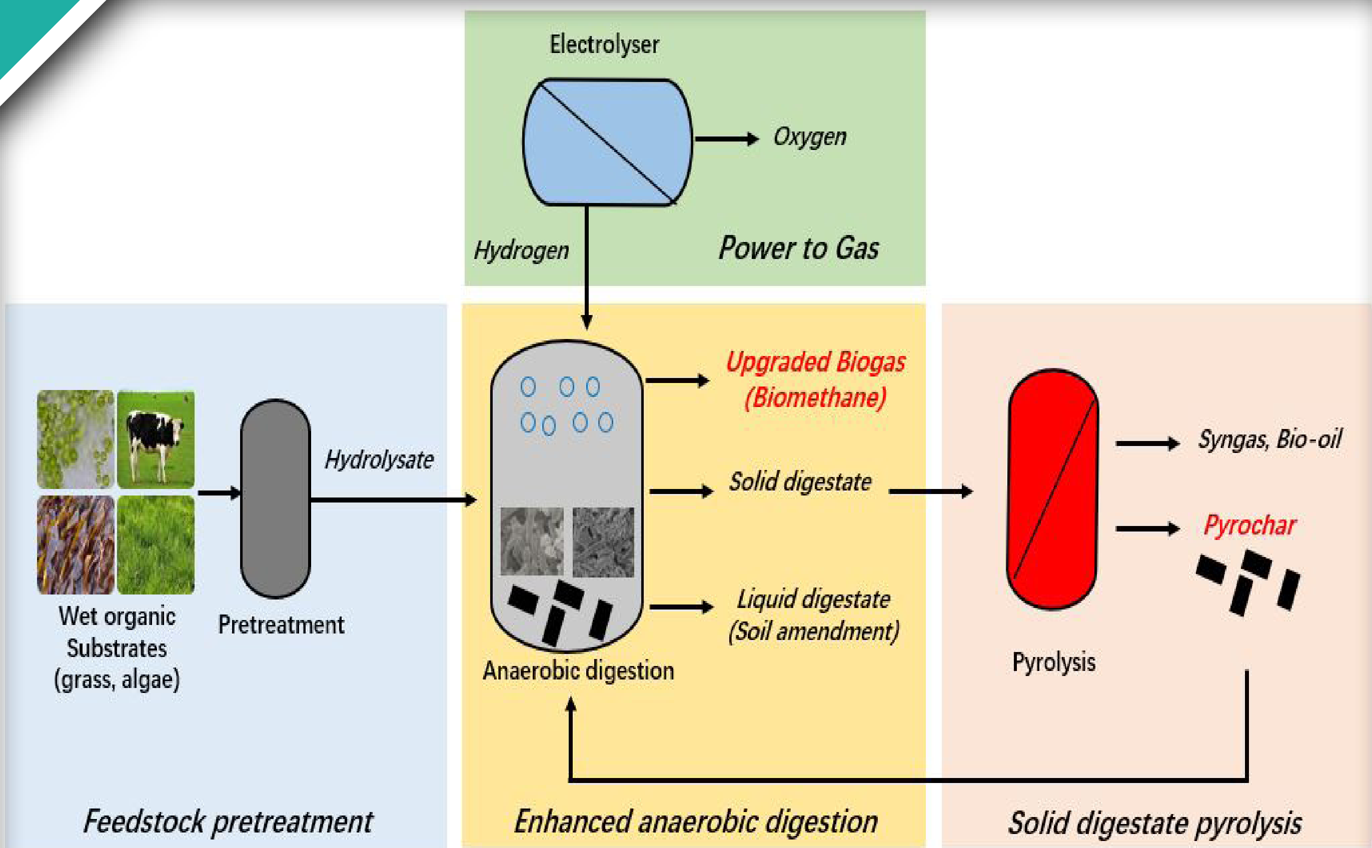
Report No. 431

epa Research

Production of Advanced Gaseous Biomethane Transport Fuel in an Integrated Circular Bioenergy System

Authors: Xihui Kang, Richen Lin, Benteng Wu, Alan Dobson and Jerry D. Murphy



Advanced biofuel production in a circular bioenergy system

www.epa.ie

Rialtas na hÉireann
Government of Ireland

Environmental Protection Agency

The EPA is responsible for protecting and improving the environment as a valuable asset for the people of Ireland. We are committed to protecting people and the environment from the harmful effects of radiation and pollution.

The work of the EPA can be divided into three main areas:

Regulation: Implementing regulation and environmental compliance systems to deliver good environmental outcomes and target those who don't comply.

Knowledge: Providing high quality, targeted and timely environmental data, information and assessment to inform decision making.

Advocacy: Working with others to advocate for a clean, productive and well protected environment and for sustainable environmental practices.

Our Responsibilities Include:

Licensing

> Large-scale industrial, waste and petrol storage activities;
> Urban waste water discharges;
> The contained use and controlled release of Genetically Modified Organisms;
> Sources of ionising radiation;
> Greenhouse gas emissions from industry and aviation through the EU Emissions Trading Scheme.

National Environmental Enforcement

> Audit and inspection of EPA licensed facilities;
> Drive the implementation of best practice in regulated activities and facilities;
> Oversee local authority responsibilities for environmental protection;
> Regulate the quality of public drinking water and enforce urban waste water discharge authorisations;
> Assess and report on public and private drinking water quality;
> Coordinate a network of public service organisations to support action against environmental crime;
> Prosecute those who flout environmental law and damage the environment.

Waste Management and Chemicals in the Environment

> Implement and enforce waste regulations including national enforcement issues;
> Prepare and publish national waste statistics and the National Hazardous Waste Management Plan;
> Develop and implement the National Waste Prevention Programme;
> Implement and report on legislation on the control of chemicals in the environment.

Water Management

> Engage with national and regional governance and operational structures to implement the Water Framework Directive;
> Monitor, assess and report on the quality of rivers, lakes, transitional and coastal waters, bathing waters and groundwaters, and measurement of water levels and river flows.

Climate Science & Climate Change

> Publish Ireland's greenhouse gas emission inventories and projections;
> Provide the Secretariat to the Climate Change Advisory Council and support to the National Dialogue on Climate Action;
> Support National, EU and UN Climate Science and Policy development activities.

Environmental Monitoring & Assessment

> Design and implement national environmental monitoring systems: technology, data management, analysis and forecasting;
> Produce the State of Ireland's Environment and Indicator Reports;
> Monitor air quality and implement the EU Clean Air for Europe Directive, the Convention on Long Range Transboundary Air Pollution, and the National Emissions Ceiling Directive;
> Oversee the implementation of the Environmental Noise Directive;
> Assess the impact of proposed plans and programmes on the Irish environment.

Environmental Research and Development

> Coordinate and fund national environmental research activity to identify pressures, inform policy and provide solutions;
> Collaborate with national and EU environmental research activity.

Radiological Protection

> Monitoring radiation levels and assess public exposure to ionising radiation and electromagnetic fields;
> Assist in developing national plans for emergencies arising from nuclear accidents;
> Monitor developments abroad relating to nuclear installations and radiological safety;
> Provide, or oversee the provision of, specialist radiation protection services.

Guidance, Awareness Raising, and Accessible Information

> Provide independent evidence-based reporting, advice and guidance to Government, industry and the public on environmental and radiological protection topics;
> Promote the link between health and wellbeing, the economy and a clean environment;
> Promote environmental awareness including supporting behaviours for resource efficiency and climate transition;
> Promote radon testing in homes and workplaces and encourage remediation where necessary.

Partnership and Networking

> Work with international and national agencies, regional and local authorities, non-governmental organisations, representative bodies and government departments to deliver environmental and radiological protection, research coordination and science-based decision making.

Management and Structure of the EPA

The EPA is managed by a full time Board, consisting of a Director General and five Directors. The work is carried out across five Offices:

1. Office of Environmental Sustainability
2. Office of Environmental Enforcement
3. Office of Evidence and Assessment
4. Office of Radiation Protection and Environmental Monitoring
5. Office of Communications and Corporate Services

The EPA is assisted by advisory committees who meet regularly to discuss issues of concern and provide advice to the Board.

Production of Advanced Gaseous Biomethane Transport Fuel in an Integrated Circular Bioenergy System

Authors: Xihui Kang, Richen Lin, Benteng Wu, Alan Dobson and Jerry D. Murphy

Identifying pressures

Ireland's Climate Action Plan 2021 (CAP21) aims to reduce greenhouse gas (GHG) emissions by 51% by 2030 and to achieve net-zero emissions by 2050. As part of this plan, the emissions reduction goal for transport is 42–50% by 2030. Transport is by far the largest source of energy-related CO_2 emissions in Ireland, accounting for over 40% of such emissions in 2019; this sector is the least decarbonised in Ireland. A newly launched EPA report suggests that the overall GHG emissions reduction in Ireland would be only 28% (against a target of 51%) by 2030, even if all measures from CAP21 were implemented. This highlights the need for a rapid transition from a linear fossil fuel-based economy to a bio-based economy that treats waste as a commodity, reduces GHG emissions, sequesters carbon and produces biofuels, biofertilisers and bioproducts. The aim of the AGB project was to develop an integrated system that produces biomethane using biomass (such as grass, silage or food waste) to fuel the transport sector cleanly and support Ireland in achieving key emissions targets.

Informing policy

To meet Ireland's CAP21 emissions targets, we propose:

1. **A circular bioeconomy**: this would involve developing a bioenergy and carbon capture and use (BECCU) system.
2. **Renewable energy and transport:** using animal manure, grass silage and renewable hydrogen from renewable electricity in Ireland, the proposed system may produce as much as 1 billion m^3 of renewable biomethane by 2035, reducing emissions by 2.6 Mt CO_2-eq per year when replacing diesel consumption in transport. This equates to over 25% of the transport-related CO_2 emissions in 2020.
3. **Sustainable agriculture:** the modelled system offers a reduced carbon footprint of farming and a more sustainable agriculture system, with improved soil quality and increased crop yields.

Developing solutions

The AGB project proposes a cascading circular system in which anaerobic digestion is the key platform technology enabling biomethane production. With the integration of biomass pyrolysis, the system can deliver advanced biofuels for the transport sector or produce high-value biochemicals, biofertilisers and biochar while also treating a variety of organic wastes. Given recent technological advancements such as increased efficiency in biochar production and the expected reduction in the cost of the hydrogen needed to run this biomass conversion system, the system has become an increasingly viable option for biomethane production. Such circular systems are widely recognised as having the potential to provide promising economic and environmentally sound solutions to achieving the ambitious targets set in CAP21.

Production of Advanced Gaseous Biomethane Transport Fuel in an Integrated Circular Bioenergy System

(2018-RE-MS-13)

EPA Research Evidence Synthesis Report

A copy of the end-of-project Technical Report is available on request from the EPA

Prepared for the Environmental Protection Agency

by

Environmental Research Institute, MaREI Centre, University College Cork

Authors:

Xihui Kang, Richen Lin, Benteng Wu, Alan Dobson and Jerry D. Murphy

ENVIRONMENTAL PROTECTION AGENCY
An Ghníomhaireacht um Chaomhnú Comhshaoil
PO Box 3000, Johnstown Castle, Co. Wexford, Ireland

Telephone: +353 53 916 0600 Fax: +353 53 916 0699
Email: info@epa.ie Website: www.epa.ie

ACKNOWLEDGEMENTS

This report is published as part of the EPA Research Programme 2021–2030. The EPA Research Programme is a Government of Ireland initiative funded by the Department of the Environment, Climate and Communications. It is administered by the Environmental Protection Agency, which has the statutory function of co-ordinating and promoting environmental research.

The authors would like to acknowledge the members of the project steering committee, namely Mark Sweeney (Enterprise Ireland), Bernhard Drosg (Bioenergy2020+ GmbH), Patrick Barrett (Department of Agriculture, Food and the Marine (DAFM)), Dorothy Stewart (EPA), Maurice Harnett (Department of Transport) and Anne Mason (Research Project Manager on behalf of the EPA).

This report is based on research carried out/data from May 2019 to July 2022. More recent data may have become available since the research was completed.

The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

EPA RESEARCH PROGRAMME 2021–2030

Published by the Environmental Protection Agency, Ireland

ISBN: 978-1-80009-099-6 April 2023

Price: Free Online version

Project Partners

Xihui Kang
Environmental Research Institute
MaREI (SFI Research Centre for Energy, Climate and Marine)
University College Cork
Cork
Ireland
Tel.: +353 83 435 1105
Email: XKang@ucc.ie

Richen Lin
Environmental Research Institute
MaREI (SFI Research Centre for Energy, Climate and Marine)
University College Cork
Cork
Ireland
Tel.: +353 21 490 1948
Email: richen.lin@ucc.ie

Benteng Wu
Environmental Research Institute
MaREI (SFI Research Centre for Energy, Climate and Marine)
University College Cork
Cork
Ireland
Tel.: +353 83 415 1524
Email: benteng.wu@ucc.ie

Alan Dobson
School of Microbiology
SSPC-SFI Research Centre for Pharmaceuticals
University College Cork
Cork
Ireland
Tel.: +353 21 490 3000
Email: A.Dobson@ucc.ie

Jerry D. Murphy
Environmental Research Institute
MaREI (SFI Research Centre for Energy, Climate and Marine)
University College Cork
Cork
Ireland
Tel.: +353 86 055 4493
Email: jerry.murphy@ucc.ie

Contents

List of Figures

List of Tables and Boxes

Tables

Boxes

Executive Summary

This report proposes an anaerobic digestion (AD)-centred integrated circular bioeconomy system for the production of advanced fuels (biomethane or biomethanol), medium-chain fatty acids (such as caproic acid), biofertiliser and biochar (with potential application for negative emission technology).

AD is a viable technology for producing biogas while treating wastes and residues and in so doing improving the environment. Animal manure is an excellent renewable feedstock that would help to avoid fugitive methane emissions from the storage of livestock manures. In an Irish context, grass silage can add greatly to the resources if the system is optimised for sustainability. The system can be broadened to integrate power to gas with AD in a system known as biomethanation. Such a system would utilise electrolysers to produce hydrogen from wind power and react the produced hydrogen with the carbon dioxide in the biogas to produce more biomethane via the Sabatier reaction ($4H_2 + CO_2 = CH_4 + 2H_2O$). This offers an innovative means of upgrading biogas to biomethane (with methane content higher than 97%) while facilitating intermittent renewable electricity (such as from wind turbines), reducing levels of curtailment and producing advanced renewable gaseous transport fuels.

AD generates not only biogas, but also liquid effluent and solid digestate, which can be used as a biofertiliser for crops, reducing emissions through the displacement of fossil fuel-based fertiliser. To reduce carbon emissions further, a broader system that employs elements of negative emission technology may be employed; this includes pyrolysis of solid digestate to produce biochar. Biochar may be used as a soil amendment to increase soil organic content, increase crop yields and increase photosynthesis, and in doing so increase carbon sequestration to soil. Prior to land application, biochar can be circulated back to both the biogas digester and the biomethanation reactor to boost the conversion of CO_2 to methane. As a carbonaceous material, biochar can be used in microbial fermentation processes (such as AD for biogas production and anaerobic fermentation for medium-chain fatty acid production). The addition of carbonaceous material such as biochar may, under certain conditions, enhance the biological production and the rate of production of biogas or medium-chain fatty acids.

The research documented in this work demonstrates that because of high electrical conductivity and the abundance of surface functional groups, carbonaceous material, such as graphene (which is very expensive) and biochar produced via pyrolysis (which is considerably cheaper), when added into the AD or fermentation systems, can (1) alleviate acidic stress (such as rapid pH drop due to the fast hydrolysis of easily degradable components) to the methane-producing microbes; (2) stabilise the biological biogas upgrading process due to intermittent hydrogen supply associated with the intermittent nature of renewable electricity from wind turbines and solar PV; and (3) enhance medium-chain fatty acid production and production rate.

Environmental analysis showed that the net greenhouse gas emissions of the pyrolysis-incorporated systems were of the order of 22 g CO_2-eq./MJ biomethane and 45 g CO_2-eq./MJ biomethanol. This suggests that biomethane is sustainable but biomethanol is not when applying the sustainability criteria for renewable transport fuels in the recast Renewable Energy Directive (RED-II). For biomethane production, including for pyrolysis and biomethanation, the minimum selling price was modelled as 15.6c/kWh under the base scenario (low capacity and a hydrogen cost price of 10.2c/kWh); this is equivalent to a marginal abatement cost of –€58/t CO_2-eq. If natural gas is priced at 10c/kWh (typical price since the beginning of the war in Ukraine), the minimum selling price could be reduced to 4.8c/kWh biomethane with the assumptions of a larger capacity and a hydrogen cost price of 3c/kWh (very optimistic future scenario); this is equivalent to a marginal abatement cost of –€111/t CO_2-eq. When methanol was sold at 7c/kWh (global weighted average value), the abatement cost (with a cost of H_2 of €1/kg) was €136.5/t CO_2-eq.; this is higher than the carbon credit of €33.5/t CO_2-eq.

To summarise, the integration of AD, biomethanation and biochar production to produce biomethane via pyrolysis could be economically and environmentally compelling, given the increased production efficiency induced by the addition of biochar and the expected decrease in the cost of hydrogen with the development of an extensive offshore renewable electricity industry in Ireland.

1 Introduction

1.1 Project Background

The Climate Action Plan of 2021 in Ireland set a target for greenhouse gas (GHG) emission reduction of 51% by 2030 (with 2018 as the base year); it further targeted net-zero emissions no later than 2050. Within this target, the emissions reduction for transport was set in the range 42–50% by 2030. Transport is by far the largest source of energy-related CO_2 emissions in Ireland and was responsible for over 40% of energy-related CO_2 emissions in 2019. In Ireland, transport is less decarbonised than the electricity and heat sector. A report recently published (2022) by the Environmental Protection Agency (EPA) suggests that the overall GHG emissions reduction by 2030 in Ireland will be only 28% (as opposed to the 51% requirement), even if all the measures set out in the Climate Action Plan of 2021 (EPA, 2022) are met. The EPA report emphasised the following five policy objectives: (1) sustainable agriculture, (2) circular economy and bioeconomy, (3) renewable energy, (4) networks for nature and (5) marine and coastal impacts of climate change. This highlights the significance of the transition from a linear fossil-based economy to a bio-based economy that treats wastes, reduces GHG emissions, sequesters carbon, and produces biofuels, biofertilisers and bioproducts.

Integrating anaerobic digestion (AD) with other technologies is seen as a promising and applicable approach to producing chemicals, materials, transport fuels, and electricity and heat from various types of biomass, such as grass silage, animal slurries, seaweed and other organic wastes (Wellinger *et al*., 2013; Wall *et al*., 2017; Fagerström *et al*., 2018). The main biofuel targeted by the AD-centred system is biogas, which is an energy-rich gas mixture that typically contains 60% methane, 40% carbon dioxide and other trace gases such as H_2S, H_2 and N_2. The production of biogas is at a high technology readiness level for a range of agricultural and municipal feedstocks, but the biological process can suffer process instability due to the accumulation of organic acids from the fast hydrolysis of easily degradable feedstocks such as food waste and distillery wastewater.

Biogas can be used for various applications, such as transport fuels after upgrading, and heat and electricity generation (Long and Murphy, 2019). The upgraded biogas, also named biomethane (methane content over 96%), is completely interchangeable with natural gas (of huge issue since the war in Ukraine) and can contribute to a significant reduction in GHG emissions in hard-to-abate sectors such as the heavy transport and heat industries, which are heavily dependent on fossil fuels and present limited opportunities for electrification (Gray *et al*., 2021, 2022). To maximise biogas for a wide range of applications, the CO_2 in the biogas should be removed (and preferably captured for reuse in an economic and sustainable way), thereby achieving a natural gas standard. Biological methanation (or biomethanation) is a multi-functional process that: can provide storage of variable renewable electricity, reducing levels of curtailment or constraint; captures CO_2 and allows for its reuse; and is a sustainable and cost-efficient biogas upgrading process that can replace tradition physiochemical upgrading technologies (Rusmanis *et al*., 2019; Voelklein *et al*., 2019). During this process, CO_2 in the biogas is biologically captured and utilised to produce neat methane streams by reacting with hydrogen ($4H_2 + CO_2 = CH_4 + 2H_2O$) ideally sourced from renewable electricity (such as wind or solar energy) (Voelklein *et al*., 2019; Wu *et al*., 2021a).

From an economic perspective, methane is of relatively low value; traditionally, energy as a product is cheap. This can make AD an economically unattractive technology without the implementation of government subsidies or enforcement of policies to support the technology. Fortunately, in addition to the production of gaseous biofuels, AD, as a versatile platform technology, can be integrated into a biorefinery system to produce other fermentation products (from residues or waste products) with higher monetary values such as medium-chain fatty acids (MCFAs) when it is integrated with other technologies (Wu *et al*., 2019; Wang *et al*., 2020). MCFAs, such as *n*-caproic acid ($CH_3(CH_2)_4COOH$) and *n*-caprylic acid ($CH_3(CH_2)_6COOH$), are important platform chemicals with a broad range of industrial and agricultural applications, including but not limited to chemicals in antimicrobials, additives in animal feed and precursors in advanced drop-in biofuels (Angenent *et al*., 2016; de Leeuw *et al*., 2019). Furthermore, the solid digestate, a by-product of the AD process, consists of a large amount of undegraded organic components (such as lignin) and valuable agricultural nutrients (such as nitrogen, potassium and phosphorus) (Seadi *et al*., 2008). It can be used as a biofertiliser or valorised into valuable products, such as pyrochar (also termed biochar) and biocrude oil, through a negative emission system utilising pyrolysis technology (Lin *et al*., 2021a; Yang *et al*., 2021). These biochars are ideally suited to soil amendment to increase its organic carbon contents; pyrochar derived from solid digestate pyrolysis can be used as an additive to enhance the production of biogas or MCFAs (Deng *et al*., 2020; Liu *et al*., 2020).

Anaerobic digestion is not only an individual stand-alone technology but the hub of the bio-based circular economy system that combines and integrates a range of technologies; the bioeconomy system enables strong synergies and complementarities between systems and can add financial and environmental benefits beyond biofuel production (Lin *et al*., 2021a,b). This report examined an AD-centred, circular, cascading bio-based system with the aim of producing biofuels and chemicals in a sustainable biorefinery scheme. The incorporation of CO_2 biomethanation, microbial fermentation and pyrolysis technologies in a bioeconomy framework was evaluated, including from economic and environmental perspectives. The concept, with AD as the core element of the integrated circular cascading bio-based system, is shown in Figure 1.1.

1.2 Objectives

The objectives of the report are to:

- investigate the application of the nanomaterial graphene and the more cost-effective pyrochar in the digestion of organic wastes in order to overcome biological stress (such as acidic shock) and to model microbial electron transfer in the AD process;
- evaluate the application of graphene and pyrochar in an *ex situ* biomethanation system, with a particular focus on their effect on biomethanation efficiency and evolution of the microbial community structure under a biological stress such as that from the intermittent supply of hydrogen associated with an intermittent supply of variable renewable electricity;
- assess the application of pyrochar in a biorefinery process to optimise the MCFA yield under differing conditions (with ranges of dosage of pyrochar addition) to gain insights into the mechanism behind improved performance with pyrochar addition;
- perform a comparative technoeconomic and environmental analysis of these circular cascading bioeconomy systems and in doing so construct a marginal abatement cost curve to visualise the GHG emissions abatement potential of the biofuels proposed.

Box 1.1. Terminology

Anaerobic digestion

Anaerobic digestion (AD) is a process in which bacteria break down organic matter (or biomass, such as animal manure, wastewater biosolids and food wastes that contain sugars, fats and proteins) and convert this biomass into methane and carbon dioxide (the two main components of biogas) in the absence of oxygen. AD for biogas production takes place in a sealed gas-tight vessel called a reactor. Complex microbial communities incubated in these reactors break down (or digest) the feedstock and produce the resultant biogas and digestate (the solid and liquid material end-products of the AD process), which is discharged from the digester. With proper treatment, both the solid and the liquid portions of digestate can be used in many beneficial applications, such as animal bedding (segregated solids), nutrient-rich biofertiliser (in both liquid and solid forms), a foundation material for bio-based products (such as bioplastics) and organic-rich compost (solids). The solid digestate contains undegradable carbon-rich material, which can also be used for biochar production through a process named pyrolysis.

Pyrolysis

Pyrolysis is an oxygen-starved thermal process whereby organic material undergoes thermal degradation into smaller, volatile molecules. Pyrolysis of biomass is usually conducted at or above 500°C, providing enough heat to deconstruct organic material. Pyrolysis of biomass produces three products: bio-oil (in liquid state), biochar (in solid state) and syngas (in gaseous state). The proportions of these products depend on several factors, including the composition of the feedstock and the process parameters. Processes that use slower heating rates are called slow pyrolysis, and biochar is usually the major product of such processes. The pyrolysis process can be self-sustained, as the combustion of the syngas and a portion of bio-oil or biochar can provide all the necessary energy to drive the reaction.

The liquid product can be refined to a drop-in hydrocarbon biofuel, an oxygenated fuel additive or a petrochemical replacement. The biochar produced can be used on farms as an excellent soil amendment that can enhance soil organic content and sequester carbon through enhanced photosynthesis and increased yield of crops or plants. Biochar production from pyrolysis is seen as a negative-emission technology, as the carbon-rich biochar can remain in the ground for centuries. As a carbon-rich material, biochar can also be used as an alternative conductive material to graphene to accelerate the degradation efficiency of organic material during microbial fermentation by enhancing the communication (electron transfer) through different bacteria.

The average price of pyrochar/biochar is of the order of €3/kg which is significantly less than the typical price of graphene, which, in the form of nanosheets, has been reported to be €664/kg (Deng *et al.*, 2020).

Extracellular electron transfer

The degradation of organic material during AD involves mutual effort from different microorganisms, namely bacteria and archaea. Conventional AD typically employs indirect electron transfer by reduced molecules such as molecular hydrogen or formate. The efficiency of this process is limited by hydrogen partial pressure. Direct interspecies electron transfer (DIET) induced by conductive carbon materials (such as carbon nanotube, biochar, carbon cloth and graphene) is more efficient and can enhance the digestion efficiency of organic material. DIET involves electron transfer directly between microbes (such as by extracellular polymeric substances contacting each other, pili or conductive material).

Box 1.1. Continued

Ex situ biomethanation

Ex situ biomethanation is an emerging biological technology used to upgrade biogas through the conversion of CO_2 into biomethane with (preferably) renewable hydrogen derived from renewable electricity. This is a "Power-to-X" technology that produces an electro-fuel. During the process, CO_2 in the biogas is converted into biomethane through reactions with hydrogen ($4H_2 + CO_2 = CH_4 + 2H_2O$). The biogas is upgraded into a high-methane-content gas with an increase in methane output of about 70%. The biomethane produced is an alternative to natural gas for energy and transport fuel and may be used to produce other chemicals.

