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Techno-economic and life cycle assessment of power-to-formic acid production using direct air capture and green hydrogen

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ABSTRACT

The chemical industry is responsible for a significant portion of global carbon emissions. Defossilising the chemical industry is crucial for achieving climate change targets. Carbon capture and utilisation (CCU) has emerged as a promising alternative for chemicals production. Formic acid is increasingly important in the global economy as a versatile chemical used in agriculture, food preservation, and as a potential hydrogen storage.

To this direction, this study assesses the environmental and the economic performance of producing formic acid (FA) through a Power-to-Formic Acid (PtFA) process, focusing on the utilisation of green hydrogen and carbon dioxide captured from direct air capture (DAC). A cradle-to-gate life cycle assessment (LCA) was conducted, focusing on the climate change, fossil depletion and water consumption, using the ReCiPe Midpoint (H) while the minimum selling price (MSP) has been used as the main economic indicator.

The economic assessment identified the DAC and the electrolyser as the major contributors to Capital expenditures (CAPEX), while catalyst and electricity cost are the main Operating expenditures (OPEX) contributors. The resulted MSP of the PtFA is more than two times higher than the price of the conventional FA, at £1290 per tonne vs £560 per tonne, respectively. Additionally, the LCA revealed that the PtFA process reduces by 92% the CO_2eq. emissions compared to the conventional production process (190.72 vs. 2190 kg CO_2eq./tonne FA), uses 94% less water, and consumes 92% fewer fossil resources. The primary drivers of carbon emissions are the chemicals consumed in FA synthesis, and electricity generation.

This study provided new and important information regarding a sustainable chemical industry and it is the first attempt to holistically assess from a technical, economic and environmental perspective a PtFA process that contributes to the defossilisation efforts of the chemicals sector.

1. Introduction

The chemical industry is one of the industries that generates a wide range of products that play a critical role in various sectors and economies such as agriculture, pharmaceutical and textile. However, it is also a significant contributor to global carbon emissions. In 2023, the chemical industry global emissions has totalled about 2 billion metric tons (MT) of CO_2, accounting for around 5% of total emissions (Gabrielli et al., 2023). This has driven R&D efforts towards solutions that can replace fossil carbon sources with sustainable carbon sources that can produce identical chemicals. Defossilisation of the chemical industry is essential to achieving global sustainability and climate targets.

One promising strategy to achieve this goal is the utilisation of captured carbon dioxide (CO_2) from air as a feedstock for chemical production through the Power-to-X (PtX) approach (de Vasconcelos and Lavoie, 2019; Decourt, 2019; Daiyan et al., 2020). This approach not only offers a pathway to reduce carbon emissions but also aligns with circular economy principles by converting waste CO_2 into valuable products (Thonemann, 2020; Chauvy and De Weireld, 2020). Among the various chemicals that can be produced using captured CO_2, formic acid (FA) stands out due to its wide range of industrial applications, including its use as a preservative, antibacterial agent, and in fuel cells (Liu et al., 2015; Supronowicz et al., 2015). Formic acid (HCOOH, FA) is the simplest carboxylic acid, a colourless liquid miscible with polar solvents.

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FA is widely used as a food additive, preservative in silage and animal feed, and as a bactericide. It also finds applications in the dyes, rubber, textile, and leather industries (Dutta et al., 2022). In the fuel industry, FA is considered a promising candidate for hydrogen storage due to its high volumetric capacity and low toxicity (Dutta et al., 2022; Kim et al., 2022; Solakidou et al., 2023; Singh et al., 2016). The global market for formic acid reached approximately 750 thousand tonnes in 2022 and is expected to grow at a rate of approximately 4.5% annually up to 2035, with China being the largest producer (ChemAnalyst, 2022). Formic acid has been the focus of several projects in Europe that apply the power-to-chemicals concept (Pérez-Fortes et al., 2016). For example, the Norwegian company DNV has developed a pilot plant for the electrochemical conversion of CO_2 into formic acid. Additionally, the European Horizon 2020-funded C2Fuel project aims to produce dimethyl ether (DME) and formic acid from renewable hydrogen (H_2) and captured CO_2 from industrial sources (Chauvy and De Weireld, 2020).

The conventional production process of formic acid involves two steps: the carbonylation of methanol in the presence of a base catalyst (such as sodium or potassium), followed by the hydrolysis of methyl formate to formic acid (Aldaco et al., 2019). This process has several drawbacks, including an unfavourable hydrolysis equilibrium, which results in high energy consumptions. Additionally, the carbon monoxide used is typically obtained from fossil resources (Aldaco et al., 2019; Artz et al., 2018).

Alternative technological routes for formic acid production, such as electrolytic CO_2 conversion, have been explored. Various studies have evaluated the feasibility of electrolytic formic acid production, but the main challenges include high electricity consumption and the use of expensive cell materials (Kim et al., 2022; Rumayor et al., 2018, 2019; Chatterjee et al., 2021; Kang et al., 2021; Thonemann and Schulte, 2019; Banu et al., 2023; Gao et al., 2023). The catalytic CO_2 conversion is a promising route for FA synthesis. Several studies have investigated the catalyst performance of CO_2 hydrogenation into formic acid using both heterogeneous and homogeneous catalysts (Chiang et al., 2018). Heterogeneous catalysts, such as Ru polymeric catalysts, have shown excellent selectivity and stability (Mura et al., 2012; Mariyaselvakumar et al., 2023). These catalysts offer the advantages of recyclability and efficient separation from products. Metal catalysts like Au, Si, Pd, Ir, and Ru, along with various support materials, have been tested with promising results (Liu et al., 2022; Nie et al., 2021; Reymond et al., 2018; Bulushev and Ross, 2018; Zhang et al., 2018). For example, Ru catalysts have demonstrated CO_2 per pass conversion efficiencies of around 44%, with favourable turnover frequencies achieved using additives such as ethanol and trimethylamine (Zhang et al., 2018; Park et al., 2020). Homogeneous catalysts also showed potential for FA synthesis, particularly due to their reversibility towards H_2 production at high rates and room temperature (Supronowicz et al., 2015). High CO_2 conversion rates (greater than 95%) can be achieved under mild conditions, with Ru-phosphine catalysts being the most commonly used due to their high turnover frequencies and selectivity (Pérez-Fortes et al., 2016; Chiang et al., 2018; Kim and Han, 2020; Kim et al., 2024).

As for any technology, it is crucial to evaluate the energy intensity, economic viability, and environmental impact of the PtFA process to ensure sustainability. Although some studies have performed economic and environmental assessments for FA production via the catalytic and electrolytic route, there is a scarcity of research addressing both economic and environmental aspects in a holistic manner that involve all the unit operations of the PtFA assembly and their integration to minimise energy requirements.

Kim and Han (2020) presented two commercial-scale processes for catalytic production of formic acid (FA) from CO_2, analysing economic, energy, and environmental indicators. The results showed that the minimum selling price (MSP) of formic acid using a Ru-Ph catalyst (process A) reached US $1029 per tonne of FA, with the primary cost drivers being hydrogen production and the catalyst consumption. They also reported net CO_2 emissions of 0.36 tonnes per tonne FA, accounting for CO_2 uptake and excluding the production of H_2 in the model. In a separate study, Perez-Fortes et al. (Pérez-Fortes et al., 2016) conducted process modelling to evaluate the techno-economic and environmental aspects of thermocatalytic production process of formic acid from captured CO_2 and renewable H_2. They found that hydrogen capital costs and the catalyst were the main contributors to an MSP of €1656 per tonne. Their environmental assessment allocated zero emissions to renewables, resulting in an underestimation of CO_2 emissions (0.166 tonnes per tonne FA). Gokberk (Gokberk and Wiebren, 2020) studied a large-scale CO_2 and biomass-based formic acid production system. They concluded that the biomass route exhibited higher energy efficiency than the CO_2-based route (37% vs. 31%, respectively). However, the CO_2 hydrogenation route involved higher capital expenditures due to reactor costs, while the biomass route had a significantly higher breakeven selling price of US $22,060 compared to US $2363 per tonne FA for the CO_2 route. This discrepancy was attributed to the higher material costs in the biomass case. A recent study by Kang et al. (2021) quantified the climate change and fossil depletion impacts of formic acid production through catalytic hydrogenation. They reported that GHG emissions could be reduced by 97%–132% and fossil resource consumption by 69%–94% compared to conventional production. The major contributor to these reductions was the CO_2 capture included in the net emission calculations. Kim and Park (Kim et al., 2024) presented a pilot-scale process for formic acid production via CO_2 hydrogenation through the catalytic route, including techno-economic and life cycle assessments (TEA/LCA). They reported CO_2 conversion rate of 82% and a formic acid purity of over 92%. Their proposed process reduced production costs by 37% and global warming impact by 42% compared to the FA fossil-based process. Barbera et al. (2020) performed a simulation model incorporating kinetics to convert CO_2 into C1 chemicals through hydrogenation. They assumed H_2 availability from renewable sources obtaining a carbon conversion rate of 88%, an energy ratio of 0.229, and carbon emissions of 0.366 tonnes CO_2 per tonne FA. Other environmental impacts beyond CO2 GWP have been assessed only in a few studies. Robledo-Diez (Robledo-Díez, 2012) reported 18 categories within the ReCiPe method including freshwater, human and marine ecotoxicity, eutrophication, metal depletion, ozone depletion, particulate matter formation among others. However, they emphasize climate change as the most relevant category. Suzuki et al. (2024) evaluated in addition to the GWP, the abiotic depletion of formic acid production. Omodara (2013). compares CCU - formic acid and conventional fossil using a sustainability framework that includes impacts on human health and pollution prevention.

The aforementioned TEA/LCA studies have evaluated the potential of producing formic acid (FA) through thermocatalytic routes using renewable sources such as green H_2 and captured CO_2, however, these studies have limitations. Many of them include fossil resources as fuels or electricity in their processes, which detracts from the overall sustainability. Additionally, these studies often rely on black-box models or simple simulations of FA reactors that do not incorporate detailed reaction kinetics. This lack of detailed modelling limits the accuracy and applicability of the findings. Moreover, these studies generally do not conduct a comprehensive TEA and LCA of the entire power-to-formic-acid (PtFA) process. They typically dismiss the full accounting of the environmental and economic impacts of the producing H_2, capturing CO_2 and generating electricity. A common practice used in previous studies in LCA is to include the carbon uptake in the capture model, but this approach can underestimate the carbon footprint in a cradle-to-gate analysis since the carbon is eventually released back into the atmosphere at the end of the product lifecycle.

This study aims to bridge these gaps by comprehensively evaluating the environmental (utilizing a life cycle approach) and economic performance of the whole PtFA assembly. Hence, this is the first study to investigate all unit operations involved including green H_2 and CO_2 captured from the air, utilizing renewable offshore wind energy as the primary electricity source and FA synthesis and purification as well as

integration of system components to minimise energy requirements. This approach offers an accurate representation of the potential of carbon capture utilisation, CCU-based, formic acid in reducing greenhouse gas emissions, water consumption, and fossil resource use compared to traditional production methods, contributing valuable insights towards the sustainable transformation of the chemical industry to numerous stakeholders such as academics, policy makers and industrialists.

