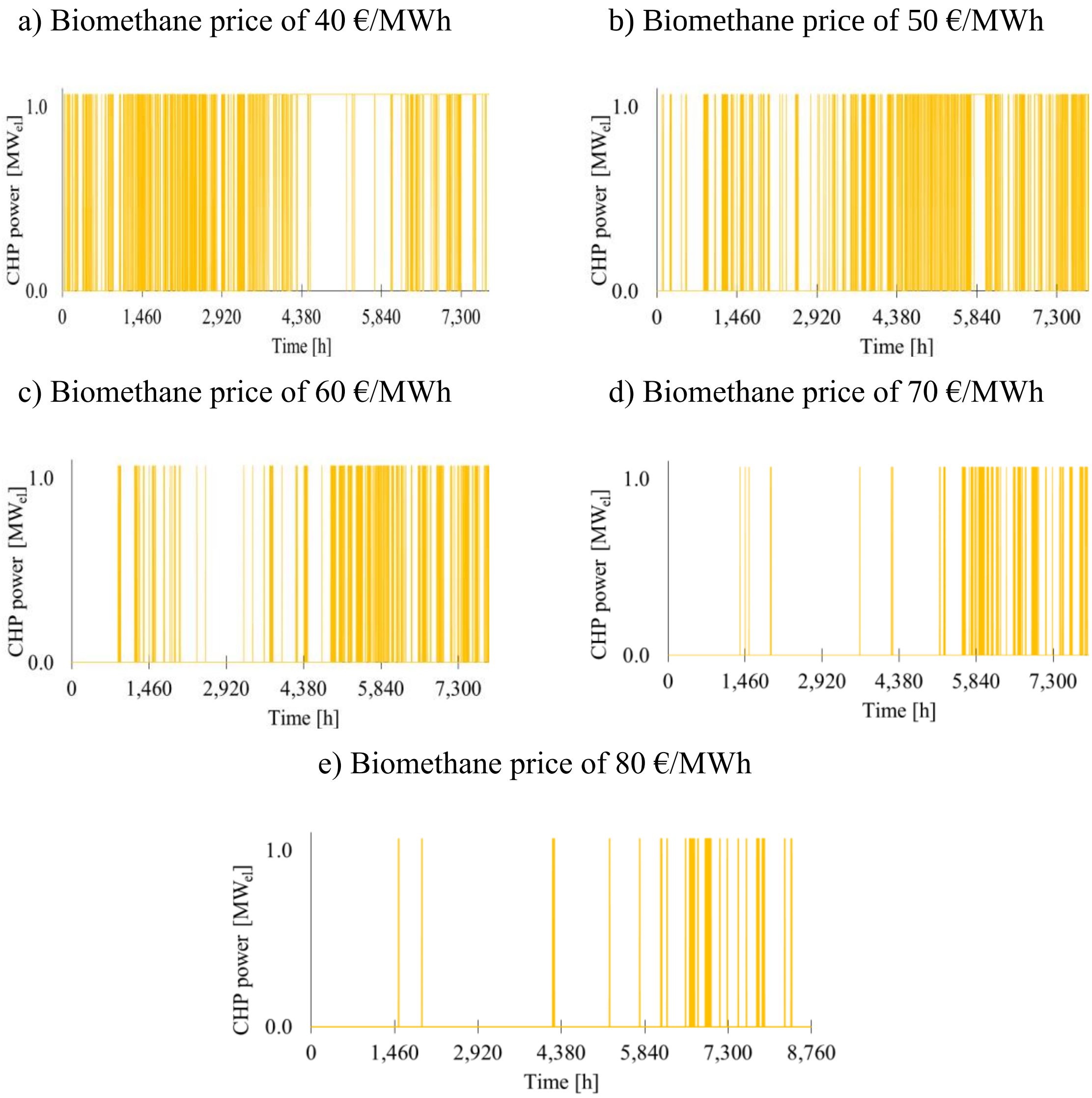


Figure 13 CHP operation on the balancing market for the biomethane price of a) 40 €/MWh, b) 50 €/MWh, c) 60 €/MWh, d) 70 €/MWh and e) 80 €/MWh [37]

It is important to stress that the results of this analysis have been tested for an electricity market (DK1) with a high penetration of wind. This study has shown that even at the very high biomethane selling price of 80 €/MWh, there are still periods in the year (112 hours) when generation of electricity and selling it on the balancing market can be more feasible than upgrading of biogas. Flexible power generation and continuous biomethane production in the case of Austrian biogas plants did not show significant profit compared to biomethane production alone [231]. Surplus to that, this analysis has shown that biomethane production could support existing biogas CHP while operating under different market conditions and enable them to keep biogas production running. Economic analysis of the proposed concepts showed that projects are profitable with high internal rate of return (*IRR*) values (between 15 and 40%) and low payback periods (between 3 and 7 years), only if biomethane is sold for the price of 60 €/MWh or above. In the present conditions, biomethane cannot be competitive to natural gas in industry processes, as the price of natural gas is still relatively low in economies with weak biogas sector [232].

2.3.2 Integration of power-to-gas with feedstock gate fee – ARTICLE 6

A robust mathematical model was developed with the goal of quantifying the integration of the P2G concept into an existing biogas plant operating under a feedstock gate fee business model. Input data for the case study considered operational features of a biogas plant taken from *ARTICLE 4* [36], and the data on potential for wind and solar energy at location from PVGIS [233] and Renewable Ninja [234]. Three scenarios for P2G integration were developed with included uncertainties of electricity production from PV and wind plants:

i) Scenario I – biogas is used in an existing CHP unit to produce heat and electricity; CO_2 after combustion is utilised with H_2 from electrolyser to produce e-CH_4 in the methanator.
ii) Scenario II – biogas is utilised with H_2 from electrolyser in methanator to produce renewable CH_4, without separating CO_2 and CH_4.
iii) Scenario III – biogas is fed to the upgrading unit to separate CO_2 and CH_4; the CO_2 stream is used in the methanator with H_2 from electrolyser to form e-CH_4, which is combined with the b-CH_4 stream from the upgrading to produce renewable CH_4.

The hourly based operation of electricity producing units to cover the electricity demand of renewable methane production in a typical winter and summer week of a year is shown in Figure 14.

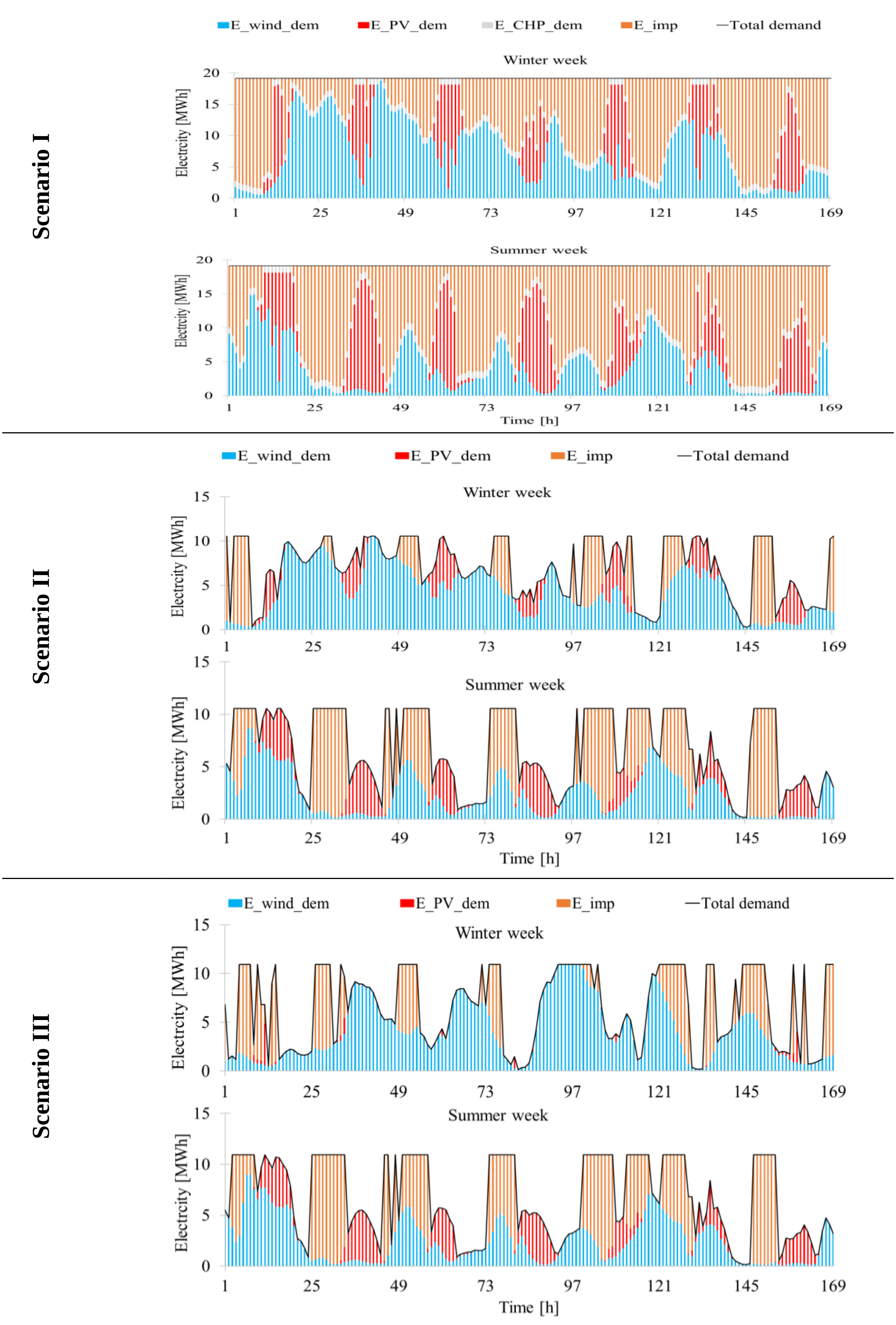


Figure 14 Hourly based operation of the system in a winter and summer week [38]

Since the cost of electricity produced in the biogas CHP was lower than that for wind and PV (the assumption was that the investment in biogas CHP had been paid out before integrating P2G), the production of CO_2 from biogas CHP was constant (flat, like the total demand curve in Figure 14), which required immediate utilisation in the P2G concept.

The optimised capacity of external storage in Scenario I was equal to 0 m^3, while the capacity of additional storage in Scenarios II and III ranged between ca. 5,000 and 8,500 m^3 in the given electricity market conditions.

On a yearly basis, for the production of 36 GWh of renewable methane, the total electricity demand in Scenario I was estimated at 167.5 GWh$_{el}$, in Scenario II at 58.6 GWh$_{el}$, and in Scenario III at 59.8 GWh$_{el}$. The analysis showed that Scenario I cannot be feasible due to the extremely high electricity demand in the process and the low integration of the P2G concept in the biogas plant whose operation should be assisted by imported electricity from the grid. In more detail, results in Figure 14 showed the hourly-based operation of the system in two characteristic weeks in the studied year.

The electricity generated by the wind farm at the location in Scenario I accounted for ca. 18% of the total demand in the summer week, and ca. 37% of the total demand in the winter week. The PV plant at the location in Scenario I covered ca. 25% of the total demand in the summer week and ca. 15% in the winter week. The biogas CHP covered ca. 7% of the total demand over the year, while the rest (ca. 40-50% of the total demand) was covered by electricity imported from the grid. In both Scenario II and III, the penetration of wind and PV in the total electricity demand was very similar, ca. 35% of the total demand in the summer week and ca. 62% in the winter week for wind, and ca. 18% of the total demand in the summer week, and ca. 14% in the winter week for PV. In Scenario II and III, the electricity imported from the grid to cover the total demand for renewable methane production accounted for ca. 25-45%.

Optimised capacity of the wind and PV plant in the given electricity market conditions and for each scenario are shown in Figure 15.

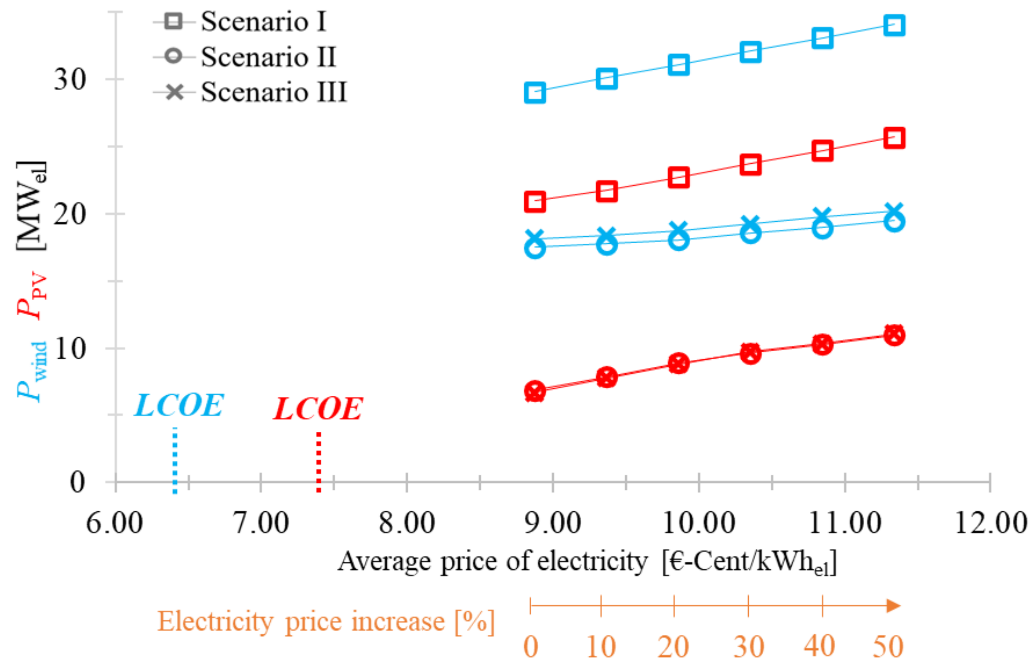


Figure 15 The impact of average electricity price on wind and PV capacity [38]

As the market price of electricity increased, the penetration of variable RES became more important to cover the energy demand of the system. As can be seen in Figure 15, the potential for wind penetration in the system was significantly higher than that of PV, since the *LCOE* for wind was found to be lower than that for PV.

Results obtained by Scenario II and Scenario III were very similar in the given electricity market conditions. In Scenario II, the optimised capacity of the methanator was calculated at 650-730 Nm^3(e-CH_4)/h, while the capacity of the electrolyser was optimised in the range 920-1,000 Nm^3(H_2)/h. The capacity of the methanator in Scenario III is optimised to the value of ca. 230-270 Nm^3(e-CH_4)/h, while the biogas upgrading unit had an optimum capacity between 660-730 Nm^3(biogas)/h.

Based on the results of the optimisation, it was estimated that the capacity factor for the electrolyser ranged between 56% and 62%, while for the methanator, the capacity factor was assessed at ca. 57-63%. Using the developed model, it was found that for the production of 900-1,100 Nm^3(H_2)/h in the electrolyser which served in the methanation to produce 36 GWh per year of renewable gas (both e-CH_4 and b-CH_4), installation of a wind plant of ca. 18-20 MW_{el} and a PV plant of 6.5-11.0 MW_{el} was required.

In the *Audi e-gas* plant [235], to meet the electricity demand for producing 1,200 $Nm^3(H_2)/h$, which is used to produce 300 $Nm^3(e\text{-}CH_4)/h$, four wind turbines were installed, each of 3.6 MW_{el} capacity, in total 14.4 MW_{el}. The capacity factor for wind at this location of the biogas plant was estimated at 22%, while in Northern Germany it was significantly higher, ca. 40% [236]. Based on the model results and comparison with data obtained from the literature, it can be concluded that the developed model for P2G integration in the biogas plant could be applicable for estimating the capacity of variable RES at the location required for these processes.

The further analysis in the study was focused on determining a threshold (*GF* level) that would indicate feasible conditions for the integration of P2G (in terms of optimized capacities) into a biogas plant for the production of renewable methane competitive with natural gas, only without subsidies. Figure 16 presents the sensitivity analysis of a variation of the feedstock *GF* on the *LCORM* value.

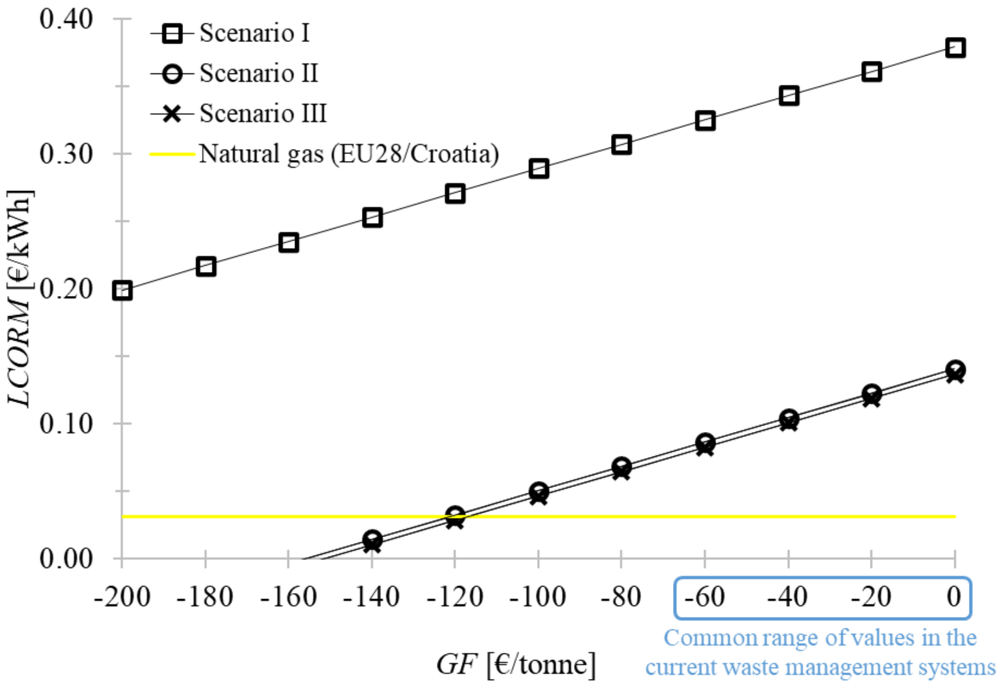


Figure 16 Sensitivity analysis of the feedstock *GF* variation on the *LCORM* [38]

The *LCORM* in Scenario II and Scenario III fitted very close to each other, while the *LCORM* in Scenario I was significantly higher. As the (absolute) value of *GF* increases, the cost of renewable methane production decreases and contributes to the economic viability of the proposed energy system. In general, the levelized cost of synthetic natural gas (SNG) generation by P2G ranged between 0.08 and 0.60 €/kWh [148]. More precisely, the cost of renewable methane produced in P2G with the direct methanation of biogas was estimated at 0.24-0.30 €/kWh [237].

If the *LCORM* in Scenarios II and III reached the average price of natural gas for non-household consumers in Croatia (which is very close to average in the EU28, ca. 0.031 €/kWh [232]), the *GF* in the proposed system should be ca. -120 €/tonne. In Scenario I, the *GF* would need to be ca. -385 €/tonne to meet the average price of natural gas in Croatia/the EU28. The calculated values of *GF* in these scenarios are significantly higher than those reported for food waste/biowaste based biogas plants in the EU, for which the common *GF* values are between -40 and -50 €/tonne [238,239].

When the *LCORM* achieves the average natural gas price for household consumers in the EU (ca. 0.067 €/kWh [232]), the *GF* should become ca. -80 €/tonne, which is closer to common *GF* values in the biogas sector. One reason that biogas plants have not yet intensified their operation in the waste management system using biodegradable fractions and biowaste is that the fee for landfilling organic waste in Europe is still rather low, between -20 and -30 €/tonne [240]. However, since landfill is no longer prioritised as a waste management solution [241], it is expected that in future the biogas sector will take over the management of biodegradable organic waste, which will apparently result in *GF* values higher than the current ones.

Moreover, further liberalisation of the natural gas market in Europe and Croatia is expected in the coming years [242]. This could result in an increase of natural gas prices, which would contribute to greater penetration of renewable methane in the gas sector.

2.3.3 Geospatial analysis and environmental impact assessment – ARTICLE 7

This study integrally analyses the geospatial availability of novel feedstocks in the replacement of maize silage in biogas production, combined with the environmental impact assessment of feedstock replacement and alternative biogas utilization pathways in future energy systems operating with a high share of RES. Methods used in the study comply of GIS mapping of an energy potential of biogas production in the studied case, combined with LCA of the studied scenarios of the biogas sector transition. The target region for testing the model was Northern Croatia, where 13 biogas plants operate mostly using maize silage and are within the *feed-in-tariffs* for electricity production. Results in Figure 17 present the assessed energy potential for biogas production from alternative substrates in the study region, and the position of existing biogas plants for which the transition from maize silage is proposed. The geospatial analysis of biogas sector included finding a natural gas network that, together with assessed biogas potential, identified the locations where new biogas plants should be installed. The analysis also included the assessment of the contribution of renewable gas production in new plants to the decarbonization of the natural gas sector.

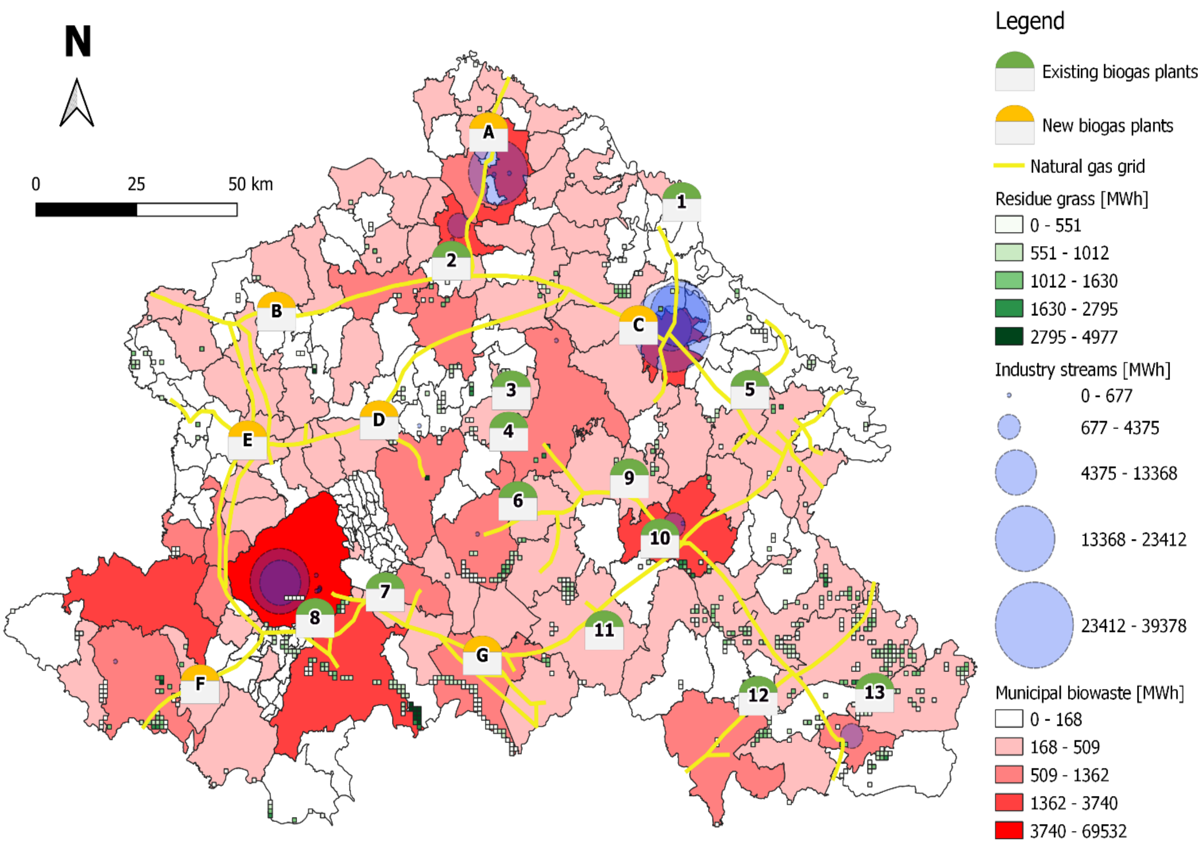


Figure 17 Geospatial analysis of the biogas sector in Northern Croatia [39]

Biowaste from municipalities (household waste) can serve as a valuable source of biogas, given the relatively high biogas yield of 100-150 m^3/tFM [84,243,244]. An experimental study by the authors of this research on using biodegradable waste from kitchen, canteen, and restaurants (similar to the composition of municipal biowaste) showed the biogas yield of such material to be equal to 0.566 Nm^3/kg TS (equal to ca. 110 m^3/tFM), with an average methane share of 60% vol [36]. A previous study showed that the biogas potential of municipal biowaste in the relevant region was assessed at 116 GWh [133]. In this study the same potential was assessed at 125 GWh, which is ca. 8% higher than in the previous report.

Lignocellulosic biomass in the form of residue grass showed a relatively high potential for biogas production. For the studied case, the potential was estimated at ca. 505 GWh. In the same region, the biogas potential from lignocellulosic biomass leftovers (straw, stalk and stover) originating from agricultural production of oat, barley, triticale, soya-beans, rapeseed, maize, and wheat was assessed at ca. 2,000 GWh [133]. As presented in the results, the given region has a surplus of residue grass potential to be utilized for biogas. However, such values are probably not economically feasible, and collection would be logistically challenging [131]. For example, for the production of 903 MWh of biogas using residue grass collected in the south-west area of the case study, the estimated length of the transport route to the nearest biogas plant (no. 7) is more than 100 km. On the other hand, to replace all maize silage with residue grass in biogas plant no. 12, the estimated radius of available feedstock amounts to ca. 11 km, resulting in a maximum transportation path of ca. 14 km. The south and south-east area of the case study shows the highest potential to be considered for biogas production from residue grass. This is because that area has many water surfaces and watercourses whose banks should be maintained by mowing and collecting the grass.

The total biogas potential of biodegradable waste originating from industry was assessed at ca. 138 GWh, of which ca. 9% was from meat processing, ca. 57% from food manufacturing and ca. 34% from the beverage and drinks industry. The most common industry waste appeared to be sludge from wastewater treatment plants, with about 44% of the mass share of the total amount of industrial waste. The methane yield for sludge was assessed between 20.6 ± 5.4 and 69.3 ± 22.3 $m^3(CH_4)/tFM$. It is known that sewage sludge and sludge from industry processes are usually poor in VS content, having a long retention time, which gives them low biogas potential [82]. In the case of the food processing industry in Northern Croatia, sludge contributes only ca. 30% to the overall biogas potential. Mixed industry biowaste mainly composed of whey, fruit and vegetable waste, pomace, yeasts, etc., showed a yield of 22.0 ± 5.0 $m^3(CH_4)/tFM$. Since such material is not rich in total solids and volatile solids, the low biogas yield was expected [87]. For more details on yield of other examined industry substrates please consider Table A1, Appendix A of the article [39].

To summarize the geospatial availability of the applied method, Table 8 presents the range of radius from each biogas plant inside which there is an energy potential for the examined feedstocks equivalent to that for maize silage. Biogas plant 8* is in fact the landfill cogeneration plant. Therefore, maize silage is not considered for replacement.

Table 8 Range of radius of equivalent energy potential to replace maize silage [39]

Biogas plant no.	Radius of equivalent energy potential [km]
1	>20
2	5-10
3	15-20
4	>20
5	5-10
6	5-10
7	0
8*	N/A
9	>20
10	15-20
11	>20
12	10-15
13	5-10

The maize silage used in biogas plants no. 1, 4, 9 and 11 would be difficult to fully replace in terms of energy content by alternative feedstocks. Either the local availability of feedstocks is poor (as for biogas plants no. 1 and 9), or the installed capacity of the biogas plant is high (>2.0 MW_{el} as for no. 4 and no. 11), which requires an excessive biogas production rate. Most of the energy potential in the replacement of maize silage comes from municipal biowaste and residue grass, while only a small share of the total potential could be generated by industry streams. The geospatial analysis of biogas plant positions showed that some are ready to integrate biogas upgrading technology and produce renewable gas, since their distance to the natural gas grid is relatively low (less than 2 km). Table 9 shows the measured distance between biogas plants and the nearest natural gas pipeline.

Table 9 Distance between examined biogas plants and the natural gas grid [39]

Biogas plant no.	Distance to natural gas grid [km]
1	7.98
2	3.51
3	14.85
4	9.44
5	1.65
6	4.37
7	1.93
8*	3.62
9	3.86
10	1.91
11	4.23
12	1.06
13	14.16

The distance of existing biogas plants to natural gas grid could serve the operators of biogas plants in assessing the total investment costs of biomethane production. The distance determines the economic feasibility of whether biomethane would be injected to natural gas grid or stored on site as a compressed gas. Overall, it would determine the further utilisation of biomethane, as well as its price [37]. Biogas plants no. 5, 7, 10 and 12 (current total installed capacity of 4.0 MW_{el}) display the highest potential for connection to the natural gas grid. Based on current biogas production in those plants, it was estimated that they could inject 19 GWh of biomethane into the grid.

Based on the analysis of actual biogas plants, three scenarios, each with two cases, were selected and evaluated in LCA. Scenario I presents the feedstock transition from maize silage to residue grass and the switch from operation in cogeneration mode to biogas upgrading using Pressure Swing Adsorption (PSA) technology and biomethane production. Scenario II demonstrates the impact of P2G integration into an existing food waste-based biogas power plant. Scenario III aims to investigate the environmental performance of replacing natural gas (in pipelines) by biomethane produced from waste and residue materials in a newly established biogas plant. Overall results of environmental performance analysis of the given scenarios are shown in Figure 18: a) Global warming potential (*GWP*) and b) Single score, for the projected electricity mix.

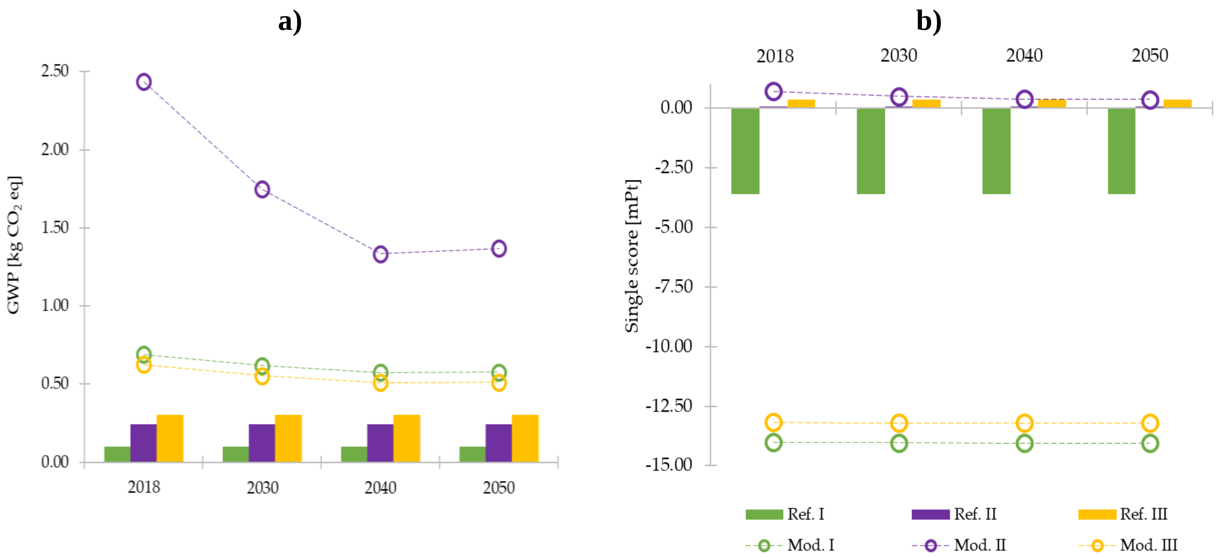


Figure 18 Lifecycle impact assessment for the functional unit of 1 m^3 of produced and utilized CH_4 for the projected electricity mix: a) *GWP* and b) Single score [39]

The comparison of LCA results for the *GWP* category showed that in all scenarios, the applied measures generated higher CO_2-eq emissions. Results for the *GWP* values for referent cases range between 0.10 and 0.30 kg CO_2-eq, while those for modified cases were between 0.51 and 2.4 kg CO_2-eq. Similar results and relations between *GWP* values (for the functional unit of 1 m^3 of biogas) were found for the comparison of biogas upgrading (1.09-1.27 kg CO_2—eq) and biogas cogeneration (0.57 kg CO_2-eq) [166]. Most emissions in the *GWP* category belong to carbon dioxide from fossil fuel combustion in the machinery and vehicles used for feedstock collection and transportation to biogas plants [34]. The referent cases were not impacted by the projected increase of RES share in the electricity mix, while in the modified cases, the *GWP* values decreased by ca. 17% in Scenario I, ca. 44% in Scenario II and ca. 18% in Scenario III in 2050, compared to the referent year. These results were expected, since all three modified cases use the electricity from the grid to produce renewable gas. In greater detail, the authors estimated that ca. 30% of the electricity demand for P2G integration in Scenario II comes from the grid [38]. However, the combination of grid assistance and installation of an electrolyser and a methanation unit [245] made Scenario II barely acceptable.

The overall results of Single score assessment showed that the measures applied to both biogas production and utilization yielded significant environmental benefits over the existing operation of biogas plants, especially in Scenarios I and III. The utilization of alternative feedstocks for biomethane resulted in a process that was ca. 36 times more environmentally improved than natural gas, and ca. 4 times better in environmental performance than biogas CHP. Results of this research can be related to a previous study (*ARTICLE 5*) by the authors in which the integration of a biogas upgrading unit into an existing biogas power plant was analysed, investigating the switch from maize silage to residue grass with the aim of mutually producing biomethane and electricity at peak power prices [37]. For that case, the thresholds for environmental benefits were determined to be -3.6 mPt and -14.0 mPt, for 1 m^3 of produced and utilized CH_4. LCA of electricity production in biogas CHP in the case of the German electricity mix, using 1 tonne of feedstock as a functional unit, gave a Single score result of -1.4 Pt for maize silage and -4.6 Pt for food residues [246]. Even though the results of this study are significantly lower (owing to another functional unit having been selected), it is interesting that the Single score results for Scenario II are higher than zero, which indicates environmental burdens greater than the generated benefits. This can be explained by the fact that the biowaste considered for biogas production has zero emissions up to the point of its creation (defined by the RED II [247]), while all other emissions and impacts on the environment come because of collecting and transporting it to the site.

2.4 Achieved scientific contributions and tested hypothesis

The scientific contributions of this doctoral dissertation were realized through the conducted research and the results of publishing in the following articles:

- By an experimental research of anaerobic digestion using novel biomass substrates the potential obstacles in biogas production like as the occurrence of an inhibition and the process stability was identified.

ARTICLE 2: It was found that lignocellulosic biomass in the form of residual grass does not contain physicochemical characteristics that would limit its use for biogas production. Moreover, it has been shown to cause improved pH control which contributes to the stability of biogas production. The disadvantage of its use is that it is necessary to apply some form of pretreatment to achieve higher yields.

ARTICLE 4: Heterogeneity of food waste affects the process and therefore it is necessary to establish a robust control of variables. It has been shown that even at the level of a biogas plant there are some variables that are not monitored on a daily basis (such as the presence of salt and metals) and can cause the inhibition of biogas production. Rendering by-products and waste in smaller quantities can contribute to increasing the rate of decomposition of food waste.

- Alternative measures for the current biogas sector will be proposed considering market prices and environmental impact analysis using Life Cycle Assessment approach.

ARTICLE 5: Alternative measures for the biogas sector in the form of biomethane production and the operation of biogas plants in the day-ahead and balancing market proved to be the most likely option after the expiry of subsidy systems for electricity generation. In such a framework, the transition from maize silage to alternative substrates will become an acceptable operational decision with additional investment in new equipment.

ARTICLE 6: The integration of variable RES into the operation of biogas plants will lead to the change of the current paradigm of biogas plants − they will no longer be just passive electricity producers but become active participants in energy markets.

ARTICLE 2: Residue grass has been shown to contribute more to ecosystem quality and human health than maize silage, although it causes higher GHG emissions, primarily due to more intensive needs for transportation still driven by fossil fuels to the biogas plant.

ARTICLE 7: LCA of the proposed measures for the biogas sector involving the replacement of maize silage with alternative biomass sources and utilisation of biogas in energy systems with a high share of RES has shown a synergistic effect in terms of reduced overall burden on the environment. The analysis also showed that the integration of P2G in the observed frameworks is still unattractive due to the complexity of the system and energy intensive processes.

- Advanced Geographical Information System model for mapping of novel biomass sources, combined with various biogas utilisation pathways integrated in high renewable energy systems under advanced energy markets, will result with robust mathematical models applicable to various biogas plant cases.

ARTICLE 6: The developed robust model of the integration of the P2G concept into the operation of a biogas plant showed a synergy between the *GF* business model and the integration of renewable electricity and heat, which were combined in the set mathematical formulation for the levelized price of renewable methane

ARTICLE 7: The proposed GIS model included the analysis of existing biogas plants and the positioning of future biomethane plants based on a geospatial analysis of available alternative substrates and the position of the gas network.

The hypothesis of the research is that applying holistic approach on biogas plants, both on the production and utilisation side, can increase economic profitability and environmental benefits over current subsidised operation. Through the conducted research, the hypothesis was tested and confirmed considering the following:

- The economic feasibility of biogas plants after exiting subsidy schemes and restrictions on the use of maize silage will be more difficult to achieve. It will include the implementation of the *GF* business model for substrates, which will require new investments in biomass pretreatment line, increase of on-site biogas storage capacity to make the plant more flexible in the electricity market and additional investments in renewable methane production system, primarily biomethane.
- The holistic approach has shown that the contribution of the future biogas sector to reducing environmental burdens will go through a double contribution: from waste management to biogas production, which will include primarily municipal and industrial biowaste in urban biogas plants, and agricultural residues in rural biogas plants, and utilization of biogas for production of renewable energy in the form of biomethane.

3 Conclusions and future work

This doctoral dissertation investigated and evaluated the position of biomass and biofuels in the energy transition, expanded with elements of environmental transition. Origin of biomass, its availability and costs are main factors in assessing biomass applicability in biofuel production. A sustainable market for biofuels contributes to the stability and expansion of the sector, the implementation of new technologies and creating feasible operation of biomass processing plants. Out of all biofuel production pathways, anaerobic digestion proved to be well-established and mature technology to produce products that can be applied for various energy and material production purposes.

As the link between the use of maize silage and electricity generation under subsidy models in biogas plants is becoming weaker, alternative biogas production and utilisation pathways were proposed in this doctoral dissertation. The holistic and comprehensive analysis demonstrated the opportunities and challenges of existing and future biogas sector. Outcomes showed that the implementation of measures would create a system far more complex than the existing one. This would include the integration of different technologies, as well as new materials and energy sources. Also, the cross-sectoral approach was presented, the implementation of new business models, focusing on the waste management systems and energy supply sectors based on the high share of renewable energy sources.

Experimental investigations showed the biogas yields of novel biomass substrates as: residue grass from landscape management − 0.192-0.275 Nm^3/kgTS; bulk food waste − 0.252-0.566 Nm^3/kgTS. Lignocellulosic biomass in the form of residue grass is a highly interesting feedstock to be utilised as a replacement to maize silage. It gains similar biodegradable properties as maize silage, which could be improved using some pretreatment methods in order to increase the rate of biomass degradation and achieve higher biogas yields. Food waste is a complex feedstock for biogas production which requires continuous monitoring of process performance. It was shown that some important process parameters such as conductivity and salt concentration are not continuously monitored in a large-scale food waste-based biogas plant. Rendering industry streams showed antagonistic effects in terms of biogas production when added to food waste by reducing the biogas yield by 12-23%. However, it was noted that their addition to food waste not only increased the reaction rate, but also improved process stability, since a narrower range of reported values was obtained between studied parallels.

The application of pyrolysis in the digestate management proved to be an interesting option from several points of view. Using the thermogravimetric analysis, it was estimated that 44-50% of hemicellulose and cellulose in residue grass was degraded under anaerobic conditions. Also, it was proved that anaerobic digestion-pyrolysis combined process contributes not only to the production of green bioenergy in the form of heat and electricity, but also to reduction of energy requirements for pyrolysis and achieving higher biochar yields.

Owing to penetration by intermittent RES like solar and wind, the prices of electricity on the day-ahead market become lower, which makes the production of heat and electricity in biogas CHP after leaving the subsidy schemes not a favourable option. Feasible operation could be achieved if biogas plant operated on market by exploiting peak power prices. However, such is limited to only short periods over the year. Replacing maize silage by low-cost residue grass and installing a biogas upgrading unit in the existing biogas plants would be a feasible operational decision, only if the price of sold biomethane was 60 €/MWh or above.

On the other hand, excess electricity from intermittent variable RES could create new possibilities for biogas plants, the most likely the integration of the power-to-gas technology. The robust optimisation of renewable methane production by methanation of biogas from food waste showed that the concept would be economically competitive with natural gas for the non-household consumers in the EU, if the gate fee for food waste became -120 €/tonne. Also, the analysis showed that such system would need the support by the electricity from the grid, on average importing 40% of the total electricity demand for the operation.

Geospatial availability of alternative feedstocks for the study case of an intensive-biogas region of Northern Croatia showed that there is enough biogas potential to replace all maize silage in current biogas production. The analysis showed that most of the examined biogas plants were well positioned for the injection of renewable gas into natural gas grid. Furthermore, the total assessed potential of biomethane from newly planned biogas plants is ca. 191 GWh, out of which the plants located nearby to the source of biodegradable industry waste would produce ca. 58% of its quantity. Environmental impact analysis of actual biogas plants showed that an integral approach to both biogas production and utilisation creates synergistic effects in terms of reduced environmental burdens. Feedstock transition and production of renewable gas in the form of biomethane showed reduced environmental burdens by 4 and 36 times compared to current operation using maize silage.

Alternative biogas utilisation pathways proposed in this dissertation showed that biogas plants could achieve feasible operation by implementing proposed measures, compared to continuing the operation on day-ahead electricity market after exiting subsidy schemes. For that, additional investments in biogas plant will be required. From an economic point of view, alternative utilisation pathways for biogas in the current market features could not create renewable gas which could be in price competitive to natural gas. However, biomethane production has significantly lower environmental burdens than natural gas. The main concern about biomethane sustainability is the transportation of studied feedstocks using fossil fuels, which results in intensive carbon footprint. The projected rise in fossil fuel prices in the near future and higher requirements for sustainable biowaste management will create market conditions in which biogas will be more competitive to natural gas. Also, the author of this dissertation believes that in the near future the term “biogas plant” would be replaced by term “biorefinery”, indicating that biogas would not be considered as the only valuable product, but rather one intermediate component to create value-added materials for various industries. Such will open space for new studies and projects, creating a scientific gap ready to be fulfilled by some other doctoral researcher.

Complex relationships between stakeholders and social component of biogas technology were not addressed in this doctoral thesis. Therefore, a continuation work in this area needs to be oriented towards engaging important stakeholders of the existing and future biogas sector to the presented concept with aim to cluster all key variables from technical, financial, and social aspects. That would include setting-up a dialogue and information exchange with biogas plant owners, feedstock producers, farmers, industry plants, waste management companies, natural gas grid operators, regulators, local, regional, and national policy and decision makers. All that in the service of keeping biogas technologies as important factor in energy and environmental transitions.

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5 Curriculum vitae

ROBERT BEDOIĆ, mag.ing.cheming. was born on the 27th March 1995 in Zagreb, Croatia. In 2013 he finished Vladimir Prelog Science School in Zagreb and started the Bachelor's course in Chemical Engineering (technical area) on the Faculty of Chemical Engineering and Technology at University of Zagreb (UNIZAG FKIT). He completed the course in 2016 and in the same year enrolled in the Master's course *Chemical Engineering*, which he finished with Cum Laude honour in 2018. From 2018 he has been employed at the Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb (UNIZAG FSB) as Project Assistant and PhD Student. The projects he has worked on mainly fall in the interdisciplinary field of chemical and mechanical engineering, with several successfully completed universities-industry collaborations. During the doctoral study he received an *Outstanding doctoral student award* at UNIZAG FSB for publishing the highest number of research articles in 2019.

He is an author and co-author of 23 scientific papers, of which 8 are articles in CC/SCI journals. His current Scopus h-index is 6. He acts as a reviewer for *Renewable and Sustainable Energy Reviews*, *Renewable Energy*, *Energy*, *Energy Conversion and Management*, *Journal of Cleaner Production*, *Journal of Environmental Management*, *Fuel*, *Bioresource Technology*, *Biomass Conversion and Biorefinery*, *Waste Management*, *Water Research*, and *Journal of Sustainable Development of Energy, Water and Environment Systems*. Since 2019 he has been involved in the organization of several SDEWES conferences.

At the moment of defending the doctoral dissertation Robert works as a Process and Technology Engineer at SAPP Management AG in Austria.

List of published scientific articles in journals:

- Bedoić, R.; Ćosić, B.; Duić, N. Technical potential and geographic distribution of agricultural residues, co-products and by-products in the European Union. *Sci. Total Environ.* **2019**, *686*, 568–579, doi:10.1016/j.scitotenv.2019.05.219.
- Bedoić, R.; Čuček, L.; Ćosić, B.; Krajnc, D.; Smoljanić, G.; Kravanja, Z.; Ljubas, D.; Pukšec, T.; Duić, N. Green biomass to biogas – A study on anaerobic digestion of residue grass. *J. Clean. Prod.* **2019**, *213*, 700–709, doi:10.1016/j.jclepro.2018.12.224.

- Bedoić, R.; Bulatović, V.O.; Čuček, L.; Ćosić, B.; Špehar, A.; Pukšec, T.; Duić, N. A kinetic study of roadside grass pyrolysis and digestate from anaerobic mono-digestion. *Bioresour. Technol.* **2019**, *292*, doi:10.1016/j.biortech.2019.121935.
- Bedoić, R.; Špehar, A.; Puljko, J.; Čuček, L.; Ćosić, B.; Pukšec, T.; Duić, N. Opportunities and challenges: Experimental and kinetic analysis of anaerobic co-digestion of food waste and rendering industry streams for biogas production. *Renew. Sustain. Energy Rev.* **2020**, *130*, doi:10.1016/j.rser.2020.109951.
- Bedoić, R.; Jurić, F.; Ćosić, B.; Pukšec, T.; Čuček, L.; Duić, N. Beyond energy crops and subsidised electricity – A study on sustainable biogas production and utilisation in advanced energy markets. *Energy* **2020**, *201*, doi:10.1016/j.energy.2020.117651.
- Bedoić, R.; Dorotić, H.; Schneider, D.R.; Čuček, L.; Ćosić, B.; Pukšec, T.; Duić, N. Synergy between feedstock gate fee and power-to-gas: An energy and economic analysis of renewable methane production in a biogas plant. *Renew. Energy* **2021**, *173*, 12–23, doi:10.1016/j.renene.2021.03.124.
- Bedoić, R.; Smoljanić, G.; Pukšec, T.; Čuček, L.; Ljubas, D.; Duić, N. Geospatial Analysis and Environmental Impact Assessment of a Holistic and Interdisciplinary Approach to the Biogas Sector. *Energies* **2021**, *14*, doi:10.3390/en14175374.
- Petrovič, A.; Vohl, S.; Cenčič Predikaka, T.; Bedoić, R.; Simonič, M.; Ban, I.; Čuček, L. Pyrolysis of solid digestate from sewage sludge and lignocellulosic biomass: kinetic and thermodynamic analysis, characterization of biochar. *Sustainability* **2021**, *13*, doi:10.3390/su13179642.

6 Summary of articles

ARTICLE 1**:** Bedoić, R.; Ćosić, B.; Duić, N. Technical potential and geographic distribution of agricultural residues, co-products and by-products in the European Union. *Sci. Total Environ.* **2019**, *686*, 568–579, doi:10.1016/j.scitotenv.2019.05.219.

Value waste chain generates a significant amount of different agricultural wastes, co-products and by-products (AWCB) that occur during three major stages of a complex path, from farm to fork. This article presents stages where and how waste occurs along the path from the ground to the table for a period of 7 years, from 2010 to 2016 in the 28 member countries of the European Union (EU28). Considering the specific conditions of the EU28 community, four different sectors with 26 commodities and waste types that occur in those sectors were analysed: 5 commodities in the Fruit sector, 10 commodities in the Vegetable sector, 7 commodities in the Cereal sector and 4 commodities in the Animal sector. The analysis consists of three stages of waste appearance: production (harvesting, farming), processing and consumption (raw, uncooked food). Production data were taken from Eurostat, import and export data were taken from FAOSTAT. Methodology and calculations consist of relations between specific values. Those specific values for every commodity are the production data, import and export data, and consumption of raw food by the inhabitants of a country. Total consumption of raw food by inhabitant is calculated from the specific consumption per capita and population. The results of the study showed that from 2010 to 2016 in the EU28 the estimated quantity of the AWCB appeared to be around 18.4 billion tonnes, with the sector percentages as follows: Animal ~31%, Vegetable ~44%, Cereal ~22% and Fruit ~2%. In the Animal sector, the most dominant were developed countries, with high population density and high level of industrialisation. The Cereal, Fruit and Vegetable sectors have shown to generate higher AWCB quantities in the countries with more available land area and appropriate climate conditions.

In *ARTICLE 1* Robert Bedoić was responsible for conceptualization, methodology, writing of original draft, editing of revised manuscript and visualization. Mr. Boris Ćosić contributed also for methodology and was responsible for funding acquisition. Professor Neven Duić supervised the research, reviewed and edited the revised manuscript.

***ARTICLE 2*:** Bedoić, R.; Čuček, L.; Ćosić, B.; Krajnc, D.; Smoljanić, G.; Kravanja, Z.; Ljubas, D.; Pukšec, T.; Duić, N. Green biomass to biogas – A study on anaerobic digestion of residue grass. *J. Clean. Prod.* **2019**, *213*, 700–709, doi:10.1016/j.jclepro.2018.12.224.

Sustainable management in the biogas production via anaerobic digestion process intents the use of alternative biomass sources that are not competitive with food production. The aim of this study is to investigate the application of the abundant-quantity residue in more sustainable production of heat and electricity along with the production of the digested substrate as a fertiliser. The study has been divided into several sequential steps. First, the grass samples have been collected at the following locations: uncultivated land, river embankment and highway verge. The greatest grass yield has been determined for the riverbank grass, with an average value of 19 t/ha of fresh mass and 2.6 t/ha of dry mass. Next, the chemical characterisation of the collected residue grass and the laboratory batch mono and co-digestion tests with maize silage and cattle slurry have been conducted. The results show that all grass samples have satisfying digestive parameters (C/N ratio between 16.6:1 to 22.8:1) with the low presence of impurities, which makes them suitable for biogas production. The following biochemical methane potential in mono-digestion of residue grass has been recorded: uncultivated land (0.275 Nm^3/kgTS), riverbank (0.192 Nm^3/kgTS) and highway verge (0.255 Nm^3/kgTS). The control of the process has been improved in co-digestion tests, by avoiding acidification in the first days of the operation. The estimation of kinetic parameters in mathematical modelling has shown that the degradation of residue grass shows some different parameters compared to the previous study. The model results for the gas phase show some small deviations compared to the experimental data. Based on the life cycle analysis results it can be concluded that there are perspectives in the use of residual grass compared to maize silage in the production of heat and electricity, especially in the improvement of ecosystem quality.

In *ARTICLE 2* Robert Bedoić was responsible for conceptualization, methodology, software, conducting experimental investigation, writing of original draft, editing of revised manuscript and visualization. Associate Professor Lidija Čuček, Mr. Boris Ćosić, Mr. Damjan Krajnc, PhD contributed to the study by conducting experimental investigation. Mr. Goran Smoljanić and Professor Davor Ljubas gave their contribution by conducting LCA. Professor Zdravko Kravanja, Assistant Professor Tomislav Pukšec, and Professor Neven Duić supervised the research, reviewed and edited the revised manuscript. Mr. Boris Ćosić was also responsible for funding acquisition.

ARTICLE 3**:** Bedoić, R.; Bulatović, V.O.; Čuček, L.; Ćosić, B.; Špehar, A.; Pukšec, T.; Duić, N. A kinetic study of roadside grass pyrolysis and digestate from anaerobic mono-digestion. *Bioresour. Technol.* **2019**, *292,* doi:10.1016/j.biortech.2019.121935.

The aim of this research is to evaluate the thermogravimetric behaviour of roadside grass and its digestate obtained from mesophilic anaerobic mono-digestion by quantifying its impacts on biomass composition and properties. Thermogravimetric measurements were conducted in a laboratory furnace under nitrogen flowrate of 100 mL/min in the temperature range from 35 to 800 °C at five different heating rates of 2.5, 5, 10, 15 and 20 °C/ min. Friedman and Kissinger-Akahira-Sunose differential and integral isoconversional models were applied to determine the distributions of activation energies and modified pre-exponential factors per reacted mass (degree of conversion). The investigation demonstrated that anaerobic digestion of roadside grass can be used to generate biochar-richer material (with significantly greater yield of final residues after pyrolysis) with less energy required for subsequent pyrolysis in comparison with raw roadside grass.

In *ARTICLE 3* Robert Bedoić was responsible for conceptualization, methodology, writing of original draft, editing of revised manuscript and visualization. Assistant Professor Vesna Ocelić Bulatović and Ms. Ana Špehar contributed to the research by conducting experimental investigation. Associate Professor Lidija Čuček, Mr. Boris Ćosić, Assistant Professor Tomislav Pukšec, and Professor Neven Duić supervised the research, reviewed and edited the revised manuscript and were responsible for funding acquisition.

ARTICLE 4**:** Bedoić, R.; Špehar, A.; Puljko, J.; Čuček, L.; Ćosić, B.; Pukšec, T.; Duić, N. Opportunities and challenges: Experimental and kinetic analysis of anaerobic co-digestion of food waste and rendering industry streams for biogas production. *Renew. Sustain. Energy Rev.* **2020**, *130*, doi:10.1016/j.rser.2020.109951.

Large amounts of food waste and sewage sludge exert a hazardous environmental impact in several countries. Producing biogas and digestate from food and industrial waste is one of the solutions for waste management, stabilization of sludge, resource and energy recovery and reductions in the amount of waste. However, biogas production from such substrates has challenges in degradation efficiency, inhibitory effects and other challenges, and thus co-digestion and pretreatment techniques could be applied to enhance biogas production. The aim of this study is to explore the effects of co-digestion of food waste, meat and bone meal and rendering wastewater sludge. First, thermal pretreatment was performed (35 °C, 5 days) by adding the rendering-industry streams to food waste in the amounts of 0, 5, 10 and 15% on a total solid basis, and further anaerobic digestion (40.5 °C, ca. 40 days) was then performed. Both experimental and kinetic analysis were conducted, and the major factors regarding opportunities and challenges in the two-stage process are discussed. Results have shown that both cosubstrates from rendering industry decreased the biogas yield of food waste. When 5% of them was added to food waste, meat and bone meal decreased biogas production by 12%, and wastewater sludge decreased it by 23%. Both co-substrates, on the other side, increased the rate of reaction of food waste digestion when applying different common kinetic models.

In *ARTICLE 4* Robert Bedoić was responsible for conceptualization, methodology, writing of original draft, editing of revised manuscript and visualization. Ms. Ana Špehar and Mr. Josip Puljko provided materials and measuring equipment for the experimental investigation. Associate Professor Lidija Čuček, Mr. Boris Ćosić, Assistant Professor Tomislav Pukšec, and Professor Neven Duić supervised the research, reviewed and edited the revised manuscript and were responsible for funding acquisition.

ARTICLE 5**:** Bedoić, R.; Jurić, F.; Ćosić, B.; Pukšec, T.; Čuček, L.; Duić, N. Beyond energy crops and subsidised electricity – A study on sustainable biogas production and utilisation in advanced energy markets. *Energy* **2020**, *201*, doi:10.1016/j.energy.2020.117651.