Biological chain elongation

Biological chain elongation is an anaerobic open-culture biotechnological process in which microbes convert short-chain fatty acids (SCFAs) (organic acids containing two to four carbon atoms, such as acetic acid and propionic acid) and an electron donor (such as ethanol, lactic acid and hydrogen) into more valuable MCFAs (organic acids containing 6–12 carbon atoms) such as caproic acid. MCFAs have multiple applications including as antimicrobials, additives in animal feed and precursors in advanced drop-in biofuels.

Examples of chemicals in stoichiometry in this report

Acetic acid: CH_3COOH

Ethanol: CH_3CH_2OH

Butyric acid (four carbon atoms): $CH_3(CH_2)_2COOH$, or in the form of $CH_3(CH_2)_2COO^-$ for the calculation of Gibbs free energy

Caproic acid (six carbon atoms): $CH_3(CH_2)_4COOH$, or in the form of $CH_3(CH_2)_4COO^-$ for the calculation of Gibbs free energy

The conversion factor of concentration (*C*, mg/L) of chemicals to chemical oxygen demand (COD) (mg/L)

Acetic acid: $COD_A = C_A \times 1.07$

Ethanol: $COD_E = C_E \times 2.09$

Butyric acid (four carbon atoms): $COD_B = C_B \times 1.82$

Caproic acid (six carbon atoms): $COD_C = C_C \times 2.21$

Energy values used in the report

$1\ Nm^3\ CH_4 = 10\ kWh$

$1\ kg\ H_2 = 33.33\ kWh$

1 kg methanol = 6.01 kWh

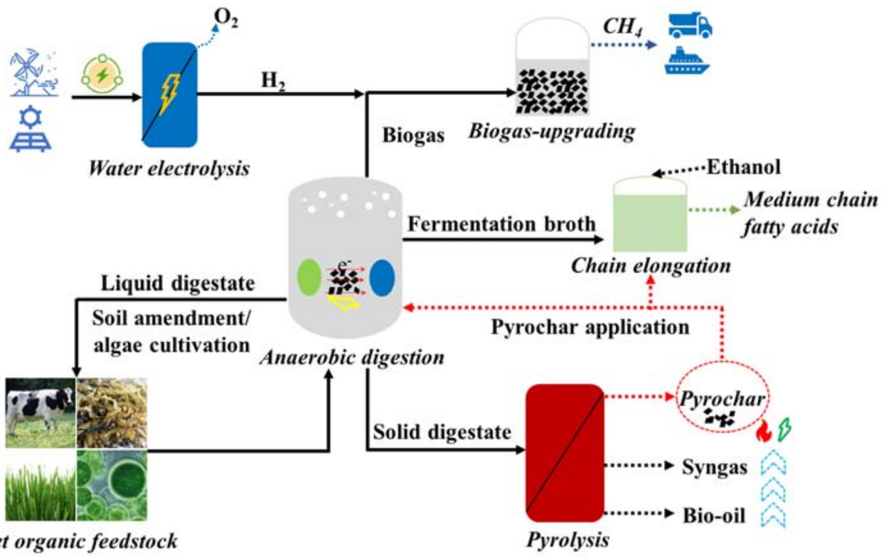


Figure 1.1. Biofuel production in an integrated circular cascading bio-based system, including for AD, pyrolysis and power-to-gas technologies. Reprinted from Wu, B., Lin, R., O'Shea, R., Deng, C., Rajendran, K. and Murphy, J.D., 2021b. Production of advanced fuels through integration of biological, thermo-chemical and power to gas technologies in a circular cascading bio-based system. *Renewable and Sustainable Energy Reviews* 135: 110371 (https://doi.org/10.1016/j.rser.2020.110371). © 2020 The Authors.

2 Research Overview

2.1 Foundations and Implications of Extracellular Electron Transfer

2.1.1 Introduction and objectives

The transport sector is one of the largest and fastest-increasing energy consumers. In addition, it is most challenging to produce climate-friendly fuels for heavy-duty vehicles such as haulage trucks, ferries and planes, which are not readily suitable for electrification. The European Union recast Renewable Energy Directive (RED-II) (2018/2001) requires the contribution of renewable energy in the transport sector to be at least 14% by 2030 and that of advanced biofuels to reach 3.5% (Bhagia *et al*., 2016). Advanced biofuels are fuels that do not require arable land for cultivation or use feedstocks that could be used for food. Typical feedstocks for advanced biofuels include animal manure, algae, crop residues and municipal solid waste (Bhagia *et al*., 2016). AD is an effective bioconversion technology that produces biomethane from wet organic materials (Voelklein *et al*., 2016; Lin *et al*., 2019). The integration of AD with a sustainable waste management system can offer GHG-negative transport fuels when considered on a whole life cycle basis (Liebetrau *et al*., 2017).

The conversion of grain to ethanol (for alcoholic beverages) is a significant industry in many countries (Dereli *et al*., 2014; Eriksson *et al*., 2016). For instance, whiskey production in Ireland has increased by 131% on a volume basis in the past 10 years (Jackson *et al*., 2020). However, in a conventional ethanol production process, up to 20 L of stillage can be generated for every litre of ethanol, producing a considerable quantity of organic by-products (Sharma *et al*., 2013). After solid/liquid separation of stillage, the liquid fraction (thin stillage) generally contains high concentrations of carbohydrates, proteins and other fermentation by-products; stillage displays a high chemical oxygen demand (COD) and a low pH (3.5–4.5) (Dereli *et al*., 2014). Unlike the solid fraction, a significant energy input is required to produce wet distillers solubles (a source of animal fodders) through the evaporation of water from stillage, due to its high water content (Murphy and Power, 2008). Considering its high biodegradability, thin stillage can be used to produce biogas, which can, in turn, be used to satisfy some of the thermal and electrical energy demands of a distillery; this improves the sustainability of alcohol production and reduces reliance on fossil-based energy (Jackson *et al*., 2020). A further use of the produced biogas is to upgrade it to biomethane for use as a sustainable climate-friendly transport fuel. Typically, transport fuels have higher exergy than heating, and higher revenue can be obtained by substituting biogas for transport fuels than for heating.

However, in practice, the digestion of readily biodegradable feedstock is subject to instability, reduced biomethane production and sometimes even failure. These issues may be attributed to the particularly lower pH within AD systems resulting from the accumulation of volatile fatty acids (VFAs) and the inhibition of subsequent methanogenesis (Wang *et al*., 2017). The inhibition of AD performance by VFAs is due to their acidity rather than direct toxicity (Kwietniewska and Tys, 2014). VFAs are not themselves toxic. Generally, they are produced and consumed as food and nutrients by microbes in a well-operated digester. Their inhibitory effects are indirect as they lower the pH to an undesirable level and subsequently inhibit methanogenesis. In this context, some strategies have been adopted to enhance the stability of AD systems (Sharma *et al*., 2013; Yang *et al*., 2015). A suitable pH within digesters may be maintained through the addition of alkaline chemicals (Yang *et al*., 2015). However, once these chemicals have been consumed, acidification may occur again. Serious events that result in the acidic suppression of microorganisms in AD necessitate long periods of operation for recovery (Zhao *et al*., 2017). To maintain the stability of AD systems treating readily degradable feedstock, especially after experiencing episodes of external stress, more sustainable and effective methods should be considered.

Recently, carbonaceous conductive materials such as pyrochar, carbon cloth and graphene have been reported as a means to enhance system stability and improve biomethane production efficiency (Lin *et al*., 2018a; Shao *et al*., 2019; Indren *et al*., 2020).

Carbon cloth could enhance AD stability by mitigating acidic inhibition (pH as low as 5.0) and accelerate the recovery of the methanogenesis function due to the promoted direct interspecies electron transfer (DIET) between microbes (Zhao *et al.*, 2017). Similar positive effects were observed when using pyrochar and granular activated carbon to alleviate ammonia (NH_4^+-N) inhibition (Lü *et al.*, 2016; Florentino *et al.*, 2019). Carbon-based conductive materials have been shown to enhance the degradation of VFAs such as butyrate and propionate, in turn leading to high methanogenesis efficiency (Barua *et al.*, 2018). In a typical syntrophic methanogenesis process, the reaction occurs close to thermodynamic equilibrium; as a result, a minor disturbance in intermediates or substrates can lead to a shift in the metabolic pathway (Leng *et al.*, 2018). Instead of hydrogen or formate being used as the electron carrier, non-biological conductive materials are able to serve as electron conduits to transfer electrons between bacteria and archaea without the requirement of synthesising electrically conductive pili (e-pili) or nanowires, which typically are the biological electron conduits that facilitate DIET (Barua and Dhar, 2017). This unique cell-to-cell electron exchange metabolism offers advantages over methane production from specific VFAs (such as propionic acid and butyric acid), which are susceptible to interference from the traditional electron carrier H_2. The degradation and methanogenesis processes for model substrates of carbohydrates, proteins and alcohols (glucose, glycine and ethanol, respectively) have been shown to be accelerated and stabilised by the establishment of DIET (Lü *et al.*, 2016; Lin *et al.*, 2018a,b). Given the high content of carbohydrates, proteins and alcohols in thin stillage, it is postulated that conductive materials can stimulate DIET in digestion of thin stillage. It is therefore hypothesised that stimulating DIET using conductive materials can alleviate the acidification stress and accumulation of VFAs, thus facilitating recovery from severe acidic shock.

The objective of this study was to investigate the application of nanomaterial graphene and the more cost-effective pyrochar (both of which are carbonaceous materials) in digestion to resist an acidic shock (pH 5.5). The mechanics of system recovery were evaluated in terms of process stability (as measured by VFA accumulation and pH change), biomethane production and responses of the microbial community. The thermodynamic advantage of DIET was exemplified using propionate (a typical VFA observed in AD) as a model substrate.

2.1.2 *Theoretical analysis of interspecies direct electron transfer and indirect hydrogen transfer*

Propionate, a typical intermediate for carbon and electron flow in the digestion of organic material, was used to investigate the syntrophic interactions in energy-limited methanogenic biosystems (Zamanzadeh *et al.*, 2013; Cruz Viggi *et al.*, 2014) and to compare mediated interspecies electron transfer (MIET) with DIET. The complete degradation of propionate to CH_4 and CO_2 needs the well-established connections between syntrophic acetogens and methanogens; these relationships determine the efficiency of the electron transfer. Figure 2.1 shows that, overall, propionate oxidation to acetate is thermodynamically more favourable via DIET than via hydrogen transfer in MIET.

In the MIET pathway, acetogenic bacteria convert propionate into acetate and H_2 (Table 2.1). Under

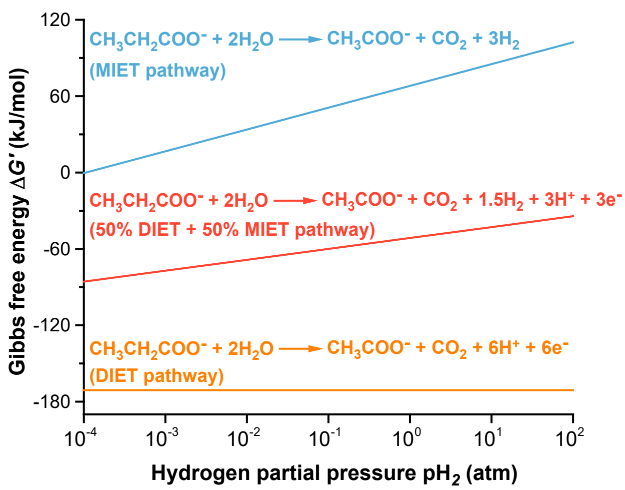


Figure 2.1. Thermodynamic comparison of propionate oxidation via MIET and DIET (pH 7, *T* = 298.15 K, [propionate] = 9.4 mM, [acetate] = 5.1 mM, pCO_2 = 0.44 atm). Reprinted from Wu, B., Lin, R., Kang, X., Deng, C., Xia, A., Dobson, A.D.W. and Murphy, J.D., 2020. Graphene addition to digestion of thin stillage can alleviate acidic shock and improve biomethane production. *ACS Sustainable Chemistry & Engineering* 8(35): 13248–13260. Copyright © 2020, American Chemical Society.

Table 2.1. Reactions and changes in Gibbs free energy values of propionate conversion to methane in different pathways

Process	Reaction	$\Delta G^{\circ\prime}$ (kJ/mol)[a]
Electron-generating reaction	MIET: $CH_3CH_2COO^- + 2H_2O \rightarrow CH_3COO^- + CO_2 + 3H_2$	+71.61
	DIET: $CH_3CH_2COO^- + 2H_2O \rightarrow CH_3COO^- + CO_2 + 6H^+ + 6e^-$	–167.37
Electron-accepting reaction	MIET: $3H_2 + 0.75CO_2 \rightarrow 0.75CH_4 + 1.5H_2O$	–98.02
	DIET: $6H^+ + 6e^- + 0.75CO_2 \rightarrow 0.75CH_4 + 1.5H_2O$	+140.96
Acetate conversion reaction	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	–35.91
Overall	$CH_3CH_2COO^- + H^+ + 0.5H_2O \rightarrow 1.75CH_4 + 1.25CO_2$	–62.32

[a]Values are computed under the conditions of $T = 298.15$ K, pH 7, pressure = 1 atm and [reactants] = 1 M based on tabulated data from Madigan *et al.* (2014).

the conditions specified (namely pH 7, $T = 298.15$ K, [propionate] = 9.4 mM, [acetate] = 5.1 mM, $pCO_2 = 0.44$ atm; values are collected from experimental data), the reaction is thermodynamically favourable only when the concentration of H_2 is below 1.0×10^{-4} atm, at which point the Gibbs free energy change equals 0. This makes propionate oxidation to acetate more vulnerable, as an increase in hydrogen partial pressure would result in the increase in the Gibbs free energy change to a level that makes the reaction unfavourable.

In the DIET pathway, the change in hydrogen partial pressure does not affect the Gibbs free energy, as it does not involve the exchange of diffusible molecules among syntrophic partners. If both MIET and DIET pathways take place, the Gibbs free energy change depends on the proportion of electrons transferred through MIET or DIET. As an example, if only half of the electrons produced from propionate oxidation to acetate are transferred through DIET at a hydrogen partial pressure of 1.0×10^{-4} atm, approximately 85 kJ/mol of energy advantage can be expected compared with that of complete MIET (Figure 2.1). It should be noted that the overall change in Gibbs free energy values of propionate conversion to methane for both the DIET and MIET pathways is theoretically the same.

The computed maximum electron carrier flux during propionate oxidation to methane demonstrated the advantage of DIET over MIET (hydrogen diffusion), indicating that the theoretical difference between them was significant with a 10^6 factor (Cruz Viggi *et al.*, 2014). It is worth mentioning that the calculations were based on numerous assumptions, several of which cannot be said to be 100% precise. For example, neither the heat loss nor the energy demand for the growth and maintenance of microorganisms was considered during computing. However, these numbers are small and, as such, the significant difference between two fluxes may still be said to be a distinct kinetic merit of DIET. Given the advantages of electron carrier flux and thermodynamics, DIET is preferable to MIET in terms of facilitating propionate oxidation among syntrophic partners in AD.

2.1.3 Performance of biomethane production from thin stillage with conductive materials amendment

The effects of conductive material addition on the performance of biomethane yield and production rate from thin stillage are illustrated in Figure 2.2. During the acidic shock phase, biomethane production increased slightly on day 1 and remained unchanged on day 2, indicating that the methanogenesis process was completely inhibited by acidic shock. In the recovery phase, the biomethane yield of the control group reached 225 mL/g COD after 18 days of digestion. With the introduction of graphene (1.0 g/L), biomethane yield increased to 250 mL/g COD, an increase of 11.0% compared with the control. However, here the addition of pyrochar did not lead to any significant effects on biomethane yield ($p > 0.05$) at either low (Pyrochar) or high (hPyrochar) doses (1 g/L and 10 g/L, respectively), generating between 219 and 230 mL/g COD, respectively. Luo *et al.* (2015) applied pyrochar with different particle sizes to evaluate the effect on AD facing various acidic stress levels. The results indicated that, compared with the

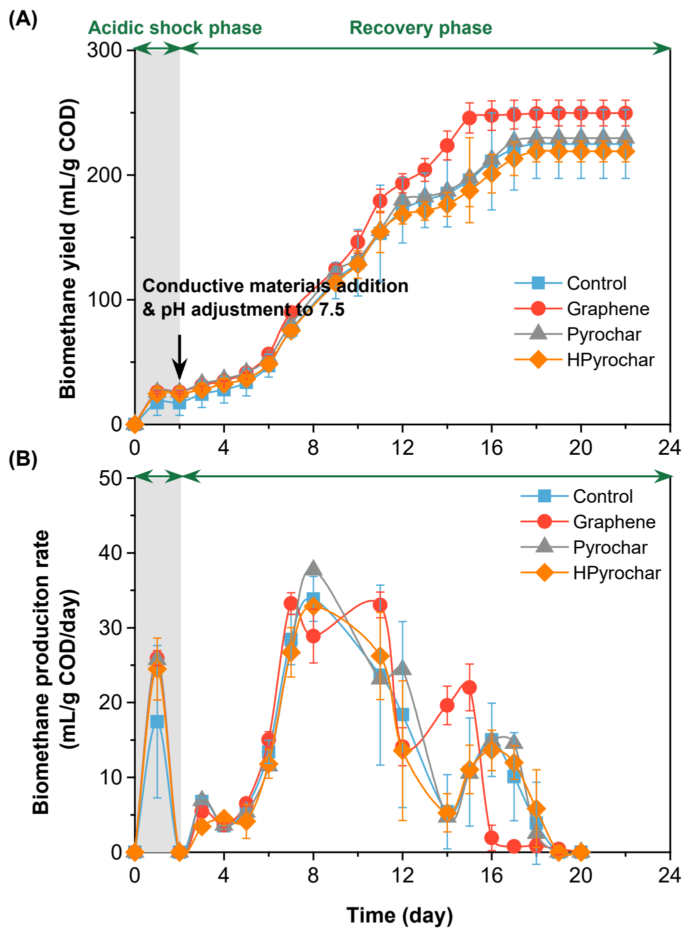


Figure 2.2. Effects of conductive material amendment on (A) biomethane yield and (B) production rate during AD of thin stillage after acidic shock. HPyrochar, high-dose (10 g/L) pyrochar. Reprinted from Wu, B., Lin, R., Kang, X., Deng, C., Xia, A., Dobson, A.D.W. and Murphy, J.D., 2020. Graphene addition to digestion of thin stillage can alleviate acidic shock and improve biomethane production. *ACS Sustainable Chemistry & Engineering* 8(35): 13248–13260. Copyright © 2020, American Chemical Society.

control, pyrochar adoption shortened the lag phase for methanation in all cases, but it also had negative impacts as the total biomethane yield was reduced by between 2.5% and 17.5% (Luo *et al*., 2015). Similarly, Wang *et al*. (2018) demonstrated that 2–15 g/L pyrochar could reduce the lag time in the treatment of a mixture of dewatered activated sludge and food waste, but there was no increase in biomethane yield. These findings are consistent with the results in this study, which showed that 1.0 g/L and 10 g/L pyrochar shortened the lag time by 18.1% and 12.2% (Table 2.2), respectively, while biomethane yield was not obviously increased.

Without the introduction of conductive materials, the biomethane production rate peaked on day 8 at 33.85 mL/g COD/day, as shown in Figure 2.2B. Among all cases, the highest peak production rate was obtained with a pyrochar introduction of 1.0 g/L, an increase of 11.5% compared with the control, reaching 37.73 mL/g COD/day on day 8. Despite the greatest promotion effects on the cumulative biomethane yield, graphene led to the highest peak production rate of only 33.23 mL/g COD/day on day 7, with no significant difference from the control ($p > 0.05$). However, during the latter recovery phase, the biomethane production rate with graphene addition still maintained a relatively higher level compared with other groups. For instance, the corresponding value of the graphene group was 22.03 mL/g COD/day on day 15, which was significantly higher than that of other groups ($p < 0.05$), with a level of approximately 10 mL/g COD/day.

Table 2.2 presents the simulated parameters of biomethane production using the modified Gompertz model. The potential biomethane yield of the graphene

Table 2.2. Estimated parameters describing biomethane production using the modified Gompertz equation

Group	$P_{measured}$ (mL/g COD)	P (mL/g COD)	R_m (mL/g COD/day)	λ (day)	T_m (day)	Adjusted R^2
Control	224.92	239.82	20.49	3.37	7.69	0.9916
Graphene	249.73	267.32	24.15	3.36	7.44	0.9878
Pyrochar	229.54	247.7	19.4	2.76	7.46	0.9911
HPyrochar	218.92	234.58	18.9	2.96	7.54	0.9908

Control, no conductive materials added; graphene, 1 g/L; HPyrochar, 10 g/L; P, maximum methane potential; $P_{measured}$, experimental methane yield; pyrochar, 1 g pyrochar/L; R_m, maximum methane production rate; T_m, peak production time; λ, lag phase time.

Reprinted from Wu, B., Lin, R., Kang, X., Deng, C., Xia, A., Dobson, A.D.W. and Murphy, J.D., 2020. Graphene addition to digestion of thin stillage can alleviate acidic shock and improve biomethane production *ACS Sustainable Chemistry & Engineering* 8(35), 13248–13260. Copyright © 2020, American Chemical Society.

group increased by 11.5%, while the peak biomethane production rate enhanced by 17.9% compared with the control. Comparatively, pyrochar addition shortened the lag time as described earlier but did not improve the total biomethane production. These results revealed that the amendment of graphene could resist acidic shock and thus stabilise and enhance the AD performance of thin stillage, but pyrochar had no evident effect in terms of recovering biomethane yield.

The proposed reason for the positive effects on biomethane production in the graphene group is that DIET was stimulated in the presence of highly conductive graphene, which possibly acted as an electron conduit between syntrophs and methanogens. In general, the electrical conductivity of pyrochar is in the range of several to 10 siemens per centimetre (S/cm) (Yu *et al*., 2015; Cheng *et al*., 2018), while the conductivity of graphene (generally tens to hundreds of S/cm) is much higher (Wu *et al*., 2009; Du *et al*., 2011). The significantly higher conductivity of graphene might be more beneficial to establishing a strong syntrophic relationship and to triggering efficient DIET between electron donating and accepting microbes, thereby enhancing cumulative biomethane production. DIET was reported to proceed via three possible pathways, namely redox mediators, e-pili adhered with cytochromes, and conductive materials (Shao *et al*., 2019; Yin and Wu, 2019). Redox mediators and e-pili are also called electron shuttles. The properties of surface structure, surface chemistry and redox mediators of pyrochar have been highlighted in other studies (Masebinu *et al*., 2019). Yu *et al*. (2015) and Wang *et al*. (2019) proved that pyrochar played a critical role in alleviating external inhibition caused by refractory compounds due to its surface redox-active moieties that might favour DIET. However, in this study, pyrochar serving as an electron shuttle mechanism might not be sufficient to trigger efficient DIET because the unique role of electron conduits cannot be replaced by electron shuttles (Liu *et al*., 2012). These findings lead to a plausible conclusion that the promoted biomethane production resulted from the electron conduit function transferring electrons between microbes rather than the electron shuttle. Meanwhile, surface functional groups of pyrochar might have a positive effect on the recovery of AD systems with acidic shock in the initial period, which shortened the lag time, but, due to its low conductivity, pyrochar failed to generate an efficient DIET process subsequently.

2.1.4 Conclusion

This experimental study demonstrated that the addition of graphene could help stabilise AD of thin stillage after acidic shock, presumably as a result of DIET. Graphene amendment (1.0 g/L) enhanced the biomethane yield by 11.0% compared with the control and accelerated the degradation of propionic acid. Thermodynamic calculations indicated that if 50% of electrons produced from propionate oxidation are transferred through DIET, approximately 85 kJ/mol of an energy advantage can be expected compared with that of indirect hydrogen transfer. By comparison, pyrochar addition (1.0 g/L and 10 g/L) shortened lag time but failed to enhance biomethane yield.

For the detailed methodology and results of this section, please refer to the published open-access journal paper at https://doi.org/10.1021/acssuschemeng.0c03484.

2.2 Biological Biogas Upgrading for Advanced Fuel Production

2.2.1 Introduction and objectives

Biological methanation can be classified into two categories or configurations: *in situ* within the AD or *ex situ* in a separate reactor with isolated hydrogenotrophic methanogens (Guneratnam *et al*., 2017; Fu *et al*., 2021). *In situ* biomethanation can lead to the accumulation of VFAs due to the increased hydrogen partial pressure associated with a reduction in the favourability of acetogenesis and elevated pH resulting from bicarbonate consumption; this is not an issue in *ex situ* systems, as the process takes place in a vessel that is separate from the original AD process (Bassani *et al*., 2015). Several studies have shown that *ex situ* biomethanation can accept higher hydrogen loading rates and obtain higher gas conversion rates than the *in situ* strategy (Rachbauer *et al*., 2016; Kougias *et al*., 2017; Voelklein *et al*., 2019).

A power-to-gas system connects electricity and gas infrastructure and ideally can optimise the overall existing energy infrastructure. McDonagh *et al*. (2019) investigated the relationship between the electricity market and the production of electro-fuels; the work highlighted that for economic production the electrolyser could not depend on just curtailed electricity but needed to operate ideally in excess of 6000 hours per year. Intermittency in hydrogen availability was shown to be due to seasonal and demand variations (Strübing *et al*., 2018; Logroño *et al*., 2021). This adds a technical challenge to the optimal operation of a biomethanation system. For example, increasing deterioration of the biomethanation process was found in restart periods in which there were increasing repetitions of intermittent gas injection; Strübing *et al*. (2018) showed that standby periods of 2 days reduced the methane production rate by 9.9%. Similar observations were also reported by Logroño *et al*. (2021), who found that a 7-day standby period resulted in a significant reduction in the restart of methane production rates, which decreased by between 5.6% and 18.8% depending on the inoculum. Effective strategies are therefore needed to minimise the adverse impact on biomethanation performance from intermittent gas supply.

In recent studies, the amendment of carbonaceous materials such as pyrochar and activated carbon has been suggested as an approach to enhance the stability and performance of AD (Deng *et al*., 2020; B. Wu *et al*., 2020). Benefits from the application of carbon-based nanocatalysts such as graphene have also been highlighted (Nizami and Rehan, 2018); their unique properties (including morphological variety, chemical stability and large surface area) are suggested to facilitate the biomethane yield or production rate during AD (Dehhaghi *et al*., 2019). Nanomaterial graphene addition was shown to improve the stability of digesters and accelerate the recovery of the methanogenesis function after it experienced external stress (for example acidic shock), possibly due to accelerated DIET (Wu *et al*., 2021b) as described in the previous section. Similar mitigatory effects were also found when pyrochar was added to alleviate the stress of ammonia and acid inhibition during AD; the immobilisation effect of pyrochar on functional microbes was highlighted (Lü *et al*., 2016). To the best of the authors' knowledge, the addition of carbonaceous materials in biological methanation systems has not been studied, with the exception of work by Yang *et al*. (2020), who used pyrochar to enhance the methane production rate during *ex situ* biogas upgrading. The large specific surface area and functional groups of pyrochar were assumed to be the main contributions to the improved methane production rate of over 70% (Yang *et al*., 2020). However, the gap in the state of the art is the potential role of carbonaceous materials in *ex situ* biomethanation systems facing flexible operation due to intermittent gas injection.

