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Novel process design for eco-efficient production of green formic acid from CO₂

Nikolaos Kalmoukidis¹, Amsalia Barus¹, Savvas Staikos¹, Maximiliano Taube¹, Farzad Mousazadeh, Anton A. Kiss^{*}

Department of Chemical Engineering, Delft University of Technology, Van der Maasweg 9, Delft 2629 HZ, the Netherlands

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ABSTRACT

The valorisation of green hydrogen and captured CO₂ to produce chemicals or energy carriers holds immense potential to reduce GHG emissions. Among them, formic acid (FA) is an essential chemical with diverse applications and a growing market demand. Furthermore, due to liquidity at ambient conditions and its chemical stability, it is a promising hydrogen carrier. However, its direct thermochemical synthesis from CO₂ hydrogenation still faces significant challenges due to a high thermodynamic barrier. This study presents a novel and eco-efficient process design for a 50 kta FA production from CO₂ and green H₂. Initially, CO₂ is converted to CO as an intermediate compound that undergoes a carbonylation reaction with methanol to form methyl formate, which is then hydrolysed into FA. The major challenges of this new proposed process lie in the purification of CO and the energy-intensive downstream separation of FA. The former is addressed by using the COPure™ technology, which combines chemical and physical absorption, while the latter requires the use of process intensification techniques to minimize the energy and capital expenses. The newly designed process achieves high molar yields of 95 % for CO₂ and 96 % for H₂ with a specific energy intensity of 21.8 MJ/kg of FA. Notably, the CO₂ emissions can be reduced by almost half as compared to the existing FA synthesis from fossil fuels, coupled with a 64 % reduction in electricity usage and 20 % decrease in steam requirements.

1. Introduction

Formic acid (FA) is a versatile chemical widely used in the food, pharmaceuticals, leather, and textile industries. Given its stability, low toxicity, and ease of handling and storage, it has also become a focal point of research, particularly as a potential hydrogen carrier (He et al., 2015; Enthaler et al., 2010). The annual global market for FA was about US\$ 760 million in 2019, and is expected to increase by 4.5 % annually until 2035, underlining its importance in economy and society. Currently, at industrial scale, FA is synthesized via methyl formate (MF) hydrolysis from fossil fuels. Specifically, synthesis gas (syngas), rich in CO, is generated via hydrocarbon reforming or coal gasification and then subjected to a carbonylation reaction to produce MF, utilizing methanol as a co-reactant (Hietala et al., 2016).

In recent years, the European Union (EU) has taken significant steps by implementing the Renewable Energy Directive (RED). Initially, the RED set a target of 32 % for renewable energy sources by the year 2030.

However, this goal has been recently revised and raised to a minimum of 42.5 % (Renewable Energy Directive, 2023). This shift highlights the critical importance of transitioning towards a low-carbon economy and efforts are already underway towards an eco-friendlier synthesis of FA. In literature, conceptual or small-scale FA production methods using sustainable feedstocks, such as biomass (Chen et al., 2020) or green Hydrogen through direct CO₂ hydrogenation (Bankar et al., 2023), have been reported. In practice, however, implementing these synthesis routes in large industrial plants remains challenging and economically unviable for a rapid transition of the chemical industry towards more sustainable FA production. Particularly, in terms of direct CO₂ hydrogenation, even recent literature has focused on methanol/DME (Vaquerizo and Kiss, 2024) or the electrochemical reduction of CO₂ (Dal Mas et al., 2024). Nonetheless, the electrochemical approach faces challenges due to low selectivity as it competes with the Hydrogen Evolution Reaction (HER). Additionally, achieving high overpotential is necessary to improve the slow kinetics associated with this process (Ewis

^{*} Corresponding author.

E-mail address: a.a.kiss@tudelft.nl (A.A. Kiss).

¹ These authors have equal contribution

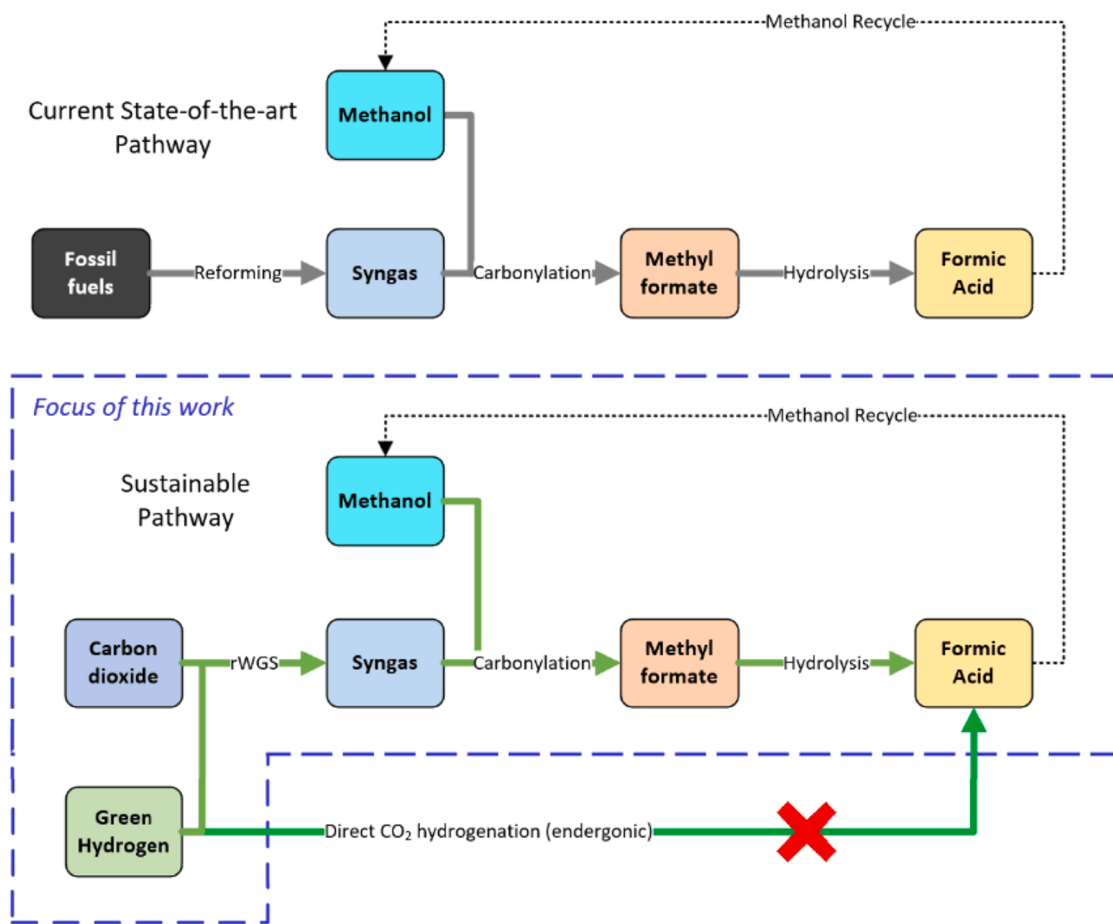


Fig. 1. Illustration of the green FA production methodology employed in this study.

et al., 2023; Al-Tamreh et al., 2021).