The combination of TEA and LCA is critical for evaluating both the environmental impact and economic feasibility of projects, particularly within emerging technologies such as PtX pathways. This integrated approach provides a robust methodology for validating the proposed PtFA process while offering a comprehensive understanding of the benefits and challenges associated with FA production. Furthermore, it facilitates the development of a scalable, sustainable framework that aligns with market demands, environmental objectives, and policy goals.

2. Methodology

The present study focuses on the techno-economic and environmental assessment of a Power to Formic Acid (PtFA) assembly. The location of the plant has been set in the Teesside region of North Yorkshire, United Kingdom where an offshore wind farm supplies around 7 MW electricity to produce around 15 ktonne FA/y. The plant size has been determined by referencing similar CCU-based formic acid production studies (Pérez-Fortes et al., 2016; Rumayor et al., 2019) and is designed to cover 5% of the installed capacity of Europe's leading formic acid producer, BASF, which currently has an installed capacity of 305 ktonne/year. The methods applied for the technical, economic and environmental assessment of the system are described in this section.

2.1. Description of the model

The model consists of an offshore wind farm that supplies electricity to the plant, an electrolysis unit where hydrogen is obtained at high purity and a DAC module that captures CO_2 from ambient air at purity >95%. The process is divided into 4 sections: Direct air capture module, hydrogen production, formic acid synthesis and formic acid purification. The plant produces 15 ktonne of FA per year. A simulation model of the PtFA plant has been developed using the process simulator Aspen plus V12.2 to establish the mass and energy balances. A block flow diagram of the PtFA is shown in Fig. 1.

The DAC system has been modelled based on the technology developed by Carbon Engineering (Keith et al., 2018). H_2 production is achieved using a PEM electrolyser system. The DAC and the PEM electrolyser provide the raw materials, i.e. CO_2 and H_2, for the synthesis of FA that is achieved through homogenous catalysis and modelled using a rigorous kinetic model. The last step incorporates the purification of FA.

2.1.1. Direct air capture model

The CO_2 capture system has been modelled according to the carbon engineering air-liquid technology. The simulation model of carbon capture have was performed using data provided by Keith et al. (2018), and Bianchi (2020). The system comprises four major unit operations: air contactor, pellet reactor, slaker and calciner. The stages are briefly described below, however, the detailed models of each section of the DAC unit are available in the supplementary information.

2.1.1.1. Air contactor. In the air contactor unit, ambient air is horizontally injected to a series of air contactor structures with plastic packaging where an alkali solution of KOH flows in a cross-flow configuration. The CO_2 is transferred to the liquid capture solution by a reaction-diffusion process, equation (1) (Keith et al., 2018).

$$2KOH(aq) + CO_2(g) \rightarrow K_2CO_{3\ (aq)} + H_2O(l) \quad (1)$$

An Electrolyte-NRTL thermodynamic model is chosen to represent the Gibbs free energy and the activity coefficients of an electrolyte system based on the alkali ionic mixture. The contactor is represented using a mixer where the atmospheric air and the KOH ionic solution are combined and fed to a separator unit that bonds the CO_2 into the alkali solution rich in carbonates. This rich solution is pumped to next section for pellets formation. The CO_2 capture efficiency of the system has been specified at 75% based on Keith et al. (2018).

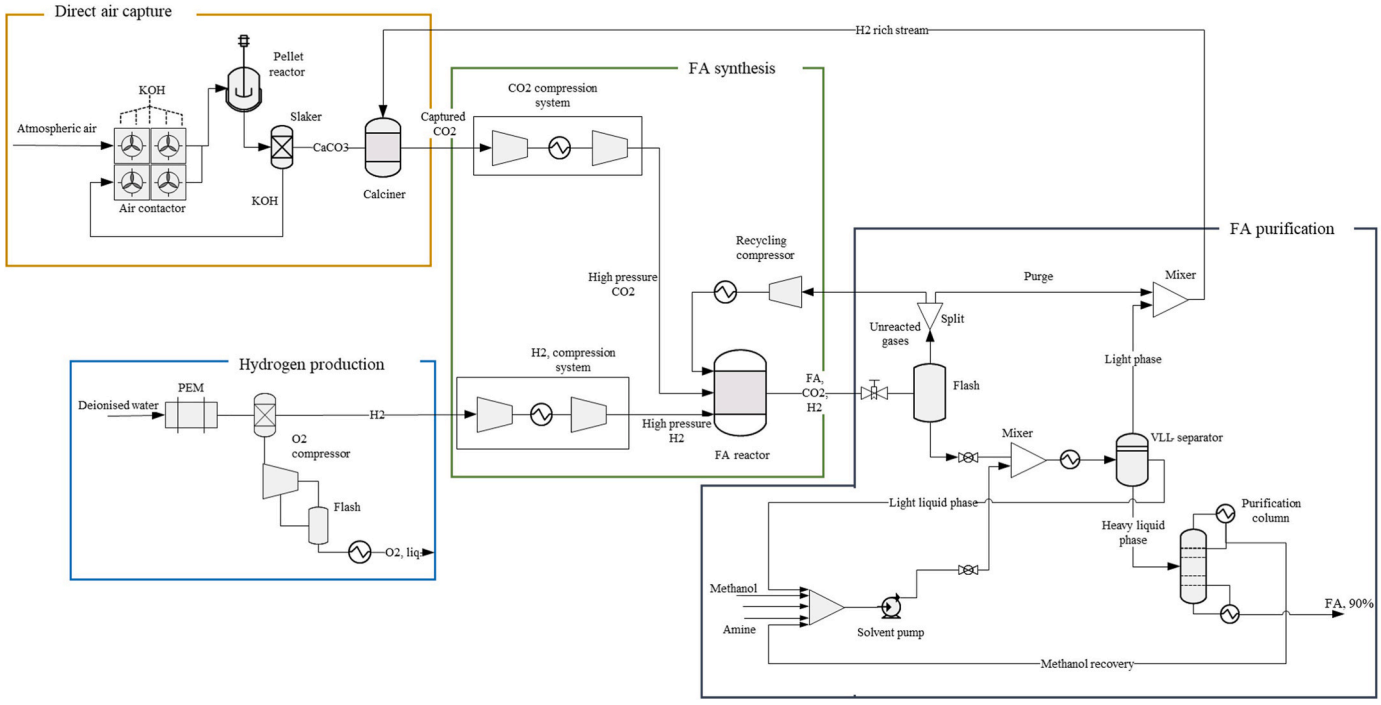

Fig. 1. The block flow diagram of the investigated PtFA assembly.

2.1.1.2. Pellet reactor. The aim of the pellet reactor is to remove the carbonate ion from the enriched solution to form carbonated pellets according to the causticization reaction in equation (2).

$$K_2CO_3 + Ca(OH)_2 \rightarrow 2KOH + CaCO_3 \quad (2)$$

The causticization is a crystallisation reaction and hence a crystallizer block was used in Aspen Plus (Bianchi, 2020). The unit operating conditions has been set as 25 °C and 1 bar. In addition, the equilibrium and dissociation reactions have been previously introduced in the Aspen properties section (see supplementary information).

The causticization reaction is carried out by injecting a slurry of 30% $Ca(OH)_2$. The Ca^{2+} ions reacts with the carbonate ions (CO_3^{2-}) formed in the air contactor dissolving the $Ca(OH)_2$ and precipitating $CaCO_3$ into pellets (Keith et al., 2018). In the simulation model, the ionic solution is fed into the crystallizer in addition to the $Ca(OH)_2$ stream that comes from the successive slaker section. Products stream is split into two streams to represent the physical separation in the pellet reactor. One of the streams contains manly the $CaCO_3$ solids that are filtrated to increase the calcium retention and recirculate the remaining liquid to the pellet reactor. The second stream is sent to a series of filters to enhance $CaCO_3$ solids recovery and obtain a KOH rich solution that is returned to the air contactor (Bianchi, 2020).

2.1.1.3. Slaker. In the steam slaker section, calcium oxide (CaO) at 674 °C from the calciner section is hydrated to form $Ca(OH)_2$ that is used in the pellet section equation (3).

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (3)$$

The calcium pellets from the previous reaction, are washed to remove residues of hydroxide liquid. Then, they are dried and preheated to 300 °C by passing through the slacker providing the steam for the reaction. The hydrated lime, $Ca(OH)_2$, product stream is cleaned from small CaO particles by passing through a series of cyclones (simulated as separator blocks). CaO particles are recirculated to the slacker while $Ca(OH)_2$ at 300 °C is cooled down from which heat is recovered and along with the heat from the slaking reaction, is used to provide heat for pellets drying (Keith et al., 2018).

2.1.1.4. Calciner. The design of the calciner has been modelled according to the design of Keith et al. (2018). Dry pellets are fed to the calciner section where CO_2 is recovered as product of the calcination reaction in equation (4).

$$CaCO_3 \rightarrow CaO + CO_2 \quad (4)$$

Carbon Engineering has designed the calciner reactor fitted with an oxy-combustion unit. For modelling purposes, these two operations have been modelled as separate units, however, in the real design both represent a single unit operation as stated in (Bianchi, 2020). Initially, $CaCO_3$ pellets at 300 °C from the slaker are passed through a heat recover system to recover heat from the exhaust gas stream. The model differs from Keith et al. (2018), since in the original model, a second heat exchanger has been used to recover heat from the outgoing stream and produce steam for power generation. In this model, the second heat exchanger for power generation has been omitted. Instead, the power requirements of the whole DAC plant is supplied by the wind farm, and the heat from the products stream is used to increase the temperature of the feed from 300 °C to 770 °C before the calciner that operates at 900 °C. The energy for calcination in the original design is provided by an oxy-fired combustion of natural gas, which is injected into the calciner releasing CO_2 and water as flue gases (Keith et al., 2018). In our proposed model, a H_2 rich stream derived from the successive formic acid synthesis section has been used as a fuel. Consequently, in this study the utilisation of external fossil resources is avoided.

After calcination, the outcome stream containing mainly CO_2 and water is sent to the CO_2 cleaning unit where water is knocked out and CO_2 reaches purity of 98%. CaO that leaves the reactor at 900 °C is cooled by exchanging heat with the oxygen from the electrolyser, which is used in the oxy-fired combustor. Finally, CaO returns to the slaker section.