The aim of this study is to investigate the operation of biogas plants in advanced energy markets after energy crops become limited in their use and biogas plants exit subsidy schemes for electricity production. Continuous biogas combined heat and power production and sale of electricity on the day ahead market could be a feasible operation strategy only in the case of low-cost substrates. When the break-even cost of electricity production in biogas power plants reaches 100 €/MWhel, selling electricity on the day-ahead market does not create profit. The study shown that a more profitable operation strategy involves coupling biogas power plant operation on the electricity balancing market with biomethane production or combining a small-scale sugar beet processing facility with a biogas upgrading plant to cover heat demand for sugar beet processing. Techno-economic analysis showed that the viability of both alternative operation strategies is severely impacted by the selling price of biomethane. In the given market conditions, a selling price of biomethane below 50 €/MWh is not feasible for a biogas plant. The model developed could be used as a guideline for biogas plant operators on how to proceed after significant changes appear in both biogas production and biogas utilisation.

In *ARTICLE 5* Robert Bedoić was responsible for conceptualization, methodology, writing of original draft, review and editing of revised manuscript and visualization. Mr. Filip Jurić was in charge of software. Mr. Boris Ćosić, Assistant Professor Tomislav Pukšec, Associate Professor Lidija Čuček and Professor Neven Duić were responsible for supervising the research, reviewing, and editing of revised manuscript and funding acquisition.

***ARTICLE 6*:** Bedoić, R.; Dorotić, H.; Schneider, D.R.; Čuček, L.; Ćosić, B.; Pukšec, T.; Duić, N. Synergy between feedstock gate fee and power-to-gas: An energy and economic analysis of renewable methane production in a biogas plant. *Renew. Energy* **2021**, *173,* 12–23, doi:10.1016/j.renene.2021.03.124.

Biogas is an instrument of synergy between responsible waste management and renewable energy production in the overall transition to sustainability. The aim of this research is to assess the integration of the power-to-gas concept into a food waste-based biogas plant with the goal to produce renewable methane. A robust optimisation was studied, using linear programming with the objective of minimising total costs, while considering the market price of electricity. The mathematical model was tested at an existing biogas power plant with the installed capacity of 1 MW_{el}. It was determined that the integration of power-to-gas in this biogas plant requires the installation of ca. 18 MW_{el} of wind and 9 MW_{el} of photovoltaics, while importing an additional ca. 16 GWh_{el} from the grid to produce 36 GWh of renewable methane. The economic analysis showed that the feedstock gate fee contributes significantly to the economic viability of renewable methane: a change in the feedstock gate fee by 100 €/tonne results in a decrease of production costs by ca. 20-60%. The robust nature of the model showed that uncertainties related to electricity production from wind and photovoltaics at the location increased the cost of gas production by ca. 10-30%.

In *ARTICLE 6* Robert Bedoić was responsible for conceptualization, methodology, writing of original draft, editing of revised manuscript and visualization. Mr. Hrvoje Dorotić gave his contribution on software. Professor Daniel Rolph Schneider, Associate Professor Lidija Čuček, Mr. Boris Ćosić, Assistant Professor Tomislav Pukšec and Professor Neven Duić had their hands on supervising the research, review and editing of revised manuscript and funding acquisition.

ARTICLE 7**:** Bedoić, R.; Smoljanić, G.; Pukšec, T.; Čuček, L.; Ljubas, D.; Duić, N. Geospatial Analysis and Environmental Impact Assessment of a Holistic and Interdisciplinary Approach to the Biogas Sector. *Energies* **2021**, *14,* doi:10.3390/en14175374.

Energy crop-based biogas production in combination with electricity generation under subsidy schemes is no longer considered a favourable business model for biogas plants. Switching to low-cost or gate fee feedstocks and utilising biogas via alternative pathways could contribute to making existing plants fit for future operations and could open up new space for further expansion of the biogas sector. The aim of this study is to combine a holistic and interdisciplinary approach on both the biogas production side and the utilisation side to evaluate the impact of integrating the biogas sector with waste management systems and energy systems operating with a high share of renewable energy sources. The geospatial availability of residue materials from agriculture, industry and municipalities was assessed using QGIS software for the case of Northern Croatia with the goal of replacing maize silage in the operation of existing biogas plants. Furthermore, the analysis included positioning new biogas plants which would produce renewable gas. The overall approach was evaluated through Life Cycle Assessment using SimaPro software to quantify the environmental benefits and identify bottlenecks of the implemented actions. Results showed that the given feedstocks could replace 212 GWh of biogas from maize silage in the relevant region and create an additional 191 GWh of biomethane in new plants. LCA revealed that the proposed measures would contribute to the decarbonization of natural gas by creating environmental benefits 36 times greater compared to a business-as-usual concept. The presented approach could be of interest to stakeholders in the biogas sector anywhere in world to encourage further integration of biogas technologies into energy and environmental transitions.

In *ARTICLE 7* Robert Bedoić, as the main author, was responsible for conceptualizing the research, conducting the investigation, collecting data, setting up the methodology, mapping biomass sources by QGIS, visualizing the results and writing the original draft. Mr. Goran Smoljanić and Professor Davor Ljubas contributed to the research by performing LCA. Assistant Professor Tomislav Pukšec and Associate Professor Lidija Čuček were responsible for supervising the research progress and administrating the project. Professor Neven Duić was in charge of providing resources and funding acquisition.

ARTICLE 1

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Technical potential and geographic distribution of agricultural residues, co-products and by-products in the European Union

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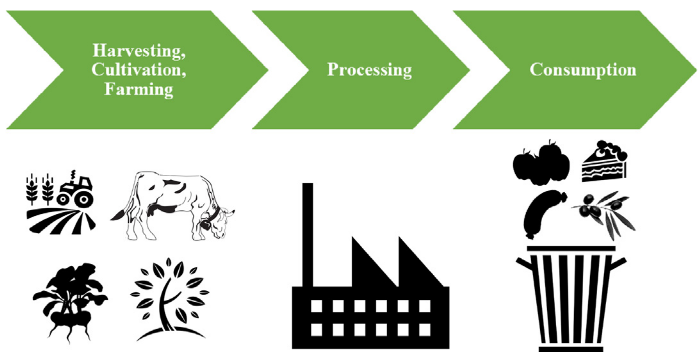
HIGHLIGHTS

- The agricultural waste, co-products and by-products potential of EU28 is analysed.
- 26 commodities from Fruit, Vegetable, Cereal and Animal sector are analysed.
- A mass ratio of the main AWCB to product ratio is presented.
- Geographically distributed AWCB potential is presented.

GRAPHICAL ABSTRACT



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ABSTRACT

Value waste chain generates a significant amount of different agricultural wastes, co-products and by-products (AWCB) that occur during three major stages of a complex path, from farm to fork. This paper presents stages where and how waste occurs along the path from the ground to the table for a period of 7 years, from 2010 to 2016 in the 28 member countries of the European Union (EU28). Considering the specific conditions of the EU28 community, four different sectors with 26 commodities and waste types that occur in those sectors were analysed: 5 commodities in the Fruit sector, 10 commodities in the Vegetable sector, 7 commodities in the Cereal sector and 4 commodities in the Animal sector. The analysis consists of three stages of waste appearance: production (harvesting, farming), processing and consumption (raw, uncooked food). Production data were taken from Eurostat, import and export data were taken from FAOSTAT. Methodology and calculations consist of relations between specific values. Those specific values for every commodity are the production data, import and export data, and consumption of raw food by the inhabitants of a country. Total consumption of raw food by inhabitant is calculated from the specific consumption per capita and population. The results of the study showed that from 2010 to 2016 in the EU28 the estimated quantity of the AWCB appeared to be around 18.4 billion tonnes, with the sector percentages as follows: Animal ~31%, Vegetable ~44%, Cereal ~22% and Fruit ~2%. In the Animal sector, the most dominant were developed countries, with high population density and high level of industrialisation. The Cereal, Fruit and Vegetable sectors have shown to generate higher AWCB quantities in the countries with more available land area and appropriate climate conditions.

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1. Introduction

The EU28 community presents a group of countries sharing the unique market of goods in Europe (European Union, 2018). Favourable climate conditions of some European countries and available land area lead to possibilities of high production of vegetables, fruits and cereals. Furthermore, the countries that are able to produce food for people and animals also focus on farming with the aim to produce meat, meat products and dairy products (Andersen, 2017). With a population of approximately 511.8 million (3/4 living in the cities and towns), the EU28 shows reputable status in the world economy and politics (Eurostat, 2019a). Agricultural production in the European Union is spread over a large area and includes diverse types of climate. Also, it is the main component of the primary sector in all Member States. Around 10 million people in the EU28 work in the agriculture sector. Almost 3/4 of the total agricultural workers are present in the countries in which the economy and politics provide good living standard and development opportunities (Eurostat, 2015).

According to the research (Esparcia, 2014), most of the waste comes from the construction sector (33.5%) and the mining and quarrying sector (29.8%) while households take up to 8% of the total waste production. Agriculture, forestry and fishing are at the bottom of the list with 1.4% of the total waste production. Authors in (Corrado et al., 2019) have estimated that the 1/3 of the food produced globally is wasted along the food chain. An important factor that was addressed in the study is the broad understanding of the context in which food waste is generated. For instance, marital status and education have a high impact on the quantity of wasted food. The analysis of food waste/losses in the supply chain models has been studied in (Muriana, 2017). The results have indicated that legal constraints, political decisions, climatic and economic factors play an important role in the minimisation and the reduction of food waste/losses. The study (Porter et al., 2016) has shown the 50-year longitude analysis (1961–2011) of food loss and waste (FLW) and the associated greenhouse gas (GHG) emissions through the entire food supply chain. The results have shown that developing economies cause an increase in food/waste losses, primarily due to increasing losses in fruits and vegetables. Authors in (Feil et al., 2017) have studied separate collection systems of plastic waste from municipal solid waste at the level of the European Union. Even though politically preferred solutions in sustainable waste management require separate collection systems, economic factors indicate that plastic recycling will hardly ever reach cost neutrality. However, the other fraction of municipal solid waste − the organic material - could be used for the production of renewable energy in the form of biogas (Mondal and Banerjee, 2015). It has been shown that pre-treatment methods increase the potential of waste used in the biogas production, and in that way reduce the negative impact of disposing waste on landfills. Furthermore, the application of vegetable and animal waste together with fractions of municipal solid waste in the anaerobic digestion, gasification and incineration has been studied in (Massimo and Montorsi, 2018). The numerical tool developed in the study proved to be helpful in improving the efficiency in the exploitation of the region-available biomass for energy recovery purposes.

Agricultural Waste, Co-products and By-products (AWCB) could have a significant role in the world's production of animal feed. In (San Martin et al., 2016) authors have reported that vegetable by-products can be potentially served as animal feed since their nutrition and sanitary properties and the report (Sortino et al., 2014) showed that municipal bio-waste could replace synthetic chemicals for the remediation of contaminated soil and waters. Furthermore, the production of medicine and high-value-added chemicals from the mixture of potato and orange peel waste has shown potential due to high protein content in the aforementioned feedstock (Matharu et al., 2016). At the same time, orange peel could be used in the production of bioelectricity via microbial fuel cell technology (Miran et al., 2016). Biomass residues have shown an important role in the production of bioenergy in the European Union (Ajanovic and Haas, 2014). The use of residue biomass improves the CO_2 balance, but resource availability, economy and policy on their utilisation have a high impact on the technical and economic potential of residue biomass. Authors in (Pereira et al., 2016) showed that the use of poplar biomass as an alternative feedstock to coal in power plants in Southern Portugal could reduce CO_2 emissions between 8.2% and 16.5%. In (Bentsen et al., 2018) authors determined that the geographical analysis of the straw used for energy purposes is highly influenced by weather conditions. Furthermore, the biomass potential from forest and agricultural residues are strongly related to the location and ecosystem services (Ooba et al., 2016) as well as on logistical, chemical, technological, economic and social issues (Scarlat et al., 2010). When considering agricultural biomass residues as a source of energy, it is important to valorise material properties (Mikulandrić et al., 2016). Authors in (Spaccini et al., 2019) have shown that biological properties and pre-known molecule structure of composted material from lignocellulose waste make a good basis for the selection of derivatives from composted materials to provide sustainable agricultural practice. In (Boeykens et al., 2018) authors have shown that agro-industrial waste could be used as a biosorbent for removal of lead and chromium as a low-cost alternative method for treating effluents. The utilisation of the olive mill wastewater (primarily carbon content) for the synthesis of luminescent nanomaterials that can be used in biological processes has been analysed in (Sousa et al., 2019). Except for the biomass residues, a high quantity of plastic waste is generated as a product of the agricultural activities, and if the plastic waste is correctly collected instead left on the ground or burned, environmental damage and economic losses can be prevented (Vox et al., 2016).

The quantities of AWCB have been estimated for 26 different commodities, previously selected according to the rate of use in each EU28 country from 2010 to 2016. The waste value chain has been divided into three characteristic groups according to the point where it occurs; harvesting and cultivation, processing and consumption. Eurostat and FAOSTAT databases have been used for the analyses, as explained in the following section, where the applied materials and methods have been described. Estimate of the generated AWCB has been based on the specific relation of the generated AWCB per kg of the commodity in each group. The result of this study gives an overview of the distribution of the technical potential of AWCB across the countries of the European Union. The interpretation of the estimated quantities of AWCB is further linked to the socioeconomic and physical factors like level of development, population density, climate conditions and available land area.

2. Materials & methods

This section gives an overview of the applied methods in calculating the AWCB quantity, made by using relations between the analysed commodity and the specific AWCB production. Key parameters for estimating the quantity of the AWCB were: produced commodity, exported and imported commodity and consumed commodity, each of them for a specific EU28 country. Consumed quantities of the commodity were calculated considering the specific consumption of a commodity per capita and year. The key assumption was that the quantity of the consumed commodity does not change over a given period. When there were two or more different values of consumption, the average value was used for calculation. The AWCB value chain was assumed to consist of the following stages: harvesting and cultivation, processing and consumption.

The notation of specific values needed for the calculation of commodity and their relations is shown below. For a country (n), notations for commodities (i) from the Fruit sector, Vegetable sector and Cereal sector were given by the Expressions (I) and (II):

$$PRC_{(i)} = \left[PRD_{(i)} + IMP_{(i)}\right] - \left[CON_{(i)} + EXP_{(i)}\right] \quad \text{(I)}$$

$$\mathrm{CON}_{(i)} = \mathrm{POP}_{(i)} \times \mathrm{PC}_{(i)} \tag{II}$$

where:

$$PRD = \text{Production of commodity (tonnes)} \tag{1}$$

$$CON = \text{Consumption of raw commodity (tonnes)} \tag{2}$$

$$IMP = \text{Imported quantity of commodity (tonnes)} \tag{3}$$

$$EXP = \text{Exported quantity of commodity (tonnes)} \tag{4}$$

$$PRC = \text{Quantity of processed commodity (tonnes)} \tag{5}$$

$$PC = \text{Consumption of commodity per capita per year (kg)} \tag{6}$$

Additionally, in the Animal sector methodology differs compared to the previous sectors. Waste value chain covers the process of breeding of animals (farming), slaughtering and consumption of meat and meat products.

Expression (III) shows the relation between values in the Animal sector:

$$\mathrm{MAN}_{(i)} = \mathrm{SPECMAN}_{(i)} \cdot \mathrm{FARM}_{(i)} \tag{III}$$

where:

$$FARM = \text{Number of farmed animals (heads)} \tag{7}$$

$$SPECMAN = \text{Manure production per animal in a year (tonnes)} \tag{8}$$

$$MAN = \text{Total manure production in a year (tonnes)} \tag{9}$$

3. Case study

In this paper, the applied methodology refers to the EU28 countries. The analyses were conducted for the period from 2010 to 2016. The data for a produced commodity were taken from the Eurostat (Eurostat, 2019b), and the data for imported and exported quantities of commodities were taken from the FAOSTAT (FAO, 2019). The population of the EU28 Member States (2010–2016) was taken from the Eurostat (Eurostat, 2019c). Consumption per capita of fresh (raw) or processed food on a national level was given in the reports of the AgroCycle project (Ćosić et al., 2018).

3.1. Commodities in the EU28

In order to select the most important commodities for analysis on the EU28 level, the FAOSTAT data of top commodities by quantity in 2016 were used (FAOSTAT, 2019). Top commodities in the EU28 community were cow milk, sugar beet and cereals. Also, some commodities were related to the geographical position of the country. Variety in size and population of countries along with a variety of top commodities together result in a variety of type and quantities of the AWCB throughout the EU28.

3.2. Commodity sectors and characteristic of AWCB

There were four analysed commodity sectors: Fruit, Vegetable, Cereal and Animal. The animal AWCB required a slightly different approach in calculation compared to the methodology shown. As it follows, a different notation was used. Stages in the animal AWCB value chain were farming, slaughtering and processing, and consumption. In the next section, characteristic of AWCBs for every commodity from every sector and for every step are briefly described.

3.2.1. Fruit sector

The Fruit sector consists of the following commodities: apples, grapes, oranges, peaches and tangerines. During the cultivation and harvesting, a certain amount of fruit is eaten or destroyed by animals (birds, rabbits, deer, wasps), or due to bad weather conditions and cannot be used as food. Furthermore, different diseases harm fruit products, stalks and trees, which can result either in lower income from the sale of fruit or in total devastation of the plant. Fruit intended for processing can result in different products depending on the type and purpose of the process. All analysed fruits can be used in the preparation of juice, whether concentrated or not. Furthermore, apples can be used for vinegar production (Viana et al., 2017), such as grapes. Citrus fruits are commonly used for food additives production, such as aroma (Madrera et al., 2015). Table 1 contains a mass ratio of the main AWCB to product ratio for the Fruit sector. The main fruit AWCB in the harvesting and cultivation step are pruning residues and leaves. The literature data estimate that citrus fruits have lower values of prunes compared to the grape. Also, many different AWCB appear in the processing step, mainly pomace and marc waste remained after pressing raw fruit.

AWCB that occur along the supply chain from the ground to table can be valorised in different ways. Peach stone has been investigated as an adsorption material for contaminants in aqueous solution (Torrellas et al., 2015). Citrus peel waste has been studied as a feedstock for anaerobic digestion and further production of biochar (Fagbohungbe et al., 2016). Sugars present in grape stalks have shown to be interesting substrates for the fermentation process and the production of bioethanol (Egüés et al., 2013). After the fermentation of apple pomace, the remaining material can be used as a feed additive in the animal breeding (Ajila et al., 2015). In the last step of the waste value chain, the estimated quantity of rotten fruits takes up to 20% of the total fruit intended for consumption (Parfitt et al., 2010). The quantity of processed fruits is calculated for every country in each given year, using expressions (I-II). An example of the calculation of the apple AWCB quantities for Germany in 2016 is given below:

PRD = 1,032,910 t
IMP = 610,955 t
EXP = 88,972 t
CON = 1,314,914 t
PRC = (1,032,910   610,955) − (88,972   1,308,938) = 239,979 t

The quantity of pruning residues is 0.10 kg per kg of harvested apples: for Germany, it was 103,291 t in 2016. Apple pomace that occurs in processing step takes 0.25 kg per kg of processed apples: for Germany, the quantity of apple pomace was 59,995 t in 2016. The quantity of the consumed apples in Germany was 1,314,914 t, and 210,386 t of apples in Germany in 2016 went mouldy (spoiled, rotten).

3.2.2. Vegetable sector

As for the Vegetable sector, the following commodities were analysed: tomatoes, cabbages, cauliflowers and broccoli, onions, carrots, potatoes, sunflower seeds, rapeseed, sugar beet and olives. Vegetables are mainly used as food for people or animals. Also, like fruits, different diseases that decrease the income and quality of the products impact vegetables. Vegetables are also used as an initial source in the production of different products and semi-products (sauces, preserved and frozen products). Table 2 contains a mass ratio of the main AWCB to product ratio for the Vegetable sector. Many different AWCB occur during the harvesting and cultivation stage. Due to the diversity of commodities that are included in the Vegetable sector, some of the AWCB primarily appear during the cultivation stage (twigs, leaves and woody branches from olives or sugar beet leaves and stones) and some during the harvesting period (damaged vegetables).

AWCB that occur along the supply chain from the ground to table can be valorised in different ways. Olive leaves have shown to be a natural source of antioxidants and sugars (Romero-García et al., 2016). With different way of processing for a certain type of vegetable, different AWCB are pomace, wastewater, skin, wash water, meal. Tomato

Table 1
Main AWCB produced from the Fruit sector.

Commodity/Fruit	Harvesting/Cultivation ratio	Source
Apple	Pruning residues and leaves to product ratio – 0.10 kg/kg	(Pellizzi, 1985)
Grape	Stalks to product ratio – 0.055 kg/kg Pruning residues and leaves to product ratio – 0.30 kg/kg	(Bacic, 2003)
Orange	Pruning residues and leaves to product ratio – 0.085 kg/kg	(Velázquez-Martí et al., 2013)
Peach	Pruning residues and leaves to product ratio – 0.12 kg/kg	(Extension, 2017)
Tangerine	Pruning residues and leaves to product ratio – 0.065 kg /kg	(Extension, 2017)

Commodity/Fruit	Processing ratio	Source
Apple	Pomace (peel, core, seed, calyx, stem) to product ratio – 0.25 kg/kg Sludge to product ratio – 0.10 kg/kg	(Dhillon et al., 2013)
Grape	Marc waste (skin, pulp, seed and stems) to product ratio – 0.22 kg/kg CO_2 to product ratio – 0.07 kg/kg Lees to product ratio – 0.03 kg/kg	(Bacic, 2003)
Orange	Orange pomace to product ratio – 0.37 ÷ 0.60 kg/kg	(Saravacos and Kostaropoulos, 2002), (Bates et al., 2001), (Goodrich and Braddock, 2006), (Siles et al., 2016)
	Orange processing water to product ratio – 4.4 ÷ 38.2 L/kg	(Bharati et al., 2017)
Peach	Processing water to product ratio – 16.4 ÷ 21.8 L/kg	(Bharati et al., 2017)
	Peach stone to product ratio – 0.10 ÷ 0.27kg/kg	(Loizzo et al., 2015), (Folinas et al., 2015), (Ordoudi et al., 2018)
	Peach pomace to product ratio – 0.30 kg/kg	(Loizzo et al., 2015)
Tangerine	Tangerine pomace to product ratio – 0.20 ÷ 0.30 kg/kg	(Nitayapat et al., 2015), (Hwang et al., 2017)
	Tangerine processing water to product ratio – 4.4 ÷ 38.2 L/kg	(Bharati et al., 2017)

Commodity/Fruit	Consumption ratio	Source
Apple	Rotten apples to product ratio – 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Grape	Rotten grapes to product ratio – 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Orange	Rotten oranges to product ratio – 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Peach	Rotten peaches to product ratio – 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
	Peach stone to product ratio – 0.10 ÷ 0.27 kg/kg	(Ordoudi et al., 2018)
Tangerine	Rotten tangerines to product ratio – 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)

processing waste has shown to be the source of lycopene (Poojary and Passamonti, 2015). Furthermore, onion skin has been recognised as a source of biosugars and quercetin (Choi et al., 2015). In the consumption stage, the estimated percentage of rotten vegetables matches the one in the fruit consumption stage. It has been shown that vegetable waste can be utilised for the synthesis of silver nanoparticles with antibacterial activity (Mythili et al., 2018). For non-edible vegetables, there is no data in the consumption stage. The quantity of processed vegetable is calculated for every country in each given year, using expressions (I-II). An example of the calculation of the tomato AWCB for Spain in 2016 is presented below:

PRD = 5,233,540 t
IMP = 145,013 t
EXP = 911,106 t
CON = 673,381 t
PRC = (5,233,540 145,013) − (911,106 673,381) = 3,794,066 t

The quantity of damaged tomatoes during cultivation and harvesting is 0.20 kg per kg of harvested tomatoes: for Spain, it was 1,046,708 t in 2016. Tomato skin that is separated during processing takes 0.10 kg per kg of processed tomatoes. For Spain, the quantity of tomato skin in 2016 was 379,407 t. Tomato pomace takes 0.05 kg per kg of processed tomatoes, and for Spain it was 189,703 t in 2010. The volume of wastewater that appears in processing is 8.2 l per kilogram of processed tomatoes. For Spain, in 2016 the volume of wastewater from tomato processing was 31,111,338 m^3. The quantity of suspended solids from tomato processing was 227,644 t. The quantity of tomatoes consumed in 2016 in Spain was 673,381 t, out of which 107,741 t went mouldy.

3.2.3. Cereal sector

The Cereal sector includes the following commodities: barley, maize, triticale, oats, rice, rye and wheat. Certain amounts of cereals are eaten or destroyed by animals (birds, rabbits, deer, wasps) and in that form cannot be used as food. Furthermore, cereals are the type of crops that generate huge amounts of AWCB during harvesting, especially straw in the case of barley, triticale, oat, wheat. Straw is mostly used as a material that provides clean area and thermal isolation for stable animals. Bran is a by-product of a multi-stage process of flour production. Husks and cobs are by-products that also often end up as burning material. Table 3 contains mass ratio of main AWCB to product ratio for the Cereal sector.

Main AWCB during the harvesting period of cereals is straw. Also, harvesting technology affects the quantities of the straw and ability to collect and properly dispose of the straw. During the processing step, the main AWCB is bran, part of the grain that could be used in a further milling process, but in the past few years, it has become an ingredient in food consumption. For rice, as the only raw cereal directly used for food consumption, estimate shows that one quarter becomes rotten and not used. The amount of fruit defected due to harvesting and handling errors is an important factor in the AWCB calculation. Traditional method using harvest workers is slow and its efficiency depends on workers' skills. Modern methods with appropriate machinery are useful in greater agricultural areas where a larger quantity of crops and fruit are being produced. Modern methods are more expensive than the traditional ones and harvesting losses can vary depending on the quality of the machinery (Magagnotti et al., 2013). The main by-product generated in the first stage of the waste value chain of Cereal sector – straw/stalk - is usually utilised as an energy source (Muazu and Stegemann, 2015). However, some further applications of those by-products have also been studied, as a construction material (Bouasker et al., 2014), or as an adsorption material (Cao et al., 2017). Cereal bran has shown to be a very interesting source of polymer macromolecules (Lee et al., 2017) and a potential resource in the production of biodiesel (Chhabra et al., 2017). The quantity of the processed cereals is calculated for every country in each given year using expressions (I-II). An example of the calculations of barley AWCB for Slovenia in 2016 is presented below:

PRD = 91,650 t
IMP = 22,117 t
EXP = 5524 t
PRC = (91,650 22,117 − 5524) = 108,243 t

Table 2
Main AWCB produced from the Vegetable sector.

Commodity/Vegetables	Harvesting/Cultivation	Source
Tomato	Damaged tomatoes to product ratio − 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Cabbage	Damaged cabbage to product ratio − 0.20 kg/kg Leaves to product ratio − 0.20 ÷ 1.51 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018), (Munhuweyi et al., 2016) (Munhuweyi et al., 2016), (Stoffella and Fleming, 1990), (Haque et al., 2016), (Nurhidayati et al., 2016), (Bajgai et al., 2014)
Cauliflower and broccoli	Damaged cauliflower and broccoli to product ratio − 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Carrot	Damaged carrot to product ratio − 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Onion	Damaged onion to product ratio − 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Potato	Damaged potatoes to product ratio − 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Sunflower seed	Damaged sunflower seed to product ratio − 0.10 kg/kg Straw to product ratio − 1.00 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018) (Bakker, 2013)
Rapeseed	Stalks to product ratio − 1.76 kg/kg Damaged rapeseed to product ratio − 0.10 kg/kg	(Islam et al., 2018)
Sugar beet	Sugar beet leaves to product ratio − 0.14 ÷ 0.91 kg/kg Stones to product ratio − 0.001 ÷ 0.04 kg/kg	(Krick, 2019)
Olives	Twigs and leaves to product ratio − 2.68 ÷ 5.15 kg/kg Woody branches to product ratio − 2.68 kg/kg	(Russo et al., 2016), (Acampora et al., 2013), (Sansoucy et al., 1985), (European Commission, 2012)

Commodity/Vegetables	Processing	Source
Tomato	Tomato skin to product ratio − 0.10 kg/kg Tomato pomace to product ratio − 0.03 ÷ 0.07 kg/kg Wastewater to product ratio − 8.20 l/kg Total suspended solids to product ratio − 0.06 kg/kg	(Kao and Chen, 2016) (Del Valle et al., 2006) (Loehr, 2012) (Loehr, 2012)
Cabbage	Outer cabbage leaves to product ratio − 0.35÷ 0.40 kg/kg	(Prokopov et al., 2015), (Agati et al., 2016)
Cauliflower and broccoli	Wastewater to product ratio − 8.20 l/kg Total suspended solids to product ratio − 0.0025 kg/kg Leaves to product ratio − 0.50 kg/kg	(Loehr, 2012) (Loehr, 2012) (Pankar and Bornare, 2018)
Carrot	Pomace and peel to product ratio − 0.12 kg/kg Wastewater to product ratio − 11.10 l/kg	(Loehr, 2012)
Onion	Wastewater to product ratio − 21.00 l/kg Total suspended solids to product ratio − 0.01 kg/kg Peel to product ratio − 0.25 kg/kg	(Loehr, 2012) (Loehr, 2012) (Committee, 2016)
Potato	Peel to product ratio − 0.10 kg/kg Process water to product ratio − 16.00 l/kg Suspended solid to product ratio − 0.27 ÷ 0.50 kg/kg	(Loehr, 2012)
Sunflower seed	Sunflower cake meal to product ratio − 0.60 ÷ 0.64 kg/kg Slurry (ugido) to product ratio − 0.015 ÷ 0.045 kg/kg	(Mogala, 2012)
Rapeseed	Cake meal to product ratio − 0.67 kg/kg	(Ivanova et al., 2016)
Sugar beet	Stones to product ratio − 0.001 ÷ 0.005 kg/kg Beet soil to product ratio − 0.04 ÷ 0.10 kg/kg Molasses to product ratio − 0.032 ÷ 0.035 kg/kg Sugar beet pulp to product ratio − 0.05 kg/kg Wash water to product ratio − 0.75 l/kg Sugar beet factory lime to product ratio − 0.04 kg/kg Sugar beet tops & tails to product ratio − 0.007 kg/kg	(Krick, 2019)
Olives	Twigs and leaves to product ratio − 2.68 ÷ 5.15 kg/kg Olive mill wastewater to product ratio − 0.50 ÷ 1.50 kg/kg Olive pomace to product ratio − 0.25 kg/kg	(Abaza et al., 2015), (Ahmad and Ayoub, 2014) (Barbera et al., 2013) (Manzanares et al., 2017)

Commodity/Vegetables	Consumption	Source
Tomato	Rotten tomatoes to product ratio − 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Cabbage	Rotten cabbage to product ratio − 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Cauliflower and broccoli	Rotten cauliflower and broccoli to product ratio − 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Carrot	Rotten carrot to product ratio − 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Onion	Rotten onion to product ratio − 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Potato	Rotten potatoes to product ratio − 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Sunflower seed	Not applicable, as sunflower seed are not consumed directly by humans	n/a
Rapeseed	Not applicable, as rapeseed is not consumed directly by humans	n/a
Sugar beet	Not applicable, as sugar beet are not consumed directly by humans	n/a
Olives	Wasted olive oil to product ratio − 0.12 ÷ 0.20 kg/kg Rotten olives to product ratio − 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)

Per 1 kg of harvested barley, between 0.68 and 1.75 kg of straw is left. With an average mass of straw of 1.22 kg per kg of harvested barley, for Slovenia, it was produced 111,813 t of straw in 2016. Bran that occurs in processing step takes 0.15 ÷ 0.49 kg per kg of processed barley. With the average value of 0.32 kg/kg for Slovenia, there were 34,638 t of bran. Furthermore, a hull that occurs in the processing step takes from 0.14 to 0.40 kg per kg of processed barley. The average value is 0.27 kg/kg, and for Slovenia, it was 29,226 t in 2016.

3.2.4. Animal sector

The last sector analysed is the Animal sector: cattle, dairy cows, pigs and chickens (broilers). Animal manure presents one of the most used by-products during the long tradition of animal farming. Before urea, the only fertiliser for crop treatment was manure. Nowadays, people still use manure as a fertiliser, but due to methane production, it should be avoided. Another source of by-products that are classified as waste is the slaughterhouse remains. In slaughterhouses, huge quantities of different types of AWCB occur, which is potentially dangerous for the

Table 3
Main AWCB produced from the Cereal sector.

Commodity/Cereals	Harvesting/Cultivation	Source
Barley	Straw to product ratio − 0.68 ÷ 1.75 kg/kg	(FAO, 2018), (McCartney et al., 2006), (Gelaw et al., 2014), (Mali et al., 2017), (Weiser et al., 2014)
Maize	Stalks to product ratio − 0.80 ÷ 3.77 kg/kg	(FAO, 2018), (Gelaw et al., 2014), (Barten, 2013), (Szalay et al., 2018)
	Husk to product ratio − 0.20 ÷ 0.30 kg/kg	(Barten, 2013), (Galanakis, 2015)
	Cobs to product ratio − 0.15 ÷ 0.86 kg/kg	(Galanakis, 2015), (Borrelli et al., 2014), (Blandino et al., 2016)
Triticale	Straw to product ratio − 0.90 ÷ 4.00 kg/kg	(FAO, 2018), (Weiser et al., 2014), (Adolfsson, 2005)
Oat	Straw to product ratio − 0.75 ÷ 2.00 kg/kg	(FAO, 2018), (McCartney et al., 2006), (Weiser et al., 2014)
Rice	Straw to product ratio − 0.42 ÷ 2.15 kg/kg	(FAO, 2018), (Weiser et al., 2014), (Szalay et al., 2018)
Rye	Straw to product ratio − 0.90 ÷ 2.00 kg/kg	(FAO, 2018), (McCartney et al., 2006), (Weiser et al., 2014)
Wheat	Straw to product ratio − 0.50 ÷ 2.37 kg/kg	(FAO, 2018), (McCartney et al., 2006), (Gelaw et al., 2014)

Commodity/Cereals	Processing	Source
Barley	Bran to product ratio − 0.15 ÷ 0.49 kg/kg	(Galanakis, 2015), (Izydorczyk et al., 2013), (Singh et al., 2015)
	Hull to product ratio − 0.14 ÷ 0.40 kg/kg	(Youssef et al., 2017), (Rosentrater and Evers, 2017)
Maize	Bran to product ratio − 0.11 ÷ 0.15 kg/kg	(Galanakis, 2015), (Puma et al., 2015)
Triticale	Bran to product ratio − 0.15 ÷ 0.17 kg/kg	(Galanakis, 2015), (Peña, 2018)
Oat	Bran to product ratio − 0.15 kg/kg	(Galanakis, 2015)
	Hull to product ratio − 0.25 ÷ 0.32 kg/kg	(Rosentrater and Evers, 2017), (Decker et al., 2014), (Mahapatra and Yubin, 2007)
Rice	Bran to product ratio − 0.08 ÷ 0.12 kg/kg	(Galanakis, 2015), (Puma et al., 2015), (IRRI, 2014)
	Husk to product ratio − 0.04 ÷ 0.36 kg/kg	(FAO, 2018), (Rosentrater and Evers, 2017), (IRRI, 2014), (Zareei et al., 2017), (Glushankova et al., 2018)
Rye	Bran to product ratio − 0.05 ÷ 0.15 kg/kg	(Galanakis, 2015), (Singh et al., 2015)
Wheat	Bran to product ratio − 0.13 ÷ 0.20 kg/kg	(Galanakis, 2015), (Puma et al., 2015), (Chalamacharla et al., 2018), (Hemdane et al., 2016)

Commodity/Cereals	Consumption	Source
Barley	Not applicable, as barley is not consumed directly by humans	n/a
Maize	Not applicable, as maize is not consumed directly by humans	n/a
Triticale	Not applicable, as triticale is not consumed directly by humans	n/a
Oat	Not applicable, as oat is not consumed directly by humans	n/a
Rice	Rotten rice to consumed ratio − 0.12 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018)
Rye	Not applicable, as rye is not consumed directly by humans	n/a
Wheat	Not applicable, as wheat is not consumed directly by humans	n/a

environment. To decrease environmental pollution, these by-products must be safely used and disposed of. Furthermore, dairy cows are farmed for milk production. After the milk is processed for different products different types of waste occur, primarily whey. Whey must be pre-treated before disposal because of environmental protection. Table 4 contains mass ratio of the main AWCB to product ratio for the Animal sector.

Types of AWCB that appear in the Animal sector are entirely different from those in the previous sectors. The main AWCB that occurs in the farming step is manure, which has been well-known to people for a significant period. As the petrochemical industry developed and still continues to grow, fertilisers have replaced manure progressively. In some rural areas, people still use manure as a natural fertiliser in the gardens and smaller fields. Cow manure can also be used in a co-composting process that can be used for biodegradation of petroleum hydrocarbons (Ahmadi et al., 2016). Chicken manure has chemical properties which have proven to be applicable to produce catalysts for the production of biodiesel from waste cooking oil (Maneerung et al., 2016). In the processing step, slaughtering remains that occur, present potential danger to the environment in case of non-adequate treatment and disposal (Um et al., 2016). As an example of the slaughterhouse by-products utilisation, slaughterhouse water has been studied as feedstock for the production of biodiesel (Hernández et al., 2016). Application of cruor (coagulated blood) in the extraction of haemoglobin and its potential use as a preservative has been studied in (Przybylski et al., 2016). In the last step, quantities of rotten meat are primarily a result of human habits and behaviour, as it was the case for all the analysed sectors. The number of processed animals is calculated for every country in each given year using expressions (I-III). An example of the calculation of the cattle AWCB for Belgium in 2016 is presented below:

FARM = 2,501,350 heads
SLAUG = 535,330 heads
SPECMAN =18.98 t/year
MAN = 47,511,875 t
CON = 205,862 t

The average quantity of manure that one animal produces during a year is 18.98 t, and the total quantity of manure that the Belgian farmers produced was 47,511,875 t in 2016. The AWCB quantities that occurred in Belgian slaughterhouses were: 11,884 t of blood; 9315 t of fatty tissue; 21,841 t of skin; 6424 t of feet; 578 t of tail; 450 t of brain and 28,265 t of bones in 2016. The quantity of the consumed cattle meat in Belgium was 205,862 t in 2016, of which 16% was calculated to go mouldy (spoiled, rotten) or 32,938 t.

4. Results and discussion

The data on the cumulative quantity of AWCB from all the sectors, generated from 2010 to 2016, has been calculated as described in the previous sub-sections. The average quantity of AWCB per population of the country and per area of the country is shown in Fig. 1 and Fig. 2.

4.1. The average quantity of AWCB per area in the EU28 countries

Fig. 1 from a to d presents the estimated quantity of the AWCB per area for selected commodities grouped in four Sectors. In the Fruit sector (Fig. 1a), the quantity of the AWCB per area below 1 t/km^2 has been estimated in countries such as Sweden, Finland, Latvia, Estonia, Ireland and Lithuania. Such a low value is the result of low agricultural activities regarding the production of analysed fruit commodities due to inappropriate climate conditions and a large country area. Smaller countries with a high level of industrialisation like the Netherlands, Belgium and Austria have shown the yields of the fruits AWCB between 4 t/km^2 and 12 t/km^2. Since analysed commodities are mostly citrus fruit, it is expected that the Mediterranean countries show the highest quantities of the fruits AWCB. Therefore, Italy (ca. 40 t/km^2) and Greece (50 t/km^2) are the most dominant countries in the EU considering the technical potential of the fruits AWCB per km^2.

The highest quantities of AWCB per area for the Vegetable sector (Fig. 1b) have been estimated for the Netherlands at 2600 t/km^2 and for Belgium at 2525 t/km^2. Since both countries have highly developed

Table 4
Main AWCB produced from the Animal sector.

Commodity/Animals	Farming	Source
Cattle	Tonnes of manure per cattle per year – 18.25 ÷ 19.71	(Shaffer and Walls, 2002), (Vegricht et al., 2017), (Mullo et al., 2018)
Dairy cow	Tonnes of manure per dairy cow per year – 16.1 ÷ 18.8	(Shaffer and Walls, 2002), (Nennich et al., 2003)
Pig	Tonnes of manure per pig per year – 1.1 ÷ 1.3	(Shaffer and Walls, 2002), (Scheftelowitz and Thrän, 2016)
Chicken	Tonnes of manure per chicken per year – 0.013 ÷ 0.095	(Shaffer and Walls, 2002), (Recebli et al., 2015)
Commodity/Animals	Slaughtering/Processing	Source
Cattle	Blood to product ratio – 0.016 ÷ 0.060 kg/kg Fatty tissue to product ratio – 0.010 ÷ 0.070 kg/kg Hide or skin to product ratio – 0.051 ÷ 0.085 kg/kg Feet to product ratio – 0.019 ÷ 0.021 kg/kg Tail to product ratio – 0.001 ÷ 0.0025 kg/kg Brain to product ratio – 0.0006 ÷ 0.002 kg/kg Bones to product ratio – 0.08 ÷ 0.30 kg/kg	(Irshad and Sharma, 2015), (Alao et al., 2017), (Ali et al., 2013), (Sannik et al., 2015)
Dairy cow	Whey to produced cheese ratio – 5.10 ÷ 6.10 kg/kg	(Nath et al., 2016), (Cheese, 2018)
Pig	Blood to product ratio – 0.02 ÷ 0.08 kg/kg	(Irshad and Sharma, 2015), (Alao et al., 2017), (Sannik et al., 2015), (Jayathilakan et al., 2012), (Nordberg and Edström, 2003)
	Fatty tissue to product ratio 0.013 ÷ 0.11 kg/kg	(Irshad and Sharma, 2015), (Romans et al., 2018)
	Organs to product ratio – 0.018 ÷ 0.077 kg/kg	(Irshad and Sharma, 2015), (Nordberg and Edström, 2003)
	Feet to product ratio – 0.015 ÷ 0.024 kg/kg	(Irshad and Sharma, 2015), (Sannik et al., 2015), (Romans et al., 2018)
	Tail to product ratio – 0.001 kg/kg	(Irshad and Sharma, 2015), (Sannik et al., 2015), (Romans et al., 2018)
	Hide or skin to product ratio – 0.023 ÷ 0.08 kg/kg	(Irshad and Sharma, 2015), (Alao et al., 2017), (Romans et al., 2018)
	Bones to product ratio – 0.085 ÷ 0.30 kg/kg	(Irshad and Sharma, 2015), (Amisy, 2018)
Chicken	Feathers to product ratio – 0.06 ÷ 0.08 kg/kg	(Irshad and Sharma, 2015), (Alao et al., 2017), (Acda, 2016)
	Heads to product ratio – 0.025 ÷ 0.03 kg/kg	(Irshad and Sharma, 2015), (Alao et al., 2017)
	Blood to product ratio – 0.032 ÷ 0.04 kg/kg	(Irshad and Sharma, 2015), (Bah et al., 2013), (Barbut, 2015)
	Feet to product ratio – 0.035 ÷ 0.084 kg/kg	(Irshad and Sharma, 2015), (Sannik et al., 2015)
Commodity/Animals	Consumption	Source
Cattle	Rotten beef to consumed beef ratio – 0.11 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018), (Grace, 2019), (Ministry of Economic Affairs, 2013)
Dairy cow	Rotten milk to consumed milk ratio – 0.07 ÷ 0.20 kg/kg Rotten butter to consumed butter ratio – 0.133 ÷ 0.20 kg/kg Rotten cheese to consumed cheese ratio – 0.133 ÷ 0.20 kg/kg	(Grace, 2019), (Ministerio de Agricultura Alimentacion y Medio Ambiente, 2013), (Stenmarck et al., 2016)
Pig	Rotten pork meat to consumed pork meat ratio – 0.11 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018), (Grace, 2019), (Ministry of Economic Affairs, 2013)
Chicken	Rotten chicken meat to consumed chicken meat ratio – 0.11 ÷ 0.20 kg/kg	(Parfitt et al., 2010), (Conrad et al., 2018), (Grace, 2019), (Ministry of Economic Affairs, 2013)

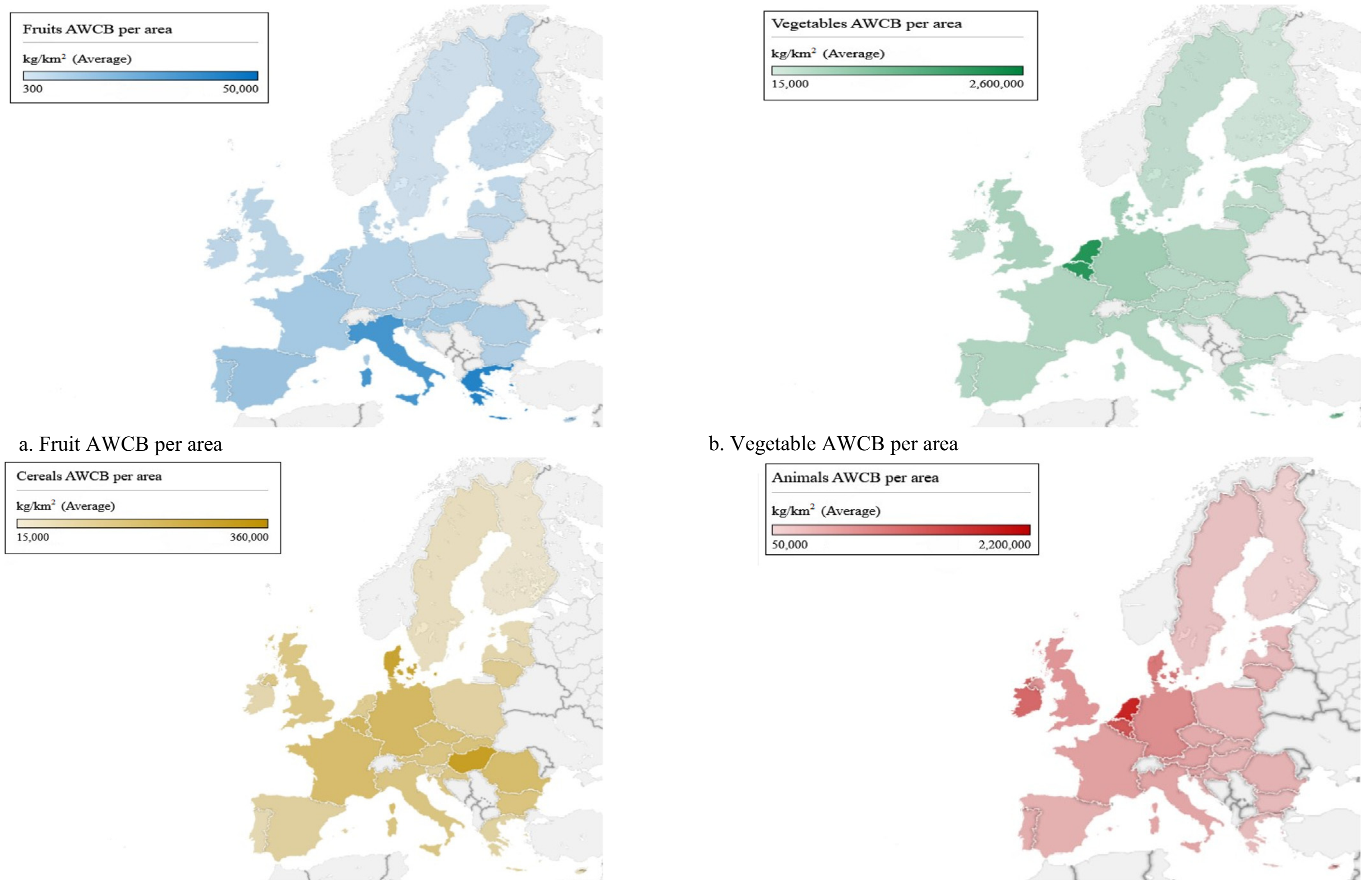
vegetable production and low land area, it brings them to the top. Other countries with more than 300 t of the vegetable AWCB per km^2 are the UK, Germany and Denmark. The lowest quantity of the vegetable AWCB has been estimated for Sweden (ca. 30 t/km^2), Latvia (ca. 23 t/km^2) and Finland (ca. 17 t/km^2), which is the result of low agricultural activities and high land area. In this analysis, highly developed European countries with high agricultural activities have shown the greatest values of the technical potential of vegetable AWCB.

The highest quantities of AWCB per area for the Cereal sector (Fig. 1c) have been estimated in Hungary (ca. 360 t/km^2), Denmark (ca. 330 t/km^2), Belgium (ca. 225 t/km^2) and Germany (ca. 220 t/km^2). The reason for such results lies in the fact that these countries have strongly developed agriculture sector regarding cereals production and lower land area, except for Germany. Romania and Bulgaria have also shown a high level of cereal production with the generated AWCB in Cereal sector slightly below 200 t/km^2. Again, the countries located in the north of Europe, Finland and Sweden, have shown the lowest AWCB quantities, below 20 t/km^2. Countries with high available land area and favourable climate conditions for cereals production and high population density have shown to be dominant in the Cereal sector.

For the Animal sector (Fig. 1d), the highest AWCB production has been estimated for the Benelux countries: the Netherlands (ca. 2200 t/km^2), Belgium (ca. 1500 t/km^2) and Luxembourg (ca. 1100 t/km^2). Denmark and Ireland generate between 1000 ÷ 1200 t/km^2 of the animal AWCB. This data points to the fact that high level of farming activities and animal processing is in the highly populated countries of Western Europe. Germany and France have also shown relatively high quantities of the animal AWCB with the average values of ca. 450 and 700 t/km^2, respectively. Countries of Central and Eastern Europe like Poland, Czech Republic, Slovakia, Slovenia, Croatia and Hungary have shown the yield of the animal AWCB between 150 ÷ 300 t/km^2, while the lowest quantities of the animal AWCB have been estimated for Northern European countries Sweden and Finland with the yield of around 50 t/km^2.

4.2. The average quantity of AWCB per area in the EU28 countries

Fig. 2 from a to d presents the estimated quantity of AWCB per capita for selected commodities grouped in four Sectors. In the Fruit sector (Fig. 2a), Greece, Italy and Spain have shown the highest quantity of



a. Fruit AWCB per area

b. Vegetable AWCB per area

c. Cereal AWCB per area

d. Animal AWCB per area

Fig. 1. a to d. The average quantity of AWCB from all sectors per area in the period 2010–2016. Fruits AWCB (a), Vegetable AWCB (b), Cereal AWCB (c), Animal AWCB (d).

the AWCB per capita and year, 600 kg, 200 kg and 130 kg. A similar trend has been reported for the estimated yield of the fruit AWCB per area. This point to the fact that the highest potential of the fruit AWCB is presented in the Southern European countries. The lowest quantity of the generated AWCB for the Fruit sector (below 10 kg per capita and year) has been estimated for Northern and Western European countries (Denmark, Finland, Sweden, Latvia, Estonia, Lithuania, Germany, the UK and Ireland). It is important to emphasize that selected Fruit commodities, except apple, are dominantly cultivated in Mediterranean climate conditions.

The highest quantity of AWCB per capita and per year for the Vegetable sector (Fig. 2b) has been estimated at around 7.0 t for the Netherlands and Belgium. Both countries have shown the highest yield of the vegetable AWCB per area, as well. This data indicates that there is high potential in the use of the residues of vegetable production, processing and consumption in those countries. Denmark follows the Benelux countries with the estimated quantities of the vegetable AWCB of ca. 3.7 t per capita. Countries of Central and Eastern Europe in this analysis have shown greater quantities of the vegetable AWCB, such as Poland, Estonia, Lithuania and Romania. This result is probably related to the low population density in the Baltic countries and high agricultural activities in Poland and Romania. The lowest yield of the vegetable AWCB per capita has been estimated in Slovakia (ca. 600 kg) and the Czech Republic (ca. 850 kg).

In the Cereal sector (Fig. 2c), the highest quantity of AWCB per capita and per year is estimated for Hungary, with around 3.5 t. Denmark is second with around 2.5 t per capita and year, followed by Romania and Bulgaria, each with 2.3 t of the cereal AWCB. Central and Eastern European countries have favourable climate conditions for the growth of cereals and therefore high technical potential for the cereal AWCB to be used. Northern European countries on average have shown the AWCB yield of 1.0 t per capita. The lowest production of the cereal AWCB per capita and per year is estimated for Malta (100 kg).

In the Animal sector (Fig. 2d), the results have shown that only six countries produce less than 2.0 t of the animal AWCB per capita (Bulgaria, Greece, Italy, Hungary, Malta and Slovakia). The Czech Republic, Spain, Croatia, Cyprus, Portugal, Romania, Germany, Sweden and the UK belong to a group of countries that produce between 2.0 and 3.0 t of the animal AWCB per capita per year. Other countries produce much bigger quantities of the animal AWCB, whereas Belgium, France, Netherlands and Denmark have shown on average between 4.0 and 7.0 t of the animal AWCB. The highest producer of the animal AWCB is Ireland, where almost 20 t of the animal AWCB is produced per capita in a year. In general, highly-developed countries of Western Europe generate the largest quantities of animal AWCB.

5. Conclusions and future research

This study gives an overview of the technical potential of agricultural co- and by- products generated from the top EU28 commodities in the agricultural value chain. The results presented in this study should be carefully analysed. The commodities have been selected due to their usage rate in the EU28. Even though they have been sorted into four different sectors, the estimated quantities of the AWCB do not represent the real situation in these sectors. The quantities of the AWCB have been calculated for every EU28 country, but their distribution over the country has not been shown, such as on the NUTS3 level. In total, this study has shown that the dispersion of the AWCB quantities is the result of land activities, climate conditions and human eating habits (consumption of goods). Countries with less available land areas, a

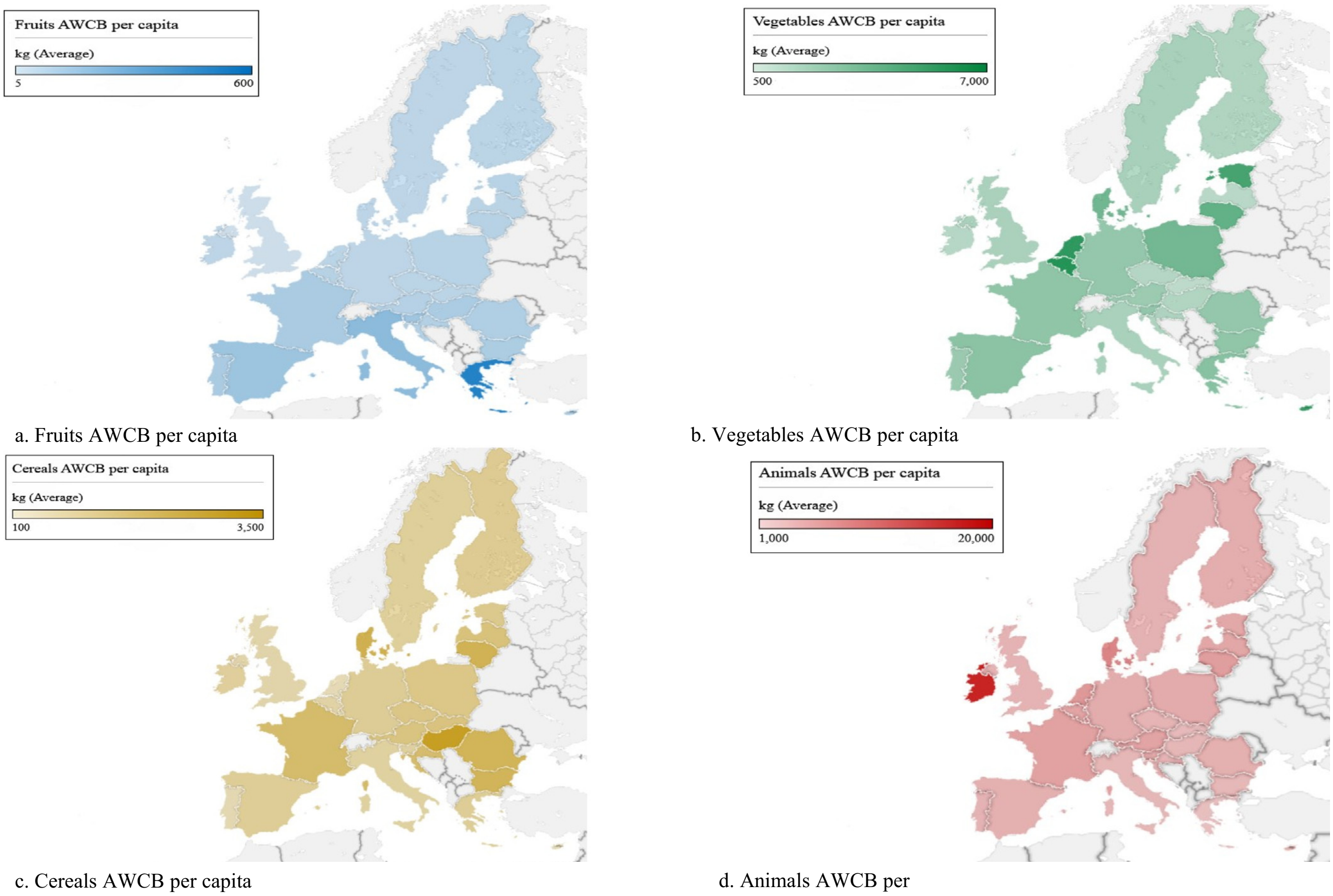


Fig. 2. a to d. The average quantity of AWCB from all sectors per capita in the period 2010–2016. Fruit AWCB (a), Vegetable AWCB (b), Cereal AWCB (c), Animal AWCB (d).

significant number of industrial zones and high population density were the biggest producers of the AWCB in the Animal sector – Belgium, France, Germany, Ireland and the Netherlands. Those countries have also shown a respective yield of AWCB generated in the Vegetable sector. Since the Animal and Vegetable sectors are highly connected due to the transfer of vegetable residues to animal feeding, the estimated distribution of their AWCB was expected. Therefore, Western European countries show a high potential of the use of co- and by- products generated in animal farming and vegetable cultivation activities. On the other hand, South European countries, with lots of land areas and mild weather conditions were shown to be more dominant in the quantities of the generated fruit AWCB. Therefore, the use of citrus fruit co- and by-products in that area should be taken for more detailed observation in further studies. The Cereal sector has shown the potential of AWCB in the countries of Central and Eastern Europe. This analysis has shown that the highest yield of the cereal AWCB was generated in the countries located in the Pannonian Basin and in France and Germany.