The direct gas-phase hydrogenation of CO_2 to FA via thermochemical pathway is also challenging, due to the endergonic nature of the reaction ($\Delta G^\circ_{300\text{ K}} = 32.9 \text{ kJ}\cdot\text{mol}^{-1}$) (Álvarez et al., 2017). Interestingly, the reaction becomes thermodynamically feasible when it occurs in (cryogenic) liquid phase ($\Delta G^\circ_{300\text{ K}} = -4.0 \text{ kJ}\cdot\text{mol}^{-1}$) (Álvarez et al., 2017). Some studies have introduced catalysts in specific solvents to overcome thermodynamic limitations, where ruthenium (Moret et al., 2014) or iridium-based catalysts (Behr and Nowakowski, 2014) have shown potential. Nevertheless, their manufacturing costs hinder their scalability for commercial applications. Furthermore, the solvent-based separation of the product adds complexity, especially in bi-phasic systems (Scott et al., 2017; Guntermann et al., 2022). Thus, direct conversion technologies of CO_2 to FA have not matured enough yet to be implemented in FA production.

Introducing MF as an intermediate compound improves the thermodynamics of the reaction, as practiced in FA synthesis state-of-the-art. The transformation of CO_2 , H_2 , and methanol into MF and H_2O is exergonic under standard conditions, with a $\Delta G^\circ = -5.3 \text{ kJ}\cdot\text{mol}^{-1}$ (He et al., 2015). Clearly, FA synthesis requires cost-effective chemical processes and affordable raw materials. The conversion of CO_2 to FA through hydrogenation represents a key industrial opportunity. Although inexpensive CO_2 is readily available from various sources (Olah et al., 2011), the availability of low-cost hydrogen remains limited. Moreover, the separation of CO and N_2 is a major challenge given that their similar molecular size prevents from implementing size-based separation, and their close boiling point discourages the use of cryogenic methods. Finally, the energy intensive downstream processing of FA needs also to be addressed and mitigated.

To overcome these challenges, this work proposes a novel process

design for the eco-efficient production of green FA from CO_2 – as shown in Fig. 1. By incorporating process intensification (PI) techniques, such as a dividing-wall column (DWC) configuration, as well as adjusting certain reaction conditions, a green FA production process can be achieved. Well-established industrial production technologies were taken into account to facilitate a smoother transition of chemical industries towards this sustainable approach. Upon completion of the simulation and technical design phase, an economic assessment was performed to determine the project's financial viability and highlight significant cost contributors. Additionally, the performance and sustainability of the process was benchmarked against conventional state-of-the-art FA chemical plants to demonstrate the overall reduction in energy consumption and in carbon footprint.

2. Process simulation

This work considers a plant producing 50 kta (168.1 kmol/h) of 85 wt% FA, by CO_2 hydrogenation using CO and MF as intermediate compounds. The required quantities of raw materials include 1.95 kta (121.1 kmol/h) of green H_2 and 43.12 kta (122.5 kmol/h) of CO_2 . Additionally, a small methanol make-up stream of 0.25 kta (1 kmol/h) is fed into the system to compensate for any methanol losses in the product and purge streams. More details are provided in the [Supplementary Information](#) file.

2.1. Thermodynamic property model

The complete process was rigorously simulated in Aspen Plus V12. The properties of the compounds utilized in this design were obtained from its database and additional literature, including the

Table 1

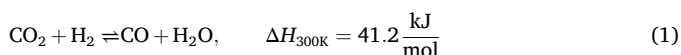
Kinetic parameters for FA synthesis simulation.

Kinetic model	k' [L ² mol ⁻² s ⁻¹]	E_a' [kJ mol ⁻¹]	k [L ² mol ⁻² s ⁻¹]	E_a [kJ mol ⁻¹]	K_c	K_d	Reference
Auto catalysed	0.002	66.4	4.33×10^{-4}	88.2	0.17		(Jogunola et al., 2010)
FA- catalysed	0.195	67.8			0.18	1.8×10^{-4}	(Jogunola et al., 2012; Skoog, 2000)

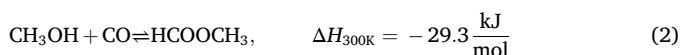
thermodynamic binary parameters essential for describing the mixtures within the design. For CO synthesis, the Peng-Robinson EOS was selected due to the low polarity of the compounds involved. In addition, the NRTL model was used for an ethylene glycol/water mixture, which serves as a thermal fluid with a low freezing point. Conversely, for the FA synthesis system, the UNIQUAC model with Hayden O'Connell equation of state for the vapor phase (UNIQUAC-HOC) was found to be the most adequate. This method considers both vapor-liquid and liquid-liquid interactions, suitable for a non-ideal system with polar compounds. The HOC variant of the method was included to handle the vapour phase dimerization of carboxylic acids. Also, Henry's law was used to account for the CO dissolved in the liquid phase, being the most suitable model for temperatures well above the critical temperature. More details are provided in the [Supplementary Information](#) file.

2.2. Chemical reactions

CO is obtained from the reverse Water Gas Shift (rWGS) reaction using CO₂ and green H₂ as feedstocks, as follows:



To prevent the formation of methane and methanol in the rWGS reaction, a H₂:CO₂ molar ratio below 3, high temperatures and near-atmospheric pressure are necessary (Kiss et al., 2016; Bown et al., 2021). Then, the CO undergoes carbonylation to yield MF, using methanol as co-reactant. MF synthesis follows the chemical reaction:



The carbonylation of CO and methanol towards MF is typically conducted in the liquid phase. High pressure is beneficial for MF production, as it significantly increases the solubility of CO in methanol, thereby enhancing the overall efficiency of the synthesis process (Reutemann and Kieczka, 2000). The reaction is exothermic which means equilibrium benefits from low temperature, while kinetics presents an opposite response (trade-off). Research on MF synthesis is primarily carried out under mild temperature conditions, typically between 60 and 110 °C, as frequently reported in literature (Chua et al., 2019). Furthermore, an excess of methanol is crucial to move the equilibrium towards the production of MF. The CH₃OH:CO molar ratio usually lies in the range of 1–5, ensuring nearly complete conversion of CO while maintaining methanol conversion levels at approximately 30 % (Kaiser et al., 2021). The excess methanol is usually recovered through distillation and recycled back to the carbonylation reactor.

In the final step, MF undergoes hydrolysis to produce FA, as shown in the next equation:



While no side reactions take place, synthesizing FA through this pathway is challenging due to equilibrium limitations. A high water-to-ester ratio is necessary to increase FA production. However, an excessive amount of water can escalate the energy costs associated with the downstream processing. As a result, the recommended ratio is between 0.8 and 7 (Hietala et al., 2016). Moreover, the reaction takes place in liquid state hence the operating pressure does not significantly impact the yield of hydrolysis. Nonetheless, elevated pressure is needed to

maintain the volatile MF in liquid phase ($T_{b, \text{MF}} = 31.8$ °C at 1 atm). Since the reaction is endothermic, higher temperatures are favourable for FA synthesis (Reutemann and Kieczka, 2000), but an optimum is reached at 120 °C due to FA thermal decomposition to CO and H₂ (Nelson and Engelder, 1926). The FA produced is then distilled to remove methanol, excess water, and unreacted MF. Because of an azeotrope between FA and water, distillation must be carried out at 3 bar to achieve the target purity of 85 wt% (Hietala et al., 2016; Chua et al., 2019). Higher pressure is avoided as it can lead to losses up to 10 % of FA due to thermal decomposition (Pasek et al., 2014).