This work assesses the potential role of carbonaceous materials in *ex situ* biomethanation systems operating with a variation in gas supply, and it has the following objectives:

- evaluate the application of carbonaceous materials (nanomaterial graphene and the more cost-effective pyrochar) in an *ex situ* biomethanation system, with a particular focus on their effect on biomethanation efficiency and evolution of microbial community with an intermittent gas supply;
- undertake microbial community profiles analysis for different operational periods, including steady-state and intermittent gas injection periods;

- provide evidence of the optimal potential functional microbes for *ex situ* biomethanation biogas upgrading.

2.2.2 *Performance of* ex situ *biomethanation systems with intermittent gas supply*

The biomethane yield and output gas contents at the end of each cycle are illustrated in Figure 2.3. For the control group without the addition of graphene or pyrochar, the inoculum exhibited an excellent capacity to convert H_2 and CO_2 into CH_4 in the initial phase, resulting in a biomethane production of 186 mL in cycle 1 (Figure 2.3A); this is 82.9% of the theoretical yield (224 mL). With continuous gas injection, the biomethane yield increased slightly, to 85.4% and 89.7% of the theoretical yield in cycles 2 and 3, respectively. This could be explained by the microbial acclimation effect, which has also been observed in other studies (Kougias *et al*., 2017; Logroño *et al*., 2021). The first intermittent gas injection was enforced in cycle 4, with a break in operation for 2 days. However, it did not have a significant influence on biomethane production. The biomethane yield in cycle 4 decreased to only 84.0% of the theoretical yield, compared with 89.7% in cycle 3. After the operation of one cycle, biomethane production in cycle 5 recovered to 197 mL, 88.1% of the theoretical yield. However, a clear reduction in upgrading performance was observed after the second break in operation for 1 day before cycle 6, leading to a biomethane production of 147 mL, 65.8% of the theoretical yield.

The proportion of methane in the output gas (Figure 2.3B) increased from 88.6% in cycle 1 to 95.1% in cycle 5, with CO_2 the dominant residual. In cycle 6, after a 1-day break in operation, the proportion of methane significantly decreased, to 58.4%, with H_2 the main residual (Figure 2.3B); this is further evidence that the main cause of gas conversion deterioration is repetitive intermittent gas injection. Similar findings were reported by Strübing *et al*. (2018), who revealed that adverse effects on restart performance were negligible during the first intermittent gas injection (with a standby period of 2 days), whereas subsequent breaks resulted in the hydrogen content

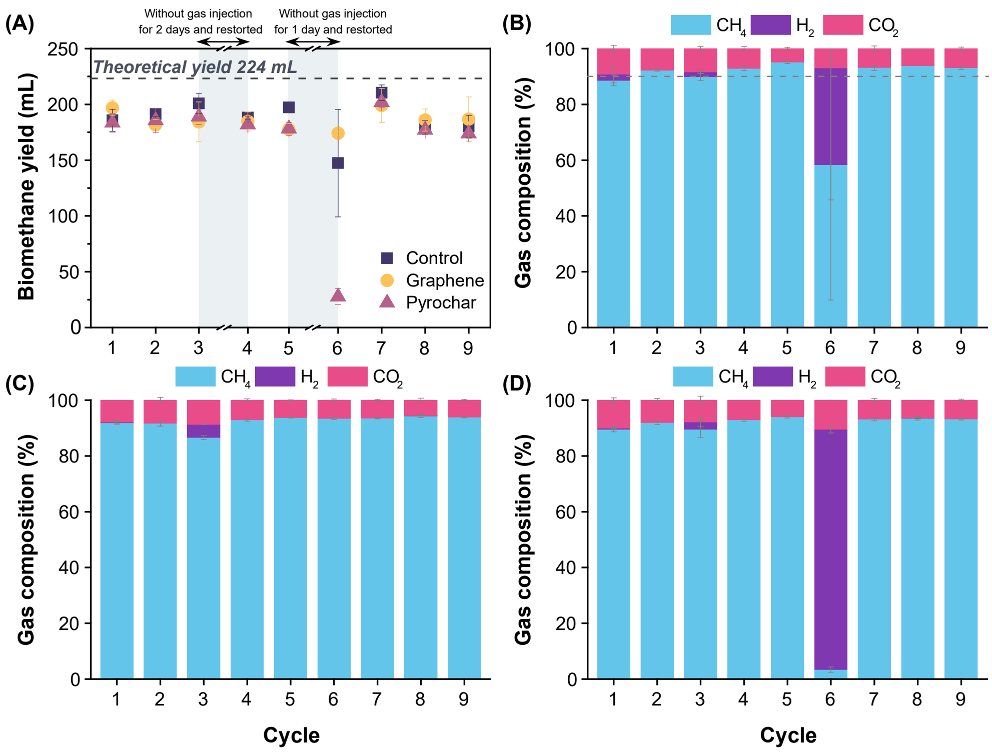


Figure 2.3. The biomethane yield (A) and methane, hydrogen and carbon dioxide contents of the control group (B), graphene group (C) and pyrochar group (D) at the end of each cycle. Error bars represent the standard deviation. Reprinted from Wu, B., Lin, R., Kang, X., Deng, C., Dobson, A.D.W. and Murphy, J.D., 2021a. Improved robustness of ex-situ biological methanation for electro-fuel production through the addition of graphene. *Renewable and Sustainable Energy Reviews* 152152: 111690. © 2021 The Authors.

of the output gas increasing up to 60%. Tsapekos *et al*. (2021) also reported a serious deterioration of upgrading performance after a longer standby period of 25 days, with a decrease in the output methane content from 90% to approximately 25%; full recovery of methanogenic activity was achieved after 6 days' continuous operation. The inhibitory effect did not last long in this study since the biomethane yield quickly reached 94.0% of the theoretical production in cycle 7 while the methane concentration reached 93.2%; this might be attributed to the shorter standby period than in other reported studies (Strübing *et al*., 2018; Tsapekos *et al*., 2021). In cycles 8 and 9, the biomethane yield and content were relatively constant, approximating 180 mL biomethane yield and 93% CH_4 in the output gas, respectively; this indicates that the biomethanation upgrading process returned to stability. The results suggested that repetitive intermittent gas injection could affect the robustness of the biomethanation system, but a recovery can be expected when continuous gas supply is restored.

With the addition of carbonaceous materials, the graphene and pyrochar group did not show a significant difference ($p > 0.05$) compared with the control in the initial four cycles (including the first intermittent gas injection of 2 days' duration), during which the average biomethane production for the control, graphene and pyrochar groups was 192 ± 7 mL, 187 ± 7 mL and 185 ± 3 mL, respectively, while the corresponding average methane content was 90.9% ± 2.0%, 90.8% ± 2.8% and 91.0% ± 1.7%, respectively. However, the second break in gas injection of a 1-day period (cycle 6) led to definite effects on the biomethanation system. For the graphene group, 174 mL of biomethane yield was obtained, 18.2% higher than that of the control. The output gas was dominated with methane accounting for 93.4% of total gases, 60.0% higher than that of the control. Surprisingly, this was not matched by the pyrochar group, in which, by contrast, suppressive effects on the restart performance occurred after the shock of repetitive intermittent gas injection phases, resulting in a significant decline in biomethane yield from 178 mL to 28 mL ($p < 0.05$). This was accompanied by a significant reduction in methane content, from 94.0% to 3.4%, with hydrogen as the main residual, highlighting that the activity of hydrogenotrophic methanogens was significantly inhibited. We postulate that this may result from the low dosage (1 g/L) and surface area (162 m^2/g) of pyrochar.

2.2.3 Insights into the stabilisation effects of carbonaceous material on ex situ biomethanation

Graphene addition was shown to be capable of stabilising the biomethanation process after experiencing intermittent gas supply when compared with the control group. Since acetate was the dominant VFA throughout the trials, thermodynamic calculations were conducted to evaluate the Gibbs free energy values of acetate conversion to methane in different pathways (Table 2.3). Compared with the MIET pathway, the DIET pathway, whereby acetate is oxidised to electrons and protons, is thermodynamically more favourable since an energy benefit of 318.64 kJ/mol exists. The generated electrons can be directly utilised by some methanogens to produce methane (Zhao *et al*., 2020). However, this DIET strategy needs the

Table 2.3. Reactions and changes in Gibbs free energy ($\Delta G^{\circ\prime}$) values of acetate conversion to methane in different pathways

Process	Reaction	$\Delta G^{\circ\prime}$ (kJ/mol)[a]
Acetate oxidation	MIET: $CH_3COO^- + H^+ + 2H_2O \rightarrow 4H_2 + 2CO_2$	+94.78
	DIET: $CH_3COO^- + H^+ + 2H_2O \rightarrow 8H^+ + 8e^- + 2CO_2$	–223.86
Methanogenesis	MIET: $4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	–130.69
	DIET: $8H^+ + 8e^- + CO_2 \rightarrow CH_4 + 2H_2O$	+187.95
Overall	$CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$	–35.91

[a]Values are calculated under the conditions of $T = 298.15$ K, pH 7, pressure = 1 atm, and [reactants] = 1 M based on tabulated data from Madigan *et al*. (2014).

Reprinted from Wu, B., Lin, R., Kang, X., Deng, C., Dobson, A.D.W. and Murphy, J.D., 2021a. Improved robustness of ex-situ biological methanation for electro-fuel production through the addition of graphene. *Renewable and Sustainable Energy Reviews* 152: 111690. © 2021 The Authors.

well-established connections between syntrophic acetogens and methanogens (Wu *et al*., 2021b). Graphene has been proven to act as an electron conduit to connect microbial populations and thereby enhance the DIET mechanism in AD systems due to its intrinsic properties of high electrical conductivity and enhanced biocompatibility (Wu *et al*., 2009; Lin *et al*., 2018b). The critical role of electrical conductivity in triggering DIET has been widely emphasised in other studies (Zhao *et al*., 2020; Tan *et al*., 2021). Compared with the control group, graphene amendment significantly enhanced the electrical conductivity of the biomethanation system. The electrical conductivity of the graphene group was 36.83 μS/cm, which is 265% higher than that of the control group. Members of the genus *Methanothermobacter* have been reported to be actively involved in the DIET process with the supplementation of carbonaceous materials (Yin *et al*., 2019; Zhao *et al*., 2020). Compared with the control group, graphene addition led to the predominance of potential syntrophic acetate oxidation (SAO) operational taxonomic units (OTUs) in the order SHA-98 and *Methanothermobacter*, which is likely to indicate enhanced connections between these via DIET and, therefore, facilitation of resistance to the shock of intermittent gas supply.

The high specific surface area of graphene itself (500 m^2/g) may be another essential factor in its stabilising of the biomethanation system. The high specific surface area of carbonaceous materials has been suggested to be responsible for improving the methane production rate during *ex situ* biomethanation (Yang *et al*., 2020). This property has also been reported to enhance and stabilise the AD process (Dang *et al*., 2017; Lü *et al*., 2019). Moreover, other physicochemical properties of carbonaceous materials, such as hydrophobicity and surface functional groups, have been suggested to positively influence the adhesion of microbes (Habouzit *et al*., 2011; Umetsu *et al*., 2020). The enrichment of functional microbes adhering tightly to the carbonaceous materials due to their porous structures is suggested to be an efficient strategy to resist external stresses (Luo *et al*., 2015; Lü *et al*., 2016). Based on the above discussion, the potential mechanism that explains the stabilisation effect of graphene on *ex situ* biomethanation is proposed and shown in Figure 2.4. With the intermittent gas injection, graphene addition possibly led to the alteration of a metabolic pathway to an SAO process with the cooperation between possible SAO OTUs within the order SHA-98 and methanogens of the genus *Methanothermobacter*. Graphene's high electrical conductivity, large specific surface area and enhanced biocompatibility are postulated to play an essential role in its ability to influence the performance of systems subjected to the shock of intermittent gas supply.

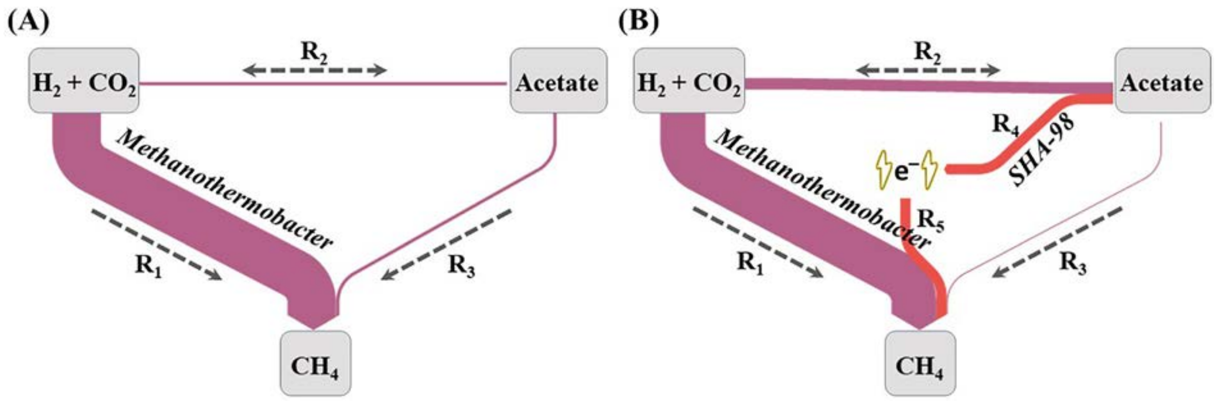


Figure 2.4. Potential reactions involved in the control group (A) and graphene group (B) with intermittent gas injection. R_1, hydrogenotrophic methanogenesis ($4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$); R_2, homoacetogenesis and acetogenesis ($4H_2 + 2CO_2 \leftrightarrow CH_3COO^- + H^+ + 2H_2O$); R_3, acetoclastic methanogenesis ($CH_3COO^- + H^+ \rightarrow CH_4 + CO_2$); R_4, acetate oxidation via DIET ($CH_3COO^- + H^+ + 2H_2O \rightarrow 8H^+ + 8e^- + 2CO_2$); R_5, methanogenesis via DIET ($8H^+ + 8e^- + CO_2 \rightarrow CH_4 + 2H_2O$). Reprinted from Wu, B., Lin, R., Kang, X., Deng, C., Dobson, A.D.W. and Murphy, J.D., 2021a. Improved robustness of ex-situ biological methanation for electro-fuel production through the addition of graphene. *Renewable and Sustainable Energy Reviews* 152152: 111690. © 2021 The Authors.

2.2.4 Conclusion

This study has demonstrated that carbonaceous material (graphene) amendment could help stabilise *ex situ* biomethanation in the event of intermittent gas supply, possibly due to the high electrical conductivity and large specific surface area of graphene. With the shock of intermittent gas injection, graphene addition enhanced the gas conversion efficiency by 18.2% and the production rate by 267% compared with the control. However, pyrochar amendment did not lead to promotional effects on the upgrading performance. Microbial analysis showed that OTUs belonging to the order SHA-98 induced by graphene addition and archaea *Methanothermobacter* potentially altered the metabolic pathway to a SAO process to stabilise the upgrading performance.

For the detailed methodology and results of this section, please refer to the published open-access journal paper at https://doi.org/10.1016/j.rser.2021.111690.

2.3 Role of Biochar in Advanced Fuel and Biochemicals Production

2.3.1 Introduction and objectives

Different bioproducts (such as biomethane, bioethanol and organic acids) can be produced from the anaerobic fermentation of organic material with different functional microorganisms. Microbial chain elongation involves the conversion of short-chain fatty acids (SCFAs) (1–5 carbon atoms) into MCFAs (6–12 carbon atoms) via open cultures of anaerobic microbial consortia. Recent studies have found that carbonaceous materials such as pyrochar and activated carbon can enhance the robustness of chain elongation systems and accelerate the process and in doing so increase the efficiency of MCFA production (Liu *et al*., 2020; Ghysels *et al*., 2021; S.-L. Wu *et al*., 2021). A previous study showed that, when using a pure culture of *Clostridium kluyveri* in chain elongation, pyrochar addition at 10 g/L shortened the lag time and increased the *n*-caproate production rate (Ghysels *et al*., 2021). Similarly, the addition of activated carbon at 30 g/L significantly enhanced the *n*-caproate yield and selectivity (Ghysels *et al*., 2021). Another study using open mixed culture also reported that pyrochar amendment at 20 g/L significantly increased the yield of *n*-caproate during chain elongation (Liu *et al*., 2017). However, the size of pyrochar particles was reported to affect chain elongation performance. A recent study revealed that only pyrochar with particle sizes smaller than 5 μm led to positive effects on chain elongation when applied at 20 g/L (Liu *et al*., 2020). The porous structure, electrical conductivity and adsorption properties of carbonaceous materials (such as pyrochar) might be attributed to such promotional effects (Liu *et al*., 2017; Ghysels *et al*., 2021). Therefore, a systematic assessment of the critical role of carbonaceous materials in the mixed culture elongation reaction was carried out.

In a typical chain elongation process, both electron acceptors and electron donors are required to effect carbon chain elongation, where SCFAs (such as acetic acid; CH_3COO^-) can function as electron acceptors, and ethanol (CH_3CH_2OH) or lactate ($CH_3CHOHCOO^-$) can function as electron donors to provide the necessary energy and carbon sources for longer MCFA production (Angenent *et al*., 2016). The molar ratio of the electron donor and electron acceptor added in chain elongation predominantly determines the type and yield of the elongated products (Liu *et al*., 2016; Spirito *et al*., 2018). A previous study showed that the highest *n*-caproate production was achieved at an ethanol to acetate molar ratio of 3 mol/mol (Liu *et al*., 2016). Similar observations were also made in continuous bioreactors in which ethanol-to-acetate ratios higher than 1.9 mol/mol led to increased MCFA production, with the highest MCFA yield achieved at a ratio of 4.5 mol/mol (Spirito *et al*., 2018). The current understanding of mechanisms by which electron donor to electron acceptor ratios affect the carbon fluxes is based on microbial chain elongation systems without the presence of carbonaceous additives. Therefore, the investigation into the combinational effect of electron donor to acceptor ratios and carbonaceous material addition in chain elongation would aid in understanding optimal chain elongation systems for longer MCFA production, such as n-caproate.

The objectives of this study were to:

- evaluate the influence of electron donor (ethanol) to acceptor (acetate) molar ratios on a pyrochar-mediated microbial chain elongation system;
- assess the influence of physicochemical properties of pyrochar (such as surface redox groups and electrical conductivity) on MCFA

production by comparing chemically reduced pyrochar and graphene;

- modify a simplified stoichiometric model to demonstrate the positive effects of pyrochar amendment to provide insights into the thermodynamic benefits.

2.3.2 Improved medium-chain fatty acid yields with pyrochar addition

At different levels of pyrochar addition, the production of MCFAs differed significantly among groups over time (Figure 2.5D). For the control group without graphene or pyrochar addition, a noticeable depletion of ethanol and acetate was observed on day 6, leading to a production of 4.55 g COD/L *n*-butyrate and 0.60 g COD/L *n*-caproate (Figure 2.5C and D). Since *n*-butyrate is reported to be a key intermediate product that can be further utilised to produce *n*-caproate (Angenent *et al*., 2016; Liu *et al*., 2020), the production of a large amount of *n*-butyrate indicated that the chain elongation process occurred in the control group. The highest MCFA production was achieved on day 10 in the control group, when 6.35 g COD/L *n*-caproate was obtained, resulting in a 43.2% MCFA conversion efficiency (MCFA conversion

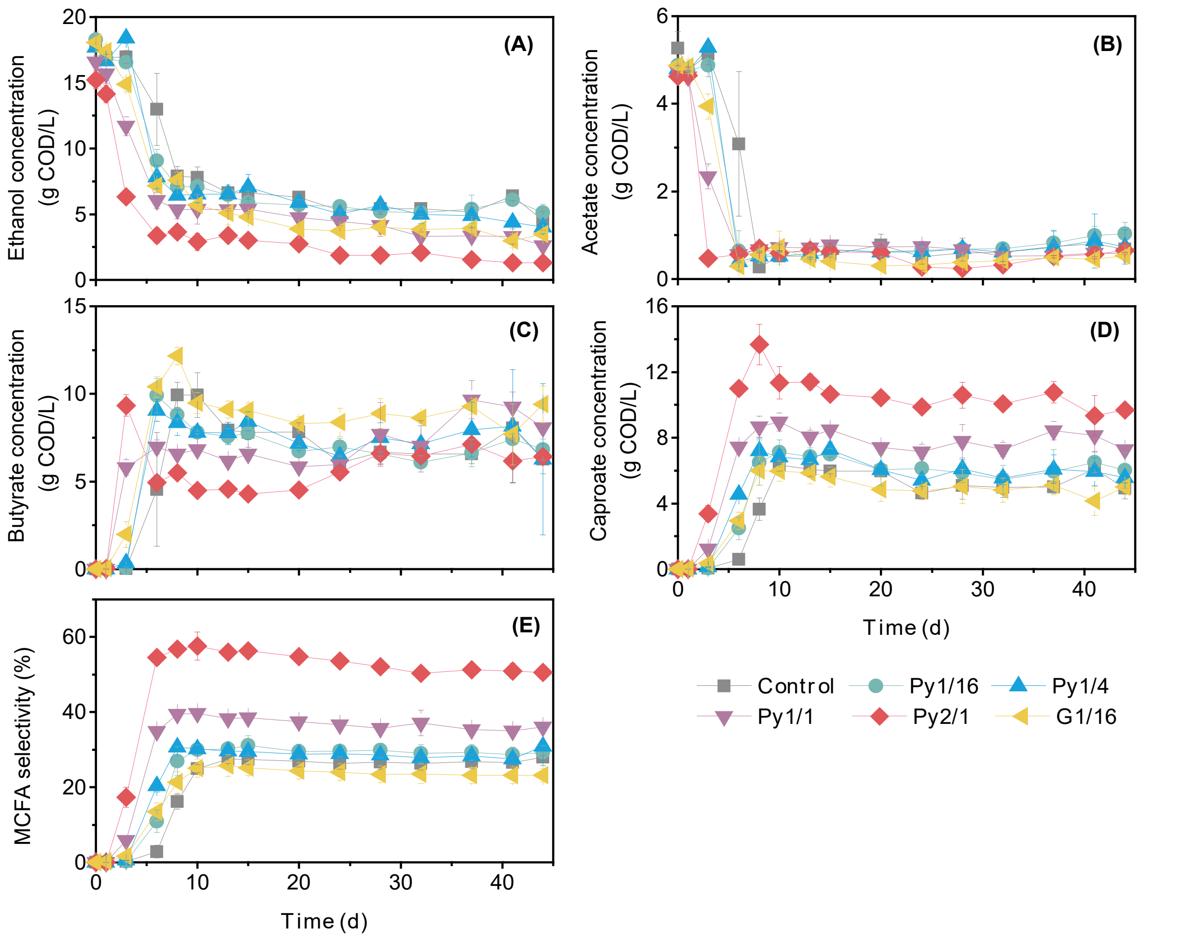


Figure 2.5. Concentration of ethanol (A), acetate (B), butyrate (C), caproate (D) and MCFA selectivity (E) in groups without carbonaceous material addition (control), and with pyrochar to substrate mass ratio of 1:16, 1:4, 1:1 or 2:1, and graphene to substrate mass ratio of 1:16. Initial ethanol to acetate carbon molar ratio is 3:1. α/β in the legend represents that pyrochar/graphene to substrate mass ratio. G represents graphene amendment; Py represents pyrochar amendment. Error bars represent the standard deviation from experimental triplicates. Reprinted from Wu, B., Lin, R., Ning, X., Kang, X., Deng, C., Dobson, A.D.W. and Murphy, J.D., 2022. An assessment of how the properties of pyrochar and process thermodynamics impact pyrochar mediated microbial chain elongation in steering the production of medium-chain fatty acids towards n-caproate. *Bioresource Technology* 358: 127294. © 2022 The Authors.

efficiency = ($COD_{caproate}$ + $COD_{caprylate}$)/($COD_{ethanol\text{-}consumed}$ + $COD_{acetate\text{-}consumed}$)) and 24.9% MCFA selectivity (MCFA selectivity = ($COD_{caproate}$ + $COD_{caprylate}$)/(COD_{total})).

The suitable addition of pyrochar to chain elongation can significantly affect the overall MCFA yield and C_{6+} carboxylate selectivity. As the fermentation proceeded to day 6, significantly higher *n*-caproate yields were achieved in all pyrochar amendment groups ($p < 0.05$), among which the Py2/1 group achieved the highest *n*-caproate production: 11.0 g COD/L, compared with only 0.60 g COD/L in the control group. This is a significant deviation (Figure 2.5D). The highest *n*-caproate production of the Py1/16, Py1/4 and Py1/1 groups was achieved at 7.11, 7.28 and 8.95 g COD/L, respectively, significant increases over the control of 12.0%, 14.6% and 40.9%. However, the standout figure was noted with pyrochar addition in the Py2/1 group, which resulted in the highest *n*-caproate production, 13.67 g COD/L, an increase of 115% compared with the control group. The corresponding MCFA selectivity and conversion efficiency was 56.8% and 88.1%, respectively; this elucidates an efficient conversion of intermediate *n*-butyrate to *n*-caproate in the chain elongation process. These results indicate that appropriate pyrochar amendment could significantly enhance the chain elongation process by reducing the lag time and enhancing MCFA conversion efficiency.

The positive effects of the carbonaceous materials-mediated chain elongation process have been reported with pure or open cultures (Liu *et al*., 2017, 2020; Ghysels *et al*., 2021; S.-L. Wu *et al*., 2021). Besides MCFAs, microbial chain elongation can also steer electrons into short-chain *n*-butyrate (Angenent *et al*., 2016). Notably, *n*-butyrate accumulation in the end products (day 44) was observed in all groups, ranging from 6.28 to 8.09 g COD/L. This indicates that the conversion of *n*-butyrate as an electron acceptor with ethanol as an electron donor to *n*-caproate is a rate-limiting step in the chain elongation process.