Future research should put the focus on the combined approach of converting the studied AWCB in biorefineries. The first stage of the combined approach should include experimental research on the production of value-added bio-applications like enzymes, biofuels, biopolymers, pigments and bioactive compounds from the studied AWCB. The second stage is GIS mapping of AWCB at national/regional level that could give a more detailed spatial distribution of AWCB. GIS mapping will be used to find an optimum transport route for AWCB utilisation in the current biorefineries, or in the planning of new biorefineries and local/regional intermediate processing facilities. Finally, the study on the techno-economic analysis of the combined approach will be used to valorise the products and the feasibility of AWCB utilisation.

In many cases, the production of value-added products from specific AWCB may not be economically feasible mainly because of the low market price of products, low quantities and seasonality of AWCB, high transportation costs and water content of AWCB. In order to overcome these problems, specific types of AWCB should be treated on-site by the same producing industry in order to produce intermediate products (such as bio-oil, biogas, bio-juice, etc.) that can be easily stored and transported to the biorefineries which production provides a large-volume product to achieve economies of scale.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.05.219.

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Green biomass to biogas – A study on anaerobic digestion of residue grass

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ABSTRACT

Sustainable management in the biogas production via anaerobic digestion process intents the use of alternative biomass sources that are not competitive with food production. The aim of this study is to investigate the application of the abundant-quantity residue in more sustainable production of heat and electricity along with the production of the digested substrate as a fertiliser. The study has been divided into several sequential steps. First, the grass samples have been collected at the following locations: uncultivated land, river embankment and highway verge. The greatest grass yield has been determined for the riverbank grass, with an average value of 19 t/ha of fresh mass and 2.6 t/ha of dry mass. Next, the chemical characterisation of the collected residue grass and the laboratory batch mono and co-digestion tests with maize silage and cattle slurry have been conducted. The results show that all grass samples have satisfying digestive parameters (C/N ratio between 16.6:1 to 22.8:1) with the low presence of impurities, which makes them suitable for biogas production. The following biochemical methane potential in mono-digestion of residue grass has been recorded: uncultivated land (0.275 Nm^3/kgTS), riverbank (0.192 Nm^3/kgTS) and highway verge (0.255 Nm^3/kgTS). The control of the process has been improved in co-digestion tests, by avoiding acidification in the first days of the operation. The estimation of kinetic parameters in mathematical modelling has shown that the degradation of residue grass shows some different parameters compared to the previous study. The model results for the gas phase show some small deviations compared to the experimental data. Based on the life cycle analysis results it can be concluded that there are perspectives in the use of residual grass compared to maize silage in the production of heat and electricity, especially in the improvement of ecosystem quality.

1. Introduction

A recent study has shown that anaerobic digestion (AD) is likely to be one of the most promising technologies for biomass energy recovery, especially on farms (Massimo and Montorsi, 2018). Also, animal manure is better suited as an AD substrate instead of its direct use as a fertiliser. It contains significant concentrations of nutrients and pathogens (Neshat et al., 2017) and could cause contamination of ground waters and soil (Holm-Nielsen et al., 2009). Storing the manure in the open air results in methane and carbon dioxide emissions through the process of self-remediation (Burg et al., 2018). Using animal manure as a feedstock for the AD, several negative impacts on the environment could be reduced; emissions of carbon dioxide, methane and nitrous oxide; reduction of waste, odour; destruction of pathogens (especially when the AD runs at thermophilic conditions) and better fertilisation effect (Bochmann and Montgomery, 2013). On the other hand, use of only animal manure in the AD has some disadvantages, and one of the major is low carbon to nitrogen ratio (C/N) (Neshat et al., 2017). Cattle manure appears to be a major substrate for biogas plants, especially in the intensive-farming countries (Franco et al., 2018). To increase relatively low biogas yield from mono-digestion of manure (10÷20 m^3/t of fresh manure) pretreatment methods could be applied, co-digestion with other biodegradable organic substrates or combination of both (Ormaechea et al., 2018).

Energy crops have been largely used as lignocellulosic biomass feedstock in the production of biogas via an AD in recent years. Abundant quantities of lignocellulosic biomass and respective

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biochemical methane potential (BMP) from biomass biodegradation, point to the promising feedstock in the production of energy-rich methane gas. It has been calculated that the annual global production of dry biomass exceeds $2.00 \cdot 10^{11}$ t (Kumar et al., 2008) and thus there is a significant potential for lignocellulosic biomass to be investigated in the AD and sequentially used in biogas production. Biodegradation of different types of lignocellulosic biomass depends on the chemical structure, primarily on the cellulose content, hemicellulose, lignin and C/N ratio, as it has been presented for various organic substrates (Karthikeyan and Visvanathan, 2013).

Residue grass belongs to a group of lignocellulosic biomass and could be profitably used for the more sustainable production of bioenergy in biorefineries (Nimmanterdwong et al., 2017). Average production of $500 \div 600$ m^3 of biogas per t of VS could be achieved from the AD of residue grass (Mattioli et al., 2017). Also, methane content of the generated biogas ranges between 52% and 56%, similar to maize silage (L.E.E. SÀRL, 2018), feedstock often used in biogas plants (Bull, 2008) while it could be used as fodder to feed ruminants. Analyses have shown that the higher biomass yields could be achieved in the low-nature quality areas and the nutrient-rich soils.

Among the promising type of residue grass in the AD supply chain is the riverbank grass (Boscaro et al., 2018). Fieldwork has shown that the average yield of green biomass on the riverbank was around 13 t/ha. The average dry matter (DM) content in the riverbank grass was 37% which gives the dry mass yield of around 4.8 t/ha. The overall results pointed to the conclusion that the energy recovery of grass biomass could decrease the dependency of the AD supply chain on the energy crops while obtaining a positive energy return (Meyer et al., 2014). Antagonistic and synergistic effects on biogas and methane production from batch anaerobic co-digestion of cattle and pig slurries with grass silage have shown that the replacement of cattle slurry with grass silage increased the biogas and methane yields (Himanshu et al., 2018).

Besides several experimental works on the AD, various studies based on mathematical modelling of the AD have been performed. Mathematical modelling of the AD of biodegradable matter describes the interactions between physical and biological mechanisms (Lauwers et al., 2013). Typically, Anaerobic Digestion Model No. 1 (ADM1) is applied for the mathematical description of the process. ADM1 describes the reactions occurring in an AD by assuming a perfect mixing and consequently homogenous reactor mixture. The components in the process are expressed regarding their Chemical Oxygen Demand (COD) or molar concentrations. Recent studies on modelling of the AD using ADM1 have been applied to several substrates: blackwater and rotten vegetable (Feng et al., 2006); grass silage (Koch et al., 2010); a mixture of municipal waste and grease (Nordlander et al., 2017); microalgae (Mairet et al., 2011) and many others. ADM1 is available in Matlab and Simulink and water-related simulation software such as WEST, BioWin and AQUASIM.

Life Cycle Assessment (LCA) is an useful tool for improving the biogas production chain, with the main focus on the environmental performance and eco-efficiency (Huttunen et al., 2014). There have been several LCA studies on biogas production, such as LCA study on co-digestion of fresh algae with animal manure (Cappelli et al., 2015). LCA-based mixed integer programming (MIP) mathematical model has been applied to investigate sustainability of the biogas production from environmentally harmful raw materials where it was shown that the integrated biogas production with included auxiliary facilities led to a significant eco-profit in the large-scale applications (Čuček et al., 2011). Evaluation of replacing energy crops with macroalgae at a real biogas plant has been performed using the LCA approach where sustainable energy production and lower environmental effects have been obtained compared to energy crops, but only if microalgae are regionally accessible (Ertem et al., 2017).

The focus of this study is on the use of residue grass as a replacement for maize silage in the AD. The grass samples have been collected from the areas that do not compete with the food production: uncultivated land, the Sava riverbank in the city of Zagreb and highway verge. The study includes determination of the fresh and dry yield of residue grass biomass, chemical characterisation of residue grass, determination of biogas yield and biogas composition from the residue grass in the AD together with the application of ADM1 model to describe the AD and compare the modelling results with the experimental results. In the end, LCA has been used to determine the environmental effects of biogas production from residue grass in the production of heat and electricity.

It is worth noting that most of the studies in this area include experimental investigations, mathematical modelling and life-cycle analysis, each of them separately, or two of them combined. A novelty in this study is combining all three approaches to evaluate the use of the alternative substrate in the sustainable production of biogas and digestate.

2. Materials and methods

In this section, an overview of applied methods is presented. First, the grass yield has been evaluated, and the sampling procedure has been determined. After the samples have been collected and stored, elemental analysis and analysis of heavy metals have been performed. Before setting up a batch AD experiment, the preparation of feedstock and inoculum has been conducted. During the AD, biogas yield, biogas composition and reactor pH have been monitored. Finally, mathematical modelling of biogas production has been performed, and the results of the mathematical model and experimental process have been compared.

2.1. Grasslands and grass sampling

Three types of grasslands have been used for valorisation in this research: uncultivated land, riverbank and highway verge. Each of the grasslands is located nearby the capital city of Croatia, Zagreb. The chosen locations of grasslands are not suitable for food crops production or feed purposes, and thus their application in the AD is in accordance with the sustainability principles. The grass samples have been collected at the end of April 2018. A metal frame of the internal area of 2 m^2 has been used to surround the grass stems which were collected using scissors. On each of the examined grasslands, nine samples have been collected. For each of the samples, the length of the grass stems and the mass of collected grass per area has been measured. Grass cutting and measuring procedures have been conducted for each of the nine samples for each of the grasslands. After the grass has been collected from the grasslands, it was stored in plastic bags. Using a tabletop vacuum device the air was removed, and the samples have been weighted and further stored in the freezer at $-15\,^{\circ}C$ to preserve grass characteristics and composition.

2.2. Chemical analysis of residue grass

Chemical analysis of the collected residue grass consists of the determination of elemental composition of grass samples and their lower (LHV) and upper heating values (UHV), and determination of metal contents in analysed grass samples.

Proximate and ultimate analyses of the residue grass have been conducted in the Central Laboratory for Chemical Technology in the

Table 1
Proximate and ultimate parameters of residue grass and applied test methods.

Parameter	Test method
Moisture	*HRN EN ISO 18134-1:2015*
Ash	*HRN EN ISO 18122:2015*
LHV	*HRN EN ISO 18125-1:2017*
UHV	*HRN EN ISO 18125-1:2017*
Sulphur	*HRN EN ISO 16994:2015*
Carbon	*HRN EN ISO 16948:2015*
Hydrogen	*HRN EN ISO 16948:2015*
Nitrogen	*HRN EN ISO 16948:2015*
Oxygen	*HRN EN ISO 16948:2015*

HEP Generation Ltd. in Croatia. Table 1 contains the analysed parameters and applied test methods.

The grass is a lignocellulosic biomass mainly composed of cellulose, hemicellulose and lignin (Paul and Dutta, 2018). Determining the elemental composition of dried grass samples, theoretical chemical oxygen demand ($COD_{theoretical}$) of each sample could be calculated. Grass has been summarised as a molecule with the following empirical formula: $C_aH_bO_cN_d$ (Gerike, 1984), where *a*, *b*, *c* and *d* present a number of carbon, hydrogen, oxygen and nitrogen atoms estimated by the elemental composition. When the molecular formula of grass samples has been estimated, the $COD_{theoretical}$ could be calculated as (Koch et al., 2010):

$$COD_{theoretical} = \frac{16(2a + 0.5(b - 3d) - c)}{12a + b + 16c + 14d}\left[\frac{kg_{O_2}}{kg_{C_aH_bO_cN_d}}\right] \quad (1)$$

As the calculation of the $COD_{theoretical}$ is independent of their digestibility and due to the presence of lignin which is not readily digestible, the real COD is always lower compared to the theoretical one.

Metals in the residue grass have been further analysed due to the challenges they might present when digestate from the AD is used as a fertiliser (Fermoso et al., 2015). The analysis of heavy metals presence in the residue grass has been conducted at the School of Public Health “Andrija Štampar” in Zagreb, Croatia. The following metals have been analysed: lead (Pb), cadmium (Cd), mercury (Hg), nickel (Ni), manganese (Mn), zinc (Zn), iron (Fe) and copper (Cu). The applied test method for all metals was *SOP-262-053 Edition 01* and the investigation technique *AAS; ICP-MS*.

2.3. Feedstock preparation

The following substrates have been used for the analysis: residue grass from the uncultivated land (RG1), residue grass from the riverbank (RG2), residue grass from the highway verge (RG3), maize silage collected from the biogas plant (MS) and cattle slurry collected from a small farm (CS).

The residue grass has been collected as described in Section 2.1, and further, it has been chopped into smaller pieces of approx. 3–6 cm in length. The inoculum and maize silage were collected 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 the municipality of Šentilj. Once collected, inoculum and cattle slurry have been filtered through a coarse filter to remove large particles and to improve the homogeneity in the reactors. All the substrates have further been dried in five parallels in an oven at 105 °C until constant weight to determine the average total solids (TS) of each substrate.

2.4. Experimental setup

Anaerobic digestion has been performed in 250 mL batch reactors for 42 days in a heated bath. The temperature in the heated bath was maintained with SC 100 immersion circulator (Thermo Scientific™) at 39 °C which is in the mesophilic range. Filter flasks for vacuum use (Witeg) have been used as reactors and were sealed with silicone cream/PTFE septa (La-Pha-Pack) to maintain anaerobic conditions.

All the samples have been prepared based on the average dry matter (DM) content of samples in triplicates. In total, 9 g of total solids (TS) has been added to each reactor. 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%. Each filter flask was filled to a working volume in reactors of 150 g. Different types of residue grass have been placed in reactors as mono-substrates for anaerobic digestion (MRG1: residue grass from the uncultivated land, MRG2: residue grass from the riverbank and MRG3: residue grass from the highway verge). For comparison with residue grasses, maize silage has been analysed as a mono-substrate for anaerobic digestion (MMS).

Furthermore, riverbank grass and maize silage have been added as a co-substrate with the animal slurry in the 1:1 ratio based on a dry mass (C1 and C5). Additionally, residue grass from the riverbank was mixed with maize silage at different ratios on dry basis (C2 - 0.75:0.25, C3 - 0.5:0.5, C4 - 0.25:0.75) together with animal slurry in the 1:1 ratio to investigate if the grass could be an alternative substrate for food-competitive maize silage in the actual biogas plants. For all the batch assay the ratio between inoculum and substrates for anaerobic digestion was 1:1. Finally, the blank assays containing only inoculum and medium (IN) were set to subtract biogas and methane production in substrate assays. The setup of samples on TS basis is shown in Table 2.

After the addition of substrates and medium, and sealing the flasks, the reactors were flushed with inert argon gas 4.8 (Messer Group GmbH) for about 30 s to achieve anaerobic conditions. During anaerobic digestion, biogas production was measured daily, and bottles were hand-mixed daily for approximately 20 s. Biogas yield was measured by a water displacement method. Methane and carbon dioxide compositions in biogas were measured five times during the process (once a week) by the gas chromatograph Varian CP4900 using argon and helium as carrier gases and were recorded on a personal computer using Galaxie Workstation software. Twice a week around 3 mL of samples were removed from the reactors using a 10 mL syringe fitted with a needle and transferred to 15 mL vials to analyse pH (Smonkar et al., 2017). pH was measured using a wireless pH sensor (Pasco) which was connected to a tablet computer via Bluetooth and recorded via the SPARKvue app. After the analysis, the samples were returned to the flasks. The schematic of the batch digester and the biogas collecting apparatus is shown in Fig. 1.

Table 2
Batch assay setup of samples on TS basis [g].

Reaction mixture	Inoculum	Residue grass	Maize silage	Cattle slurry
MMS	4.500	/	4.500	/
MRG1	4.500	4.500	/	/
MRG2	4.500	4.500	/	/
MRG3	4.500	4.500	/	/
C1	4.500	2.250	/	2.250
C2	4.500	1.687	0.563	2.250
C3	4.500	1.125	1.125	2.250
C4	4.500	0.563	1.687	2.250
C5	4.500	/	2.250	2.250
IN	4.500	/	/	/

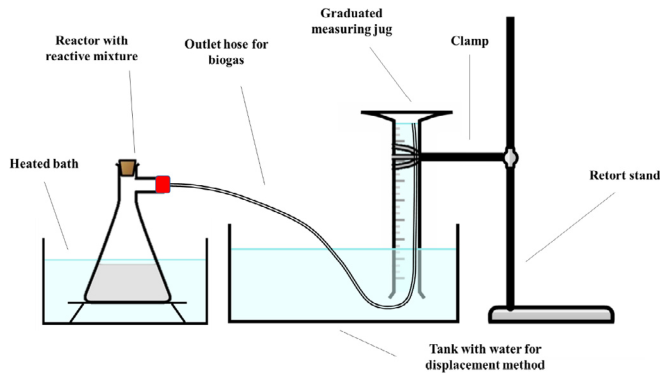

Fig. 1. Laboratory experimental set-up for anaerobic digestion.

2.5. Anaerobic Digestion Model No. 1

The ADM1 was published in 2002 by the IWA Task Group for mathematical modelling of anaerobic digestion (Page et al., 2008). The model is highly complex and includes 19 chemical and biological conversion processes with 24 dynamic state variables. Simulations and parameter estimation procedures have been conducted in Aquasim 2.0. The values of parameters used in the calculation have been adopted from literature (Batstone et al., 2008). The set of sensitive kinetic parameters in the ADM1 for the grass degradation has been chosen and presented in Table 6 in Section 3.3. These parameters have been estimated and fitted to the degradation of grass using the experimental data recorded in the laboratory.

2.6. Life Cycle Assessment (LCA) study

The Life Cycle Assessment (LCA) of the biogas production was conducted according to ISO 14040/14044 standards (International Standards Organization, 2006a, 2006b) using SimaPro v7.3.3 software. The study aimed to estimate and compare the environmental effects of the biogas production from co-digestion of riverbank grass with cattle slurry and maize silage in mass ratios presented in Table 2 and its usage in combined heat and power plant.

The system boundary includes all the processes regarding maize silage and grass collection and transportation, production of biogas in the anaerobic digestion plant and co-generation of heat and electricity in combined heat and power plant. Three different grass types (grass from the uncultivated land area, riverbank grass and verge next to the highway) were collected from uncultivated lands. The grass is assumed to be mowed and formed into round bales of 175 kg of DM each and transported to an AD plant, where a transport distance of 50 km has been assumed.

The functional unit for this study was defined as the production of "1 kWh of useful energy "(heat and electricity). The impact assessment methods selected were Impact 2002+ (Jolliet et al., 2003), the method that evaluates several midpoint categories grouped in four damage categories: Human health, Ecosystem quality, Climate change and Resources, and Global Warming Potential (GWP) calculated over 100 y time horizon (GWP100).

The data used in the study regarding the grass and maize silage quality and the biogas production by anaerobic digestion were obtained from laboratory analyses. All other data have been obtained from Ecoinvent v2.2 (Frischknecht et al., 2007) database. The results of the LCA analysis are shown in Section 3.4.

3. Results and discussions

In this section, the results from the residue grass characterisation and the batch AD process are presented. The results of the ADM1 are further shown which provide the view of kinetic parameters in the AD and show the comparison between the experimental and predicted behaviour of the process. In the end, the results of the conducted LCA provide the environmental impacts associated with a grass application in anaerobic digestion.

3.1. Residue grass characterisation

The results of the grass yield determination, the length of stems and the chemical composition of the examined fresh and dry grass are shown in Table 3.

Field measurements have shown that the greatest yield of fresh grass is present for the riverbank grass RG2. Other two samples have shown similar fresh grass yield, where the yield for RG3 appeared to be a bit higher compared to RG1. At the same time, by using the moisture content in grass samples, the yield of dry matter on grasslands is similar for RG2 and RG3. The higher moisture content of grass sample RG2 compared to samples RG1 and RG3 can be explained by the fact that the river bank area is occasionally flooded.

The analyses of residue grass types have shown significant differences in proximate parameters when expressed over the fresh matter. On the other side, when parameters were expressed on a dry basis, the values of proximate parameters of three grass samples (RG1, RG2 and RG3) were more similar. The reason for such phenomenon lies in the fact that all grass samples have shown significant variations in moisture contents. As expected, the highest moisture content has been determined for riverbank residue grass, grown in the partially flooded area. On the other side, residue grass collected on the highway verges has shown the lowest dry matter content, probably because it grows on the sloping terrain, where water drains more easily compared to the flat riverbank terrain.

The results from the ultimate analysis of grass samples for all elements except sulphur showed to be very similar for all the examined grass samples. Deviations in the term of sulphur content could be due to different positions of grasslands and the soil type on which the examined grass grows. Higher sulphur contents in residue grasses from the riverbank and highway verge are due to the sulphur presence in the Sava River (Kanduč and Ogrinc, 2007) and the uptake of sulphur dioxide emissions from vehicles by plants (WHO Regional Office for Europe, 2000).

The results of the metal presence analysis have shown that metal presence is the highest for the grass collected on the highway verges (RG3). Large traffic volumes and consequently high vehicle pollutant emissions are the probable cause. The grass from the uncultivated land has also shown the relatively high presence of heavy metals. The reason for such a trend could be found in the fact that the uncultivated land is located near the state road with a relatively high traffic concentration. Current studies of the presence of metals in roadside grass have been successfully conducted in Denmark (Meyer et al., 2014), the UK (Delafield, 2006), and Northern Germany (Werner, 2010). The differences in the results of the metal presence of roadside grass indicate that their presence is primarily a function of the traffic density and past activities in that area.

The lowest presence of heavy metals was found in the grass samples collected from the riverbank of the Sava River. Although the riverbank grass has shown the lowest share of heavy metals, the data were not drastically lower compared to the other grass samples, except for the iron presence. As the Sava riverbank is

Table 3
Results from field measurements, proximate and ultimate analysis and heavy metal presence analysis of residue grass, fresh (dry) matter basis.

Characterisation	Parameter	RG1	RG2	RG3
Field measurements	Average yield [kg/m^2]	0.74 (0.14)	1.90 (0.26)	1.01 (0.23)
	Average stems length [m]	0.28	0.68	0.49
Proximate analysis	Moisture [%]	80.9 (/)	86.3 (/)	77.5 (/)
	Ash [%]	2.0 (10.4)	1.6 (11.2)	1.9 (8.4)
	LHV [MJ/kg]	1.48 (18.08)	0.25 (17.23)	2.07 (17.61)
	UHV [MJ/kg]	3.69 (19.34)	2.53 (18.45)	4.24 (18.85)
Ultimate analysis [%]	Carbon	8.9 (47.1)	6.3 (44.7)	10.4 (46.2)
	Hydrogen	1.1 (5.8)	0.8 (5.6)	1.3 (5.7)
	Nitrogen	0.54 (2.84)	0.31 (2.18)	0.46 (2.03)
	Oxygen	8.5 (44.2)	6.3 (47.2)	10.3 (45.9)
	Sulphur	0.017 (0.089)	0.039 (0.278)	0.033 (0.146)
Metal presence analysis [mg/kg]	Lead	0.019 (0.10)	0.010 (0.07)	0.081 (0.36)
	Cadmium	0.002 (0.01)	0.001 (0.01)	0.002 (0.01)
	Mercury	0.004 (0.02)	0.003 (0.02)	0.005 (0.02)
	Chromium	0.124 (0.65)	0.064 (0.47)	0.173 (0.77)
	Nickel	0.145 (0.76)	0.095 (0.69)	0.196 (0.87)
	Manganese	1.459 (7.64)	0.486 (3.55)	1.928 (8.57)
	Zinc	1.119 (5.86)	0.682 (4.98)	2.520 (11.20)
	Iron	10.390 (54.40)	2.617 (19.10)	21.060 (93.60)
	Copper	0.711 (3.72)	0.393 (2.87)	1.024 (4.55)

occasionally flooded (Gilja et al., 2010), heavy metals from the river accumulate in the soil and grass. As the Sava River springs in Slovenia where it passes through an area that has been strongly industrialised in the past, the presence of heavy metals in the river is not unexpected. Several mines, car, chemical and pharmaceutical industries, as well as the nuclear plant in Slovenia have contaminated the river in the past (Žibret and Gosar, 2017). The past activities related to mining in that area have thus caused significant pollution of the Sava River and its banks.

Table 4 further presents the estimated empirical formula of grass samples and theoretical oxygen demand, determined by Equation (1).

The range of the theoretical oxygen demand of grass according to the chemical composition is limited between 1.2 ÷ 1.6 kgO_2/kgTS (Koch et al., 2010). The results of this study are fluctuating around the lower limit. RG2 sample has shown the lowest theoretical oxygen demand, due to the low content of oxidable compounds and higher oxygen content, in comparison to the other two samples. An important factor for anaerobic digestion, carbon to nitrogen ratio (C/N), has the following values: 16.6:1 (RG1); 20.5:1 (RG2) and 22.8:1 (RG3). It has been determined that the grass show C/N values between 10:1 to 25:1 (Steffen et al., 1998). Ultimate analysis has given valuable data which show that the residue grass collected on different grasslands has the potential to serve as feedstock in anaerobic digestion.

Significant yield, favourable biodegradability and low content of impurities indicate that the use of residue grass could be attractive in the bioenergy production.

Table 4
Estimated empirical formula and theoretical oxygen demand of the analysed grass samples.

Parameter	RG1	RG2	RG3
a	19.3	23.9	26.5
b	28.3	35.6	38.9
c	13.6	19.0	19.8
d	1.0	1.0	1.0
$COD_{theoretical}$	1.23	1.13	1.19

3.2. Laboratory batch test

In this study, the stress has been put on the examination of the gas phase (biogas) because of organic matter degradation. The results presented in this section give the view of the generated biogas and biomethane quantity expressed regarding the biochemical biogas potential (BGP) and biochemical methane potential (BMP). Also, the pH values of reaction mixtures (digested substrates) have been monitored over time. The impact of substrate properties on the pH value in anaerobic digestion is shown in Fig. 2 where the average values for each sample (analysis has been performed in triplicates) are presented.

Each of the pH profiles for analysed samples shows a common trend; in the initial days, the drop of pH values occurred due to the generation of acids, and after the rise of pH values was observed due to degradation of acids and the biogas generation. All grass mono-digestion samples, shown in Fig. 2 a), have shown a similar behaviour of the pH values over time; only the MRG2 sample has shown a little bit lower pH values compared to others. The pH values for mono-digestion of grass silage with the inoculum ratio of 1:1 were in the range between 7.31 and 8.00. The results of the conducted experiments were in line with the previous studies (Abu-Dahrieh et al., 2011), with some slight deviations that could have been the result of different substrate and inoculum type. Mono-digestion of maize silage (MMS), see Fig. 2 a), has shown much lower pH values compared to grass samples (with a minimum of 6.5 on the 8th day of the AD). That resulted in a significant decrease in the biogas production after five days of operation. As methanogenesis and thus the biogas production is the most efficient in the pH range between 6.5 and 8.2 (Mao et al., 2015), in order to avoid inhibitory effects, the pH value was raised when it reached the value close to 6.5. Sodium hydroxide (10 mL of solution with pH of 13) has been added on the 8th day of the AD to each parallel of MMS sample. After the addition of a strong base, a significant rise of the pH to approximately 7.7 has occurred, as shown in Fig. 2 a). After a few days, the process returned to the usual production of biogas.

Co-digestion samples, shown in Fig. 2 b), have not shown inhibitory effects because the animal slurry serves as a buffer and in that way controls the pH in the system and prevents the occurrence

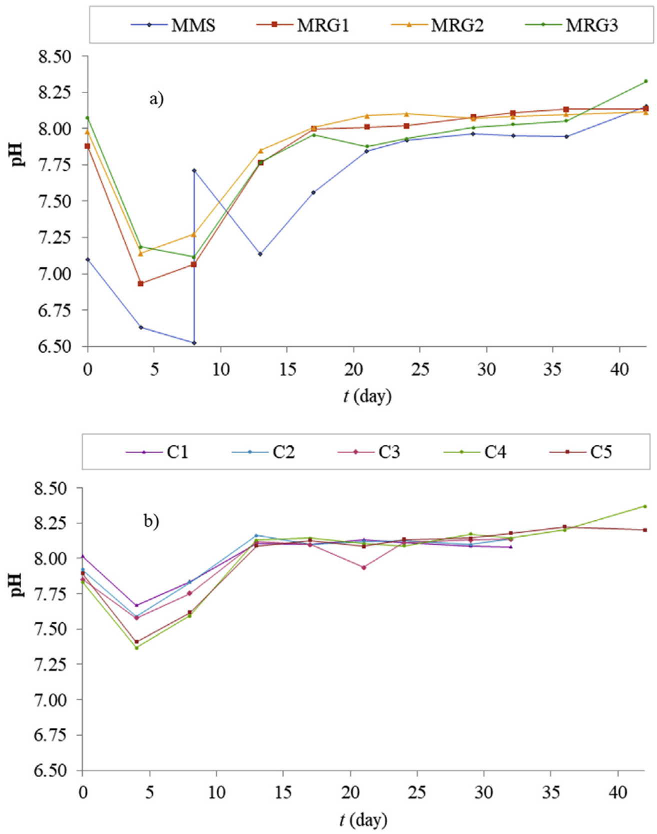

Fig. 2. Profiles of pH values in digested substrates during a) mono- and b) co-digestion.

of inhibition in the process (Husted and Husted, 1995). The missing data for the samples C3, C4 and C5 after the 31st day of operation are the result of removing the flask content from the reactor when the biogas production stopped.

Table 5 shows average data on BGP and BMP of the analysed samples after 40 days of operation under mesophilic conditions.

All grass samples (MRG1, MRG2 and MRG3) have shown both lower BGP and BMP compared to the mono-digestion of maize silage (MMS), which was expected. The riverbank grass (MRG2) has shown the lowest potential for biogas and biomethane production, which could be related to the lowest COD value as shown in Table 4. Also, the higher COD value-the higher BGP and BMP trend has been observed for the grass samples RG1 and RG3. Even though the sample RG2 has shown the lowest production of biogas, it has been selected for further analysis in co-digestion tests with maize silage and cattle slurry since it has shown the highest yield on the grasslands (Table 3). Therefore, the potential of replacing the part of maize silage by riverbank grass has been investigated in the samples C1 to C5. The results point to the expected situation, as the share of maize silage in the feedstock increases, both increase the BGP and BMP. In general, it can be stated that the riverbank grass gives the lower quantity of the biogas compared to maize silage. At the same time, it is non-competitive with food production, and as a residue material it can be cheaper feedstock compared to maize silage, and thus it could reduce the operating cost of biogas plants. In terms of the environmental impacts of residue grass application in the biogas production at larger scale, the results are presented in Section 3.4.

3.3. ADM1 model predicted data for gas phase in grass mono-digestion

Substrate parameters for ADM1 have been based on the previous research (Koch et al., 2010) with the following composition assumed: proteins (f_Pr_Xc) = 0.187; lipids (f_Li_Xc) = 0.033; carbohydrates (f_Ch_Xc) = 0.401, and inerts (f_Xi_Xc) = 0.379. To estimate the sensitive kinetic parameters of grass degradation, the following recorded data have been used: methane and carbon dioxide content in biogas and the biogas production for grass mono-digestion sample RG2 shown in Table 6.

In the parameter estimation procedure, it is important to find the optimal set of parameters for a model structure that will result in a good data fit. The set of parameters shown in Table 6 includes the hydrolysis step, as it has been recognised as an important step in the degradation of lignocellulosic biomass. Other parameters have been selected due to the following facts; acetate degrades directly to methane in the methanogenesis step, and hydrogen is a compound in anaerobic degradation that is generated in the hydrolysis and acetogenesis step, but at the same time consumed by bacteria in the acidogenesis and methanogenesis step. The results of the parameter estimation procedure show that both disintegration and hydrolysis steps for lignocellulosic biomass are slower compared to the default values in the model, which was expected. Furthermore, for the degradation of acetate default and the estimated value of half-saturation constants (K_S) do not differ significantly, but the estimated kinetic parameter for the Monod maximum specific uptake rate constant (k_m) is significantly lower compared to the default value. Combined, the model assumes that in the methane generation from degrading acetate has a lower rate compared to the default assumption. On the other side, both higher estimated values of half-saturation constants and Monod maximum specific uptake rate constant in comparison to the default values cannot point to the conclusion whether the hydrogen uptake, in general, has higher or lower rate. Using the estimated parameters shown in Table 6, the share of methane in the biogas and the BGP values have been estimated for all grass samples as shown in Table 7. The ADM1 model considers that the biogas is composed of methane, carbon dioxide and hydrogen (Batstone et al., 2002). The laboratory measurements of the biogas composition give the share of methane and carbon dioxide. Due to the fact that the hydrogen share in the biogas is typically measured in ppm (Gaida, 2014), the assumption that the biogas is hydrogen-free has been made. Therefore, all the results for measured and estimated data are fitted to 100% content of methane and carbon dioxide in biogas.

The highest methane content in biogas has been recorded for mono-digestion of the grass sample RG1 (MRG1) – grass collected on the uncultivated land. As it is shown in Table 5, MRG1 exhibits also the highest BMP and BGP compared to the other grass samples (MRG2 and MRG3). To present deviations between the experimental data and ADM1 data, the relative error has been determined, as it is shown in Fig. 3.

Table 5
Measured biochemical biogas and biochemical methane potentials of the analysed samples.

Parameter	MMS	MRG1	MRG2	MRG3	C1	C2	C3	C4	C5
BGP [$Nm^3/kgTS$]	0.4744	0.4361	0.3482	0.4131	0.2888	0.3211	0.3268	0.3861	0.4029
BMP [$Nm^3/kgTS$]	0.2896	0.2750	0.1921	0.2552	0.1724	0.1965	0.1952	0.2514	0.2521

Table 6
Estimated kinetic parameters in the grass degradation.

Parameter	Initial values (default) Batstone et al. (2002) Batstone et al. (2002)	Estimated by MRG2 experimental data	Unit
k_{dis}	0.50	0.17	1/d
k_{hyd_Ch}	10	7.07	1/d
k_{hyd_Li}	10	4.31	1/d
k_{hyd_Pr}	10	6.29	1/d
k_{m_Ac}	8	1.70	$kgO_2/(kgO_2 \cdot d)$
k_{m_H2}	50	70.2	$kgO_2/(kgO_2 \cdot d)$
K_{s_Ac}	0.15	0.12	kgO_2/m^3
K_{s_H2}	$7 \cdot 10^{-6}$	$4.7 \cdot 10^{-4}$	kgO_2/m^3

Parameters shown in Table 6 present: k_{dis} – disintegration constant, k_{hyd} – hydrolysis constant k_m – Monod maximum specific uptake rate constant, K_S – half-saturation constant.

Table 7
Results of measurements of methane content in biogas and ADM1 estimated values.

Period [day]	MRG1		MRG2		MRG3	
	Measured	ADM1	Measured	ADM1	Measured	ADM1
7	38.1	38.3	42.4	37.8	38.3	38.0
16	75.9	68.7	73.8	69.7	72.6	69.3
23	76.3	74.4	73.9	74.2	72.1	74.0
31	77.0	73.6	74.6	72.2	75.6	72.8
36	77.5	70.9	75.4	69.4	75.3	70.1

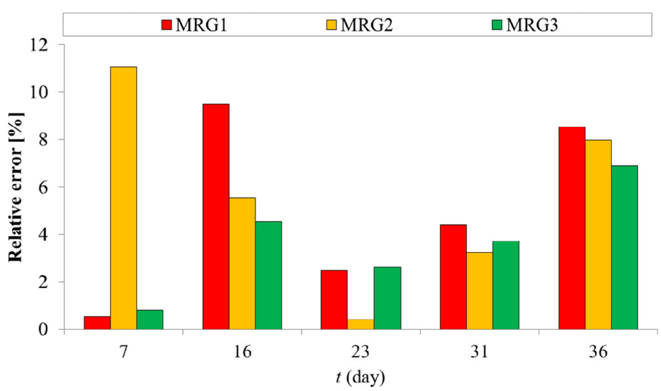

Fig. 3. The relative error values between measured and modelled methane content data in the gas phase.

There are no significant fluctuations in the methane content in biogas around the 23rd day of the AD process, while some fluctuations occurred at the start of the process and its end. To obtain a better fit of the experimental results to the model data, more frequent measurements on the gas phase should be conducted, preferably once a day or even twice a day.

The comparison between simulation and experimental data has been investigated in various studies. The threshold for a maximum relative standard error to 10% has been set (Poggio et al., 2016). Some examples of the previous studies: batch and semi-continuous anaerobic digestion of green and food waste has been performed and 10 (maximum 26.4%) and 2% (maximum 9.7%) average standard errors have been obtained (Poggio et al., 2016); for batch anaerobic digestion of agro-waste it has been shown that the correlation for several types of waste is very good while for some the simulation data showed higher values than experimental data (Galí et al., 2009). In case of a semi-continuous process, the relative error has been up to 9%; anaerobic digestion of cane-molasses vinasse has been studied and a mean absolute relative error ranging from 1% to 26% has been obtained (Barrera et al., 2015).

The production of biogas predicted by the ADM1 model, expressed as BGP, is shown in Table 8.

According to the results shown in Table 8, it can be stated that the ADM1 correctly describes the production of biogas in the mono-digestion process for the RG2 sample. Since the experimental data for MRG2 have been used to estimate the kinetic parameters in the ADM1, such results were expected. On the other side, the ADM1 results of BGP for mono-digestion of the RG1 and RG3 have shown higher deviation, around 20%. Although these fluctuations appear to be significant, when modelling the phenomena in the organic system as the ones examined, then compared to the inorganic systems, the error values are higher.

3.4. Environmental impacts of residue grass application in the anaerobic digestion

The environmental impact analysis has been performed for nine analysed samples (all studied reaction mixtures except inoculum) with the ratios between substrates as shown in Table 2. For the LCA study it was assumed that the biogas produced is used for heat and electricity generation. The following two impact categories have been considered: GWP100 expressed as carbon dioxide equivalents (CO_2-eq) to indicate the effects on climate change, and a single score characterisation expressed in μPt to determine contributions of four damage categories; Resources, Climate change, Ecosystem quality and Human health. The results are shown in Fig. 4 and Fig. 5.

The results by the single score characterisation identify the ecosystem quality category as a category that makes a significant difference among all studied cases (Fig. 4). Negative results should be interpreted as an environmental benefit. Compared to maize silage, the grasses grow naturally without using any agricultural inputs and without cultivating the soil, and therefore, the results in Aquatic ecotoxicity, Terrestrial ecotoxicity and Land occupation (all are part of the Ecosystem quality category) show beneficial effects to the ecosystem quality. Comparing only the results obtained from the processes with co-digestion (C1–C5), it can be noted that the ecosystem quality arising from the process C1 and carried out with the residue grass and cattle slurry is 3.8 times environmentally better than the process C5, carried out with the maize silage and cattle slurry. The results in terms of greenhouse gas (GHG) emissions are shown in Fig. 5.

Table 8
Results of BGP predicted by the ADM1 and error value compared to the experimental data.

Parameter	MRG1	MRG2	MRG3
BGP [$Nm^3/kgTS$]	0.3578	0.3515	0.3465
Relative error [%]	21.9	0.9	19.2

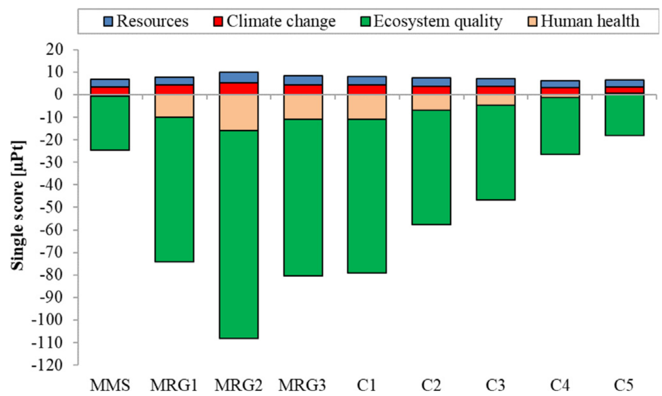

Fig. 4. The single score results of the life cycle impact assessment.

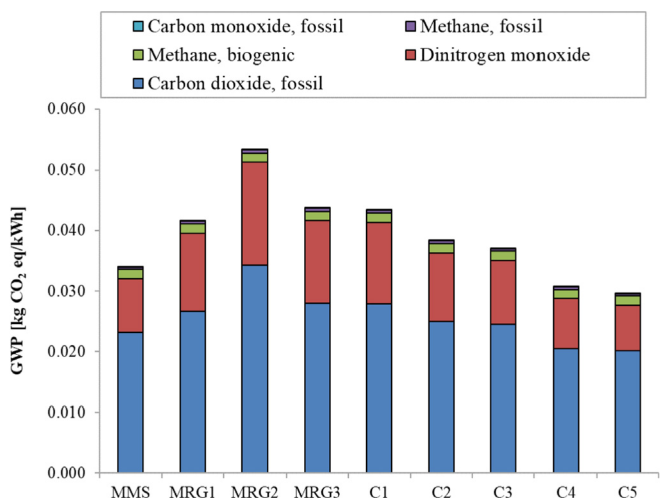

Fig. 5. Global warming potential (GWP) results.

Most of the emissions belong to carbon dioxide from fossil fuels used for agricultural machinery and grass and maize silage transportation. GHG emissions related to grass collection are the result of quite high energy inputs (fossil fuels) for collecting and baling of grass. Compared to the GHG emissions from maize silage, all studied grass types have lower biogas yield potential which increases the emissions for transportation since more grass needs to be transported to the AD plant to produce the same amount of energy. For that reason, the process C1 resulted in 32% higher GHG emissions than the process C5. It should be noted that the benefit of using grass from the uncultivated lands for biogas production instead of its natural decomposition on the field, resulting in avoiding GHG emissions, was not considered in this study. Also, GHG emissions related to land use changes were not considered.

4. Conclusions

Investigations of residue grass utilisation in anaerobic digestion have been successfully carried out. Based on the grass yields and analysis of the presence of chemical compounds in grass samples on the examined grasslands it could be concluded that the position of grassland influences the grass properties and consequently behaviour during anaerobic digestion. Even though riverbank grass has shown the highest grass yield, it has also shown the lowest quality and production of the biogas, in comparison to the other two grass types. Monodigestion of maize silage has shown the greatest yield of biogas, but on the other side, it has shown that issues regarding process control exist, especially in terms of the pH regulation. Analysis of the co-digestion samples points to the conclusion that cattle slurry increases the degradation of riverbank grass residue. Co-digestion processes stopped producing biogas earlier than mono-digestion processes, after 30 days of operation instead of after 42 days. That phenomenon could be analysed in more details in further analyses.

Modelling of the gas phase in the anaerobic digestion has given the view of the rate of chemical reactions which occur during the process. Especially the first stages of digestion, disintegration and hydrolysis are attractive for further observation due to the estimated kinetics parameters. This work has shown that the disintegration and hydrolysis of biomass occur at lower rates of reactions compared to initial assumptions. The investigation has also shown the importance of knowing the feedstock composition for mathematical modelling by using mechanistically inspired model, in this study the ADM1 model.

Investigation of mono- and co-digestion processes could be extended by applying different pre-treatment methods to improve the digestion of green biomass. The LCA analysis has provided the results which should be explained carefully due to the complexity of the analysis and quality and quantity of the data that are to be used. In general, the residue grass has shown lower BMP compared to the maize silage which leads to the increase of the required quantity of grass to produce the same amount of energy as when using maize silage. The residue grass has the potential to serve as a replacement for maize silage in the production of heat and electricity, and therefore some further investigations should be aimed at the way to increase the digestibility of grass.

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Nomenclature

Abbreviations

AAS	Atomic absorption spectroscopy
Ac	Acetate
ADM1	Anaerobic Digestion Model No. 1
BGP	Biochemical biogas potential
BMP	Biochemical biomethane potential
C	Co-digestion
C/N	Carbon to nitrogen ratio
Ch	Carbohydrates
COD	Chemical Oxygen Demand
dis	Disintegration
DM	Dry matter
EROEI	Energy return on energy invested index
GHG	Greenhouse gas
GWP	Global Warming Potential
hyd	hydrolysis
ICP-MS	Inductively coupled plasma - mass spectrometry
IN	Inoculum
LCA	Life Cycle Assessment

LHV	Lower heating value
Li	Lipids
M	Mono-digestion
MS	Maize silage
Nm^3	Normalized cubic meter (for gases: 101,325 Pa and 0 °C)
OLR	Organic load rate
Pr	Proteins
RG	Residue grass
TS	Total solids
UHV	Upper heating value
VFA	Volatile fatty acids
VS	Volatile solids
Xc	Composite material
Xi	Inerts

Symbols

a	Number of carbon atoms [−]
b	Number of hydrogen atoms [−]
c	Number of oxygen atoms [−]
d	Number of nitrogen atoms [−]
f_Ch_Xc	Carbohydrates from composite material [−]
f_Li_Xc	Lipids from composite material [−]
f_Pr_Xc	Proteins from composite material [−]
f_Xi_Xc	Inerts from composite material [−]
k_{dis}	Disintegration constant [1/d]
k_{hyd}_Ch	Hydrolysis constant for carbohydrates degradation [1/d]
k_{hyd_Li}	Hydrolysis constant for lipids degradation [1/d]
k_{hyd_Pr}	Hydrolysis constant for proteins degradation [1/d]
k_{m_Ac}	Monod maximum specific uptake rate constant for acetate [$kgO_2/(kgO_2 \cdot d)$]
k_{m_H2}	Monod maximum specific uptake rate constant for hydrogen [$kgO_2/(kgO_2 \cdot d)$]
K_{s_Ac}	Half saturation coefficient of acetate [kgO_2/m^3]
K_{s_H2}	Half saturation coefficient of hydrogen [kgO_2/m^3]

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ARTICLE 3

A kinetic study of roadside grass pyrolysis and digestate from anaerobic mono-digestion

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Abstract

The aim of this research is to evaluate the thermogravimetric behaviour of roadside grass and its digestate obtained from mesophilic anaerobic mono-digestion by quantifying its impacts on biomass composition and properties. Thermogravimetric measurements were conducted in a laboratory furnace under nitrogen flowrate of 100 mL/min in the temperature range from 35 to 800°C at five different heating rates of 2.5, 5, 10, 15 and 20°C/min. Friedman and Kissinger-Akahira-Sunose differential and integral isoconversional models were applied to determine the distributions of activation energies and modified pre-exponential factors per reacted mass (degree of conversion). The investigation demonstrated that anaerobic digestion of roadside grass can be used to generate biochar-richer material (with significantly greater yield of final residues after pyrolysis) with less energy required for subsequent pyrolysis in comparison with raw roadside grass.

Keywords:
Roadside grass; roadside grass digestate; anaerobic digestion; pyrolysis; kinetic study; thermogravimetric measurements; isoconversional models

1. Introduction

Grass is a sustainable source of lignocellulosic material which can be cultivated on non-arable lands, making it non-competitive with other crops for food production (Rodriguez et al., 2017). The location of the area where grass is collected impacts its chemical composition and further application. Grass collected on non-arable lands has been shown to be an abundant and environment-friendly source of material to produce bioenergy in the form of biogas (Bedoić et al., 2019). Another efficient and environmentally attractive process for converting biomass and different types of waste to energy products is pyrolysis (Campuzano et al., 2019). Besides anaerobic digestion and pyrolysis, biomass can be converted to energy and bioproducts through combustion, gasification and biochemical processing (Akhtar et al., 2018).

Pyrolysis is one of the most thoroughly researched thermochemical conversion processes of biomass into valuable hydrocarbon and alternative fuels (Dhyani and Bhaskar, 2018). Slow pyrolysis producing charcoal has been successfully utilised for waste-to-energy and waste-to-liquid purposes (Rostek and Biernat, 2013). Pyrolysis can be studied under different atmospheric conditions (inert or reactive) that affect the complexity of the thermal behaviour of feedstock (Mikulcic et al., 2019). Gaseous products that appear during pyrolysis contain variable chemical constituents based on the feedstock used (Stančin et al., 2019).

Pyrolysis of biomass and waste is widely examined with thermogravimetric analysis (TGA) together with kinetic studies (Zhang et al., 2017). To evaluate the effects of different waste materials on pyrolysis, various experiments have been performed using the TGA (Oyedun et al., 2014). Thermochemical processes (pyrolysis, gasification and combustion) of different types of lignocellulosic biomass have shown that for describing their kinetics, different approaches/models are suggested (Senneca, 2007). Generally, there are two types of kinetic methods which have been used for the description of biomass and waste pyrolysis kinetics, model-fitting and isoconversional or model-free methods (Jain et al., 2016).

Isoconversional methods are more popular in the analysis of biomass pyrolysis kinetics than model-fitting methods (Burnham and Dinh, 2007). The advantages of isoconversional methods include computation of kinetic parameters without modelling assumptions (Ramajo-Escalera et al., 2006) and better suitability for more complex and multiple step reactions (Sánchez-Jiménez et al., 2013). Isoconversional methods can be divided into differential and integral methods (Wang et al., 2017). The Friedman (FR) differential isoconversional model is among the most widely used (Burnham and Dinh, 2007). It has shown adequacy and high matching to experimental data in the pyrolysis of corn stalk (Cai et al., 2018), and has been used to describe the kinetics of Miscanthus grass pyrolysis (Cortés and Bridgwater, 2015). Kissinger-Akahira-Sunose (KAS) and Ozawa-Flynn-Wall (OFW) integral isoconversional models have been applied in the pyrolysis of different grass types, such as Para grass (Al Ayed et al., 2016) and Camel grass (Mehmood et al., 2017).

Product yields by pyrolysis of lignocellulosic biomass can be improved by pretreatment, such as by the application of heat, chemicals or different pretreatment times (Wang et al., 2018) or by integration of aerobic and anaerobic digestion (Juchelková et al., 2015). Pyrolysis is an attractive option for the treatment of digestate due to its seasonal applicability as a fertilizer (Losak et al., 2014), and in cases when digestates contain heavy metals, pathogens and other toxic compounds (Wiśniewski et al., 2015). Pyrolysis of digestate is an interesting option because of the benefits it confers (Li et al., 2017) such as reduction of weight and volume of digestate and elimination of pathogens and odour (Nansubuga et al., 2015). As biochar from digestate can effectively be used for various applications, a combined anaerobic digestion – pyrolysis process might be beneficial because of the low economic value of digestate (Egieya et al., 2019); thus, subsequent pyrolysis of digestate offers an opportunity to improve the profitability of biogas production processes (Egieya et al., 2018).

Digestate has recently attracted significant attention as a potential feedstock for pyrolysis (Wei et al., 2018). Various kinetic studies have been performed on the combined anaerobic digestion - pyrolysis process for biomass/waste material with its digestate, for corn stover and its digestate (Zhang et al., 2017), for food waste and its digestate (Opatokun et al., 2015), and for different organic solid wastes (sewage sludge, food waste, vinasse and cow manure) and their digestates (Li et al., 2017).

This paper presents the continuation of the previous experimental study on anaerobic digestion of two types of roadside residue grass, residue grass from the uncultivated land (next to minor road) and from the highway verge (Bedoić et al., 2019). This research contains two novel scientific contributions, such as the study on pyrolysis of residue roadside grass and its digestate and the study on determination of degraded organic matter during anaerobic process based on the analysis of thermogravimetric curves. Estimation of the organic matter degradation is studied in relation to biochemical biogas potential of grasses, which was determined previously (Bedoić et al., 2019). Two isoconversional models, differential FR model and integral KAS model are used to quantify the impacts of anaerobic digestion of two types of roadside residue grass on parameters of pyrolysis kinetics. Verification of the applied models based on the experimental data and estimated kinetic parameters is finally conducted with the aim to reconstruct the kinetic behaviour of studied feedstocks in the pyrolysis. The study determines the share of compounds in two types of roadside grass and in its digestates without using any chemical solvents and performs the research on the energy recovery of residue grass.

2. Materials and methods

In this section, we present an overview of the methods applied, along with a brief description of TGA; two further linear isoconversional models used in the study are introduced. Our research is linked with a previous investigation on anaerobic digestion of different types of residue grass (Bedoić et al., 2019). Regarding residue grass sampling, preparation and characterisation, and laboratory results from anaerobic digestion, readers are referred to Bedoić et al. (2019).

2.1. Substrates used in the study

We focused on the use of two roadside grass types. The first was collected on the verge next to a minor road (RG-MR), while the second was collected on the verge next to a highway (RG-H). In our previous study (Bedoić et al., 2019) they were marked as RG1 (now RG-MR) and RG3 (now RG-H). Both grasslands are located near Zagreb, the capital city of Croatia, on locations not suitable for food and/or feed purposes. Nine samples were collected on each of the grasslands examined, which were then stored in plastic bags in a vacuum in a freezer at −15°C (Bedoić et al., 2019).

The proximate and ultimate analysis and analysis of heavy metals presence of residue grasses have been performed. The results, including results from field measurements, are presented in Bedoić et al. (2019). Both types of grass (see RG1 and RG3 in Table 1 by Bedoić et al., 2019) showed similar chemical composition; RG-H exhibited higher yield on both a fresh and dry basis, longer stem length, lower moisture and ash contents, higher heating values and higher carbon content, compared to RG-MR. Significant differences were obtained in terms of heavy metal concentrations, where RG-H showed much higher values than RG-MR. On dry basis, RG-H sample contains 93.60 mg/kg of iron, 11.20 mg/kg of zinc, 8.57 mg/kg of manganese and 4.55 mg/kg of copper. On the other side, RG-MR sample contains on dry basis 54.40 mg/kg of iron, 5.86 mg/kg of zinc, 7.64 mg/kg of manganese and 3.72 mg/kg of copper. Other elements like lead, cadmium, mercury and nickel have shown lower concentrations, below 1 mg/kg of dry grass. As expected, higher concentrations of metals were detected for the grass collected in the intense traffic area (highway verge).

For this study, raw grass samples were reduced into smaller pieces of approx. 3–6 cm in length and were dried in a laboratory oven at 105°C until constant weight before use.

Besides the two types of roadside residue grass, their digestates obtained by mono-digestion were used as substrates for the analysis. For anaerobic digestion, substrates were chopped into smaller pieces of approx. 3–6 cm in length. They were placed in 250 mL batch reactors in triplicate together with inoculum, where the ratio between inoculum and grass for anaerobic digestion was 1:1 on a dry basis. In total, 9 g of total solids (TS) were added to each reactor, and the dry matter in each reactor was 6%. Anaerobic digestion was performed for 42 days at 39°C. During the process of anaerobic mono-digestion no inhibition could be observed, despite relatively high concentration of heavy metals in the studied grass samples.