2.3. Catalysts and kinetics

Typical catalysts for the rWGS reaction include transition metals such as iron, cobalt, and nickel, as well as metal oxides like copper oxide or cerium oxide (Roy et al., 2018). Molybdenum Carbide (Mo₂C) has been reported as one of options for its relatively cheap price and high activity in C=O bond scission and H₂ dissociation (Porosoff et al., 2014). The selected catalyst in this work is 1 K-5Cu/β-Mo₂C, which was reported to deliver 100 % CO selectivity and 48 % one-pass CO₂ conversion (close to equilibrium) under operating conditions of 600 °C, 1 bar, and WHSV of 84000 mL/g/h (Xu et al., 2021) (please refer to the [Supplementary Information](#) file for more details).

For MF synthesis commercial sodium methoxide catalyst was chosen. The high purity of the previously produced CO is crucial, given the catalyst's susceptibility to residual water and CO₂ (Kaiser et al., 2021). The kinetics that dictate MF synthesis under this catalyst were inferred from a previous study (Chua et al., 2019), which considers both the forward and backward reactions. In line with the parameters from that study, the catalyst concentration used for the process was 0.408 mol/L_{reactor} of sodium methoxide (2.5 wt%), with a residence time of 0.717 h. The MF reaction kinetic is:

$$[\text{MF}] = 1.414 \cdot 10^9 e^{-\left(\frac{70748}{RT}\right)} [\text{cat}]_L [\text{CH}_3\text{OH}]_L [\text{CO}]_L - 2.507 \cdot 10^{12} e^{-\left(\frac{92059}{RT}\right)} [\text{cat}]_L [\text{MF}]_L \quad (4)$$

The hydrolysis of MF takes place in two reactors with distinct kinetic models (Leonard, 1981). Initially the hydrolysis is auto-catalysed, following the kinetics outlined below (Jogunola et al., 2010):

$$r = \bar{k} e^{-\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_R}\right)\right)} \left\{ 1 + \frac{\bar{k}'}{\bar{k}} e^{-\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_R}\right)\right)} \left(\frac{1}{T} - \frac{1}{T_R}\right) \right\} C_C \quad (5)$$

$$\left(C_A C_B - \frac{1}{K_C} C_C C_D \right)$$

When a sufficient amount of FA is available, an excess of water is added to the reactor and the reaction proceeds with FA as the catalyst. The kinetic model in this case is given by (Jogunola et al., 2012):

$$r = \bar{k}' (K_d C_C)^{0.5} e^{-\left(\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_R}\right)\right)} \left(C_A C_B - \frac{1}{K_C} C_C C_D \right) \quad (6)$$

Table 1 includes all the kinetic parameters that were considered for simulating the two chemical reactors in Aspen Plus V12 (Chua et al., 2019).

3. Equipment sizing and economic assessment

In this work, an economic evaluation was conducted to assess the financial feasibility and robustness of the process. This involves estimating costs (capital and operational) and projecting revenues, as well as understanding how these costs and revenues are affected over time. For this reason, a rigorous assessment of the process, comparing its economic aspects between 2020 and a future projection, 2030, was carried out. The chronological period 2021–2023 was not considered due to uncertainties and unprecedented price increases during the pandemic and the energy crisis that followed.

Initially, the capital expenditure (CAPEX) was estimated, which is a sum of the fixed capital investment (FCI) and the working capital. The former can be divided into direct costs and indirect costs of the facility. Both are commonly calculated using a percentage fraction of the bare equipment cost (BEC), which represents the cost of purchasing the major equipment needed to operate the plant (excluding any costs associated with installation, operation, or maintenance). BEC is typically derived from vendor quotes or cost-estimating charts and databases that provide average costs for various types of equipment and can be influenced by several factors, including the type, size and capacity of the equipment, the materials of construction, as well as market conditions.

Note that the purge implemented in the CO section was adjusted to maintain a 5 % molar inert level at the reactor inlet for both the typical and the limit CO₂ composition case. Details are provided in the [Supplementary Information](#) file. As a result, many of the sizing input parameters, such as volumetric/mass flow rates and duties, are identical. However, there are some exceptions. The membrane, for instance, requires a greater capacity for the limit case, while the turbines (and the turbine inter heater) need larger capacity in the typical case due to a larger proportion of the recycled hydrogen that can be expanded in the turbine rather than being recovered in the membrane. For all the other equipment, the limit case was consistently used for sizing.

All methods for estimating costs rely on historical data and, in essence, are forecasts of future costs. The prices of the construction materials and labor costs are subject to inflation (cost escalation). The majority of the equipment estimation methods employed are those depicted in Sinnott's book ([Towler and Sinnott, 2013](#)). The prices in this book are based on the year 2013. Only the cost calculations for the polymeric H₂ membrane ([Jansen et al., 2009](#)) and the CO separation (COPure™) ([Lim et al., 2016](#)) are based on the years 2009 and 1988, respectively. A CEPCI value of 709 for 2030 was determined by plotting a trendline using data from 1960 to 2020. Similarly, the costs were adjusted for other years and the extrapolation graph are provided in the [Supplementary Information](#) file.

The primary drivers influencing the cost of raw materials in this process are CO₂ and H₂, which are used directly as feedstocks, and sodium methoxide, which is used in the synthesis of MF. However, various other raw materials are also integral to the overall process.

In the COPure™ process, the toluene recovery units use activated carbon for adsorption and operate in a quasi-continuous operation. A 1.7 % loss of the toluene directed to the two adsorbers was calculated for make-up calculations based on available pilot plant data ([Dingler, 1983](#)). Given the rigorous feed pre-treatment the loss of activity of the chemisorbent is considered negligible. Since decomposition would be the only source of losses here (due to its low volatility), continuous make-up of the chemisorbent is not considered. Lastly, the operational expenses (OPEX) can be calculated, again using a percentage portfolio of already calculated costs.

Finally, the revenues for the FA production plant are estimated for both the average purchase cost of 85 %wt. FA in 2020 and a rough projection towards 2030. Profit was calculated as:

$$\text{Profit (€)} = \text{Revenues} - \text{Manufacturing cost} \quad (7)$$

where manufacturing cost equals the sum of OPEX and annualized

capital cost (ACC):

$$\text{ACC} \left[\frac{\text{€}}{\text{yr}} \right] = \text{CAPEX} \times \frac{i(1+i)^n}{(1+i)^n - 1} \quad (8)$$

A six-tenth rule was applied to predict the CAPEX in larger plant size. The same method was used to simulate capital-related expenses in depreciation and maintenance, where the 0.25 exponent rule was used to account for labour-related costs, such as direct labour and overhead cost. More details are provided in the [Supplementary Information](#) file.

4. Results and discussion

This section provides the main results related to process design, process intensification, energy requirements, economic assessment, process benchmarking and sensitivity analysis.

4.1. Process design

CO₂ is acquired from the Porthos CCUS network pipeline at 25 °C and 35 bar, with two compositions considered: typical and limit cases of post-combustion capture quality. Pure and dry green H₂ at 25 °C and 30 bar is utilized from the Hydrohub Gigawatt electrolyser project (please refer to the [Supplementary Information](#) file for more details). The endothermic rWGS reaction occurs in a tubular reactor (modelled by a conversion reactor). The selected catalyst was considered to give same performance at the reactor condition of 1.2–1.4 bar, temperature range of 573–600 °C, and H₂:CO₂ molar ratio of 2.5 as similar conditions were reported in literature ([Xu et al., 2021](#)). Ideal isothermal operation poses challenges due to the complexity of controlling the high temperatures necessary for the process. Hence, a pragmatic approach involves employing five adiabatic stages with inter-heating, utilizing a fired heater, to simulate the process realistically. The number of stages was determined to minimize the adiabatic temperature drop (and thus keep the average temperature close to 600 °C).

