

Circular Economy: Recovery, Reuse & Valorisation

Renewable Fuels & Chemicals

Solid-Liquid Waste Streams to Biogas

KEYWORDS: Biogas / Agro-industrial Residues / Fruit Wastes / Glycerol / Waste Activated Sludge / Organic Wastes / Technology

Anaerobic digestion of various types of waste, including agro-industrial by-products, kiwi waste, and glycerol, towards sustainable energy production. Technology for the pre-treatment of waste-activated sludge to foster biogas production, combining the effect of radiation (solar light), mild temperature (60-80 °C), and equipment design (raceway pond reactor). Overall, these studies have provided insights into sustainable waste management and renewable energy production.

Objectives

Treatment and potential high-quality biogas production of different residue types (agro-industrial, kiwi, effluent from agro-industrial and dairy plants, and glycerol from the biodiesel production industry) through anaerobic digestion, utilizing a range of reactor systems, including batch reactors and upflow anaerobic sludge digesters (UASB). Pre-treatment of waste activated sludge, to foster sludge disintegration, enhancing hydrolysis, the rate-limiting step of anaerobic digestion.

Current Development

In an extensive exploration of sustainable waste management and energy production, various types of residues, including agro-industrial by-products, kiwi waste, effluent from agro-industrial and dairy plants, and glycerol from the biodiesel production industry, have been subjected to anaerobic digestion. This innovative approach is aimed at both treating these residues and economically valorizing them through the generation of high-quality biogas.

The optimization efforts were multifaceted, focusing on crucial operating conditions such as substrate composition for co-digestion, diverse substrate pre-treatment methods (physical, chemical, and biological), and controlling factors such as temperature, alkalinity, pH, carbon:nitrogen:phosphorous (C:N:P) ratio, hydraulic retention time (HRT), organic load, volumetric flow rate (VF), and agitation. Notably, the challenges posed by high concentrations of glycerol, which is known to inhibit microorganisms, were addressed through a comprehensive evaluation of various HRTs and organic loading rates (OLR).

Glycerol Anaerobic Digestion Study

Experimental anaerobic digestion of crude glycerol was conducted under semi-continuous mesophilic conditions. The study revealed a significant 11% increase in methane (CH₄) production by extending the HRT, reaching optimal conditions at an OLR of 2 g chemical oxygen demand (COD) L⁻¹ d⁻¹ and HRT of 23 days. This resulted in a methane production of 256 mL CH₄ g⁻¹ COD removed, maintaining a volatile solids-to-total solids ratio (VS/TS) of 0.62 and achieving a final COD removal efficiency of 86%.

Kiwifruit Agro-Industrial Residue Study

The energetic potential of kiwifruit agro-industrial residues was thoroughly assessed through ten experiments in a perfectly mixed batch reactor (PMBR) (Fig 1). This study investigated various operational factors, including substrate/inoculum ratios, distinct C:N ratios, inoculum sources, and collection times. Particularly interesting results were obtained, showing the highest quality biogas (85% CH₄) from the 5% kiwifruit residue. Under optimal conditions, up to

102 € in gross monetary income could be generated per ton of kiwifruit residue.



Fig 1. Biogas production system at mesoscale.

Agro-Industrial Effluent Valorization Study

An upflow anaerobic sludge digester (UASB) was used for the valorization of agro-industrial effluents (Fig 2). The digester's performance was evaluated at the Sortegel agro-industrial company wastewater treatment plant (WWTP), utilizing different HRT and VF values: 0.66 d/1509 L m⁻³ d⁻¹, 1.33 d/755 L m⁻³ d⁻¹, and 2.41 d/415 L m⁻³ d⁻¹. The assessment encompassed the 5-day biochemical oxygen demand (BOD₅) and total suspended solids (TSS) parameters, along with the analysis of the CH₄ content and biogas production rate. The average COD removal efficiency achieved significant levels of 69%, 82%, and 75%, accompanied by the associated BOD₅ removal efficiencies of 84%, 91%, and 70% for HRT values of 0.66, 1.33, and 2.41 d, respectively. Additionally, the digester exhibited high CH₄ production rates, ranging from 2500 to 4800 L CH₄ kg⁻¹ COD removed d⁻¹. Notably, biogas consistently showed high CH₄ concentrations of 66-75%, 70%, and 75%, depending on the adopted HRT value.



Fig 2. Experimental setup – upflow anaerobic sludge blanket digester reactor (UASB).

Integrated Glycerol Valorisation Study

Another study focused on enhancing the methane yield of crude glycerol anaerobic digestion by integrating ultrasound or aerobic biodegradation using *A. niger*/*E. coli* (Fig 3). This

innovative approach led to an improved methane yield, with ultrasound and *A. niger* biodegradation steps showing promising results. The system achieved an energy gain of 0.48 kWh d⁻¹ and increased methane production rates under specific conditions.