The complete *n*-butyrate elongation to *n*-caproate could be theoretically achieved with an ethanol to *n*-butyrate molar ratio of 2:1, as per the following equation:

$$5CH_3CH_2OH + 2.5CH_3(CH_2)_2COO^- \rightarrow 10/3CH_3(CH_2)_4COO^- + 5/6H^+ + 5/3H_2 + 10/3H_2O \quad \Delta_r G' = -131.58\ \text{kJ/mol} \tag{2.1}$$

Taking the control group as an example, the transformed Gibbs free energy ($\Delta_r G'$) based on the actual carboxylates concentration on day 44 (as per Figure 2.5A) was calculated as –131.58 kJ/mol, which is less thermodynamically favourable than that of acetate elongation to *n*-caproate of –198.20 kJ/mol at a molar ratio of 3:1:

$$7.5CH_3CH_2OH + 2.5CH_3COO^- \rightarrow 10/3CH_3(CH_2)_4COO^- + 5/6H^+ + 5/3H_2 + 35/6H_2O \quad \Delta_r G' = -198.20\ \text{kJ/mol} \tag{2.2}$$

This suggests that, compared with acetate, *n*-butyrate is thermodynamically disadvantaged in achieving chain elongation when ethanol is used as the electron donor. This is supported by Wu *et al*. (2018), who demonstrated that *n*-butyrate did not present advantages for chain elongation performance, as MCFA production and selectivity were lower than when acetate was used as the electron acceptor. Furthermore, the high content of undissociated carboxylic acids might be another reason for inhibiting *n*-butyrate elongation to *n*-caproate.

For the control group, the maximum *n*-caproate concentration was 6.35 g COD/L (24.80 mM; day 10; Figure 2.5D). At a pH of 5.38 (Figure 2.6D; assuming that the pH on day 10 was the same as on day 8), this translates to an undissociated caproic acid concentration of 5.67 mM as per calculations presented in Wu *et al*. (2022). Although this value is lower than the reported inhibition limit of 7.5 mM for chain elongation (Angenent *et al*., 2016), considering the combined toxicities from other undissociated carboxylic acids such as 13.49 mM of undissociated *n*-butyric acid (calculated from Figure 2.5C (group G1/16), day 10), the toxic limit of undissociated *n*-caproic acid in a mixed solution is expected to be lower than the reported limit of 7.5 mM. Ge *et al*. (2015) found that, even though the undissociated *n*-caproic acid concentration was significantly reduced by in-line product extraction, inhibition of the chain elongation process still occurred, and they attributed this to the large amount of undissociated *n*-butyric acid (maximum at 13.5 mM). As the pH variation significantly affects the undissociated carboxylic acid concentration as per calculations in Wu *et al*. (2022), the elevated pH resulting from pyrochar amendment compared with the control, ranging from 5.41 to 5.61 on day 8 (Figure 2.6D), could greatly reduce the undissociated caproic acid concentration. The elevated pH of pyrochar-amended groups is suggested to be a result of the buffer capacity of pyrochar resulting from the alkali and alkaline earth metals (such as calcium, magnesium and iron) (Shen *et al*., 2017; Wu *et al*., 2021b). However, even given the consideration of high pH values, the maximum undissociated caproic acid concentration in pyrochar-amended groups still ranged from 5.94 to 7.94 mM, which is 4.8–40.0% higher than that in the control, indicating that pyrochar considerably enhanced the robustness of the chain elongation system.

2.3.3 *Unique properties of pyrochar attributed to enhanced medium-chain fatty acid selectivity*

The results of the present study suggest that pyrochar addition affects the chain elongation process, with the level of impact dependent on the level of addition. Previous studies have attributed the ability of pyrochar or biochar to mediate biological reactions to its redox capacities, electrical conductivity and porous structures (Zhang *et al*., 2019; Deng *et al*., 2020). In this study, the electrical conductivity and extracellular polymeric substances (EPS) content of the bulk sludge and their correlation with the MCFA yield were assessed, and the results are shown in Figure 2.6. The superior electron transfer ability of graphene was demonstrated in this study, as a small amount of graphene addition (G1/16: 0.83 g/L) presented an electrical conductivity of 31.34 μS/cm, comparable to that (42.42 μS/cm) obtained with a higher amount of pyrochar addition (Py1/1: 13.20 g/L). Notably, a strong linear correlation was observed between MCFA production and electrical conductivity in the pyrochar-amended groups (Figure 2.6A). The results showed that MCFA production was positively correlated with the electrical conductivity of the

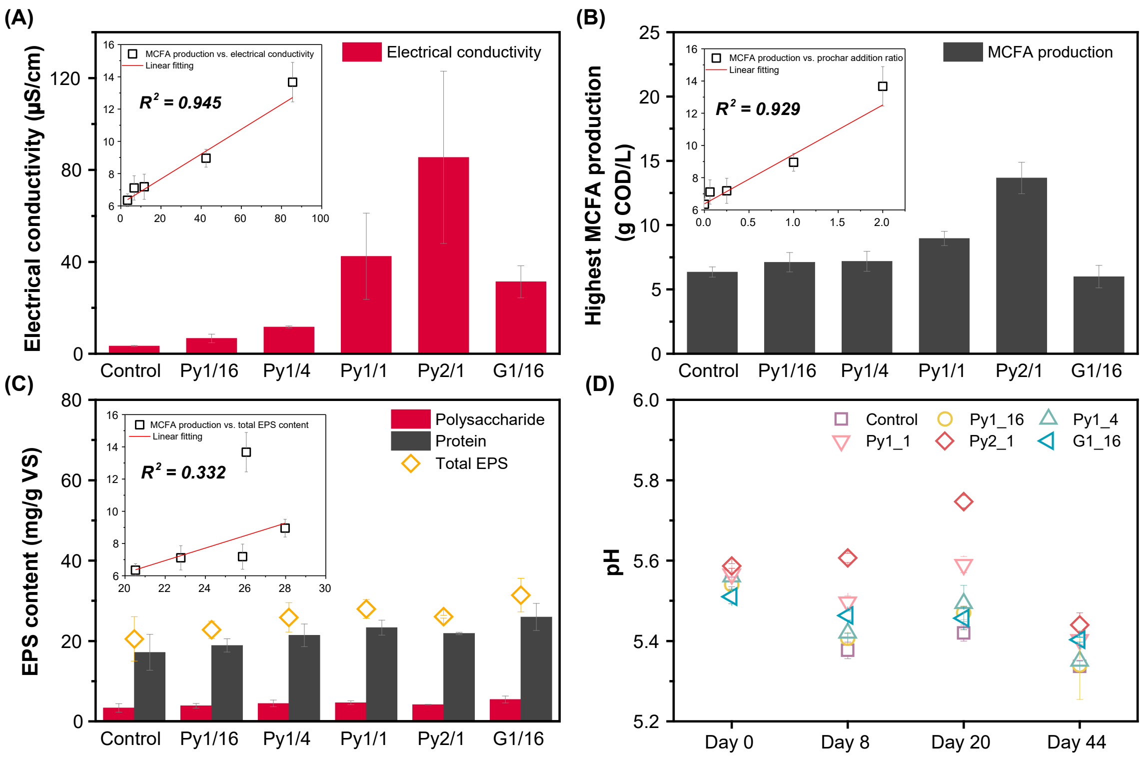


Figure 2.6. (A) Electrical conductivity of the mixture of sludge and material at the end of the experiment, (B) the highest MCFA production during the chain elongation process, (C) EPS content of the bulk sludge at the end of experiment and (D) pH variations during the chain elongation process. α/β in the *x*-axis of A, B and C represents the pyrochar/graphene to substrate mass ratio; Py and G represent groups amended with pyrochar and graphene, respectively. Error bars represent the standard deviation from experimental triplicates. Reprinted from Wu, B., Lin, R., Ning, X., Kang, X., Deng, C., Dobson, A.D.W. and Murphy, J.D., 2022. An assessment of how the properties of pyrochar and process thermodynamics impact pyrochar mediated microbial chain elongation in steering the production of medium-chain fatty acids towards n-caproate. *Bioresource Technology* 358: 127294. © 2022 The Authors.

sludge and material mixture ($R^2 > 0.945$). Relatively high electrical conductivity of pyrochar has been commonly discussed and is highlighted during biological fermentation and AD (Deng *et al*., 2020; S.-L. Wu *et al*., 2021). Liu *et al*. (2017) observed that, when 20 g/L pyrochar was added to a semi-continuous chain elongation reactor using ethanol and acetate as substrates, caproate production was 286% higher than in the control group. The enhanced microbial system conductivity due to pyrochar addition was postulated to be the critical reason (Liu *et al*., 2017). It should be mentioned that although a high-conductive system was achieved by graphene amendment (Figure 2.6A), the MCFA yield was not significantly enhanced compared with the control group and nor was the yield of the same order of the Py1/16 group (Figure 2.6B), suggesting that the electrical conductivity of carbonaceous materials is not the sole parameter affecting MCFA production.

Extracellular polymeric substances play a critical role in protecting microorganisms from adverse conditions and can also facilitate extracellular electron transfer among syntrophic microbial partners (Yan *et al*., 2018). Figure 2.6C shows the EPS content, including polysaccharides and proteins, of the bulk sludge in different groups. A weak correlation ($R^2 < 0.34$) was observed between the total EPS content and the MCFA production in the pyrochar-amended groups. With the increase in pyrochar dosage, the total EPS content of the bulk sludge increased gradually but reached a peak in the Py1/1 group. High secretion of EPS is considered a strategy by which microbes protect themselves from undissociated carboxylic acids (Q. Wu *et al*., 2020). The results suggested that pyrochar amendment can improve the system robustness by promoting EPS secretion, resulting in a more efficient chain elongation process. Interestingly, the G1/16 group achieved the highest EPS content among all of the groups, at 31.41 mg/g volatile solids, indicating an effective response of microbes to the high concentration of undissociated carboxylic acids. However, low dosages of graphene, even with its high electrical conductivity and EPS content, did not lead to a particularly high MCFA selectivity. This suggests that the promotional effect of pyrochar on chain elongation amendment did not depend solely on the enhanced electrical conductivity and high EPS content. Other parameters of pyrochar, such as its porous structure and redox properties, might also contribute to the efficient chain elongation, and these are discussed in the following sections.

2.3.4 Insights into pyrochar-enhanced medium-chain fatty acid yields with microbial analysis

As shown in Figure 2.7, the control group was dominated by the genera *Aminivibrio* (6.2%), *Syntrophobacter* (10.6%), *Rummeliibacillus* (5.0%) and *Sporanaerobacter* (9.3%) and an OTU belonging to the order *Clostridiales* (10.5%). Compared with the inoculum, a more even microbial community composition was observed in the control group, which was supported by the fact that the Shannon index (a parameter that indicates community evenness) of the control group was 0.67, which is higher than that of the inoculum (at 0.59). Compared with the control group, similar microbial communities were observed in the Py1/16 and G1/16 groups. Considering the chain elongation performance observed in the Py1/16 and G1/16 groups, the similarities in the microbial compositions could explain the insignificant difference in MCFA production led by the low dosage of pyrochar and graphene amendments. Interestingly, the genera *Syntrophobacter, Aminivibrio* and *Rummeliibacillus* predominated in all pyrochar-amended groups, among which the Py1/1 group achieved the highest total relative abundance of 53.8% of these three genera, followed by the Py2/1 group at 44.3%.

The genus *Syntrophobacter* has been widely reported to be a propionate-utilising bacterium and to be capable of establishing syntrophic metabolism with hydrogenotrophic methanogens to convert ethanol, propionate and butyrate to acetate and hydrogen (Cao *et al*., 2021; Wang *et al*., 2021). As a metabolic competitor in chain elongation, *Syntrophobacter* has been suggested to be negatively related to the efficiency of *n*-caproate production (Liu *et al*., 2017; Bao *et al*., 2019). The control group presented a 10.6% relative abundance of the genus *Syntrophobacter*, whereas no significant change was observed in the pyrochar-amended groups, as evidenced by the similar relative abundance of 11.2–15.2%. However, the proportion of *Syntrophobacter* significantly increased to 22.2% in the G1/16 group, which indicated the potentially high activity of competitive metabolic pathways as opposed to chain elongation, thereby leading to lower *n*-caproate production. Bacterial

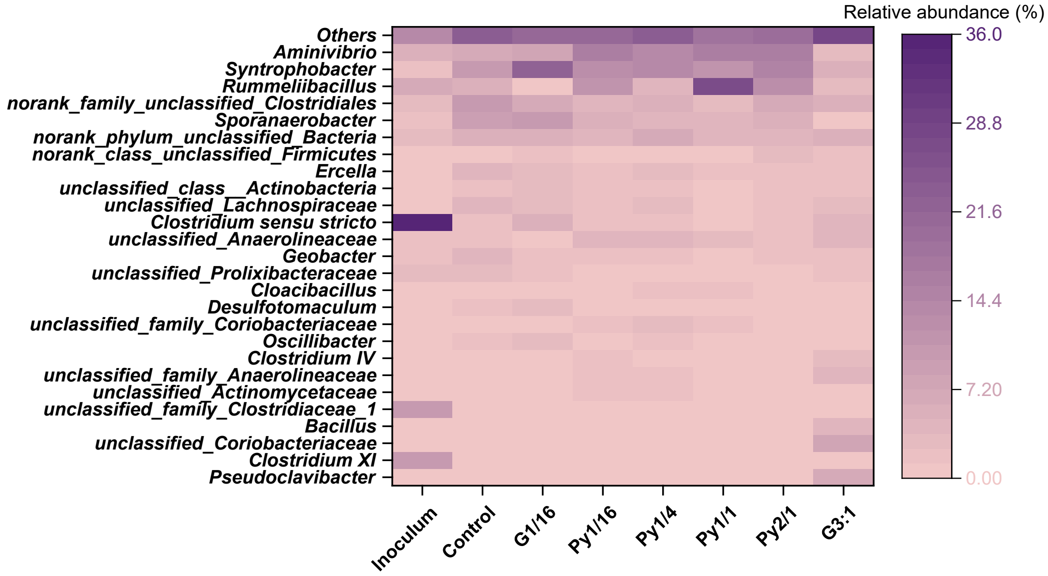


Figure 2.7. Heatmap of relative abundances at the genus level in different groups. Relative abundance (%) is shown by the colour gradient. OTUs with <2% relative abundance in all samples are classified into "Others". α/β in the *x*-axis represents pyrochar/graphene to substrate mass ratio; 3:1 in the *x*-axis represents molar ratio of ethanol to acetate; Py and G represent groups with pyrochar and graphene amendment, respectively. Reprinted from Wu, B., Lin, R., Ning, X., Kang, X., Deng, C., Dobson, A.D.W. and Murphy, J.D., 2022. An assessment of how the properties of pyrochar and process thermodynamics impact pyrochar mediated microbial chain elongation in steering the production of medium-chain fatty acids towards n-caproate. *Bioresource Technology* 358: 127294. © 2022 The Authors.

members affiliated to the *Aminivibrio* genus have been reported to act as fermentative bacteria that utilise amnio acids and organic acids (Honda *et al*., 2013; Yi *et al*., 2020), and their presence is rarely reported in the chain elongation system. However, compared with the control group (6.2% relative abundance), a predominance of *Aminivibrio* was observed in all pyrochar-amended groups (14.4–16.4%), indicating its essential role in a pyrochar-mediated chain elongation process. The genus *Rummeliibacillus* is believed to be a critical *n*-caproate producer that enables the elongation of ethanol and acetate to MCFAs (Zhang *et al*., 2022). Liu *et al*. (2017) found that species affiliated to the genus *Rummeliibacillus* maintained predominance in a pyrochar-mediated chain elongation system. In addition, its spore-forming ability provides *Rummeliibacillus* with the capacity to alleviate the adverse effects resulting from undissociated carboxylic acids (Liu *et al*., 2017). Compared with the control group (5.0% relative abundance), the relative abundance of *Rummeliibacillus* increased significantly after pyrochar amendment, especially in the Py1/1 and Py2/1 groups, at 26.5% and 12.7%, respectively. Given the significant increase in MCFA production observed in the Py1/1 and Py2/1 groups, it is reasonable to infer that the genus *Rummeliibacillus* was actively involved in enhancing the MCFA production efficiency in a pyrochar-mediated chain elongation process.

Surprisingly, the most apparent modification to the bacterial community composition was observed in the G3:1 group, in which the microbes were primarily distributed in 15 major genera and their proportions ranged from 2.0% to 8.2%, resulting in the highest Shannon index, 0.69, among all groups. Among these genera, members of the genera *Clostridium sensu stricto* (4.8% relative abundance) (Coma *et al*., 2016), *Bacillus* (4.4%) (Zagrodnik *et al*., 2020), *Rummeliibacillus* (3.3%) (Zhang *et al*., 2022) and *Clostridium IV* (2.7%) (Duber *et al*., 2018; Q. Wu *et al*., 2021) and the family Coriobacteriaceae (8.2%) (Duber *et al*., 2018, 2020) were present, all of which have been reported to be capable of participating in the chain elongation process. Clearly, the microbial community structure in different chain elongation groups was a consequence of several factors, including (1) the types of materials added to the chain elongation system and (2) the toxicity of the undissociated carboxylic acids. Compared with pyrochar amendment, the microbes in the high graphene dosage group are likely to have adopted a different strategy to alleviate external stresses and improve microbial electron transfer efficiency.

2.3.5 Conclusion

Pyrochar amendment in chain elongation could achieve 115% more MCFA yield than no pyrochar addition. Such improvements could be attributed to the high electrical conductivity and surface redox groups of pyrochar, with a thermodynamic advantage of 93.50 kJ/mol reaction presented compared with the control group under the ethanol to acetic acid ratio of 2:1. Moreover, the ethanol-to-acetate molar ratio of 2 mol/mol achieved the highest *n*-caproate production in a pyrochar-mediated chain elongation system. By comparison, graphene addition yielded a comparable MCFA yield to pyrochar amendment, but a significant prolongation of lag time (15 days) was observed. Bacteria *Rummeliibacillus* and *Aminivibrio* were the dominant genera in the pyrochar-mediated chain elongation microbiome.

For the detailed methodology and results of this section, please refer to the published open-access journal paper at https://doi.org/10.1016/j.biortech.2022.127294.

3 The Marginal Abatement Costs of Liquid and Gaseous Transport Biofuels Produced in Circular Cascading Bioeconomy Systems

3.1 Introduction and Objectives

AD, which employs microorganisms under anaerobic conditions, has shown itself to be a mature, proven bioconversion technology for sustainable gaseous biofuel production from biodegradable feedstock (such as grass silage, animal slurry, and other organic residues and waste materials) (Wu *et al*., 2020a; Kang *et al*., 2021). The produced energy-rich gas mixture, known as biogas (typically containing 60% methane, 40% carbon dioxide and other trace gases such as H_2S, H_2 and N_2), can be used for various applications such as transport fuels after upgrading, and heat and electricity generation (Xia *et al*., 2016; Vo *et al*., 2018a; Voelklein *et al*., 2019). For biogas to be used in the transport sector, carbon dioxide needs to be removed or sequestered, resulting in a methane-rich gas mixture (methane content higher than 96%) named biomethane (Alamia *et al*., 2016). Among the biogas-upgrading technologies, CO_2 utilisation via biomethanation (also known as power to gas), which can facilitate variable renewable electricity by reducing electricity curtailment while capturing and utilising CO_2, is considered potentially sustainable and cost-efficient (Parra *et al*., 2017; Lin *et al*., 2021a; Wu *et al*., 2021b). During this process, CO_2 in the biogas is biologically captured and utilised to produce neat methane streams by reacting with hydrogen, ideally sourced from renewable electricity (such as wind or solar energy) (Voelklein *et al*., 2019; Wu *et al*., 2021a).

Bioenergy, carbon capture and sequestration (BECCS) is a negative emission technology; such technologies are seen as essential to reduce global GHG emissions (EASAC, 2018). Digestate, another product of the AD process, consists of a significant amount of undegraded organic components (such as lignin) and valuable agricultural nutrients (such as nitrogen, potassium and phosphorus). Compared with direct use as biofertiliser, the solid digestate can be valorised into pyrochar, syngas and biocrude oil utilising pyrolysis technology, maximising carbon capture and allowing for concentration of CO_2 in the pyrochar (Monlau *et al*., 2015; Neumann *et al*., 2015). Pyrochar is a versatile product. The application of pyrochar as a soil amendment is regarded as a negative emission technology (EASAC, 2018). In addition to soil amendment, recent advances have demonstrated that pyrochar can be used as an additive to AD to enhance biomethane production (via DIET) from various feedstocks due to its relatively high specific area, electrical conductivity and surface functional groups (Deng *et al*., 2020, 2021). Improvements in biomethane production have been reported to range from 5% to 72%, depending on the feedstock and pyrochar characteristics and dosages (Deng *et al*., 2021; Wu *et al*., 2021b). Biocrude oil can be used as a diesel replacement after further treatment (Neumann *et al*., 2015), while syngas can be burned to compensate for the heat demand in pyrolysis (Monlau *et al*., 2015; Deng *et al*., 2020).

In this context, the integration of AD, CO_2 biomethanation and solid digestate pyrolysis technologies may be optimised to produce sustainable renewable gaseous biofuel (biomethane) while achieving carbon recycling through pyrochar. The produced biomethane, with a significantly reduced carbon intensity, can be compressed or liquefied as an alternative to compressed natural gas or liquefied natural gas or can be converted into biomethanol, which is also a versatile liquid transport fuel. One of our previous studies reported the synergistic benefits of the above-mentioned bio-based system, in which, when renewable hydrogen was used in CO_2 biomethanation, the net energy output increased by 70% compared with a conventional biomethane system (Wu *et al*., 2021b). Gray *et al*. (2022) reported that gross energy was increased by 62.6% by combining AD with CO_2 biomethanation and by 50% by integrating AD and methanol synthesis. Deng *et al*. (2020) proposed a cascading circular bioenergy system consisting of AD and pyrolysis processes. Compared with individual technology, the proposed system increased biomethane production by 17% and biocrude oil by 10% while reducing digestate mass flow by 26% (Deng *et al*., 2020). Several studies have explored the technoeconomics of combining AD with CO_2 biomethanation (Vo *et al*., 2018b; Kassem *et al*., 2020; Lawson *et al*., 2021) and its life cycle impacts (Vo *et al*., 2018a). Technoeconomic analysis of using AD-sourced biogas to produce liquid fuels has been carried out in a small number of studies (Dimitriou *et al*., 2015; Sheets and Shah, 2018). However, there is a gap in knowledge regarding the evaluation of the economic and environmental benefits of a circular cascading bioeconomy system integrating AD, CO_2 biomethanation and pyrolysis technologies for the production of transport biofuels.

Figure 3.1 illustrates the different C1 biofuel production systems that underwent technoeconomic and environmental assessment in this study. Specifically, biomethane and biomethanol are the targeted biofuels from bio-based systems incorporating carbon capture, sequestration and utilisation. The objectives of this study are to:

- design process configurations for the production of biomethane and biomethanol using grass silage and cattle slurry as the raw feedstock in circular cascading bioeconomy systems;
- perform a comparative technoeconomic and environmental analysis of the configurations and identify the key economic parameters affecting the minimum selling price of biofuels through sensitivity analysis;
- perform environmental/sustainability assessment of biofuels including GHG emissions and identify the key environmental drivers of the carbon intensity;
- construct a marginal abatement cost curve to visualise the GHG emissions abatement potential of biofuels proposed from circular cascading bioeconomy systems.

3.2 Mass and Energy Balance in the Bioeconomy Systems

Figures 3.2 and 3.3 show the mass balance of the considered systems. For all evaluated cases, the mass input of grass silage and cattle slurry was the same, so the results can be directly compared. The anaerobic digestion–carbon utilisation (AD-CU) system (Figure 3.2A), which uses CO_2 from the biogas stream to produce biomethane, as modelled produced 400 Nm³/h biomethane (purity of 97.6%), equivalent to an energy content of 3893 kWh (lower heating value (LHV) basis). The LHV of CH_4 and H_2 is 50 MJ/kg and 120 MJ/kg, respectively (The Engineering Tool Box, 2003). For the AD-Py-CU case, the biomethane yield of the pyrochar-mediated AD process (4.6 g of pyrochar per litre of substrate) was modelled as 422 Nm³/h (4104 kWh). In addition to pyrochar, 16.2 kg/h biocrude oil (dry basis) was obtained from the model of the solid digestate process. Assuming that the LHV of biooil is 22.05 MJ/kg (dry basis), the energy content of biocrude oil was 98.9 kWh (Monlau *et al*., 2015).

When biomethanol was the target product, the AD-CU-MeOH case as modelled (Figure 3.3A), which incorporated biomethane steam reforming and methanol synthesis processes, resulted in a biomethanol yield of 383 kg/h (99.84% purity), which is equivalent to 2121 kWh when considering a LHV of 20 MJ/kg methanol (The Engineering Tool Box, 2003).

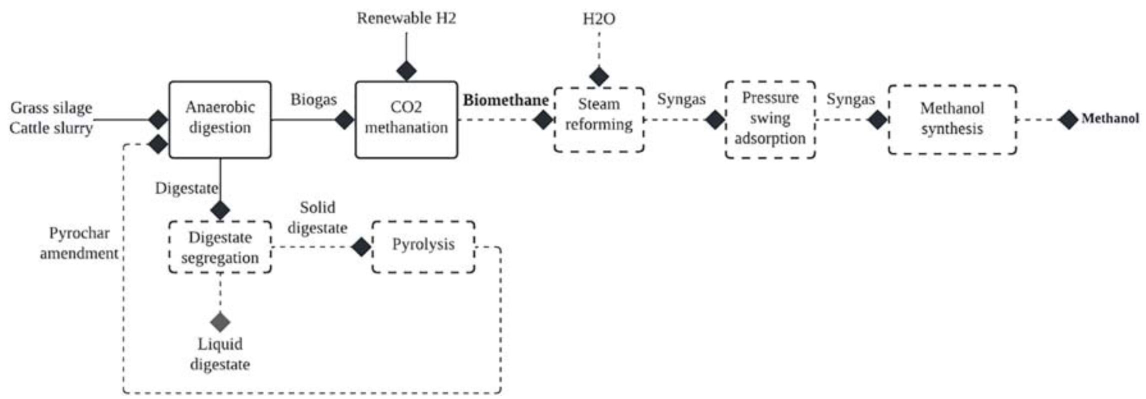


Figure 3.1. An overview of the circular cascading bioeconomy systems for the production of biomethane or biomethanol (dashed lines represent variable processes/steps in different design cases).