2.1.2. Green H_2 production

The hydrogen production has been modelled using a polymer electrolytic membrane (PEM) unit. It exhibits multiple advantages over other electrolysers such as high efficiency and high product purity (Hank et al., 2018; Shiva Kumar and Himabindu, 2019). The PEM unit has been simulated as a stoichiometric reactor unit using conditions stated in (Shiva Kumar and Himabindu, 2019). Initially, deionized water is delivered at a flowrate of 0.01 m^3/kg H_2 (Lundberg, 2019), then the electrical supply initiates reaction where water is split into oxygen and hydrogen. Hydrogen product is purified in a separation unit that removes oxygen. The water and H_2 that remain in the stream are passing through a heat exchanger where temperature is reduced to 25 °C to facilitate flash separation, increasing hydrogen purity to 99.9%. The O_2 that has been separated in the separator unit is used for two purposes: 1) oxygen is sent to the DAC system where serves in the oxy-combustion for energy recovery and 2) it is liquefied to obtain commercial oxygen with an economic value. The liquefaction stage is configured as in Johnson et al. (2018) consisting in a flash unit, a multiple compressors that operating at 51 bar followed by cryogenic cooling at temperature of −123 °C and final expansion to 1.2 bar. The model is not a rigorous simulation model but it provides the mass and energy balance for the equipment cost estimation. Thus, the PEM electricity consumption is estimated by the H_2 high heating value (HHV), a 75% electrolyser efficiency (Harrison et al., 2014) and the amount of hydrogen required by the FA synthesis. Other electricity requirements for water purification has a minor contribution to the overall energy requirement and it is included in the balance of plant (BoP) (Terlouw et al., 2022). Finally, the lifetime of the equipment has been set as 80,000 h (Shiva Kumar and Himabindu, 2019).

2.1.3. Offshore wind power supply

The power supply has been modelled as an offshore wind farm located near the FA plant, in the Teesside region. The System Advisor Model (SAM) is used to estimate power generation by inputting the wind profile at specific location that includes temperature, pressure, wind speed, and direction. These profile conditions have been obtained from Meteonorm v7.2 software and then ingested into SAM software to estimates the hourly power output using a commercial turbine model. The turbine model selected was the Senvion 6.2M126 offshore that has a turbine height of 80 m, while wind profile is given at a default height of 10 m. Therefore, the wind speed has to be adjusted to the actual turbine height using equations in (Manwell et al., 2010).

As the actual power output from the wind farm is estimated according to the wind and the PtFA plant requires a continuous energy supply, a backup energy strategy is proposed. The energy grid network is used as a storage system in order to storage electricity when wind farm electricity production exceeds demand, but drawing it when generation in the farm is insufficient to supply PtFA needs. Thus, the wind farm is designed to balance the electricity that is sent to and recovered from the grid. Moreover, the cost of the grid network use is included in the economic analysis to reflect this expense.

2.1.4. FA synthesis

In this study, a conceptual design of the catalytic conversion to produce high purity formic acid (90%) from CO_2 is presented. The model has been developed using Aspen Plus simulator V12.2 and using the conditions described in Mantoan et al. (2019). This section involves the CO_2 and hydrogen compression, FA reaction synthesis, solvent recovery, and FA purification.

2.1.4.1. Compression system. The CO_2 coming from the DAC module at 60 °C and 1 bar is compressed to reactor conditions (105 bar and 50 °C) through a series of four compressors with intermediate cooling to control the temperature before entering the reactor. The isentropic efficiency has been set at 92%. Similarly, the H_2 stream from the electrolysis unit at 25 °C and 35 bar is compressed to 105 bar using a compressor unit and it is cooled down to the reactor temperature through a heat exchanger.

2.1.4.2. Reaction synthesis. The formic acid synthesis is based on the studies of Barbera et al. (2020), Mantoan (Mantoan et al., 2019) and Perez-Fortes et al. (Pérez-Fortes et al., 2016) which attempted to reproduce the commercial BASF patent (Schaub et al., 2014) for CO_2 hydrogenation into formic acid. The process comprises a homogenous catalytic reaction of CO_2 and H_2 in presence of a tertiary amine and a polar solvent. equation (5) takes place at high pressure of 105 bar and 50 °C as reported in (Barbera et al., 2020; Surywanshi et al., 2022).

$$CO_2 + H_2 + C_{15}H_{33}N \leftrightarrow C_{15}H_{33}N - HCOOH \quad (5)$$

The triamylamine ($C_{15}H_{33}N$) is used to stabilize the formic acid product as a 2:1 adduct; water/methanol mixture has been used as polar solvent additive which is known to accelerate the reaction (Thomas et al., 2001). The catalyst chosen is the complex Ru/Ph as indicated in (Singh et al., 2016; Schaub et al., 2014; Wang et al., 2023). The reactor has been simulated as an isothermal continuous stirred tank reactor (CSTR) using the kinetic parameters presented in the supplementary information. Matlab has been used to solve the kinetic equations while Excel serves as the intermediate to transfer data from and to Aspen plus. Additional details on the simulation model of the reactor can be found in Supplementary Information.

2.1.4.3. Solvent recovery and FA purification. The product stream of the reactor is cooled down to 90 °C and then it is flashed to separate unreacted gases such as CO_2 and H_2 that are recirculated to the reactor. Further, the solvent mixture of methanol/water and amine is pumped from 1 to 105 bar. In the real process, the mixture is fed to the reactor for enhancing FA formation. However, due to lack of information about thermodynamic equilibrium in the reactor, the solvent mixture is simulated separately from the reactor and conditioned to the same temperature and pressure only to account for the energy requirements of the separation and purification system as suggested in (Barbera et al., 2020; Mantoan et al., 2019). The stream is cooled down to 50 °C and laminated at 1 bar before being mixed with FA product. A purge of 5% is considered to avoid accumulation of components. This purge is a H_2-rich stream, and it is sent to the DAC-calciner system to provide heat.

Product stream and solvent stream are mixed and sent to a vapour liquid-liquid (VLL) separator. Here, the remaining gases are separated and sent them to the purge stream while the liquid phase forms two immiscible liquid phases (Mantoan et al., 2019). The light liquid phase, comprising mostly the triamylamine, is recovered and sent it back to the reactor. The heavy liquid phase containing formic acid, methanol and water is sent to a distillation column for further purification. The column is designed as an equilibrium Radfrac unit with 20 stages and operating at 1 bar (Barbera et al., 2020). The reflux ratio has been set at 1.5. Methanol and water are recovered in the distillate and recycled while purified formic acid is recovered at the bottom. The amount of solvent required for the separation of FA has been determined by a design specification tool in Aspen plus based on the amount that is recirculated from the VLL streams and the column, and preserve the ratio 2:1 between solvents and FA.

It has been assumed that methanol solvent is renewed once every ten years while catalyst is renewed once per year. It is also assumed that catalyst is completely recovered as stated in Perez-Fortes et al. (Pérez-Fortes et al., 2016) and Surywanshi et al. (2022). The simulation of the catalyst recovery is not considered in this study, but the equipment cost data has been taken into account in the economic analysis. Table 1 summarises the parameters for FA synthesis.

2.2. Key performance indicators (KPIs)

2.2.1. Carbon efficiency

The carbon efficiency is the fraction of the initial carbon dioxide that is found in the final product, i.e. formic acid. equation (6) indicates the moles of carbon present in the FA product per unit of carbon in the feedstock.

$$C_e = \frac{\dot{n}_{CFA}}{\dot{n}_{C_{CO_2}} + \dot{n}_{C_{met+amine}}} x100\% \quad (6)$$

2.2.2. CO_2 conversion efficiency

In this study, both per pass, equation (7), and the overall CO_2 conversion, equation (8) have been calculated as technical indicators.

$$\eta_{CO2-R} = \frac{CO_{2-in} - CO_{2-out}}{CO_{2in}} x100\% \quad (7)$$

$$\eta_{CO2-P} = \frac{CO_{2-in} - CO_{2-out}}{CO_{2-in}} x100\% \quad (8)$$

Where $CO_{2\text{-in}}$ indicates the moles of CO_2 that is fed to the reactor or in the system, and $CO_{2\text{-out}}$ denotes the moles of CO_2 that leaves the reactor (R) or the whole process (P).

2.2.3. Energy efficiency

The energy efficiency correspond to the total output energy to the total input energy (Kim and Han, 2020). Equation (9):

Table 1
Main equipment design specifications of formic acid synthesis.

Equipment	Parameters	Reference
Compressor & turbine efficiencies	Isentropic = 0.92 Mechanical = 0.99	Aspen plus
Compressor 1	Isentropic P = 4 bar	Aspen Plus
Compressor 2	Isentropic P = 15 bar	Aspen Plus
Compressor 3	Isentropic P = 50 bar	Aspen Plus
Compressor 4	Isentropic P = 105 bar	Aspen Plus
H_2 compressor	Isentropic P = 105 bar	Aspen Plus
Recycling compressor	Isentropic P = 105 bar	Aspen Plus
Solvent pump	Centrifugal P = 105	Robledo-Díez (2012)
FA reactor	Type = CSTR (model user 3) T = 50 °C P = 105 bar	Terlouw et al. (2022)
Catalyst	Ru = 38.1 kg/y Ph = 19.1 kg/y	Calculated from (Pérez-Fortes et al., 2016), (Manwell et al., 2010)
Flash	T = 90 °C Duty = 0	Terlouw et al. (2022)
Split	Purge = 5%	Robledo-Díez (2012)
VLL flash	Type = Pressure & duty P = 1 bar Duty = 0	(Robledo-Díez, 2012; Terlouw et al., 2022)
Separation column	Calculation type = Equilibrium Stages = 20 Distillate rate = 3.5 ton/h Reflux ratio = 1.5 P = 1 bar	Robledo-Díez (2012)

$$\eta = \frac{E_{FA}}{E_{H2} + E_{amine} + E_{sol.} + E_{heat} + E_{elect}} x100\% \quad (9)$$

Where E_{FA} is the heating value of formic acid, E_{H2}, E_{amine} and E_{sol} are the heating values of the H_2, amine and solvent fed to the system, and E_{heat}, E_{elect} are heating values from required energy streams such as heat and electricity.

2.2.4. Specific energy consumption (SEC)

The specific energy consumption indicates the amount of energy requirement in form of heat or electricity that is required for the manufacture per unit of mass of final product. It is determined by equation (10).

$$SEC\ [MWh/tonne] = \frac{Energy\ consumption\ [MW]}{Mass\ flowrate\ of\ products\ [tonne/h]} \quad (10)$$

2.3. Economic analysis

The economic analysis is performed as a typical discounted cash flow to appraise the financial performance of the PtFA system. The capital and operating expenditures (CAPEX/OPEX) have been included in the estimation. The total CAPEX has been computed using data from the simulations results and relevant literature data. The general assumptions for the PtFA economic analysis are listed in Table 2.

The CAPEX estimation include computing for the main equipment used in the facility. The purchased equipment cost of the four stages of the PtFA has been estimated using relevant literature and adjusted to the current year and size using the scaling factor method (see supplementary information). The assumptions for the specific DAC and electrolyser unit are described as follows: In the DAC system, the equipment cost of the subsystems is given by Keith et al. (2018). As the air contactor and pellet reactor are considered modular units, the reference suggests for capacities up to 100 ktonne CO_2/year, use a scaling factor of one. In turn, for the calciner and slaker units, the costs is highly dependent on size, therefore, multiple studies (Mostafa et al., 2022; Fasihi et al., 2019; Sabatino et al., 2021; Peters et al., 2019; Prats-Salvado et al., 2022; McQueen et al., 2020) suggesting an exponent of 0.7 as a conservative value.