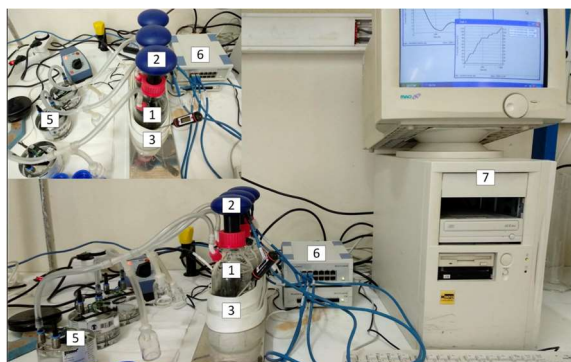


Fig 3. Experimental layout (batch reactor and methane sensor).

Co-Digestion of Kiwifruit and Wine Leaves

Energetic valorization studies were conducted through anaerobic co-digestion (AcoD) using kiwi waste and wine lees. Kiwi, scientifically known as *Actinidia deliciosa*, is a fruit with extensive production in Portugal (2,369 ha), generating an estimated 25% waste. Wine production also contributes significantly to waste generation, with approximately 3.5-8.5% of wine production ending up as waste. The literature indicates that anaerobic digestion has the potential to treat 38×10³ ton year⁻¹ of wine production waste, and wine sludge alone can produce 1.06×10⁶ m³ of biogas annually. Experimental runs using kiwi fruit and wine lees in batch reactors were conducted via AcoD, with substrate percentage and C:N ratio variations. Nine lab-scale digesters, each fed with one material (2.5 g inoculum plus 1.0 g kiwi or wine lees), were used for anaerobic digestion. Additionally, 12 digesters were fed with a mixture of inoculum (2.5 g) and substrates in different proportions (kiwi/wine lees: 0.2 g/0.7 g; 0.2 g/0.8 g; 0.8 g/0.2 g; 0.5 g/3.3 g). Analysis of variance (ANOVA) was applied to the anaerobic digestion and AcoD treatment results, followed by Tukey's test ($p < 0.05$) to identify the best treatment. In the anaerobic digestion experiments, the assay with kiwi waste showed superior results (27.0 mL biogas g⁻¹ VS) compared with wine lees (16.9 mL biogas g⁻¹ VS). Concerning AcoD tests, the highest biogas production (40.5 mL g⁻¹ VS) was achieved using 0.5 g kiwi plus 3.3 g wine lees, but statistically, all co-digestion experiments were deemed equal. Consequently, the AcoD process led to a 50% increase in the biogas production.

Technology for Waste Activated Sludge Pre-Treatment

The present invention discloses a technology for the pre-treatment of waste activated sludge (WAS) using an innovative unit configuration driven by a renewable and readily resource, solar light, complemented, when necessary, with artificial radiation to foster the cell lysis and sludge disintegration, enhancing hydrolysis, the rate-limiting step of anaerobic digestion processes, maximizing biogas production, sludge dewatering, stabilization, and disinfection. The advanced technology combines the effect of radiation, mild temperature (60-80 °C), and equipment design (raceway pond reactor - RPR). The technology is based on a series of thermal, catalytic, photochemical, and photocatalytic reactions driven by solar light in combination with endogenous metals (e.g., iron) present in WAS. The proof-of-concept was assessed as regards waste activated sludge disintegration (soluble chemical oxygen demand-SCOD) and biomethane potential (BMP), evaluating the effect of illumination time, radiation power (solar light), liquid level, and temperature. The RPR device showed a COD solubilization of 18% (SCOD of 5200 mg O₂ L⁻¹) after 70 kJ of UV solar radiation per liter of WAS (19.4 kWh m⁻³), considering a

temperature of 70 °C, liquid level = 5 cm, paddlewheel velocity = 30 rpm, providing an increment on BMP of 100% when compared to the sludge without pre-treatment. The initial characteristics of the WAS were: (i) total suspended solids of 17 g L⁻¹; (ii) SCOD= 370 mg O₂ L⁻¹; (iii) COD_{total} =22000 mg O₂ L⁻¹. Temperature was controlled using an external heat source.

Future Perspectives

Biogas or biomethane is conventionally generated through anaerobic digestion and, more recently, through thermochemical processes or a combination of thermochemical and biological processes using syngas (CO and H₂) fermentation. However, certain wastes exhibit recalcitrant structures that are challenging to digest, contain toxic compounds (such as fruit flavors or high ammonia content), or are entirely nondigestible (e.g., plastics). To address these challenges, innovative strategies for economically enhancing biogas production are under investigation. These strategies include commonly known physical pre-treatment, rapid decompression, autohydrolysis, acid or alkali pre-treatments, solvent (e.g., for lignin or cellulose) pre-treatments or leaching, and supercritical, oxidative, or biological pre-treatments.