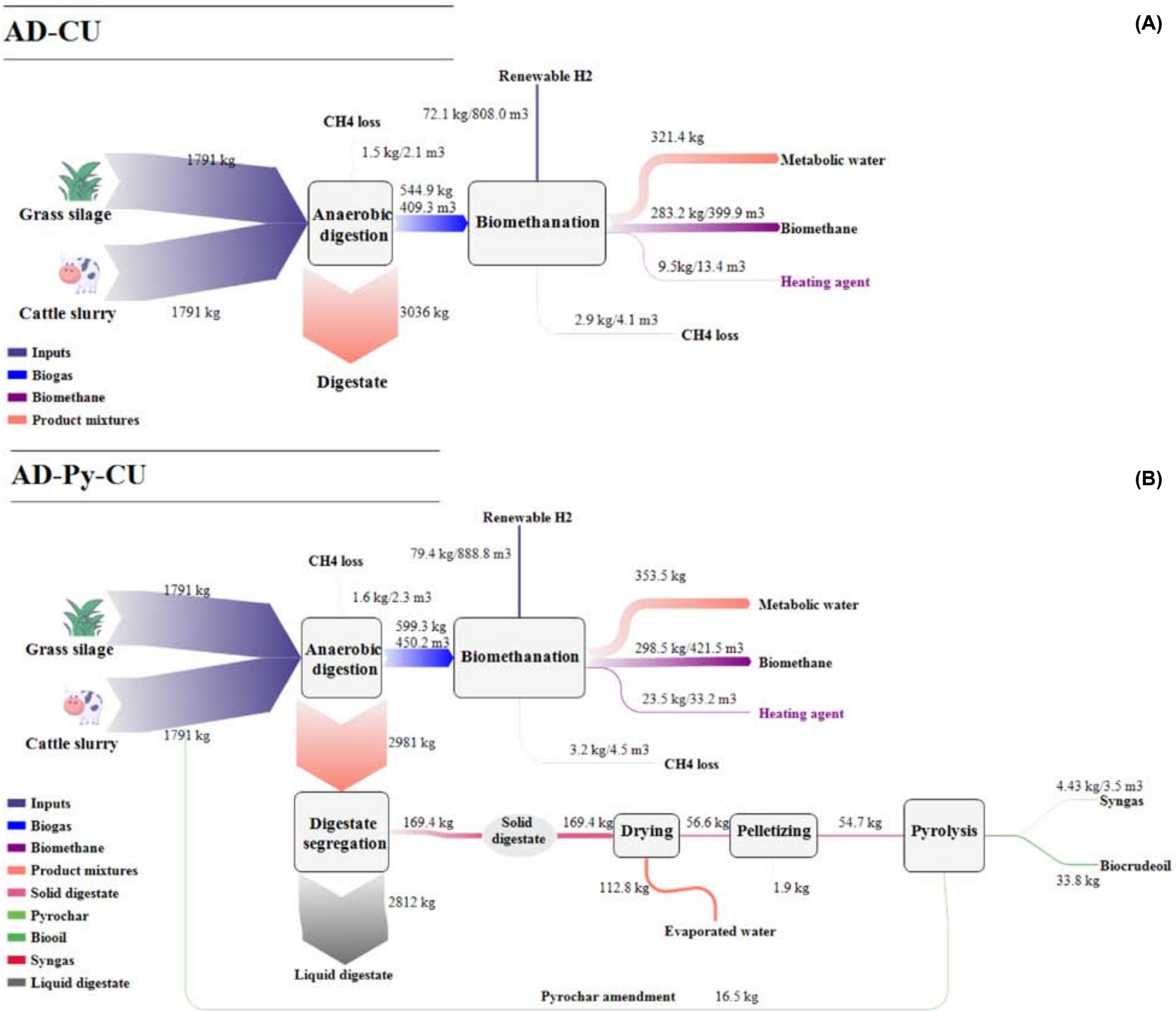


Figure 3.2. Hourly mass balance of the AD-CU (A) and AD-Py-CU (B) cases. CU, CO_2 utilisation (via biomethanation); Py, (solid digestate) pyrolysis.

The AD-Py-CU-MeOH case as modelled produced 403 kg/h or 2236 kWh of biomethanol, which is 5.4% higher than the AD-CU-MeOH case because of the larger amount of biomethane processed in the methanol synthesis unit. In the case of AD-CU-MeOH and AD-Py-CU-MeOH, the amount of hydrogen produced from the methane steam reformer was larger than the hydrogen demand of the methanol synthesis reactor. Therefore, the surplus hydrogen was sent to the CO_2 biomethanation unit, where external hydrogen was also required.

Table 3.1 summarises the mass and energy balances of all four evaluated systems. To measure the percentage of energy originally present in the feedstock that ends up in the biofuels, including biomethane, biomethanol and biocrude oil (Dimitriou *et al*., 2015; Deng *et al*., 2020), the plant energy efficiency was calculated based on the following equation:

$$\eta_{plant} = \frac{M_{biofuels} \times LHV_{biofuels}}{M_{feedstock} \times LHV_{feedstock} + V_{H_2} \times 4.4 \times PEF_{RE} + E_{el} \times PEF_{el}} \quad (3.1)$$

where M_i is the mass flow (kg/h), LHV_i is the lower heating value (MJ/kg) of the materials (grass silage, cattle slurry, biomethane, biomethanol and biocrude oil), V_{H2} is the volume flow (Nm³/h) of hydrogen, 4.4 kWh/Nm³ H_2 is the conversion factor indicating that 4.4 kWh of electricity was needed to produce 1 Nm³ H_2, PEF_{RE} is the primary energy factor of renewable electricity, assumed to be 1.0 for renewable electricity (Wu *et al*., 2021b; SEAI, 2022), E_{el} is the grid electricity

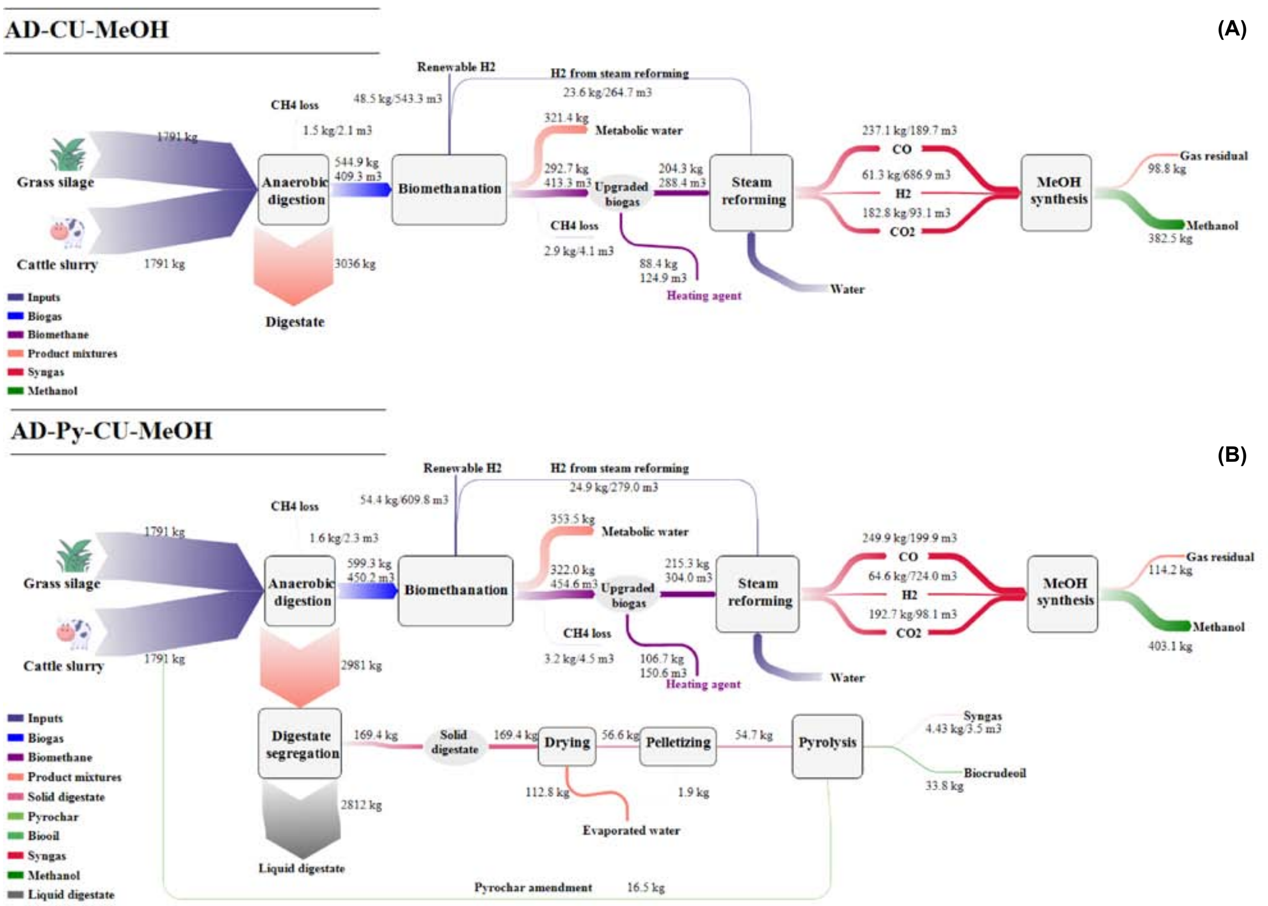


Figure 3.3. Hourly mass balance of the AD-CU-MeOH (A) and AD-Py-CU-MeOH (B) cases. CU, CO_2 utilisation via biomethanation; MeOH, methanol synthesis; Py, (solid digestate) pyrolysis.

consumed at the plant (kWh_{el}) and PEF_{el} is the primary energy factor of grid electricity, assumed to be 1.83 (SEAI, 2022).

As shown in Table 3.1, synergistic effects were obtained from integrating the pyrolysis and AD processes. The AD-Py-CU case achieved the highest plant energy efficiency, at 57.6%, followed by the AD-CU case, at 56.8%. This estimation was supported by Deng *et al*. (2020), who reported that a higher plant efficiency (59.7%) than that of AD alone (38.1%)

Table 3.1. Summary of mass and energy balances for the circular cascading bio-based systems

Plant inputs	AD-CU	AD-Py-CU	AD-CU-MeOH	AD-Py-CU-MeOH
Grass silage (kg/h)	1791	1791	1791	1791
Cattle manure (kg/h)	1791	1791	1791	1791
Renewable hydrogen (kg/h)	72.1	79.4	48.5	54.4
Electricity (kW_{el})	280.9	325.9	762.2	833.2
Plant outputs				
Biomethane (Nm^3/h)	399.9	421.5	–	–
Biomethanol (kg/h)	–	–	382.5	403.1
Biocrude oil (kg/h)[a]	–	16.2	–	16.2
Efficiency				
Plant energy efficiency (%)	56.8	57.6	32.3	33.4

[a]**Dry weight basis.**

CU, CO_2 utilisation via biomethanation; MeOH, methanol synthesis; Py, (solid digestate) pyrolysis.

was obtained when integrating AD and the pyrolysis technology. However, the plant energy efficiency decreased significantly when the targeted biofuel was biomethanol. The plant energy efficiency of the AD-CU-MeOH and AD-Py-CU-MeOH cases was 32.3% and 33.4%, respectively. The primary reason for the lower energy efficiencies of the two systems is that the steam reforming and methanol synthesis processes consumed extra electricity and biomethane to cover the energy requirements of the plant. Similar estimations were reported by Dimitriou *et al.* (2015), who evaluated a plant including AD, amine scrubber biogas upgrading, steam reforming and reverse water gas shift processes to synthesise Fischer–Tropsch fuels; here, a plant energy efficiency of 26.4% was calculated. The results indicated that, from the energy perspective, steam reforming biomethane to produce biomethanol did not benefit the overall plant performance.

3.3 The Cost in the Base and Optimistic Scenarios

Table 3.2 presents a summary of the economics of the four evaluated process designs. The minimum selling price of the targeted biofuels was calculated when the net present value was zero. The minimum selling price of biomethane for the AD-CU and AD-Py-CU cases was €1.54/Nm^3 (15.82c/kWh) and €1.59/Nm^3 (16.28c/kWh), respectively, which was comparable to the reported minimum selling price of biomethane at €1.43/Nm^3 (14.67c/kWh) when AD and biological upgrading were combined (Vo *et al.*, 2018b). However, the minimum selling price of biomethane estimated in this study was more than five times higher than the business gas price in 2020, at 2.94c/kWh natural gas (EU weighted average value) (SEAI, 2021). Incorporating solid digestate pyrolysis processes led to a higher minimum selling price of biomethane (€1.59 vs. €1.54/Nm^3), which was because of the higher equipment and utility requirements associated with the pyrolysis process. Under current conditions, integrating AD, pyrolysis and CO_2 biomethanation technologies to produce biomethane was not competitive with natural gas as of 2021. However, the war in Ukraine and the limitation on gas exports from Russia to Europe, and in particular to Germany, has changed the natural gas market significantly. The highest price for natural gas was projected to be €1.03/Nm^3 (10c/kWh) in 2022.

The minimum selling price of biomethanol for the AD-CU-MeOH and AD-Py-CU-MeOH cases was €1730/t (28.49c/kWh) and €1775/t (29.24c/kWh), respectively. The produced biomethanol was not economically competitive compared with fossil-based methanol, which has a market price of €425/t (7c/kWh, global weighted average value). The industry is unlikely (without significant policy drivers or economic stresses) to invest in a plant using biomethane as the feedstock to produce biomethanol when it can use natural gas at a lower cost. Key economic drivers need to be identified for the process designs. Again, however, the recent natural gas price rises (March/April 2022) associated with the war in Ukraine will drive up not only natural gas prices but those of the significant range of natural gas-derived products such as methanol. With climate-neutral targets there is a longer-term goal in the EU to significantly reduce and eventually eliminate fossil fuels. Both energy security (the war in Ukraine) and the climate emergency will be game-changers for the biomethane market and greatly improve the economic argument for the replacement of natural gas with biomethane (and hydrogen).

A sensitivity analysis was conducted for each evaluated process design by varying major input parameters from their base-case values. Several key parameters were considered, including capital expenditure, operating hours, discount rate, debt

Table 3.2. Summary of overall economics of the four evaluated systems

	AD-CU	AD-Py-CU	AD-CU-MeOH	AD-Py-CU-MeOH
Capital expenditure (€m)	9.24	10.05	11.31	12.22
Operating costs (€m/year)	3.11	3.42	3.15	3.46
Biomethane production (MNm^3/year)	3.17	3.34	–	–
Biomethanol production (t/year)	–	–	3029	3193
MSP of biomethane (€/Nm^3)	1.54	1.59	–	–
MSP of biomethanol (€/t)	–	–	1730	1775

CU, CO_2 utilisation; MeOH, methanol; MSP, minimum selling price (tax is excluded); Py, pyrolysis.

ratio, yearly increment in operating costs, yearly decrease in product yields, electricity, and hydrogen and grass prices. Figure 3.4 shows the dependence of the minimum selling price of targeted biofuels on the selected parameters of all four assessed process designs. The bars indicate the model parameter variances from their base-case values. Longer bars represent a higher sensitivity to a specific parameter. The capital expenditure was the second most sensitive parameter when biomethane was the targeted biofuel, but it was the most sensitive parameter when biomethanol was targeted. The minimum selling price of biofuels could be reduced by 5.8–6.6% when the capital expenditure was decreased by 20%. CO_2 biomethanation is a novel and developing technology, which is only at the beginning of its commercial application (Rafrafi *et al*., 2021). The high sensitivity to changes in capital costs highlighted the importance of scale since expanding the system capacities can reduce the capital costs per unit output of energy (Dimitriou *et al*., 2015).

For all evaluated systems, the hydrogen price was a significant parameter affecting the minimum selling price of targeted biofuels. If the hydrogen price reduced by 20% from a base of €3.4/kg hydrogen, the minimum selling price of biomethane could drop by 9.2% (the AD-CU case) or 9.3% (the AD-Py-CU case) compared with the base-case value in the two biomethane production systems, while the minimum selling price of biomethanol could decrease by 5.7% (the AD-CU-MeOH case) or 5.9% (the AD-Py-CU-MeOH case) in the two biomethanol production systems. This emphasises the importance of reducing renewable hydrogen prices with technological developments. According to the EU hydrogen strategy, the investment costs of electrolysers are expected to decrease significantly by 2030, by which time the price of renewable hydrogen could be cost competitive with fossil-based hydrogen in some regions (EU, 2020). The US Department of Energy launched an initiative in 2021 to reduce the cost of renewable hydrogen by 80% to $1/kg (€0.85/kg) within a decade. This is a very low value, equivalent to 3c per kWh of hydrogen; considering an electrolyser efficiency of 75%, this equates to a maximum price of 2.25c per $kW_{el}h$ of electricity. When we take into account the cost of the electrolysers, the price paid to electricity production is minimal. This is an issue; the cheaper the hydrogen, the lower the price paid for the electricity and the more

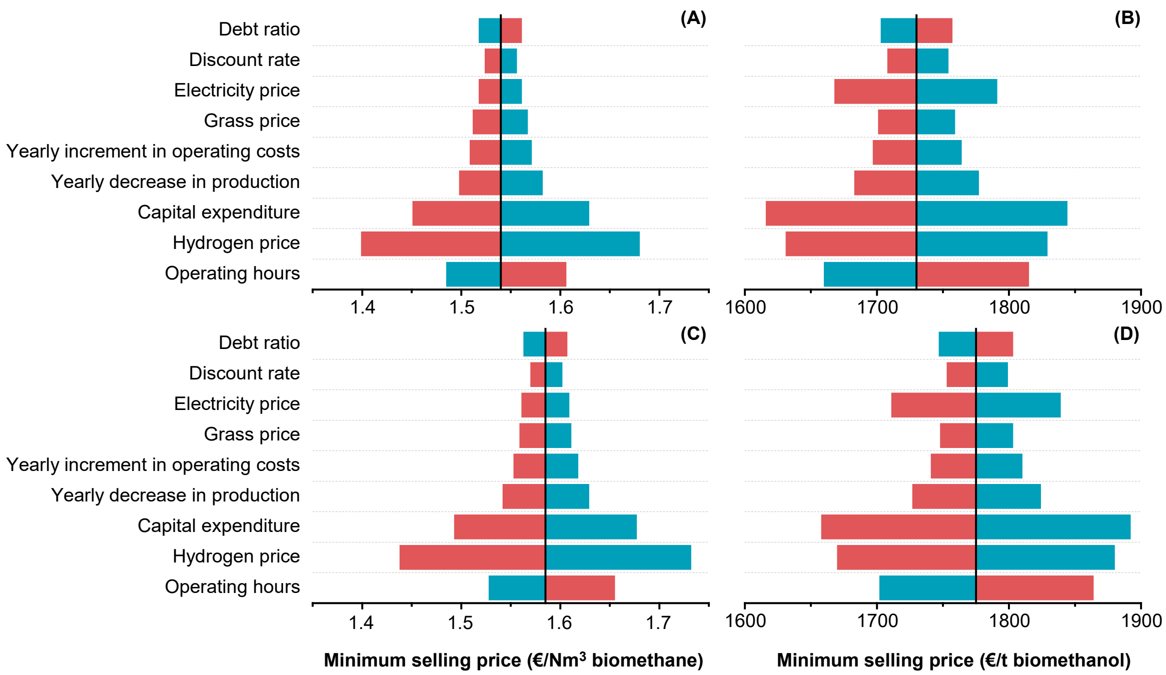


Figure 3.4. Sensitivity analysis of the minimum selling price of the targeted biofuels to variations in selected technical and economic parameters under different cases: (A) AD-CU, (B) AD-CU-MeOH, (C) AD-Py-CU and (D) AD-Py-CU-MeOH. Variations are ±20% for all parameters except operating hours, in which case it is ±10%. The red bar represents a decrease of 20% in each parameter while the blue bar represents an increase of 20% in each parameter.

challenging the financial sustainability of the renewable energy or electricity producer. In regions where energy from renewables, such as wind and solar power, is relatively low cost and produced at scale, there is potential to produce hydrogen at minimum cost associated with high load factors of electrolysis (Hydrogen Council, 2020) and through maximising the use of electricity that may otherwise be curtailed or constrained. The Hydrogen Council suggests that, under optimistic conditions, the cost of hydrogen will be reduced to \$1.2/kg (€1.02/kg) by 2030 (Hydrogen Council, 2020). Furthermore, by combining electricity from renewable sources such as wind and solar power with surplus electricity due to intermittency, the production of hydrogen can be competitive, and in an optimal scenario the cost of hydrogen is estimated in an International Energy Agency report to be as low as \$1.0–1.5/kg (€0.85–1.28/kg) (Philibert, 2017). In this context, a very optimistic future scenario was discussed in section 3.5 with consideration of renewable hydrogen at €1/kg, which is an average price for fossil-based hydrogen (Parkinson *et al*., 2019).

The operating hours were the third most sensitive parameter in all processes. A 10% increase in operating hours could reduce the minimum selling price of biofuels by 3.6–4.1%. The minimum selling price was less sensitive to the electricity price, discount rate, debt ratio, yearly increment in operating costs, yearly decrease in production and grass prices.

An optimistic scenario modifying key parameters identified in the sensitivity analysis was considered in analysing the potential economic competitiveness of biofuels compared with conventional fuels. The first factor that significantly affected the minimum selling price of biofuels was the hydrogen price. For this reason, a lower renewable hydrogen cost of €1/kg was assumed in the optimistic scenario. Another significant factor is the capital expenditure (the bigger the plant, the lower the capital costs per unit output of energy). Therefore, a larger plant capacity was assumed in the optimistic scenario. For the AD-Py-CU case, a system capacity of 19.80 MNm^3 CH_4/year, which is 5.9 times larger than that of the present study (3.34 MNm^3 CH_4/year), was considered. The large capacity was based on Electrochaea's BioCat biomethanation plant, one of the first demonstrated biomethanation plants in the world (Electrochaea, 2021). For the other three cases, the same scaling level was selected. The six-tenths factor rule was used to estimate the capital costs of the scaled-up systems, in accordance with Dimitriou *et al*. (2015), as follows:

$$C_2 = C_1 \times \left(\frac{S_2}{S_1}\right)^{0.6}, \qquad (3.2)$$

where C_1 and C_2 are the CAPEX of the base and large systems, respectively, S_1 and S_2 are the capacities of the base and large systems, respectively, and 0.6 is the scaling factor. When assuming a renewable hydrogen price of €1/kg, the operating costs for the AD-CU, AD-Py-CU, AD-CU-MeOH and AD-Py-CU-MeOH cases were 18.8%, 19.0%, 19.7% and 19.8% of the capital costs, respectively. In this study, the same contribution percentages were assumed when estimating the operating costs of the scaled-up systems.

Table 3.3 summarises the overall economics of the scaled-up systems in comparison with the base case. In the large system, the minimum selling price of biomethane was reduced by more than 62% compared with that of the base system. The minimum selling price of biomethane was the same in the two biomethane production systems, at €0.50/Nm^3 CH_4 (c5.1 /kWh), obtained from the scaled-up AD-Py-CU case. By comparison, the EU weighted average market price of natural gas was c2.94 /kWh in 2020 (July to December) (SEAI, 2021), which is still 1.7 times lower than the minimum selling price in this study. However, the scaled-up system may well be very profitable when future natural gas prices are considered. Based on Dutch TTF Gas Futures, natural gas prices are expected to be around c10/kWh in 2022 and c6.8/kWh in 2023 (ICE Endex, 2022). This indicates that biomethane from a plant including AD, CO_2 biomethanation and solid digestate pyrolysis technologies can compete against natural gas in future natural gas markets.

The minimum selling price of biomethanol for the large system was more than 2.6 times lower than that of the base system. The minimum selling price of biomethanol was €663/t MeOH, obtained from the scaled-up AD-Py-CU-MeOH case. The current market situation for methanol is €425/t in 2022 (Methanol Institute, 2022), which is 56% lower than the minimum selling price in this study (€663/t MeOH). A further increase in the system capacity along

Table 3.3. Capital expenditure and minimum selling prices of the scaled-up system in comparison with the base case

	Capital expenditure	System capacity	Minimum selling price
Base AD-CU	€9.24m	3.17 MNm³ CH_4/year	€1.54/Nm³ CH_4
Large AD-CU	€26.88m	18.79 MNm³ CH_4/year	€0.50/Nm³ CH_4
Base AD-Py-CU	€10.05m	3.34 MNm³ CH_4/year	€1.59/Nm³ CH_4
Large AD-Py-CU	€29.25m	19.80 MNm³ CH_4/year	€0.50/Nm³ CH_4
Base AD-CU-MeOH	€11.31m	3029 t MeOH/year	€1730/t MeOH
Large AD-CU-MeOH	€32.92m	17,968 t MeOH/year	€661/t MeOH
Base AD-Py-CU-MeOH	€12.22m	3193 t MeOH/year	€1775/t MeOH
Large AD-Py-CU-MeOH	€35.55m	18,938 t MeOH/year	€663/t MeOH

CU, CO_2 utilisation; MeOH, methanol; Py, pyrolysis.

with the introduction of government subsidies and incentives can benefit the economics of the proposed biomethanol production system (Dimitriou *et al*., 2015), but this is out of the scope of this study. Overall, the scaled-up biomethanol production system was not cost competitive with fossil-based methanol, but adjunct benefits such as GHG emission reductions need to be analysed to allow a full evaluation of the scaled-up biomethanol system. Again, the economics will benefit from the rise in natural gas prices.