The PEM electrolyser cost is estimated from literature using a scaling factor and an additional 28% of the electrolyser cost to account for the balance of the plant and auxiliaries (Buttler and Spliethoff, 2018). Similarly, the equipment cost data for the FA synthesis have been estimated using literature scaling factors and is detailed in the Supplementary information.

As equipment cost is reported for specific year, the Chemical Engineering Plant Cost Index (CEPCI) was utilised to update the cost plant equipment to the base year of the study. Moreover, costs that are reported in a different currency than GBP (£), are first converted to GBP using the exchange rate and then updated to the actual year. The Lang factor methodology in Table 3 is applied to estimate the capital expenditures of a typical chemical plant (Pérez-Fortes et al., 2016; Zhang et al., 2015).

The operating expenditures (OPEX) comprises accounting for variable and fixed costs. The variable costs include raw materials, process water, catalyst, and disposals. These variables costs are calculated considering the market prices and flowrates of the inputs which are derived from literature and simulation results, respectively. The amount of catalysts needed in the FA synthesis, is accounted for a renewal once per year while methanol solvent and amine are renewed every ten years. The levelized cost of electricity (LCOE) from wind farm power supply is retrieved from SAM software. The fixed operating costs, such as maintenance, insurance, and general plant overhead are calculated using default factors based on the PEC. Additionally, the labour cost is estimated using the empirical equation proposed by Peter and Timmerhaus in (Peters and Timmerhaus, 2002). The variable and fixed costs used in

Table 2
Main assumptions for the PtFA economic evaluation.

Parameter	Units	Value
Plant location	–	United Kingdom
Base year	–	2023
Production rate	ktonne/y	15.3 ktonne/y
Lifetime of the project	years	20
Discount rate	%	10
Depreciation method	–	straight line
Operating time	h/y	8000

Table 3
CAPEX estimation methodology.

Component	Lang factor
Purchased Equipment Cost (PEC)	1
Installed direct costs (IDC)	PEC + (1) + (2) + (3) + (4) + (5)
(1) PEC installation	0.47*PEC
(2) Instrumentation and controls	0.36*PEC
(3) Piping	0.68*PEC
(4) Electrical systems	0.11*PEC
(5) Service facilities	0.70*PEC
Non-installed direct costs (NIDC)	(6) + (7)
(6) Buildings	0.18*PEC
(7) Yard improvements	0.10*PEC
Total direct costs (TDC)	(ICD) + (NIDC)
Indirect costs (IDC)	(8) + (9) + (10) + (11) + (12)
(8) Engineering and supervision	0.33*PEC
(9) Construction expenses	0.41*PEC
(10) Legal expenses	0.04*PEC
(11) Contractor's fee	0.22*PEC
(12) Contingency	0.44*PEC
Fixed Capital Investment (FCI)	TDC + IDC
Working Capital (WC)	0.05*FCI
CAPEX	FCI + WC

Table 4
Fixed and variable costs.

Fixed operating and maintenance costs (O&M)	*Basis*	*Factor*	Reference
Operating Labour (OL)	Plant capacity	–	Peters and Timmerhaus (2002)
Operating Supervision (OS)	OL	0.25	Pérez-Fortes et al. (2016)
Direct overhead (DO)	OL + OS	0.5	Pérez-Fortes et al. (2016)
General overhead	OL + OS + DO	0.45	Pérez-Fortes et al. (2016)
Maintenance labour	FCI	0.015	Gokberk and Wiebren (2020)
Maintenance materials	FCI	0.015	Pérez-Fortes et al. (2016)
Insurance and tax	FCI	0.01	Herz et al. (2021)
Financing working capital	WC	0.1	Herz et al. (2021)
Variable costs	***Unit***	***Value***	***Reference***
Catalyst price (Ru)	£/kg	120,000	Sigma Aldrich (2023)
Catalyst price (Ph)	£/kg	81,180	Thermo Scientific Chemicals (2023)
Solvent Methanol	£/kg	0.44	Methanex (2016)
Amine	£/kg	0.212	Pérez-Fortes et al. (2016)
Oxygen price	£/kg	0.044	Bellotti et al. (2022)
Electricity wind	£/kWh	0.051	SAM software
Electricity grid[a]	£/kwh	0.025	Eurostat (2021)
Wastewater treatment	£/tonne	0.42	Peters and Timmerhaus (2002)
Cooling water	£/tonne	0.03	Peters and Timmerhaus (2002)
Process water	£/m^3	0.08	Keith et al. (2018)
Ca disposal and make up	£/tonne CO_2	0.16	Keith et al. (2018)

[a] Only the cost for the grid network use is computed.

PtFA are summarized in Table 4.

2.3.1. Minimum selling price of FA

The minimum selling price (MSP) of the formic acid product is defined as the break-even point at which net present value (NPV) is equal to zero. equation (11) indicates the minimum price of which formic acid production is economically feasible (Olefins paper).

$$NPV = \sum_{n=1}^{20} \left(\frac{Cash\ flow}{(1+i)^n} \right) = 0 \quad (11)$$

Where cash flow is the sum of incomes and depreciation after taxes. In other words, the revenue generated from the sale of formic acid, subtracting all expenses (such as operating costs) and taxes. The discount rate i is assumed as 10%, and the number n has been set as 20 years over which the cash flow is evaluated.

2.3.2. Sensitivity analysis

A sensitivity analysis has been applied to the key parameters that may have a significant effect over the formic acid MSP. The analysis is conducted by applying a ±25% and ±50% change of the original economic parameters. The parameters of interest are listed in Table 5.

2.4. Life cycle assessment (LCA)

A life cycle assessment approach has been applied evaluate the environmental performance of the PtFA system. The ISO-14040/44 standard is employed as the framework of the assessment. The four stages considered are: goal and scope definition, inventory analysis, impact assessment, and interpretation (Von Der Assen et al., 2013).

2.4.1. Goal and scope

The goal of this LCA is to quantify the environmental impacts of formic acid production through CO_2 hydrogenation and green H_2 including climate change, and fossil depletion (FD) and water consumption to identify the main system contributors. Further, a comparison of the climate change impact with conventional fossil-based formic acid production process is also discussed.

2.4.1.1. Functional unit and allocation procedure. In this paper, the functional unit (FU) is 1 tonne of formic acid produced through PtX. All inputs and environmental impacts results are normalized to the FU. The O_2 produced in the water electrolysis is considered as by-product and this necessitates the utilisation of an allocation procedure. In the ISO-14044 guidelines, the recommendation is to avoid or minimise allocation whenever possible by subdividing the system (Ekvall and Tillman, 1997). Therefore, the approach followed herein is the subdivision of the PEM electrolysis from the DAC and FA synthesis as in Fig. 2. Thus, the allocation approach for the H_2 and O_2 is through an exergy analysis which can be found in the Supplementary Information.

Table 5
Main assumptions for PtFA sensitivity analysis.

	Base value	*Units*	*Reference*
LCOE	0.040	£/kWh	SAM software
PEM Installed cost	750	£/kW	(Element Energy, 2018; Marí et al., 2023)
Discount rate	10	%	–
O_2 price	0.044	£/kg	Bellotti et al. (2022)
CO_2 CAPEX	294	£/tonne-CO_2	Keith et al. (2018)
Catalyst price:			
Ruthenium	120	£/tonne	Sigma Aldrich (2023)
Phosphine	81	£/tonne	Thermo Scientific Chemicals (2023)

2.4.1.2. System boundaries. The system boundaries of the PtA has been specified as cradle to gate (Fig. 2). Thus, the distribution, use and final disposal are excluded. The reason behind this is because the formic acid produced through PtFA has the same physical properties as conventional fossil-based FA and therefore they have similar end use phase (Robledo-Díez, 2012; Sternberg et al., 2017a). The LCA includes all materials and energy inputs in addition to the outputs including emissions to soil, water and air during the processing stage. The CO_2 captured is not considered as negative emissions because, at the product end-of-life, it is released back into the atmosphere as positive emissions, resulting in a net-zero effect within the carbon neutrality cycle (Rosental et al., 2020). The infrastructure for DAC, FA synthesis, and the PEM electrolyser is excluded due to their minimal environmental impact (Lundberg, 2019). However, emissions from the offshore wind farm infrastructure were considered.

2.4.2. Life cycle inventory

The life cycle inventory for the PtFA steps has been composed of the mass and energy balances simulation model results, literature data and datasets available in the Ecoinvent database v3.6. (Ecoinvent, 2021). Process emissions have been taken into account through the entire system. Emissions to the air have been retrieved from simulation of the combustion process while wastewater treatment has been assumed for emissions to water. The catalyst LCA impact is usually neglected (Althaus et al., 2007) within chemical processes, therefore, the same approach if considered here. The plant infrastructure has not been included in the analysis due to its minimal contribution to the overall carbon footprint.

2.4.3. Impact assessment

The environmental impacts of the CCU-based formic acid process were evaluated using the ReCiPe Midpoint (H) level methodology available in Simapro v9.4.0.2. This method includes 18 impact categories: Climate change (CC) abiotic depletion (ADP), Ozone depletion (ODP), Terrestrial acidification (TAP), Freshwater eutrophication (FEP), Marine eutrophication (MEP), Human toxicity (HTP), Photochemical oxidant formation (POP), Particulate matter formation (PM), Terrestrial ecotoxicity (TEP), Freshwater ecotoxicity (FWEP), Marine ecotoxicity (MEP), Ionising radiation (IR), Agricultural land occupation (ALO), Urban land occupation (ULO), Natural land transformation (NLT), metal depletion (MD) and fossil depletion (FD). Water consumption is calculated from accounting the water needed in the production or raw materials as well as cooling water loss and water used in the electrolyser unit.

2.4.4. Interpretation

The environmental impact, water consumption and fossil depletion impact of the power-to-formic acid process has been included and compared with fossil-based formic acid production coming from natural gas in order to raise the benefits of PtFA. The model for conventional FA has been retrieved from Ecoinvent database v3.6 running the same impact method and the specific *module "Formic acid {RER}| production, methyl formate route | Cut-off, U"*. The module represents the standard industrial process of FA production.

Additionally, a sensitivity analysis of the electricity carbon intensity on the climate impact of the PtFA process has been conducted to understand its significance. The analysis is prime of importance due to the reliability of the process in the electricity consumption. The sensitivity includes various electricity sources such as offshore wind, hydropower, nuclear, and solar power. Each of these energy sources has a distinct carbon intensity and, consequently, a different impact on the overall greenhouse gas emissions associated with the PtFA process.