Additionally, approaches such as combined gasification and fermentation, integrated biogas production and pre-treatment, innovative biogas digester design, co-digestion, and bio-augmentation have been considered.

In this context, the forthcoming studies will focus on intensifying biogas production from wastewater treatment plant sludge using thermal processes, ultrasound, the Fenton process, and ozone, with an emphasis on understanding the effects of operating parameters.

Related Sustainable Development Goals



Outputs

PhD Theses

[1] Joana Pinto Monteiro, Tecnologia avançada de maximização da performance energética de ETAR, potenciando a sua autossuficiência, através da integração de processos de pré-tratamento de lamas com radiação solar/artificial na etapa de digestão anaeróbia, FEUP, 2020-2024, on-going

Master Dissertations

- [1] Camila Gabrielle Queiroz, Produção de biogás por digestão anaeróbia de glicerol bruto, MEQ, ESTIG-IPB, 2020
- [2] Lis Geraldine Zschach, Production of biogas from crude glycerol using ultrasound as pre-treatment in a batch reactor, MEQ, ESTIG-IPB, 2019
- [3] Mariana Ferrari Giacon, Valorização energética dos resíduos de kiwi e borra de vinho por meio de co-digestão anaeróbia, MTA, ESA-IPB, 2019
- [4] Mateus Baumguertner, Valorização energética de resíduos de kiwi por meio da digestão anaeróbia, MTA, ESA-IPB, 2018

Selected Publications

- [1] R.J. Martins, J. Jilin University (Eng and Techn Edition) 42, 35 (2023)
- [2] R.J. Martins, L.G. Zschach, J. Jilin University (Eng and Techn Edition) 34, 11 (2023)
- [3] M. Giacon et al., J. Jilin University (Eng and Techn Edition) 34, 18 (2023)

Patent

[1] Vítor Vilar, Joana Monteiro, Isabel Saraiva, Diana Lopes, Nuno Brôco, Method device and system for treatment of waste activated sludge, Date of Application: 30-11-2023, Application number: 20232005624053.

Team

Ramiro J. Professor; Vítor Vilar Principal Researcher; Rui Boaventura Principal Researcher, Joana Monteiro, PhD Student, **Lis Zschach**, MSc Student; **Mariana Giacon**, MSc Student; **Camila Queiroz**, MSc Student; **Matheus Baumguertner**, MSc Student

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 LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023
 LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019
 LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984, 2013-2018
 FCT Scholarships: 2020.04887.BD

Circular Economy: Recovery, Reuse & Valorisation

Renewable Fuels & Chemicals

Liquid Waste Streams

KEYWORDS: Lignin / Glycerol / Value-Added Products / Selective Oxidation / (Photo)Electrocatalysis / Reactor Design

Development of technologies for the valorization of liquid waste streams to produce value-added organic chemicals based on electrocatalysis and photoelectrocatalysis processes employing novel (photo)anode materials and a novel NETmix-based electrochemical flow reactor. Black liquor, a pulp mill effluent rich in lignin, has been converted into phenolic compounds, with a highlight on vanillin and syringaldehyde. Crude glycerol, a by-product of transesterification reactions in biodiesel production, has been used to mainly produce dihydroxyacetone, glyceraldehyde, and hydroxyppyruvic acid.

Introduction

Lignin is the second most abundant polymer on Earth after cellulose, and its primary industrial source is black liquor, a pulp mill effluent with 15-18% wt. solids, mostly lignin. Black liquor has been concentrated in multi-stage evaporation units to reach a solids content of 65-75% and then burned as low-value fuel to generate electricity and heat. The oxidation of the lignin present in the black liquor can lead to the production of various phenolic compounds, with a highlight on vanillin (V) and syringaldehyde (S). V is widely used as a flavoring and fragrance agent in food and cosmetics, while S is a valuable starting chemical for the pharmaceutical industry.

Crude glycerol has been experiencing an oversupply in the world market, and consequently, its value has been drastically reduced. This compound is a by-product of transesterification reactions in biodiesel production, which has been continually growing. By 2029, global biodiesel production is projected to reach almost 46 billion L, with around 34% in the European Union. The production of 100 kg of biodiesel brings out approximately 10 kg (10% wt.) of crude glycerol. Dihydroxyacetone (DHA), glyceraldehyde (GAD), and hydroxyppyruvic acid (HPA) are major valuable compounds from glycerol oxidation. DHA is widely applied as a tanning agent in cosmetics, GAD is used as an anti-aging agent in the production of advanced glycation end-products, and HPA is an important intermediate in pharmaceutical and chemical industries.