After the reaction, CO is separated from unreacted feedstock and impurities, where the CO and N₂ separation is particularly challenging due to their similar properties. While a purge stream may mitigate N₂ accumulation, a separation step is necessary to prevent excessive loss of product and raw materials. Chemical absorption using a chemical agent that can selectively bind CO without affecting N₂ is proposed as the best solution. This process is commonly known as COPure™ technology and it involves the selective chemisorption of CO with a CuAlCl₄ salt dissolved in toluene, achieving a minimum CO purity of 99 % and a CO recovery of 98 % ([Sato et al., 1988](#)). The chemical reactions that occur in COPure™ process are as follows:



The operating conditions in the absorption column, chosen based on pilot plant data ([Go et al., 2019](#)), adjust the pressure to 27 bar to compensate for the slightly lower CO concentration in the feed. After CO is chemically bound to CuAlCl₄ at a low temperature (12–52 °C), other gases dissolved in the toluene are desorbed in a flash vessel at 90 °C and atmospheric pressure. Finally, the CO-CuAlCl₄ complex is dissociated in a stripper, in which the reboiler operates at 2 bar and 135 °C ([Bierhals, 2001](#)).

Although the reaction conversion is not expected to be affected by inert dilution, a high level of inert can significantly increase capital and operational costs. Therefore, a purge is incorporated to maintain a 5 % inert level in the reactor inlet. Furthermore, the pressure difference between the pressurized rWGS reaction feedstock and the low pressure rWGS reaction is utilized towards power generation using turbines. Additionally, this pressure difference facilitates hydrogen recovery from the inert purge through a polymeric membrane, which is also selective

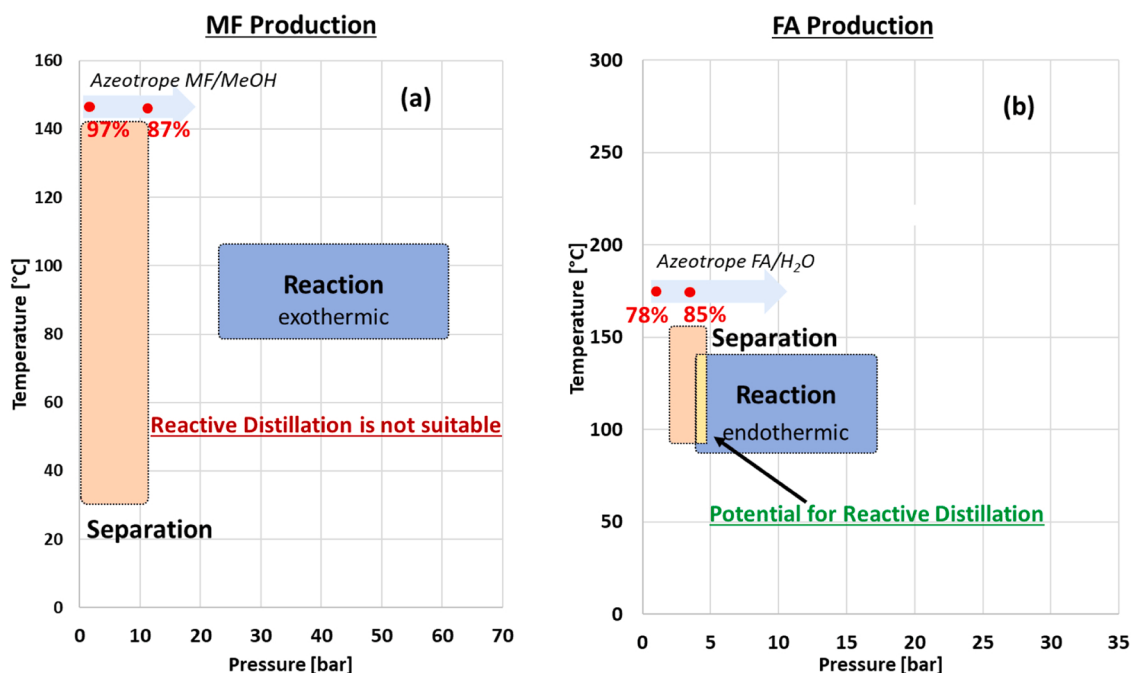


Fig. 2. RD potential in synthesis and separation of: (a) methyl formate and (b) formic acid.

to reject impurities such as CH_4 and N_2 .

Regarding to energy savings, heat integration was also implemented in the CO synthesis section. The CO synthesis reactor's outlet stream which has temperature of 573 °C was used to generate 6 bar steam, which was then utilized to replace the reboiler in the stripper. Additionally, the regeneration of refrigerant via the turbines during feed-stock depressurization was included, avoiding the requirement for chilled water.

A CSTR reactor was employed for MF production, operating at a methanol-to-CO ratio of 5, under conditions of 40 bar and 80 °C. An immersed coil cooling system was chosen to fulfil this requirement due to its affordability and its compatibility with the low viscosity (dynamic viscosity of 0.3 mPa·s) of the process fluid. Methanol and CO exhibit per-pass conversions of 14.8 % and 74 %, respectively, while preserving 100 % selectivity towards the production of MF. As the reaction progresses, a fraction of the catalyst degrades due to CO_2 poisoning. To maintain consistent reaction performance, a continuous supply of fresh catalyst, making up 3 % of the total catalyst weight, is introduced into the reactor. The reactor's outlet is distilled, and the excess of methanol is retrieved and recycled back into the reactor. The MF stream is then subjected to hydrolysis to synthesize FA.

To avoid accumulation, inert CO_2 needs to be removed, which is accomplished by introducing a purge stream with a flow ratio of 0.1. This leads to a minor loss of 3.3 % of the CO molar flow. By maintaining a 10 % purge ratio, the circulating CO_2 levels are kept low at 1.3 % mol, effectively minimizing the risk of sodium methoxide poisoning and preserving the MF yield.

Given that for the last reaction the reactants must remain in a liquid state, the pressure and temperature have been set at 18 bar and 120 °C, respectively (Chua et al., 2019; Jogunola et al., 2011). The L/D ratio is fixed at 30 to ensure turbulent flow in the PFR (Sauer et al., 2013). The ratio of MF-to-water at the reactor is kept around 1.8, as determined by the reaction conditions from the kinetic model used.

In the first reactor, 10 % of MF reacts with water to produce FA, acting as a catalyst for subsequent reactions. The second reactor achieves 30.5 % per-pass conversion of MF, with 100 % selectivity towards FA. Following this, the reactor outlet undergoes decompression. Leading to the partial vaporization of MF and methanol and instant cooling, which prevents the re-esterification reaction. Subsequently, MF and

methanol are separated from FA and water. The re-esterification reaction is avoided if the contact time between methanol and FA is minimized (Hietala et al., 2016). The top distillate stream is further separated into MF and methanol, each of which is recycled back to the hydrolysis and carbonylation reactors, respectively. The bottom distillate of water and FA is further distilled at 3 bar to overcome the azeotrope. More information about the selection parameters of the operating units and process sections can be found in [Supplementary Information](#) file.