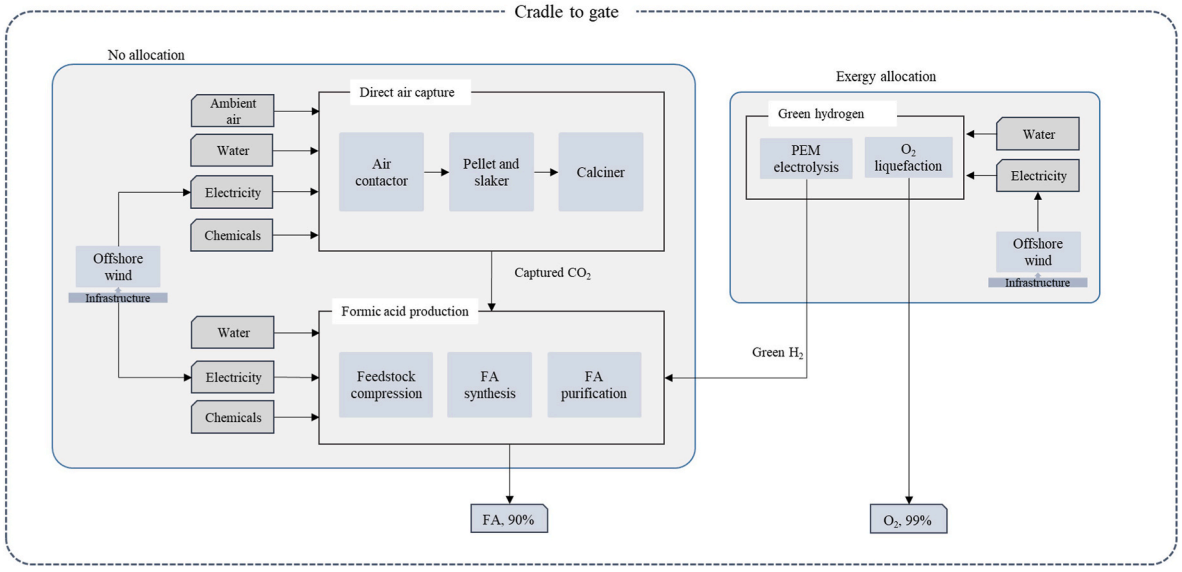

Fig. 2. The system boundaries for the LCA of the investigated PtFA process.

3. Results and discussion

3.1. Key performance indicators results

As described in the methodology section, compressed CO_2 and H_2 are synthetized into formic acid through thermocatalytic route. The mass and energy balance of the main inputs and outputs of the PtFA process are summarized in Table 6.

The process involves handling approximately 25,149 ktonne of atmospheric air to capture 10.98 ktonne of CO_2 annually. This captured CO_2, combined with an additional 2.96 ktonne of CO_2 recovered from the combustion of off-gases during formic acid synthesis, results in a total of 14.2 ktonne of CO_2 available per year. Additionally, 868 tonne/year of hydrogen is produced from 9.37 ktonne of deionized water through electrolysis. The process also generates 7.22 ktonne of oxygen, which is partially utilised in the combustion process within the calciner unit (57%), with the remaining 43% being considered a by-product available for sale. The small quantities of amine and methanol listed in Table 6 represent the renewal of the solvent that compensates for any losses incurred during the recycling process. While the majority of methanol and amine solvent are recovered and recycled within the plant, a minor fraction is inevitably lost due to factors such as evaporation, degradation, or addition in product streams. These losses require the addition of fresh solvent to maintain the desired operational levels and ensure the efficiency and stability of the process. The reported amounts thus reflect the make-up quantities required to sustain the continuous operation of the plant.

Table 6
Annual inputs and outputs of PtFA plant.

Mass balance	Value	Units
Inputs		
Air	25,149	ktonne/y
CO_2 available	14.2	ktonne/y
Water	9.37	ktonne/y
H_2 produced	868	tonne/y
Methanol	861	tonne/y
Amine	130	tonne/y
Outputs		
FA	14.01	ktonne/y
O_2	7.22	ktonne/y
CO_{2-R}	45.4%	–
CO_{2-P}	99.9%	–
Carbon efficiency	73.4%	–
Energy balance		
Electricity	4.49	MWh/tonne
Heating	3.6*	MWh/tonne
Cooling	3.9*	MWh/tonne
Total SEC (w/o integration)	12.01	MWh/tonne
Total SEC (w/integration*)	4.49	MWh/tonne
Energy efficiency	22	%

3.1.1. CO_2 conversion efficiency

The process achieves complete CO_2 conversion into formic acid (99.9%), primarily due to the continuous recycling of unreacted materials throughout the entire system. This approach significantly enhances the overall efficiency of the CO_2 utilisation, making the process highly effective in converting the greenhouse gas into valuable products. However, it is important to note that the reactor itself, does not achieve full conversion in a single pass. According to the process model, the CO_2 conversion rate within the reactor is fixed at approximately 45%, as reported by Mantoan et al. (2019). This lower conversion rate in the reactor highlights the challenges in achieving high efficiency in a single stage of the process. Despite this, the overall system compensates for the reactor limitations through the recycling strategy, which ensures that unreacted CO_2 is reprocessed until it is completely converted into formic acid.

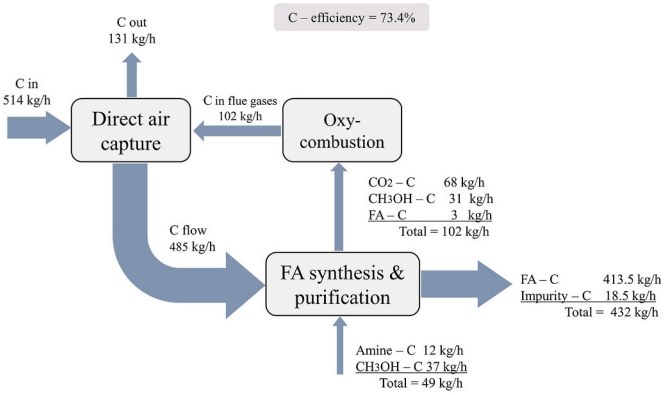

Fig. 3. The carbon balance of the PtFA system.

3.1.2. Carbon balance

The carbon balance of the PtFA process, illustrated in Fig. 3, reveals a carbon efficiency of 73.43%. The process begins with the injection of approximately 514 kg/h of carbon into the DAC unit, sourced from atmospheric CO_2. Due to the DAC capture efficiency of 74.6%, a portion of this carbon (131 kg/h) is not captured and then released as exhaust gas back to the atmosphere.

In addition to the DAC-sourced carbon, an extra carbon stream of 49 kg/h is introduced in the system from the methanol and amine solvent make-up stream in the FA synthesis and purification stage. This accounts for the solvent volumes that are not recovered during recycling and must be replaced to sustain the reaction cycle. As part of the energy integration strategy, the fraction of solvents not recovered along with the unreacted gases from the FA synthesis and purification unit, are subjected to an oxy-combustion with the purpose of recover energy for the process and supply additional carbon to the DAC unit, thus enhancing the overall carbon input (102 kg/h).

As a result, the total carbon leaving the DAC system is 485.6 kg/h, which is directed to the synthesis and purification unit. In this stage, carbon is distributed between the unreacted compounds (CO_2, methanol, FA), and the main product stream. The final product stream consists of 413.5 kg/h of formic acid at a purity of 96%, and 18.5 kg/h of impurities derive from the solvent mixture (4%). This efficient management of carbon flows within the PtFA process emphasizes the potential of integrated carbon capture, solvent recycling, and energy recovery to optimize the production of formic acid while maximizing carbon utilisation.

3.1.3. Energy balance

The energy consumption per tonne of FA is also summarized in Table 6. Energy efficiency and the specific energy consumption have been included in the same table.

The electricity consumption is responsible for around 37% of the total energy consumption, followed by heating requirements which constitute about 30% and cooling demands which make up the remaining 33% of the total. As detailed, the total energy consumption of the PtFA process without any heat integration was found to be 12.01 MWh per tonne of formic acid produced. This high energy requirement is primarily driven by the electricity needs of the electrolyser, and the DAC modules. However, by implementing heat integration strategies, the SEC can be significantly reduced by 62.5%, bringing it down to 4.49 MWh/tonne FA. This reduction is achieved mainly by recovering and reusing the available heat from various process streams, thereby minimizing the external energy input required for heating and cooling. The reduction in SEC through heat integration not only lowers operating costs but also enhances the sustainability of the process by reducing its overall energy footprint. Also, this heat recovery strategy helps in optimizing energy flows within the plant, reducing dependency on external energy sources, and improving the overall energy efficiency of the PtFA system. Other studies such as the one conducted by Kim and Han (2020) have reported a SEC of 5.3 MWh/tonne FA which is in line with this study. This comparison remarks the importance of incorporating heat integration strategies in PtX processes.

Compared to the conventional formic acid production process, the PtFA approach demonstrates a different energy profile. The total electricity consumption in conventional methods ranges between 3.5 and 11.79 MWh/tonne of FA, along with a significant steam consumption of 4.13–93.8 MWh/tonne of FA produced (Pérez-Fortes et al., 2016; Sternberg et al., 2017b). This evidences the substantial energy requirements of traditional FA production, where both electricity and steam are critical inputs. In contrast, the PtFA process focuses on optimizing electricity consumption through the use of renewable energy sources and implementing heat integration techniques to reduce overall energy demand. The reduction in steam consumption, achieved through these strategies, makes PtFA a more energy-efficient and environmentally friendly alternative to conventional processes.

Fig. 4 displays the breakdown of the electricity consumption within the PtFA process. The most significant portion of the electricity consumption, approximately 89% is attributed to hydrogen production in the PEM electrolyser unit. The remaining 11% of electricity use is distributed among the other components. Specifically, 4.2% is consumed by compressors used by conditioning H_2 and CO_2 feed while the compressor in the FA purification column accounts for 3.7%. Additionally, the DAC unit requires 1.7% of the total electricity, and the solvent pump used in the FA synthesis contributes 1.6%.

The energy efficiency of the PtFA process reflects the ratio of the total energy output in the form of produced formic acid to the total energy input required for its production. This efficiency has been calculated by considering the heating values of FA, H_2, and methanol, as reported in prior studies (Gao et al., 2023; Kibria Nabil et al., 2021). The heating value of the amine solvent is excluded from the calculation due to its minimal energy value contribution to the overall. The PtFA process has an energy efficiency of 22%, indicating that significantly more energy is consumed than what is recovered in the final product. This low efficiency is expected, given the substantial energy demands of the electrolysis stage and the high energy content of the hydrogen used. The obtained energy efficiency is consistent with findings by Kim and Han, who reported an efficiency of 23% for a formic acid production process via CO_2 hydrogenation. In contrast, Gokberk (Gokberk and Wiebren, 2020) reported a higher energy efficiency of around 31%. The discrepancy in efficiency between the current study and that of Gokberk can be attributed to the greater electricity consumption per tonne of formic acid observed in this study compared to the values reported by Gokberk (0.29 MWh/tonne FA excluding CO_2 and H_2).