The digestates, RGD-MR - digestate of roadside grass collected on the verge next to the minor road (marked as MRG1 in Bedoić et al., 2019), and RGD-H – digestate of roadside grass collected on the verge next to the highway (marked as MRG3 in Bedoić et al., 2019) were used for this investigation. Before performing TGA analysis, digestates were dried in a laboratory oven at 105°C until constant weight.

More details regarding the residue grass substrates and anaerobic digestion process can be found in Bedoić et al. (2019).

2.2. Thermogravimetric analysis

Thermogravimetric measurements of dried samples (RG-MR, RG-H, RGD-MR and RGD-H) were conducted using a TA Instruments Q500 at the heating rates β_i of 2.5, 5, 10, 15 and 20°C/min at a temperature range from 35 to 800°C under a steady flow of nitrogen (100 mL/min) to maintain an inert atmosphere. Samples weighing approximately 10 mg were used for the analysis. Three replicates were run for each sample, and the average value is reported. TGA data (mass weights and derivative mass weights) were recorded with respect to temperature and time for the five heating rates considered.

2.3. Analysis of hemicellulose and cellulose degradation

To calculate the degradation of hemicellulose (*hc*) and cellulose (*c*) in residue grass samples – $X_{\mathrm{RG}}(hc+c)$ (%) based on the analysis of thermogravimetric curves of grass and digestate, the following relation was used:

$$X_{\mathrm{RG}}(hc+c) = \frac{\bar{x}_{\mathrm{RG}}(hc+c) - \bar{x}_{\mathrm{RGD}}(hc+c) \cdot \dfrac{\bar{x}_{\mathrm{RG}}(l)}{\bar{x}_{\mathrm{RGD}}(l)}}{\bar{x}_{\mathrm{RG}}(hc+c)} \times 100 \tag{1}$$

where $\bar{x}_{\mathrm{RG}}(hc+c)$ is the average share of hemicellulose and cellulose in residue grass sample (before anaerobic digestion), $\bar{x}_{\mathrm{RGD}}(hc+c)$ is the average share of hemicellulose and cellulose in digestate sample (after anaerobic digestion), $\bar{x}_{\mathrm{RG}}(l)$ is the average share of lignin in residue grass sample (before anaerobic digestion) and $\bar{x}_{\mathrm{RGD}}(l)$ is the average share of lignin in digestate sample (after anaerobic digestion). The term "average share of components" is related to the arithmetic mean of a component's share determined at the selected heating rates. Factor $\dfrac{\bar{x}_{\mathrm{RG}}(l)}{\bar{x}_{\mathrm{RGD}}(l)}$ is introduced in the calculation since the relative share of components during anaerobic digestion changes.

2.4. Analysis of kinetic parameters

Two linear isoconversional models (Li et al., 2017) were used for the determination of kinetic parameters of roadside grass and roadside grass digestate pyrolysis, as shown in Table 1. In Table 1 β_{i} is the heating rate (°C/min), α is the degree of conversion (/ or %), T is the temperature as a general parameter of process (°C or K), $(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,\mathrm{i}}$ is the conversion derivative per temperature at the given degree of conversion and heating rate, $A_\alpha f(\alpha)$ is a modified pre-exponential factor in the Friedmann isoconversional model (1/s), $A_\alpha/g(\alpha)$ is the modified pre-exponential factor in the Kissinger-Akahira-Sunose isoconversional model (1/s), E_α is the activation energy (J/mol), $T_{\alpha,\mathrm{i}}$ is the temperature at the given degree of conversion and heating rate required for model application (K), and R is the universal gas constant (8.314 J/(mol·K)).

Table 1: Linear isoconversional kinetic models applied on the pyrolysis of roadside grass and roadside grass digestate

To conduct a kinetic analysis using the models in Table 1, it is necessary to determine the degree of conversion at a certain temperature $\alpha(T)$, as:

$$\alpha(T) = \frac{m_0 - m(T)}{m_0 - m_f} \tag{2}$$

where m_0 is the mass at temperature T_0, $m(T)$ is the mass at temperature T, and m_f is the mass at the final temperature T_f. Since biomass sample contains retained water and could also contain light volatile compounds, the first stage is a dehydration stage. Pyrolysis occurs in the second and third stages, which are called active and passive pyrolysis. Both pyrolysis stages correspond to the decomposition of cellulose, hemicellulose and lignin. It has been reported that the dehydration stage ends at about 150°C, and pyrolysis of lignocellulosic biomass starts (Chen et al., 2013).

When applying the Friedman isoconversional model in the kinetic study of pyrolysis, it is necessary to determine the derivative conversion curve $(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,i}$. Since the curve has been reported to have many fluctuations, it is recommended to apply some smoothing tool to reduce the impact of the noisy data (Vyazovkin et al., 2011). In this study, the Moving Average of data in Excel was applied (Hogarth, 2014) to smooth the experimental derivative conversion curves.

After the degree of conversion has been determined, the calculations of parameters based on the thermogravimetric measurements follows. For the Friedman isoconversional model, at the given α, E_α and $\ln[A_\alpha f(\alpha)]$ are obtained from the slope and intercept of the plot of $\ln[\beta_\mathrm{i}(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,\mathrm{i}}]$ versus $(-1/RT_{\alpha,\mathrm{i}})$. For the Kissinger-Akahira-Sunose isoconversional model, at the given α, E_α and $\ln[A_\alpha/g(\alpha)]$ are obtained from the slope and intercept of the plot of $\ln[\beta_\mathrm{i}/T^2_{\alpha,\mathrm{i}}]$ versus $(-1/RT_{\alpha,\mathrm{i}})$.

To represent the deviations of activation energy and modified pre-exponential factor (based on linear regression) at the given degree of conversion, the confidence interval has been used (Cai et al., 2018). The specific level of confidence was set at 95% to present a range of values of activation energy and modified pre-exponential factor within the selected probability (Bartocci et al., 2019).

To reconstruct the kinetic behaviour of pyrolysis of the selected feedstocks, the average values of kinetic parameters at the given degree of conversion are used.

3. Results and discussion

In this section, the results of our experiments of biomass pyrolysis and modelling of pyrolysis kinetics are presented.

3.1. Thermogravimetric analysis

The results of thermogravimetric analysis of roadside grass (RG) and roadside grass digestate (RGD) in terms of thermogravimetric (TG) and derivative TG (DTG) curves are presented in Figure 1 for five different heating rates (β_i of 2.5, 5, 10, 15 and 20°C/min), where the temperature range is from 35 to 800°C. TG shows the loss of weight during heating, while DTG shows the first derivative of TG which indicates the main devolatilization stages more clearly (Ceylan and Kazan, 2015). TG curves for analysed samples (RG-MR, RG-H, RGD-MR and RGD-H) show steady or decreasing trends with increased temperature, while the changes in TG curves (weight loss) are shown as peaks in DTG curves.

Figure 1: TG-DTG curves of RG and RGD samples at different heating rates: a) 2.5 °C/min, b) 5 °C/min, c) 10 °C/min, d) 15 °C/min, e) 20 °C/min

All the samples underwent three main stages of weight loss, which indicate the processes of dehydration, active and passive pyrolysis (Slopiecka et al., 2012). The stages are the drying, devolatilization and char formation stages (Chandrasekaran et al., 2017). In the dehydration stage, evaporation of water and light volatile compounds occurs; in the active pyrolysis stage, the degradation of hemicellulose and cellulose takes place, and in the final stage, decomposition of lignin occurs (Chandrasekaran et al., 2017). Hemicellulose and cellulose degrade at a similar temperature range (simultaneously) and thus only one peak is typically obtained in the DTG curve (Parthasarathy and Narayanan, 2014). The last stage typically shows slow continued loss of weight, as solid residue is slowly decomposed (Peng et al., 2001). The final residue at 800°C consists of biochar and ash (Peng et al., 2001).

In Figure 1 it can be seen that RG-H shows the highest peak of the DTG curve at the highest temperature at each of the applied heating rates, and exhibits a more intense peak shoulder compared to

RG-MR. Unlike the RG samples, peak shoulder in the DTG curves in the case of RGDs is not clearly visible. We assume that this is because both cellulose and hemicellulose from RG are partly degraded under anaerobic conditions, which impact the DTG curves of RGD by fading the peak shoulder. Similar observations have been reported in the analysis of food waste and its digestate pyrolysis (Opatokun et al., 2015).

According to the TG curves, all the RGDs show higher amounts of residues or lower weight loss during pyrolysis due to lower cellulose and hemicellulose content in the samples. In terms of grass samples, RG-MR shows a slightly higher yield of the final residue compared to RG-H. This result can be explained through the higher share of ash and carbon in the RG-MR sample (10.4% of ash and 47.1% of carbon, on dry basis) than in the RG-H sample (8.4% of ash and 46.2% of carbon, on dry basis) (Bedoić et al., 2019).

More detailed information regarding the mass loss intervals and characteristic temperature zones (Ye et al., 2010) of all samples is shown in Tables 2 and 3. Table 2 shows five characteristic temperature zones during different stages of decomposition of RG and RGD samples at five different heating rates. *T1* in Table 2 represents the end of the dehydration stage or the start of the biomass pyrolysis process. The active pyrolysis stage occurs at temperatures between *T1* and *T5*. This stage (stage II) can be divided into zones I and II, where zone I occurs at temperatures *T1* – *T3*, and zone II at temperatures *T3* – *T5*, with maximum weight loss at *T2* and *T4*. For more details regarding characteristic temperature zones, see (Ye et al., 2010). As mentioned previously, the upper limit of the temperature range, 800°C, is applied.

Table 2: Characteristic temperature zones during different stages of decomposition of RG and RGD samples

Table 3: Weight loss (in wt.%) during different stages of decomposition of RG and RGD samples

Results show that the dehydration stage occurs from the starting temperature to about 136 to 191°C for RG samples, and to about 137 to 189°C for RGD samples. The active pyrolysis stage is observed to be in the following temperature ranges:

- RG-MR: start from ca. 136°C (2.5 °C/min) to ca. 191°C (20°C/min), end from ca. 343°C (2.5°C/min) to ca. 396°C (20°C/min),
- RG-H: start from ca. 139°C (2.5°C/min) to ca. 191°C (20°C/min), end from ca. 356°C (2.5°C/min) until ca. 418°C (20°C/min),
- RGD-H: start from ca. 137°C (2.5°C/min) to ca. 187.5°C (20 °C/min), end from ca. 332°C (2.5°C/min) until ca. 394°C (20°C/min),

• RGD-H: start from ca. 141°C (2.5°C/min) to ca. 189°C (20°C/min), end from ca. 364°C (2.5°C/min) until ca. 415°C (20°C/min),

Table 3 shows the weight loss during different stages of decomposition for all the analysed samples for the five heating rates considered. From Table 3 it can be seen that the first dehydration stage shows slightly higher weight loss for RGD samples (ca. 6 to 8%) than for RG samples (ca. 4 to 5.5%). RG-H samples on average contain slightly more cellulose and hemicellulose, $\bar{x}_{\text{RG-H}}(hc+c)$=60%, compared to RG-MR samples, $\bar{x}_{\text{RG-MR}}(hc+c)$=56%. Since temperatures *T2* and *T3* could not be determined for the RGD samples due to the shoulder fading in DTG curves, the share of cellulose and hemicellulose is calculated by subtracting the share of moisture, lignin and final residue from the total amount (100 wt.%). Therefore, the amount of hemicellulose and cellulose in digestate samples is estimated on average, $\bar{x}_{\text{RGD-MR}}(hc+c)$=37% and $\bar{x}_{\text{RGD-H}}(hc+c)$=42%.

The degradation of lignin at the observed heating rates started at ca. 340 to 400°C in the RG-MR sample, at ca. 360 to 420°C for the RG-H sample, at ca. 330 to 390°C for the RGD-MR sample and at ca. 360 to 415°C for the RGD-H sample. The mass loss caused by lignin degradation and charring is as follows: $\bar{x}_{\text{RGD-MR}}(l)$=17%, $\bar{x}_{\text{RG-MR}}(l)$=13%, $\bar{x}_{\text{RGD-H}}(l)$=15%, and $\bar{x}_{\text{RG-H}}(l)$=12%. The differences in mass loss during the lignin degradation and biochar formation stage between RGD samples and raw RG samples are 3 and 4%, on average. Since the relative share of components during anaerobic digestion changes, this could be the reason for the measured deviations. However, estimation of the amount of lignin in samples should be taken with caution, since it was obtained by using experimental data and theoretical background related to pyrolysis of lignocellulosic biomass (Carrier et al., 2016). It has been reported that partial degradation of lignin under inert atmosphere starts at 200°C, while at 400°C it starts to be intensified (Carrier et al., 2011).

When Eq. (1) is applied, the results show that during monodigestion of RG-MR, ca. 50% of cellulose and hemicellulose was converted to biogas ($X_{\text{RG-MR}}(hc+c)$=49.5%), and in the case of RG-H, degradation of cellulose and hemicellulose is estimated at $X_{\text{RG-H}}(hc+c)$=44.0%). Degradation is similar for both grass types, which is also supported by the fact that for both, similar biochemical biogas potential values (BGP) were obtained, 0.436 Nm^3/kgTS for RG-MR and 0.413 Nm^3/kgTS for RG-H (Bedoić et al., 2019).

The results show that mono-digestion has been incomplete (49.5 and 44 % conversion of cellulose and hemicellulose). To further increase the degradability of biomass and enhance biogas production, co-digestion and addition of additives such as bio-based carbon materials (Yun et al., 2018) and accelerants such as for example urea, plant ash (Zhang et al., 2018) or steel slag (Han et al., 2019) to substrates have been recognised to be more efficient than mono-digestion (Wang et al., 2019). Similar conclusions have been obtained by thermogravimetric analysis of digested residue from aloe peel waste and dairy manure (Huang et al., 2016).

At 800°C, the average final residue yields for RG-MR and RG-H are ca. 25% and 23%. However, RGD samples have shown a higher yield of final residue at 800°C; for RGD-MR, the yield was ca. 38%, and for RGD-H, ca. 37%. Both RGD-MR and RGD-H have shown much higher yields of the final residues at 800°C than the RG feedstocks. Similar conclusions were obtained when using food waste as feedstock (Opatokun et al., 2015).

This study has shown that significant quantities of final residue (mainly biochar) are obtained from pyrolysis of roadside grass and its digestate. Biochar could have various applications, such as it could be used as an additive material for improving stability of anaerobic digestion, as an approach to carbon sequestration, in animal husbandry, as a soil conditioner, in the building sector, in treatment of drinking and waste waters and in many other applications (Schmidt, 2012). Combined anaerobic digestion – pyrolysis process from roadside grass might also improve the profitability of biogas production processes (Egieya et al., 2018).

3.2. Kinetic analysis

Thermogravimetry and isoconversional models can provide an estimation of kinetic data (activation energy and pre-exponential factor) from reaction parameters such as temperature and heating rate without estimation of reaction mechanisms (Damartzis et al., 2011). The activation energy and modified pre-exponential factors were obtained using FR and KAS methods. Their distribution for RG and RGD samples has been determined based on the performed thermogravimetric analysis data for conversions between 20 and 70% in step sizes of 5%. Degrees of conversion lower than 20% and higher than 70% are not shown because of significant fluctuations observed (especially for digestate samples), which were probably associated with the thermal behaviour of lignin (Carrier et al., 2016). In addition, verification of the applied models was performed, and average values of kinetic parameters obtained by this study were used to verify models with the experimental data.

3.2.1. Friedman (FR) model

The values of activation energy (E_α) and modified pre-exponential factor in logarithmic expression ($\ln[A_\alpha f(\alpha)]$) for pyrolysis of RG and RGD samples were obtained using the FR isoconversional model, as shown in Figure 2. The error bars in Figure 2 represent confidence intervals with a confidence level of 95%.

Figure 2: Distribution of E_α and $\ln[A_\alpha f(\alpha)]$ per the degree of conversion by means of FR model

Estimated values of E_α in the studied range of conversions vary between 160 and 600 kJ/mol for RG-MR samples, and between 170 and 380 kJ/mol for RG-H samples. Both RG samples show a slight increase in the values of E_α from $\alpha = 0.20$ to 0.30; between $\alpha = 0.30$ to 0.50, a stagnation/slight decline of E_α is shown, and after $\alpha = 0.50$, a significant increase in the E_α can be observed. Such a trend in the distribution of E_α using the FR model was also reported for corn stalk pyrolysis (Cai et al., 2018) and for miscanthus pyrolysis (Cortés and Bridgwater, 2015).

On the other hand, RGD samples have shown much lower values of E_α in the considered ranges of conversions; for RGD-MR it is between 20 and 170 kJ/mol, while for RGD-H it is between 10 and 170 kJ/mol. RGD samples show the highest E_α at the lowest value of α, and with an increase in the degree of conversion, E_α continuously declines in the case of RGD-MR, while RGD-H declines up to $\alpha = 0.45$, and then stagnation appears.

Similar trends as for E_α are observed for the change of $\ln[A_\alpha f(\alpha)]$ with the degree of conversion. The highest value of $\ln[A_\alpha f(\alpha)]$ is for RG-MR, about 110 s^{-1}, while the highest value for RG-H is around 60 s^{-1}. RGD samples show negative values of $\ln[A_\alpha f(\alpha)]$, with the lowest value around -8 s^{-1}.

To reconstruct the kinetic process using the FR model, Eq. (3) is used in the non-logarithmic form. The results of the verification process are presented in Figure 3.

Figure 3: Experimental and FR kinetic model based on E_α and $\ln[A_\alpha f(\alpha)]$ data for grass and digestate pyrolysis at 2.5, 5, 10, 15 and 20 °C/min

At all heating rates, the FR model shows high-level matching with the experimental data for RG samples. Higher fluctuations of the model compared to the experimental data are shown for RGD samples. The peaks of the curves for RG samples move to higher temperatures with an increase in heating rate. That observation is not seen for RGD samples. Furthermore, RGD samples show a wider range of temperatures in terms of the $\beta_i(d\alpha/dT)$ distribution. Since the weight loss in the active pyrolysis stage (stage II) is significantly lower for RGD samples, and the residue yield greater than for RG samples, this observation is supported by the analysis of TG curves. The kinetic parameters obtained with the FR model show a better fit for RG samples than for RGD samples. At lower heating rates of 2.5 and 5°C/min, RGD samples show a good model fit to the experimental data.

3.2.2. Kissinger-Akahira-Sunose (KAS) model

Using the KAS isoconversional model, the values of activation energy (E_α) and modified pre-exponential factor in logarithmic expression (ln[$A_\alpha/g(\alpha)$]) for pyrolysis of RG and RGD samples are obtained, as shown in Figure 4Figure 4.

Figure 4: Distribution of E_α and ln[$A_\alpha/g(\alpha)$] with the degree of conversion by means of KAS model

E_α estimated by the KAS model for RG samples in the studied range of conversions vary between 150 and 430 kJ/mol for RG-MR, and between 160 and 260 kJ/mol for RG-H samples. Similar results were obtained for the pyrolysis of Para grass (between 180 and 230 kJ/mol, (Al Ayed et al., 2016)) and Camel grass with the KAS model (between 150 and 190 kJ/mol, (Mehmood et al., 2017)). The results obtained in this study and by analyses of specific grass types show a narrower range of activation energies for specific grass types than for unclassified species of grass. On the other hand, RGD samples again show lower values of E_α compared to RG samples; for RGD-MR the range is between 30 and 170 kJ/mol, while for RGD-H it is between 20 and 175 kJ/mol. Again, RGD samples show the highest E_α at the lowest value of α. KAS modeling shows that with an increase of the degree of conversion, E_α continuously declines in the case of both RGD samples.

Similar trends with the degree of conversion as for E_α are obtained for ln[$A_\alpha/g(\alpha)$] for both RG and RGD samples. The highest value of ln[$A_\alpha/g(\alpha)$] is obtained for RG-MR, about 80 s^{-1}, while the highest value for RG-H is about 45 s^{-1}. It should be noted that modified pre-exponential factors obtained with FR and KAS models cannot be compared directly, since the expressions of functions are slightly different. RGD samples again show both positive and negative values of ln[$A_\alpha/g(\alpha)$], where the lowest value is about -5 s^{-1}.

To reconstruct the kinetic process with the KAS model, Eq. (4) is used in the non-logarithmic form. The results of the verification process are shown in Figure 5.

Figure 5: Experimental and KAS kinetic model based on E_α and ln[$A_\alpha/g(\alpha)$] for grass and digestate pyrolysis at 2.5, 5, 10, 15 and 20 °C/min

The KAS model shows matching with the experimental data for the middle temperature range of 450 to 700 K in the case of RG samples, and between 500 and 1,050 K for RGD samples. At lower temperatures, the KAS model deviates significantly from the experimental data. Again, more intense fluctuations of the model compared to the experimental data are shown for RGD samples. For all the analysed samples, the highest match of KAS model to experimental data is at the lowest heating rate (2.5°C/min). Slowly heating the samples leads to a better and more effective heat transfer to the inner layers of biomass (Mani et al., 2010). Therefore, the model results match the experimental data best at lower heating rates. Kinetic parameters obtained with the KAS model are more effective in the case of RG samples than in the case of its digestate.

4. Conclusions

The analysis of TG and DTG curves of selected feedstocks shows that estimated amount of degraded cellulose and hemicellulose in roadside grass during the AD process is around 44 to 50%. Roadside grass digestate has shown a greater yield of final residues (ca. 38%) than roadside grass samples (ca. 24%). The combined process, anaerobic digestion of roadside grass and pyrolysis of its digestate, contributes to the production of green bioenergy in the form of heat and electricity, while reducing energy requirements (activation energy and pre-exponential factor) for pyrolysis.

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Symbols

$(\mathrm{d}\alpha/\mathrm{d}T)_{\alpha,i}$	Conversion derivative per temperature at the given degree of conversion and heating rate
0	Initial (mass or temperature)
$A_\alpha/g(\alpha)$	Modified pre-exponential factor in KAS isoconversional model (s^{-1})
$A_\alpha f(\alpha)$	Modified pre-exponential factor in FR isoconversional model (s^{-1})
f	Final (mass or temperature)
m	mass (kg)
R	Universal gas constant, 8.314 J/(mol·K)
T	Temperature, general parameter of process (°C or K)
$T_{\alpha,i}$	Temperature at the given degree of conversion and heating rate required for model application (K)
X	degradation of hemicellulose and cellulose during anaerobic digestion of roadside grass

	(/ or %)
$\bar{x}$	average share of a component in a biomass sample (/ or %)
α	Degree of conversion (/or %)
β_i	Heating rate (°C/min)

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Table 1 Linear isoconversional kinetic models applied on the pyrolysis of roadside grass and roadside grass digestate

Isoconversional model	Linear equation	
Friedman (FR)	$\ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right]=\ln\left[A_\alpha f\left(\alpha\right)\right]-\frac{E_\alpha}{RT_{\alpha,i}}$	(3)
Kissinger-Akahira-Sunose (KAS)	$\ln\left[\frac{\beta_i}{T_{\alpha,i}^2}\right]=\ln\left[\frac{RA_\alpha}{E_\alpha g\left(\alpha\right)}\right]-\frac{E_\alpha}{RT_{\alpha,i}}$	(4)

Table 2 Characteristic temperature zones during different stages of decomposition of RG and RGD samples

Samples	Temperatures (°C)	Heating rate (°C/min)				
		2.5	5	10	15	20
RG-MR	*T1*	135.8	141.5	165.5	172.3	190.9
	T2	226.8	234.9	260.3	267.1	276.3
	T3	239.1	246.9	268	274.9	287.7
	T4	248.8	295.6	321.9	330.3	334.7
	T5	343.2	349.1	371.8	384.2	395.8
RG-H	*T1*	139	149.7	168.8	178.5	191.4
	T2	255.5	270.2	271.7	283.1	297.5
	T3	271.8	276.8	294.8	308.3	318
	T4	312.4	321.6	334.8	344.8	361.3
	T5	356.3	376.3	393.3	404.2	418.2
RGD-MR	*T1*	137	142.3	163.1	175.9	187.5
	T2	N/A	N/A	N/A	N/A	N/A
	T3	N/A	N/A	N/A	N/A	N/A
	T4	275.1	283.2	290.9	300	314.5
	T5	332.2	334.3	373.3	382.1	393.8
RGD-H	*T1*	140.5	145.1	166.8	179.8	188.5
	T2	N/A	N/A	N/A	N/A	N/A
	T3	N/A	N/A	N/A	N/A	N/A
	T4	288.9	306	299.8	312.1	328.1
	T5	363.9	377.3	373.9	401.1	414.5

Table 3 Weight loss (in wt.%) during different stages of decomposition of RG and RGD samples

Samples	Stages	Heating rate (°C/min)				
		2.5	5	10	15	20
RG-MR	Dehydration (I)	5.20	4.70	4.81	4.17	4.06
	Active pyrolysis (II)	56.12	57.47	57.24	57.69	56.2
	Passive pyrolysis (III)	16.52	15.73	11.24	10.50	11.75
	Final residues	22.16	22.10	26.71	27.64	27.99
RG-H	Dehydration (I)	5.52	3.94	4.40	4.05	3.82
	Active pyrolysis (II)	59.89	58.73	60.76	59.63	61.94
	Passive pyrolysis (III)	14.16	14.04	10.96	11.37	11.28
	Final residues	20.43	23.29	23.88	24.95	22.96
RGD-MR	Dehydration (I)	6.73	7.94	7.38	7.84	6.59
	Active pyrolysis (II)	34.00	39.53	33.10	35.64	43.9
	Passive pyrolysis (III)	24.68	21.55	17.01	13.57	8.70
	Final residues	34.59	30.98	42.51	42.95	40.81
RGD-H	Dehydration (I)	6.68	7.43	6.93	6.57	6.73
	Active pyrolysis (II)	44.52	48.03	33.80	35.66	43.61
	Passive pyrolysis (III)	22.69	13.48	14.68	12.91	12.43
	Final residues	26.11	31.06	44.59	44.86	37.50

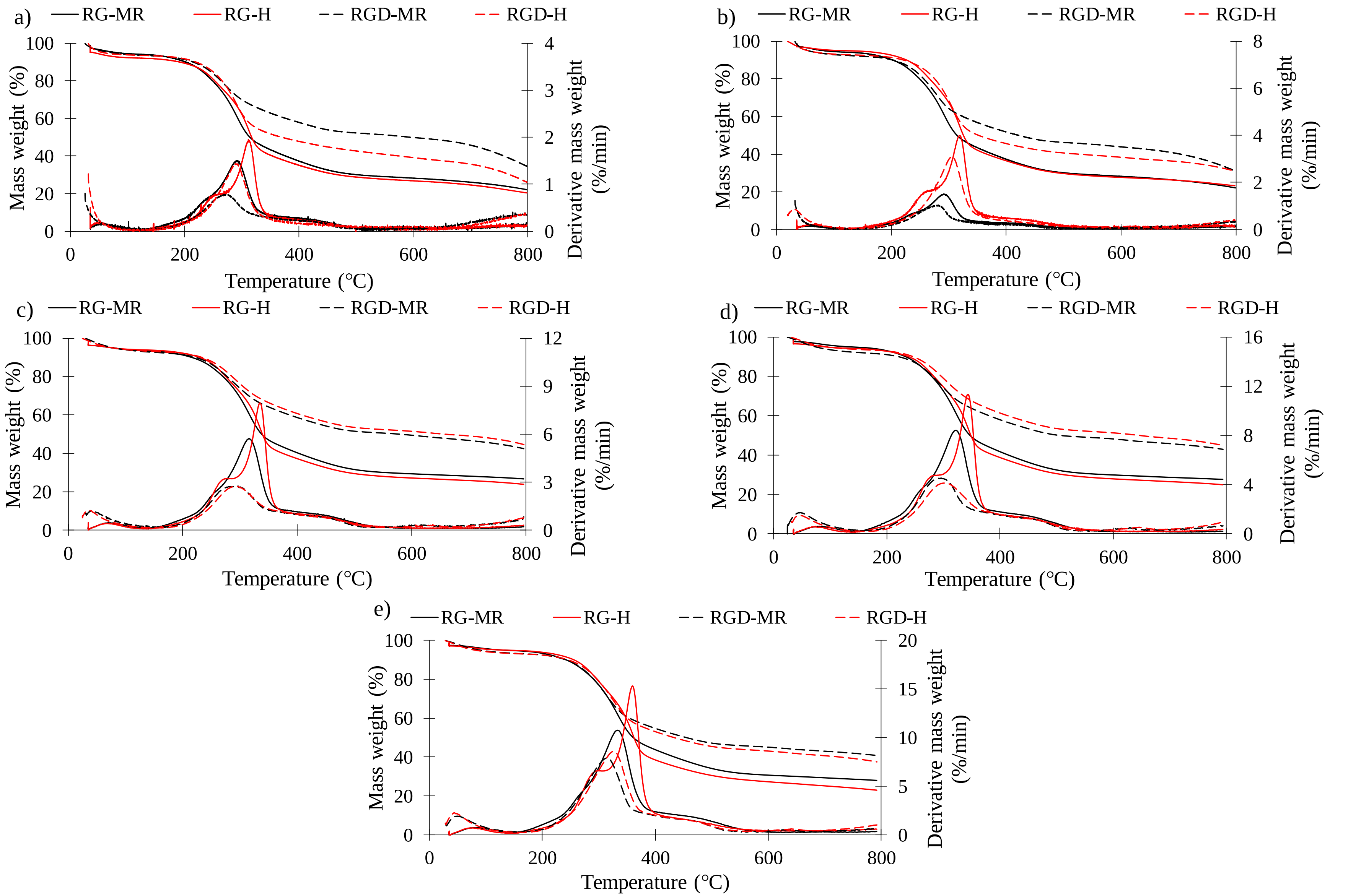

Figure 1 TG-DTG curves of RG and RGD samples at different heating rates: a) 2.5 °C, b) 5 °C/min, c) 10 °C/min, d) 15 °C/min and e) 20 °C/min

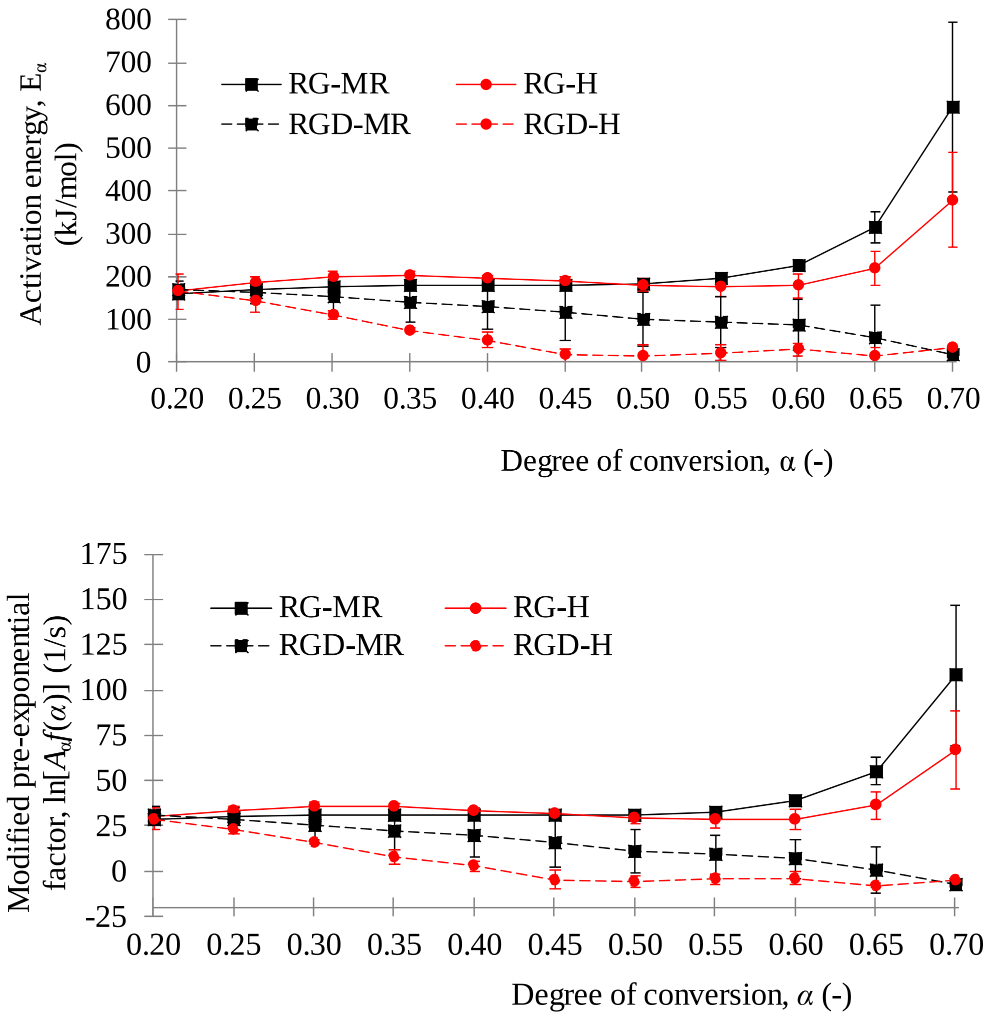

Figure 2 Distribution of E_α and $\ln[A_\alpha f(\alpha)]$ with the degree of conversion by means of FR model

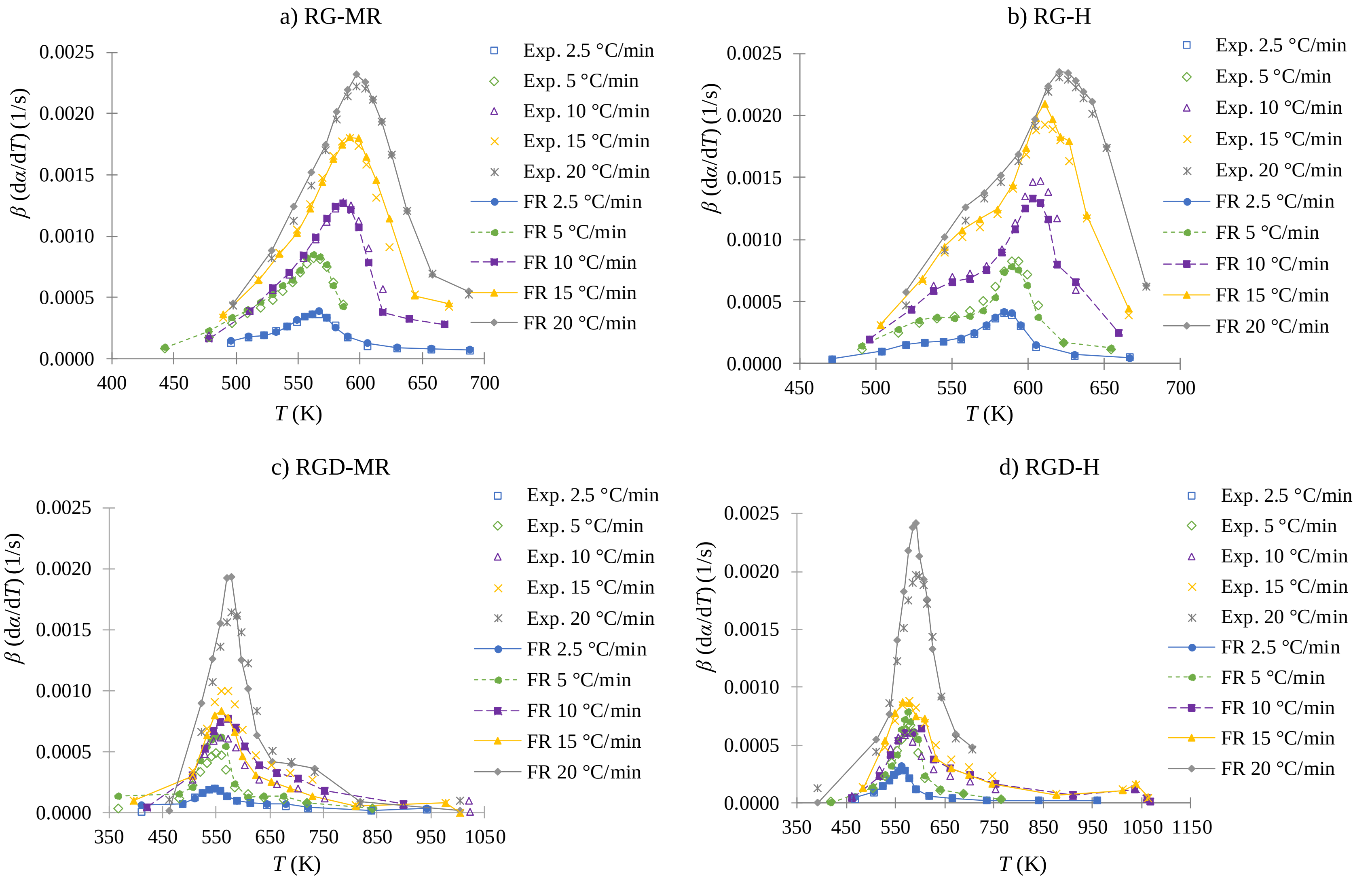

Figure 3 Experimental and FR kinetic model based on E_α and $\ln[A_\alpha f(\alpha)]$ data for grass and digestate pyrolysis at 2.5, 5, 10, 15 and 20 °C/min

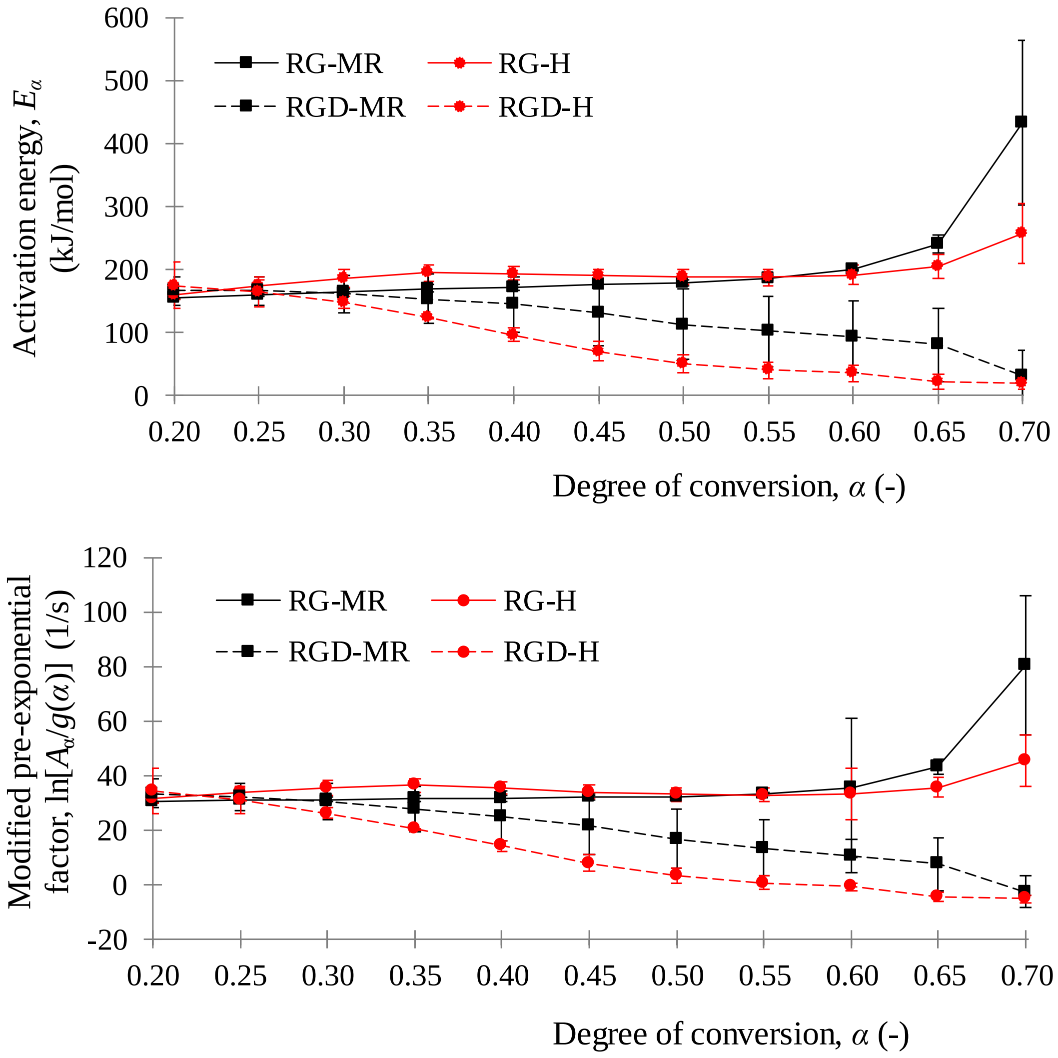

Figure 4 Distribution of E_α and ($\ln[A_\alpha/g(\alpha)]$) with the degree of conversion by means of KAS model

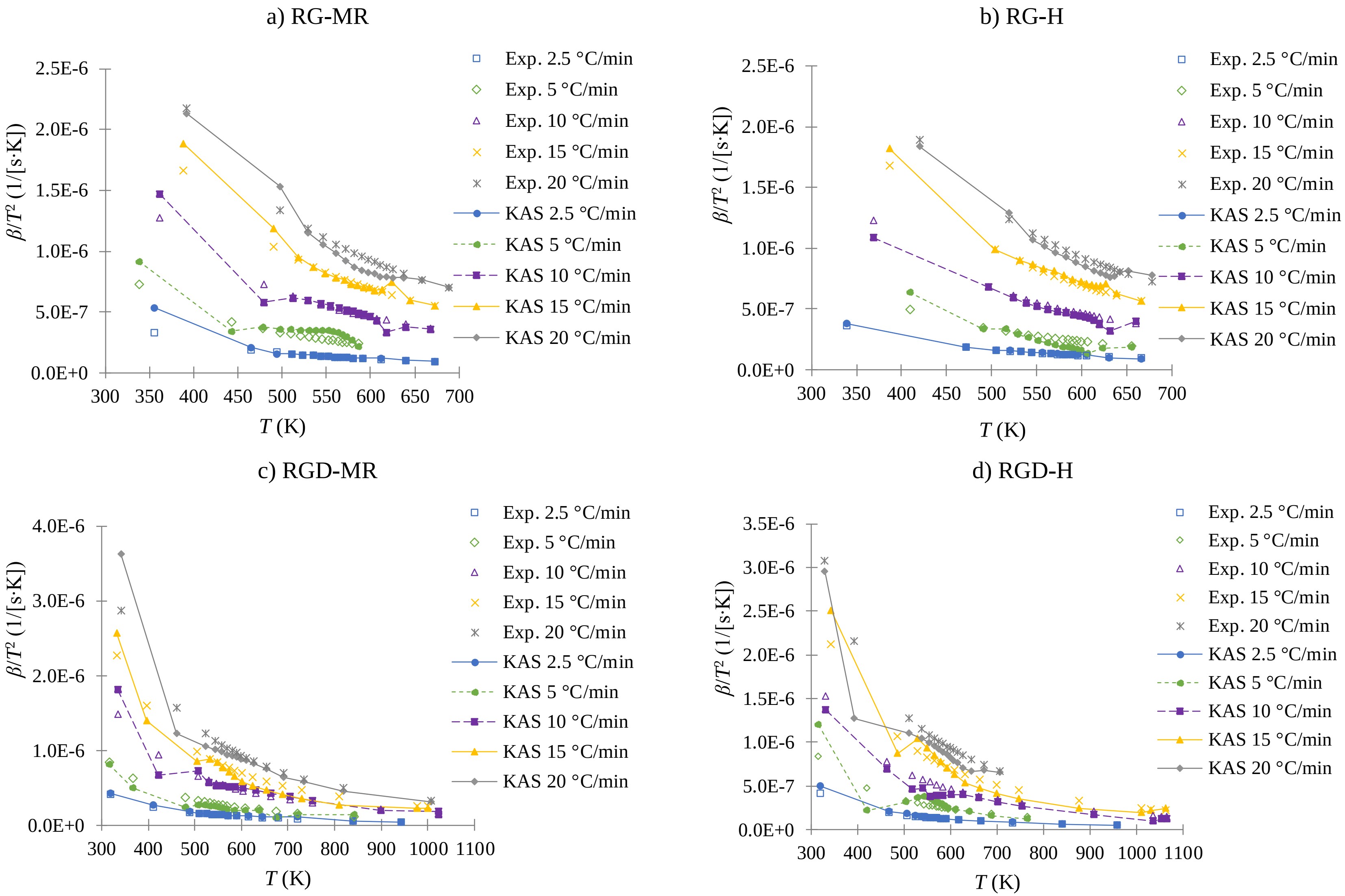

Figure 5 Experimental and KAS kinetic model based on E_α and $\ln[A\alpha/g(\alpha)]$ for grass and digestate pyrolysis at 2.5, 5, 10, 15 and 20 °C/min

ARTICLE 4

Opportunities and challenges: experimental and kinetic analysis of anaerobic co-digestion of food waste and rendering industry streams for biogas production

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Abstract

Large amounts of food waste and sewage sludge exert a hazardous environmental impact in several countries. Producing biogas and digestate from food and industrial waste is one of the solutions for waste management, stabilization of sludge, resource and energy recovery and reductions in the amount of waste. However, biogas production from such substrates has challenges in degradation efficiency, inhibitory effects and other challenges, and thus co-digestion and pretreatment techniques could be applied to enhance biogas production. The aim of this study is to explore the effects of co-digestion of food waste, meat and bone meal and rendering wastewater sludge. First, thermal pretreatment was performed (35°C, 5 days) by adding the rendering-industry streams to food waste in the amounts of 0, 5, 10 and 15% on a total solid basis, and further anaerobic digestion (40.5°C, ca. 40 days) was then performed. Both

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experimental and kinetic analysis were conducted, and the major factors regarding opportunities and challenges in the two-stage process are discussed. Results have shown that both co-substrates from rendering industry decreased the biogas yield of food waste. When 5% of them was added to food waste, meat and bone meal decreased biogas production by 12%, and wastewater sludge decreased it by 23%. Both co-substrates, on the other side, increased the rate of reaction of food waste digestion when applying different common kinetic models.

Highlights

- Rendering streams were studied as co-substrates to food waste for biogas production
- Experimental study of thermal pretreatment and anaerobic digestion was performed
- Food waste could cause inhibition of the anaerobic digestion process
- Kinetic parameters were estimated for anaerobic digestion of selected mixtures
- Rendering streams decrease biogas production, while increase the rate of reaction

Keywords

Food Waste; Rendering Industry Streams; Thermal Pretreatment; Anaerobic Co-Digestion; Biogas Production; Experimental Research; Kinetic Analysis

Word Count (excluding title, author names and affiliations, keywords, abbreviations, table/figure captions, acknowledgements and references): **8,284 words**

Abbreviations

AE Agroproteinka Energija; AD Anaerobic Digestion; EU European Union; FW Food Waste; IN Inoculum; LCFAs Long Chain Fatty Acids; MBM Meat and Bone Meal; SCOD Soluble Chemical Oxygen Demand; TS Total Solids; VFAs Volatile Fatty Acids; VS Volatile Solids; WWS Wastewater Sludge

Nomenclature

COD	*Chemical Oxygen Demand (g/L)*
k	*Reaction Rate Constant* (d^{-1})
m	*Mass (g, kg)*
N	*Number of Data Points*
n	*Shape Factor (−)*
NH_4-*N*	*Ammonium Nitrogen (g/L)*
pH	*Power of Hydrogen (−)*
R	*Biogas Production Rate* ($Nm^3/(kg\ TS \cdot d)$)
RMSE	*Root Mean Square Error* ($Nm^3/kg\ TS$)
S	*Biogas Yield* ($Nm^3/kg\ TS$)
t	*Time (d)*
TIC	*Total Inorganic Carbon* ($g\ CaCO_3/L$)
V	*Volume of Gas* (Nm^3)
VFAs	*Volatile Fatty Acids* ($g\ CH_3COOH/L$)

Subscripts

exp	*Experimental*
i	*Data Point*
m	*Maximum*
mod	*Model*

Greek Symbols

λ	*Lag phase (d)*

1 Introduction

A circular economy and a "closing the loop" approach have been recognised in EU energy policy as very important factors in the security of energy supply and the threat to climate change [1]. Implementation of a multi-waste management concept has shown that it is possible to treat various waste streams at the same facility [2], where anaerobic digestion technology has shown the highest applicability level of all energy recovery methods.

The latest European directive on the promotion of the use of energy from renewable sources (REDII) positions future biogas production towards the utilisation of more sustainable feedstocks, such as lignocellulosic materials and the biomass fraction of waste and residues [3]. The rationale behind the decision to consider only such substrates in anaerobic digestion (AD) has been related to the unfavourable side effects of currently used substrates, which are mainly cultivated crops, such as maize [4]. Among the side effects are increasing food prices [5] and the environmental footprint of the biogas industry because of crop production [6].

Among all bio-waste types in the EU28, food waste (FW) is the most interesting on account of worldwide trends towards landfill reduction [7] and increasing separate collection of waste that can be further used in the production of renewable heat and electricity [8], or renewable gas [9]. The European Commission has estimated that around $88 \cdot 10^6$ t/y of FW are generated in the EU28, which is equal to ca. 173 kg/y of FW per person [10].

Energy recovered from FW (food waste and loss) can significantly contribute to better energy self-sufficiency and to a reduction in fossil energy consumption [11]. There are many conversions pathways for FW to produce energy and value-added materials [12]. Compared with disposal methods such as landfill, incineration and composting, AD is a promising technology for FW management, since FW is a wet organic material. Co-digestion with animal manure and sewage sludge are practical options for AD of FW for biogas production [13]. AD is a conversion process from which versatile uses of products, methane and digestate, are possible, in the industrial, domestic and transport sectors. Emphasis in this work will be placed on the experimental analysis of two-stage AD, its kinetics and on the limitations of the AD process relating to FW.

The paper is structured as follows. First, the comprehensive review is presented and focuses on the presentation of FW resources, pretreatment and degradation of FW, co-digestion of FW and the common co-substrates in the two-stage AD, and on an overview of the use of animal and rendering by-products in AD (Section 1.1). Further, in Section 1.2 limiting factors in AD of FW are presented, focusing on the inhibition affecting biogas production, caused by the compounds like ammonia, long chain fatty acids (LCFAs), volatile fatty acids (VFAs) and metal elements. The last Section of the review presents commonly applied kinetic models and estimated kinetic parameters in AD of FW.

The second part of the paper is devoted to testing the scientific contribution and objectives of this research through an experimental and modelling study of the two-stage AD of FW, where in the first stage rendering industry streams were thermally pretreated and added as co-substrates for AD (second stage). Finally, four of the common kinetic models were applied to perform kinetic analysis of biogas yield, and to estimate kinetic parameters of the mixtures for AD.

1.1 Resource and energy recovery from food waste

In general, there are two types of FW; the first is edible FW that is generated during food consumption by consumers and could be reduced or avoided, while the second is inedible FW which cannot be avoided, such as peels, bones, stalks and skin [14]. FW represents a significant part of food consumption; around one third of all food intended for human consumption becomes FW [15]. FW is generated mostly in homes, restaurants and in food services (schools, hospitals, old people’s homes etc.), but also in distribution and in food stores, and along the production supply chain [16]. FW that is collected is mostly processed in biogas plants, followed by processing in composting plants [17].

The complex origins of raw FW result in a wide and heterogenous composition, where the main component of raw FW is water, ca. 70-90%. The dry matter basis is ca. 5-50% lipids, ca. 0-20% starch and ca. 2-20% proteins [18]. The high share of water in FW makes it unsuitable for incineration, gasification or pyrolysis, while at the same time, it is highly applicable in a wet AD process [19]. Utilising FW for wet AD has shown high potential in reducing environmental burdens: for instance 6,600 t of FW can be substituted for 9,900 t of maize silage, resulting in a carbon footprint reduction of 42% [20].

However, the approach to AD of FW is slightly different compared to AD of energy crops and animal manure [4], which is usually performed as a single-stage process [21]. In comparison to maize silage and cattle manure, FW has characteristics that vary considerably, depending on the source of the FW. Multi-stage AD of FW offers higher stability [22] and more efficient conversion of biomass to biogas [23]. The first stage of AD, also known as hydrolysis, is usually the rate-limiting step in the case of FW that defines the overall biogas production rate [24]. To achieve more efficient hydrolysis and avoid low conversion rates, pretreatment methods are introduced [25]. After pretreatment, the second stage includes degradation of organic material under anaerobic conditions where biogas is produced.

1.1.1 Pretreatment of food waste

Prior to the pretreatment, raw FW is ground or milled into smaller particles to improve the carbon accessibility [25]. There are several applicable pretreatment methods for FW, such as thermal, mechanical, thermo-chemical, chemical and biological pretreatment [26]. Thermal hydrolysis has been recognised as the most efficient and least complex method of hydrolysing macromolecules in FW for easier degradation [27].

1.1.2 Degradation of organic material under anaerobic conditions

The second stage includes anaerobic degradation of organic material. AD has been recognised as an economic and effective option to reduce FW landfill, groundwater pollution and emission of toxic gases [28]. In addition, AD of FW is considered a recycling method [29] that additionally contributes to its promotion in the framework of sustainable development and circular economy.

Two-stage AD could enhance conversion and thus increase the yield of biogas. A study on anaerobic degradation of kitchen FW showed an increase in biogas production of ca. 30-40% when thermal pretreatment was performed using temperatures of 90-120°C with durations of 70 and 50 min [30]. Synthetic FW (a mixture of fruits/vegetables, pasta/rice, bread/baked goods, meat and fish) yielded negative effects in terms of biogas production when thermal pretreatment was performed at temperatures higher than 120°C and a pretreatment time longer than 4 h [31].

On the other hand, thermal pretreatment of canteen FW and waste activated sludge at temperatures higher than 200°C resulted in reduced biogas production [32]. At higher temperatures, complex polymer compounds are formed which inhibit the second stage (AD process) [31]. Based on a literature review, thermal pretreatment of FW is recommended at lower temperatures and prolonged duration, since increasing temperature does not significantly increase biodegradation but rather decreases the potential for biogas production by forming inhibitory intermediate compounds.

1.1.3 Anaerobic digestion of food waste and co-substrates

Several studies have been performed regarding anaerobic co-digestion of FW and co-substrates. It was found that, especially in batch processes, the substrate to inoculum ratio has a significant impact on the process performance of FW digestion. In the case of batch AD of FW, the substrate to inoculum ratio has varied as follows 1:1 [4], 1.4:1 [33] and 3.0:1 [34].

Some examples of co-digestion studies of FW are as follows: Canteen FW and parthenium weed were studied for biogas production using microwave irradiation and steam pretreatment on a laboratory scale [35], where by adding pretreated parthenium weed to FW, pH control was improved as compared to untreated weed. Canteen FW in co-digestion with rice straw showed an approximately 70% higher biogas yield compared to mono-digestion of FW [36]. Thermally pretreated canteen FW and waste activated sludge were studied for biogas production, where the results showed that 24 h pretreatment using fungal mash resulted in a 6% increase in soluble chemical oxygen demand (SCOD), and the SCOD removal during biogas production was estimated to be between 70 and 90% [37].

The co-digestion of pretreated FW and yard waste gave a biogas yield of 431 NmL/g VS, while untreated FW and yard waste had a biogas yield of 335 NmL/g VS [38]. Adding sewage sludge and yard waste to cafeteria FW showed synergistic effects in terms of biogas production compared to mono-digestion of FW [39]. Co-digestion of FW composed of bread, rice, spaghetti, vegetables, fruits and meat gave a 1.4-fold higher methane yield compared to sludge mono-digestion. Adding organic FW to sludge increases the organic content in the mixture and improves the digestibility of the mixture [40]. Anaerobic co-digestion of restaurant FW and sewage sludge showed that, when adding 10% of sludge to FW, biogas production is stable [41].

Based on the literature review, it was found that substrates in second-generation biogas production like FW, various sludge types and other waste types are highly heterogenous, and thus process behaviour is highly unpredictable. Therefore, it is important to investigate limiting factors and obstacles to their use in AD.

1.1.4 Animal and rendering industry streams in anaerobic digestion

The rendering industry processes animal by-products into more valuable materials with the goal of preventing land and water pollution caused by irresponsible handling of those by-products [42]. Animal by-products are classified in three categories [42]:

- Category 1 – materials with the highest risk for public health, animals, or the environment (animals affected by diseases, e.g. mad cow disease) that cannot be utilised in AD in any kind of form [43];
- Category 2 – animal by-products that can be recovered in biogas plants approved by national rules (manure or digestive tract content) and
- Category 3 − animal by-products that could be used for human consumption; however, for commercial reasons, they are not intended for human consumption. Such products are fully suitable to be recovered in biogas plants.