4.2. Process intensification

Reactive distillation (RD) was considered for MF and FA synthesis. In the carbonylation reactor, given the conditions chosen – high pressure at the reactor and ambient pressure at the distillation – there is no overlap between reaction and separation conditions, making the use of RD not possible (as illustrated in Fig. 2). In FA synthesis the overlap of reaction and separation operating conditions is too narrow, to successfully employ a RD configuration without a significant trade-off. Namely, if elevated pressure is used for both the hydrolysis reaction which is needed to ensure liquid state and higher yield, and the separation section, then thermal decomposition of FA is promoted due to excessive temperature (149 °C) (Sharma et al., 2018). Despite of this challenge, numerous articles have reported RD application in MF hydrolysis (FA synthesis) (Sharma et al., 2018; da Cunha et al., 2018a; Ge et al., 2020; Novita et al., 2015, 2018; Patle et al., 2021; Ge et al., 2021). The tight operating window could be the main reason of several PI-based FA synthesis publications focus on plantwide process control design (Ge et al., 2020; Patle et al., 2021; Ge et al., 2021). RD is feasible through an ion-exchange resin embedded in the distillation column tray (Ge et al., 2020). However, the data available for the catalyst is limited in literature and may result in calculation inaccuracies. In this work, the MF hydrolysis is auto-catalysed, thus, eliminating additional catalyst costs and the formation of by-products due to catalyst decomposition. Furthermore, the product losses due to thermal decomposition at proposed RD operating condition are not considered in literature, hence, overestimating total FA yield (Sharma et al., 2018; Patle et al., 2021). These limitations potentially hinder RD and its variation from practical implementation in industry.

Another PI option worth to be evaluated is DWC, which is an

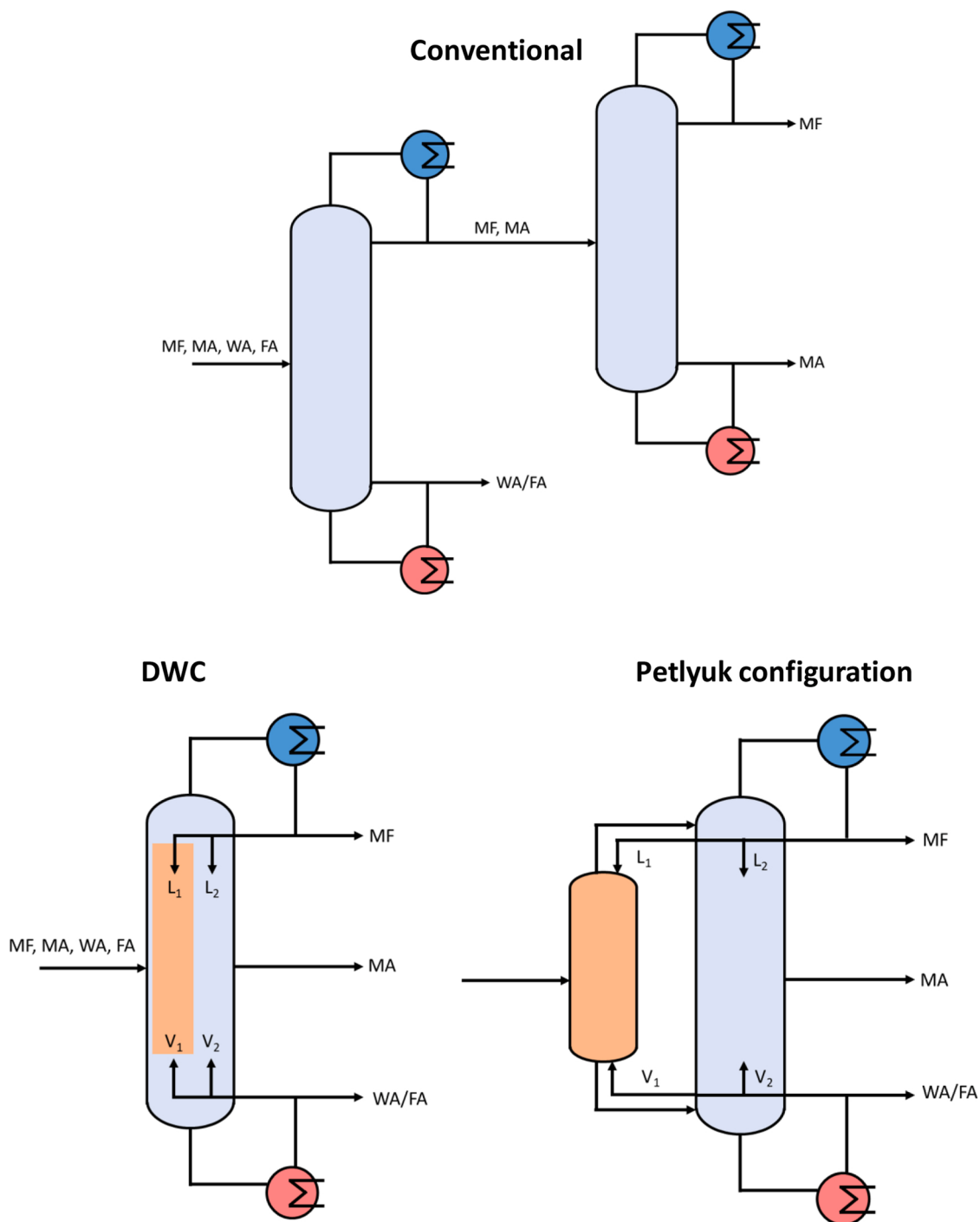


Fig. 3. Conventional indirect sequence vs dividing-wall column and equivalent Petlyuk configuration for the FA separation.

intensified distillation technology that combines the functions of two conventional columns into one. The vertical divider within the column structure enables the simultaneous separation of multiple components within a single column setup. As a result, the DWC could notably reduce both capital and operational costs, requiring only one reboiler or condenser to function (Chua et al., 2019). Compared to RD, DWC gives more flexibility as the reaction and separation are done in different system. DWC has already been evaluated in literature in the downstream processing of FA, but only as a retrofit alteration for existing formic acid plants. Since it is regarded as inappropriate for retrofitting (da Cunha et al., 2018b) due to increased total costs, in this work DWC is evaluated as an improvement in a newly constructed plant. The separation of MF,

methanol and water-FA streams requires ambient pressure, and their boiling points differ enough to apply a DWC configuration. The goal of this design is to determine if DWC is an economically feasible option and quantify its impact on capital and operational costs, as compared with the conventional configuration with three distillation columns.

The DWC is modelled in Aspen Plus using an equivalent Petlyuk column setup. The energy required to separate a multicomponent mixture using a three-product Petlyuk arrangement is comparable to that needed to separate top/middle or middle/bottom products in a conventional single column (Halvorsen and Skogestad, 2003). Fig. 3 illustrates the proposed DWC used for the MF / methanol / FA-H₂O separation. The initial step in DWC design involves the construction of