3.1.3.1. Heat integration. The integration of the DAC and Formic Acid synthesis processes has been achieved through strategic heat integration between the available hot and cold streams within the system. This approach aims to maximize energy efficiency by utilizing residual heat from one part of the process to meet the thermal demands of another. The primary energy-intensive component was identified as the calciner, which operates at a high temperature of 900 °C. To meet this significant thermal requirement, the system utilizes the oxy-combustion of off-gases generated during the FA synthesis. These off-gases, consisting of unreacted compounds such as H_2, methanol, and FA, are combusted with oxygen, providing the necessary heat for the calciner.

Another critical thermal integration occurs within the slaker dryer, which is responsible for drying the carbonate pellets by removing the majority of the water content. The heat needed for the slaker dryer is supplied by integrating it with hot streams from the calcium hydroxide production and the water cooling system. By spending these hot streams, the process reduces the need for external heat sources, thus enhancing overall energy efficiency.

The FA purification process requires a significant amount of energy, specifically 3.03 MW of heat for the reboiler. To meet this demand, a heat pump system has been integrated within the purification column.

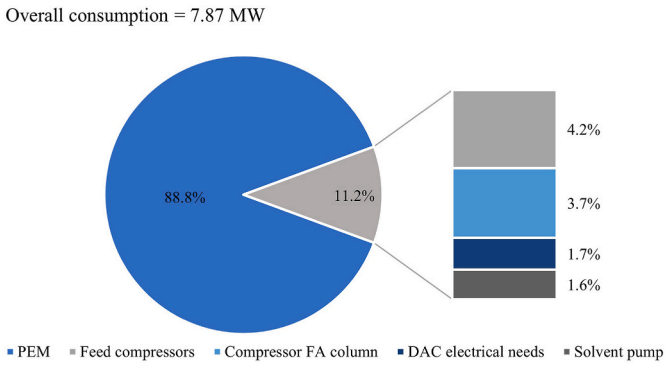

Fig. 4. The electricity consumption breakdown of PtFA.

This approach leverages the heat released in the condenser to provide the necessary heat for the reboiler (Bruinsma, 2010). The system employs a Vapour Recompression Column (VRC) configuration, where a compressor is installed before the condenser. This compressor increases the temperature and pressure of the vapour exiting the column. By elevating these parameters, the vapour thermal energy is enhanced, enabling the recovery of heat through a dedicated heat exchanger. This recovered heat is then redirected to the reboiler, supporting the evaporation process while simultaneously condensing the vapour. The specifications of the VRC system are presented in Fig. 5.

This comprehensive heat integration contributes to reducing operating costs and minimizing the environmental impact by efficiently utilizing available energy resources within the system.

3.2. Economic analysis

3.2.1. Capital expenditures

The main economic results are presented in Table 7. The total CAPEX of the PtFA process is estimated at £33.6 Million GBP. The major components include equipment cost including installation (53%), while non-installed direct costs such as buildings, and yard improvements accounted for 6%. Indirect costs such as engineering, supervision, construction and legal expenses, contractor's fee and contingency represent 33%. Finally, working capital contributes with 8% of the total CAPEX.

The equipment cost is the most significant portion of the CAPEX due to the specialized machinery needed. Fig. 6 provides the major equipment cost breakdown by stage and equipment type.

The DAC process is a significant contributor to the overall equipment cost, accounting for 54% of the total cost, with the air contactor and calciner units being the primary cost drivers. The PEM equipment cost constitutes 29% of the total, comprising stack cost and balance of plant (BoP), indicating that advancements in PEM technology could enhance the economic feasibility of the process. The FA synthesis has a relatively smaller contribution to the overall cost (17%), with compressors and pumps being the most expensive components. Fig. 6 indicates the critical areas where cost reductions can be most impactful. The prominence of electrolyser and DAC costs suggests that innovations in these technologies could not only reduce costs but also improve environmental performance by increasing efficiency and reducing energy consumption.

3.2.2. Operating expenditures

The total operating expenditures (OPEX) for the PtFA plant is estimated at £11.2M annually. Fig. 7 illustrates the breakdown of operating expenditures for the plant. Each bar represents the percentage

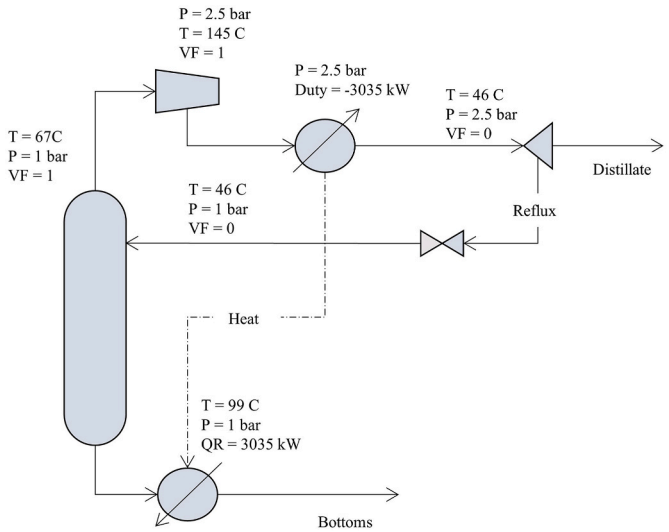

Fig. 5. The design of the FA purification column using a VCR configuration.

Table 7
Economic results.

Component	Cost, Million GBP	Share
Installed equipment cost	19.8	53%
Non-direct cost	2.4	6%
Indirect cost	12.3	33%
Working capital	3.2	8%
CAPEX	37.61	-

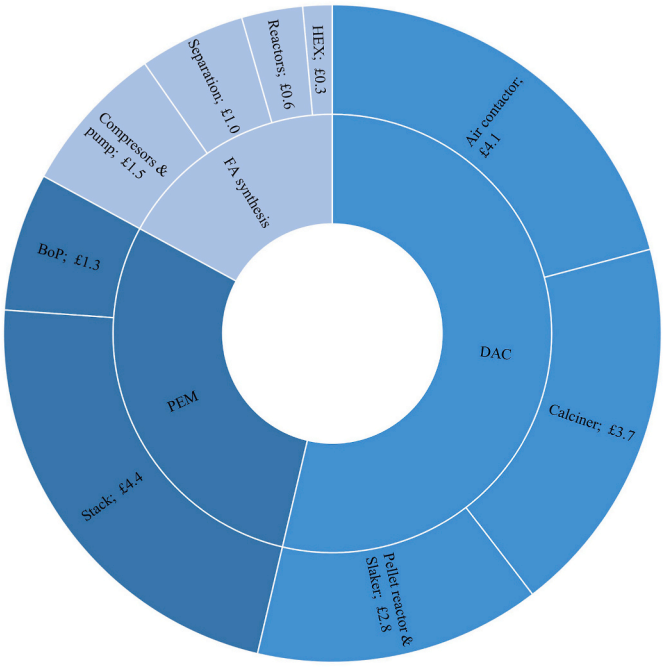

Fig. 6. Breakdown of the installed equipment cost, data in million GBP.

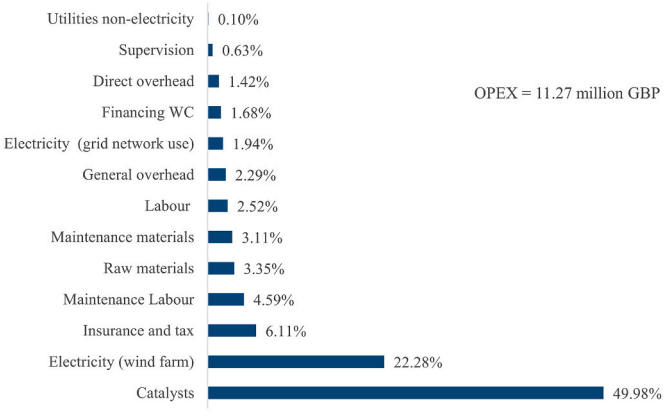

Fig. 7. The breakdown of the OPEX.

contribution of various cost components to the total OPEX.

The catalyst cost is the primary factor influencing OPEX contributing around 50% of the total OPEX. This is due to the use of expensive ruthenium and phosphine catalysts, this contribution has been previously reported by Perez-Fortes et al., (Pérez-Fortes et al., 2016). This indicates that catalyst costs are the most significant factor in the overall cost of the PtFA process. The high contribution suggests a need for innovations in catalyst technology or alternative catalyst to reduce this cost significantly. The next largest cost contributor is electricity sourced from the wind farm, accounting for 22% of the total OPEX. This result is

expected given that electricity is a major energy input, particularly for powering the PEM electrolyser unit in the PtFA process.

The remaining 27.7% is distributed among various other costs. The cost of insurance and taxes, maintenance labour and materials, other raw materials such as methanol and the amine solvent, overhead, grid network use, supervision and other utilities such as processing water while not as substantial as electricity or catalysts, still represents a notable portion of the overall costs.

The prominent role of catalyst costs suggests that efforts should focus on exploring cost-effective catalyst alternatives. Various studies (Zhang et al., 2018; Thomas et al., 2001; Wang et al., 2023; Maru et al., 2018) are actively developing novel catalysts to optimize FA production and improve its economic performance, though the research is still in its early stages. The OPEX analysis presented here highlights critical areas where cost reductions can have a substantial impact, indicating that innovations in energy efficiency and catalyst technology could yield significant economic benefits.

3.2.3. Minimum selling price

The minimum selling price has been calculated through a break-even analysis. The minimum selling price of formic acid (MSP) has been estimated in £1290 per tonne FA. This is 2.3 times higher than the market price in Europe of £560 (€650) per tonne (Kim et al., 2024). This result indicates the production cost needs to be reduced to achieve a more competitive price. Formic acid production cost through PtX have been reported in a range of £802 - £1872 per tonne (Pérez-Fortes et al., 2016; Kim and Han, 2020; Kim et al., 2024; Gokberk and Wiebren, 2020), where electricity, catalyst and the amine cost denote as the main contributors.

Additionally, the cost breakdown of formic acid production illustrated in Fig. 8 reveals that 53% of the total cost arises from the formic acid synthesis process, primarily driven by the high cost of the catalyst. Hydrogen production accounts for 26% of the cost, largely due to the significant electricity required for its generation. Finally, 22% of the cost is attributed to CO_2, with DAC technology contributing substantially due to its high capital expenses. This distribution underscores the critical impact of these parameters on the overall economics of formic acid production.