After processing animal by-products, the main rendering industry streams are wastewater sludge (WWS), meat and bone meal (MBM) and grease trap sludge, which is mostly used in biodiesel production [44].

In the meat and rendering industry, the AD process acquires a high potential for renewable energy production and reduction of greenhouse gas emissions [45]. However, relatively high financial investment and the inappropriateness of some streams like fat, oil and grease for biogas production have been recognised as major concerns in installing AD technology in a rendering plant [45].

Meat processing by-products have shown high yields in biogas production when co-digested with pig manure and process water from a rendering facility [46]. To keep such an AD process stable, a limit has been set on a maximum 10% of MBM share in a mixture. MBM has proven to have high TS content of approximately 98.5% and a relatively low carbon to nitrogen ratio (C/N) of 4.19 [47], which could significantly contribute to ammonia inhibition during AD

[48]. Therefore, MBM can be added to lignocellulosic substrates with a very high C/N ratio, like wheat straw and pine wood [49], to achieve the optimum C/N value for biodegradation. WWS from meat waste processing showed both ammonia and VFAs inhibition in AD when loaded higher than 3.8 g COD/g VS [50]. At lower loadings, inhibition was not detected, and the biogas yield of WWS achieved values of 0.53-0.55 Nm^3/kg VS. From the literature review, it was found that rendering industry streams can only be utilised for AD if they meet safety regulations to be utilised in biogas production and if they are added to a base substrate in smaller portions to maintain stability during the process.

1.2 Limiting factors in anaerobic digestion of food waste

Inhibition has been identified as the main obstacle to using FW as a substrate for AD [51]. Owing to the complex nature of FW, there are many inhibitory compounds that can affect AD and the biogas production rate. Some of the most frequent inhibitory compounds are presented and analysed in the subsections below.

1.2.1 Ammonia

One of the most important inhibitory compounds related to AD of FW is the excess nitrogen (protein) content in FW [52]. To quantify the share of nitrogen in a substrate and to estimate its potential for ammonia inhibition, the C/N ratio is usually used. A wide range of C/N values for FW is reported, between 16.5 and 46.8 [53]. Usually, an optimum C/N ratio for biodegradation is between 27 and 32 [52], which makes FW as a substrate for AD highly unpredictable in terms of whether or not it will lead to ammonia inhibition during the process.

When considering ammonia inhibition, it is important to distinguish two different concentrations of nitrogen that are usually used. The first is total ammonia nitrogen (TAN), which refers to both nitrogen from ammonia (NH_3-N) and ammonium (NH_4-N) that is present in the liquid phase during the process. Free ammonia refers to the concentration of unionised ammonia (NH_3) in the same liquid phase. Free ammonia is a toxic form of ammonia that causes ammonia inhibition during AD. The threshold concentration for ammonia inhibition depends on the type of substrate and inoculum [53], and on AD conditions like temperature and pH [54]. When quantifying the ammonia inhibition in AD of FW, the threshold is usually expressed in terms of NH_4-N concentration, since it is easily measurable. Several reports have shown that a wide range of threshold concentration for ammonia inhibition exists, between 2 and 6 g/L [53,55].

1.2.2 Long Chain Fatty Acids (LCFAs)

During the hydrolysis of FW, lipids are degraded into long chain fatty acids (LCFAs) [56], of which palmitic, stearic and oleic acids are reported to be the most common [57]. The theoretical methane potential of lipids is higher than that of carbohydrate and proteins, between approximately 850 and 1,050 NL/kg VS [58]. However, lipids are usually not suitable for mono-digestion, owing to LCFAs inhibition, which is caused by an accumulation of LCFAs due to the slow lag phase of acidogenesis [58]. An excess of LCFAs results in physical adsorption on the cell membrane of microorganisms and in stagnation of the molecular transfer [51]. Since FW is usually rich in lipids (ca. 5 g/L [51]), LCFAs inhibition can be expected. The reported threshold for LCFAs inhibition during AD is 0.5-1.5 g COD/L [59]. If there is no LCFAs inhibition in the acidogenesis stage, then volatile fatty acids (VFAs) are being produced.

1.2.3 Volatile Fatty Acids (VFAs)

As the concentration of VFAs increases during acidogenesis [60], the pH value in the system drops and can cause inhibition in acetolactic methanogenesis. Such a phenomenon has been reported for AD of kitchen FW, where the pH was reported in the range of 2.3-5.1 [61]. The optimum pH range for the acetogenesis of FW is estimated between 6.8 and 7.6 [62]. A study on AD of canteen FW showed that propionic acid is the most responsible VFA for causing inhibition [63]. Moreover, the same research showed that manual adjustment of pH by adding chemicals could not reverse VFA inhibition but could only delay the process failure.

On the other hand, if the concentration of VFAs in the system is too low, it indicates that acidogenesis was inhibited and no acids were produced [64]. Such an observation was determined using the VFAs/SCOD ratio, which showed that strong acid conditions (pH=4.0) favour inhibition of acidogenesis and delay conversion of soluble acids to acetic acid that is further converted to methane [64]. Therefore, to avoid inhibition caused by VFA in two-stage anaerobic digestion, it is important to adjust the pH value to be in a range of 6.4-7.8 [62]. An experimental study on co-digestion of FW and pig manure revealed that the threshold inhibition concentration of VFAs ranged between 16.5 and 18.0 g/L [65].

1.2.4 Metal elements

Metal elements are essential for a stable and efficient AD process [51]. In general, there are two groups of metals important for AD: light and heavy metals. Iron, nickel, selenium and cobalt have proven to be the most important heavy metals responsible for the stable AD of FW. Their excess can cause disruption in the function and structure of enzymes that lead to inhibition [66]. However, inhibition caused by heavy metals is not usually a concern in AD of FW, since they are usually not sufficiently present in FW [51].

In contrast, light metals like sodium (Na), potassium (K) and calcium (Ca) are more present in FW and could be the cause of salt inhibition [51]. The threshold for sodium inhibition in AD of kitchen FW was between 8 g Na/L [67] and 12 g Na/L [68]. In the case of a calcium presence in AD of FW, the threshold was set at a value of 7 g Ca/L, while the optimum concentration of calcium was reported at between 0.15 and 0.30 g Ca/L [69]. The threshold for potassium inhibition is estimated at approximately 7.5 g K/L [70].

In laboratory conditions, salt inhibition can be detected by measuring electrical conductivity [68]. To avoid salt stress during AD and inhibition in biogas production, the overall conductivity should be maintained below 30 mS/cm, which has been estimated as the general threshold value [71].

A summary of limiting factors that impact the anaerobic digestion of food waste through an inhibition is presented in Table 1.

Table 1. A summary of limiting factors in anaerobic digestion of food waste

Limiting factor	Inhibition threshold
Ammonia	2-6 g NH_4-N/L
LCFAs	0.5-1.5 g COD/L
VFAs	16.5-18.0 g CH_3COOH/L
Salts	30 mS/cm

1.3 Kinetic modelling of anaerobic digestion of food waste

Kinetic analysis and estimation of the kinetic parameters of AD are important in predicting the behaviour of an anaerobic system and in optimising biogas production [72]. Results of the kinetic analysis quantify the impact of changing process variables like pH, total solids, added co-substrate and others on the rate of biogas production and biogas yield [73]. The most common kinetic models for AD of organic biomass are ADM1, Modified Gompertz, Monod [74], the First-order model and the Cone model [75].

Estimated kinetic parameters for AD of FW performed in a batch mode [75] yielded a value of the first-order kinetic parameter equal to 0.099 d^{-1}, while the Modified Gompertz kinetic parameter was equal to 0.126 d^{-1}. Changing the FW composition and finding its impact on the value of kinetic parameters constituted an attractive method in studying FW capacity for AD [76]. It was established that using an exponential model (First-order model) resulted in a wide range of rate constant values for VS reduction, between 0.55 and 3.63 d^{-1}.

Application of more complex models like the original Anaerobic Digestion Model No. 1 (ADM1) [77] or modified ADM1 [78] to simulate AD of FW showed well-predicted methane production. In addition, these complex models can identify which processes within AD have the most effect on biogas production and are the possible cause of inhibition.

It is important to emphasise, however, that as the complexity of the applied model increases, there are certain limitations, such as the necessity for more data regarding the substrate and the process and more time to successfully apply the model.

1.4 Scientific contribution of the research

Based on the detailed literature review, there is no reported research on AD of FW using rendering industry streams as co-substrates. This study presents a comprehensive experimental and modelling study of the two-stage AD of FW on a laboratory scale when rendering industry streams are added as co-substrates during thermal pretreatment in portions up to 15% on a TS basis. The "closing the loop" approach between the biogas plant and the rendering plant via integrated waste management will be evaluated with the following objectives:

(i) to assess the impact of rendering plant industry streams, MBM and WWS, on the efficiency of thermally-pretreated FW collected from the biogas plant handling FW as a base substrate;

(ii) to determine the yield of biogas and to evaluate the stability and efficiency of AD of selected FW, MBM and WWS mixtures by monitoring several important process variables over time, and

(iii) to estimate kinetic parameters for AD of selected mixtures.

2 Materials and methods

In this section, an overview of applied materials and methods is presented. First, the substrate sampling in the biogas and rendering plant is described, followed by description of chemical analyses and the laboratory set-up. The last part describes the kinetic modelling of the AD process.

2.1 Substrate and inoculum sampling

The substrates were collected from two companies located near the city of Zagreb, Croatia. FW and inoculum were sourced from the Agroproteinka Energija biogas plant, and MBM and WWS from waste of categories 2 and 3 were collected from the Agroproteinka rendering plant. The inoculum was sampled in an anaerobic digester of the biogas plant and had slightly less than 5% of TS. WWS is sampled at the rendering plant after a decanter centrifuge for dewatering in the wastewater treatment facility [79]. Two sets of experiments were carried out. For the first set of experiments, FW (FW1), the co-substrate MBM and the inoculum (IN1), were sampled on February 15, 2019, while for the second set of experiments, FW (FW2), the co-substrate WWS and the inoculum (IN2) were sampled on April 15, 2019.

2.2 Chemical analysis

First, TS content of substrates and inoculum were determined in an oven (Universal Oven UN 30) at 105°C. Around 30 g of raw substrate was placed in a ceramic crucible and dried in an oven until constant weight. TS content was determined in three parallels.

During the two-stage process (pretreatment and AD), an analysis of the gas and liquid phases was conducted, using the standard equipment found in biogas plants. Gas phase composition was analysed by an OPTIMA 7 biogas analyser, and the following gases were measured: methane (CH_4), carbon dioxide (CO_2) and hydrogen sulphide (H_2S). For the liquid phase, several analyses were performed. COD was determined by Hach LCK cuvette tests and LT 200 Series COD reactor for digestion. Temperature was set at 148°C and time was set to 120 min. The concentration of NH_4-N was also analysed by Hach LCK cuvette tests. A DR 3900 spectrophotometer with RFID technology was used to measure concentrations of COD and NH_4-N. pH was measured by a Hach HQ440d pH-meter. The concentration of VFAs and total inorganic carbon (TIC) was measured by a TitraLab AT1000 Series Potentiometric Titrator. Before each use, the instruments were calibrated according to the declared procedure. Analysis of both the gas and liquid phases were conducted in triplicate, and the average values are presented.

2.3 Experimental set-up

Two experiments were conducted, where first the substrates (FW and MBM and FW and WWS) were hydrolysed at 35°C for 5 days, and further AD was performed on pretreated substrates to possibly replicate biogas production in Agroproteinka Energija (AE) company.

2.3.1 Thermal pretreatment

In the first stage, MBM and WWS were added to FW in the amounts of 0, 5, 10 and 15% on a TS basis. The reason for adding co-substrates in such small fractions as compared to some previous reports [33,34] is to maintain process stability. The mixtures were prepared in triplicate with a total mass of 60 g TS added to a container of 1.0 L volume. After adding the mixtures to the containers and sealing them with parafilm, the containers were placed in a heated bath. Thermal pretreatment of mixtures was conducted for 5 days at a temperature of 35.0°C, which was maintained by a SC 100 immersion circulator (Thermo Scientific™). Substrates for the second stage (AD) were then selected based on measured changes to the variables in the liquid phase.

2.3.2 Anaerobic digestion

In the second stage, AD of pretreated mixtures was performed. Two mixtures were selected for AD: a control mixture (with no added co-substrate, thus only FW) and a mixture with the overall best parameters according to the selection criteria as analysed after thermal pretreatment. AD was performed in 500 mL volume filter flasks, which were placed in a heated bath where the temperature was set and maintained at 40.5°C.

In total, 20 g of TS was added to each reactor. For all the batch assays, the ratio between substrate (mixture after thermal pretreatment) and inoculum was set to 1:1 on a TS basis. At the start of the process, the pH value in the reactor was set to 7.8 (as in an anaerobic digester of AE company) using an NaOH solution (pH=13). Finally, demi-water was added so that 5% of the TS content in the reactor (also, as in an anaerobic digester of AE company) was achieved.

Biogas production was measured according to the DIN 38414-8 standard method [80] using a graduated 400 mL eudiometer in 5 mL increments, water as a confining liquid and a levelling bottle of 1.0 L. To subtract biogas production in substrate assays, the blank assay containing only inoculum was set. Figure 1 presents the schematics for batch-mode two-stage AD composed of a) thermal pretreatment and b) anaerobic digestion.

Biogas yield (S, expressed in Nm^3/kg TS) of each mixture is calculated using the following equation [81]:

$$S = \frac{V(\text{biogas})}{m(\text{substrate})} \tag{1}$$

where V(biogas) is the cumulative biogas production given at 101,325 Pa and 0°C (also called normalized volume of biogas, Nm^3 [82]) and m(substrate) is the mass of the studied mixture expressed in kg TS.

a) Thermal pretreatment at 35.0°C

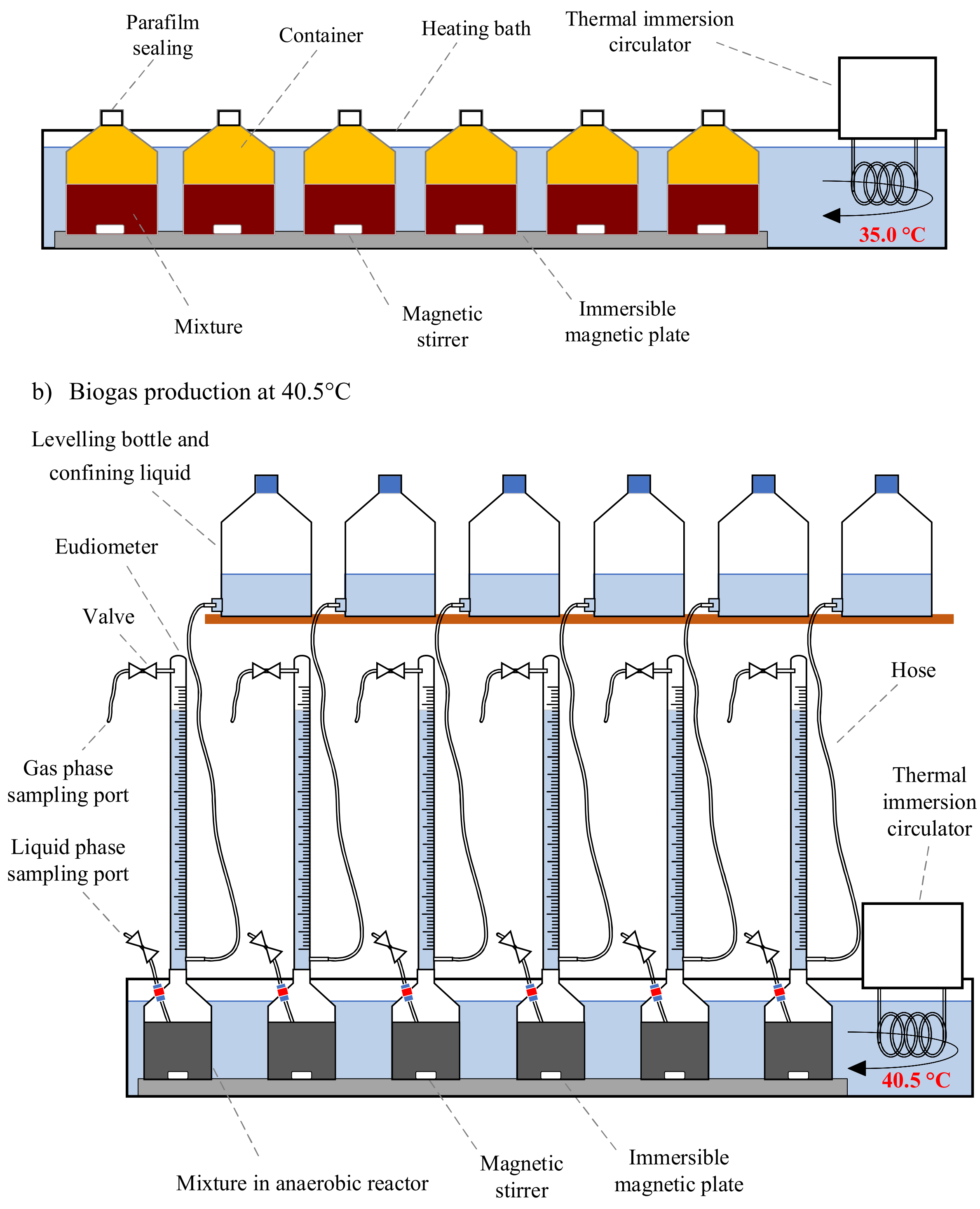

Figure 1 Schematic diagram for batch-mode a) thermal pretreatment and b) biogas production

2.4 Kinetic modelling

Kinetic study of AD from FW and rendering industry streams was carried out, using four different models. Cumulative biogas production during batch AD [83] was being estimated, using the models as presented in Table 2.

Table 2. Kinetic models for AD

Model	Mathematical definition	
First-order [84]	$S(t) = S \cdot \left(1 - \exp\left(-k \cdot t\right)\right)$	(2)
Monod [85]	$S(t) = S \cdot \left(\frac{k \cdot t}{1 + k \cdot t}\right)$	(3)
Modified Gompertz [86]	$S(t) = S \cdot \exp\left(-\exp\left(\frac{R_{\mathrm{m}}}{S} \cdot \exp\left(\lambda - t\right) + 1\right)\right)$	(4)
Cone [75]	$S(t) = \frac{S}{1 + \left(k \cdot t\right)^{-n}}$	(5)

$S(t)$ is the time reported biogas yield [Nm^3/kg TS]; k is the first-order reaction constant (First-order model) or rate constant (Monod and Cone model) [d^{-1}]; R_{m} is the maximum biogas production rate [Nm^3/(kg TS·d)], λ is the lag time [d] and n is the dimensionless shape factor.

Root-mean square error (*RMSE*) was used to indicate the quality of the model's fit to experimental data, which was calculated using the following equation [38]:

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}\left(S_{\mathrm{exp,i}} - S_{\mathrm{mod,i}}\right)^2}{N}} \quad (6)$$

where $S_{\mathrm{exp,i}}$ is the average biogas yield obtained in the experiment, $S_{\mathrm{mod,i}}$ is the biogas yield obtained by the model, and N is a number of measurements (data points). To find the optimum value of kinetic parameters (k, R_{m}, λ, n) using these models, the values of kinetic parameters were such to achieve the highest match of the model with the experimental data, and thus the lowest value of *RMSE*.

3 Results and discussion

In this section, the results of experimental and kinetic analysis are presented. The authors would like to note that data on the chemical composition and physical properties of substrates are confidential, while the results of the research, such as TS content, parameters measured before and after pretreatment and during AD are shown in the following.

3.1 Total solid content of substrates and inoculum

Table 3 shows the TS content of the substrates and inoculum that were used for two-stage hydrolysis and AD.

Table 3. TS content of substrate and inoculum samples

Substrate/Inoculum	Total solid content [%]
FW1	19.58 ± 2.23
FW2	19.98 ± 0.31
MBM	99.30 ± 0.52
WWS	12.60 ± 0.03
IN1	4.44 ± 0.01
IN2	4.53 ± 0.01

FW has a TS content of approximately 20%, which is in the range of values found in the literature: 7.6-39.5%. [37–39,87–89]. The wide span of TS in FW is mainly due to FW composition. In an AE biogas plant, the TS content of 5% is achieved by adding water or some waste liquid stream such as spoiled milk, juice, waste soup from restaurants, or any liquid waste available for use.

MBM showed the share of TS to be almost 100%, while WWS had a much lower TS content, ca. 13%. The moisture content in MBM is usually around 5% [90] or even below 2% [47], as in this study. Such a high TS content makes MBM highly suitable for incineration as a supplement to or replacement for coal [91]. MBM is typically incinerated when it fails to meet the standards for use as animal feed (waste category 1) [42].

WWS shows TS content to be in a range, as reported previously, between 10.8-16.9% [37,39,87]. The inoculum has a TS content slightly less than 5%, which is in the range of the TS content in biogas plants [92], and is a relatively common value for digestion of FW [93].

3.2 Thermal pretreatment of food waste and rendering industry streams

Thermal pretreatment of FW and rendering industry streams, MBM and WWS, was evaluated by monitoring the change in pH, NH_4-N and COD. Values of parameters measured before and after pretreatment are shown in Figure 2 left, for the first experiment (co-substrate MBM, inoculum IN1, sampled on February 15, 2019) and in Figure 2 right, for the second experiment (co-substrate WWS, inoculum IN2, sampled on April 15, 2019). The coloured bar in Figure 2 represents the average value of the variable for the given mixture, while range bars delimit the actual range of values measured in the experiments [94].

The results in Fig. 2 a) show that both FW (FW1 and FW2, collected at different times) show a similar range of pH during the pretreatment, between 3.40 and 3.50. According to the literature, the reported pH range of FW is very wide, between 3.7 and 6.1 [38,64,87,95]. Adding MBM to FW1 slightly increases the pH, from about 3.5 (0% MBM) to about 3.9 (15% MBM). Such a trend was anticipated, since MBM is the product of alkaline hydrolysis where NaOH is used to dissolve animal industry streams in rendering plants [96]. On the other hand, WWS showed no significant change in pH. The results also show that after pretreatment, the pH values remain similar to those before pretreatment in all the cases analysed.

Figure 2 b) show the impact of adding rendering industry streams to FW in terms of NH_4-N concentration. The FW2 sample (right) had a greater share of nitrogen-rich material than the FW1 sample (left). Values are slightly higher compared to previously reported values, which are about 0.203 g/L [89]. With more MBM, and especially WWS, in the substrate, NH_4-N concentration increased, since both animal industry streams are rich in proteins [97] that hydrolyse during the pretreatment and increase NH_4-N concentration.

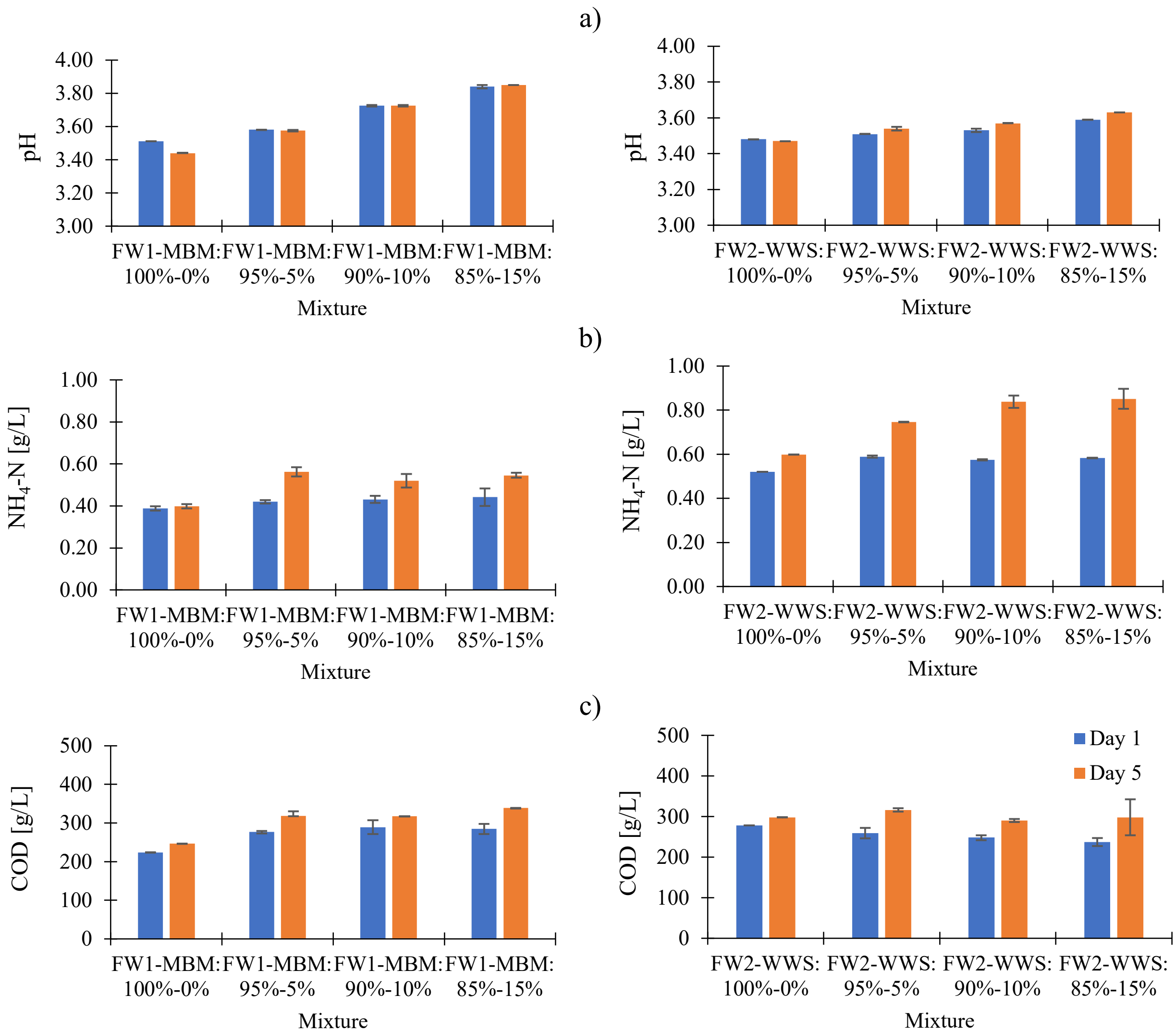

Figure 2 Change in a) pH, b) NH_4-N and c) COD during pretreatment of FW1 and MBM (left) and FW2 and WWS (right)

COD values for the samples are shown in Figure 2 c). FW2 has a slightly higher COD value (298 g/L) compared to FW1 (224 g/L). Results of the research are in line with results obtained for cafeteria FW with a pH of 4.2 ± 0.3, where COD was 197 ± 42 g/L [98].

As a result of the pretreatment, COD increased by 7 - 26%, more in the case of FW2-WWS. When adding MBM to FW1, an increasing trend of COD occurs, while in the case of

FW2-WWS, a decreasing trend is obtained, which is expected, since WWS is a low-organic material [99].

Based on these results, selection criteria were determined to decide which samples to select to reveal their impact in terms of AD. The mixture with the highest relative increase in COD and the lowest relative increase in NH_4-N concentration during pretreatment was selected. The first indicator stands for the higher amount of degradable organic matter, which in theory corresponds to higher biogas yield. The second criterion is related to prevention of ammonia inhibition during AD. Based on the chosen criteria, mixtures FW1-MBM: 95%-5% and FW2-WWS: 95%-5% were selected for the second AD stage.

3.3 Anaerobic digestion of food waste and rendering industry streams

In the second stage, AD of FW1, FW1-MBM (95%-5%), FW2 and FW2-WWS (95%-5%) were carried out. During the process, analyses were performed for both gas and liquid phases. In the gas phase, biogas yield and composition were measured, while in the liquid phase, pH, VFAs, TIC, NH_4-N, COD and electrical conductivity were analysed.

3.3.1 Gas phase

Figure 3 a) - d) shows the results of variables for the gas phase of AD for thermally pretreated mixtures of FW and rendering industry streams.

For the AD of FW, the reported biogas yield is 0.27-0.64 Nm^3/kg VS [100] that amounts to 0.24-0.58 Nm^3/kg TS, using an average VS/TS ratio of 0.90 [100]. In this research, the following biogas yields were obtained: for FW1 – 0.566 Nm^3/kg TS, for FW1-MBM – 0.499 Nm^3/kg TS, for FW2 – 0.252 Nm^3/kg TS and 0.195 Nm^3/kg TS for FW2-WWS. Such a wide range of values is a result of the FW heterogeneity (taken at two different times).

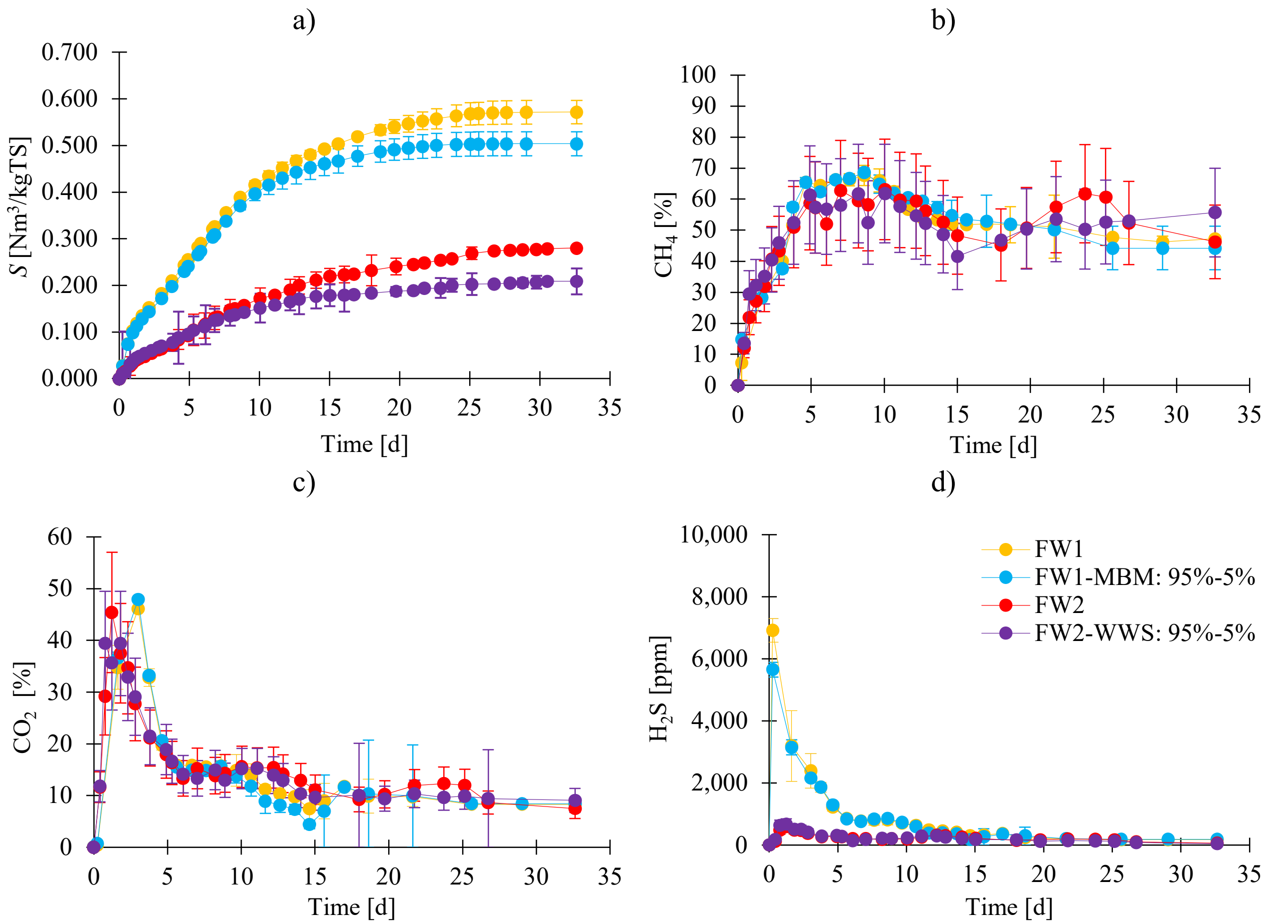

Figure 3 Variables in a gas phase, a) biogas yield, and concentrations of b) CH_4, c) CO_2 and d) H_2S during AD

In this research, it is estimated that sample FW2 is not very different from FW1, since the material that biogas plant receives usually comes from the same sources, and analysis of the liquid phase (see Figure 4) contributes to that statement. Based on the shape of the biogas yield profiles [101] shown in Figure 3a), it can be concluded that inhibition in AD of FW2 occurred, resulting in about 2.25-fold lower biogas yield compared to FW1. More detailed discussion of the causes of inhibition in the process will be provided in the following subsection on analysis of the liquid phase.

This research showed that both rendering industry streams have decreased biogas yield of FW when added in portions of 5% on a TS basis. It has been stated that FW contains fungi and yeast that enhance its biodegradability during AD [102]. MBM and WWS are sterile industry streams of alkaline hydrolysis, and when added to FW in AD, they could possibly decrease the size of the bacterial community of fungi and yeast in FW, which is reflected in a slightly lower biogas yield.

According to the previous report, in the steady state period, the biogas produced from FW reported CH_4 concentrations to be approximately between 53% and 59%, while the CO_2 concentration in biogas was in the range of around 40-47% [88]. In this study, similar concentrations of the main biogas components in the steady state period (after day 20) was observed. By comparing CH_4 and CO_2 profiles in Figures 3b) and 3c), it can be observed that the FW2 and FW2-WWS mixtures showed slightly lower CH_4 and slightly higher CO_2 content in biogas before stabilizing (days 5-20).

The profiles of H_2S concentration in biogas during the AD showed that the FW1 sample had a much higher content of sulphur-rich materials than the FW2 sample. The highest reported H_2S concentration in the experiments was obtained one day from the start of the process and reached approximately 7,000 ppm. According to the literature, raw biogas can have up to 10,000 ppm of H_2S [103]. In both cases, rendering industry streams reduced H_2S generation during AD of FW, which could be a promising topic for further exploration in the future, since high H_2S concentration during combustion produces high amounts of SO_2, which affects biogas engines on account of corrosion [104].

It is also important to note that for both batch experiments, as biogas was produced, it displaced the air which was trapped in the reactor headspace at the start of the process and decreased the share of oxygen in the gas phase. By displacing oxygen and other gases by biogas, anaerobic conditions in reactors were achieved and maintained. Other contaminants such as nitrogen, water vapour and oxygen can be present in raw biogas in amounts up to 15, 3 and 5% [103]. In this research, the maximum oxygen content in produced biogas was 5%, while concentrations of nitrogen and water vapours were not measured.

3.3.2 Liquid phase

Figure 4 a) - f) shows the results of variables for the liquid phase of AD of thermally pretreated mixtures of FW and rendering industry streams.

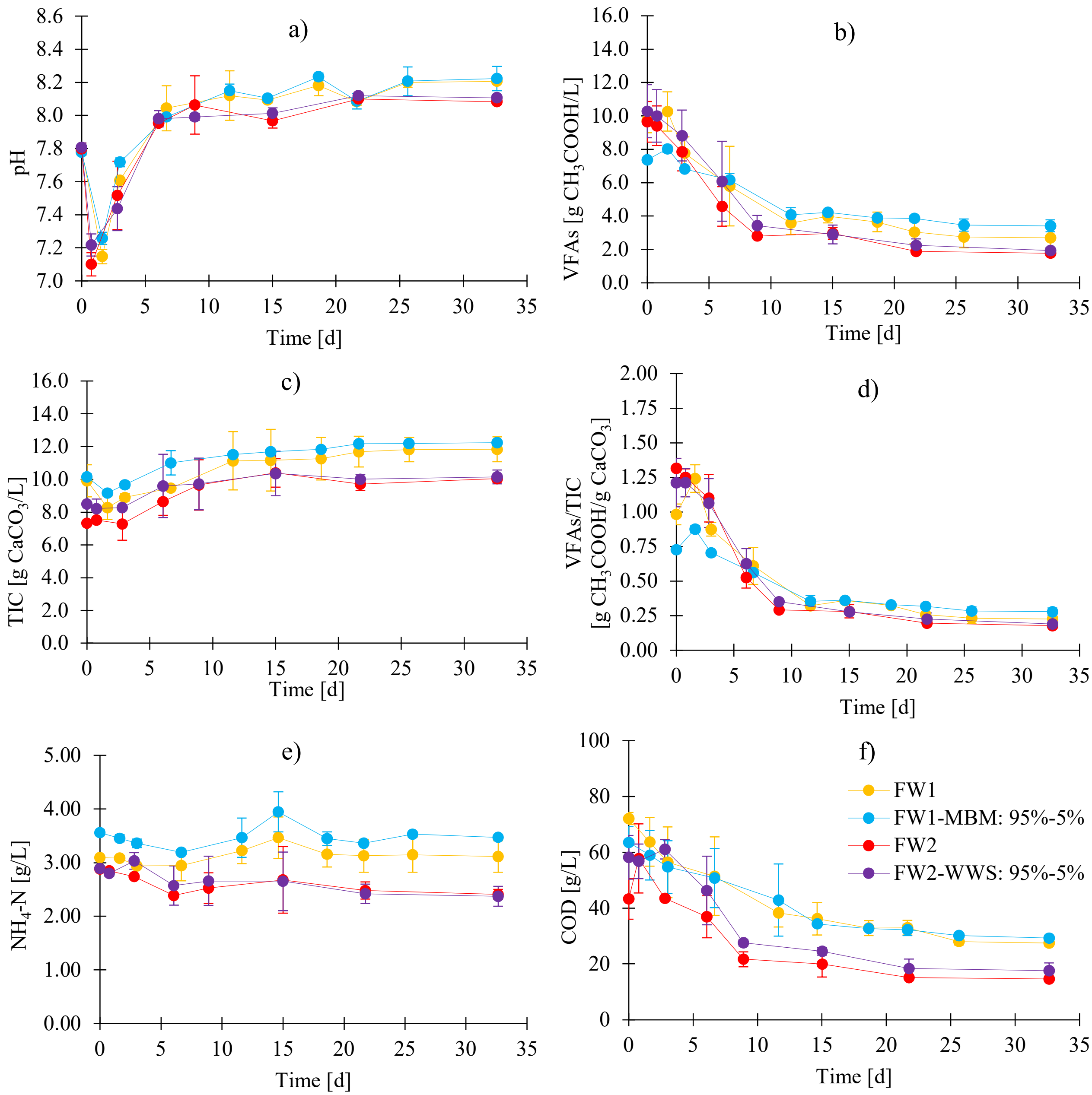

Figure 4 The change in variables in a liquid phase, a) pH, b) VFA, c) TIC, d) VFA/TIC, e) NH_4-N and f) COD during AD of selected mixtures

The profile of pH values determined in this research follows the theoretical pathway. During the first days of the process, pH value drops because of acidogenesis and acetogenesis, while it subsequently increases as VFAs are consumed to produce CH_4 and CO_2 [105]. As mentioned before, MBM is a product of alkaline hydrolysis of animal industry streams [96], and when added as a co-substrate to FW, it slightly increases pH (see Figure 4a). FW2 showed a similar range of pH values to that of FW1. As with MBM, WWS slightly increased the pH of FW. According to some previous studies, the pH values for AD of FW ranged between 6.0 and 8.5 [35,106]. The pH values obtained in this research showed that there was no indication of inhibition in biogas production caused by poor pH control for FW2 and WWS [107].

Figure 4b) shows the reported profile of VFAs during AD of selected FW mixtures. VFAs are generated during the acidogenesis stage, which causes the drop in pH as shown in Figure 4a). For the AD of FW, it was reported that the concentration of VFAs ranged between ca. 10.0 to 11.0 g/L, while pH ranged between 7.5 and 9.0 [108]. However, another study showed that the maximum value of VFA concentration during AD of FW was even below 5.0 g/L, while pH was above 8.0 [89]. During the entire process, FW1 achieved a VFA conversion of 81.8%, while FW1-MBM achieved a VFA conversion of 57.5%. Adding MBM to FW causes lower generation of VFAs, which was reflected in lower levels of conversion to biogas and consequently lower biogas yield, as shown in Figure 3a). The VFA conversion was 81.6% for FW2, and 81.2% when WWS was added to FW2. Results show that VFAs in all mixtures under analysis were converted successfully, which is an indication of non-inhibited acidogenesis and acetogenesis steps. Based on that, it can be concluded that inhibition of biogas production for FW2 and FW2-WWS cannot be caused by LCFA or VFA accumulation [109].

The profile of TIC in these mixtures shown in Figure 4c) follows similar trends as the pH profile shown in Figure 4a), since the TIC value represents the buffering capacity of the mixture (ability to change pH by adding acids or alkaline) [93]. The range of TIC values during AD of FW was reported to be between 8.0 and 9.5 g $CaCO_3$/L [110]. Results of this research have proven to be in a slightly broader range: for FW, between 8.272 ± 0.715 g $CaCO_3$/L and 11.835

± 0.933 g $CaCO_3$/L, while for FW2, the range was between 7.285 ± 1.006 g $CaCO_3$/L and 10.396 ± 1.613 g $CaCO_3$/L. In both cases, the addition of MBM and WWS yielded slightly increased TIC values.

Usually, a high VFAs/TIC ratio (<0.4) is an indicator that the AD reactor is overfed by substrate and that the process is unstable [106]. Such an interpretation is valuable only if AD is studied in continuous operation. In this research, a batch AD was performed, which showed that the VFAs/TIC ratio can go above 1.0 with the process remaining stable. Adding MBM to FW1 decreased the VFAs/TIC ratio, since MBM showed a negative effect in term of VFA production. On the other hand, WWS did not significantly affect the VFAs/TIC ratio for FW2. In the case of batch AD of food-processing industrial waste, the VFAs/TIC ratio at the start of the process was approximately 0.70; after 6 days it increased to around 2.3 and later dropped, reaching the final value of ca. 0.25 after 30 days from the start of the process [111].

Ammonia inhibition of biogas production using FW is a relatively common inhibition type in AD, caused by protein-rich material present in FW [112]. It has been determined that, in the case of AD of FW, there is a wide range in the NH_4-N inhibition threshold concentration, between 2 and 6 g/L [55]. As expected, adding MBM to FW1 increased the release of ammonia during AD, similar to what was observed during the pretreatment stage. However, these higher concentrations of NH_4-N when MBM was added to FW did not affect the stability of AD, since the biogas production was not inhibited, as shown in Figure 3a). It can be seen in Figure 4e) that the highest NH_4-N concentration is achieved when adding MBM to FW1. Among the reasons for stable behaviour (despite a comparably high NH_4-N concentration) is adaptation of the microbial community in a digester over time to operation at higher NH_4-N concentrations (compared to others) without causing a failure in the process [113]. The FW2 and FW2-WWS mixtures had much lower concentrations of NH_4-N than FW1, from which we can conclude that ammonia inhibition cannot be the reason why FW2 gave such a reduced biogas production.

Figure 4f) shows the change in COD of these mixtures during the AD. According to the literature, FW shows a wide range of COD values at the start of the process, between 69.92 and 181.05 g/L [55,89,114]. The efficiency of COD removal during AD was approximately the following: 61.9% for FW1, 53.9% for FW1-MBM, 74.7% for FW2, and 71.2% for FW2-WWS. In the literature, it has been reported that COD removal efficiency of two-stage AD of dining hall FW was 78.7% [115], while the COD removal efficiency during AD of canteen FW was slightly lower, between 51 and 62% [109].

Based on the results presented in Figure 4, there is no indicative measure in the liquid phase of what caused the inhibition in AD of the FW2 and FW2 mixtures with WWS, since those samples showed almost identical parameter values as FW1 and FW1-MBM.

Finally, to further explore the possible cause of inhibition, electrical conductivity was measured at the end of the process, which could show possible salt inhibition [67]. The explanation of salt-inhibition mechanisms is that a high presence of sodium ions during AD reduces the conversion of acetate to products (inhibition of methanogenesis) and reduces the potential to produce biogas [116]. In this study, it was noticed that the measured biogas composition (Figure 3b) showed lower methane and higher CO_2 concentrations in the biogas for FW2 and its mixture with WWS. Since the last stage of AD, methanogenesis is related to conversion of acetate and CO_2 to methane, methanogenesis of FW2 is shown to be relatively inefficient.

Measurements of electrical conductivity gave the following results, for FW1 8.99 ± 0.54 mS/cm, for FW1-MBM 9.00 ± 0.39 mS/cm, for FW2 9.96 ± 0.63 mS/cm and for FW2-WWS 9.60 ± 0.44 mS/cm. Results indicate that higher conductivity (higher concentrations of salts [117]) is obtained for FW2. However, the values are still way below the general threshold for salt inhibition of 30 mS/cm [71]. It is possible that a slightly higher concentration of salts in

FW2 resulted in the lower biogas yield, but it is highly improbable to expect that an approximately 10% higher electrical conductivity resulted in 2.25-fold lower biogas yield.

After experimental analysis of two-stage AD of FW and rendering industry streams, a high-level of heterogeneity for FW was confirmed. Analysis revealed that most process variables display the usual behaviour; however, despite that, the AD process was inhibited for a certain FW sample. Rendering industry streams showed antagonistic effects in terms of biogas production when added to FW. It was also noted that their addition to FW slightly improved stability, since a narrower range of reported values was obtained between studied parallels.

3.4 Kinetic parameters of AD

The kinetic parameters of AD for the mixtures were further estimated. Results of the applied kinetic models with the lowest *RMSE* are shown in Figure 5, while Table 4 displays the calculated kinetic parameters.

The best fit of a model to the experimental data for all these mixtures was obtained by the First-order kinetic model, where the estimated reaction rate constant for FW1 was 0.135 d^{-1} and for FW2, 0.097 d^{-1}. As expected, the rate constant for FW2 is lower (by 28%) compared to FW1, owing to the occurrence of inhibition. These results are in line with previous reports. The first-order reaction rate constant for AD of FW has shown a wide range of values, between 0.027 $d^{-}1$ and 0.49 d^{-1} [72,75,118–120].

In this study, Monod kinetics proved to be the least applicable among the models studied, because of the highest *RMSE* values. Application of the Modified Gompertz model in AD of thermally pretreated FW gave a lag phase (λ) equal to 0 d, which was also reported in some previous studies [72,120,121]. Kinetic analysis using the Cone model showed that FW has a shape factor equal to n=1.6, and a reaction rate constant between 0.145 and 0.200 d^{-1}. A previous report on the application of a Cone model in AD of FW gave a similar shape factor (1.3) and rate constant (0.126 d^{-1}) [75].

Previous studies have shown that adding co-substrates like seaweed [119], waste cardboard [122], distillery grains [123], pig manure [65] and certain types of wastewater biosolids [124] to FW decreases the value of kinetic parameters. On the other hand, co-substrates like sewage sludge [125], rice straw [36] and dairy manure [126] increase the reaction rate of AD when added to FW.

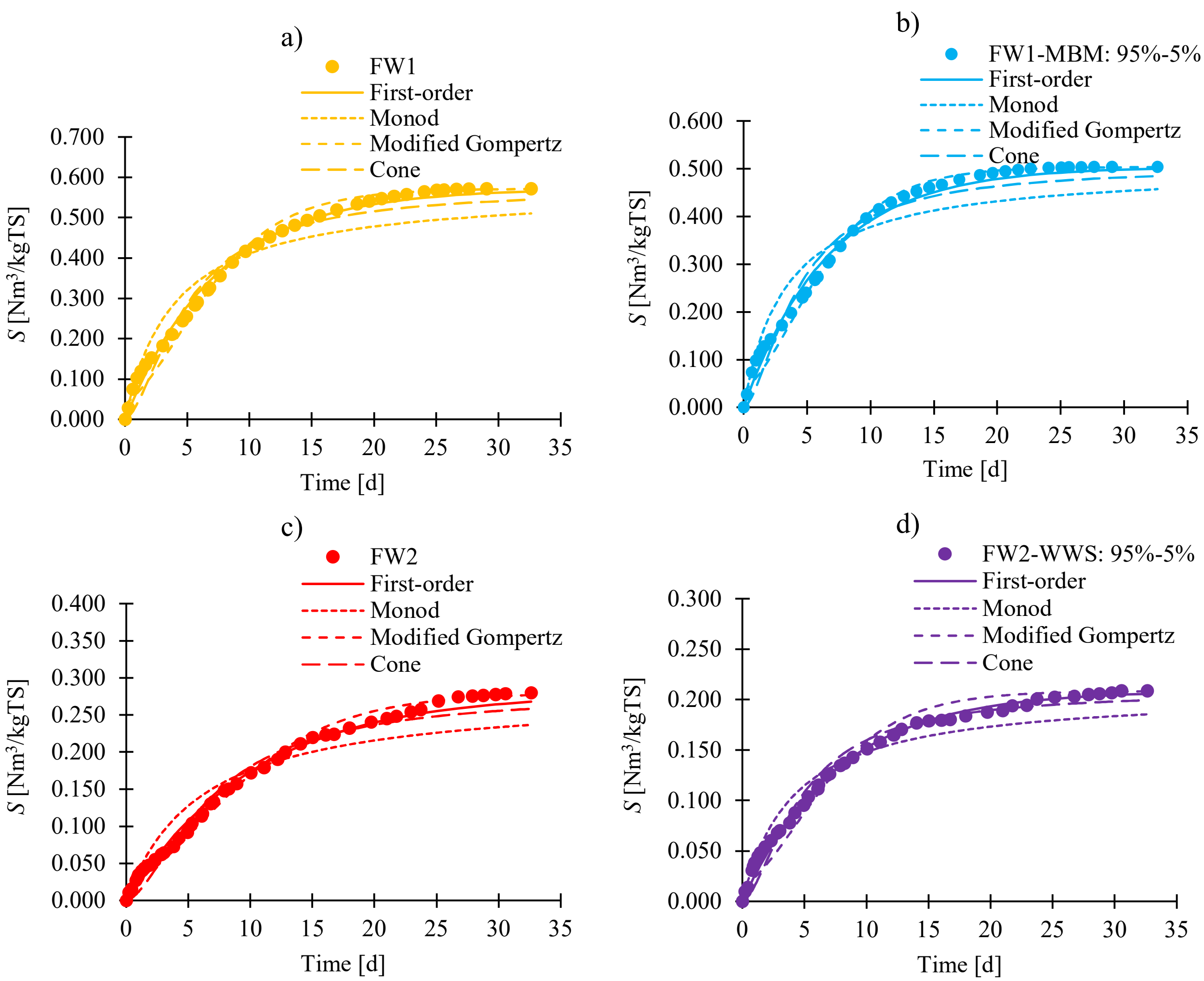

Figure 5 Kinetic analysis of biogas yield for a) FW1, b) FW1-MBM, c) FW2 and d) FW2-WWS

Table 4. Estimated kinetic parameters for AD of selected mixtures

Model	Parameters	Mixtures			
		FW1	FW1-MBM 95%-5%	FW2	FW2-WWS 95%-5%
First-order	k [d^{-1}]	0.135	0.150	0.097	0.131
	$RMSE$ [Nm^3/kg TS]	0.0150	0.0153	0.0079	0.0052
Monod	k [d^{-1}]	0.255	0.300	0.168	0.245
	$RMSE$ [Nm^3/kg TS]	0.0512	0.0476	0.0259	0.0146
Modified Gompertz	R_m [Nm^3/(kg TS·d)]	0.0845	0.0950	0.0623	0.0850
	λ [d]	0	0	0	0
	$RMSE$ [Nm^3/kg TS]	0.0218	0.0171	0.0090	0.0112
Cone	k [d^{-1}]	0.200	0.230	0.145	0.210
	n [−]	1.6	1.6	1.6	1.6
	$RMSE$ [Nm^3/kg TS]	0.0305	0.0288	0.0136	0.0106

4 Conclusion

This study has investigated the thermal pretreatment of rendering industry streams, MBM and WWS with FW obtained from a biogas plant, and further biogas production potential has been explored. Thermal pretreatment of these mixtures at a temperature of 35°C for a 5-day duration showed no impact on the pH, while concentrations of both COD and NH_4-N increased. AD of both samples containing MBM or WWS causes antagonistic effects in terms of biogas production when added to FW. Adding 5% MBM to FW1 decreased biogas production by 12%, while adding 5% WWS to FW2 decreased biogas production by 23%.

This research has also shown that there is a relatively high probability of inhibition during AD of FW, on account of the variety and complexity of FW. In addition, it was found that a certain inhibition could occur that could not be detected using the standard equipment applied in biogas plants.

Based on kinetic analysis, rendering industry streams showed an increase in the reaction rate of AD from FW, determined by means of the different kinetic models used in this study.

In this research, First-order kinetics showed the highest match between the experimental and model data, where the reaction rate constant increased from 0.135 d^{-1} to 0.150 d^{-1} when MBM was added in 5% share to FW, and from 0.097 d^{-1} to 0.131 d^{-1} when WWS was added to FW.

The experimental approach has also shown that process variables, such as pH, LCFAs, VFAs, VFAs/TIC ratio, NH_4-N and electrical conductivity behave as usual, although the AD process might be inhibited. The research has proved that utilisation of waste and residue materials to produce advanced biofuels, such as biogas, is more complex and requires higher level analysis, compared to the use of common substrates to produce biogas, e.g. cultivated energy crops.

Future research should focus on analysing more detailed causes of inhibition during AD of FW and on exploring how to prevent such inhibitions.

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ARTICLE 5

Beyond energy crops and subsidised electricity – A study on sustainable biogas production and utilisation in advanced energy markets

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ABSTRACT

The aim of this study is to investigate the operation of biogas plants in advanced energy markets after energy crops become limited in their use and biogas plants exit subsidy schemes for electricity production. Continuous biogas combined heat and power production and sale of electricity on the day-ahead market could be a viable operation strategy only in the case of low-cost substrates. When the break-even cost of electricity production in biogas power plants reaches 100 €/MWh_{el}, selling electricity on the day-ahead market does not create profit. The study shown that a more profitable operation strategy involves coupling biogas power plant operation on the electricity balancing market with biomethane production or combining a small-scale sugar beet processing facility with a biogas upgrading plant to cover heat demand for sugar beet processing. Techno-economic analysis showed that the viability of both alternative operation strategies is severely impacted by the selling price of biomethane. In the given market conditions, a selling price of biomethane below 50 €/MWh is not viable for a biogas plant. The model developed could be used as a guideline for biogas plant operators on how to proceed after significant changes appear in both biogas production and biogas utilisation.

KEYWORDS

Anaerobic Digestion, Biomethane, Electricity markets, Heat utilisation, Sugar beet

1 INTRODUCTION

Biogas is a renewable energy fuel produced during the degradation of complex organic matter in an oxygen-free atmosphere [1]. Biogas composition is ca. 50-75% methane and 25-45% carbon dioxide, with small amounts of water vapour, oxygen, nitrogen, ammonia, hydrogen and hydrogen sulphide [2]. Over the years, production of biogas was based on utilising energy crops, of which maize silage was (and still is) the most common [3]. However, the European Commission has recently adopted an assessment that beyond 2020, the application of maize silage to biogas production will be limited or even restricted, owing to future sustainability policies [4].

Cultivation of maize silage involves environmental burdens related to the consumption of energy and fertilisers, as well as changes in indirect land use [5]. As an alternative to cultivated energy crops, other biomass sources have shown potential to produce biogas, such as residues from agriculture and industry, municipal organic waste and various sludge types [6]. Agricultural waste and industry co-products and by-products have been recognised as a wide source of sustainable biomass in the European Union [7]. Of all these, animal manure has proven to have the highest biomass technical potential (in t/km^2) compared to other agricultural residues such as harvest leftovers, processing by-products and food waste [7]. Although animal manure has been recognised as a sustainable substrate for biogas production, it has a relatively low biogas yield of only about 0.09 m^3/kg total solids (TS) [8]. To increase the biogas production of cattle manure, co-digestion with other biomass sources is usually performed [9].