Currently, the most applied processes for lignin and crude glycerol valorization include chemical alkaline oxidation and catalytic oxidation, respectively, under high temperature and pressure. Furthermore, the existing electrochemical reactors typically exhibit mass transfer limitations. The current research project aims to challenge this scenario by fostering disruptive and green technologies based on 1) electrocatalysis (EC) and photoelectrocatalysis (PEC) processes, 2) innovative (photo)anode materials, and 3) a disruptive electrochemical continuous-flow reactor of micro/meso dimensions based on the NETmix static mixer technology. EC and PEC processes provide unique opportunities to use clean and inexpensive reaction drivers - the electrons - and carry out reactions under mild conditions of temperature and pressure. The (photo)anodes employed in these processes are crucial for high efficiency.

Current Development

Our research has been focused on the development of a novel NETmix-based electrochemical flow reactor. The NETmix is a static mixer characterized by a network of cylindrical chambers interconnected by prismatic channels arranged at

45° angles, capable of promoting convective mixing and the development of a laminar chaotic flow regime. The new reactor has one compartment and is composed of a 316-grade stainless-steel plate with a machined NETmix network for fluid circulation working as the cathode, and (ii) a flat plate anode that can be of any material. Fig 1 illustrates the reactor.

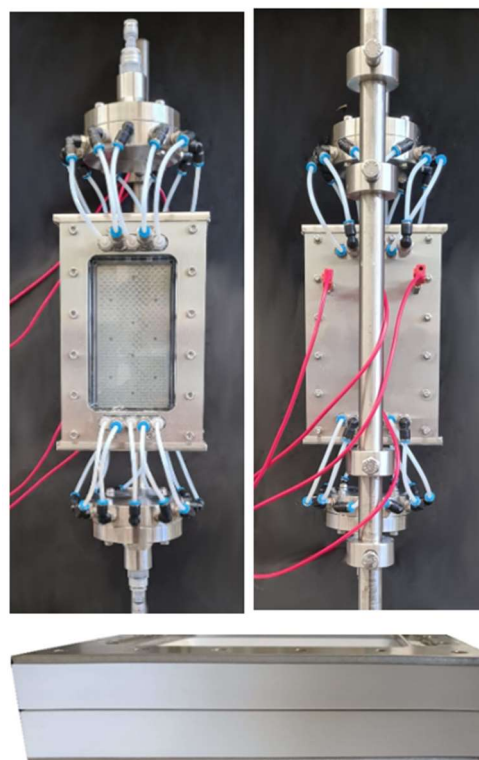


Fig 1. Images of the NETmix-based electrochemical flow reactor.

The proof-of-concept of the novel reactor in terms of global mass transfer properties was done by applying the limiting current technique for the ferricyanide-ferrocyanide reaction at different Reynolds numbers (Re). For Re from 100 to 1750, the volumetric mass transfer coefficients ($k_m A$) ranged from $\sim 1.3 \times 10^{-1} \text{ s}^{-1}$ to $\sim 5.1 \times 10^{-1} \text{ s}^{-1}$, and the mass transfer coefficients (k_m) ranged from $\sim 6.8 \times 10^{-5} \text{ m s}^{-1}$ to $\sim 2.7 \times 10^{-4} \text{ m s}^{-1}$. A comprehensive comparison of the new reactor with a commercial electrochemical flow reactor, the MicroFlowCell from ElectroCell (Denmark), revealed $k_m A$ and k_m values ~ 63 -fold and ~ 8.6 -fold higher in the new reactor, respectively, for similar Re . Moreover, the novel reactor showed mass transfer superiority over most existing reactors reported in the literature, allowing the attainment of $k_m A$ values up to ~ 54 -fold higher for similar mean linear fluid velocities (v_{avg}) and k_m values up to ~ 24 -fold higher for equal Re . Fig 2 compares the novel reactor with the MicroFlowCell and the various reactors reported in the literature. The exceptional performance of the NETmix-based electrochemical flow reactor gave rise to the filing of a provisional patent application. Part of this study was carried out together with the Collaborative Laboratory NET4CO2, Portugal.

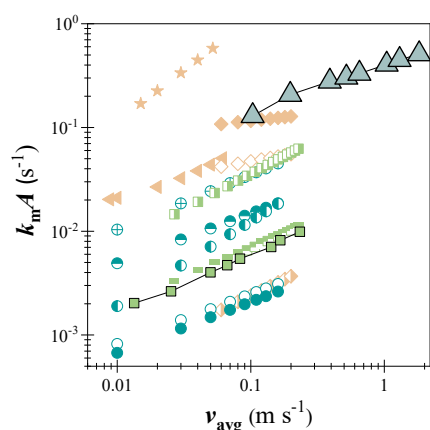


Fig 2. $k_m A$ of the NETmix-based electrochemical flow reactor versus MicroFlowCell versus literature data for various electrochemical flow reactors as a function of the v_{avg} .