3.4 Greenhouse Gas Emissions in the Bioeconomy Systems

The net GHG emissions for all evaluated systems are shown in Figure 3.5. For systems producing biomethane (Figure 3.5A), the highest GHG emissions came from feedstock cultivation (grass), accounting for 35.2% and 32.9% of the total GHG emissions in the AD-CU and AD-Py-CU cases, respectively. Methane loss constituted the second largest

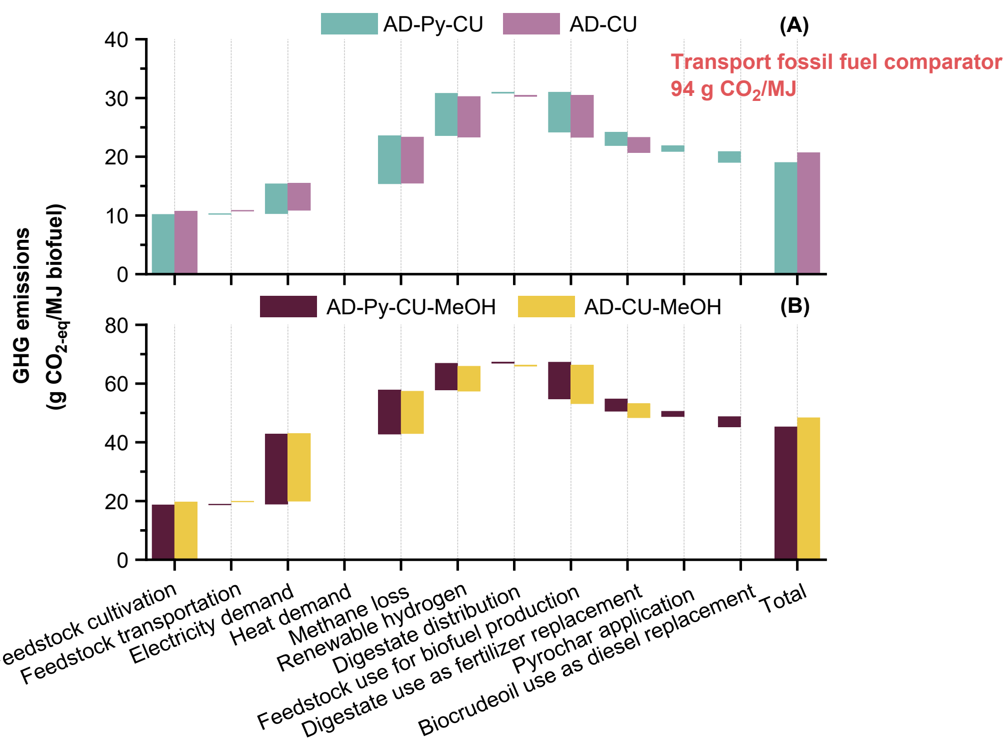


Figure 3.5. Net GHG emissions for (A) biomethane and (B) biomethanol targeted systems and the detailed breakdown of GHG emissions and savings from different categories. The fossil fuel comparator required for the transport end use is based on the RED-II (EU, 2018).

fraction of the total emissions from biomethane production systems (25.8% for the AD-CU case and 26.5% for the AD-Py-CU case) since 1% of methane loss was assumed in both the AD and the CO_2 biomethanation units. GHG emissions from renewable hydrogen contributed 22.6% and 23.2% of the total emissions in the AD-CU and AD-Py-CU cases, respectively. Even though relatively low specific emissions from renewable hydrogen were assumed (1.34 g CO_2-eq./g H_2 (Parkinson *et al.*, 2019), equivalent to 11.2 g CO_2/MJ hydrogen or 40.2 g CO_2/kWh), the large amounts of hydrogen required for CO_2 biomethanation resulted in significant GHG emissions. Electricity demand accounted for 15.2–16.4% of the total emissions from the two biomethane production systems. Among the emission savings during the process, the highest savings, of 7.18 g CO_2-eq./MJ biomethane (25.9 g CO_2/kWh) (the AD-CU case) and 6.81 g CO_2-eq./MJ biomethane (24.5 g CO_2/kWh) (the AD-Py-CU case), resulted from the use of slurry for biomethane production (e_{sca}). Considering the benefits of emission savings from the use of digestate as a fertiliser replacement, the net GHG emissions of the AD-CU case were 20.69 g CO_2-eq./MJ biomethane (74.5 g CO_2/kWh). This result is comparable to those reported in the literature, ranging from 6 to 29 g CO_2-eq./MJ biomethane (21.6 to 104.4 g CO_2/kWh) (Parra *et al.*, 2017), in which the wind energy-sourced hydrogen was used to upgrade the biogas. For the AD-Py-CU case, emission savings from the pyrolysis process, including the pyrochar application to the land (1.01 g CO_2-eq./MJ biomethane) and the use of biocrude oil as a diesel replacement (1.88 g CO_2-eq./MJ biomethane), offset the high emissions from the heat consumption of drying solid digestate, leading to lower net GHG emissions of 19.01 g CO_2-eq./MJ biomethane (68.4 g CO_2/kWh).

In contrast to biomethane production systems, in biomethanol production systems electricity demand constituted the largest fraction of GHG emissions (Figure 3.5B), making up 34.7% and 35.5% of the total GHG emissions in the AD-CU-MeOH and AD-Py-CU-MeOH cases, respectively. The carbon intensity of grid electricity was assumed to be 230.7 g CO_2-eq./kWh (EEA, 2021). The high electrical energy demand for methanol synthesis was the main reason for such significant GHG emissions. Emissions from grass cultivation and methane loss were the second and third largest contributors to the total. Net GHG emissions of the AD-CU-MeOH case were 48.36 g CO_2-eq./MJ biomethanol (174.1 g CO_2/kWh) taking into consideration emission savings from the feedstock used for biomethanol production and from the use of digestate as a fertiliser replacement. Meanwhile, the AD-Py-CU-MeOH case achieved net GHG emissions of 45.28 g CO_2-eq./MJ biomethanol (163.0 g CO_2/kWh) when the benefits of emission savings from the pyrochar and biocrude oil were further considered.

As shown in Figure 3.5, the integration of the solid digestate pyrolysis process proved to be carbon beneficial to the bioenergy systems since lower net GHG emissions were obtained in all pyrolysis-incorporated cases. Combining AD, CO_2 biomethanation and pyrolysis processes, maximum CO_2 sequestration and biomethane production can be achieved (Wu *et al.*, 2021b), leading to a more carbon beneficial bioenergy system. Compared with the fossil fuel comparator (FFC) required for the transport end use, the biomethane produced from the AD-Py-CU system had a significantly lower carbon intensity, since 73.31 g CO_2-eq./MJ biomethane (263.9 g CO_2/kWh) can be abated when biomethane is used as the transport fuel (20.69 vs. 94 g CO_2-eq./MJ). Based on the RED-II sustainability criteria, the allowed emissions of biofuels for transport end use are 32.9 g CO_2-eq./MJ to meet a 65% reduction in GHG emissions in 2026 ($94 \times (1 - 65\%)$) (EU, 2018; Long *et al.*, 2021). The net GHG emissions of biomethanol in the AD-Py-CU-MeOH system were 45.28 g CO_2-eq./MJ MeOH (163.0 g CO_2/kWh), lower than those in the non-pyrolysis-incorporated system (48.36 g CO_2-eq./MJ MeOH, or 174.1 g CO_2/kWh). However, the AD-Py-CU-MeOH system did not meet the sustainability criteria even when a lower carbon intensity biomethane was used as the raw feedstock for methanol synthesis. The electricity demand made up the largest fraction of GHG emissions for biomethanol production systems. As discussed previously, high electricity consumption can largely be attributed to the energy required for cooling during methanol synthesis. Lower cooling energy demand can be achieved with optimised heat exchanger designs (Pérez-Fortes *et al.*, 2016). It has been suggested (Vo *et al.*, 2018a) that system optimisation, for example by minimising methane loss and using electricity from low GHG emission sources, would help reduce the total emissions of bioenergy systems

(Vo *et al*., 2018a). Regardless of the optimisation of electricity demand, if there were no methane loss in the CO_2 biomethanation process, and the carbon intensity of electricity were reduced to 109 g CO_2-eq./kWh (which was the carbon intensity of the much lauded electricity system in Denmark in 2020 (EEA, 2021)), the net GHG emissions of the AD-Py-CU-MeOH system could be reduced to 22.56 g CO_2-eq./MJ MeOH, which would meet the sustainability criteria required by the RED-II. These results indicate that the use of biomethane produced by the proposed system as a transport fuel is sustainable, but other strategies for the use of biomethanol in transport, such as minimising methane loss and using electricity with low GHG emission intensity, are needed to reduce the carbon intensity of such biomethanol.

3.5 Marginal Abatement Cost Analysis

Figure 3.6 shows the discounted marginal abatement cost curve of the evaluated systems under optimistic scenarios in which the system capacity was scaled up 5.9 times and the corresponding capital expenditure was estimated using the six-tenths factor rule. For replacing fossil fuels in transport, the AD-CU-MeOH system had the potential to reduce GHG emissions by 0.22 Mt CO_2-eq., while incorporating the pyrolysis process could abate 13.6% more GHG emissions, at 0.25 Mt CO_2-eq. in the AD-Py-CU-MeOH system. In the model using biomethane as the alternative to transport fossil fuels, similar environmental benefits of the pyrolysis technology were obtained; the AD-Py-CU system reduced GHG emissions by 7.6% more than the AD-CU system (0.71 vs. 0.66 Mt CO_2-eq.).

The impact of the hydrogen price is significant in the assessment of the marginal abatement cost. At a renewable hydrogen cost of €3.4/kg H_2 (Figure 3.6A), the GHG abatement cost was assessed at €262.4/t CO_2-eq. in the AD-CU-MeOH case and €253.5/t CO_2. in the AD-Py-CU-MeOH case. Reducing the renewable hydrogen cost to €1.0/kg H_2 significantly lowered the abatement cost of the AD-CU-MeOH design to €145.0/t CO_2-eq. (Figure 3.6B). The pyrolysis-incorporated system dropped to €136.5/t CO_2-eq. These values for the methanol systems give marginal abatement costs in excess of current and projected carbon credits, at €33.5/t CO_2 and €80/t CO_2, respectively (EPA, 2021; Irish Tax and Customs, 2022). This indicates that unless significant reductions are achieved in the GHG savings, along with the introduction of government subsidies and incentives, biomethanol produced from these systems will not be desirable in the long term.

When the renewable hydrogen cost was considered to be €3.4 kg H_2 (Figure 3.6A), incorporating the solid digestate pyrolysis process did not lead to clear climate and economic benefits for the system since the abatement costs were practically the same. When the methane selling price increased to €47.5 MWh (2024 price), the levelised cost of abatement of the two biomethane production systems ranged from €62.7 to €64.3/t CO_2-eq., which is lower than the projected carbon tax for 2030 (€80/t CO_2) resulting from the new climate mitigation policies and measures. This indicates that the two biomethane production systems could be cost desirable even at a hydrogen cost of €3.4/kg H_2.

Taking into consideration a low hydrogen cost of €1.0/kg H_2, lower abatement costs were achieved in the AD-Py-CU system when biomethane was sold at €20.5/MWh (2021 price) and €36.0/MWh (2025 price). At a sale price of biomethane of €20.5/MWh, the levelised cost of abatement of the two biomethane production systems ranged from €66.3 to €67.3/t CO_2-eq., which is higher than the current carbon credits but lower than the projected carbon credits by 2030, indicating bright prospects for biomethane production in the longer term (Figure 6.9B). An increase in the gas selling price to €106.1/MWh in 2022 significantly improved the feasibility of the proposed bioenergy system. However, a slightly higher abatement cost was achieved in the AD-Py-CU system (–€111.1/t CO_2-eq.) than in the AD-CU system (–€114.2/t CO_2-eq.), which was due to the large amount of produced biomethane consumed to dry the solid digestate as required by the pyrolysis process, thus reducing the biomethane revenues when the methane selling price was high. The AD-Py-CU and AD-CU systems were still cost beneficial when the future gas selling prices of 2023, 2024 and 2025 were considered since the abatement costs ranged from –€35.3 to €31.2/t CO_2-eq., lower than the current and future carbon credits.

As can be seen in Figure 3.6, regardless of the targeted biofuels, the pyrolysis-incorporated systems compare very well with the non-pyrolysis-incorporated systems, indicating the economic and environmental

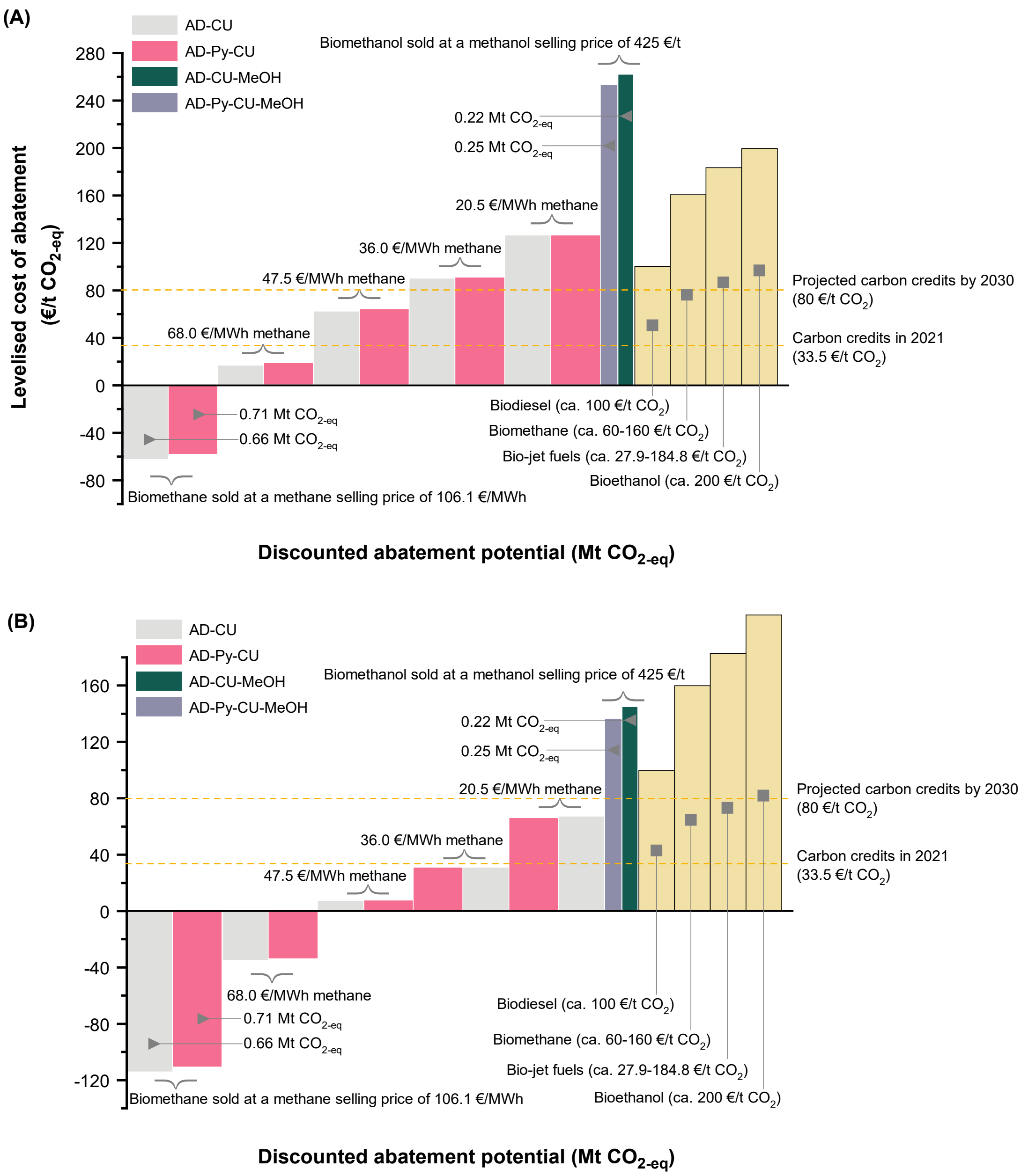


Figure 3.6. Marginal abatement cost curve of four scaled-up bioeconomy systems with renewable hydrogen at (A) €3.4/kg H_2 and (B) €1.0/kg H_2. The abatement costs of other alternative technologies are also indicated. The width of the bar represents the abatement potential of each system. Please note that GHG reductions from the cited alternative technologies were not available. Abatement costs below the carbon credits indicate that the system is cost desirable. The levelised costs of abatement of biomethane (IEA, 2020), biodiesel (Teagasc, 2019), bio-jet fuels (Baral *et al.*, 2019) and bioethanol (Teagasc, 2019) were cited from other studies. Current carbon credits (2021) were obtained from the government of Ireland (Irish Tax and Customs, 2022) and projected carbon credits by 2030 were sourced from the Environmental Protection Agency (EPA, 2021).

advantages of the pyrolysis technology in the circular cascading bioeconomy system. These results suggest that the proposed systems could be implemented as a circular bioeconomy system for biomethane production as a result of its benefits on cost and sustainability, but the methane selling price and the price of green hydrogen are major influencers of such benefits.

3.6 Conclusion

The evaluated systems considered AD and CO_2 utilisation (CU) via biomethanation units to produce biomethane from grass silage, cattle slurry and renewable hydrogen, or biomethanol by incorporating subsequent biomethane steam reforming and methanol synthesis (MeOH) processes. Solid digestate pyrolysis technology (Py) was incorporated to investigate its effects on the technoeconomic and environmental benefits of the system.

The sensitivity analysis revealed that the minimum selling prices of biofuels were mainly affected by variations in hydrogen prices and capital costs. A comparison of the optimistic scenario (larger capacity and a hydrogen price of €1/kg) with the base case (lower capacity and a hydrogen price of €3.40/kg) for the pyrolysis-incorporated systems showed a reduction in the minimum selling price from €1.56 to €0.48/Nm^3 biomethane (AD-Py-CU case) and from €1744 to €638/t biomethanol (AD-Py-CU-MeOH case), respectively.

Environmental analysis showed that the net GHG emissions of the pyrolysis-incorporated systems were 21.69 g CO_2-eq./MJ biomethane and 45.28 g CO_2-eq./MJ biomethanol. This would suggest that biomethane is sustainable and biomethanol is not when using the sustainability criteria in the RED-II when assessing renewable transport fuels. When hydrogen was purchased at €1 /kg, the marginal abatement cost for the AD-Py-CU case was –€111.1/t CO_2-eq. with a contract gas price of €1.03/Nm^3. When hydrogen was purchased at €3.40/kg, this cost rose to –€58.2/t CO_2-eq. When methanol was sold at €425/t (global weighted average value), the abatement cost of the AD-Py-CU-MeOH case (for H_2 at €1/kg) was €136.5/t CO_2-eq.; this is higher than the carbon credit at €33.5/t CO_2. The integration of AD, CO_2 biomethanation and pyrolysis technologies could be economically and environmentally compelling to produce biomethane, while, for biomethanol production, the minimisation of methane loss and the use of low-carbon electricity were necessary to lower the abatement cost.

4 Key Findings, Policy Implications and Recommendations

4.1 Key Research Findings

Biofuel production in an integrated circular cascading bio-based system, including for AD, pyrolysis and power-to-gas technologies, was assessed (Figure 4.1).

The laboratory work investigated a range of applications of carbonaceous materials in the proposed systems, and the primary learning points are described below.

Anaerobic digestion of thin stillage after an acidic shock improved with addition of graphene. The application of graphene addition at 1 g/L was shown to be beneficial for stabilising an anaerobic process under stress from excessive loading leading to an acidic stress on the biological process. The addition of graphene increased the biomethane yield by 11%, postulated as due to induced DIET. By comparison, pyrochar amendment reduced the lag phase time by 12–18%, while not displaying benefits in biomethane yield.

Biological CO_2 methanation systems under stress from intermittent loading associated with hydrogen production for variable renewable electricity improved with addition of graphene. Graphene addition at 1 g/L had stabilisation effects on the biomethanation process with stop–start operation associated with intermittent gas supply, as would be likely in the real-world application of such a system. The laboratory work mimicked intermittent gas injection to create such a stress, and the system with graphene addition enhanced the gas conversion efficiency by 18% and production rate by 267% compared with the control.

Addition of pyrochar improved microbial medium-chain fatty acid production. In this work pyrochar addition was shown to be preferable to graphene addition. Pyrochar addition increased the MCFA yield by 115% compared with the group without addition. Graphene addition led to a comparable MCFA yield to that from pyrochar amendment but with a significant longer lag time. It is postulated that the characteristics of both high electrical conductivity and abundant surface redox groups add to the enhancing effect.

A technoeconomic-environmental analysis was carried out on circular cascading bioeconomy systems for the production of biomethane or biomethanol (Figure 4.2).

The primary findings are outlined below.

The minimum selling prices of biofuels from integrated systems were primarily affected by

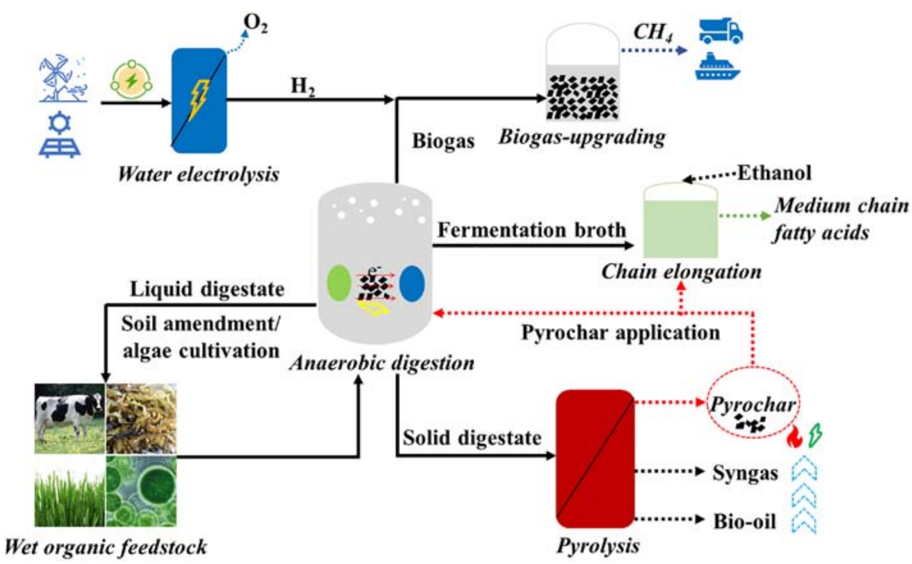


Figure 4.1. Biofuel production in an integrated circular cascading bio-based system, including for AD, pyrolysis and power-to-gas technologies.

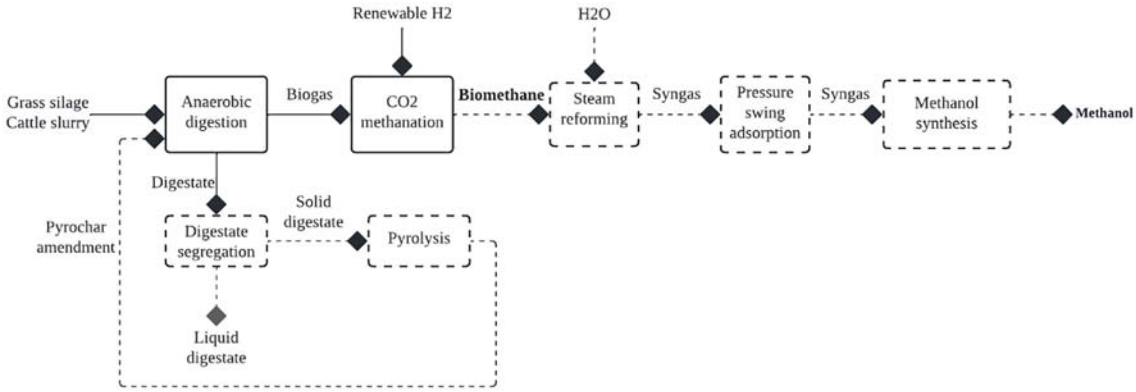


Figure 4.2. An overview of the circular cascading bioeconomy systems for the production of biomethane or biomethanol (dashed lines represent variable processes/steps in different design cases).

variations in hydrogen prices and capital costs. For biomethane production through the pyrolysis incorporated system (AD-Py-CU case), the minimum selling price was €1.56 Nm^3 biomethane (15.6c/kWh) under the base scenario of a lower capacity and a hydrogen price of €3.40/kg H_2 (10.2c/kWh); this would be reduced to €0.48/Nm^3 biomethane (4.8c/kWh) with a higher capacity and a hydrogen price of €1/kg (3.0c/kWh, optimistic scenario). For biomethanol production (AD-Py-CU-MeOH case), the minimum selling price could be reduced from €1744/t biomethanol (28.7c/kWh) under the base scenario to €638/t biomethanol (10.5c/kWh) under the optimistic scenario.

Biomethane can meet the sustainability criteria for renewable transport fuel, while biomethanol will struggle to do so. The carbon footprint of the pyrolysis-incorporated systems was 21.69 g CO_2-eq./MJ biomethane and 45.28 g CO_2-eq./MJ biomethanol, respectively. Compared with the allowed emissions of biofuels for transport end use outlined in the RED-II (32.9 g CO_2-eq./MJ), biomethane meets the sustainability criteria, whereas biomethanol does not. Other strategies, such as minimising methane loss and using electricity with lower GHG emission intensity, are needed to further reduce the carbon intensity of biomethanol.

The cost of CO_2 reduction (marginal abatement cost) was beneficial for biomethane systems, with hydrogen purchase price and methane selling price of greatest impact. Marginal abatement costs that are negative or at least lower than the proposed carbon tax or credit are deemed advantageous. For biomethane production, when hydrogen was purchased at €1/kg (optimistic future scenario) the marginal abatement cost for the AD-Py-CU case was –€111.1/t CO_2-eq. with a contract gas price of €1.03/Nm^3 (associated with the war in Ukraine and the energy security emergency). The marginal abatement cost rose to –€58.2/t CO_2-eq. when hydrogen was purchased at €3.40/kg; this is still very favourable. However, for biomethanol production, when biomethanol was sold at €425/t (global weighted average value), the abatement cost of the AD-Py-CU-MeOH case (for H_2 at €1/kg) was €136.5/t CO_2-eq., which is higher than the carbon credit at €33.5/t CO_2.

4.2 Policy Implications

The 2021 Climate Action Plan for Ireland has set GHG emission reduction targets of 51% by 2030 (with 2018 as the base year) and net-zero emissions no later than 2050. Within this target, the emissions reduction by 2030 is set in the range 42–50% for transport and 22–30% for agriculture. However, a newly launched EPA report suggests that the overall GHG emission reduction in Ireland would be only 28% (against 51%) by 2030 if all the measures from the 2021 Climate Action Plan (EPA, 2022) were satisfied; the assessment indicates that implementation of all climate plans and policies, plus further new measures, are needed for Ireland to achieve the ambitious target set in the Climate Action Plan 2021, with emphasis on the following five policy objectives: (1) sustainable agriculture, (2) circular economy and bioeconomy, (3) renewable energy, (4) networks for nature and (5) marine and coastal impacts of climate change.

The present report proposes a low-carbon AD-centred cascading bioeconomy system. With the integration of pyrolysis for biochar production (with its associated potential for negative emission technology), the system can deliver advanced biofuels for transport or high-value biochemicals and produce biofertiliser (minimising the requirement for fossil-fuel-based fertilisers with their associated emissions) and the aforementioned biochar while treating a variety of organic wastes (that may otherwise produce fugitive methane emissions and have an impact on water quality). The proposed system can contribute to meeting the targets in the Climate Action Plan 2021 of Ireland in the following areas.

4.2.1 Circular bioeconomy

The proposed system shown in Figure 4.1 is an integrated circular cascading bio-based system including for AD, pyrolysis and power-to-gas technologies. The system can produce advanced gaseous transport fuel (biomethane) from a wide array of advanced feedstocks as defined in the RED-II (such as perennial ryegrass and animal manures). Other products may include biochemicals, biofertiliser and biochar depending on the system set-up. Surplus renewable electricity to produce hydrogen (termed a gaseous fuel from non-biological origin in the RED-II) may be utilised as a means of upgrading biogas and using CO_2 to increase methane output by, typically, 70% via the Sabatier equation ($4H_2 + CO_2 = CH_4 + 2H_2O$). This is a bioenergy and carbon capture and use (BECCU) system. As a carbonaceous material, biochar can also be circulated back to the digester to improve conversion efficiency via DIET; this can increase biological stability and increase the rate and overall yield of biomethane production. It may also be used to improve the stability of the *ex situ* biomethane system if this is under stress from stop–start operations associated with hydrogen production from intermittent renewable electricity. After they are used to enhance the DIET pathway, biochar and biofertiliser can be returned to the soil to increase the soil's organic content, increase photosynthesis and increase the yield of crops (such as grass silage) that then may be returned as feed to the digester (this is itself a negative emission technology).