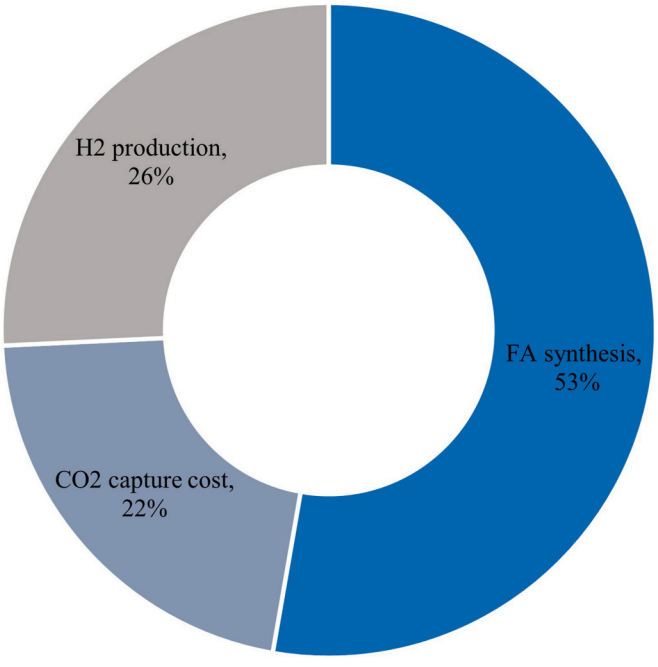

Fig. 8. The cost breakdown of FA production per process area, i.e. green H_2 production, CO_2 capture through DAC and FA synthesis plant.

3.2.4. Sensitivity analysis

Fig. 9 depicts the sensitivity results of the main parameters used in the economic analysis to the formic acid MSP. The parameters used for the base economic analysis are: catalyst price, H_2 cost, CO_2 cost, discount rate, levelised cost of electricity (LCOE), and oxygen selling price. Parameters have been varied in ±25% (grey bars) and ±50% (blue bars) of base value.

The catalyst price is the parameter with the most substantial impact on the MSP. Variations in the catalyst price cause the MSP to fluctuate between £1070 and £1520 per tonne when adjusted by ±50%. A change of ±25% in catalyst price affects the MSP in a range of £1180 - £1400 per tonne of FA. This results evidenced the catalysts price as the most critical parameter among those evaluated emphasizing their substantial role in determining the overall production cost.

Additionally, the cost of H_2 production is the second main driver of the FA price with ranges from £1109 to £1477 per tonne and from £1211 to £1385 per tonne when variation of ±25% and ±50%, respectively. Similarly, a variation of the CO_2 capture cost in ±50% lead to a formic acid price range of £1136 - £1450 per tonne. This result is important as it can be associated with other technologies for CO_2 capture and if a capture technology with a 50% lower cost (i.e. £139/tonne CO_2) is used, then this will result in a reduction of 14.03% to the formic acid MSP. An additional sensitivity analysis of the CO_2 cost over the formic acid MSP is available in the Supplementary Information.

The LCOE has a moderate effect on the MSP, with the cost of formic acid ranging between £1184 and £1400 per tonne when the electricity price and network cost are varied by ±50%. For a ±25%, the MSP fluctuates between £1240 and £1347 per tonne. Lastly, the selling price of oxygen has the least impact on the MSP, with a change of around ±0.7% from the baseline MSP of £1290 per tonne when a ±50% change is applied.

3.2.5. Economies of scale

The individual scaling factors have been used to estimate the CAPEX in order to measure the effect of scale to the MSP of the FA. The OPEX has been calculated using labour, catalyst, raw materials and utilities assuming to increase linearly to the different plant capacities. The capacities have been defined from 1 tonne/h to 200 tonne/h. Each capacity has been run in the system and the formic acid MSP was recalculated. Fig. 10 illustrates the effect of economies of scale to the formic acid MSP.

At highest capacity (200 tonne/h) an 8.6% reduction in the MSP can be achieved. However, the MSP of formic acid stabilizes at price of 1180 £/tonne. As plant capacity increases, the anticipated cost reductions from scaling up become negligible. This is primarily because, beyond 80 tonne/h, the OPEX dominate the overall costs, and their linear relationship with scale negates the advantages typically associated with larger operations. Consequently, the cost savings expected from economies of scale are not realized in these larger plants.

3.3. Life cycle assessment

In this section, the environmental impact of CCU-based formic acid is analysed and compared to fossil-based FA. The ReCiPe Midpoint (H) V1.13 impact calculation method was applied and estimated for the functional unit of 1 tonne of formic acid.

3.3.1. Life cycle inventory (LCI)

Table 8 presents the main inputs and outputs converted to the functional unit. It includes material and utility sources.

3.3.2. Environmental impact results

The environmental impacts of FA production through green H_2 and DAC relative to 1 tonne of product are shown in Table 9.

The PtFA production process has a climate change of approximately 190.27 kg CO_{2e} per tonne of FA, a water use of 8.17 m^3 per tonne of FA,

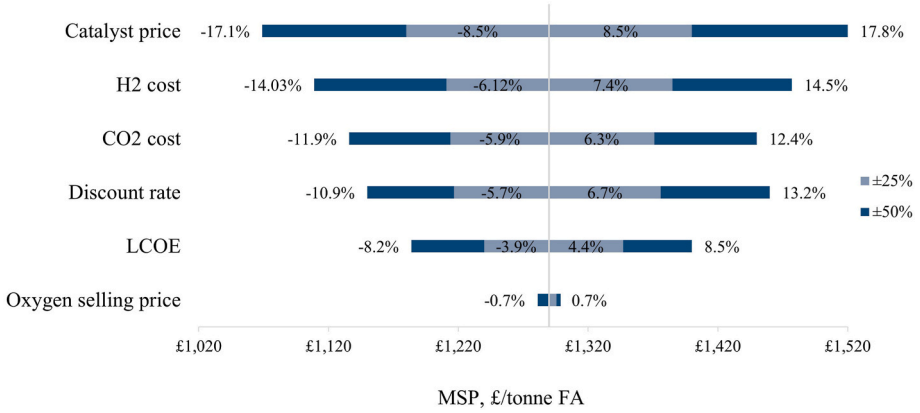

Fig. 9. Economic sensitivity analysis on the MSP.

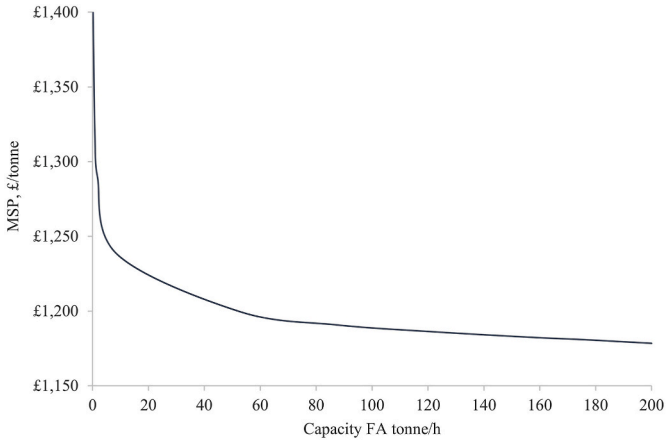

Fig. 10. The economies of scale effect on the PtFA process.

Table 8
Life cycle inventory of PtFA system.

Input/output	Value	Units	Source
Electrolyser			
Deionized water	0.66	tonne	Harrison et al. (2014)
Electricity	3.99	MWh	Harrison et al. (2014)
Output			
Hydrogen	0.07	tonne	Aspen Plus
Oxygen	0.52	tonne	Aspen Plus
DAC system			
Electricity	0.08	MWh	Aspen Plus; (Keith et al., 2018)
Process water	4.79	tonne	Aspen Plus
$CaCO_3$ make-up	0.07	tonne	Aspen Plus
KOH make up	2.04E-4	tonne	Aspen Plus
Output			
CO_2	0.99	tonne	Aspen Plus
$CaCO_3$ disposal	0.07	tonne	Aspen Plus, (Keith et al., 2018)
KOH disposal	2.04E-4	tonne	Aspen Plus
FA synthesis			
CO_2	0.99	tonne	Input from DAC
H_2	0.07	tonne	Input from PEM
Methanol	0.06	tonne	Aspen plus, (Pérez-Fortes et al., 2016)
Amine	0.01	tonne	Aspen plus, (Pérez-Fortes et al., 2016)
Water	0.08	tonne	Aspen plus, (Pérez-Fortes et al., 2016)
Electricity	0.43	MWh	Aspen plus
Output			
FA	1.00	tonne	–

Table 9
Environmental impacts of formic acid through PtFA (FU: 1 tonne FA).

Impact category	Unit	Total
Climate change	kg CO_2 eq	190.27
Ozone depletion	kg CFC-11 eq	2.22E-05
Terrestrial acidification	kg SO2 eq	0.74
Freshwater eutrophication	kg P eq	0.01
Marine eutrophication	kg N eq	0.09
Human toxicity	kg 1,4-DB eq	47.20
Photochemical oxidant formation	kg NMVOC	0.66
Particulate matter formation	kg PM10 eq	0.39
Terrestrial ecotoxicity	kg 1,4-DB eq	0.02
Freshwater ecotoxicity	kg 1,4-DB eq	0.56
Marine ecotoxicity	kg 1,4-DB eq	0.59
Ionising radiation	kBq U235 eq	3.90
Agricultural land occupation	m^2a	4.24
Urban land occupation	m^2a	2.76
Natural land transformation	m^2	0.03
Water consumption	m^3	8.17
Metal depletion	kg Fe eq	66.31
Fossil depletion	kg oil eq	89.77

and a fossil depletion of 89.77 kg oil-equivalent per tonne of FA. In Fig. 11, the impact values for conventional fossil-based FA are set to 100%, and the CCU-based FA impacts are presented as relative emissions. When PtFA impacts are compared to the conventional methyl formate route (as shown in Fig. 11), CCU-based formic acid evidences to

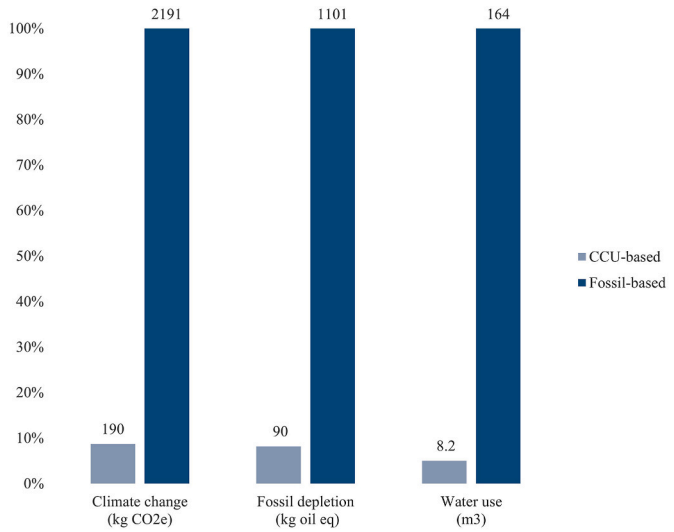

Fig. 11. Climate change, fossil depletion and water consumption of formic acid production through PtFA and fossil-based per FU.

be more environmentally beneficial.

A reduction of more than 90% of the impacts is achieved by producing CCU-based formic acid compared to the conventional methyl formate route using fossil resources. Individual impacts in the figure are discussed below.