Legend: NETmix-based electrochemical flow reactor (Δ); MicroFlowCell with ElectroCell turbulence promoter (TP) (\square , \blacksquare) and with Ni 100 mesh (\blacksquare); customized cells (with nickel (Ni) foam 3D electrode (\oplus), with nanostructured Ni electrode + type D TP (\blacklozenge), with nanostructured Ni electrode without TP (\diamond), with mirror polished planar Ni electrode + type D TP (\blacklozenge), with 3D Ni/stainless steel porous electrode (\blacktriangleleft), with titanium (Ti) mesh (\circ), with Ti mesh + TP (\bullet), with Ti micromesh (\ominus), with Ti fine mesh (\odot), with Ti felt (\oplus)).

Before the application of the novel reactor to the valorization of lignin and crude glycerol, its performance was assessed for a model reaction of organic electrocatalysis: the selective electrochemical oxidation of 4-methoxybenzyl alcohol (4-MBA) to *p*-anisaldehyde (PAA). A fluorine-doped tin oxide (FTO) anode was applied for this purpose. The efficiency of the process was assessed for distinct current densities (j), Re , supporting electrolyte contents, and substrate initial contents. The new reactor was extensively compared to the commercial MicroFlowCell. The main outcomes revealed that the novel reactor facilitated the use of a broader range of j (0.8-2.0 mA cm^{-2} versus 0.8 mA cm^{-2}) together with smaller Re (≥ 190 versus > 1750), supporting electrolyte contents (≥ 1 mM versus ≥ 30 mM), and substrate initial contents (≥ 2.0 mM versus ≥ 3.0 mM) with no loss of PAA production or energy consumption. Fig 3 compares the effect of Re on the efficiency of the 4-MBA selective oxidation to PAA for the NETmix-based electrochemical reactor and the MicroFlowCell. These findings underscore the remarkable suitability of this new reactor for organic electrocatalysis.

So far, the lignin selective oxidation has been assessed by the PEC process using distinct photoanodes. Highlight can be given to the photoanode made of a glass plate coated on one side by a fluorine-doped tin oxide (FTO) thin film, further by a niobium-doped titanium dioxide ($TiO_2:Nb$) thin film. Among all tested photoanodes, this photoanode provided the highest contents of V, S, and phenolic compounds. An in-depth study is currently being carried out to optimize the operational conditions to maximize production. The fabrication and characterization of photoanodes for lignin oxidation have been counting on the collaboration of the LEPABE/FEUP, the University of Minho, Portugal, and the Arizona State University, USA. Furthermore, this study has been carried out in collaboration with RAIZ – Forest and Paper Research Institute, part of The Navigator Company, Portugal.

Research on the development of the NETmix-based electrochemical flow reactor, photoanodes, and lignin selective oxidation has been carried out within the LigTech project (reference EXPL/EAM-AMB/0216/2021).

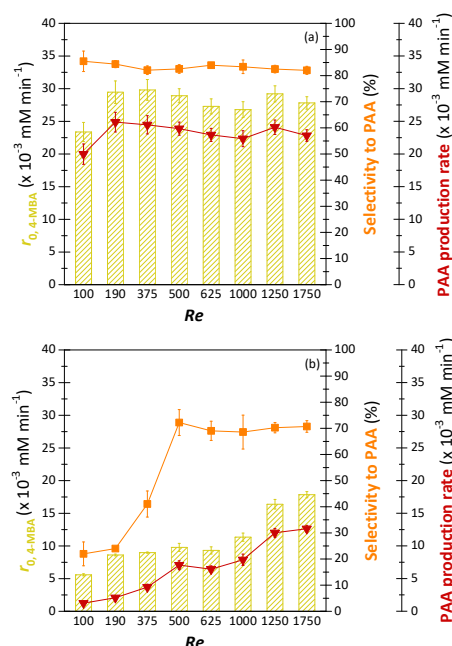


Fig 3. 4-MBA selective oxidation to PAA as a function of Re in the NETmix-based electrochemical flow reactor (a) and MicroFlowCell (b). 4-MBA initial oxidation rate ($r_{0,4-MBA}$) (hatched bars), selectivity to PAA (\blacksquare), PAA production rate (\blacktriangledown). Values for 50% 4-MBA conversion. Conditions: current density = 0.8 mA cm^{-2} , $[Na_2SO_4] = 50$ mM, $[4-MBA]_0 = 1.0$ mM, $T = 25 \pm 1$ $^\circ C$, $pH = 7.0 \pm 0.2$. Error bars are representative of deviations from duplicate trials.

Future Perspectives

The development of improved and stable (photo)anodes for lignin and glycerol selective oxidation will continue, together with the optimization of the EC and PEC operational conditions. Furthermore, the adaptation of the NETmix-based electrochemical flow reactor for a two-compartment reactor will be carried out, enabling reduction reactions at the cathode side, such as carbon dioxide reduction and hydrogen generation.