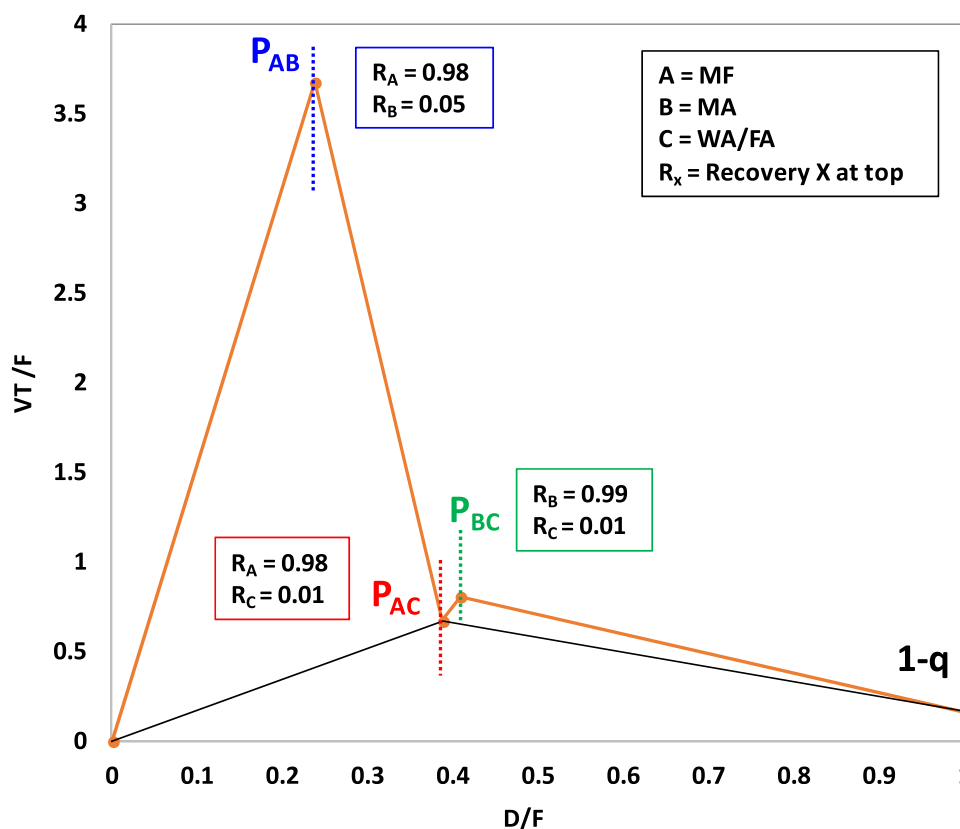


Fig. 4. $V_{\min}$ diagram of the feed to the DWC.

the $V_{\min}$ diagram using the short-cut model (DWSTU) in the Aspen Plus simulator. This diagram outlines the minimum vapor flow rates required for effective separation within the column. Despite the feed containing four components, the DWC design was simplified to focus on the separation of methanol, MF, and the FA-H₂O mixture. In this context, three key separation points are identified: P_{AB} (separating components A and B), P_{AC} (separating components A and C), and P_{BC} (separating components B and C) where A is MF, B is methanol, and C represents the water-FA mixture. The $V_{\min}$ diagram, depicted in the Fig. 4, showcases these essential separations. Notably, P_{AC} and P_{BC} are closely located in terms of V_T/T and D/F compared to P_{AB} , suggesting a relatively simpler separation of MF-methanol and water-FA compared to MF and methanol. P_{AB} represents the minimum energy requirement, as evidenced by its highest peak in the diagram. The detailed $V_{\min}$ data acquisition from Aspen Plus can be found in [Supplementary Information](#) file.

4.3. Energy requirements

The simplified process diagram in Fig. 5 illustrates the production of FA with an annual yield of 50 kta, achieving mass-based process yields of 95 % for CO₂ and 96 % for H₂. The most energy-intensive step is the separation of FA, mainly due to the substantial energy needed to separate water and FA.

The composition profile within the DWC (shown in Fig. 6), clearly demonstrates the achievement of the separation objectives. In the pre-fractionator, there is a noticeable concentration of MF and methanol in the upper section, while the components of FA and water are predominantly found in the lower stages. Towards the main column, a more refined separation process unfolds: MF is effectively drawn off from the top, followed by the additional separation of methanol and the FA-water mixture in the middle section. Simultaneously, the remaining FA-water mixture descends to the bottom of the column.

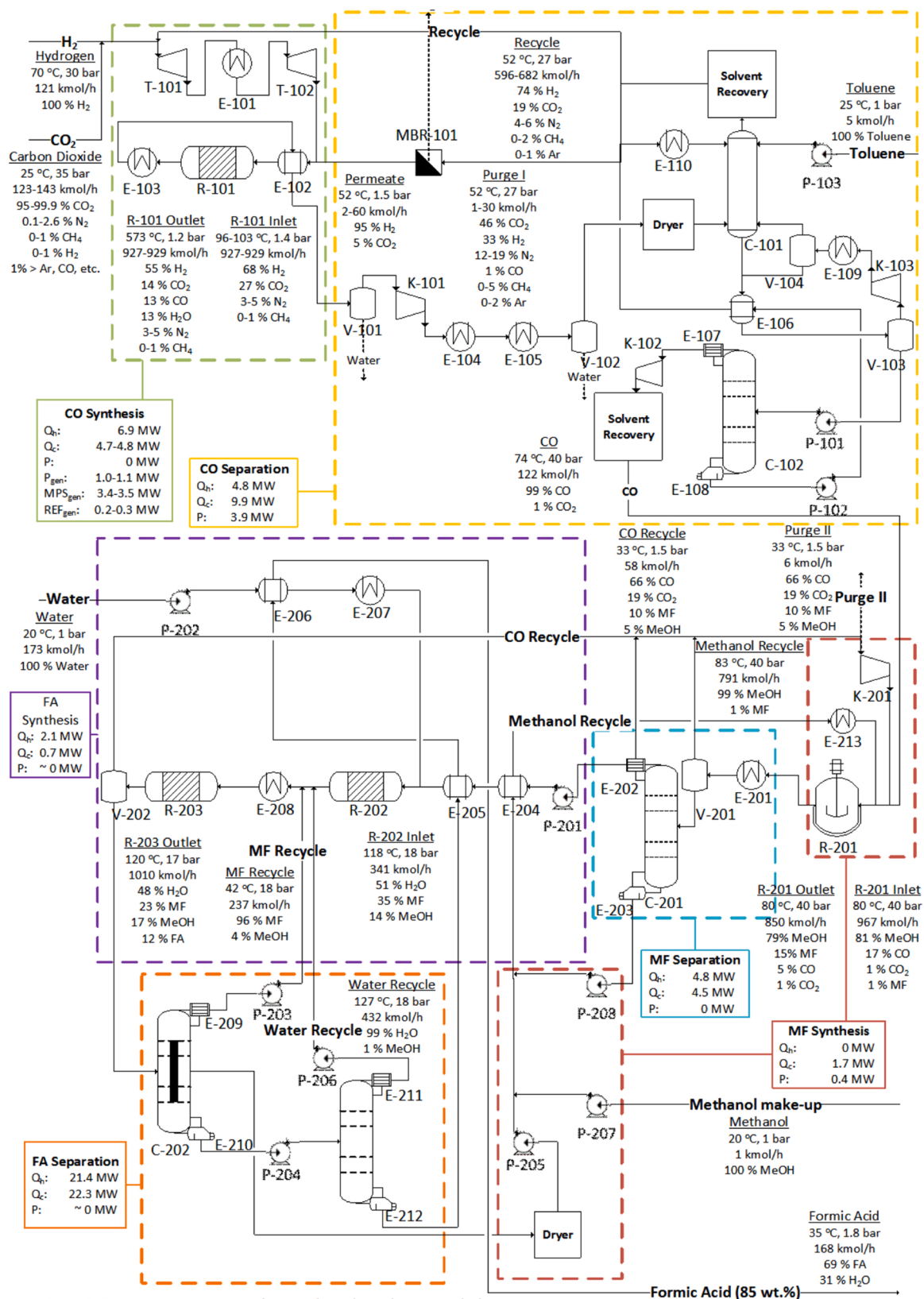
4.4. Economic assessment

This section discusses the results of the economic evaluation of the suggested design. It is important to note that state-of-the-art FA production plants are typically constructed within chemical complexes, allowing for integration with other processes and thereby considerably reducing production costs. However, for the scope of this study, the proposed process design was evaluated as a standalone system.