4.2.2 Renewable energy and transport

Using the potential resources of animal manure, grass silage and renewable hydrogen from renewable electricity in Ireland, the proposed system may, according to calculations based on a Sustainable Energy Authority Ireland report, produce in the order of 1 billion m^3 of renewable biomethane by 2035 (SEAI, 2016). The proposed resource of grass silage of 1200 kt of dry solids per annum is equivalent to c. 170,800 ha or 3.9% of agricultural land, while the resource of slurry proposed (2400 kt) is equivalent to about 7% of the cattle herd or 25% of the dairy herd (see Box 4.1). An EPA report estimated that the CO_2 emissions from the transport sector would be 10.4 million tonnes (Mt) CO_2-eq. by 2030 in Ireland (EPA, 2022). If the methane produced as per the SEAI report (including for digestion of grass silage and slurry coupled with biomethanation) were used for transport (see Box 4.1), it could fuel approximately 18,295 trucks with an annual running distance of 120,000 km (3.8 kWh/km) (Gray *et al*., 2021), or 23,792 buses with an annual running distance of 54,000 km (0.65 kWh/km) (DTTS, 2019). This should reduce emissions by 2.2 Mt CO_2-eq. per year when replacing diesel consumption in transport; this equates to about 21% of the transport-related CO_2 emissions in 2020.

4.2.3 Sustainable agriculture

GHG emissions from the agriculture sector in Ireland arise from enteric fermentation (c. 61%), manure management (c. 12%) and nitrogen and urea application to soil (c. 25%) (EPA, 2022). Through AD of animal manure (2.4 Mt in 2035) (see Box 4.1), the core element of the proposed bioenergy system, the methane emissions avoided could lead to an annual emissions reduction of 0.13 Mt CO_2-eq. (see Box 4.1). Thus, the circular cascading bioeconomy system properly manages manure and produces a more effective biofertiliser than raw slurry while minimising fugitive methane emissions from open slurry holding tanks. The biomethane produced may be used on site for combined heat and power or injected into the gas grid for transport or heat production elsewhere on the gas grid, providing extra income for farmers while reducing the carbon footprint of the farm. Moreover, the digestate from AD can be used as a biofertiliser, an eco-friendly replacement for chemical fertilisers, reducing the emissions associated with the application of fossil-based nitrogen and urea. The system may produce 280 kt of biochar from solid digestate in 2035, which can potentially store about 0.57 Mt CO_2-eq. (see Box 4.1). The biochar can also

Box 4.1. Methane production and methane-powered transport in Ireland by 2035

Table 4.1. Potential of biogas production in the proposed system with the resource as suggested by SEAI (2016)

Feedstock	Resource (kt, fresh matter)[a,b]	Biomethane production potential from AD ($\times 10^6$ m^3)[c]	Biogas production potential ($\times 10^6$ m^3)	Biogas production (ktoe)	Enhanced biomethane production potential ($\times 10^6$ m^3)[d]	Energy production ($\times 10^6$ kWh)[e]
Grass silage[a]	1200 (dry matter)	441.6	736.0	379.7	771.3	7713
Animal manure[b]	2400 (as is)	38.6	64.3	33.2	67.3	673
Total	–	480.2	800.3	412.9	838.7	8387

[a]Equivalent to 170,800 ha of land at 7 t dry solids production per hectare per annum or 3.9% of all agricultural land (4.44 million ha) in Ireland.

[b]Say 1.5 t of fresh matter per dairy cow per month at 4 months' storage is equivalent to 6 t per cow. This quantity of manure is equivalent to 400,000 dairy cows; this is 7% of the total cattle herd or 25% of the dairy herd. The solid content of animal manure is assumed as 8.75%.

[c]Say 1,200,000 t dry solids, of which 92% is volatile solids, and methane yield is 400 m^3 CH_4/t VS = 441.6 × 10^6 m^3 CH_4 (Wall *et al.*, 2013). Assuming that the content of methane and CO_2 is 60% and 40%, respectively, the biogas production is 736 × 10^6 m^3.

[d]Assuming that the biochar addition increased the methane production by 10% and the conversion efficiency of CO_2 and H_2 to CH_4 is 97%. For example, the total biomethane from grass silage is calculated as [736 × 60% × (100% + 10%)] + [736 × 40% × 97%] = 771.3 × 10^6 m^3.

[e]The energy content of methane is assumed as 10 kWh/m^3.

Calculations

1. Calculations of numbers of trucks and buses fuelled by biomethane produced from the system:

- For trucks: methane-fuelled internal combustion engine (energy efficiency) = 3.82 kWh/km; the distance one truck travels a year = 120,000 km/year; energy consumption for one truck travels a year = 458,400 kWh/year (Gray *et al.*, 2021).
  - Number of trucks that can be fuelled from biomethane produced from the system = 8387 × 10^6 kWh/(458,400 kWh/year) = 18,295 trucks.
- For buses: energy efficiency = 6.53 kWh/km; the distance one bus travels a day = 150 km; the distance one bus travels a year = 54,000 km/year; energy consumption for one bus travels a year = 352,502.8 kWh/year (DTTS, 2019).
  - Number of buses that can be fuelled from biomethane produced from the system = 8387 × 10^6 kWh/(352,502.8 kWh/year) = 23,792 buses.

2. Calculation of GHG emissions reduction by replacing diesel with methane in transport:

- 8387 × 10^6 kWh × 263.9 gCO_2/kWh = 2.2 million tonnes CO_2.

3. Calculation of methane avoided by managing animal manure (the avoided CO_2 emissions from untreated slurry is suggested as 54 kg CO_2/t fresh manure (EU, 2018)):

- 2400 kt manure × 54 kg CO_2/t fresh manure (EU, 2018) = 129.6 × 10^6 kg CO_2 = 0.13 Mt CO_2.

Box 4.1. Continued

4. Calculation of CO_2 stored in the biochar produced from the system:

- Biochar production is assumed as 20% from the dry matter of feedstocks, and the carbon content in biochar is assumed as 55%. CO_2 fixed in biochar: 1 t C = 3.67 t of CO_2.
- CO_2 stored in grass silage-derived biochar = 1200 kt dry solids × 20% to biochar × 55% carbon × 3.67 tCO_2/t C= 484.4 ktCO_2 = 0.48 MtCO_2.
- CO_2 stored in manure-derived biochar = 2400 kt × 8.75% dry solids × 20% carbon × 55% carbon to biochar × 3.67 tCO_2/t C = 84.4 ktCO_2 = 0.08 MtCO_2.
- CO_2 fixed in biochar in total = 0.48 Mt + 0.08 Mt = 0.57 Mt CO_2.

be applied to soil to increase the soil organic content, enhancing the growth of plants or crops with increased photosynthesis capacity. The modelled system offers a reduction in the carbon footprint of farming and a more sustainable agriculture system with improved soil quality and increased crop yields.

4.3 Recommendations and Outlook

This report has proposed systems that integrate the decarbonisation of agriculture and fuel. The potential of circular cascading bioeconomy systems to produce sustainable biofuel production has been highlighted, with enhanced performance associated with strong synergy and complementarity between different components of the system. Not all of the range of components in the system are commercially available and nor are any such integrated systems in operation. The carbonaceous material amendment has shown to be promising in enhancing the stability and performance of AD, CO_2 biomethanation and microbial chain elongation processes; however, it could not be said to be a mature technology. The following recommendations are made to further advance the potential commercialisation of such systems, creating opportunities for future research.

- Further work is needed to identify the quantitative correlations between the properties of pyrochar and the enhanced biological stability and productivity in the anaerobic digestion system. This would provide guidance and potentially standard operating procedures for tailoring pyrochar's characteristics to achieve maximum benefits in terms of reducing digestion lag time and promoting biomethane production, thereby reducing the cost of the bespoke AD systems.
- Research is needed to investigate combining pyrochar-mediated chain elongation systems with inline product extraction technologies to enable the continuous production of large amounts of MCFAs without significant inhibition of microbial activity. A comprehensive technoeconomic analysis (TEA) of the fermentation-based system incorporating inline product extraction and solid digestate pyrolysis technologies for MCFA production is essential for assessing the economic and environmental sustainability of such systems and identifying potential bottlenecks in commercial practice.
- A detailed life cycle assessment (LCA) needs to be carried out to evaluate the overall potential of the proposed system incorporating AD, CO_2 biomethanation and solid digestate pyrolysis technologies to produce biomethane or biomethanol, biofertiliser and biochar. TEA and LCA studies of the proposed systems with alternative configurations using different AD feedstocks need to be performed. The marginal abatement cost presented per configuration could be expanded to assess the optimal applications of the proposed bio-based system. This could be accompanied by multi-criteria analysis methodologies to assess the optimal solutions for bespoke applications.

References

Alamia, A., Magnusson, I., Johnsson, F. and Thunman, H., 2016. Well-to-wheel analysis of bio-methane via gasification, in heavy duty engines within the transport sector of the European Union. *Applied Energy* 170: 445–454.

Angenent, L.T., Richter, H., Buckel, W., Spirito, C.M., Steinbusch, K.J.J., Plugge, C.M., Strik, D.P.B.T.B., Grootscholten, T.I.M., Buisman, C.J.N. and Hamelers, H.V.M., 2016. Chain elongation with reactor microbiomes: open-culture biotechnology to produce biochemicals. *Environmental Science & Technology* 50: 2796–2810.

Bao, S., Wang, Q., Zhang, P., Zhang, Q., Wu, Y., Li, F., Tao, X., Wang, S., Nabi, M. and Zhou, Y., 2019. Effect of acid/ethanol ratio on medium chain carboxylate production with different VFAs as the electron acceptor: insight into carbon balance and microbial community. *Energies* 12: 3720.

Baral, N.R., Kavvada, O., Mendez-Perez, D., Mukhopadhyay, A., Lee, T.S., Simmons, B.A. and Scown, C.D., 2019. Techno-economic analysis and life-cycle greenhouse gas mitigation cost of five routes to bio-jet fuel blendstocks. *Energy & Environmental Science* 12: 807–824.

Barua, S. and Dhar, B.R., 2017. Advances towards understanding and engineering direct interspecies electron transfer in anaerobic digestion. *Bioresource Technology* 244: 698–707.

Barua, S., Zakaria, B.S. and Dhar, B.R., 2018. Enhanced methanogenic co-degradation of propionate and butyrate by anaerobic microbiome enriched on conductive carbon fibers. *Bioresource Technology* 266: 259–266.

Bassani, I., Kougias, P.G., Treu, L. and Angelidaki, I., 2015. Biogas upgrading via hydrogenotrophic methanogenesis in two-stage continuous stirred tank reactors at mesophilic and thermophilic conditions. *Environmental Science & Technology* 49: 12585–12593.

Bhagia, S., LI, H.J., GAO, X.D., Kumar, R. and Wyman, C.E., 2016. Flowthrough pretreatment with very dilute acid provides insights into high lignin contribution to biomass recalcitrance. *Biotechnology for Biofuels* 9.

Cao, L., Cox, C.D. and He, Q., 2021. Patterns of syntrophic interactions in methanogenic conversion of propionate. *Applied Microbiology and Biotechnology* 105: 8937–8949.

Cheng, Q.W., De Los Reyes, F.L. and Call, D.F., 2018. Amending anaerobic bioreactors with pyrogenic carbonaceous materials: the influence of material properties on methane generation. *Environmental Science-Water Research & Technology* 4: 1794–1806.

Coma, M., Vilchez-Vargas, R., Roume, H., Jauregui, R., Pieper, D.H. and Rabaey, K., 2016. Product diversity linked to substrate usage in chain elongation by mixed-culture fermentation. *Environmental Science & Technology* 50: 6467–6476.

Cruz Viggi, C., Rossetti, S., Fazi, S., Paiano, P., Majone, M. and Aulenta, F., 2014. Magnetite particles triggering a faster and more robust syntrophic pathway of methanogenic propionate degradation. *Environmental Science & Technology* 48: 7536–7543.

Dang, Y., Sun, D., Woodard, T.L., Wang, L.-Y., Nevin, K.P. and Holmes, D.E., 2017. Stimulation of the anaerobic digestion of the dry organic fraction of municipal solid waste (OFMSW) with carbon-based conductive materials. *Bioresource Technology* 238: 30–38.

De Leeuw, K.D., Buisman, C.J.N. and Strik, D.P.B.T.B., 2019. Branched medium chain fatty acids: Iso-caproate formation from iso-butyrate broadens the product spectrum for microbial chain elongation. *Environmental Science & Technology* 53: 7704–7713.

Dehhaghi, M., Tabatabaei, M., Aghbashlo, M., Kazemi Shariat Panahi, H. and Nizami, A.-S., 2019. A state-of-the-art review on the application of nanomaterials for enhancing biogas production. *Journal of Environmental Management* 251: 109597.

Deng, C., Lin, R., Kang, X., Wu, B., O'Shea, R. and Murphy, J.D., 2020. Improving gaseous biofuel yield from seaweed through a cascading circular bioenergy system integrating anaerobic digestion and pyrolysis. *Renewable and Sustainable Energy Reviews* 128: 109895.

Deng, C., Lin, R., Kang, X., Wu, B., Wall, D.M. and Murphy, J.D., 2021. What physicochemical properties of biochar facilitate interspecies electron transfer in anaerobic digestion: a case study of digestion of whiskey by-products. *Fuel* 306: 121736.

Dereli, R.K., Van Der Zee, F.P., Heffernan, B., Grelot, A. and Van Lier, J.B., 2014. Effect of sludge retention time on the biological performance of anaerobic membrane bioreactors treating corn-to-ethanol thin stillage with high lipid content. *Water Research* 49: 453–464.

Dimitriou, I., García-Gutiérrez, P., Elder, R.H., Cuéllar-Franca, R.M., Azapagic, A. and Allen, R.W.K., 2015. Carbon dioxide utilisation for production of transport fuels: process and economic analysis. *Energy & Environmental Science* 8: 1775–1789.

DTTS (Department of Transport, Tourism and Sport), 2019. *Report on Diesel-and Alternative-Fuel Bus Trials*. DTTS.

Du, J.H., Zhao, L., Zeng, Y., Zhang, L.L., Li, F., Liu, P.F. and Liu, C., 2011. Comparison of electrical properties between multi-walled carbon nanotube and graphene nanosheet/high density polyethylene composites with a segregated network structure. *Carbon* 49: 1094–1100.

Duber, A., Jaroszynski, L., Zagrodnik, R., Chwialkowska, J., Juzwa, W., Ciesielski, S. and Oleskowicz-Popiel, P., 2018. Exploiting the real wastewater potential for resource recovery – n-caproate production from acid whey. *Green Chemistry* 20: 3790–3803.

Duber, A., Zagrodnik, R., Chwialkowska, J., Juzwa, W. and Oleskowicz-Popiel, P., 2020. Evaluation of the feed composition for an effective medium chain carboxylic acid production in an open culture fermentation. *Science of The Total Environment* 728: 138814.

EASAC (European Academies Science Advisory Council), 2018. *Negative Emission Technologies: What Role in Meeting Paris Agreement Targets?* EASAC. Available online: https://easac.eu/fileadmin/PDF_s/reports_statements/Negative_Carbon/EASAC_Report_on_Negative_Emission_Technologies.pdf (accessed 23 March 2022).

EEA (European Environment Agency), 2021. *Greenhouse Gas Emission Intensity of Electricity Generation in Europe.* EEA. Available online: https://www.eea.europa.eu/ims/greenhouse-gas-emission-intensity-of-1 (accessed 20 February 2022).

Electrochaea, 2021. *Electrochaea Data Sheet*. Electrochaea. Available online: https://www.electrochaea.com/press-resources/ (accessed 20 February 2022).

EPA (Environmental Protection Agency), 2021. *Ireland's Greenhouse Gas Emissions Projections 2020–2040.* EPA, Johnstown Castle, Ireland. Available online: https://www.epa.ie/publications/monitoring--assessment/climate-change/air-emissions/EPA-Irelands-Greenhouse-Gas-Emissions-Projections-report-2020–2040v2.pdf (accessed 18 April 2022).

EPA (Environmental Protection Agency), 2022. *Ireland's Greenhouse Gas Emissions Projections 2021–2040*. EPA, Johnstown Castle, Ireland.

Eriksson, O., Jonsson, D. and Hillman, K., 2016. Life cycle assessment of Swedish single malt whisky. *Journal of Cleaner Production* 112: 229–237.

EU (European Union), 2018. Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the promotion of the use of energy from renewable sources (recast). Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=uriserv:OJ.L_.2018.328.01.0082.01.ENG&toc=OJ:L:2018:328:TOC (accessed 20 February 2022).

EU (European Union), 2020. Communication from the Commission to the European Parliament, the Council, the European Economic and Social Committee and the Committee of the Regions: a hydrogen strategy for a climate-neutral Europe (COM/2020/301 final). Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52020DC0301 (accessed 19 March 2022).

Fagerström, A., Al Seadi, T., Rasi, S. and Briseid, T., 2018. The role of anaerobic digestion and biogas in the circular economy*. IEA Bioenergy Task* 37.

Florentino, A.P., Sharaf, A., Zhang, L. and Liu, Y., 2019. Overcoming ammonia inhibition in anaerobic blackwater treatment with granular activated carbon: the role of electroactive microorganisms. *Environmental Science-Water Research & Technology* 5: 383–396.

Fu, S., Angelidaki, I. and Zhang, Y. 2021. *In situ* biogas upgrading by CO_2-to-CH_4 bioconversion. *Trends in Biotechnology* 39: 336–347.

Ge, S., Usack, J.G., Spirito, C.M. and Angenent, L.T., 2015. Long-term n-caproic acid production from yeast-fermentation beer in an anaerobic bioreactor with continuous product extraction. *Environmental Science & Technology* 49: 8012–8021.

Ghysels, S., Buffel, S., Rabaey, K., Ronsse, F. and Ganigué, R., 2021. Biochar and activated carbon enhance ethanol conversion and selectivity to caproic acid by *Clostridium kluyveri*. *Bioresource Technology* 319: 124236.

Gray, N., McDonagh, S., O'Shea, R., Smyth, B. and Murphy, J.D., 2021. Decarbonising ships, planes and trucks: an analysis of suitable low-carbon fuels for the maritime, aviation and haulage sectors. *Advances in Applied Energy* 1: 100008.

Gray, N., O'Shea, R., Smyth, B., Lens, P.N.L. and Murphy, J.D., 2022. What is the energy balance of electrofuels produced through power-to-fuel integration with biogas facilities? *Renewable and Sustainable Energy Reviews* 155: 111886.

Guneratnam, A.J., Ahern, E., Fitzgerald, J.A., Jackson, S.A., Xia, A., Dobson, A.D.W. and Murphy, J.D., 2017. Study of the performance of a thermophilic biological methanation system. *Bioresource Technology* 225: 308–315.

Habouzit, F., Gévaudan, G., Hamelin, J., Steyer, J.-P. and Bernet, N., 2011. Influence of support material properties on the potential selection of *Archaea* during initial adhesion of a methanogenic consortium. *Bioresource Technology* 102: 4054–4060.

Honda, T., Fujita, T. and Tonouchi, A., 2013. *Aminivibrio pyruvatiphilus* gen. nov., sp. nov., an anaerobic, amino-acid-degrading bacterium from soil of a Japanese rice field. *International Journal of Systematic and Evolutionary Microbiology* 63: 3679–3686.

Hydrogen Council, 2020. *Path to Hydrogen Competitiveness: A Cost Perspective*. Hydrogen Council. Available online: https://hydrogencouncil.com/en/path-to-hydrogen-competitiveness-a-cost-perspective/ (accessed 1 March 2022).

ICE Endex, 2022. *Dutch TTF Gas Futures.* ICE Endex. Available online: https://www.theice.com/products/27996665/Dutch-TTF-Gas-Futures/data?marketId=5889446 (accessed 23 March 2022).

IEA (International Energy Agency), 2020. *Outlook for Biogas and Biomethane: Prospects for Organic Growth*. IEA. Available online: https://iea.blob.core.windows.net/assets/03aeb10c-c38c-4d10-bcec-de92e9ab815f/Outlook_for_biogas_and_biomethane.pdf (accessed 17 April 2022).

Indren, M., Birzer, C.H., Kidd, S.P. and Medwell, P.R., 2020. Effect of total solids content on anaerobic digestion of poultry litter with biochar. *Journal of Environmental Management* 255: 109744.

Irish Tax and Customs, 2022. *Natural Gas Carbon Tax.* Irish Tax and Customs. Available online: https://www.revenue.ie/en/companies-and-charities/excise-and-licences/energy-taxes/natural-gas-carbon-tax/rate-of-tax.aspx (accessed 20 February 2022).

Jackson, S.A., Kang, X., O'Shea, R., O'Leary, N., Murphy, J.D. and Dobson, A.D., 2020. Anaerobic digestion performance and microbial community structures in biogas production from whiskey distillers organic by-products. *Bioresource Technology Reports* 12: 100565.

Kang, X., Lin, R., Li, L., Wu, B., Deng, C., O'Shea, R., Sun, Y. and Murphy, J.D., 2021. Assessment of pretreatment and digestion temperature on anaerobic digestion of whiskey byproducts and microbial taxonomy. *Energy Conversion and Management* 243: 114331.

Kassem, N., Hockey, J., Lopez, C., Lardon, L., Angenent, L.T. and Tester, J.W., 2020. Integrating anaerobic digestion, hydrothermal liquefaction, and biomethanation within a power-to-gas framework for dairy waste management and grid decarbonization: a techno-economic assessment. *Sustainable Energy & Fuels* 4: 4644–4661.

Kougias, P.G., Treu, L., Benavente, D.P., Boe, K., Campanaro, S. and Angelidaki, I., 2017. *Ex-situ* biogas upgrading and enhancement in different reactor systems. *Bioresource Technology* 225: 429–437.

Kwietniewska, E. and Tys, J., 2014. Process characteristics, inhibition factors and methane yields of anaerobic digestion process, with particular focus on microalgal biomass fermentation. *Renewable and Sustainable Energy Reviews* 34: 491–500.

Lawson, N., Alvarado-Morales, M., Tsapekos, P. and Angelidaki, I., 2021. Techno-economic assessment of biological biogas upgrading based on Danish biogas plants. *Energies* 14: 8252.

Leng, L., Yang, P., Singh, S., *et al*., 2018. A review on the bioenergetics of anaerobic microbial metabolism close to the thermodynamic limits and its implications for digestion applications. *Bioresource Technology* 247: 1095–1106.

Liebetrau, J., Reinelt, T., Agostini, A. and Linke, B., 2017. Methane emissions from biogas plants. Methods for measurement, results and effect on greenhouse gas balance of electricity produced. In Murphy J.D. (ed.), *IEA Bioenergy Task* 37: 12.

Lin, R., Deng, C., Cheng, J., Xia, A., Lens, P.N.L., Jackson, S.A., Dobson, A.D.W. and Murphy, J.D., 2018a. Graphene facilitates biomethane production from protein-derived glycine in anaerobic digestion. *iScience* 10: 158–170.

Lin, R., Cheng, J., Ding, L. and Murphy, J.D., 2018b. Improved efficiency of anaerobic digestion through direct interspecies electron transfer at mesophilic and thermophilic temperature ranges. *Chemical Engineering Journal* 350: 681–691.

Lin, R., Deng, C., Ding, L., Bose, A. and Murphy, J.D., 2019. Improving gaseous biofuel production from seaweed *Saccharina latissima*: the effect of hydrothermal pretreatment on energy efficiency. *Energy Conversion and Management* 196: 1385–1394.

Lin, R., Deng, C., Zhang, W., Hollmann, F. and Murphy, J.D., 2021b. Production of bio-alkanes from biomass and CO_2. *Trends in Biotechnology* 39: 370–380.

Lin, R., O'Shea, R., Deng, C., Wu, B. and Murphy, J.D., 2021a. A perspective on the efficacy of green gas production via integration of technologies in novel cascading circular bio-systems. *Renewable and Sustainable Energy Reviews* 150: 111427.

Liu, F.H., Rotaru, A.E., Shrestha, P.M., Malvankar, N.S., Nevin, K.P. and Lovley, D.R., 2012. Promoting direct interspecies electron transfer with activated carbon. *Energy & Environmental Science* 5: 8982–8989.

Liu, Y., Lü, F., Shao, L. and He, P., 2016. Alcohol-to-acid ratio and substrate concentration affect product structure in chain elongation reactions initiated by unacclimatized inoculum. *Bioresource Technology* 218: 1140–1150.

Liu, Y., He, P., Shao, L., Zhang, H. and Lü, F., 2017. Significant enhancement by biochar of caproate production via chain elongation. *Water Research* 119: 150–159.

Liu, Y., He, P., Han, W., Shao, L. and Lü, F., 2020. Outstanding reinforcement on chain elongation through five-micrometer-sized biochar. *Renewable Energy* 161: 230–239.

Logroño, W., Popp, D., Nikolausz, M., Kluge, P., Harms, H. and Kleinsteuber, S., 2021. Microbial communities in flexible biomethanation of hydrogen are functionally resilient upon starvation. *Frontiers in Microbiology* 12.

Long, A. and Murphy, J.D., 2019. Can green gas certificates allow for the accurate quantification of the energy supply and sustainability of biomethane from a range of sources for renewable heat and or transport? *Renewable and Sustainable Energy Reviews* 115: 109347.

Long, A., Bose, A., O'Shea, R., Monaghan, R. and Murphy, J.D., 2021. Implications of European Union recast Renewable Energy Directive sustainability criteria for renewable heat and transport: case study of willow biomethane in Ireland. *Renewable and Sustainable Energy Reviews* 150: 111461.

Lü, F., Luo, C., Shao, L. and He, P., 2016. Biochar alleviates combined stress of ammonium and acids by firstly enriching *Methanosaeta* and then *Methanosarcina*. *Water Research* 90: 34–43.

Lü, F., Liu, Y., Shao, L. and He, P., 2019. Powdered biochar doubled microbial growth in anaerobic digestion of oil. *Applied Energy* 247: 605–614.

Luo, C., Lü, F., Shao, L. and He, P., 2015. Application of eco-compatible biochar in anaerobic digestion to relieve acid stress and promote the selective colonization of functional microbes. *Water Research* 68: 710–718.

Madigan, M.T., Martinko, J.M., Bender, K.S., Buckley, D.H. and Stahl, D.A., 2014. *Brock Biology of Microorganisms*. Pearson Education.