Related Sustainable Development Goals



Outputs

PhD Theses

- [1] Daniela Filipa Sousa Morais, A continuous-flow photoelectrocatalytic static mixer microreactor applied to the synthesis of high-value organic chemicals, PDEQB, FEUP, on-going, 2020-2024
- [2] Leonardo Almeida Delgado, Breakthrough photoelectrocatalytic technology for glycerol valorization, PDEQB, on-going, 2022-2026

Patents

- [1] J. C. B. Lopes, V. J. P. Vilar, M. F. C. Moreira, M. M. Q. Dias, R. J. N. Santos and R. F. S. Maia, Electrochemical device and respective uses (tentative title). Provisional Patent Application no. 118751, June 2023.

Team

Francisca Moreira, Junior Researcher; **Vitor Vilar**, Principal Researcher; Rui Boaventura, Principal Researcher; Alirio Rodrigues, Emeritus Professor; Carina Almeida, Junior Researcher; **Daniela Morais**, PhD Student; **Leonardo Delgado**, PhD Student; **Clarissa Rosa**, PhD Student; **Gabriel Cerron-Calle**, PhD Student

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 LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023
 LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019
 LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984, 2013-2018
 FCT Grants: CEECIND/02196/2017, CEECIND/01317/2017
 FCT Scholarships: SFRH/BD/146476/2019, SFRH/BD/07258/2021
 Other Scholarships: CNPq/200860/2018-6

Circular Economy: Recovery, Reuse & Valorisation

Renewable Fuels & Chemicals

Gaseous Waste Streams

KEYWORDS: CO₂ Utilization / SO₂-Depolarized Electrolysis / N₂ Fixation / Materials / Thermo-Photocatalysis / Electrocatalysis

Development of state-of-the-art technologies to unlock the potential of gaseous waste streams rich in carbon dioxide (CO₂), nitrogen (N₂), and sulfur dioxide (SO₂) to produce renewable fuels and energy carrier vectors, permitting to achieve the European Green Deal, Europe's clean energy transition, and carbon neutrality by 2050.

Introduction

In recent decades, the escalating consumption of fossil fuels and anthropogenic greenhouse gas emissions have led to an energy crisis and global warming. Intergovernmental Panel on Climate Change has issued a stark warning, emphasizing the imperative for urgent actions in pursuit of an energy transition to mitigate climate change. Responding to the pressing need for heightened global climate action, the European Parliament has ratified the European Climate Law (Regulation (EU) 2018/1999), mandating a binding target of collectively achieving net-zero greenhouse gas emissions by 2050 for EU member states. This research project is aligned with these pivotal policies by intending to unveil the potential of converting gaseous waste streams into valuable resources, not only offering a pathway to cleaner energy alternatives but also contributing to a more sustainable and circular economy. The experimental focus of this endeavor revolves around the development of novel materials, designing computer fluid dynamics (CFD) models, and testing breakthrough reactors for the valorization of carbon dioxide (CO₂) into renewable ethanol (EtOH) and methane (CH₄), nitrogen (N₂) into ammonia (NH₃), and sulfur dioxide (SO₂) into hydrogen (H₂) and sulfuric acid (H₂SO₄).

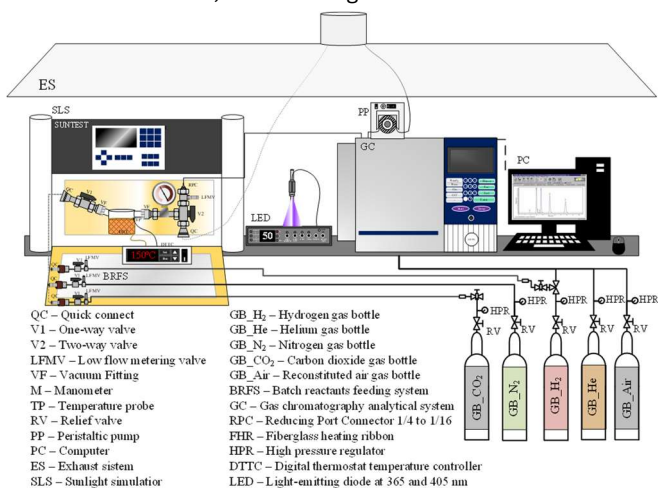
Current Development

Under this project's scope, the following approaches were addressed as regards CO₂ valorization via solar-driven thermo-photocatalysis: (1) oxidative dehydrogenation of ethane (C₂H₆) with CO₂ into EtOH over strontium titanate (SrTiO₃) co-loaded with ruthenium oxide (RuO₂) and nickel oxide (NiO), in close collaboration with the Polytechnic University of Valencia, Spain; and (2) hydrogenation of CO₂ into CH₄ over hybrid catalysts composed of (2.1) mesostructured silica SBA-15 functionalized with titanium dioxide (TiO₂) and further loaded with RuO₂, and (2.2) zeolite 13X impregnated with either RuO₂-loaded TiO₂ or RuO₂-loaded SrTiO₃, under the CO₂-to-CH₄ project.