A summary of the estimated BEC is given in the [Supplementary Information](#) file. The main attributors are compressors and columns, accounting for roughly 60 % of the total BEC. The cost of raw materials, particularly H₂, is a major factor in the feasibility of this process. By 2030, the price of green H₂ is predicted to fall to 2500 €/ton ([Statista, 2023](#)), although this could be heavily influenced by regional policies and countries' commitment to reducing greenhouse gas emissions following the Paris Agreement ([The Paris Agreement, 2015](#)). Yet, the price of CO₂ is expected to remain steady as the supply-demand ratio is likely to stay the same. The [Supplementary Information](#) file provides detailed costs of raw materials, utilities, and waste treatment.

Additional costs for estimating CAPEX and OPEX were based on empirical methods outlined in Peters and Timmerhaus ([Peters et al., 1991](#)). The [Supplementary Information](#) file includes a detailed cost estimation of CAPEX and OPEX, while Table 2 provides a summary of these. The total CAPEX is projected at 73.8 M€ in 2030, marking a 19 % increase compared to 2020. This increase over these years can be attributed to the escalation of purchase costs as indicated by CEPCL. On the other hand, OPEX follows a different trend, with total costs of 42.0 M€ in 2020 and 43.9 M€ in 2030. The increase in OPEX is smaller (~5 %) due to the anticipated price decrease of H₂.

As for revenues, the price of FA was ~700 €/ton in 2020 and is projected to be around 1200 €/ton in 2030 ([ChemAnalyst, 2023](#)). This study conducted a basic profit and loss analysis using a 10 % interest rate and a 20-year plant lifespan. In 2020, an annual loss of 14.3 M€/yr



Note 1: Some compressors condensate (not shown) are recycled

Note 2: Q_h and Q_c account for total hot and cold duties without discounting integration savings

Note 3: Components with molar concentration < 1 % not shown

Fig. 5. Process flowsheet of the proposed FA synthesis from CO₂ and green H₂.

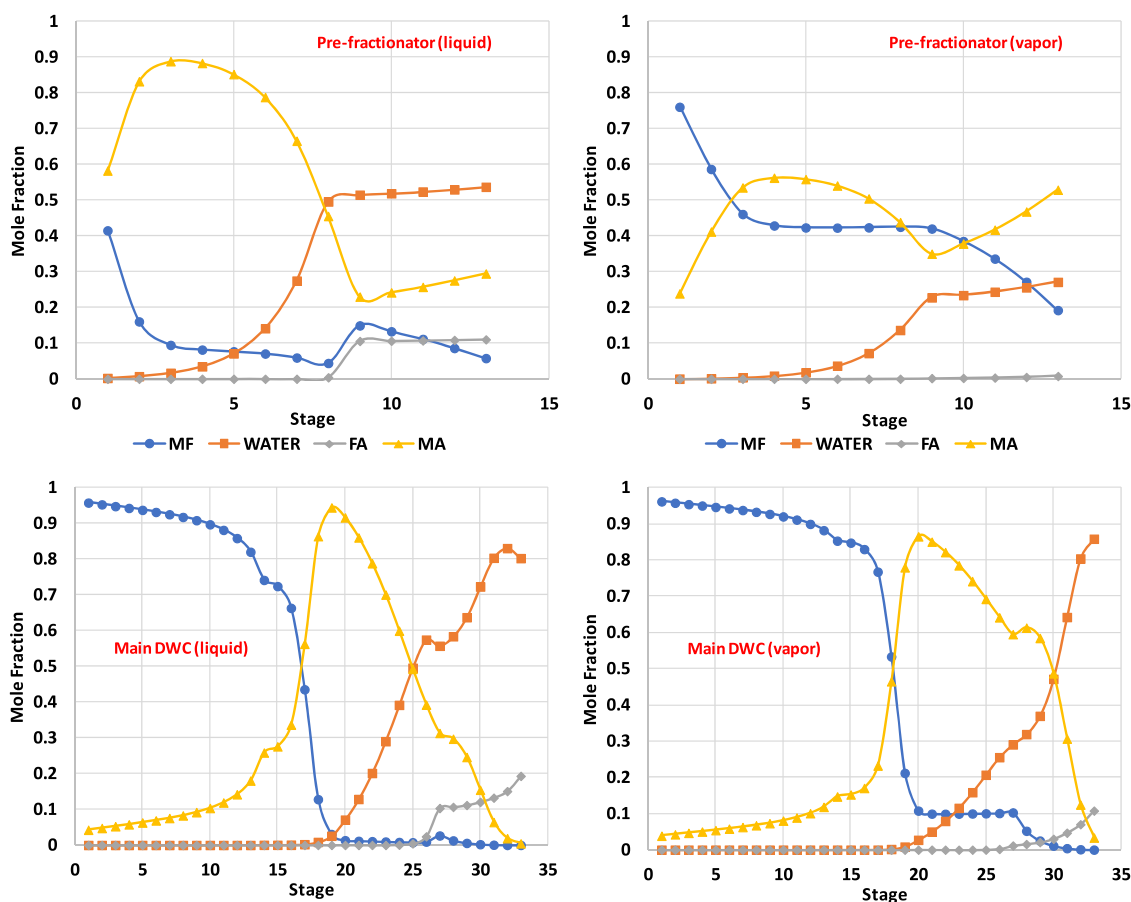


Fig. 6. Molar composition profiles across the DWC.

Table 2
Summary of CAPEX and OPEX.

Expenses	Remarks	2020	2030
CAPEX		Cost [M€]	
Total Direct Plant Cost	272 % of BEC (a)	42.2	50.2
Total Indirect Plant Cost	76 % of BEC (b)	11.8	14.0
Fixed Capital Investment	Sum (a + b)	54.0	64.2
Working Capital	15 % of FCI	8.1	9.6
Total Capital Investment		62.1	73.8
OPEX		Cost [M€/yr]	
Direct Production Costs	(c)	34.7	35.8
Fixed Charges	7 % of FCI	3.8	4.5
Plant Overhead	Based on (c)	1.7	1.7
General Expenses	Based on (c) and 4 % of OPEX	1.9	2.0
Total Operating Expenses		42.0	43.9

was estimated, but this loss is expected to decrease significantly and by 2030 a profit of 7.4 M€/yr is forecasted. This indicates that this approach of green FA production will become substantially more viable in the future. Despite this design being more energy-efficient in producing FA compared to conventional methods, it still poses an economic challenge due to the high cost of raw materials, especially green H₂.

4.5. Process benchmarking with conventional distillation configuration

A key novelty in the proposed process design lies on the eco-friendly FA production and the implementation of PI, which aims to reduce capital and energy costs. This is achieved by using a single DWC, which has lower equipment cost and energy requirements. In the conventional

Table 3
Utility consumption in conventional and intensified process.