Residue grass from landscape management has the potential to serve as a sustainable source of biomass to produce biogas. In the case of river embankments, current practice shows that riverbank grass is mowed a couple of times per year and usually left on the riverbank. The digestion that occurs within the piles of grass left on the bank causes methane and carbon dioxide release into the atmosphere [10]. To avoid unnecessary GHG emissions, riverbank residue grass has been studied as a potential replacement for maize silage in biogas production in Croatia [11]. The biogas yield of riverbank grass co-digested with cattle manure in a 1:1 ratio on a dry basis was about 0.289 Nm^3/kg TS, which was about 28% lower, compared to co-digestion with maize silage. On the other hand, residue grass shows better pH control during the process, compared to maize silage.

Except for animal manure and energy crops, biogas can be produced using industry co-products and by-products as co-substrates. Dairy waste from the dairy processing industry has shown high energy potential to serve as a feedstock for biogas production in Poland [12]. A study has shown that dairy whey produces about 0.86 Nm^3 of biogas per kg of volatile solids (VS), dairy sludge yields biogas production of about 0.48 Nm^3/kg VS, while fatty sludge produces about 1.2 Nm^3 biogas/kg VS. Grease trap sludge has shown synergistic effects in increasing the methane yield of sewage sludge from 0.18 to 0.35 Nm^3/kg VS during anaerobic digestion [13]. Food waste [14] and the organic fraction of municipal solid waste [15] have also attracted attention as sustainable substrates for biogas production. The composition of food waste and organic municipal solid waste is significantly affected by seasonal changes, geographical position, cooking procedures and consumption patterns [16]. These variables strongly effect the AD in terms of process control and inhibition occurrence, usually caused by compounds like salts, heavy metals, ammonia, long chain fatty acids, etc. Looking at the variety of feedstocks available to produce biogas, it is clear that biogas can act as a sustainable alternative to fossil fuels in energy production [17].

According to the latest EU directive (2018/2001) on promoting the use of energy from renewable sources [18], the future use of biogas will be aimed toward biofuel production to be used in industry and the transport sector. Therefore, biogas will play an important role in reaching the future energy policy targets of the European Union (EU). In 2015, the installed capacity of biogas in the EU was ca. 15 GW_{el}, with more than 17,400 biogas plants [19]. Most biogas plants currently use biogas for combined heat and electricity production (CHP), for which biogas plants receive financial support for the energy produced in the form of a Feed-in-Tariff (FIT) or a Premium Tariff (PT) system [20]. The highest incentive for biogas plants is found in Bulgaria, where biogas plants earn 248 EUR/MWh_{el}, while the lowest is reported for the Netherlands, at 85 EUR/MWh_{el} [21]. In the case of Croatia, FIT for 1 kWh of produced electricity using biogas is about 1.20 HRK, or 160 EUR/MWh_{el} [22]. It is important to emphasise that the period of a guaranteed electricity price for biogas CHP is between 12 and 14 years, depending on the country [23].

Soon, biogas plants in the EU will be facing operational issues. Besides the regulations on limited use of maize silage in biogas production, loss of subsidy schemes for electricity production will make possible new options for biogas utilisation. A possible solution for keeping electricity production in biogas CHP after subsidies expire is an orientation towards the operation of biogas plants on the electricity energy market, since biogas plants are flexible in their operation in the power sector, compared to other renewable energy sources [24].

The International Energy Agency has recognised the energy from biomass as a stabilising element in balancing the electricity grid and providing options for energy storage in the EU [25]. The flexible operation of biogas-driven CHP units in terms of load and frequent starts and stops is growing in importance, owing to the increasing share of variable RES in energy systems [26]. The potential of biogas plants to balance the power supply from wind power plants was examined in the case of Latvia [27]. Results showed that the surplus of wind power capacity could be balanced using currently installed biogas CHP plants. In the case of Germany's power system [28], it has been shown that the flexible power generation of biogas plants, integrated with the substitution of fossil fuels in the heating sector, could contribute to economic benefits, compared to subsidised electricity production. Dynamic analysis of the operation of biogas plants in the peak power reserve market in Germany [29] has shown that biogas plants with excess capacity can profitably exploit peak power prices. Results of the study have also shown that a single oversized CHP unit (2 MW_{el}) is economically more feasible than two smaller CHP units (2 x 1 MW_{el}). The market-based optimisation model for biogas plants operating on the spot market [30] showed that biogas facilities can control electricity production through their storage capability and flexible operation in time, duration and amount. For flexible operation of a biogas plant using a CHP of 1.36 MW_{el} and an upgrading unit of 600 Nm^3/h capacity, the size of installed gas storage of 4,800 m^3 proved to be sufficient to provide control reserves and biomethane simultaneously [31].

Another option for maintaining the profitability of biogas plants after loss of the subsidy scheme for electricity production is the upgrading of biogas to biomethane, a gas with more than 95 vol.% of CH_4 [32], as an alternative to heat and electricity production in cogeneration plants [33]. Biogas upgrading in general consists of two steps [34]. The first step is "biogas cleaning", where toxic compounds like hydrogen sulphide, volatile organic compounds, and ammonia are removed. The next step is the separation of carbon dioxide from methane, which is usually achieved through absorption, adsorption or membrane separation. The cost of upgrading depends heavily on the amount of upgraded biogas and the economy of scale [34]. The total cost of biogas upgrading is estimated to be between 58 and 78 EUR/MWh of upgraded biogas. Energy analysis of biomethane and biogas CHP [35] has shown that the energy efficiency of biomethane production is about 90%, which is much greater compared to the electricity efficiency in CHP (35-40%). Moreover, it has been shown that the incentivising instrument (subsidy) required for biomethane production is at the level of about 30 EUR/MWh, while in the case of electricity from CHP, the lowest subsidy is at the level of about 80 EUR/MWh_{el} [35]. Production of heat from biogas CHP and its utilisation in a small local district heating network, combined with biogas upgrading to biomethane and its injection into a local gas grid, has proven to be a more advantageous option for biogas plant operation compared to electricity production alone [36]. Apart from a district heating network, biogas heat can also be utilised in greenhouses, farming stables, industry, etc [36]. The market potential of biomethane is very broad, since it can be used either in energy production (power generation, vehicle fuel), or as a raw material for the chemical industry, replacing natural gas [37]. The unitary value of subsidies for biomethane and the selling price depend on the business model [38]. In Germany, biomethane producers do not receive FIT for feeding biomethane into the gas grid [39]. However, the German Energy Agency supports biomethane producers through a bonus system for guaranteeing biomethane origin when sustainable substrates like manure and waste are used for biogas production. Such an approach in the biogas sector is given in the latest Renewable Energy Directive recast (RED II) [40], where the guarantee of origin for biomethane production is not declared as a support scheme and should be distinguished from the green certificates for biomethane that are used in support schemes. The selling price of sustainably produced biomethane under the guarantee of origin in Germany is between 65 and 80 €/MWh [41]. Other recent studies have reported that, on average, the selling price of biomethane is ca. 70 €/MWh [42,43]. Detailed analysis of biomethane production and its economic viability has revealed that there are many advantages over biogas CHP in reaching the EU climate and energy goals. Still, the main reasons why biogas upgrading is not currently the dominant biogas utilisation technology are the relatively high subsidy support for biogas CHP and the relatively high capital and operational cost of the upgrading process.

In this study, the economic viability of biogas plant operation in advanced energy markets integrated with sugar production will be analysed. The production of sugar is among the most energy-intensive industries within the agri-food sector [44]. Sugar beet processing constitutes the most energy-intensive phase in sugar production because of its high demand for electricity and heat [44]. Intensive energy users during sugar beet processing are extraction, juice heating, evaporating crystallisation and sugar drying [45]. The specific electricity consumption during sugar beet processing varies between 17 and 30 kWh_{el}/t of processed sugar beet, while specific heat demand varies between 140 and 200 kWh_{th}/t of processed sugar, excluding sugar beet pulp drying [46]. Currently, natural gas is the most common fossil-based fuel for energy production in sugar beet factories [47]. The latest report in 2019 from the European Association of Sugar Manufacturers [48] stated that renewable energy producers should coordinate their operation with the sugar industry to reduce dependency on fossil fuels and reduce GHG emissions. Therefore, anaerobic digestion and biogas technologies have shown high potential for integration within the sugar industry to reduce the requirement for natural gas [49]. Integration of anaerobic digestion technology in a sugar beet processing facility has proven to be more feasible in the case of small-scale, decentralised sugar production [50] than in the case of large, robust centralised facilities. By-products from sugar production like sugar beet pulp, sugar beet tops and tails can be used to reduce waste and give additional value to sugar [51]. Dried sugar beet pulp has been successfully applied in mesophilic co-digestion with animal manure, where it has been shown to increase the methane yield of manure by almost 130% [52].

The contribution of this research is to develop operational methods for existing biogas plants that currently operate in CHP mode once they lose subsidies for energy production in terms of feed-in-tariffs, based on the use of alternative substrates to maize silage in biogas production (sugar beet by-products, riverbank residue grass and cattle manure) and biogas utilisation in advanced energy markets, combined with a small-scale sugar beet processing plant. Objectives of the research are as follows:

(i) to evaluate the viability of biogas CHP plant operation on the day-ahead electricity market after feed-in-tariffs expiry relative to the cost of substrate;

(ii) to determine the threshold of the biomethane selling price relative to the investment in the biogas upgrading unit and biogas CHP operation on the balancing electricity market;

(iii) to assess the economics of integrating biogas plants with industry processes in order to establish sustainable energy and mass flows.

The hypothesis of the research states that the operation of biogas plants using sustainable substrates in advanced energy markets integrated with industry processes can yield economic benefits even after existing biogas plants which have paid out their investment lose support for electricity production by using food-competitive energy crops.

2 MATERIALS & METHODS

In this section, an overview of applied materials and methods is presented. First, biogas yields of alternative substrates to those energy crops in the study are presented. Second, the analysis of biogas production and utilisation under advanced energy markets integrated with sugar production is given.

2.1 Feedstock for biogas production

Riverbank residue grass is selected to be an alternative feedstock to maize silage in biogas production, based on the research already conducted [11]. The daily production of biogas, Q(biogas), using riverbank grass and cattle manure is defined using the following relation:

$$Q(\text{biogas}) = q_{\text{RG+CM}} \cdot M_{\text{RG+CM}} \tag{1}$$

where $M_{\text{RG+CM}}$ represents the daily input of riverbank residue grass and cattle manure to the digester and $q_{\text{RG+CM}}$ represents the biogas yield of residue riverbank grass and animal manure co-digestion. According to previous research, the $q_{\text{RG+CM}}$ was estimated on 80 Nm^3/t of fresh feedstock [11].

The production period of sugar beet in a small-scale factory (capacity of 100 t/day of processed sugar beet) is assumed to be between October and March. Sugar beet pulp takes around 25% of the mass of processed sugar beet, while the waste plant is around 1.6% of processed beet mass [53]. During sugar production, the biogas plant utilises sugar beet by-products additional to riverbank grass and cattle manure in biogas production:

$$Q(\text{biogas}) = q_{\text{RG+CM}} \cdot M_{\text{RG+CM}} + q_{\text{SBP}} \cdot M_{\text{SBP}} + q_{\text{WP}} \cdot M_{\text{WP}} \tag{2}$$

where M_{SBP} and M_{WP} represent the daily quantity of sugar beet pulp and the waste plant generated during beet processing, while $M_{\text{RG+CM}}$ represents the daily input of riverbank residue grass and cattle manure to the digester. The average specific biogas yield of sugar beet pulp (q_{SBP}) was found to be 105 Nm^3/t of raw sugar beet pulp, while the average specific biogas yield of the waste plant (q_{WP}) at the same time is 40 Nm^3/t of raw waste residue [53].

2.2 Biogas plant operation under advanced markets integrated with sugar production

In the MATLAB/Simulink® models, all processes inside the anaerobic digester are assumed to be continuous processes, with average biogas production in the unit of time [54]. The computational time of the models was one year, with time intervals of one hour, where the operating point in all scenarios was switch-controlled in real-time, based on market prices. A complementary approach was implemented for the experimental switch-controlled energy harvesting in LabView® [55]. Electricity and heat production (E_{CHP}, H_{CHP}) based on the utilisation of biogas in the CHP unit can be calculated using:

$$E_{\text{CHP}} = \Delta H(\text{biogas}) \cdot \eta_{\text{el}} \int_{0}^{8760\ \text{h}} Q_1(\text{biogas})\ \text{d}t \tag{3}$$

$$H_{\text{CHP}} = \Delta H(\text{biogas}) \cdot \eta_{\text{th}} \int_{0}^{8760\ \text{h}} Q_1(\text{biogas})\ \text{d}t \tag{4}$$

where Q_1(biogas) is the intake flow of biogas to the CHP unit, ΔH (biogas) is the lower calorific value of biogas estimated on 6 kWh/Nm^3 [56], η_{el} is the efficiency of electricity production in the CHP (40%), and η_{th} is the efficiency of thermal energy (heat) in the CHP (50%) [4].

To ensure flexible operation of the biogas CHP on the electricity market, additional biogas storage is included as part of the post-feed-in era investment. Currently, digester headspace is used as temporary storage for biogas for several hours [57], usually not longer than 4 hours. The dynamics of biogas storage depends on the electricity price on the market; the biogas from anaerobic digestion is stored or utilised in the CHP unit to generate electricity. The storage fill percentage is calculated as:

$$x_{storage\%} = \int \left(Q_1 - Q_1^{*}\right) dt \tag{5}$$

where $Q_1^{*}$is the biogas storage outflow, which is zero for electricity prices on the day-ahead market and lower than the marginal price. If the electricity price is above the break-even cost of electricity production, the Q_1^{*} will increase up to the maximum flow at which the CHP unit can operate. If biogas storage falls below 20%, the Q_1^{*} is limited to the maximum value of Q_1 in order to avoid a completely empty biogas storage unit.

The system dynamics is determined by the electricity price and biomethane price, where the biogas is supplied to storage, the upgrading unit or the CHP, in order to maximize profit, known as advanced unit commitment with economic dispatch [58]. A similar approach is described in [59], where the combined operation between wind power generation and pumped hydro energy storage was analysed, employing MATLAB/Simulink®. For biogas upgrading, a membrane separation system was selected, also known as gas permeation technology, owing to its suitability for smaller upgrading capacities (250 - 750 Nm^3/h) [60]. The specific membrane upgrading electricity consumption for raw biogas ranges between 0.35 and 0.40 kWh_{el}/Nm^3 [60]. The total energy potential of biomethane outflow from upgrading is:

$$H_{up} = \Delta H(\text{biogas}) \cdot \eta_{up} \int_0^{8760\ \text{h}} Q_2(\text{biogas})\ \mathrm{d}t \tag{6}$$

where Q_2(biogas) is the intake flow of biogas to the upgrading unit, and η_{up} is the efficiency of the upgrading unit, 90 % [60].

Specific heat demand for sugar beet processing is set at h_{SB}=170 kWh_{th}/t of processed sugar beet when the sugar beet pulp is not dried [46]. This study considerers a small-scale sugar beet processing facility [50] with an average daily input of sugar beet set at M_{SB}=100 t. To calculate the daily heat demand (H_{SB}) for the daily processing of sugar beet, the following relations were used:

$$H_{SB} = h_{SB} \cdot M_{SB} \tag{7}$$

A constraint in the calculation is set on the production of heat to fulfil the heat requirements in the sugar beet processing:

$$H_{SB} = \Delta H(\text{biogas}) \cdot \eta_{gb} \int_0^{8760\ \text{h}} Q_3(\text{biogas})\ \mathrm{d}t \tag{8}$$

where Q_3(biogas) is the volume flow rate of biogas required to achieve the proposed heat demand, and the efficiency of the gas boiler (η_{gb}) used in beet processing facility is set at 90% [46].

3 CASE STUDY

The study follows a virtual biogas plant that operated in the past using maize silage and animal manure as substrates, while selling heat in the local district heating network and electricity under a Feed-in-Tariff. The biogas plant operates with two anaerobic digesters, each with a capacity of 4,500 m^3. An installed CHP electric power is 1.00 MW_{el} with electric power efficiency of CHP 40% and thermal power efficiency of 50% [4]. To maintain the heat and electricity production performance, it is required to utilise 10,000 Nm^3/day of biogas in CHP. It is assumed that the biogas CHP engine works for 60,000 h [61] in the period between general overhauls. The capacity of the upgrading unit was assumed at 420 Nm^3/h of upgraded biogas.

3.1 Scenario selection

After the prohibition of maize silage for use in biogas production and the end of the existing subsidy scheme, biogas plants will need to apply different operation strategies. The following three strategies (scenarios) are considered in this work (a schematic representation of these scenarios is shown in Figure 1):

- *Scenario I):* the reference case, where an existing biogas plant continues its operation after a general CHP overhaul and starts to sell electricity on the day-ahead market. Maize silage is replaced by riverbank residue grass, while animal manure further remained to be used for anaerobic digestion. To ensure the flexible operation of CHP on the day-ahead electricity market, given fluctuating prices, an additional investment in biogas external storage is included. The heat produced is sold to a local district heating network.
- *Scenario II):* investment in an upgrading unit to produce biomethane and in the compressor to inject biomethane into a local natural gas grid are considered. The upgrading unit operates in the period when the potential profit obtained by selling electricity on the electricity market is below the biomethane profit from the upgrading unit. The restored CHP unit produces electrical energy during peak power needs and sells it on an hour-ahead electricity market (a balancing market). In this scenario selling heat to the local district heating network is rather limited by the energy production in CHP which is driven by fluctuating conditions on the electricity market. Feedstock for biogas production is the same as in Scenario I).

- *Scenario III):* connection between a biogas plant and a small-scale sugar beet processing plant with a capacity of 100 t/d of processed sugar beet. In the period when sugar beet is not processed in the plant (March-October), biogas will be produced by digestion of residue riverbank grass and animal manure, as in Scenarios I and II, using the biogas produced as a biomethane. In the period when sugar beet is processed, biogas will be produced from sugar beet by-products (wet exhausted sugar beet pulp and beet plant residues), riverbank residue grass and animal manure. Part of the biogas produced will be sold to the sugar beet processing facility as a replacement for natural gas in covering the heat demand for sugar beet processing, while the other part will be upgraded to biomethane and injected into the natural gas grid.

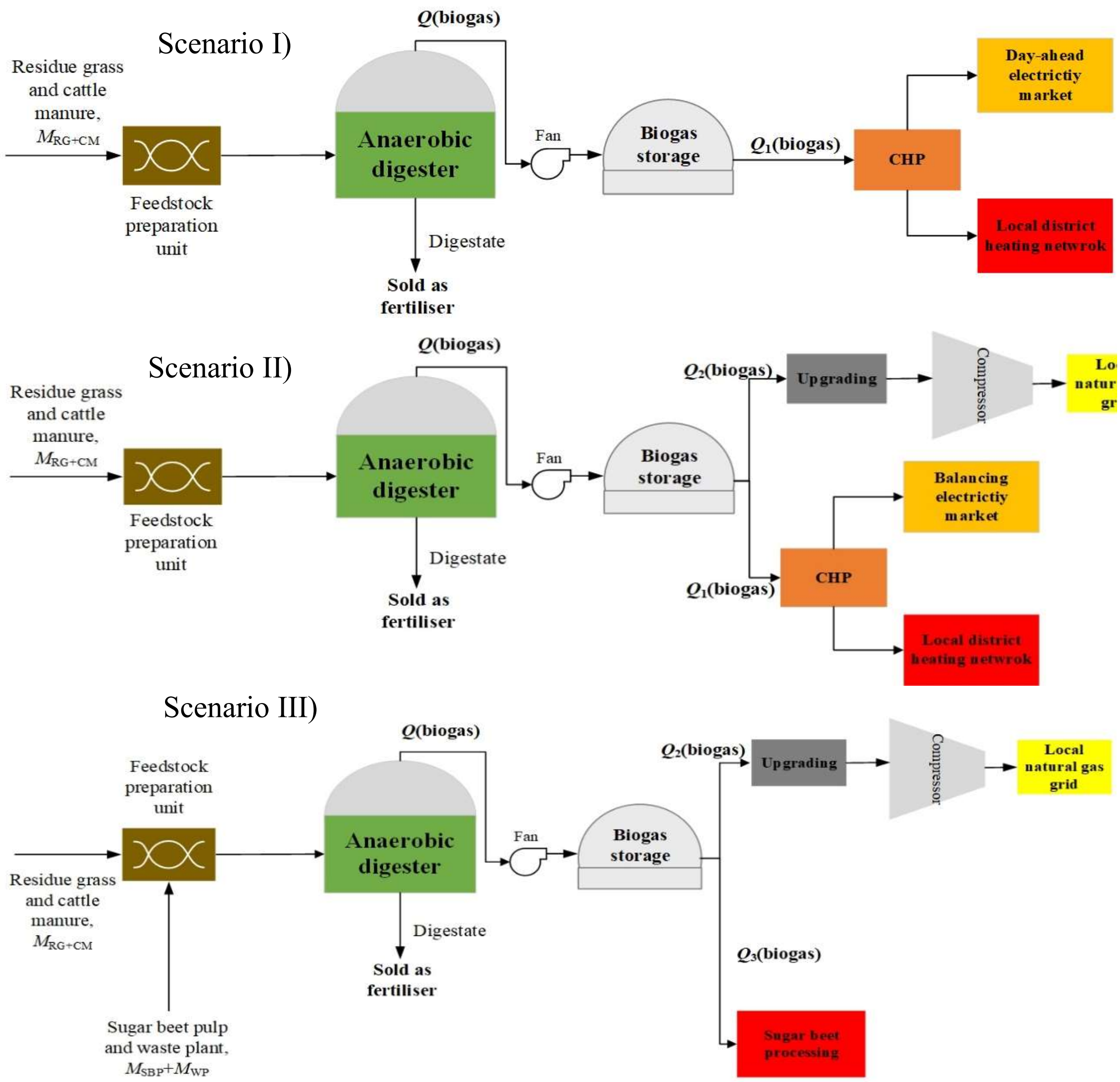

Figure 1 A schematic representation of the 3 scenarios

3.2 Process economics

To earn profit under the new market conditions, the biogas plant must sell electricity on the day-ahead market − prices adopted from Nord Pool [62] for the case of Denmark (DK1) in 2018, only when the price is higher than the break-even cost of electricity production ($BECP_{\mathrm{el}}$), which can be calculated using (9):

$$BECP_{\mathrm{el}} = \frac{OPEX - p(\mathrm{heat}) \cdot H_{\mathrm{CHP}}}{E_{\mathrm{CHP}}} \tag{9}$$

where *OPEX* represents the daily cost of feedstock (which includes harvesting and transport of the feedstock [63]), and the daily cost of maintenance, salaries and other costs not associated with the purchase of substrates, or their harvesting and transport [64], as shown in Eq. (10); $p($heat) is the biogas heat price(€/$\mathrm{MWh_{th}}$); H_{CHP} is the daily production of heat ($\mathrm{MWh_{th}}$). and E_{CHP} is the daily production of electricity ($\mathrm{MWh_{el}}$). Equation (9) considers the continued dispatching of the biogas plant based on the $BECP_{\mathrm{el}}$, after the payback period of the investment, on the day-ahead electricity market. The structure of the *OPEX* is as follows (10):

$$OPEX = \sum_{i=1}^{N} p_i(\mathrm{substrate}) \cdot M_i(\mathrm{substrate}) + MSO \tag{10}$$

where p(substrate) is the price of substrates from Table 1 (€/t) and M(substrate) is the mass of substrate put in the digester, and *MSO* is the cost of maintenance, salary and other costs found in Table 2. In Scenario I) and Scenario II), the daily input of riverbank grass and cattle manure can be calculated using (1) and corresponds to $M_{\mathrm{RG+CM}}$=125 t/day, or 62.5 t/day each. In Scenario III), the daily amount of sugar beet pulp and plant waste utilised in anaerobic digestion is M_{SBP}=25 t/day and M_{WP}=1.6 t/day. To achieve the daily biogas production of 10,000 Nm^3 in Scenario III) when sugar beet is processed, it is required to utilise an additional 45.5 t/day of riverbank grass and cattle manure each, or in total $M_{\mathrm{RG+CM}}$=91 t/day.

Table 1. Price of fuels and substrates

Substrate/fuel	Price
Natural gas for industry [65]	30 €/MWh
Biomethane	40-80 €/MWh
Biogas heat [66,67]	20-40 €/MWh$_{th}$, on average 30 €/MWh$_{th}$
Waste sugar beet plant [65]	4 €/t
Pressed sugar beet pulp [65]	15 €/t
Cattle manure [68]	0.60 €/t
Riverbank grass transport [69]	16.1 €/t
Digestate [8]	2.24-4.48 $/t, on average 3.0 €/t

The transportation cost of delivering grass to the biogas plant is estimated at ca. 16.1 €/t of fresh grass [69]. In Germany, cultivated grass silage costs ca. 30 €/t [70], while in Ireland, the price of grass silage paid by biogas plants ranges between 15 and 40 €/t [71]. The lower limit relates to grass from uncultivated land, while the upper limit refers to cultivated grass. In this study, the price of grass consists of the transportation cost for the grass. The price of animal (cattle) manure is lower, about 0.6 €/t [68].

The total profit of the system operation in Scenario II) (P_2) is defined with the following term:

$$P_2 = \begin{cases} p(\text{electricity}) \cdot E_{\text{CHP}} + p(\text{heat}) \cdot H_{\text{CHP}} & , p(\text{electricity}) > p(\text{biomethane}) \,\&\, BECP_{el} \\ p(\text{biomethane}) \cdot H_{\text{up}} & , p(\text{biomethane}) > p(\text{electricity}) \,\&\, BECP_{el} \\ 0 & , BECP_{el} > p(\text{electricity}) \,\&\, p(\text{biomethane}) \end{cases} \quad (10)$$

where p(electricity) is the hourly based price of electricity on the balancing market adopted from Nord Pool [62] for the case of Denmark (DK1) in 2018. The operating point for each hour is selected based on the conditions in the previous Equation, where change in the electricity price was the primary determinant for the operating model.

In Scenario III), the total profit P_3 can be estimated as:

$$P_3 = \begin{cases} p(\text{biomethane}) \cdot (1-f) \cdot H_{\text{up}} + p(\text{heat}) \cdot H_{\text{SB}} \cdot f & \text{, during sugar beeet processing} \\ p(\text{biomethane}) \cdot H_{\text{up}} & , \quad p(\text{biomethane}) > BECP_{el} \\ 0 & , \quad BECP_{el} > p(\text{biomethane}) \end{cases} \qquad (11)$$

where f is the part of the biogas flow that is sent to the sugar plant during the processing period when the demand for natural gas is high. An additional determiner for the operating mode of Scenario III is the biogas price, which is related to the electricity price, through the parameter marginal price, and provides a more profitable solution in that time period.

The costs of substrates on a yearly basis are calculated based on the amounts required to produce biogas using (1) and (2). All capital and operating costs for all scenarios are presented in Table 2.

Table 2. Economic specifications of the scenarios in the study

Investment	Cost [€]
1 MW_{el} biogas engine overhaul [72]	458,200
Membrane upgrading unit of ca. 420 Nm^3/h biogas capacity [60]	1,400,000
External biogas storage of 2,500 m^3 capacity and biogas fan [73]	100,000
Compressor to inject biomethane into the local gas grid at 10 bar [74]	165,000
Operation	**Cost [€/year]**
Maintenance, salaries and other costs (*MSO*) [75]	100,000
Membrane upgrading electricity cost and maintenance [60]	340,000

To perform the techno-economic analysis, cumulative cashflow, Payback Period (PBP) and Internal Rate of Return (IRR) were used. The discount rate for cumulative cash flow calculation was set at 10% and the tax profit at 18% [76]. The period of the studied investment for the techno-economic analysis was set at 15 y. Furthermore, a sensitivity analysis was performed to study the impact of natural gas price changes on the project economics in Scenario III).

4 RESULTS AND DISCUSSION

This section presents the results of the analysis considering the three scenarios under analysis, where the dynamic biogas dispatching operation scenarios and the techno-economic analysis are discussed.

4.1 Break-even cost of electricity production on the day-ahead electricity market

Results of the analysis of the $BECP_{el}$ impact on the CHP operational time using day-ahead electricity prices are shown in Figure 2.

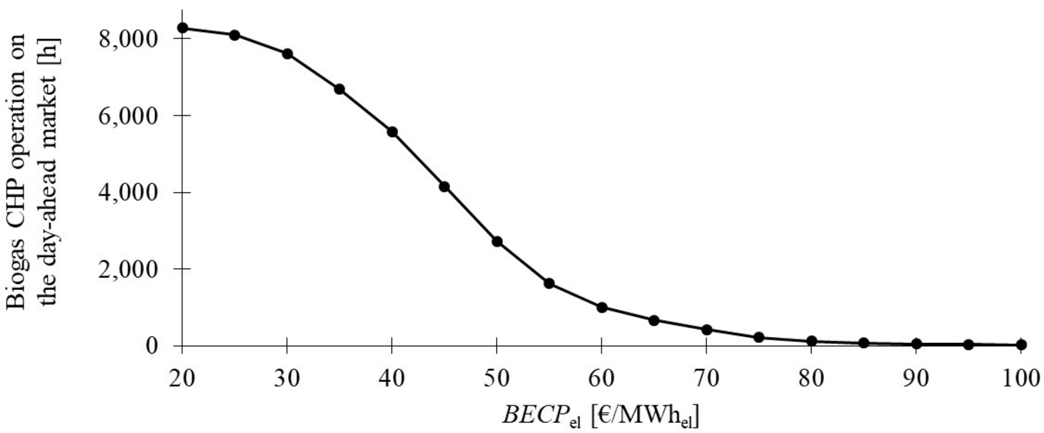

Figure 2 The impact of $BECP_{el}$ value on CHP operational time on the day-ahead electricity market

CHP operation on the day-ahead market is seriously impacted by the $BECP_{el}$ value. Beyond the value of 40 €/MWh$_{el}$, the CHP operational time decreases significantly, even below 4,000 h/y. At the price of 100 €/MWh$_{el}$, biogas energy production equals the biogas production costs, and the operation is no longer viable. In current conditions in Germany, the $BECP_{el}$ value for maize silage is estimated at ca. 100 €/MWh$_{el}$ [77]. Without subsidies for electricity production, biogas plants could not make a profit while operating using relatively expensive raw materials, such as maize silage. In addition, biogas plants should instead utilise cheaper substrates or even substrates with a negative price, like food waste from canteens, restaurants, etc. [5] to make their operation profitable. The highest gradient in Figure 2 is shown for an approximately 45 €/MWh$_{el}$, which can be attributed to the median electricity price on the day-ahead market. Additionally, in Figure 2 the inflection point is at approximately 45 €/MWh$_{el}$, where the rate of gradient change is maximal, which indicates the $BECP_{el}$ for which the CHP system will experience the most starting up and shutting down of the system.

4.2 Dynamic operation of the biogas plant under advanced energy markets

Results of dynamic operation of the biogas plant analysed through the three scenarios are given in the subsections below.

4.2.1 Scenario I)

The break-even cost of electricity production using riverbank grass and cattle manure is calculated for two cases, when both electricity and heat are sold on the market, and when only electricity is sold. Using the prices given in Table 1, the $BECP_{el}$ including heat sold is about 20 €/MWh$_{el}$, and when heat is not sold, the $BECP_{el}$ is about 40 €/MWh$_{el}$. In the case of AD of manure and agro-industrial waste, the break-even cost of electricity production ranges from 25 to 60 €/MWh$_{el}$ [78]. Based on the comparison between $BECP_{el}$=40 €/MWh$_{el}$ and day-ahead electricity prices in this study, the longest period of CHP non-operation is estimated at ca. 10 h. Therefore, external storage for biogas will be added to hold produced biogas for an additional 6 h. Based on hourly biogas production (417 Nm^3/h), its volume should be ca. 2,500 m^3. For low-pressure biogas storage (biogas dome), the specific investment price ranges between 25 and 55 €/m^3 [73]. Using the average cost of 40 €/m^3 and defined storage volume, the investment is estimated at 100,000 €. In total, a digester headspace and the added external storage together form a 10 h capacity storage that has a volume of about 4,500 Nm^3. Total storage dynamics based on $BECP_{el}$ values and market conditions is given in Figure 3. The dynamics for two representative $BECP_{el}$ values is shown in Figure 3, where the biogas storage is fully filled during the operating time of low electricity prices, which is more pronounced in the case of $BECP_{el}$=40 €/MWh$_{el}$. In contrast, in the case of $BECP_{el}$=20 €/MWh$_{el}$, the storage level for most of the time is not fully filled across the whole operating time. The period when both cases do not store the biogas indicates a high electricity price, during which the all biogas is dispatched to the CHP. The selected prices show the price boundaries from which the CHP unit is dominantly operating or secondarily, on the day-ahead market.

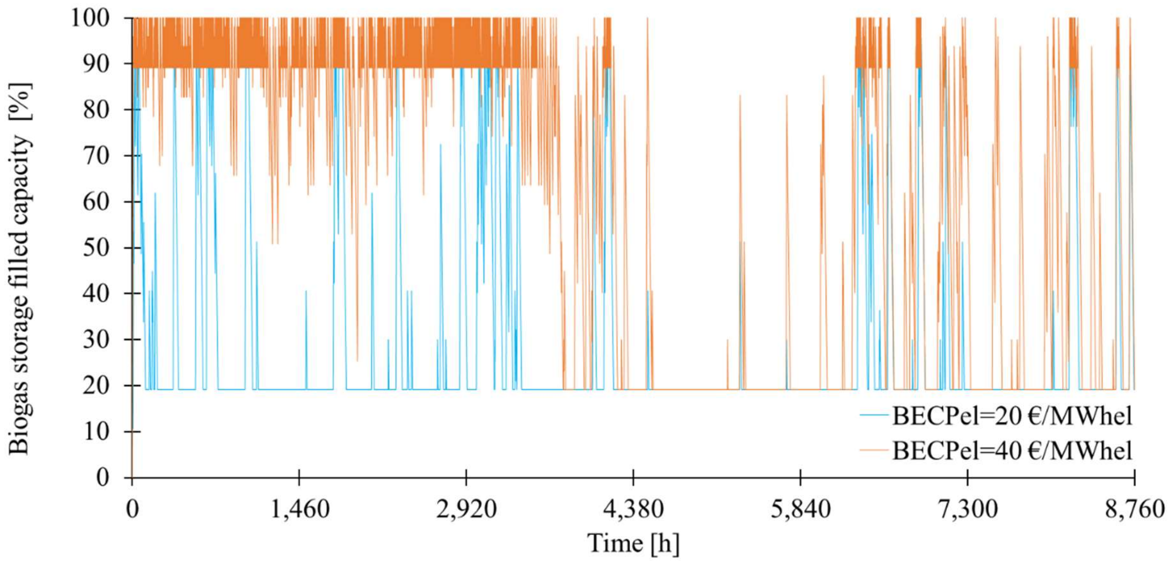

Figure 3 Biogas storage dynamics due to fluctuating market conditions and the break-even cost of electricity production

Selling heat in Scenario I) (lower $BECP_{el}$ value) has a significant impact on biogas storage dynamics, and on CHP operation. There are only short periods when energy production in the CHP is not viable, owing to fluctuating market conditions. On the other hand, if heat selling is not included in the CHP operation on the day-ahead electricity market (higher $BECP_{el}$), there are many periods when biogas is not utilised in the CHP and stored. In addition, using biogas heat in a district heating application gains a saving in GHG emissions and contributes to waste reduction [79]. Therefore, it can be observed that in the post-feed-in-tariff era, biogas plants should become more attractive for biogas heat utilisation, owing to low electricity prices on the market. The impact of $BECP_{el}$ value on the electrical energy and heat produced in biogas CHP in Scenario I) is given below.

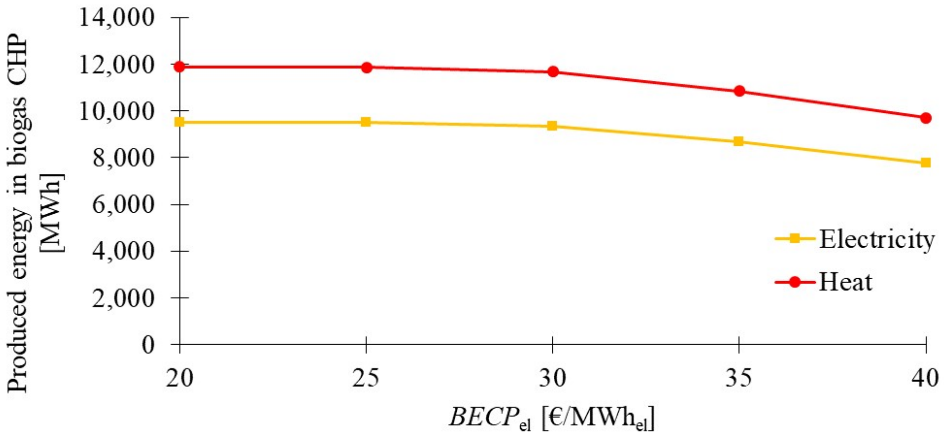

Figure 4 Energy produced in biogas CHP, Scenario I)

For the $BECP_{el}$ value of 20 €/MWh$_{el}$, energy produced in CHP accounts for ca. 9,508 MWh$_{el}$ and ca. 11,900 MWh$_{th}$. If the $BECP_{el}$ value is doubled, energy generation decreases by 18.5%. Based on the analysis, it was determined that the biogas plant in the study can still achieve profitable operation after exiting the subsidy scheme if the price of substrate for AD is not too high and if heat is utilised. More detailed analysis of the application of biogas in the heating processes is given in Scenario III).

4.2.2 Scenario II)

In Scenario II), the analysis of the biogas operation strategy was studied by changing the selling price of biomethane from 40 €/MWh to 80 €/MWh, at intervals of 10 €/MWh. The operation proposed in Scenario II) is not sensitive to change in the $BECP_{el}$ value, since the primary target is to produce biomethane, and biogas CHP is viable only when the price of electricity is high. Overall, because the market price of biomethane needs to be high enough to yield profit in continuous operation, biogas storage does not occur. As a result, the biogas storage is continuously charging and discharging with the same flow of biogas. An example of CHP operation on the balancing market is given in Figure 5 for defined prices of biomethane. For the period between 5,500 h and 7,000 h, when the CHP is mainly working, for all biomethane prices in Figure 5, a high electricity price is present, which was also visible in Figure 3. The different dispatching in operation of the scenario is between the biomethane price of 40 €/MWh and 50 €/MWh, which corelate to the largest gradients from Figure 2, and a greater difference in the overall electricity generated.

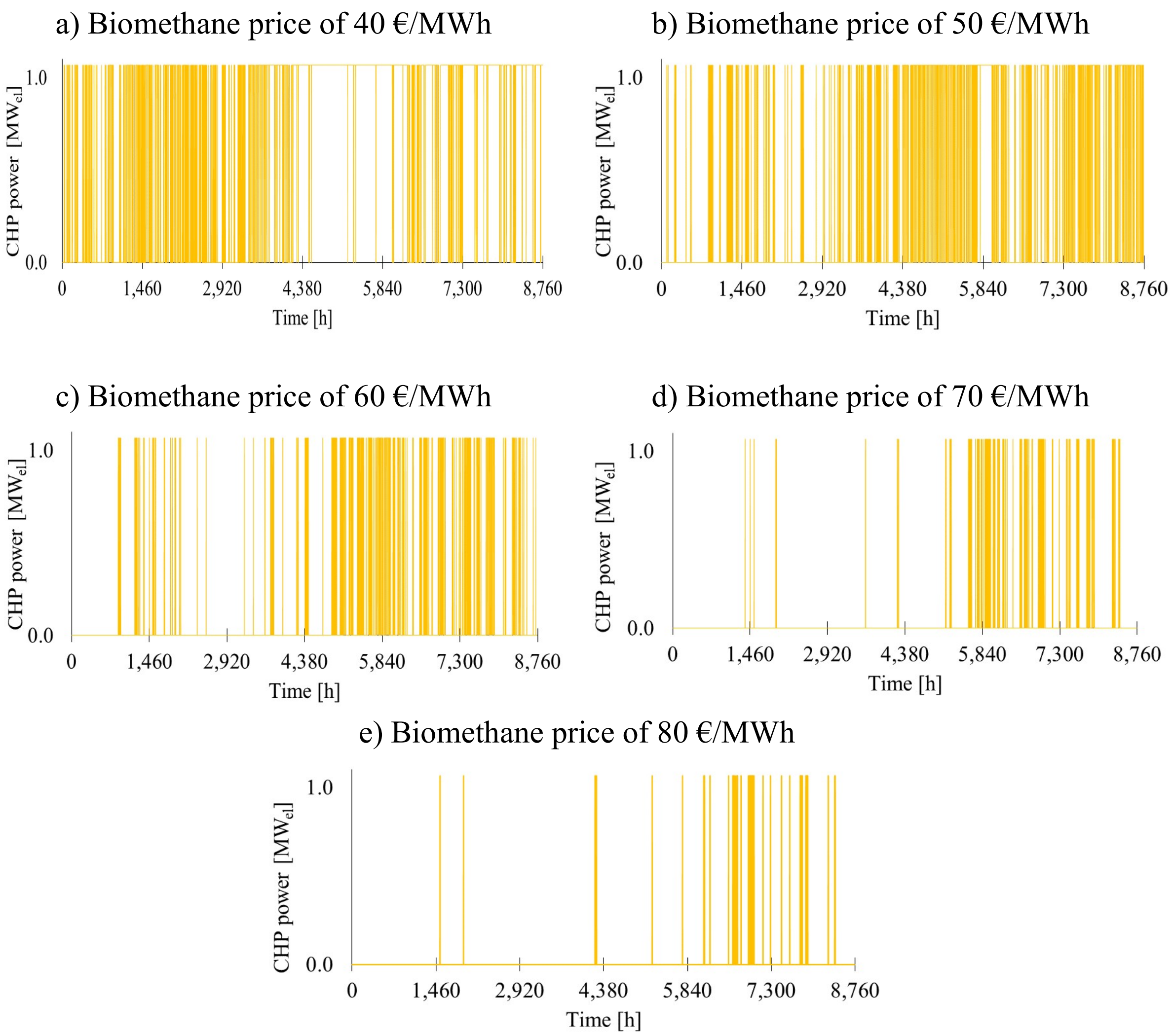

Figure 5 CHP operation on the balancing market for the biomethane price of a) 40 €/MWh, b) 50 €/MWh, c) 60 €/MWh, d) 70 €/MWh and e) 80 €/MWh

For the lowest biomethane selling price (40 €/MWh), biogas CHP has an operational time close to 5,600 hours/year, while for the biomethane price of 80 €/MWh, the CHP operational time is 112 hours. The analysis results show that the most frequent operation of CHP on that balancing market was detected in the last quarter of the year, between hours 6,000 and 8,000. Electricity prices on the DK1 balancing market are significantly influenced by wind penetration, the influence of which is especially marked in the fall period (September, October, November) [80]. The impact of the biomethane selling price on the energy produced in CHP and biomethane itself on the yearly level is given in Figure 6.

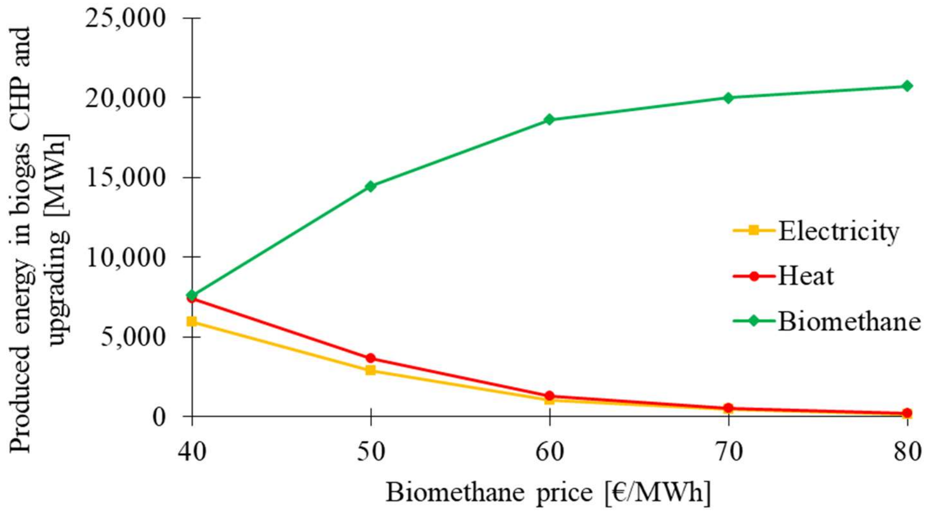

Figure 6 The impact of biomethane selling price on energy production in CHP and biomethane production

For the biomethane price of 40 €/MWh, the electricity generation (5,953 MWh_{el}) is still competitive with upgrading and biomethane production (7,616 MWh). As the biomethane price rises, the electricity and heat generation in CHP become non-viable, and the biogas plant turns to biomethane production. At the highest biomethane price of 80 €/MWh, electricity generation is at its lowest −152 MWh_{el}, while biomethane production is ca. 21,000 MWh. However, results indicate that in the post-feed-in-tariff era, the biogas operation on the electricity balancing market could in some periods be even more viable than production of biomethane, even though those periods are rare. It is important to stress that the results of this analysis have been tested for an electricity market (DK1) with a high penetration of wind. Flexible power generation and continuous biomethane production in the case of Austrian biogas plants did not show significant profit compared to biomethane production alone [81]. The market conditions under which the CHP will operate in the future will have a serious impact on the viability of its operation. Major European economies are already promoting biomethane grid injection as an environmentally acceptable solution and a viable path for biogas plant operation [21]. Surplus to that trend, this analysis has shown that biomethane production could support exiting biogas CHP while operating under different market conditions and enable them to keep biogas production running.

4.2.3 Scenario III)

Scenario III) shows how the current biogas plants could be combined with the processing industry to replace the use of natural gas with biogas. Figure 7 shows the operational strategy of biogas plant upgrading, combined with the sugar beet processing industry.

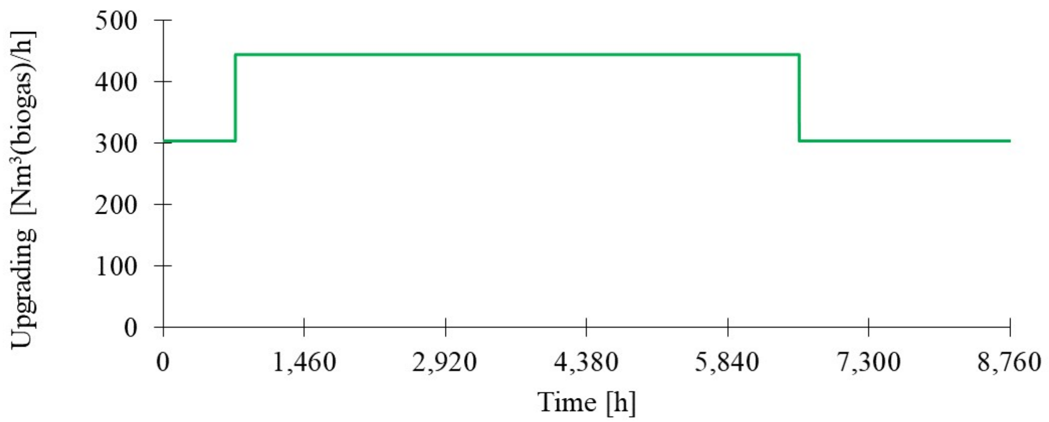

Figure 7 The operation strategy for upgrading at the biogas plant combined with sugar beet processing

At the start of the year and in the last quarter of the year, sugar beet is processed into sugar. Part of the biogas produced in the biogas plant during that period is utilised in the heat demand for sugar beet processing as a replacement for natural gas. The daily amount of biogas used in sugar beet processing to replace natural gas is calculated using (8), and it is Q_3=3,150 Nm^3. In that period, the biogas upgrading unit works with 32% lower biomethane production. Scenario III) presents an option for substituting natural gas in two ways: in the natural gas grid by producing biomethane, and in the processing industry by replacing natural gas with biogas. In addition, production of biogas using sugar beet by-products in a digester is ca. 2,700 Nm^3, which is very close to the self-consumption of biogas for heating purposes. This analysis has shown that the sugar beet processing industry could replace almost 85% of natural gas consumption by using their own by-products in biogas production. In the Netherlands, sugar beet processing plants are building new digesters to utilise sugar beet by-products for biogas and to use it on site, as part of the decarbonisation process [82]. Therefore, small-scale processing industries should take advantage of biogas production using their own biomass sources and invest part of their profit in building an AD plant.

4.3 Techno-economic analysis of biogas operation

In this section, a techno-economic analysis of the scenarios is presented and discussed. Figure 8 gives the cumulative cashflow of the investment for Scenario II) and Scenario III) with reference to Scenario I) at a duration of 15 years. The selling price of biogas in Scenario III) is set at 30 €/MWh, which corresponds to the price of natural gas that the industry is currently charged [65].

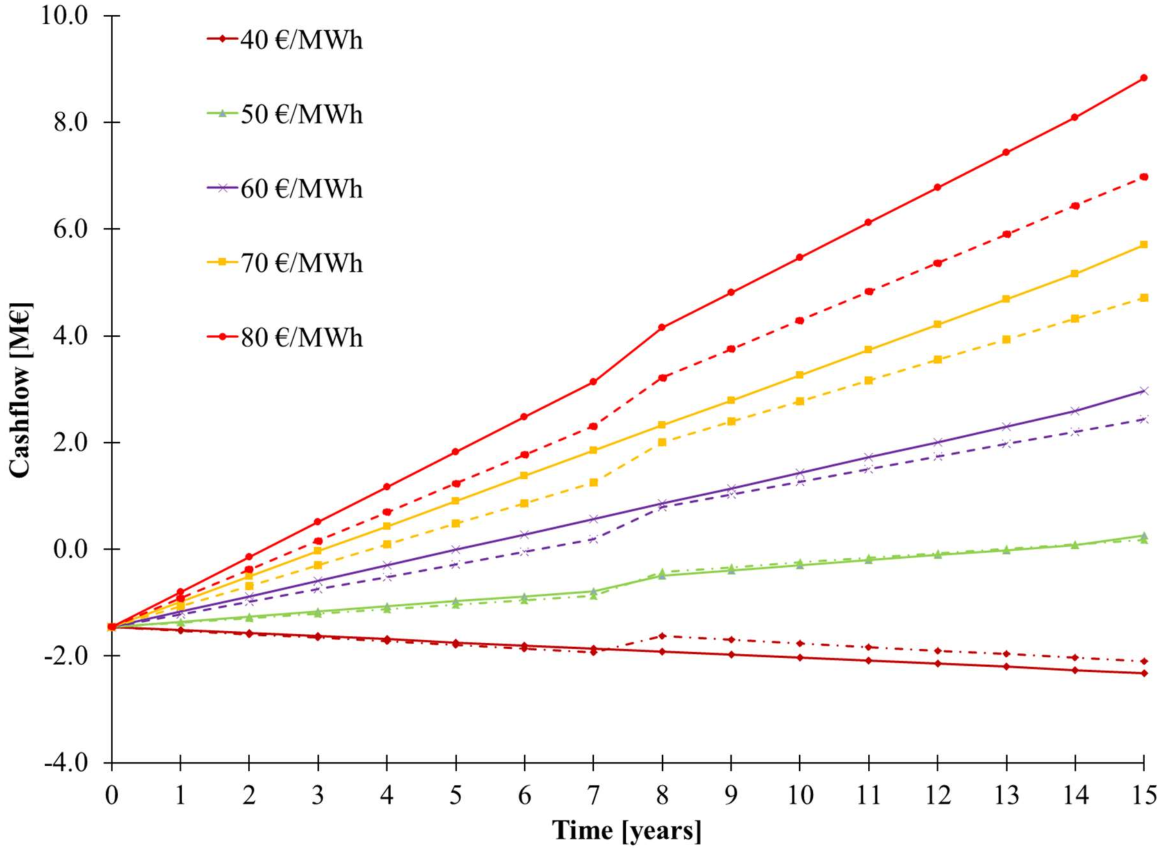

Figure 8 Generated cashflow of the investment for Scenario II) with reference to Scenario I) (solid line) and generated cashflow of the investment for Scenario III) with reference to Scenario I) (dashed line) in the 15-year period, discount rate 10%

Scenario II) yields higher revenue compared to Scenario III) for the same biomethane selling price. For the lowest price of biomethane (40 €/MWh), there is no possibility of paying back the investment in the upgrading unit and CHP general overhaul for either Scenario II) or Scenario III). As presented in the previous section for Scenario II), with the price of biomethane at 40 €/MWh, the CHP operates for ca. 5,600 hours, which indicates that market conditions for electricity production are more viable than biomethane production and its utilisation. The bottom-line total cost of biomethane production is estimated to be ca. 0.46-0.49 €/Nm^3 (46-49 €/MWh) [83]. As shown by the results presented, when the price of biomethane rises to 50 €/MWh, the operation strategy in Scenario II) and Scenario III) is more profitable, but still not very promising. The payback period for both scenarios is almost 14 years. When the selling price of biomethane reaches 60 €/MWh, the investment in the upgrading unit becomes feasible, and the payback period is ca. 6.0 years in Scenario II) and ca. 6.7 years for Scenario III). For higher biomethane prices, 70 and 80 €/MWh, the payback period is 4.0 and 3.2 years in Scenario II) and 4.6 and 3.7 years in Scenario III). The payback period of the investment in water-scrubbed biogas upgrading and biomethane grid injection for the biomethane price of 0.74 €/Sm^3 (it corresponds to the price of ca. 80 €/MWh) was estimated to be ca. 4.2 years [84]. Results of the analysis show that the biomethane selling price has a significant impact in both Scenario II) and Scenario III), where slightly higher revenues come from CHP operation on the electricity balancing market combined with biogas upgrading, in comparison to biogas upgrading combined with selling biogas to the process industry. The sensitivity analysis of the biogas selling price (corresponds to price of natural gas) for Scenario III) is given in Figure 9.

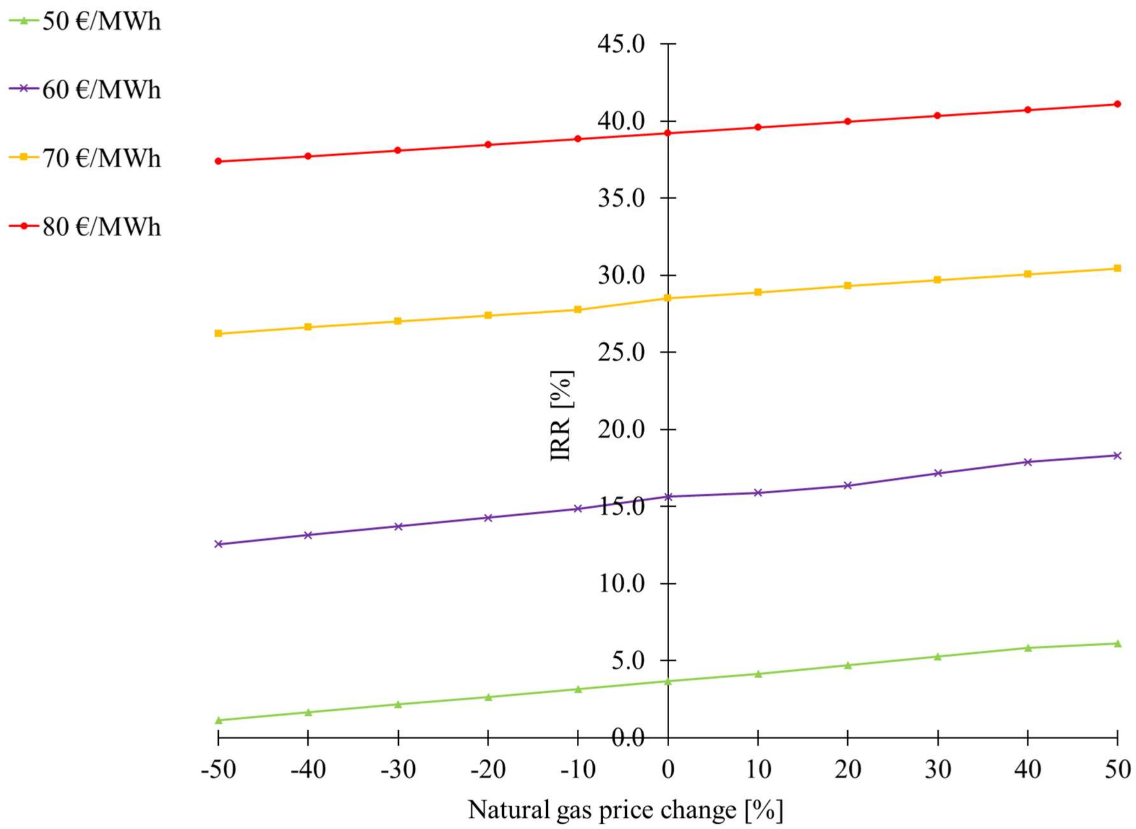

Figure 9 Sensitivity analysis of IRR on the price change in the system inputs and outputs

Sensitivity analysis was performed for the biomethane price of 50 €/MWh and above, since the biomethane price of 40 €/MWh is not viable in operation at all. Even a biomethane price of 50 €/MWh is not profitable, since its IRR value is lower than the initial discount rate of 10%. The analysis showed that, as the biomethane selling price increases, the IRR values in Scenario III) also increase. Biogas upgrading projects are reported to have an IRR value between 16.4 and 29.2%, with the PBP between 3 and 5 years [85]. Similar results were obtained by this study. Additionally, this research showed that the change in IRR value follows the change in natural gas price linearly. Reported changes in IRR values due to changes in the natural gas price are not significant, since a higher portion of biogas generated in the biogas plant is upgraded to biomethane, a value-added material that earns a higher selling price.