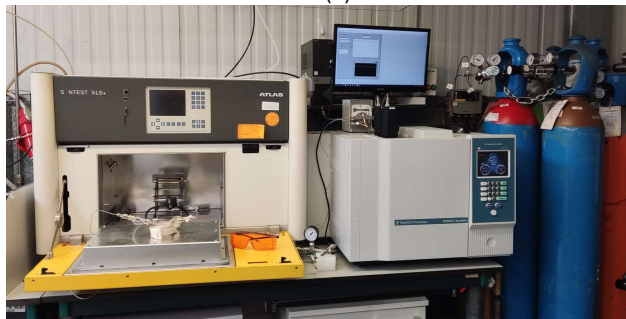
To assess the thermo-photocatalytic activity of the novel materials towards CO₂ hydrogenation, a lab-scale batch-mode prototype was designed and constructed, as displayed in Fig 1. The experimental apparatus included: (i) a cylindrical quartz photoreactor (40 mL); connected to (ii) a feed system consisting of H₂/CO₂ gas bottles and Swagelok connections (tubing, fittings, and valves); (iii) a pressure control system (up to 4 bar) to regulate the reactor pressure/reactants feed; (iv) a temperature control system (up to 300°C) consisting of a fiberglass heating ribbon (FHR), surrounding the reactor, coupled to a digital thermostat temperature controller (DTTC); (v) an irradiation source, which could be a xenon (Xe) lamp equipped in a sunlight simulator (Atlas, Suntest XLS+) emitting polychromatic radiation between 280 and 800 nm, or a light emitting diode (LED) emitting monochromatic

radiation at 365 nm or 405 nm; and (vi) an online gas chromatography (GC) analytical system to analyze the gas samples directly withdrawn from the reactor headspace using a peristaltic pump.

From the three abovementioned approaches for the valorization of CO₂, the following results were obtained.



(a)



(b)

Fig 1. (a) Sketch and (b) photograph of the batch-mode gas-phase thermo-photocatalytic methanation system.

Approach 1. It was observed that: (i) the functionalization of the SrTiO₃ with RuO₂ and NiO allows the visible light harvest and narrows the band gap energy (ca. 14–20%); (ii) the selectivity towards EtOH depends on the presence of Ni and irradiation; (iii) the catalyst photoresponse is mainly due to the visible photons; (iv) the photocatalyst loses > 50% efficiency right after the 2nd use; (v) the reaction mechanism is based on the photogenerated electron-hole pair charge separation; and (vi) a maximum yield of 85 μmol EtOH g_{cat}⁻¹ h⁻¹ under simulated solar irradiation (1,000 W m⁻² between 200–700 nm) at 200 °C, using 0.4 g L⁻¹ of NiO(0.6%):RuO₂(1.0%):SrTiO₃. Despite its exploratory nature, this study offers an alternative route to solar fuel synthesis from underutilized C₂H₆ and CO₂.

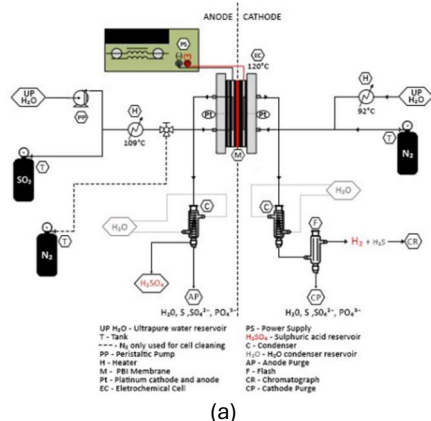
Approach 2.1. The best methanation yields were attained for the RuO₂(6.4%):TiO₂(16.9%)/SBA-15 nanocomposite at 150 °C, under simulated sunlight (0.21 W between 280–800 nm) and stoichiometric [H₂]:[CO₂] molar ratio (4:1), reaching: a specific CH₄ production rate of 13.6 mmol g_{cat}⁻¹ h⁻¹; 99.8% selectivity; 96.8% CO₂ conversion (110-min; reactor volume

of 40 mL); and apparent photonic efficiency/quantum yield of 39.5%/42.1%. Considering only the active RuO₂:TiO₂ photocatalyst mass (23.3%), the CH₄ production rate increased to 58.6 mmol g_{active_cat}⁻¹ h⁻¹. Besides, this highly-active photocatalyst featured excellent UV-Vis-IR light absorbance, a high surface area, and stability for reuse when moist gas was removed between cycles.