3.3.3. Climate change (CC)

The climate change impact as illustrated in Fig. 11 results in 190.27 kg CO_{2e} per tonne of FA. A 92% less than conventional formic acid through methyl formate production process which exhibits a carbon emission of 2191 kg CO_{2e} per tonne FA (Ecoinvent, 2021).

Fig. 12 breaks down carbon emissions by stage and type. As shown, the climate change is primarily driven by fossil-derived chemical inputs in the DAC and FA synthesis stages, such as methanol, calcium carbonate, and tertiary amine that together contribute to nearly 60% of the total FA emissions. Although the quantities of these chemicals are relatively small, their contribution to the overall carbon emissions is significant because of the fossil consumption involved in their production. Additionally, electricity consumption which is dominant in the electrolyser stage, accounts for 36% of the total FA climate change, this is attributed to the materials employed in the offshore wind infrastructure.

One alternative to reduce chemical emissions in the PtFA is the utilisation of renewable methanol from the PtM (Power-to-Methanol) approach. For example, carbon emissions for green methanol have been reported to range from 19.1 to 280 kg CO_{2e} per tonne methanol, for systems employing DAC and green hydrogen (Rosental et al., 2020; Arnaiz del Pozo et al., 2022). Incorporating this renewable methanol in the PtFA production process can further decrease the climate change impact of PtFA by 23%–36%, respectively i.e., 154 and 139 kg CO_{2e}/-tonne FA. However, due to variations in the technologies of methanol production and differences in the stages included or excluded, it is recommended to include a comprehensive simulation and LCA models when combining with PtFA, as their implications on other environmental and economic performances must be considered.

The GHG intensity of the electricity source is of prime importance due to its significant contribution to overall PtFA emissions. Consequently, a comparison of different electricity generation technology GHG intensities is shown in Fig. 13. The assessed technologies include solar photovoltaics, hydro from reservoirs, offshore wind, and nuclear from pressurized water reactors. The carbon intensities of each source have been taken from the library of the Simapro software for 1MWh of electricity in the UK, with the exception of solar and hydro based which are available for the rest of the world (Ecoinvent, 2021). The bars in Fig. 13 represent the GHG per tonne of formic acid, while the white dots indicate the electricity carbon intensity (CI) of each energy source in kg CO_{2e} per kWh.

Electricity generation technology with low GHG intensity, such as nuclear power, reduces the climate change of PtFA from 190 to 112 kg

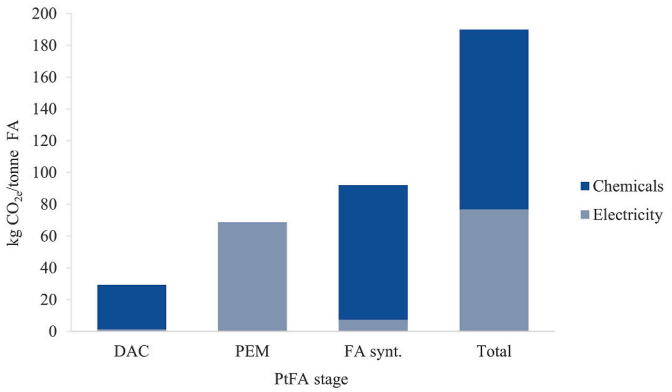

Fig. 12. The climate change breakdown by stage and component.

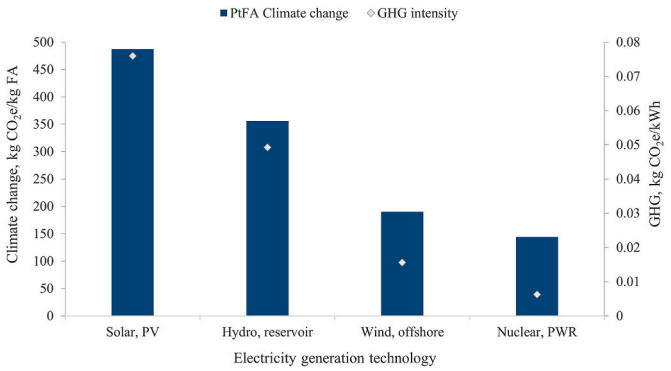

Fig. 13. Effect of the energy carbon intensity on the global warming potential of PtFA.

CO_{2e} per tonne of FA, a 41% reduction compared to offshore wind. Conversely, if solar energy is used, emissions increase by approximately 124%, reaching 425 kg CO_{2e} per tonne of FA. The choice of electricity source is highly location-dependent. Therefore, countries with developed nuclear energy infrastructure benefit from significantly lower carbon emissions.

3.3.4. Fossil depletion (FD)

The PtFA process has a fossil depletion of 89.77 kg oil-equivalent per tonne of FA, with around 71% attributed to FA synthesis. This is primarily due to the methanol and amine chemicals, sourced from non-renewable resources, which, despite their small quantities, significantly impact the system's environmental performance. One way to reduce the use of fossil resources in the PtFA process is by incorporating green methanol. Conversely, the conventional fossil methyl formate route involves higher fossil depletion due to the primary use of methanol and CO as feedstock, which are derived from fossil sources. This leads to significant consumption of oil resources, as shown in Fig. 11. Other studies have reported similar results, for instance, Ahn et al. (2019), evaluated a CCU-formic acid production pathway against conventional. The results showed fossil depletion of CCU around 28% compared to conventional due to the feedstock. The difference is caused by the use of non-renewable energy in the CCU model. Kang et al. (Kang et al., 2021), reported catalytic method strategy had lower FD compared to conventional strategy (0.23 vs 0.83 kg oil-e/kg FA).

3.3.5. Water consumption

Water use is an important indicator of the environmental performance in a sustainable project. The investigated CCU-based formic acid consumes around 8.17 m^3 water per tonne FA. The main contributor of this is the DAC with 68% of total. The use of non-renewable chemicals such as methanol, the tertiary amine led to a higher consumption in water that comes primary from fossil chemicals. Compared to the conventional production method, CCU-based formic acid consumes 95.4% less water, this is because in the conventional method, the water accounts for the feedstock coming from non-renewables including electricity.

3.3.6. Other environmental impact categories

Fig. 14 compares the environmental impact categories of CCU and fossil - based FA production method across various categories. The axis represents a different category, the fossil-based FA has been set as 100% while the CCU-based FA is calculated as relative emissions.

The CCU-based formic acid under the PtFA production process is more environmentally friendly compared to the conventional fossil-based method, including TAP, FEP, HTP, POP, PM, TEP, ME, IR, ALO, ULO, and NLT. The categories that do not show a substantial reduction are MD, FWEP, and MEP which are likely influenced by specific materials like chromium utilised in the electricity production. Overall, the

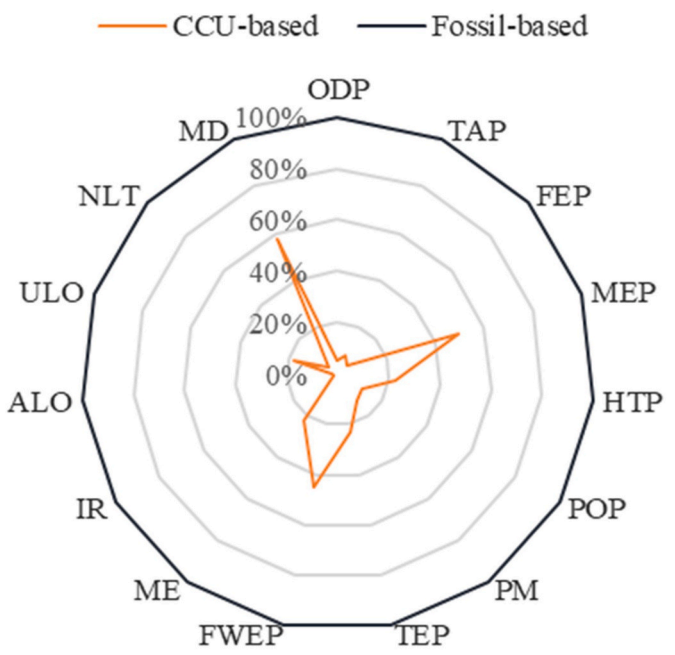

Fig. 14. Relative comparison of the environmental impacts of CCU-based (orange line) with the fossil-based formic acid (black line, from Ecoinvent v3.6).

CCU-based formic acid through PtFA performs better environmentally, highlighting the benefits of using renewable sources and complete heat integration in the production process.

In addition to mitigating climate change, these results underscore the potential of the PtFA process to reduce water consumption, fossil depletion and other environmental impacts compared to fossil-based FA production.

4. Conclusions

The study represents the first effort to comprehensively evaluate both the economic and environmental feasibility of a PtFA assembly that includes a DAC unit, a PEM electrolyser and catalytic synthesis of FA through CO_2 hydrogenation. It includes exhaustive process modelling and heat integration, techno-economic assessment and a cradle to gate LCA.

The PtFA process achieves an overall carbon efficiency of 73.4%. Most carbon losses occur in the DAC unit, due to the CO_2 capture efficiency of 75% (Suzuki et al., 2024). Additionally, it requires 1.01 tonne of CO_2 to produce 1 tonne of formic acid. The DAC heat requirement, 1.87 MWh per tonne of CO_2, was met internally through heat integration, eliminating the need for external fossil fuels. The specific energy consumption of the entire PtFA system is lower than that of fossil-based production, due to the fact that only electricity is used whereas a large amount of steam is employed in the fossil-based system.

A standard discounted cash flow analysis indicates that the minimum selling price (MSP) of the PtFA is twice as the conventional FA, at £1290 per tonne compared to £560 per tonne. The sensitivity analysis revealed that catalysts cost along with hydrogen costs are the primary cost drivers. Thus, efforts should be focused on cost-effective catalyst alternatives and a more affordable hydrogen production. A cradle-to-gate life cycle assessment (LCA) estimated that the PtFA process significantly reduces carbon emissions, lowering the climate change by 95% compared to fossil-based production. The primary sources of carbon emissions were formic acid synthesis due to the non-renewable methanol employed and the electricity in the electrolysis, which together accounted for around 85% of the carbon emissions. Additionally, the CCU-based formic acid process has the potential to reduce water and fossil resource depletion by more than 90% compared to fossil-based formic acid production.

The study proposed and evaluated an innovative, integrated design for a low-carbon formic acid synthesis route, aiding the research on defossilising the chemical industry. The holistic assessment presented herein provided results that can guide policy formulation and engineering decisions.

CRediT authorship contribution statement

Gabriela A. Cuevas-Castillo: Writing – original draft, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Stavros Michailos:** Writing – review & editing, Validation, Supervision, Software, Methodology, Investigation, Conceptualization. **Kevin Hughes:** Writing – review & editing, Supervision, Resources. **Derek Ingham:** Writing – review & editing, Supervision, Resources, Project administration. **Freddy Navarro-Pineda:** Writing – review & editing, Validation. **Mohamed Pourkashanian:** Writing – review & editing, Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.clet.2025.100929.

Data availability

Data will be made available on request.

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