5 CONCLUSION

The study of the post-feed-in-tariff era for biogas plants was successfully carried out. Three scenarios were developed to reveal the potential for biogas plants to operate under advanced energy markets, an electricity balancing market, a process heat market and a biomethane market to replace natural gas. Replacement of energy crops on the biogas production side by alternative substrates like residue grass and processing by-products yields better prospects and lower production costs. As even more attractive substrates, biogas plants should consider substrates with a negative price, like food waste, to earn higher profits and whose energy recovery can contribute to GHG mitigation. Production of heat and electricity in biogas CHP after leaving the subsidy schemes does not seem like a favourable option. Owing to penetration by intermittent renewables like solar and wind, the prices of electricity on the day-ahead market are very low, which makes biogas operation non-viable. On the other hand, high penetration of intermittent renewables in energy systems opens the space for biogas CHP to be in operation only in the short period of time when balancing prices are high. This study has shown that even at the very high biomethane selling price of 80 €/MWh, there are still periods in the year (112 hours) when generation of electricity and selling it on the balancing market can be more viable than upgrading of biogas. In general, it was established that viable operation in these cases can be achieved if the price of biomethane is 50 €/MWh or above. Using biogas to replace natural gas in industry processes in the case of a small-sugar beet processing facility could be viable if the processing facility decides to invest in their own AD plant. Thus, the studied biogas plant pays for the substrate and sells the biogas relatively cheaply, instead of converting it to biomethane. Economic analysis of these scenarios showed that projects are profitable with high IRR values (between 15 and 40%) and low payback periods (between 3 and 7 years), only if biomethane is sold for the price of 60 €/MWh or above.

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ARTICLE 6

Synergy between feedstock gate fee and power-to-gas: An energy and economic analysis of renewable methane production in a biogas plant

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ABSTRACT

Biogas is an instrument of synergy between responsible waste management and renewable energy production in the overall transition to sustainability. The aim of this research is to assess the integration of the power-to-gas concept into a food waste-based biogas plant with the goal to produce renewable methane. A robust optimisation was studied, using linear programming with the objective of minimising total costs, while considering the market price of electricity. The mathematical model was tested at an existing biogas power plant with the installed capacity of 1 MW_{el}. It was determined that the integration of power-to-gas in this biogas plant requires the installation of ca. 18 MW_{el} of wind and 9 MW_{el} of photovoltaics, while importing an additional ca. 16 GWh_{el} from the grid to produce 36 GWh of renewable methane. The economic analysis showed that the feedstock gate fee contributes significantly to the economic viability of renewable methane: a change in the feedstock gate fee by 100 €/tonne results in a decrease of production costs by ca. 20-60%. The robust nature of the model showed that uncertainties related to electricity production from wind and photovoltaics at the location increased the cost of gas production by ca. 10-30%.

Keywords: Biogas; food waste; optimisation; uncertainty; renewable gas

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1 INTRODUCTION

Biogas is a renewable source of energy produced by decomposition of organic materials (feedstocks) under an oxygen-free atmosphere and controlled temperature in the process known as anaerobic digestion (AD) [1]. Commonly used feedstocks to produce biogas are animal manure and agricultural residues [2], energy crops [3], combined with various waste streams originating from food processing value chains [4].

In 2018 the European Commission adopted a recast of the Renewable Energy Directive, which stated that the biomass fraction of municipal waste, biowaste and streams from industry should play a greater role in future biogas production, since they have low indirect land-use change impact to produce biofuel [5]. In recent years, the developed biogas sectors among the European countries have limited the utilisation of energy crops, like maize silage and corn, to a share of 30-50% of the total input feedstock [6,7].

Since the cost of feedstock accounts for the highest share of operating costs for AD, biogas plants are exploring a transition towards low-cost source material suitable for biogas production [8]. The purchase price for the most common feedstocks in the biogas sector − maize and grass silage fluctuates between 15 and 40 €/tonne of raw material [9], depending on the country and the crop quality. In addition, energy crops in biogas production give rise to environmental, social and economic issues due to the competition with food production on arable land [10].

Energy recovery of organic waste materials using biogas technology as a replacement for landfilling has shown to avoid environmental burdens [11] and contributes to the perspective of circular economy [12]. Agri-food waste and animal manure have a zero cost, while the purchase price for food waste and other bio-waste types is between -60 and 0 €/tonne [9]. The minus sign indicates that the biogas plant receives a "gate fee − *GF*" from the waste producers to receive and handle their biodegradable waste [8]. The amount of the *GF* depends on the origin and complexity of the waste [13], and in some cases it can be as high as 100 $/tonne [8].

From an economic point of view, the introduction of *GF* in the operation of biogas plants has proven to be a promising business model, as it can amount to 80% of the total biogas plant income [13]. International Energy Agency projects that food waste disposal on landfills will be banned by 2040, which could be an attractive opportunity for biogas plants to consider more using food waste in biogas production [8]. In addition, such measures will result in increased separate waste collection costs, which will ultimately lead to increased gate fees in biogas plants and additional financial income [14].

The main component of biogas is methane (45-70% vol. share of CH_4), which makes biogas applicable as an alternative to natural gas [15]. In past decades, strong public subsidy mechanisms [16] for electricity production in the form of feed-in-tariffs and feed-in-premiums have resulted in a high level of biogas penetration in the European electricity sector [17]. The level of subsidies depends on the country, and in all European countries is not lower than 8.0 €-Cent/kWh_{el} [18], which is almost the twice the average wholesale market price of electricity in the EU.

Part of the heat produced in biogas combined heat and power (CHP) unit is used to maintain a constant temperature in the digester [19], while residual high-grade heat is used for various heating purposes like district heating [20], Organic Rankine Cycle [21], for drying of materials and heating greenhouses [22].

According to the European Biogas Association, at the end of 2017, there were 17,783 biogas plants in Europe operating in CHP mode [23]. Since subsidies are granted only for a certain period, usually not longer than 15 years [18], biogas plant owners have started seeking alternative biogas utilisation pathways [24].

It has been shown that in the post-subsidy era, the operation of biogas plants on the day-ahead electricity market is not viable [25], since the cost of electricity production in CHP meets the price of electricity on the market [13]. On the other hand, a minority of biogas plants in

Europe, only 540 of them [23], operate in the biogas upgrading mode, removing non-methane components from biogas and producing biomethane, a gas with a 99% share of CH_4 [26], which can be directly injected into the natural gas grid. Biogas upgrading technologies require electricity for their operation, on average ca. 0.30 kWh_{el} per Nm^3 of fed biogas, while some also require solvents, water and heat [26]. The relatively high level of subsidies for biogas CHP and the high investment costs in the upgrading units have resulted in a rather low number of upgrading installations compared to biogas CHP.

In the transition by the biogas sector towards low-cost sustainable feedstocks and viable operation on energy markets, the integration of variable renewable energy sources (RES) [27], primarily wind and photovoltaics (PV), seems an attractive option, since their capacity is continuously on the increase globally, providing low-cost electricity [28].

In Germany, utilisation of excess electricity from wind farms for biogas upgrading has shown potential for converting and storing of surplus electricity without long transport routes [29]. Utilising 0.70 $TW_{el}h$ of excess electricity to 480 biogas plants could produce $100 \cdot 10^6$ Nm^3/y of upgraded CH_4.

Apart from covering the electricity demand in a certain process, excess electricity from variable RES is also utilised to produce hydrogen (H_2) through the process of water electrolysis [30]. The integration of renewable H_2 in fuel production can reduce the demand for biomass, while simultaneously increasing the flexibility of the energy system by enabling higher penetration of variable RES in energy systems [31].

The surplus energy generated by wind turbines or PV modules can also be used in a technology called power-to-gas (P2G), where the carbon dioxide (CO_2) and H_2 produced in electrolysers are converted to synthetic natural gas (synthetic methane/e-methane, e-CH_4) in the methanation process [32]. Since both biogas CHP and biogas upgrading act as sources of

CO_2, the integration of the P2G concept together with sustainable biomass management offers a high gain perspective [33].

Installing a P2G unit near the biogas CHP unit ensures that both units can operate independently: when there is demand for P2G operations, biogas is used for methanation, and when it is not required, biogas is used in the CHP unit [34]. Moreover, electrolysers and methanators are sources of heat, where electrolysers usually provide low-grade heat [35], while methanators produce high-grade heat that can be used in local district heating appliances or in industrial processes [36].

The examples of integrating variable RES in renewable gas production are the *WindGas Falkenhagen* methanation plant [37] and the *Audi e-gas* plant [38], both located in Germany, where wind supplies electricity to run the P2G facilities. In Denmark, the *BioCat* plant uses CO_2 from biogas upgrading and renewable H_2 to produce synthetic CH_4, which is fed to the national gas grid [39]. Compared to biogas upgrading and separate CO_2 utilisation in P2G, the direct methanation of biogas [40] has proven the more efficient and less energy demanding process [41], enabling full carbon utilisation from biomass [42].

Synthetic natural gas produced in the direct methanation of biogas from the wastewater treatment plant has a CH_4 share of ca. 90%, with ca. 5% of H_2 [43]. The second P2G project by the *Audi e-gas* company in Germany, with direct methanation of raw biogas using renewable H_2, produces renewable methane with a 98% share of CH_4 [38]. Previous economic analyses have shown that the renewable gas produced by integrating P2G into biogas plants cannot be competitive in price with natural gas, unless there are subsidies [44].

The efficiency of the P2G concept is highly dependent on the metrological conditions at the location where wind and PV are studied [45]. Such energy systems usually operate connected to the electricity grid (on-grid), purchasing electricity from the grid at times when no wind/PV electricity is available and exporting electricity excess to the grid.

Finding the capacity of energy production units in the P2G concept is an optimisation problem [46] that requires system modelling on an hourly level, because of the variable nature of electricity generation and electricity market features [47]. In addition, optimising power production from wind and PV includes the involvement of uncertainties [48] due to variability in input data, which makes the developed mathematical model robust [49]. When optimising energy systems, the common objective functions (OF) are minimisation of total cost (or maximisation of total profit), minimisation of energy loss (maximisation of energy efficiency) and minimisation of environmental impact (usually expressed through CO_2-equivalent emissions) [50]. From the perspective of new technology integration in existing facilities, the choice to minimise the energy system's costs is commonly accepted [51], as long as it guarantees the security of supply and ensures technical-feasible operation.

Based on the detailed literature review of the biogas sector including available feedstocks, biogas utilisation pathways and integration of variable RES , there is no reported research that combines all these elements of the biogas chain into a holistic approach that integrally analyses the transition of the biogas sector after expiry of subsidy mechanisms for electricity production. To address this gap in the scientific literature, this study will develop a robust mathematical model with the goal of quantifying the integration of the P2G concept into an existing biogas plant operating under a feedstock gate fee business model. To develop and test the model, the following research objectives were appointed:

i) to optimise the integration of the variable RES in the operation of the existing biogas plant, using total cost minimisation as an objective function;
ii) to quantify the impact of the feedstock gate fee in the biogas plant on the cost of renewable methane production, with the aim of making it economically competitive with natural gas;

iii) to reveal the impact of uncertainty in electricity production from variable RES on the optimal economic solution and system operational features.

The hypothesis of this research is that the synergy between a feedstock gate fee business model and the integration of the P2G concept at the biogas plant can contribute to a significant reduction of renewable methane cost generation, which could be considered an alternative to subsidy mechanisms in the production of renewable gas.

2 MATERIALS & METHODS

This section provides a brief description of the methods applied in the study. The model for P2G integration into an existing biogas plant is presented, analysing key features of the system operation. The description of an optimisation problem includes variables, energy and mass equations and the objective function. The last part describes the assessment tool to evaluate the economic viability of P2G integration in the existing biogas plant.

2.1 Power-to-gas integration in a biogas plant operation

The integration of the P2G concept supported by wind and PV electricity in an on-grid biogas plant is presented in Figure 1, which was derived from previous studies [34,52]. Green lines indicate the flow of electricity, black lines indicate the flow of gases and red lines indicate heat flows. The electricity imported from the electricity market to cover the total demand is shown in orange. The studied model is arranged to select which electricity supply unit with its energy flow is most appropriate to be chosen, based on the defined objective function (OF). The assumption is that the size of the plant is small enough so that its operation on the market does not impact the electricity price. The results of the model are presented in the form of interval values, for a defined set of input data.

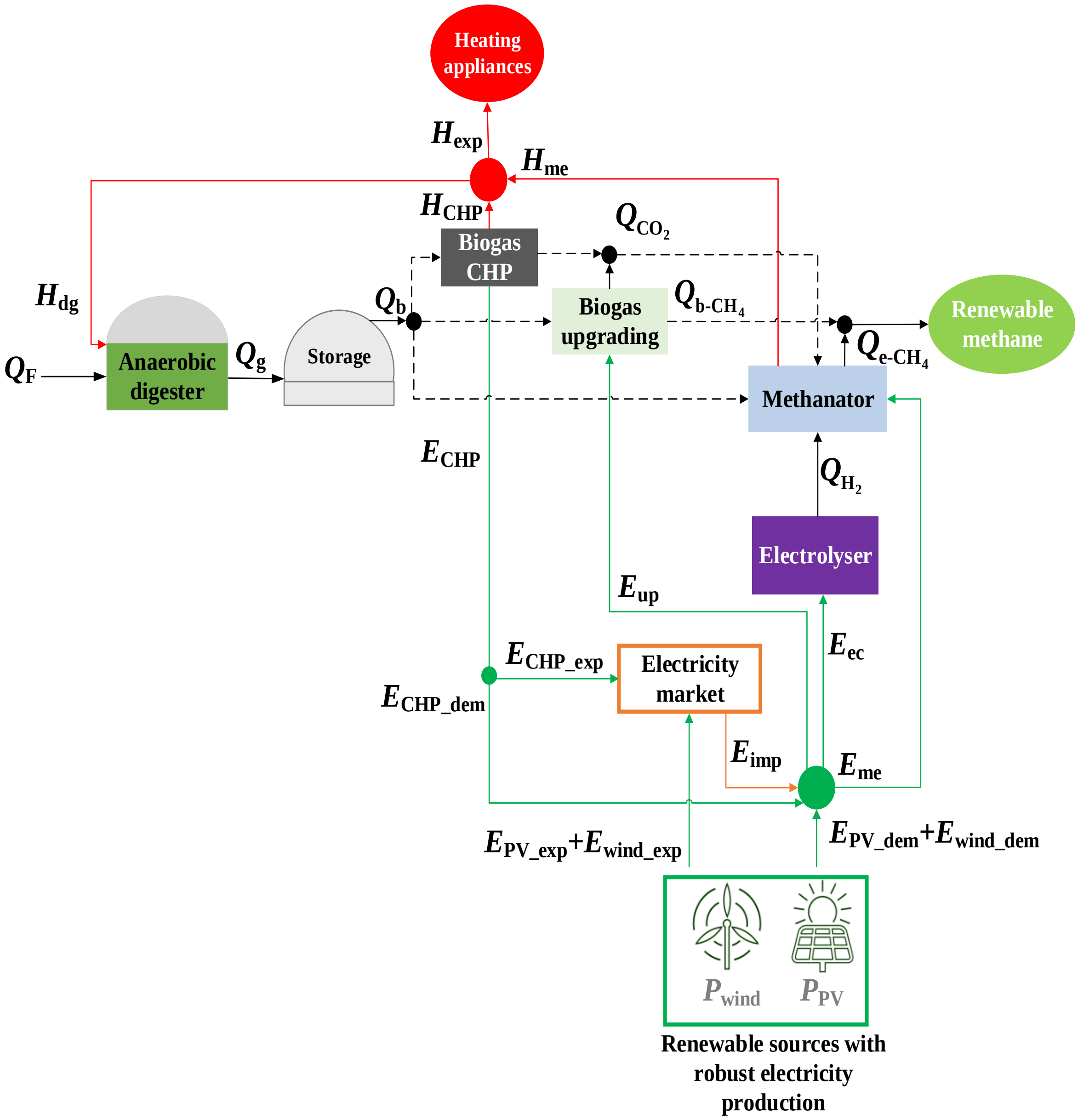

Figure 1: Power-to-gas integration in a biogas plant

2.2 Optimisation variables

A single objective optimisation model for a whole year time horizon [53] was used to optimise the energy flow and the capacity of the wind farm (P_{wind} [kW$_{el}$]) and PV plant (P_{PV} [kW$_{el}$]), the size of additional atmospheric biogas storage (V_{st} [m^3]), the capacity of an upgrading unit (c_{up} [Nm^3(biogas)/h]), an electrolyser (c_{ec} [Nm^3(H_2)/h]) and a methanation unit (c_{me} [Nm^3(e-CH_4)/h]), For solving the optimisation problem, the open-source programming language, Julia,

[54] and the JuMP modelling framework for mathematical optimisation [55] were used with the Clp solver for LP and Cbc for MILP.

2.3 Optimisation constraints

To produce renewable methane in the advanced biogas plant operation, the mathematical model must satisfy the hourly electricity demand in [kWh_{el}] for biogas upgrading ($E_{up,t}$), the H_2 production in the electrolyser ($E_{el,t}$) and the methanation process ($E_{me,t}$), which is the sum of demanded electricity produced in existing biogas CHP and in the newly installed wind and PV plants ($E_{wind\_dem,t}$+$E_{PV\_dem,t}$), plus the electricity imported from the electricity market ($E_{imp,t}$):

$$E_{\mathrm{up},t} + E_{\mathrm{ec},t} + E_{\mathrm{me},t} = E_{\mathrm{CHP\_dem},t} + E_{\mathrm{wind\_dem},t} + E_{\mathrm{PV\_dem},t} + E_{\mathrm{imp},t} \tag{1}$$

To calculate the electricity demand for biogas upgrading [56], the following relation was considered [26,57]:

$$E_{\mathrm{up},t} = \frac{Q_{b,t} \cdot e_{\mathrm{up}}}{\eta_{\mathrm{up}}} \tag{2}$$

where $Q_{b,t}$ is the biogas flowrate entering the upgrading unit [Nm^3/h]; e_{up} is the specific electricity consumption [kWh_{el}/Nm^3], and η_{up} is the upgrading efficiency [−]. The biogas flowrate supplied to the upgrading unit at any time cannot exceed the installed upgrading capacity:

$$Q_{\mathrm{b},t} \le c_{\mathrm{up}} \tag{3}$$

For the purpose of this research, an estimation was taken into account that, at the exit of the biogas upgrading unit, only two streams are present: bio-methane (b-CH_4) and pure CO_2 [58]:

$$Q_{\mathrm{b},t} = Q_{\mathrm{b\text{-}CH_4},t} + Q_{\mathrm{CO_2},t} \tag{4}$$

To calculate the flowrate of biomethane produced, the volume share of CH_4 in the biogas, $x(CH_4)$ is multiplied by the biogas fed to the upgrading unit.

The capacity of the atmospheric biogas storage placed between the anaerobic digester and the upgrading unit is defined using the following relations [59]:

$$SOC_t \leq V_{\mathrm{st}} \tag{5}$$

$$SOC_t = SOC_{t+1} + Q_{\mathrm{f},t} - Q_{\mathrm{b},t} \tag{6}$$

where SOC_t is the state of charge of the biogas storage [m^3], and $Q_{\mathrm{f},t}$ is the biogas production rate in the anaerobic digester [Nm^3/h]. The *SOC* in the initial moment (t=0 h) is the same as at the end of the year (t=8760 h), which means that biogas storage is not a source of biogas generation.

The energy required for electrolysing H_2O to produce H_2 [60] is defined by the following relation [57]:

$$E_{\mathrm{ec},t} = \frac{Q_{\mathrm{H_2},t} \cdot e_{\mathrm{ec}}}{\eta_{\mathrm{ec}}} \tag{7}$$

where $Q_{\mathrm{H_2},t}$ is the H_2 production rate [Nm^3/h]; e_{ec} is the specific electricity consumption of the electrolyser [kWh$_{\mathrm{el}}$/Nm^3], and η_{ec} is the electrolysis process efficiency [−]. Coupling P2G directly to the wind farm and the PV plant can result in a very small size of H_2 storage [61]. In this research, hydrogen storage has not been considered in the analysis. The amount of H_2 to convert captured CO_2 from biogas in the methanation process can be calculated based on the stoichiometric relation [62]:

$$Q_{\mathrm{H_2},t} = 4 \cdot Q_{\mathrm{b},t} \cdot x(\mathrm{CO_2}) \tag{8}$$

The H_2 flowrate from the electrolyser cannot exceed the installed capacity of the electrolyser:

$$Q_{\mathrm{H_2},t} \leq c_{\mathrm{ec}} \tag{9}$$

The energy required for the methanation reaction to produce e-CH_4 [60] is as [57]:

$$E_{\mathrm{me},t} = \frac{Q_{\text{e-CH}_4,t} \cdot e_{\mathrm{me}}}{\eta_{\mathrm{me}}} \tag{10}$$

where $Q_{\text{e-CH}_4,t}$ is the e-CH_4 production rate [Nm^3/h]; e_{me} is the specific electricity consumption of methanation [kWh_{el}/Nm^3], and η_{me} is the methanation process efficiency [−]. The e-CH_4 flowrate from methanation at any time cannot exceed the installed capacity of the methanator (c_{me}):

$$Q_{\text{e-CH}_4,t} \leq c_{\mathrm{me}} \tag{11}$$

Since methanation is a highly exothermic chemical reaction with a heat release of −165 kJ/mol [35], the following relation presents the amount of heat released by the methanator:

$$H_{\mathrm{me},t} = h_{\mathrm{me}} \cdot Q_{\mathrm{CO}_2,t} \tag{12}$$

where h_{me} is the specific heat released during methanation [kWh_{th}/Nm^3] [35] and $Q_{\mathrm{CO}_2,t}$ is the CO_2 flowrate [Nm^3/h].

Electricity and heat produced in biogas CHP are defined using the following relations [25]:

$$E_{\mathrm{CHP},t} = \Delta H(\mathrm{biogas}) \cdot \eta_{\mathrm{el}} \cdot Q_{\mathrm{b},t} \tag{13}$$

$$H_{\mathrm{CHP},t} = \Delta H(\mathrm{biogas}) \cdot \eta_{\mathrm{th}} \cdot Q_{\mathrm{b},t} \tag{14}$$

where ΔH(biogas) is the lower calorific value of biogas [kWh_{th}/Nm^3] [63], $Q_{\mathrm{b},t}$ is the biogas outflow from the storage to the CHP unit [Nm^3/h], η_{el} is the efficiency of electricity production in the CHP, and η_{th} is the efficiency of heat in the CHP [64]. The biogas CHP operation is studied by the MILP approach, using B_{in} as a binary variable (0 or 1):

$$E_{\mathrm{CHP},t} = P_{\mathrm{CHP}} \cdot B_{\mathrm{in}} \tag{15}$$

The assumption was that biogas CHP operates either at the nominal power, or that it does not operate at all [25]. Moreover, it was calculated that the investment in the biogas plant was paid out before integrating the P2G concept and that running costs of the biogas CHP include maintenance, salaries and other costs [25], while the feedstock gate fee is considered as additional income.

Heating demand for the digester operation depends on the amount of input feedstock in the process [35] and can be estimated as:

$$H_{\mathrm{dg},t} = h_{\mathrm{dg}} \cdot Q_{\mathrm{F},t} \tag{16}$$

where h_{dg} is the specific heat demand for the AD process [kWh$_{\mathrm{th}}$/tonne] and $Q_{\mathrm{F}.t}$ is the amount of feedstock fed to the digester [tonne/h] for which the biogas plant receives a *GF*.

The excess heat exported to various heating appliances is defined by the following relation [19]:

$$H_{\exp,t} = H_{\mathrm{CHP},t} + H_{\mathrm{me},t} - H_{\mathrm{dg},t} \tag{17}$$

The electricity generation in the PV plant can be defined as [58]:

$$E_{\mathrm{PV},t} = P_{\mathrm{PV}} \cdot a_{\mathrm{PV},t} \tag{18}$$

where P_{PV} is the installed capacity of the PV plant [kW$_{\mathrm{el}}$] and a_{PV} is an exogenous parameter representing the hourly electricity generation from the PV plant per installed capacity at the location [kWh$_{\mathrm{el}}$/kW$_{\mathrm{el}}$]. To assess the uncertainties in electricity production from PV at the location, the robust optimisation (RO) approach was considered [65], and its expression (17) is modified accordingly by using the set of equations below [66,67]:

$$E_{\mathrm{PV},t} = P_{\mathrm{PV}} \cdot a_{\mathrm{PV},t} - \beta_{\mathrm{PV},t} \cdot \Gamma_{\mathrm{PV}} - \zeta_{\mathrm{PV},t} \tag{19}$$

$$\beta_{\mathrm{PV},t} + \zeta_{\mathrm{PV},t} \geq D_{\mathrm{PV},t} \cdot \lambda_{\mathrm{PV},t} \tag{20}$$

$$\beta_{\mathrm{PV},t}, \zeta_{\mathrm{PV},t}, \lambda_{\mathrm{PV},t} \geq 0 \tag{21}$$

$$\lambda_{\mathrm{PV},t} \geq P_{\mathrm{PV}} \tag{22}$$

where $\beta_{\mathrm{PV},t}$ [$\mathrm{kWh_{el}}$], $\zeta_{\mathrm{PV},t}$ [$\mathrm{kWh_{el}}$] and $\lambda_{\mathrm{PV},t}$ [$\mathrm{kW_{el}}$] are auxiliary variables of the robust mathematical model [66], Γ_{PV} is the robustness control parameter for PV, the value which reflects the ability of the system to cope with risk and that obtains values between 0 and 1 ($\Gamma_{\mathrm{PV}} \in [0,1]$), and $D_{\mathrm{PV},t}$ is any deviation by the PV system power profile from the mean value. Part of the electricity produced in the PV plant meets the demand for system operation ($E_{\mathrm{PV\_dem},t}$), while the rest is exported to the electricity grid ($E_{\mathrm{PV\_exp},t}$).

The total energy produced in the wind farm (E_{wind}) can be calculated as [58]:

$$E_{\mathrm{wind},t} = P_{\mathrm{wind}} \cdot a_{\mathrm{wind},t} \tag{23}$$

where P_{wind} is the installed capacity of the wind farm [$\mathrm{kW_{el}}$] and $a_{\mathrm{wind},t}$ is an exogenous parameter representing the hourly electricity generation in the wind farm per installed capacity at the location [$\mathrm{kWh_{el}/kW_{el}}$]. The robust nature of electricity generation in the wind farm [65] can be defined as [66,67]:

$$E_{\mathrm{wind},t} = P_{\mathrm{wind}} \cdot a_{\mathrm{wind},t} - \beta_{\mathrm{wind},t} \cdot \Gamma_{\mathrm{wind}} - \zeta_{\mathrm{wind},t} \tag{24}$$

$$\beta_{\mathrm{wind},t} + \zeta_{\mathrm{wind},t} \geq D_{\mathrm{wind},t} \cdot \lambda_{\mathrm{wind},t} \tag{25}$$

$$\beta_{\mathrm{wind},t}, \zeta_{\mathrm{wind},t}, \lambda_{\mathrm{wind},t} \geq 0 \tag{26}$$

$$\lambda_{\mathrm{wind},t} \geq P_{\mathrm{wind}} \tag{27}$$

where $\beta_{\text{wind},t}$ [kWh$_{\text{el}}$], $\zeta_{\text{wind},t}$ [kWh$_{\text{el}}$] and $\lambda_{\text{wind},t}$ [kW$_{\text{el}}$] are auxiliary variables of the robust mathematical model [66], Γ_{wind} is the robustness control parameter for wind ($\Gamma_{\text{wind}} \in [0,1]$), and $D_{\text{wind},t}$ is any deviation by the wind power profile from the mean value. Part of the electricity produced by the wind farm meets the demand for system operation ($E_{\text{wind\_dem},t}$), while the rest is exported to the electricity grid ($E_{\text{wind\_exp},t}$).

2.4 Objective function

The minimisation of the total system cost was used in a single-objective function (f_{econ}) defined as follows [59]:

$$\min(f_{\text{econ}}) = \min\left(\sum_{j=1} CRF \cdot CAPEX_j + \sum_{t=0}^{8760}\sum_{j=1} C_{\text{imp},t} + OPEX_{j,t}\right) \tag{28}$$

where $CRF{\cdot}CAPEX_j$ is the total discounted investment cost of the technology j [€]; $C_{\text{imp},t}$ is the total cost of imported electricity based on electricity demand and day-ahead electricity market prices [€], and $OPEX_{j,t}$ is the total cost for operation and maintenance of the technology j [€] in time step t. Since the capital cost is paid only once, at the start of the project, it does not have a temporal summation sign. To calculate the discounted investment cost of the technology, the capital price of investment was multiplied by a capital recovery factor (CRF) [68]:

$$CRF = \frac{i \cdot (1+i)^n}{(1+i)^n - 1} \tag{29}$$

where i is the interest rate, and n is the number of annuities received, in this case the number of operational years.

2.5 Levelized cost of electricity and renewable methane

To estimate the cost of electricity production from wind and PV at the location, the levelized cost of electricity ($LCOE$) [69] was used:

$$LCOE_j = \frac{CRF \cdot capex_j + opex_j}{\dfrac{E_j}{P_j}} \tag{30}$$

where $capex_j$ is the specific investment cost in the technology j [€/kW$_{el}$], $opex_i$ is the specific operational cost of the technology j on a yearly basis [€/kW$_{el}$)], E_j is the amount of electricity generated by the technology j [kWh$_{el}$], and P_j is the installed capacity of the technology j [kW$_{el}$].

The levelized cost of renewable methane (*LCORM*) produced in the proposed energy system which accounts for capital and operating expenditures, purchases and income from the studied energy and materials [70] can be estimated as:

$$LCORM = \frac{\sum_{j=1} CAPEX_j + \sum_{t=0}^{8760} \sum_{j=1} \frac{OPEX_{j,t} + C_{\mathrm{imp},t} - R_{\mathrm{exp},t} - H_{\mathrm{exp},t} \cdot p_{\mathrm{exp}} + Q_{\mathrm{F},t} \cdot GF}{(1+i)^t}}{\sum_{t=1}^{N} \frac{G_t}{(1+i)^t}} \quad (31)$$

where $R_{\mathrm{exp},t}$ is the revenue from electricity exported to the grid [€], $H_{\mathrm{exp},t} \cdot p_{\mathrm{exp}}$ is the revenue generated from the heat sold in variable appliances [€]; $Q_{\mathrm{F},t} \cdot GF$ is the revenue of the biogas plant arising from the gate fee for feedstocks [€], which is negative, and G_t represents the amount of renewable methane produced by this model [kWh].

3 CASE STUDY

The present method was tested on the biogas plant which uses food waste and industry waste in its operation and is located near the city of Zagreb, Croatia. This biogas plant was chosen as a case study, since the authors of this research have already done several experimental and modelling studies on biogas production at the plant [71].

This research does not consider the current economic position of the biogas plant, as it operates under a subsidy agreement. This analysis is focused on determining a threshold (GF in Equation 31) that would indicate feasible conditions for the integration of P2G (in terms of optimised capacities) into a biogas plant for the production of renewable methane competitive with natural gas, only without subsidies.

3.1 Input data from the biogas plant

An experimental study at the biogas plant [71] showed that the average total solid (TS) content of food waste was ca. 20% and that biogas production from food waste is estimated at 0.566 Nm^3/kgTS. Multiplying these numbers and scaling to the biogas plant size shows that the average biogas production rate at the plant is 110 Nm^3 per tonne of raw feedstock.

According to the data obtained from the plant owner, the biogas production in digester is estimated at 10,000 Nm^3 per day, or Q_f=417 Nm^3/h, with the average share of methane being $x(CH_4)$=0.65 and ΔH(biogas)=6.4 kWh/Nm^3 [63]. Dividing the daily biogas production by the experimentally obtained biogas potential from food waste [71] results in an input amount of feedstock equal to Q_F=90 tonnes/day, or 3.75 tonnes/h.

The digester headspace has a storage capacity equivalent to 6 h of biogas production, or ca. 2,500 m^3. The specific heat demand of the digester to maintain a constant temperature during the process is estimated at h_{dg}=18.60 kWh_{th}/tonne of input feedstock [35].

Biogas produced at the plant is used in a gas engine of the power P_{CHP}=1,000 kW_{el} and efficiency η_{el}=0.40 and η_{th}=0.50. The operational costs for a biogas CHP plant include running costs (maintenance, salaries and other diverse operational costs, *MSO*), while the cost/gate fee associated with the feedstock for biogas is not included in operational costs [72]. For the 1 MW_{el} biogas plant, the *MSO* was estimated at ca. 200,000 € per year [73].

After every 60,000 operating hours, the biogas engine goes for an overhaul that costs ca. 500,000 € [25]. The electricity produced in CHP is sold to the electricity grid, while excess heat is used in a nearby rendering plant. The heat demand of the rendering plant is many times higher than the heat currently supplied from the biogas CHP. To cover the total heat demand of the rendering plant, natural gas boilers are used. The selling price of high-grade heat from biogas plant, which sold to the nearby company, is classified information. Nevertheless, for the purpose of this study, that price was estimated at p_{exp}=2.0 €-Cent/kWh_{th} [22]. Also, the revenues of the biogas plant due to the received waste (the current gate fee) and the electricity sold to the grid are also confidential information.

3.2 Input data for power-to-gas integration

To find the potential for electricity production from PV and wind, the following coordinates were used: 45°47'56''N, 16°10'51''E. Characteristic values a_{PV} and a_{wind} at the location were obtained from PVGIS [74] and Renewable Ninja [75]. To investigate the impact of uncertainty in power generation, the model was studied through two subcases:

- Subcase A: Deterministic case in which no uncertainty in electricity production was taken into account.
- Subcase B: Robust case in which the uncertainty in electricity production is considered in the model. Deviation of the wind and PV power profile from the mean data at the location is set to 10%, since this proved to be the common value [66].

The specific investment costs for wind and PV installation were taken, on average, as 1,000 €/kW$_{el}$ for wind and PV installation, while *opex* for the PV plant represents 3% of *capex* per year and 1% for the wind farm [76]. The *capex* for additional biogas storage operating at atmospheric pressure is estimated at 180 €/m^3, with no significant *opex* required [77]. The *capex* and *opex* values for the upgrading unit, electrolyser and methanator are shown in Table 1. The specific electricity consumption (*e*) of these units includes both the electricity consumption of the unit itself and the power supply for instruments, valves and other peripherals [78].

Table 1 Input data for upgrading unit, electrolyser and methanator installation

Input parameters	Biogas upgrading (Pressure Swing Adsorption)	Electrolyser (Proton Exchange Membrane)	Methanator
e [kWh_{el}/Nm^3]	0.17 – 0.45 [26,38,56]	3.9 – 5.6 [38,60,79,80]	12.3 – 15.8 [60,81,82]
η [%]	84 – 96 [26,56]	60 – 80 [60,79]	55 – 85 [38,60,81]
capex [€/(Nm^3/h)]	3,200 – 4,500 [56]	(1,000 – 2,000 €/kW_{el}) 6,950 [83,84]	(650 – 660 €/kW_{el}) 6,250 [38,61]
OPEX [% of *CAPEX*/y]	4 [85]	3 [83]	10 [86,87]

The price of electricity on the day-ahead market was obtained from the Croatian Power Exchange (CROPEX) [88]. For 2019, the average price for electricity on the wholesale market was 4.93 €-Cent/kWh_{el}. In the case of importing electricity from the grid, the regulated component was added to the wholesale price (in Croatia it accounts for ca. 80% of the wholesale electricity price [89]), which resulted in a total average price of electricity equal to 8.87 €-Cent/kWh_{el}. In the case when excess electricity from the system is exported to the grid, a regulated component was not considered.

The heat released during methanation was estimated at between 1.6 and 2.1 $kWh_{th}/Nm^3(CO_2)$ [35], and in this study the average value of 1.9 was used. To estimate the economic viability of the proposed model, the *LCOE* and *LCORM* values were calculated for a period of 20 years and the discount rate of 5%, which are common values for these technologies [90].

3.3 Scenario analysis

In this study, three scenarios for P2G integration into an existing biogas plant were developed referring to Subcase A and Subcase B. The scenarios differ based on electricity demand and utilisation of biogas technology:

i) Scenario I – biogas is used in an existing CHP unit to produce heat and electricity; CO_2 after combustion is utilised with H_2 from electrolyser to produce e-CH_4 in the methanator.

ii) Scenario II – biogas is utilised with H_2 from electrolyser in methanator to produce renewable CH_4, without separating CO_2 and CH_4.

iii) Scenario III – biogas is fed to the upgrading unit to separate CO_2 and CH_4; the CO_2 stream is used in the methanator with H_2 from electrolyser to form e-CH_4, which is combined with the b-CH_4 stream from the upgrading to produce renewable CH_4.

To investigate the level of variable RES penetration and the capacity of the gas processing units in this model, the price of electricity purchased from the day-ahead market was increased by 10, 20, 30, 40 and 50% compared to average price from 2019. In the end, the levelized cost of renewable methane production was estimated by alternating the feedstock *GF*.

4 RESULTS AND DISCUSSION

This section presents the results of the analysis of the P2G concept integration into the biogas plant operating under a feedstock *GF* business model.

The first set of results is presented for the analysis performed under Subcase A, with no uncertainty included in the model, analysing the *LCOE* for wind and PV, hourly based operation of the system, assessed capacity of all energy units and economic analysis of renewable methane production at the location. The second set of results includes uncertainty in the model

(Subcase B), presenting the impact of robustness in electricity production on the total cost of the energy system.

The result figures presented in the manuscript are intended for biogas plant operators in order to quantify the techno-economic conditions of RES integration with the aim of achieving the profitable operation even in the post-subsidy period. The assessed capacities of photovoltaic and wind plants, electrolysers and methanators represent technical requirements for the integration of the P2G concept into the advanced operation of existing biogas plant. The level of the gate fee for a received substrate indicates at what level advanced biogas plants can produce renewable gas that is economically competitive with natural gas.

4.1 Subcase A

4.1.1 Cost of electricity production from variable energy sources

For wind electricity, the *LCOE* value was calculated at 6.4 €-Cent/kWh$_{el}$ and for PV at 7.4 €-Cent/kWh$_{el}$, which are both in the range of data from previous literature [91], for wind 4.0-8.2 €-Cent/kWh$_{el}$ and 3.7-11.5 €-Cent/kWh$_{el}$ for PV. Based on the estimated potential for electricity production at the location, the capacity factor [92] for wind was estimated at 22% and 16% for PV. That explains why in this case study, the *LCOE* for wind was lower than that for PV.

4.1.2 Operation and capacity of energy units

The hourly based operation of electricity producing units to cover the electricity demand of renewable methane production in a typical winter and summer week of a year is shown in Figure 2.

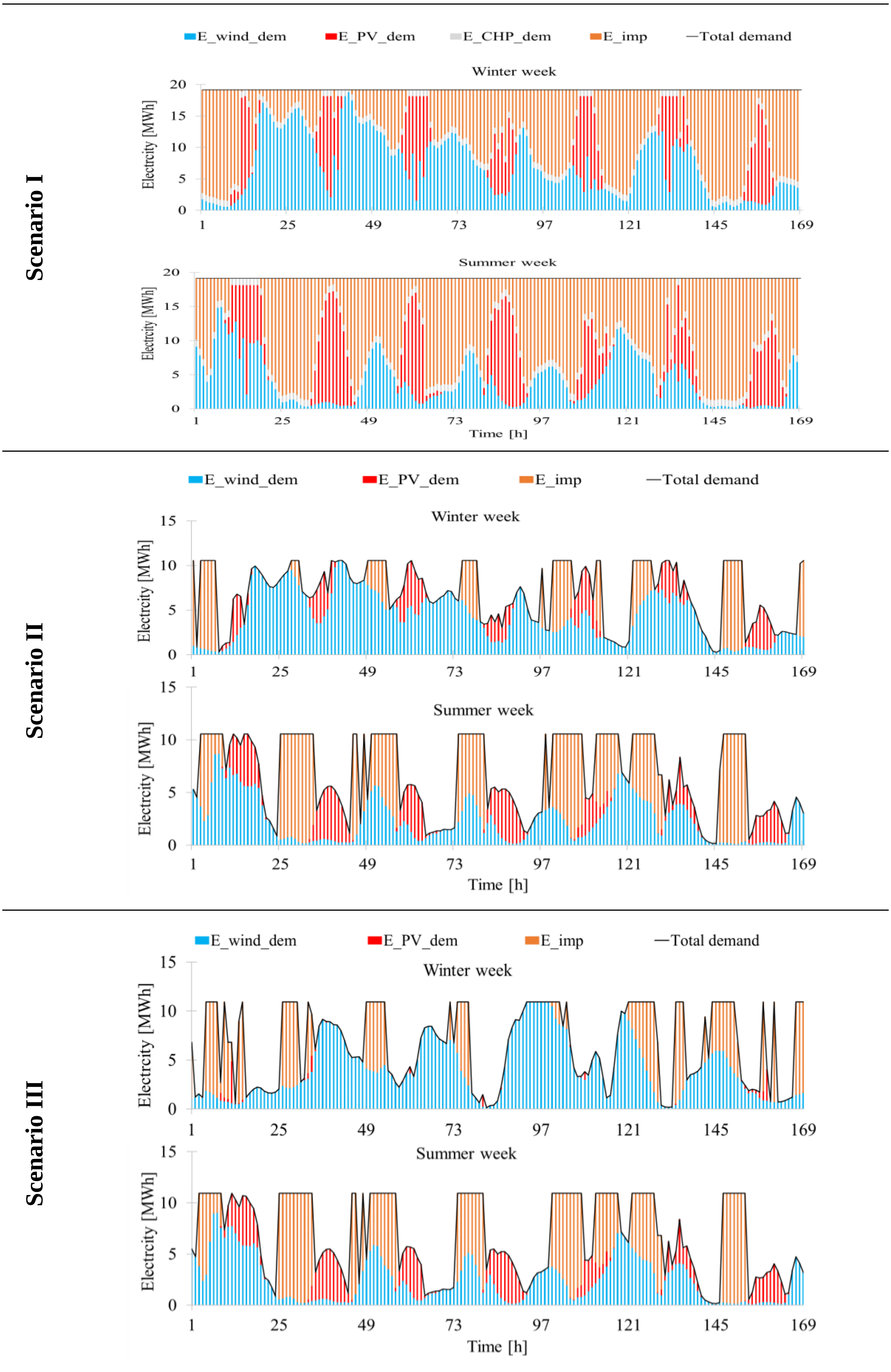

Figure 2: Hourly based operation of the system in a typical winter and summer week, Subcase A

Since the cost of electricity produced in the biogas CHP was lower than that for wind and PV (the assumption was that the investment in biogas CHP had been paid out before integrating P2G), the production of CO_2 from biogas CHP was constant (flat, like the total demand curve in Figure 2), which required immediate utilisation in the P2G concept.

The optimised capacity of external storage in Scenario I was equal to 0 m^3, while the capacity of additional storage in Scenarios II and III ranged between ca. 5,000 and 8,500 m^3 in the given electricity market conditions.

On a yearly basis, for the production of 36 GWh of renewable methane, the total electricity demand in Scenario I was estimated at 167.5 GWh_{el}, in Scenario II at 58.6 GWh_{el}, and in Scenario III at 59.8 GWh_{el}. The analysis showed that Scenario I cannot be feasible due to the extremely high electricity demand in the process and the low integration of the P2G concept in the biogas plant whose operation should be assisted by imported electricity from the grid. In more detail, results in Figure 2 showed the hourly-based operation of the system in two characteristic weeks in the studied year.

The electricity generated by the wind farm at the location in Scenario I accounted for ca. 18% of the total demand in the summer week, and ca. 37% of the total demand in the winter week. The PV plant at the location in Scenario I covered ca. 25% of the total demand in the summer week and ca. 15% in the winter week. The biogas CHP covered ca. 7% of the total demand over the year, while the rest (ca. 40-50% of the total demand) was covered by electricity imported from the grid. In both Scenario II and III, the penetration of wind and PV in the total electricity demand was very similar, ca. 35% of the total demand in the summer week and ca. 62% in the winter week for wind, and ca. 18% of the total demand in the summer week, and ca. 14% in the winter week for PV. In Scenario II and III, the electricity imported from the grid to cover the total demand for renewable methane production accounted for ca. 25-45%.

Optimised capacity of the wind and PV plant in the given electricity market conditions and for each scenario are shown in Figure 3.

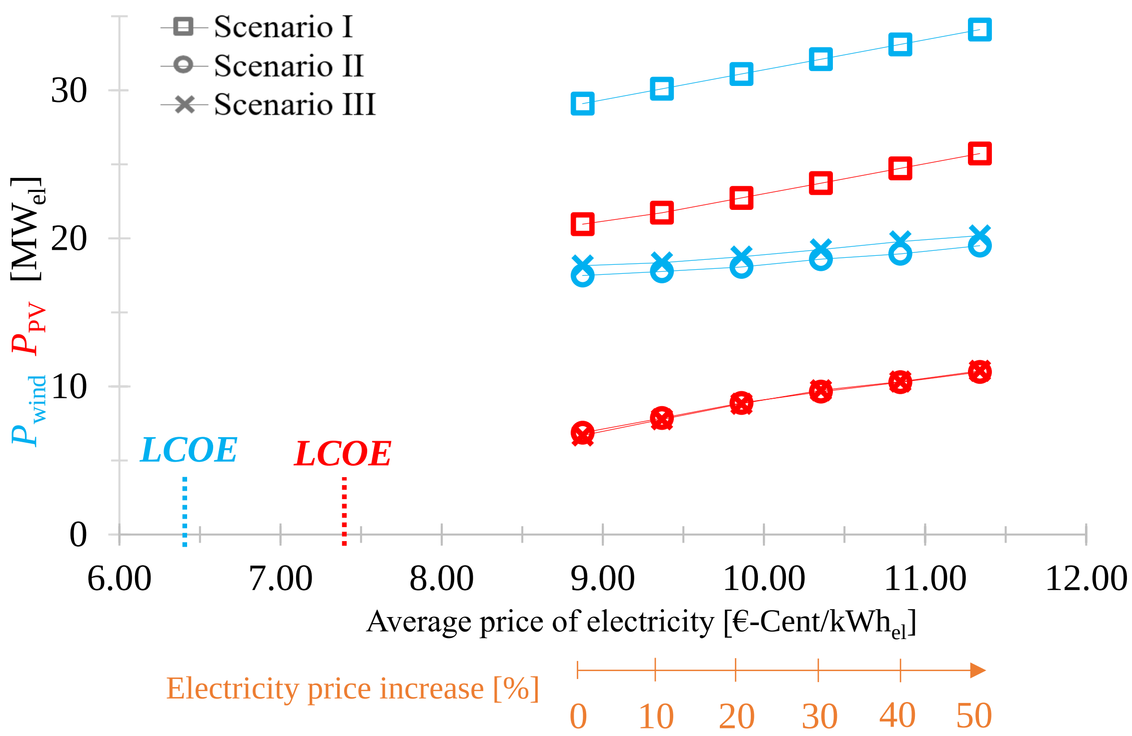

Figure 3: The impact of average electricity price on wind and PV capacity, Subcase A

As the market price of electricity increased, the penetration of variable RES became more important to cover the energy demand of the system. As can be seen in Figure 3, the potential for wind penetration in the system was significantly higher than that of PV, since the *LCOE* for wind was found to be lower than that for PV.

Results obtained by Scenario II and Scenario III were very similar in the given electricity market conditions. In Scenario II, the optimised capacity of the methanator was calculated at 650-730 Nm^3(e-CH_4)/h, while the capacity of the electrolyser was optimised in the range 920-1,000 Nm^3(H_2)/h. The capacity of the methanator in Scenario III is optimised to the value of ca. 230-270 Nm^3(e-CH_4)/h, while the biogas upgrading unit had an optimum capacity between 660-730 Nm^3(biogas)/h.

Based on the results of the optimisation, it was estimated that the capacity factor for the electrolyser ranged between 56% and 62%, while for the methanator, the capacity factor was assessed at ca. 57-63%. Using the developed model, it was found that for the production of 900-1,100 $Nm^3(H_2)/h$ in the electrolyser which served in the methanation to produce 36 GWh per year of renewable gas (both e-CH_4 and b-CH_4), installation of a wind plant of ca. 18-20 MW_{el} and a PV plant of 6.5-11.0 MW_{el} was required.

In the *Audi e-gas* plant [38], to meet the electricity demand for producing 1,200 $Nm^3(H_2)/h$, which is used to produce 300 Nm^3(e-CH_4)/h, four wind turbines were installed, each of 3.6 MW_{el} capacity, in total 14.4 MW_{el}. The capacity factor for wind at this location of the biogas plant was estimated at 22%, while in Northern Germany it was significantly higher, ca. 40% [93].

Based on the model results and comparison with data obtained from the literature, it can be concluded that the developed model for P2G integration in the biogas plant could be applicable for estimating the capacity of variable RES at the location required for these processes.

4.1.3 Economic analysis of the energy system

In Scenarios II and III, the cost of electricity imported from the electricity grid to the system decreased from ca. $1.4 \cdot 10^6$ € (at an average electricity price of 8.87 €-Cent/kWh_{el}) to ca. $1.1 \cdot 10^6$ € when the electricity price increased by 50%. In Scenario I, the cost of imported electricity from the grid in the same range of prices was calculated to be much higher, between $7.4 \cdot 10^6$ and $9.3 \cdot 10^6$ €.

In Scenario II and Scenario III, it was estimated at ca. $1.1 \cdot 10^5$ € (at the electricity price of 8.87 €-Cent/kWh_{el}), and it increased by almost 200% when the electricity price increased by 50%. The higher revenue was achieved in Scenario I, between 2.8 and $4.5 \cdot 10^5$ €. In Scenarios

II and III, the revenue from heat sold to the nearby rendering plant was around $3.5 \cdot 10^4$ €, while in Scenario I, this figure was significantly higher, ca. $3.5 \cdot 10^5$ €.

The analysis showed that heat exported to the rendering plant accounted for ca. 12-25% of the overall revenue from selling the energy in Scenarios II and III, while in Scenario III the heat represented ca. 44-45% of the total revenue. As expected, Scenario I yielded higher revenue from selling the heat from the biogas CHP, but it also resulted in higher demand for importing electricity, as the amount of CO_2 used in the methanator was much higher than in Scenarios II and III.

All capital and operating costs in the system, costs and revenues from imported and exported electricity and revenues from the exported heat were counted, adding the feedstock *GF* as additional revenue according to Eq. (31). The sensitivity analysis took a variation of the feedstock *GF* from 0 €/tonne to -200 €/tonne, and the results are shown in Figure 4.

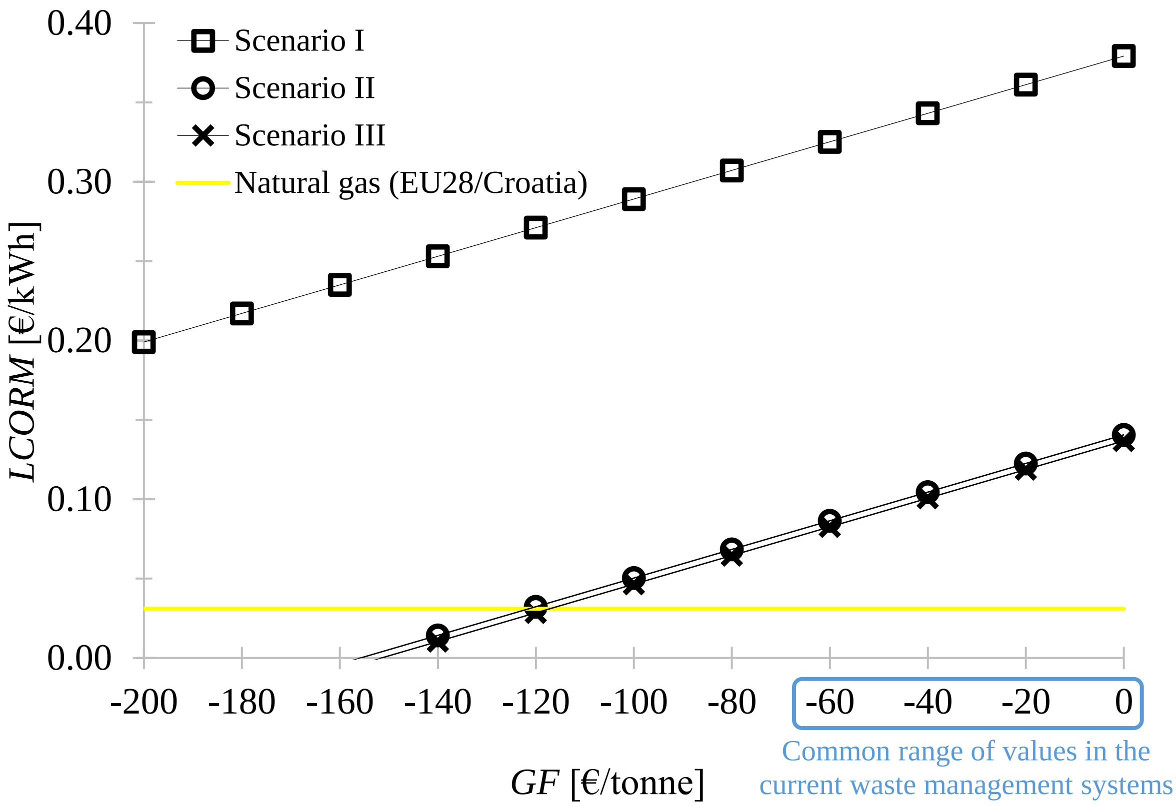

Figure 4: Sensitivity analysis of the feedstock *GF* variation on the *LCORM*

The *LCORM* in Scenario II and Scenario III fitted very close to each other, while the *LCORM* in Scenario I was significantly higher. As the (absolute) value of *GF* increases, the cost of renewable methane production decreases and contributes to the economic viability of the proposed energy system. In general, the levelized cost of SNG generation by P2G ranged between 0.08 and 0.60 €/kWh [32]. More precisely, the cost of renewable methane produced in P2G with the direct methanation of biogas was estimated at 0.24-0.30 €/kWh [94].

If the *LCORM* in Scenarios II and III reached the average price of natural gas for non-household consumers in Croatia (which is very close to average in the EU28, ca. 0.031 €/kWh [95]), the *GF* in the proposed system should be ca. -120 €/tonne. In Scenario I, the *GF* would need to be ca. -385 €/tonne to meet the average price of natural gas in Croatia/the EU28. The calculated values of *GF* in these scenarios are significantly higher than those reported for food waste/biowaste based biogas plants in the EU, for which the common *GF* values are between -40 and -50 €/tonne [96,97].

When the *LCORM* achieves the average natural gas price for household consumers in the EU (ca. 0.067 €/kWh [95]), the *GF* should become ca. -80 €/tonne, which is closer to common *GF* values in the biogas sector. One reason that biogas plants have not yet intensified their operation in the waste management system using biodegradable fractions and biowaste is that the fee for landfilling organic waste in Europe is still rather low, between -20 and -30 €/tonne [98]. However, since landfill is no longer prioritised as a waste management solution [99], it is expected that in future the biogas sector will take over the management of biodegradable organic waste, which will apparently result in *GF* values higher than the current ones.