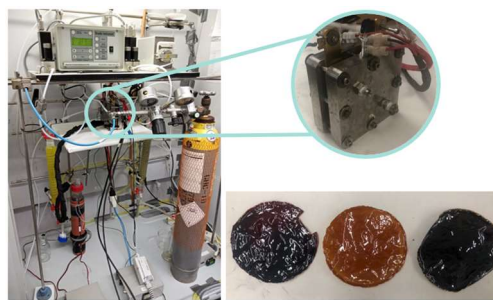
Approach 2.2. The hybrid RuO₂(4.0%):TiO₂(26.3%)/Z13X material (30 mg), synthesized by solid-state impregnation method, showed the best results under simulated sunlight (0.75W) at 150 °C, achieving a 88% CO₂ thermo-photoreduction after 100 min (40 mL), corresponding to a specific CH₄ production of 29.2 mmol g_{active_cat}⁻¹ h⁻¹ (309 mmol g_{Ru}⁻¹ h⁻¹) and apparent quantum yield of 20.7%. Adsorption equilibrium isotherms demonstrated that enhanced methanation performance at 150 °C can be attributed to the synergistic action of CO₂ capture and thermo-photoconversion boosted by the bifunctional material.

Regarding the artificial N₂ photocatalytic fixation into NH₃, a worldwide fertilizer and emerging energy vector, bio-inspired materials were developed in collaboration with the University of Bayreuth, Germany. In this context, iron (Fe) and molybdenum (Mo)-based catalysts were tested in the liquid-phase under semi-batch operation mode. Both Mox-Fe₃S₄ and Mox-Fe₃S₄@TiO₂ composites have demonstrated good photoactivity. While the composites tend to exhibit higher performance for the hydrogen evolution reaction than Mox-Fe₃S₄ materials, reaching a maximum H₂ production of ~1000 μmol L⁻¹, the Mox-Fe₃S₄ exhibits greater activity for NH₃ conversion than the composites, reaching contents between 1200 and 1600 μg L⁻¹. However, blank experiments using argon instead of N₂ indicated that the generated NH₃ might result from the reaction with N contained in the catalyst rather than the gaseous N₂ feed to the reactor, suggesting that different precursors must be used for the photocatalysts synthesis.

SO₂ stream was valorized into H₂ and H₂SO₄ via SO₂-depolarized water electrolysis based on the electrochemical step of the Westinghouse cycle, using proton exchange membranes (PEM) in a lab-scale single-cell electrolyzer unit (Fig 2a). This work was carried out in collaboration with the University of Castilla-La Mancha, Spain.



(a)



(b)

Fig 2. (a) Sketch and (b) photographs of the (left) laboratorial single cell electrolyzer and (right bottom) the thermally cured standard PBI membrane, standard PBI membrane, and PBI membrane with 2% GO (from left to right).

Three types of PEMs were applied and characterized: (i) standard polybenzimidazole-based membrane (PBI); (ii) PBI with 2% graphene oxide (GO); and (iii) thermally cured PBI, all of them doped with H₃PO₄ (Fig 2b). Water electrolysis using a PBI membrane with 2% GO provided the generation of higher amounts of H₂ and lower amounts of hydrogen sulfide (H₂S), an undesired reaction by-product, compared to the use of a standard PBI membrane, ultimately leading to a higher process efficiency. The higher efficiency for H₂ production, achieved for the PBI membrane with 2% GO, can be attributed to its higher content of H₃PO₄ and higher capacity to retain this acid, which contributed to a higher conductivity. The new membrane also showed to be more chemically stable in the presence of persulphate. An additional characterization of a thermally cured PBI membrane showed promising results for H₂ production.

Future Perspectives

CO₂-to-CH₄ project, supported by the Portuguese Foundation for Science and Technology: A continuous-flow solar-driven thermo-photocatalytic reactor is being constructed, and it will be applied to foster CO₂/N₂ hydrogenation under gas-phase at low onset temperatures. Novel nanostructured materials will also be synthesized to improve CO₂/N₂ conversion efficiency.

ATE Agenda, the Alliance for Energy Transition, supported by the Portugal's Recovery and Resilience Plan: new solutions for hydrogen production using the Westinghouse process, including (i) development of an electrochemical cell based on the NETmix technology for SO₂-depolarized electrolysis, targeting the paired synthesis of H₂ and H₂SO₄; and (ii) transfer strategies of the Westinghouse process using integrated process simulation tools, targeting a competitive hydrogen cost, considering the direct valorization of SO₂ industrial streams or industrial units with heat production (nuclear power plants and solar concentrators).

Related Sustainable Development Goals



Outputs

PhD Theses

- [1] Larissa Oliveira Paulista, Solar-driven thermo-photocatalytic CO₂ valorisation into value-added fuels, PDEA, FEUP, 2023
- [2] Fabiane Soares Lira, A step forward in photocatalytic nitrogen fixation: towards a more sustainable future, PDEA, FEUP, 2021-2025, on-going

Master Dissertations

[1] Inês Lopes Pinho, Electrochemistry for water remediation and energy production, MIEQ, FEUP, 2021

[2] Rui Daniel Gonçalves Matias, Photo-thermocatalytic hydrogenation of CO₂ into methane driven by sunlight, MIEQ, FEUP, 2023

Selected Publications

[1] L.O. Paulista et al., Catalysts 11, 461 (2021)

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