Masebinu, S.O., Akinlabi, E.T., Muzenda, E. and Aboyade, A.O., 2019. A review of biochar properties and their roles in mitigating challenges with anaerobic digestion. *Renewable and Sustainable Energy Reviews* 103: 291–307.

McDonagh, S., Deane, P., Rajendran, K. and Murphy, J.D., 2019. Are electrofuels a sustainable transport fuel? Analysis of the effect of controls on carbon, curtailment, and cost of hydrogen. *Applied Energy* 247: 716–730.

Methanol Institute, 2022. Methanol price and supply/demand. Methanol Institute. Available online: https://www.methanol.org/methanol-price-supply-demand/ (accessed 20 February 2022).

Monlau, F., Sambusiti, C., Antoniou, N., Barakat, A. and Zabaniotou, A., 2015. A new concept for enhancing energy recovery from agricultural residues by coupling anaerobic digestion and pyrolysis process. *Applied Energy* 148: 32–38.

Murphy, J.D. and Power, N.M. 2008. How can we improve the energy balance of ethanol production from wheat? *Fuel* 87: 1799–1806.

Neumann, J., Binder, S., Apfelbacher, A., Gasson, J.R., Ramírez García, P. and Hornung, A., 2015. Production and characterization of a new quality pyrolysis oil, char and syngas from digestate – introducing the thermo-catalytic reforming process. *Journal of Analytical and Applied Pyrolysis* 113: 137–142.

Nizami, A.-S. and Rehan, M., 2018. Towards nanotechnology-based biofuel industry. *Biofuel Research Journal* 5: 798–799.

Parkinson, B., Balcombe, P., Speirs, J.F., Hawkes, A.D. and Hellgardt, K., 2019. Levelized cost of CO_2 mitigation from hydrogen production routes. *Energy & Environmental Science* 12: 19–40.

Parra, D., Zhang, X., Bauer, C. and Patel, M.K., 2017. An integrated techno-economic and life cycle environmental assessment of power-to-gas systems. *Applied Energy* 193: 440–454.

Pérez-Fortes, M., Schöneberger, J.C., Boulamanti, A. and Tzimas, E., 2016. Methanol synthesis using captured CO_2 as raw material: techno-economic and environmental assessment. *Applied Energy* 161: 718–732.

Philibert, C., 2017. *Renewable Energy for Industry: From Green Energy to Green Materials and Fuels*. International Energy Agency (IEA).

Rachbauer, L., Voitl, G., Bochmann, G. and Fuchs, W., 2016. Biological biogas upgrading capacity of a hydrogenotrophic community in a trickle-bed reactor. *Applied Energy* 180: 483–490.

Rafrafi, Y., Laguillaumie, L. and Dumas, C., 2021. Biological methanation of H_2 and CO_2 with mixed cultures: current advances, hurdles and challenges. *Waste and Biomass Valorization* 12: 5259–5282.

Rusmanis, D., O'Shea, R., Wall, D.M. and Murphy, J.D., 2019. Biological hydrogen methanation systems – an overview of design and efficiency. *Bioengineered* 10: 604–634.

Seadi, T.A., Rutz, D., Prassl, H., Köttner, M., Finsterwalder, T., Volk, S. and Janssen, R., 2008. *Biogas Handbook*. University of Southern Denmark Esbjerg.

SEAI (Sustainable Energy Authority of Ireland), 2016. *Bioenergy Supply in Ireland 2015–2035*. SEAI. Available online: https://www.seai.ie/publications/Bioenergy-Supply-in-Ireland-2015-2035.pdf (accessed 27 January 2023).

SEAI (Sustainable Energy Authority of Ireland), 2021. *Electricity & Gas Prices in Ireland —2nd Semester (July–December) 2020*. SEAI. Available online: https://www.seai.ie/data-and-insights/seai-statistics/key-publications/ (accessed 18 March 2022).

SEAI (Sustainable Energy Authority of Ireland), 2022. Conversion factors. SEAI. Available online: https://www.seai.ie/data-and-insights/seai-statistics/conversion-factors/ (accessed 9 February 2022).

Shao, L., Li, S., Cai, J., He, P. and Lü, F., 2019. Ability of biochar to facilitate anaerobic digestion is restricted to stressed surroundings. *Journal of Cleaner Production* 238: 117959.

Sharma, D., Espinosa-Solares, T. and Huber, D.H., 2013. Thermophilic anaerobic co-digestion of poultry litter and thin stillage. *Bioresource Technology* 136: 251–256.

Sheets, J.P. and Shah, A., 2018. Techno-economic comparison of biogas cleaning for grid injection, compressed natural gas, and biogas-to-methanol conversion technologies. *Biofuels, Bioproducts and Biorefining* 12: 412–425.

Shen, Y., Forrester, S., Koval, J. and Urgun-Demirtas, M., 2017. Yearlong semi-continuous operation of thermophilic two-stage anaerobic digesters amended with biochar for enhanced biomethane production. *Journal of Cleaner Production* 167: 863–874.

Spirito, C.M., Marzilli, A.M. and Angenent, L.T., 2018. Higher substrate ratios of ethanol to acetate steered chain elongation toward n-caprylate in a bioreactor with product extraction. *Environmental Science & Technology* 52: 13438–13447.

Strübing, D., Moeller, A.B., Mößnang, B., Lebuhn, M., Drewes, J.E. and Koch, K., 2018. Anaerobic thermophilic trickle bed reactor as a promising technology for flexible and demand-oriented H_2/CO_2 biomethanation. *Applied Energy* 232: 543–554.

Tan, L.C., Lin, R., Murphy, J.D. and Lens, P.N.L., 2021. Granular activated carbon supplementation enhances anaerobic digestion of lipid-rich wastewaters. *Renewable Energy* 171: 958–970.

Teagasc, 2019. *An Analysis of Abatement Potential of Greenhouse Gas Emissions in Irish Agriculture 2021–2030*. Available online: https://www.teagasc.ie/media/website/publications/2018/An-Analysis-of-Abatement-Potential-of-Greenhouse-Gas-Emissions-in-Irish-Agriculture-2021-2030.pdf (accessed 18 April 2022).

The Engineering Tool Box, 2003. *Fuels – Higher and Lower Calorific Values.* The Engineering Tool Box. Available online: https://www.engineeringtoolbox.com/fuels-higher-calorific-values-d_169.html (accessed 20 February 2022).

Tsapekos, P., Treu, L., Campanaro, S., Centurion, V.B., Zhu, X., Peprah, M., Zhang, Z., Kougias, P.G. and Angelidaki, I., 2021. Pilot-scale biomethanation in a trickle bed reactor: process performance and microbiome functional reconstruction. *Energy Conversion and Management* 244: 114491.

Umetsu, M., Sunouchi, T., Fukuda, Y., Takahashi, H. and Tada, C., 2020. Functional group distribution of the carrier surface influences adhesion of *Methanothermobacter thermautotrophicus*. *Archaea* 9432803.

Vo, T.T.Q., Rajendran, K. and Murphy, J.D., 2018a. Can power to methane systems be sustainable and can they improve the carbon intensity of renewable methane when used to upgrade biogas produced from grass and slurry? *Applied Energy* 228: 1046–1056.

Vo, T.T.Q., Wall, D.M., Ring, D., Rajendran, K. and Murphy, J.D., 2018b. Techno-economic analysis of biogas upgrading via amine scrubber, carbon capture and ex-situ methanation. *Applied Energy* 212: 1191–1202.

Voelklein, M.A., Jacob, A., O'Shea, R. and Murphy, J.D., 2016. Assessment of increasing loading rate on two-stage digestion of food waste. *Bioresource Technology* 202: 172–180.

Voelklein, M.A., Rusmanis, D. and Murphy, J.D., 2019. Biological methanation: strategies for *in-situ* and *ex-situ* upgrading in anaerobic digestion. *Applied Energy* 235: 1061–1071.

Wall D.M., O'Kiely, P. and Murphy, J.D., 2013. The potential for biomethane from grass and slurry to satisfy renewable energy targets. *Bioresource Technology* 149: 425–431.

Wall, D.M., McDonagh, S. and Murphy, J.D., 2017. Cascading biomethane energy systems for sustainable green gas production in a circular economy. *Bioresource Technology* 243: 1207–1215.

Wang, D., AI, J., Shen, F., Yang, G., Zhang, Y., Deng, S., Zhang, J., Zeng, Y. and Song, C. 2017. Improving anaerobic digestion of easy-acidification substrates by promoting buffering capacity using biochar derived from vermicompost. *Bioresource Technology* 227: 286–296.

Wang, G., Li, Q., Gao, X. and Wang, X.C., 2018. Synergetic promotion of syntrophic methane production from anaerobic digestion of complex organic wastes by biochar: performance and associated mechanisms. *Bioresource Technology* 250: 812–820.

Wang, G., Gao, X., Li, Q., Zhao, H., Liu, Y., Wang, X.C. and Chen, R., 2019. Redox-based electron exchange capacity of biowaste-derived biochar accelerates syntrophic phenol oxidation for methanogenesis via direct interspecies electron transfer. *Journal of Hazardous Materials* 121726.

Wang, T., Zhu, G., Kuang, B., Jia, J., Liu, C., Cai, G. and Li, C., 2021. Novel insights into the anaerobic digestion of propionate via *Syntrophobacter fumaroxidans* and *Geobacter sulfurreducens*: process and mechanism. *Water Research* 200: 117270.

Wang, Y., Wei, W., Wu, S.-L. and Ni, B.-J., 2020. Zerovalent iron effectively enhances medium-chain fatty acids production from waste activated sludge through improving sludge biodegradability and electron transfer efficiency. *Environmental Science & Technology* 54: 10904–10915.

Wellinger, A., Murphy, J.D. and Baxter, D., 2013. *The Biogas Handbook: Science, Production and Applications*. Elsevier.

Wu, B., Lin, R., Kang, X., Deng, C., Xia, A., Dobson, A.D.W. and Murphy, J.D., 2020. Graphene addition to digestion of thin stillage can alleviate acidic shock and improve biomethane production. *ACS Sustainable Chemistry & Engineering* 8: 13248–13260.

Wu, B., Lin, R., Kang, X., Deng, C., Dobson, A.D.W. and Murphy, J.D., 2021a. Improved robustness of ex-situ biological methanation for electro-fuel production through the addition of graphene. *Renewable and Sustainable Energy Reviews* 152: 111690.

Wu, B., Lin, R., O'Shea, R., Deng, C., Rajendran, K. and Murphy, J.D., 2021b. Production of advanced fuels through integration of biological, thermo-chemical and power to gas technologies in a circular cascading bio-based system. *Renewable and Sustainable Energy Reviews* 135: 110371.

Wu, B., Lin, R., Ning, X., Kang, X., Deng, C., Dobson, A.D.W. and Murphy, J.D., 2022. An assessment of how the properties of pyrochar and process thermodynamics impact pyrochar mediated microbial chain elongation in steering the production of medium-chain fatty acids towards n-caproate. *Bioresource Technology* 358: 127294.

Wu, Q., Guo, W., Bao, X., Meng, X., Yin, R., Du, J., Zheng, H., Feng, X., Luo, H. and Ren, N., 2018. Upgrading liquor-making wastewater into medium chain fatty acid: insights into co-electron donors, key microflora, and energy harvest. *Water Research* 145: 650–659.

Wu, Q., Bao, X., Guo, W., Wang, B., Li, Y., Luo, H., Wang, H. and Ren, N., 2019. Medium chain carboxylic acids production from waste biomass: current advances and perspectives. *Biotechnology Advances* 37: 599–615.

Wu, Q., Feng, X., Guo, W., Bao, X. and Ren, N., 2020. Long-term medium chain carboxylic acids production from liquor-making wastewater: parameters optimization and toxicity mitigation. *Chemical Engineering Journal* 388: 124218.

Wu, Q., Feng, X., Chen, Y., Liu, M. and Bao, X., 2021. Continuous medium chain carboxylic acids production from excess sludge by granular chain-elongation process. *Journal of Hazardous Materials* 402: 123471.

Wu, S.-L., Wei, W., Xu, Q., Huang, X., Sun, J., Dai, X. and Ni, B.-J., 2021. Revealing the mechanism of biochar enhancing the production of medium chain fatty acids from waste activated sludge alkaline fermentation liquor. *ACS ES&T Water* 1: 1014–1024.

Wu, Z.-S., Ren, W., Gao, L., Zhao, J., Chen, Z., Liu, B., Tang, D., Yu, B., Jiang, C. and Cheng, H.-M., 2009. Synthesis of graphene sheets with high electrical conductivity and good thermal stability by hydrogen arc discharge exfoliation. *ACS Nano* 3: 411–417.

Xia, A., Cheng, J. and Murphy, J.D. 2016. Innovation in biological production and upgrading of methane and hydrogen for use as gaseous transport biofuel. *Biotechnology Advances* 34: 451–472.

Yan, W., Sun, F., Liu, J. and Zhou, Y., 2018. Enhanced anaerobic phenol degradation by conductive materials via EPS and microbial community alteration. *Chemical Engineering Journal* 352: 1–9.

Yang, H.-J., Yang, Z.-M., Xu, X.-H. and Guo, R.-B. 2020. Increasing the methane production rate of hydrogenotrophic methanogens using biochar as a biocarrier. *Bioresource Technology* 302: 122829.

Yang, L., Huang, Y., Zhao, M., Huang, Z., Miao, H., Xu, Z. and Ruan, W., 2015. Enhancing biogas generation performance from food wastes by high-solids thermophilic anaerobic digestion: effect of pH adjustment. *International Biodeterioration & Biodegradation* 105: 153–159.

Yang, Q., Zhou, H., Bartocci, P., Fantozzi, F., Mašek, O., Agblevor, F.A., Wei, Z., Yang, H., Chen, H., Lu, X., Chen, G., Zheng, C., Nielsen, C.P. and McElroy, M.B., 2021. Prospective contributions of biomass pyrolysis to China's 2050 carbon reduction and renewable energy goals. *Nature Communications* 12: 1698.

Yi, Y., Wang, H., Chen, Y., Gou, M., Xia, Z., Hu, B., Nie, Y. and Tang, Y., 2020. Identification of novel butyrate- and acetate-oxidizing bacteria in butyrate-fed mesophilic anaerobic chemostats by DNA-based stable isotope probing. *Microbial Ecology* 79: 285–298.

Yin, C., Shen, Y., Yuan, R., Zhu, N., Yuan, H. and Lou, Z., 2019. Sludge-based biochar-assisted thermophilic anaerobic digestion of waste-activated sludge in microbial electrolysis cell for methane production. *Bioresource Technology* 284: 315–324.

Yin, Q. and Wu, G. 2019. Advances in direct interspecies electron transfer and conductive materials: electron flux, organic degradation and microbial interaction. *Biotechnology Advances* 37: 107443.

Yu, L., Yuan, Y., Tang, J., Wang, Y. and Zhou, S., 2015. Biochar as an electron shuttle for reductive dechlorination of pentachlorophenol by *Geobacter sulfurreducens*. *Scientific Reports* 5: 16221.

Zagrodnik, R., Duber, A., Łężyk, M. and Oleskowicz-Popiel, P., 2020. Enrichment versus bioaugmentation – microbiological production of caproate from mixed carbon sources by mixed bacterial culture and *Clostridium kluyveri*. *Environmental Science & Technology* 54: 5864–5873.

Zamanzadeh, M., Parker, W.J., Verastegui, Y. and Neufeld, J.D., 2013. Biokinetics and bacterial communities of propionate oxidizing bacteria in phased anaerobic sludge digestion systems. *Water Research* 47: 1558–1569.

Zhang, X., Xia, J., Pu, J., Cai, C., Tyson, G.W., Yuan, Z. and Hu, S., 2019. Biochar-mediated anaerobic oxidation of methane. *Environmental Science & Technology* 53: 6660–6668.

Zhang, Y., Pan, X., Zuo, J. and Hu, J., 2022. Production of n-caproate using food waste through thermophilic fermentation without addition of external electron donors. *Bioresource Technology* 343: 126144.

Zhao, Z., Zhang, Y., LI, Y., Dang, Y., Zhu T. and Quan, X., 2017. Potentially shifting from interspecies hydrogen transfer to direct interspecies electron transfer for syntrophic metabolism to resist acidic impact with conductive carbon cloth. *Chemical Engineering Journal* 313: 10–18.

Zhao, Z., Li, Y., Zhang, Y. and Lovley, D.R., 2020. Sparking anaerobic digestion: promoting direct interspecies electron transfer to enhance methane production. *iScience* 23: 101794.

Abbreviations

AD	Anaerobic digestion
CAPEX	Capital expenditure
COD	Chemical oxygen demand
CU	CO_2 utilisation
DIET	Direct interspecies electron transfer
EPS	Extracellular polymeric substance
GHG	Greenhouse gas
LCA	Life cycle assessment
MCFA	Medium-chain fatty acid
MeOH	Methanol synthesis
MIET	Mediated interspecies electron transfer
OTU	Operational taxonomic unit
Py	Pyrolysis
RED-II	Renewable Energy Directive (recast)
SAO	Syntrophic acetate oxidation
SCFA	Short-chain fatty acid
TEA	Technoeconomic analysis
VFA	Volatile fatty acid
VS	Volatile solids

Appendix 1 Peer-reviewed Publications

The following papers were published in the course of this research project:

Deng, C., Lin, R., Kang, X., Wu, B., O'Shea, R., Murphy, J.D., 2020. Improving gaseous biofuel yield from seaweed through a cascading circular bioenergy system integrating anaerobic digestion and pyrolysis. *Renewable and Sustainable Energy Reviews* 128: 109895.

Deng, C., Lin, R., Kang, X., Wu, B., Wall, D., Murphy, J.D., 2022. Improvement in biohydrogen and volatile fatty acid production from seaweed through addition of conductive carbon materials depends on the properties of the conductive materials. *Energy* 239: 122188.

Deng, C., Lin, R., Kang, X., Wu, B., Wall, D.M., Murphy, J.D., 2021. What physicochemical properties of biochar facilitate interspecies electron transfer in anaerobic digestion: a case study of digestion of whiskey by-products. *Fuel* 306: 121736.

Lin, R., Deng, C., Zhang, W., Hollmann, F., Murphy, J.D., 2021. Production of bio-alkanes from biomass and CO_2. *Trends in Biotechnology* 39: 370–380.

Lin, R., O'Shea, R., Deng, C., Wu, B., Murphy, J.D., 2021. A perspective on the efficacy of green gas production via integration of technologies in novel cascading circular bio-systems. *Renewable and Sustainable Energy Reviews* 150: 111427.

Wu, B., Lin, R., Kang, X., Deng, C., Dobson, A.D.W., Murphy, J.D., 2021. Improved robustness of ex-situ biological methanation for electro-fuel production through the addition of graphene. *Renewable and Sustainable Energy Reviews* 152: 111690.

Wu, B., Lin, R., Kang, X., Deng, C., Xia, A., Dobson, A.D.W., Murphy, J.D., 2020. Graphene addition to digestion of thin stillage can alleviate acidic shock and improve biomethane production. *ACS Sustainable Chemistry & Engineering* 8: 13248–13260.

Wu, B., Lin, R., Ning, X., Kang, X., Deng, C., Dobson, A.D.W., Murphy, J.D., 2022. An assessment of how the properties of pyrochar and process thermodynamics impact pyrochar mediated microbial chain elongation in steering the production of medium-chain fatty acids towards n-caproate. *Bioresource Technology* 358: 127294.

Wu, B., Lin, R., O'Shea, R., Deng, C., Rajendran, K., Murphy, J.D., 2021. Production of advanced fuels through integration of biological, thermo-chemical and power to gas technologies in a circular cascading bio-based system. *Renewable and Sustainable Energy Reviews* 135: 110371.

An Ghníomhaireacht Um Chaomhnú Comhshaoil

Tá an GCC freagrach as an gcomhshaol a chosaint agus a fheabhsú, mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ar thionchar díobhálach na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialáil: Rialáil agus córais chomhlíonta comhshaoil éifeachtacha a chur i bhfeidhm, chun dea-thorthaí comhshaoil a bhaint amach agus díriú orthu siúd nach mbíonn ag cloí leo.

Eolas: Sonraí, eolas agus measúnú ardchaighdeáin, spriocdhírithe agus tráthúil a chur ar fáil i leith an chomhshaoil chun bonn eolais a chur faoin gcinnteoireacht.

Abhcóideacht: Ag obair le daoine eile ar son timpeallachta glaine, táirgiúla agus dea-chosanta agus ar son cleachtas inbhuanaithe i dtaobh an chomhshaoil.

I measc ár gcuid freagrachtaí tá:

Ceadúnú

> Gníomhaíochtaí tionscail, dramhaíola agus stórála peitril ar scála mór;

> Sceitheadh fuíolluisce uirbigh;

> Úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe;

> Foinsí radaíochta ianúcháin;

> Astaíochtaí gás ceaptha teasa ó thionscal agus ón eitlíocht trí Scéim an AE um Thrádáil Astaíochtaí.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil

> Iniúchadh agus cigireacht ar shaoráidí a bhfuil ceadúnas acu ón GCC;

> Cur i bhfeidhm an dea-chleachtais a stiúradh i ngníomhaíochtaí agus i saoráidí rialáilte;

> Maoirseacht a dhéanamh ar fhreagrachtaí an údaráis áitiúil as cosaint an chomhshaoil;

> Caighdeán an uisce óil phoiblí a rialáil agus údaruithe um sceitheadh fuíolluisce uirbigh a fhorfheidhmiú

> Caighdeán an uisce óil phoiblí agus phríobháidigh a mheasúnú agus tuairisciú air;

> Comhordú a dhéanamh ar líonra d'eagraíochtaí seirbhíse poiblí chun tacú le gníomhú i gcoinne coireachta comhshaoil;

> An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Dramhaíola agus Ceimiceáin sa Chomhshaol

> Rialacháin dramhaíola a chur i bhfeidhm agus a fhorfheidhmiú lena n-áirítear saincheisteanna forfheidhmithe náisiúnta;

> Staitisticí dramhaíola náisiúnta a ullmhú agus a fhoilsiú chomh maith leis an bPlean Náisiúnta um Bainistíocht Dramhaíola Guaisí;

> An Clár Náisiúnta um Chosc Dramhaíola a fhorbairt agus a chur i bhfeidhm;

> Reachtaíocht ar rialú ceimiceán sa timpeallacht a chur i bhfeidhm agus tuairisciú ar an reachtaíocht sin.

Bainistíocht Uisce

> Plé le struchtúir náisiúnta agus réigiúnacha rialachais agus oibriúcháin chun an Chreat-treoir Uisce a chur i bhfeidhm;

> Monatóireacht, measúnú agus tuairisciú a dhéanamh ar chaighdeán aibhneacha, lochanna, uiscí idirchreasa agus cósta, uiscí snámha agus screamhuisce chomh maith le tomhas ar leibhéil uisce agus sreabhadh abhann.

Eolaíocht Aeráide & Athrú Aeráide

> Fardail agus réamh-mheastacháin a fhoilsiú um astaíochtaí gás ceaptha teasa na hÉireann;

> Rúnaíocht a chur ar fáil don Chomhairle Chomhairleach ar Athrú Aeráide agus tacaíocht a thabhairt don Idirphlé Náisiúnta ar Ghníomhú ar son na hAeráide;

> Tacú le gníomhaíochtaí forbartha Náisiúnta, AE agus NA um Eolaíocht agus Beartas Aeráide.

Monatóireacht & Measúnú ar an gComhshaol

> Córais náisiúnta um monatóireacht an chomhshaoil a cheapadh agus a chur i bhfeidhm: teicneolaíocht, bainistíocht sonraí, anailís agus réamhaisnéisiú;

> Tuairiscí ar Staid Thimpeallacht na hÉireann agus ar Tháscairí a chur ar fáil;

> Monatóireacht a dhéanamh ar chaighdeán an aeir agus Treoir an AE i leith Aeir Ghlain don Eoraip a chur i bhfeidhm chomh maith leis an gCoinbhinsiún ar Aerthruailliú Fadraoin Trasteorann, agus an Treoir i leith na Teorann Náisiúnta Astaíochtaí;

> Maoirseacht a dhéanamh ar chur i bhfeidhm na Treorach i leith Torainn Timpeallachta;

> Measúnú a dhéanamh ar thionchar pleananna agus clár beartaithe ar chomhshaol na hÉireann.

Taighde agus Forbairt Comhshaoil

> Comhordú a dhéanamh ar ghníomhaíochtaí taighde comhshaoil agus iad a mhaoiniú chun brú a aithint, bonn eolais a chur faoin mbeartas agus réitigh a chur ar fáil;

> Comhoibriú le gníomhaíocht náisiúnta agus AE um thaighde comhshaoil.

Cosaint Raideolaíoch

> Monatóireacht a dhéanamh ar leibhéil radaíochta agus nochtadh an phobail do radaíocht ianúcháin agus do réimsí leictreamaighnéadacha a mheas;

> Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha;

> Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta;

> Sainseirbhísí um chosaint ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Ardú Feasachta agus Faisnéis Inrochtana

> Tuairisciú, comhairle agus treoir neamhspleách, fianaise-bhunaithe a chur ar fáil don Rialtas, don tionscal agus don phobal ar ábhair maidir le cosaint comhshaoil agus raideolaíoch;

> An nasc idir sláinte agus folláine, an geilleagar agus timpeallacht ghlan a chur chun cinn;

> Feasacht comhshaoil a chur chun cinn lena n-áirítear tacú le hiompraíocht um éifeachtúlacht acmhainní agus aistriú aeráide;

> Tástáil radóin a chur chun cinn i dtithe agus in ionaid oibre agus feabhsúchán a mholadh áit is gá.

Comhpháirtíocht agus Líonrú

> Oibriú le gníomhaireachtaí idirnáisiúnta agus náisiúnta, údaráis réigiúnacha agus áitiúla, eagraíochtaí neamhrialtais, comhlachtaí ionadaíocha agus ranna rialtais chun cosaint chomhshaoil agus raideolaíoch a chur ar fáil, chomh maith le taighde, comhordú agus cinnteoireacht bunaithe ar an eolaíocht.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil

Tá an GCC á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóir. Déantar an obair ar fud cúig cinn d'Oifigí:

1. An Oifig um Inbhunaitheacht i leith Cúrsaí Comhshaoil
2. An Oifig Forfheidhmithe i leith Cúrsaí Comhshaoil
3. An Oifig um Fhianaise agus Measúnú
4. An Oifig um Chosaint ar Radaíocht agus Monatóireacht Comhshaoil
5. An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tugann coistí comhairleacha cabhair don Ghníomhaireacht agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

epa Research

EPA Research

Webpages: www.epa.ie/our-services/research/
LinkedIn: www.linkedin.com/showcase/eparesearch/
Twitter: @EPAResearchNews
Email: research@epa.ie

www.epa.ie