Moreover, further liberalisation of the natural gas market in Europe and Croatia is expected in the coming years [100]. This could result in an increase of natural gas prices, which would contribute to greater penetration of renewable methane in the gas sector.

4.2 Subcase B

The impact of introducing uncertainty into the mathematical model using the gamma parameter in electricity production at the location, on the optimal economic results and the imported electricity from the grid is shown in Figure 5.

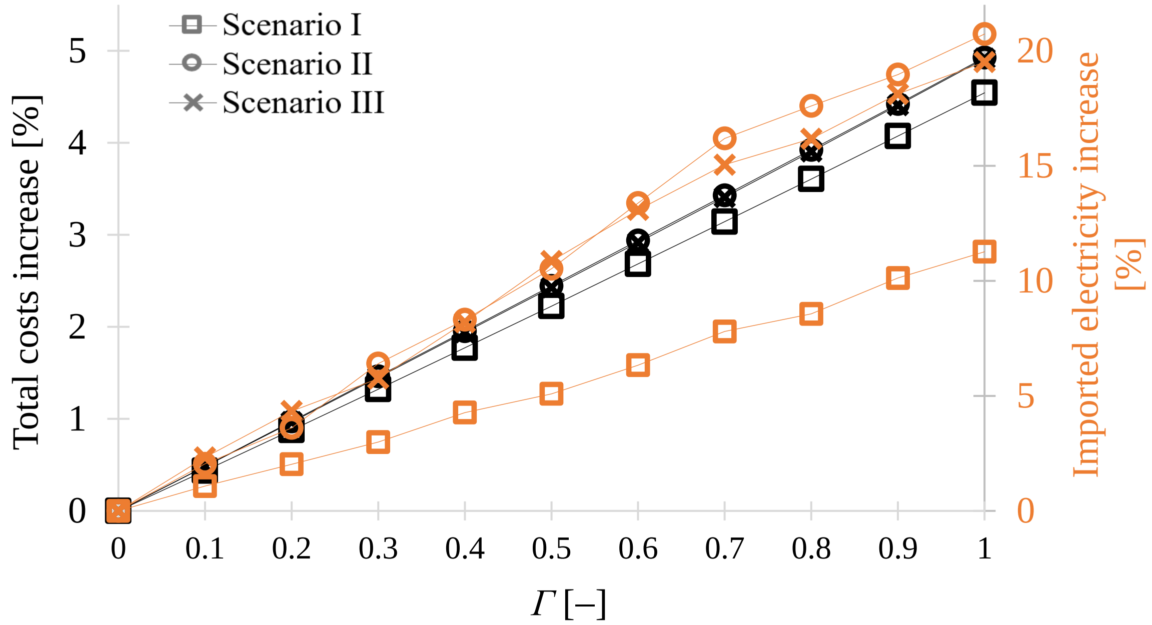

Figure 5: Increase in the total costs of the system operation and imported electricity in relation to robustness level

As presented in Figure 5, introducing uncertainty into electricity production resulted in a decrease in the economic benefits of the system and in an increase in the amount of electricity imported from the grid. When the robustness level met the most conservative case, the total costs increased by ca. 5% in all examined scenarios.

Regarding electricity import, the most conservative approach resulted in an increase of 11% in Scenario I, ca. 21% in Scenario II and ca. 20 % in Scenario III. Introducing uncertainty in Scenario I was shown to have a lower impact on the increase in the amount of imported electricity, compared to Scenario II and Scenario III. This was explained by the fact that the imported electricity in Scenario I constituted almost half the total electricity demand (Figure

2), while in Scenarios II and III, the energy systems relied more on electricity from wind and PV (also Figure 2), and therefore were more influenced by uncertainty in electricity production.

The increase in the system's robustness results in higher *LCOE* values for wind and PV [101], making the system more grid-dependent. In the present analysis it was reported that, for the most conservative case, the average increase in the *LCOE* at the location for wind was 14% and for PV 44%, compared to the case where no uncertainties were examined (Subcase A). In addition, the analysis showed that uncertainty decreased the load factor of renewable plants. On average, it was determined that the decrease for wind was from 22% to 16%, and for PV from 16% to 10%.

The overall impact of system robustness on the increase in *LCORM* (as presented in Figure 4, without uncertainties considered) was determined to be ca. 8-12% in Scenario I, ca. 3-32% in Scenario II and ca. 4-20% in Scenario III. Results indicated that the production of renewable methane in both Scenarios II and III was more affected by the uncertainties in electricity production than Scenario I. However, the cost of renewable methane production in both Scenarios II and III remained much lower than those in Scenario I, pointing to the conclusion that the concept of direct biogas methanation synergised with the feedstock *GF* in biogas production has a higher potential to be economically competitive with natural gas than CO_2 capture from flue gasses, utilised with renewable electricity [102].

From the technical point of view, the CO_2 utilisation concept presented in Scenario I has several shortcomings, the major one being the separation of relatively low concentrations of CO_2 from the large amounts of nitrogen in the flue gasses, which was not considered in this study but represents an important investment and operational factor in the process. It was determined that capturing post-combustion CO_2 at a biogas plant cannot be feasible in any case to the biogas upgrading process [103].

5 CONCLUSION

The robust mathematical model developed in this study was successfully tested on a real biogas plant, analysing key features of the implementation of the power-to-gas concept. Direct methanation of biogas has proven to be economically attractive option for the integration of power-to-gas concept driven by the PV and wind plant. About 60% of the total electricity demand to produce renewable methane can be obtained from variable RES, while the rest should be covered by the electricity from the grid.

The hypothesis of the study was successfully confirmed, as the feedstock gate fee significantly reduced the cost of renewable methane production, bringing additional viability to the plant operation. The research showed that the gate fee level for food waste below which the advanced operation of biogas plants becomes viable is around -120 €/tonne.

The analysis showed that the studied energy system becomes more grid-dependent and the cost of renewable methane production becomes higher if the uncertainty in electricity production from wind and PV at the location intensifies. The projections indicate that an increase in landfill gate fees for biodegradable waste, a liberalisation of the natural gas market and a reduction in investment costs for renewables (wind and PV plants) will eventually contribute to creating renewable methane that is economically competitive with natural gas.

In future research, the authors are inclined to study the integration of demand-response in the existing robust model, especially considering hydrogen production in the electrolyser and market prices.

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ARTICLE 7

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Article

Geospatial Analysis and Environmental Impact Assessment of a Holistic and Interdisciplinary Approach to the Biogas Sector

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Abstract: Crop-based biogas energy production, in combination with electricity generation under subsidy schemes, is no longer considered a favourable business model for biogas plants. Switching to low-cost or gate fee feedstocks and utilising biogas via alternative pathways could contribute to making existing plants fit for future operations and could open up new space for further expansion of the biogas sector. The aim of this study was to combine a holistic and interdisciplinary approach for both the biogas production side and the utilisation side to evaluate the impact of integrating the biogas sector with waste management systems and energy systems operating with a high share of renewable energy sources. The geospatial availability of residue materials from agriculture, industry and municipalities was assessed using QGIS software for the case of Northern Croatia with the goal of replacing maize silage in the operation of existing biogas plants. Furthermore, the analysis included positioning new biogas plants, which would produce renewable gas. The overall approach was evaluated through life cycle assessment using SimaPro software to quantify the environmental benefits and identify the bottlenecks of the implemented actions. The results showed that the given feedstocks could replace 212 GWh of biogas from maize silage in the relevant region and create an additional 191 GWh of biomethane in new plants. The LCA revealed that the proposed measures would contribute to the decarbonisation of natural gas by creating environmental benefits that are 36 times greater compared to a business-as-usual concept. The presented approach could be of interest to stakeholders in the biogas sector anywhere in the world to encourage further integration of biogas technologies into energy and environmental transitions.

Keywords: biogas; feedstocks; energy potential; GIS; future energy systems; LCA

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1. Introduction

The paradigm of development for the European biogas sector has changed significantly in recent years owing to higher sustainability requirements and cost production reduction as the main drivers of new trends in biogas production and utilisation [1]. Most biogas plants (especially in less mature biogas systems) still use cultivated energy crops (primarily maize silage), which increase the inefficient use of arable land and compete with food production [2]. Since such a practice is not in line with the principles of sustainable development, the biogas sectors among the European countries limited the utilisation of maize silage and corn to a share of 30–50% of the total input feedstock [3,4], and a further decrease in the use of maize silage is expected.

In 2018, the European Commission adopted a revised version of the Renewable Energy Directive (RED II), which stated that the biomass fraction of municipal waste, biowaste and streams from industry and agriculture [5] should play a greater role in future biogas production since they have a low indirect land-use change impact to produce biofuel [6]. In addition, the RED II determined that wastes and residues from agricultural activities and processing shall be considered to have zero life cycle greenhouse gas (GHG) emissions up to the process of the collection of those materials. This opens a space for these materials to enter the biogas sector and contribute to the transition towards more sustainable and efficient waste management systems [7].

In addition to facing the feedstock-changing policy, biogas plant owners and operators also look towards alternative biogas utilisation pathways compared with producing heat and electricity under subsidy models [8]. The biogas sector in the EU28 recorded a rapid increase in the number and capacity of installed plants in the period 2009–2012 [9]. The earliest of these biogas plants are near the completion of their subsidised operation, as these subsidies were granted for 12–20 years, depending on the country [10]. In the post-subsidy era, the operation of biogas plants on the day-ahead market could only be viable in the case of low-cost feedstocks or by implementing the feedstock gate fee business model [11]. Among the most likely alternatives after the expiry of subsidies are biogas upgrading, the production of biomethane [12] and/or the integration of the power-to-gas (P2G) concept using variable electricity from wind and solar to produce e-methane [13]. Renewable methane with natural gas quality (ca. >96% CH_4 [14]) can be directly injected into the gas grid or stored on location as compressed or liquified gas [15].

A geographical information system (GIS) was recognised as a valuable tool for the detailed mapping and planning of new energy projects [16] and in assessing the environmental and economic benefits of renewable energy source (RES) integration [17]. In the context of bioenergy, geospatial investigation contributes to the assessment of the physico-chemical properties of biomass, facilitating the choice of the best technologies for application in the studied region [18]. The geospatial assessment of the energy potential of crop residues and manure for biogas production in the EU showed the yearly availability of 0.7 EJ (ca. 195 TWh) [19], which was ca. double the EU production of biogas from agricultural feedstocks in 2016. The bottom-up GIS model applied in the assessment of biomass potential from grasslands in Northwest Europe showed that ca. 45% of the sustainable grass could be utilised for energy production purposes in the model region [20]. Another bottom-up analysis of using animal manure from various husbandry operations in East Croatia showed the potential of feedstock to produce 6.5 GWh of biogas, which could generate double the yearly electricity consumption of that municipality [21]. The top-down mapping of agricultural residues in Croatia using Quantum GIS (QGIS) software [22] showed that stover, straw and stalk could generate biogas potential up to 3000 MWh/(km^2·a) in the extensive agricultural regions of Croatia. ArcGIS software was applied to reveal the potential of renewable electricity generation from municipal solid waste, including organic and dry material in Iran [23]. The results showed that the studied region could produce ca. 2% of the total household electricity consumption, while achieving the avoidance of 6.7 thousand tons of CO_2eq/year due to the proposed measures. Integrated tools in GIS software allow users to determine important factors when assessing the availability of feedstocks for biogas production, such as the length of transportation routes from the biomass harvesting location to the biogas plant and the optimal location for setting up a new biogas plant. [24]. In this sense, QGIS was successfully applied when determining the optimum area for establishing the biogas hub in Karditsa, Greece [25]. The results showed that the optimal distance between the available biomass sources and the planned hub was ca. 20 km in order to maintain a feasible hub operation. ArcGIS was applied when finding an optimal biogas plant sited on the territory of Ohio in the United States for the case of corn stover and wheat straw [26]. It was found that the average biomass availability radius for that case ranged between 22 and 34 km in the case of 10 newly examined biogas plants. The same software was applied to the case of Southern Finland with the goal of quantifying the relationship between the length of transportation distances to deliver feedstocks to existing biogas plants and an increase in their production capacity [27]. Increasing the radius of biomass collection from 10 to 40 km could increase biogas plant production capacity by ca. 10–127%. However, the study did not reveal the impact of a capacity extension on the environmental performance of plants.

From environmental and economic points of view, the penetration of bioenergy into energy production systems (especially the ones based on fossil fuels) could bring multiple contributions and benefits [28]. As the price of the carbon tax increases, so will the switch to carbon-neutral and carbon-sink resources. In the context of this research, the application of a life cycle assessment (LCA) can reveal the actual environmental impact of feedstock-changing policies in biogas production and utilisation related to future energy systems [29]. It was shown that sugar beet generates ecological effects that are similar to those of maize crops in bioenergy production [30], while intercropping forage sorghum with maize contributes to a lower environmental impact than a maize monoculture [30]. Examining the environmental impact assessment of replacing maize silage with marine macroalgal biomass using SimaPro (an LCA software) showed a reduction in the environmental burden in almost all the impact categories that were examined. However, the significantly longer transport route for algae (150 km) compared to maize silage (12 km) resulted in higher values in the global warming potential (GWP) category, from 140 g CO_2-eq/kg(energy crops), to 160 g CO_2-eq/kg(macroalgae). A similar observation was also found by the authors of the present study in the case of applying residue grass from landscape management as a replacement for maize silage in existing biogas production [31]. Biogas plants that are fed with agro-industry by-products and waste, such as distiller's waste, rapeseed cake, cheese whey, pulp, seeds, peel, and fruit and vegetable residues, yielded better environmental performances than those fed with cereal silage [32]. Nevertheless, the overall environmental performance also depends on the variability in terms of the total solids/volatile solids (TS/VS) content, specific biogas yield, origins and other factors [32]. A comparison of the LCA performance for a biogas plant fed with animal manure and energy crops for various biogas utilisation pathways [33] showed that biogas for electricity generation saves around 300 kg CO_2/MWh(electricity), while upgrading biogas to biomethane and its injection into the gas grid saves 191 kg CO_2-eq/MWh(biomethane). Another study of LCA claimed that using biogas in cogeneration achieved better overall environmental results compared to biogas upgrading [34]. In both studies, the details about the considered electricity mix in the study were not provided, and the results were not presented using the same reference point. Projections from the Joint Research Centre (JRC) of the European Commission (EC) showed that by 2030, the further penetration of renewable energy sources (primarily wind and solar photovoltaic) will decrease the overall GHG emissions of the electricity generation sector [35]. The integration of P2G and methanation in a biogas plant to fully exploit biogenic CO_2 potential yielded better environmental performance, with a projected European electricity mix for 2030 compared to 2016 [36]. In the case of Ireland, an LCA of a biogas upgrade with P2G integration showed that using an electricity mix with an 85% share of renewables could satisfy the GHG savings of 70% compared to fossil fuels [37]. Future development of P2G efficiency and the integration of renewable credits from CO_2 valorisation could increase the competitiveness of the biogas sector in future energy systems [38].

Based on the detailed literature review, there is no reported research that integrally analyses the geospatial availability of novel feedstocks in the replacement of maize silage in biogas production, combined with the environmental impact assessment of feedstock replacement and alternative biogas utilisation pathways in future energy systems operating with a high share of RES. To address this gap in the scientific literature, the research objectives were as follows:

- To assess the energy potential for biogas production using lignocellulosic residues, agri-food industry streams and the biodegradable fraction of municipal waste;
- To present the geospatial distribution of the energy potential of novel feedstocks using a GIS mapping approach and to determine which existing and newly added biogas plants are suitable to contribute to natural gas decarbonisation;
- To estimate the environmental impact via using an LCA of novel operational measures on the biogas production side and the utilisation side, while using actual biogas plants as test cases.

The hypothesis of this research was that applying a holistic approach to biogas plants, on both the production and utilisation sides, can increase environmental benefits over the current operation based on maize silage utilisation and baseload electricity production.

2. Materials and Methods

This section presents the materials and methods that were applied in this research. The first step was to determine the quantity of alternative feedstocks for biogas production and their energy potential. The second step included the mapping and data processing in QGIS software to present the geospatial availability. The final step was the assessment of the environmental impact of the proposed measures on the biogas sector using SimaPro software.

2.1. Alternative Feedstocks to Maize Silage

The target feedstocks in this research were divided into three specific types by place of origin and approach when estimating their potential for biogas production. Their selection was based on previous studies conducted by the authors and on the objective of using waste material sources in biogas production that are not competitive with food production.

The technical potential of biodegradable municipal waste ($P_{\text{tech,biowaste}}$) in tonnes was estimated at the municipality level (i) using the following relation:

$$P_{\text{tech,biowaste}(i)} = D_{\text{pop}(i)} \times Area_{(i)} \times S_{\text{biowaste}(i)} \tag{1}$$

where

$D_{\text{pop}(i)}$ is the population density (cap/km^2);

$Area_{(i)}$ is the area of the municipality (km^2);

$S_{\text{biowaste}(i)}$ is the specific biowaste generation per person (t/cap) living in the studied municipality.

The second group of feedstocks included residue grass (RG) originating from landscape management and generated on uncultivated land, riverbanks and highway verges [31]. The technical potential of residue grass ($P_{\text{tech,RG}}$) in tonnes on the examined grasslands (j) was assessed using Equation (2):

$$P_{\text{tech,RG}(j)} = N_{\text{cut}(j)} \times Area_{(j)} \times S_{\text{RG}(j)} \tag{2}$$

where

$N_{\text{cut}(j)}$ is the number of cuts per year, usually between 2 and 4 [20];

$Area_{(j)}$ is the area of the pasture (km^2);

$S_{\text{RG}(j)}$ is the specific yield of grass on the grassland (t/km^2).

The third group of feedstocks included industry waste, co-products and by-products from crop and animal processing, as well as food and beverage manufacturing. These included wastewater sludge, fat, oil and grease, spent materials, the biodegradable fraction of industry waste and co- and by-products that cannot be used as animal feed [39]. The authors sought actual data on waste generation in the processing plants. This was done using technical annual reports, recent environmental impact studies, master's theses and the national registry for environmental pollution. In several cases, these sources were unavailable; instead, the authors estimated the amount of generated waste using the yearly production capacity and specific ratios of generated waste per unit of processed raw material [40]. All details regarding the assessed biogas potential and the relevant literature sources are given in Supplementary Material.

To assess the biogas potential using the above-mentioned feedstocks in an anaerobic digestion process ($E_{\text{feedstock}}$), the following relation was used:

$$E_{\text{feedstock}} = P_{\text{tech,feedstock}} \times Y_{\text{feedstock}} \times LHV_{\text{methane}} \tag{3}$$

where

$Y_{\text{feedstock}}$ is the methane potential of the studied feedstock expressed over fresh material (FM) (m^3/tFM);

LHV_{methane} is the lower heating value of methane (kWh/m^3).

2.2. GIS Mapping and Data Processing

Georeferenced data on settlement boundaries and land-use maps were used to perform GIS mapping of the biogas potential. An open-source QGIS software, version 3.10.4-A Coruña [41], was used to conduct this stage. This included the use and creation of raster and vector layers, as well as the application of the integrated tools, which are elaborated further in the article. The advantages of using QGIS over some other software for GIS mapping are its free availability, stability during data processing and numerous accessible plugins and modules that allow users to create added value for the project [42]. Data on the yearly availability of biogas potential that was calculated in the previous stage was joined to the georeferenced layer of the case layer. The CORINE Land Cover inventory [43] was used to perform a spatial distribution of biogas potential from residue grass in the given region. The category 2.3.1 Pastures was selected for the mapping of residue grass potential since it presents the data on permanent grassland (pastures and meadows) [20]. The analysis included uncultivated land, riverbanks and highway verges, while other pastures were not considered. To present the distribution of the biogas potential of yearly residue grass biomass, the following equation was used:

$$E_{\text{RG}(m)} = Area_{(j)}/Area_{(\text{tot})} \times E_{\text{RG}(j)} \tag{4}$$

where

$E_{\text{RG}(m)}$ is the biogas potential for the examined area that uses the grid (MWh);

$Area_{(j)}$ is the area of specific grassland (1 km^2);

$Area_{(tot)}$ is the total grassland area (km^2);

$E_{\text{RG}(j)}$ is the biogas potential for the relevant grassland (MWh).

In the case of biodegradable industry waste, the point source layer was used, while municipal biowaste was presented at the level of the municipality. To determine which of the existing biogas plants would be suitable to switch from electricity production towards renewable methane production alone (as proposed in our previous research [13]), the position of the natural gas grid was determined. More details on how the natural gas grid was extracted are presented in Section 3.2. To estimate the distance between the feedstock position and the biogas plant, an *Online Routing Mapper* tool was used, while to find the shortest path to connect the biogas plant to the natural gas grid, a *Measure Line* tool in QGIS was used. The *Buffer* tool and *Join attributes by location (sum)* were applied to estimate the area with the same energy potential of examined feedstock as the one with maize silage. In the end, an optimal location for setting up new biomethane-producing plants was determined based on the availability of feedstocks and the distance to the natural gas grid.

2.3. Life Cycle Assessment

The life cycle assessment was conducted according to International Standard Organization (ISO) 14040/14044 standards [44] using SimaPro software (v7.3.3, PRé Sustainability, Amersfoort, The Netherlands). The study aimed to estimate and compare the environmental effects of applying the proposed measures to both the biogas production side and the utilisation side using actual biogas plants as test cases. The system boundary included all the processes regarding feedstock collection and transportation, the production of biogas in the anaerobic digestion plant and biogas utilisation in a combined heat and power (CHP) unit or to produce renewable gas. The analysis did not include the environmental features of electricity, heat and renewable gas utilisation in any energy sector specifically. To be in line with the RED II, all pre-collection processes for waste and residues were considered to have zero emissions. The feedstock properties and the biogas production via anaerobic digestion were obtained from previous laboratory analyses and published articles. In addition, the calculated biogas potential and location features obtained by processing the data in QGIS software were taken as inputs. All other data were obtained from the Ecoinvent v2.2 [45] database.

The functional unit for this study was defined as the production of 1 m^3 of CH_4 during the anaerobic digestion of selected feedstocks, which would be further utilised in various pathways, as presented in the scenarios. The chosen impact assessment methods were Impact 2002+ [46], which is a method that evaluates several midpoint categories that re grouped as a single score and a global warming potential (GWP) that was calculated over a 100 y time horizon (GWP100). The results of the LCA analysis are shown in Section 4.2.

3. Case Study

The region of Northern Croatia [47] was selected for the case study and is shown in Figure 1.

Figure 1. Case study—Northern Croatia.

In 2019, the region was home to 1,622,651 people (ca. 40% of the total population of Croatia) [48] living in an area of 11,309 km^2 (ca. 20% of total Croatian land). The average population density in the region is 144.1 cap/km^2, which is double the average population density of Croatia. Food processing, production of goods and agricultural activities are highly developed in the region. There are 13 biogas plants in the area, which operate mostly using maize silage.

3.1. Biogas Plants in Northern Croatia

The installed capacity of biogas plants operating under the subsidy mechanism (feed-in-tariff) in Northern Croatia was taken from the annual report of the Croatian Energy Market Operator Ltd. (HROTE) [49], as shown in Table 1. References related to the feedstocks in use and quantity were taken from publicly available data (only in Croatian), such as master's theses, environmental management studies and reports and biogas plant webpages.

Table 1. Biogas plants in the case.

Biogas Plant No.	Installed Capacity (MW_{el})	Utilised Feedstocks and Quantity (t/a)	Type of Process and Temperatures	References
1	1.0	Chicken manure (5000), maize silage (8000), grain dust (3400)	Single-stage at 40 °C	[50]
2	0.3	Cattle and swine manure (14,400), maize silage (3600)	Single-stage at 40 °C	[51]
3	1.2	Cattle and swine manure (10,000), maize silage (13,000)	Single-stage at 40 °C	[52]
4	2.4	Maize silage (28,400), animal manure (21,300), animal dung (21,300), chicken manure (1775), biodegradable waste (3550)	Single-stage at 38 °C	[53]
5	1.0	Maize silage (6000), animal manure (30,000)	Single-stage at 38 °C	[54]
6	2.0	Maize silage (29,750), animal manure (50,750), biowaste (35,000), animal by-products (14,000)	Two-stage: pretreatment at 133 °C and AD at 37 °C	[55]
7	1.0	Biowaste from canteens and restaurants, expired food (25,000)	Two-stage: pretreatment at 35 °C and AD at 40.5 °C	[56]
8	3.7	Landfill plant	N/A	[57]
9	1.0	Animal manure (16,285), maize silage (24,700)	Single-stage at 38 °C	Scaled using [58]
10	1.0	Animal manure (16,285), maize silage (24,700)	Single-stage at 38 °C	Scaled using [58]
11	2.0	Animal manure (32,570), maize silage (49,400)	Single-stage at 38 °C	[58]
12	1.0	Animal manure (16,285), maize silage (24,700)	Single-stage at 38 °C	Scaled using [58]
13	1.0	Animal manure (16,285), maize silage (24,700)	Single-stage at 38 °C	Scaled using [58]

By applying Equation (3) to the data presented in Table 1 and their specific methane yield shown in Supplementary Material, the total energy potential of feedstocks in the given biogas plant was shown in Table 2. Furthermore, the contribution (share) of maize silage to the total biogas energy production of each biogas plant is presented.

Table 2. Energy produced in the biogas plants.

Biogas Plant No.	Biogas Produced (MWh)	Energy Contribution of Maize Silage to Total Biogas Production (%)
1	16,917	44.3
2	5350	63.0
3	13,543	89.8
4	43,087	61.7
5	9741	57.7
6	64,469	43.2
7	15,125	0.0
8	N/A	N/A
9	25,358	91.2
10	25,358	91.2
11	50,717	91.2
12	25,358	91.2
13	25,358	91.2

Even though the overall share of maize silage in the biogas plants corresponded to ca. 40% of the input feedstock mass, it produced ca. 70% of the total energy in these biogas plants. Biogas plant no. 7 was the only one in this case that operated without using maize silage. The plant was designed to operate using biodegradable waste from canteens, restaurants and kitchens in a two-stage mesophilic process [39]. Landfill plant no. 8 [57] operated using mixed municipal waste from the city of Zagreb.

3.2. Input Data

The biogas yield of the given feedstocks is shown in Supplementary Material. For Equations (1)–(3), the input data was taken as follows:

- $D_{pop(i)}$ was taken from the Croatian Bureau of Statistics [59] (available only in Croatian);
- $S_{biowaste(i)}$ was estimated using the data on the total generation of municipal waste per capita (kg/cap) (Table 9 in [60]), with the estimation that 32% of municipal waste is biodegradable [61];
- *Area*—determined using QGIS;
- $N_{cut(j)}$—in this study, this was considered to be 2 for a 1 km × 1 km grid;
- $Y_{feedstock}$—assessed in previous studies (Supplementary Material);
- $LHV_{methane}$—10 kWh/m^3 [21].

The layer of the existing natural gas transportation grid in this region was created using the *Georeferencer* tool in QGIS [62] and the map was taken from the Environmental Justice Atlas [63].

The electricity generation mix was taken from the report by the Ministry of Economy and Sustainable Development of the Republic of Croatia and the Hrvoje Požar Energy Institute (available only in Croatian) [64]. The reference year was 2018, and the data on electricity mix projections were taken for 2030, 2040 and 2050, as shown in Table 3.

Table 3. Electricity mix projections for Croatia.

Electricity Source	Contribution to Electricity Mix (%)			
	2018 (Reference Year)	2030	2040	2050
Net import	28.3	2.6	2.6	7.2
Industrial cogeneration plants	2.1	1.3	1.1	0.5
District heating plants	13.6	14.8	8.9	2.9
Thermal power plants	7.9	14.4	7.4	3.7
Geothermal power plants	0.0	3.5	4.1	4.5
Solar power plants	0.5	3.9	20.4	24.8
Wind power plants	6.8	23.6	26.3	29.6
Hydropower plants	40.8	35.8	29.3	26.7

4. Results and Discussion

This section presents the main results and the related discussion in terms of this study and its research objectives. First, the assessment of biogas potential and a model of geospatial distribution are presented. The results of the data processing using integrated tools were disseminated in terms of a transition towards alternative solutions for both the biogas production and utilisation aspects. The assessment of environmental impact verified the hypothesis of the study.

4.1. Biogas Potential Assessment and GIS Map

Figure 2 presents a map of the biogas potential from the given yearly feedstocks for municipalities in Northern Croatia. Due to its size and complexity, the results for the city of Zagreb are presented at the settlement level.

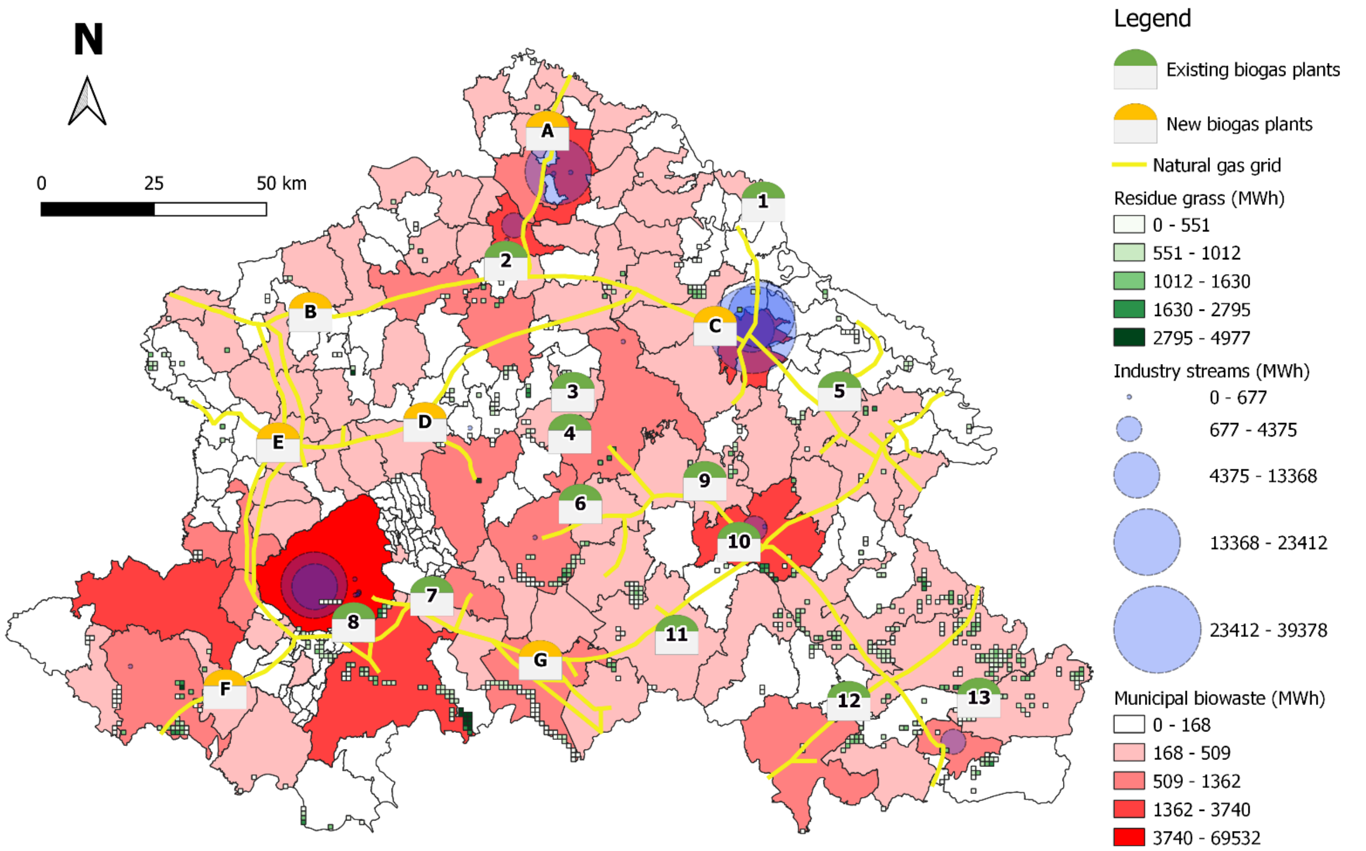


Figure 2. Geospatial analysis of the biogas sector in Northern Croatia.

The results shown in Figure 2 represent the assessed energy potential for biogas production from alternative substrates in the study region and the position of existing biogas plants for which the transition from maize silage is proposed. Next, the geospatial analysis of the biogas sector included finding a natural gas network that, together with the assessed biogas potential, identified the locations where new biogas plants should be installed. The analysis also included an assessment of the contribution of renewable gas production in new plants towards the decarbonisation of the natural gas sector. Overall, the results of this study demonstrated the scientific contribution in terms of an interlinked GIS model and LCA tool to investigate the role of the biogas sector in the future energy systems in more detail; the presented approach could also be of interest for stakeholders and the actual implementation of proposed measures. A comprehensive analysis of all results is given in the following subsections.

4.1.1. Biowaste from Municipalities

Biowaste from municipalities (household waste) can serve as a valuable source of biogas given the relatively high biogas yield of 100–150 m^3/tFM [7,65,66] An experimental study by the authors of this research on using biodegradable waste from kitchens, canteens and restaurants (similar to the composition of municipal biowaste) showed the biogas yield of such material to be equal to 0.566 Nm^3/kg TS (equal to ca. 110 m^3/tFM), with an average methane share of 60 vol% [39]. Another previous study showed that the biogas potential of municipal biowaste in the relevant region was found to be 116 GWh [22]. In this study, using the data presented in Annex 1 and the methods described, the same potential was found to be 125 GWh, which is ca. 8% higher than in the previous report. The amount of separately collected biowaste (the organic fraction of municipal solid waste) from the municipality of Zagreb amounted to 59,136 t [61]. In this research, the authors found the overall amount of biowaste generation in Zagreb to be ca. 120,000 tones. The gap between the collected and amount of the assessed biowaste corresponded with the fact that not all organic waste generated by Zagreb households is separately collected and considered as biowaste. Namely, for materials like processed (cooked) food, meat left-overs, dairy products, oils and fats, it is not mandatory to separate these as biowaste under the present waste management system [67]. Moreover, based on these numbers, it can be concluded that the capital city of Croatia recovers only 50% of its total biowaste potential. To increase the exploitation of biowaste for biogas, companies that are responsible for biowaste collection should implement additional measures to increase the awareness of citizens regarding biowaste separation. Moreover, it is necessary to apply the proper infrastructure for biowaste collection (e.g., hermetically sealable containers, as in the case of Vienna [68]) in order to obtain the maximum amount of energy from biowaste. In this sense, the assessed potential was found to be 70 GWh of biogas from municipal biowaste in the city of Zagreb, which would be sufficient to run the existing cogeneration plant for the production of electricity [57]. In this sense, the installation of biogas fermenters would be required after closing the landfill. It was found that for the energy recovery of 120,000 tons of municipal biowaste per year, an installation of 13,200 m^3 of fermenter equivalent capacity is required, using an average of 40 days of feedstock retention time [69].

In a previous study, the authors of this research investigated the integration of the P2G concept in the operation of a food-waste-based biogas plant (no. 7) with the goal of producing renewable methane [13]. The same biogas plant was studied in LCA by the current research to assess the environmental impact of replacing electricity generation with the production of renewable gas in an energy system operating with a high share of RES.

4.1.2. Lignocellulosic Biomass from Landscape Management

Lignocellulosic biomass in the form of residue grass showed a relatively high potential for biogas production. For the studied case, the potential was estimated to be ca. 505 GWh. In the same region, the biogas potential from lignocellulosic biomass leftovers (straw, stalk and stover) originating from the agricultural production of oat, barley, triticale, soya-beans, rapeseed, maize and wheat was found to be ca. 2000 GWh [22]. As presented in the results, the given region had a surplus of residue grass potential to be utilised for biogas. However, such values are probably not economically feasible, and collection would be logistically challenging [20].

For example, analysis of the map in Figure 1 shows that, for the production of 903 MWh of biogas using residue grass collected in the south-western area of the case study, the estimated length of the transport route to the nearest biogas plant (no. 7) is more than 100 km. On the other hand, to replace all maize silage with residue grass in biogas plant no. 12, the estimated radius of the available feedstock amounted to ca. 11 km, resulting in a maximum transportation path of ca. 14 km. As presented in Figure 1, the southern and south-eastern areas of the case study showed the highest potential to be considered for biogas production from residue grass. This was because these areas have many water surfaces and watercourses whose banks should be maintained by mowing and collecting the grass.

The latest economic and energetic evaluation of using maize silage (with a purchase price of 54 EUR/t) in anaerobic digestion showed that a transportation distance of up to 18 km is convenient to ensure feasible biogas plant operation in Italy [70]. In the Croatian case, the latest price of maize silage of 34 EUR/t determined that a transportation distance between 24 and 38 km is still feasible for those biogas plants operating under the feed-in tariff [71]. This study revealed that locally available residue material, such as grass, with no actual cost of materials (except harvesting and transport, which are in total estimated at ca. 16 EUR/t [11]), could replace maize silage in the actual biogas production within the same, and even lower, transportation distances. Therefore, biogas plant no.12 was selected to be further evaluated in the LCA by replacing maize silage with residue grass and utilising biogas for biomethane instead for electricity and heat generation.

4.1.3. Biodegradable Streams from the Food-Processing Industry

The total biogas potential of biodegradable waste originating from industry was found to be ca. 138 GWh, of which, ca. 9% was from meat processing, ca. 57% from food manufacturing and ca. 34% from the beverage and drinks industry.

The most common industrial waste appeared to be sludge from wastewater treatment plants, with about 44% of the mass share of the total amount of industrial waste. The methane yield for sludge was found to be between 20.6 ± 5.4 and 69.3 ± 22.3 $m^3(CH_4)/tFM$ (more details are provided in Table S1, Supplementary Material). It is known that sewage sludge and sludge from industrial processes are usually poor in VS content since they have a long retention time, which gives them low biogas potential [72]. In the case of the food-processing industry in Northern Croatia, sludge contributes only ca. 30% to the overall biogas potential. Mixed industry biowaste, which is mainly composed of whey, fruit and vegetable waste, pomace, yeasts, etc., showed a yield of 22.0 ± 5.0 $m^3(CH_4)/tFM$. Since such material is not rich in total solids and volatile solids, the low biogas yield was expected [73]. For coffee pulp and spent brewery grains, the methane yields were found to be 59.2 ± 12.4 and 66.4 ± 23.3 $m^3(CH_4)/tFM$, respectively. Fat, oil and grease waste showed a relatively high range of biogas potential at 138.0 ± 43.8 $m^3(CH_4)/tFM$, while materials like husks, bran and pastry residues had a biogas potential of 138.4 ± 16.0 $m^3(CH_4)/tFM$.

The highest methane yield was found for meat and bone meal (272.6 ± 11.2 $m^3(CH_4)/tFM$). Since such a substrate was studied in previous research by the corresponding author [39], it was determined that in the present biogas production, MBM could not be used as a mono-substrate, owing to the high share of nitrogen, but rather as a co-substrate to municipal biowaste. In this sense, it was found that MBM did not interrupt the stability of the process if it added up to 5% of the TS share, which corresponded to 1% of the total FM share. Therefore, the assessment was made that only 1% of the available MBM could be used in onsite biogas production. On the other hand, in the present case, the MBM was entirely exported from the facility and used as fuel in thermal processes (pyrolysis and combustion) [74].

4.1.4. Replacement of Maize Silage in Biogas Production

To summarise the geospatial availability of the applied method, Table 4 presents the range of the radius from each biogas plant inside which there is an energy potential for the examined feedstocks that is equivalent to that for maize silage.

Table 4. Range of the radius of equivalent energy potential to replace maize silage.

Biogas Plant No.	Radius of Equivalent Energy Potential (km)
1	>20
2	5–10
3	15–20
4	>20
5	5–10
6	5–10
7	0
8	N/A
9	>20
10	15–20
11	>20
12	10–15
13	5–10

The maize silage that is used in biogas plant nos. 1, 4, 9 and 11 would be difficult to fully replace in energy content using alternative feedstocks. Either the local availability of feedstocks is poor (as for biogas plant nos. 1 and 9), or the installed capacity of the biogas plant is high (>2.0 MW_{el} as for nos. 4 and 11), which requires an excessive biogas production rate. Most of the energy potential in the replacement of maize silage comes from municipal biowaste and residue grass, while only a small share of the total potential could be generated by industry streams. The reason for this was that the biogas plants were relatively far from industrial sites (>20 km), which calls into question the feasibility of transporting such feedstock over long distances.

4.1.5. Connecting Existing and New Biogas Plants to the Natural Gas Grid

The length of the natural gas transport system in this case was 1151 km, which corresponded to ca. 43% of the total length of the natural gas transport system (2693 km) [75].

The geospatial analysis of biogas plant positions showed that some were ready to integrate biogas upgrading technology and produce renewable gas since their distances to the natural gas grid were relatively low (less than 2 km). Table 5 shows the measured distance between the biogas plants and the nearest natural gas pipeline.

Table 5. Distances between examined biogas plants and the natural gas grid.

Biogas Plant No.	Distance to Natural Gas Grid (km)
1	7.98
2	3.51
3	14.85
4	9.44
5	1.65
6	4.37
7	1.93
8	3.62
9	3.86
10	1.91
11	4.23
12	1.06
13	14.16

The distance of existing biogas plants to the natural gas grid could serve the operators of biogas plants in assessing the total investment costs of biomethane production. The distance determines the economic feasibility regarding whether biomethane would be injected into the natural gas grid or stored on-site as a compressed gas. Overall, it would determine the further utilisation of biomethane, as well as its price [11]. Biogas plants nos. 5, 7, 10 and 12 (current total installed capacity of 4.0 MW_{el}) displayed the highest potential for connection to the natural gas grid. Based on the current biogas production in those plants, it was estimated that they could inject 19 GWh of biomethane into the grid.

Apart from connecting existing plants to the natural gas grid, the analysis included assessing the position of newly added biogas plants operations using the examined feedstocks (within the 15 km feedstock availability zone) in this region. In addition, new biogas plants were positioned directly on the natural gas transport grid. The position of new biogas plants was determined in accordance with the European Biogas Association, which assumes that future biogas plants will operate to produce renewable gas and contribute to the decarbonisation of the gas sector [76]. Table 6 presents the potential of biomethane production in newly added biogas plants.

Table 6. Biomethane production potential in newly planned biogas plants in this case.

New Biogas Plants	Biomethane Potential (MWh)
A	25,097
B	8211
C	85,228
D	13,013
E	6755
F	33,652
G	19,676

The total potential for biomethane production in the relevant region (after replacing maize silage with the specified feedstocks in existing biogas plants) was found to be ca. 191 GWh. The highest potential for biomethane production was assessed for the new biogas plant C, which would be positioned near the highest availability of industry streams (ca. 50% of the total industry potential found in the case study). Therefore, biogas plant C was evaluated using an LCA as a replacement for natural gas imports with the goal of assessing the environmental impact of using these feedstocks combined with a biomethane pathway.

Adding the potential of 191 GWh for the new plants to 19 GWh of biomethane for existing ones, the region could integrate ca. 210 GWh of biomethane into the grid, which is, however, only ca. 0.7% of the natural gas consumption in Croatia (ca. 30 TWh) [77]. Based on the brief analysis, it can be concluded that the existing capacity of biogas plants in the region, together with the newly added ones, cannot make a significant contribution to the decarbonisation of natural gas.

4.2. Environmental Impact Assessment

Based on the analysis of actual biogas plants, three scenarios, each with two cases, were selected and evaluated using an LCA, as shown in Table 7.

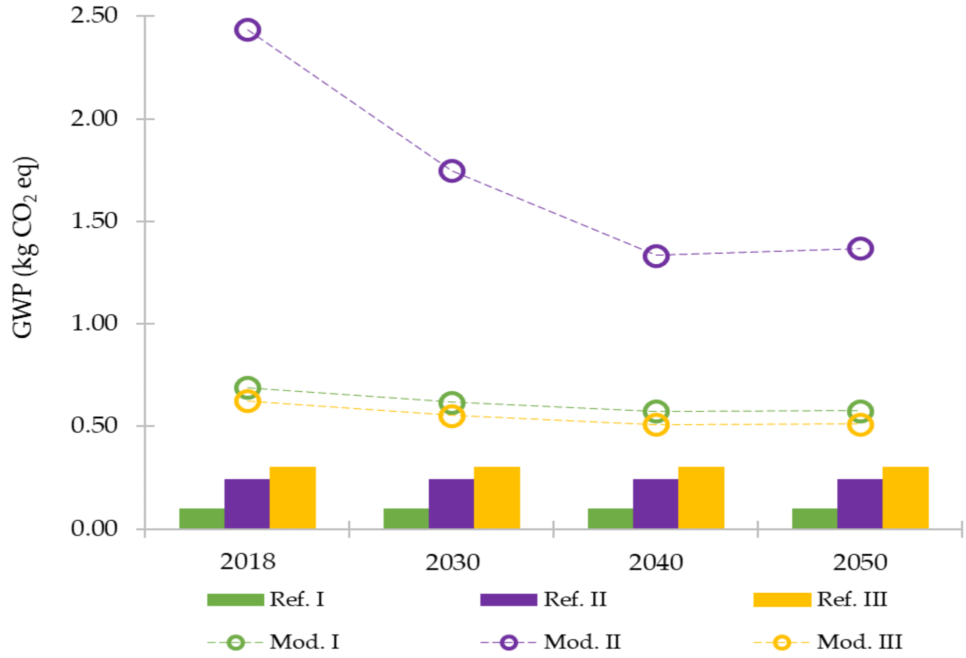
Table 7. Biomethane production potential in newly planned biogas plants in the case study.

Actual Biogas Plant	Scenario	Case	Feedstock	Utilisation
No. 12	I	Referent I Modified I	Animal manure, maize silage Animal manure, residue grass	CHP Biomethane
No. 7	II	Referent II Modified II	Biowaste/food waste Biowaste/food waste	CHP Biomethane + e-methane
New plant C	III	Referent III Modified III	N/A Residue grass, biowaste, industry waste	Natural gas Biomethane

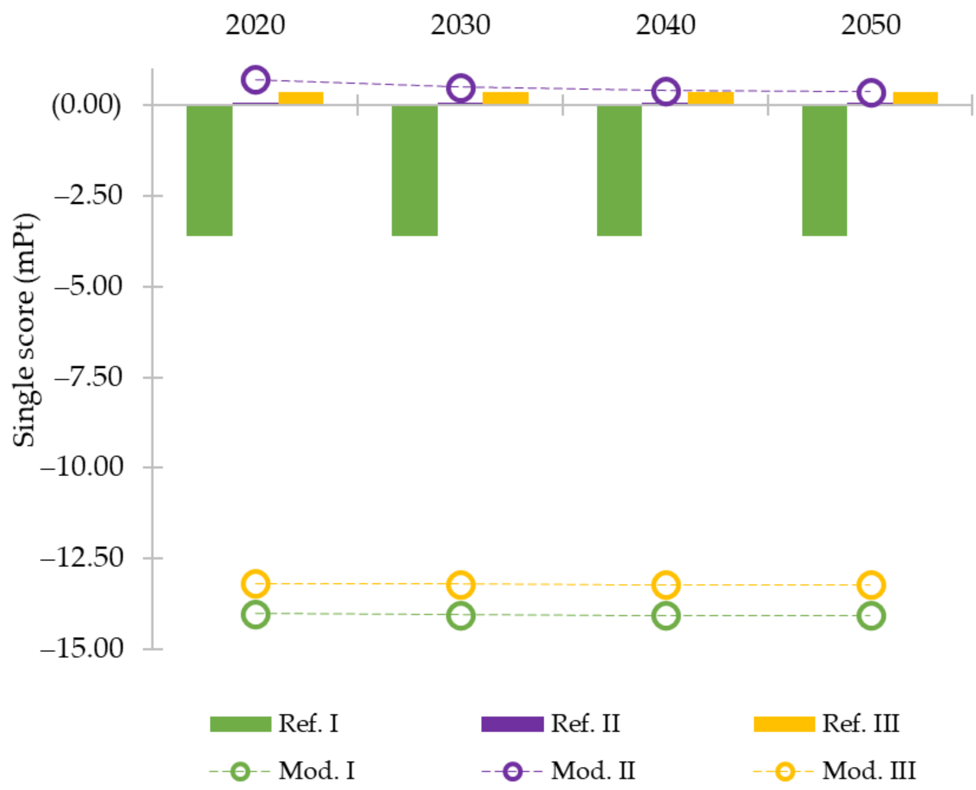
Scenario I presented the feedstock transition from maize silage to residue grass and the switch from operation in cogeneration mode to biogas upgrading using pressure swing adsorption (PSA) technology and biomethane production. Scenario II demonstrated the impact of P2G integration into an existing food-waste-based biogas power plant. Scenario III aimed to investigate the environmental performance of replacing natural gas (in pipelines) using the biomethane produced from waste and residue materials in a newly established biogas plant.

The LCA yielded results that should be explained carefully given the complexity of the analysis and the quality and quantity of the data that were used. In general, alternative feedstocks showed lower methane yield compared to that for maize silage, which led to an increase in the required quantity of feedstock to produce the same amount of energy as when using maize silage. Digestate, as another product of anaerobic digestion, was considered for application as a fertiliser in all the scenarios and cases being examined. It should be noted that the benefits of using alternative feedstocks for biogas production instead of their decomposition on the field (landfilling), which results in avoiding GHG emissions, was not considered in this study, nor were GHG emissions related to land-use changes considered.

The overall results of the environmental performance analysis of the given scenarios are shown in Figure 3: (a) GWP and (b) single score, for the projected electricity mix.



(**a**)



(**b**)

Figure 3. Lifecycle impact assessment results for (**a**) GWP and (**b**) single score, for the functional unit of 1 m^3 of produced and utilised CH_4.

The comparison of the LCA results for the GWP category showed that in all scenarios, the applied measures generated higher CO_2eq emissions. The results for the GWP values for the referent cases ranged between 0.10 and 0.30 kg CO_2eq, while those for the modified cases were between 0.51 and 2.4 kg CO_2eq. Similar results and relations between the

GWP values (for the functional unit of 1 m^3 of biogas) were found for the comparison of biogas upgrading (1.09–1.27 kg CO_2eq) and biogas cogeneration (0.57 kg CO_2eq) [34]. Most emissions in the GWP category were carbon dioxide from fossil fuel combustion in the machinery and vehicles used for feedstock collection and transportation to biogas plants [31]. The referent cases were not impacted by the projected increase in RES share in the electricity mix, while in the modified cases, the GWP values decreased by ca. 17% in scenario I, ca. 44% in scenario II and ca. 18% in scenario III in 2050 compared to the referent year. These results were expected since all three modified cases used the electricity from the grid to produce renewable gas. In greater detail, the authors estimated that ca. 30% of the electricity demand for P2G integration in scenario II came from the grid [13]. The combination of grid assistance and installation of an electrolyser and a methanation unit [78] resulted in GWP values that were significantly higher than expected, which made scenario II barely acceptable if the GWP category was the only one analysed.

For the evaluation of overall environmental impact (not just GHG emissions), aggregation of the differing impacts of the category results should be done through normalisation and weighting the impact categories and then summing the results in the form of a single score. In this sense, the overall results showed that the measures applied to both biogas production and utilisation yielded significant environmental benefits over the existing operation of biogas plants, especially in scenarios I and III. The utilisation of alternative feedstocks for biomethane resulted in a process that was ca. 36 times more environmentally improved than natural gas and ca. 4 times better in terms of environmental performance than the production of heat and electricity in cogeneration mode. The results of this research can be related to a previous study by the authors in which the integration of a biogas upgrading unit into an existing biogas power plant was analysed to investigate a switch from maize silage to residue grass with the aim of mutually producing biomethane and electricity at peak power prices [11]. For that case, the thresholds for environmental benefits were determined to be −3.6 mPt and −14.0 mPt, for 1 m^3 of produced and utilised CH_4, respectively. The LCA of electricity production in biogas cogeneration plants in the case of the German electricity mix when using 1 tonne of feedstock as a functional unit gave a single score result of −1.4 Pt for maize silage and −4.6 Pt for food residues [79]. Even though the results of this study were significantly lower (owing to another functional unit having been selected), it is interesting that the single score results for scenario II were higher than zero, which indicates that the environmental burdens were greater than the generated benefits. This can be explained by the fact that the biowaste (in the form of food waste) considered for biogas production has zero emissions up to the point of its creation (defined by the RED II), while all other emissions and impacts on the environment came as a result of collecting the biowaste and transporting it to the site. Since a comparison with biowaste landfilling was not conducted in this study, the emissions that were avoided were not considered, which would have created additional environmental benefits. Regarding the integration of the P2G concept, it was revealed that the penetration of renewable electricity into the energy mix exerted a higher impact on the reduction of GHG emissions than on the overall environmental performance of the system.

In its present form, the studied concept lacked the integration of the social component in the analysis of the transition of the biogas sector and its role in future energy systems [80]. Therefore, the next step on this topic should include elaborating the achieved results to all stakeholders engaged in the existing sector, as well as to those that will come up in the future. To assess such a dynamic complexity in the future operation of biogas plants, causal loops were identified as a powerful tool that will open up additional perspectives on how to achieve a more sustainable and just transition of the biogas sector [81].

5. Study Limitations

The methods and materials presented here were applied to a case study of Northern Croatia. Therefore, the results of the study should be cautiously disseminated, bearing in mind the regionality factors and the case-specific nature of the data.

Analysis of the methane yield from feedstocks presented in Supplementary Material was done using previous studies and available literature sources. Based on that data, the range of values was set up and the average value used in biogas potential assessment calculations.

The injection of renewable gas was evaluated by considering the connection of biogas plants to the natural gas transport grid. The position and features of the distribution grid for this case were not considered.

6. Conclusions

The link between the use of maize silage and electricity generation under subsidy models in biogas plants is becoming weaker as the new sustainability requirements are raised. The holistic and comprehensive analysis carried out in this study showed the opportunities and challenges that existing biogas plants would face if alternative measures for both biogas production and its utilisation were implemented to contribute to EU climate and energy targets.

The geospatial availability of alternative feedstocks was shown to have a potential in Northern Croatia that was high enough to replace all maize silage in current biogas production, which is ca. 212 GWh. Moreover, after the expiration of support schemes and guaranteed prices for electricity, the analysis showed that most of the examined biogas plants were well positioned for the injection of renewable gas into the natural gas grid (<2 km of distance). Others would have to consider the installation of a storage system if applying the upgraded technology. The total potential of biomethane from newly planned biogas plants was found to be ca. 191 GWh, out of which, the plants located nearby to the source of biodegradable industry waste would produce ca. 58% of its quantity.

The environmental impact analysis of actual biogas plants showed that an integrated approach to both biogas production and utilisation created synergistic effects in terms of reduced environmental burdens, which directly verified the hypothesis of the study. Scenarios that included feedstock transition and production of renewable gas in the form of biomethane showed reduced environmental burdens by 4 and 36 times compared to baseline scenarios (current operation), respectively. The analysis also showed that the integration of the P2G concept is recognised as a complex process from both the economic and the environmental point of view.

The operation of biogas plants based on sustainable feedstocks in future energy systems with a high share of RES showed that the role of the biogas sector in the energy transition should receive greater emphasis since it generates multiple positive effects for energy and the environment. There is still considerable scope for the improvement of existing processes, applying other biological feedstocks and integrating biogas technologies further in all energy sectors.

Future work in the studied area will be pointed towards engaging important stakeholders of the existing and future biogas sector to the presented concept with the aim to cluster all key variables from technical, financial and social aspects. This would include setting up a dialogue and information exchange with biogas plant owners; feedstock producers; farmers; industry plants; waste management companies; natural gas grid operators; regulators; and local, regional and national policy and decision makers. In this sense, causal loops were recognised as an attractive tool for managing the complex relationships between stakeholders and maintaining biogas technologies as an important factor in energy and environmental transitions.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en14175374/s1, Table S1: Biogas yield of feedstocks from food processing industry.

Author Contributions: R.B., as the main author, was responsible for conceptualising the research, conducting the investigation, collecting data, setting up the methodology, mapping biomass sources by QGIS, visualising the results and writing the original draft. G.S. and D.L. contributed to the research by performing the LCA. T.P. and L.Č. were responsible for supervising the research progress and administrating the project. N.D. was in charge of providing resources and fundraising. All authors read and agreed to the published version of the manuscript.

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