Type	Without DWC	With DWC	Difference (%)
	Cost [M€]	Cost [M€]	
Heat exchangers	1.52	0.95	38
Distillation columns	3.86	3.37	13
Utilities	16.9	15.5	9
Maintenance	2.04	1.93	5
Utilities		Energy Consumption [MW]	(%)
CW	35.6	28.4	15
LP 2.5 bar Steam	19.8	11.4	42
LP 6 bar Steam	13.9	15.3	10
Cost attribute		Cost [M€/yr]	(%)
Annualized CAPEX	9.2	8.7	5
OPEX	46.8	43.9	6

configuration (without DWC), the heat exchangers for downstream processing of FA were estimated to cost 1.52 M€; but this purchase cost is reduced to 0.95 M€ in the DWC setup (38 % reduction). Additionally, the purchase cost of the distillation columns is reduced from 3.86 M€ to 3.37 M€ by using a DWC (13 % savings).

Furthermore, the utilities consumption in both cases has been analyzed (see Table 3). The DWC configuration yields significant savings of 8.4 MW and 5.5 MW regarding the 2.5 bar steam usage and cooling water duty, respectively. In the conventional distillation configuration, the total cost of utilities has been estimated to be 16.9 M€, whereas in the DWC configuration, it has been decreased to 15.5 M€. Thus, process intensification results in 9 % savings in total utilities cost.

Table 4

Process performance comparison.

KPI	Unit	Reference Case (Mar Perez-Fores and Tzimas, 2016)	This Work	Difference (%)
Electrical energy	kWh/kg FA	1.55	0.56	64
Thermal energy (steam)	MJ/kg FA	19.25	15.34	20
Cooling water usage	kg H ₂ O/kg FA	375.50	501.59	34
Process water usage	kg H ₂ O/kg FA	0.60	0.50	17
Total CO ₂ emission**	kg CO _{2eq} /kg FA	2.18	1.05	51

* The reference used to compare the thermal energy with our proposed process does not indicate different quality of steam used in the process.

* Scope 1 and Scope 2.

4.6. Process benchmarking with traditional fossil fuels pathway

The proposed design has been also compared with the conventional production of FA from fossil fuels. The reference case used in this comparison is FA synthesis from natural gas and the key performance indicators (KPI), on which the two cases have been assessed, have been obtained from European Commission - JRC Science for Policy Report (Mar Perez-Fores and Tzimas, 2016). The comparison result is presented in Table 4. The proposed design outperforms the conventional FA synthesis pathway in almost every KPI, proving its potential as a sustainable alternative for FA production in the near future. Specifically, the CO₂ emissions are halved compared to the reference case, which is primarily attributed to the low direct CO₂ emissions from the purge streams with comparatively low mass flow. To compare the total OPEX saving, the cost of each KPIs has been calculated following the utility prices applied in the economic evaluation of this case study, resulting in 13 M€ OPEX savings per year.

4.7. Process benchmarking with existing RD and R-DWC literature

Section 4.2 mentioned there are several publications about FA synthesis with RD. In this section we also compared our result to the work done by others (Sharma et al., 2018). The design in this work exhibits higher specific cooling duty (609 MJ/kmol product) and heating duty (582 MJ/kmol product), where the RD could achieve much lower values (cooling duty of 527 MJ/kmol product and heating duty of 558

MJ/kmol product). It is worth mentioning that their work only considers CO carbonylation and MF synthesis sections with pure CO stream as feed. In this work, we also include the CO synthesis step with CO stream inlet purity of 99 %, which is considered to give a more realistic condition. The CO composition difference is one of the contributing factors of the higher energy requirement in the design proposed here, in addition to differences in kinetic equation employed for calculating the FA produced.

4.8. Sensitivity analysis

A sensitivity analysis was conducted to determine the influence of several key parameters on the total annual profit. These parameters encompass the price of green H₂, CO₂, electricity, product, natural gas, CAPEX, plant size, and CO₂ tax. Fig. 7 illustrates the impact on annual profits when these key parameters are adjusted by ± 30 %.

A 30 % increase in the price of electricity, CO₂, green H₂, CO₂ tax, CAPEX, and natural gas price leads to a decrease in profitability. Among these, electricity is the least sensitive while natural gas is the most, with a 0.7 M€/yr and a 4.7 M€/yr reduction compared to the base case, respectively. Conversely, a 30 % decrease in these parameters results in an increase in profitability, depicted in green, with electricity being the least sensitive (8.1 M€/yr) and natural gas the most (11.3 M€/yr).

On the other hand, a 30 % increase in plant size and product price, leads to the most significant profit increases, specifically 25.4 M€/yr, as shown in light green in Fig. 7, whereas, a 30 % decrease could lead to losses in the process of up to 10.6 M€/yr. This aligns with the economic assessment for 2020, where the price for FA was 700 €/ton. It is plausible that future aggressive carbon taxation could drive up the product price. However, the proposed process would be more shielded from these taxation costs. Given this trend, it is unlikely that a future price decrease that would result in losses will occur.

5. Conclusions

By employing process intensification techniques (e.g., DWC and heat integration), substantial savings of 3.4 M€/yr in the annualized CAPEX and OPEX are possible (as compared to conventional production), leading to an energy intensity of 21.8 MJ/kg of FA. Energy savings of 12.2 % were achieved due to lower steam usage. This novel process is more sustainable and aligns with future environmental requirements, as it effectively reduces CO₂ emissions by half to 1.05 kg CO_{2eq}/kg of FA. Given the fact that the technologies included have sufficiently high technological readiness level, the design can be readily used in existing industries.

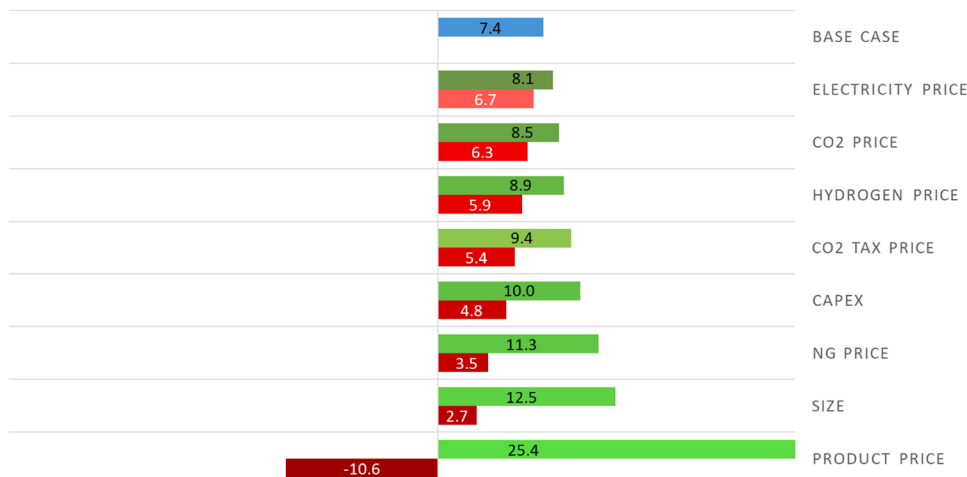


Fig. 7. Sensitivity analysis on profitability impact of key parameter variations (in M€/yr).

The economic assessment of FA synthesis in 2030 yields positive financial outcomes (7.4 M€/yr) for a 50 kta FA capacity and the sensitivity analysis shows that under most conditions the process would be profitable. It is projected that the price of FA, which is the most sensitive factor, will be increased by 2030 compared to 2020, and the green hydrogen will be more readily available and less expensive. The advent of electric heaters could also decrease indirect CO₂ emissions, leading to a reduction in CO₂ tax payments. In fact, the CO₂ tax value may increase in the future, which is likely to push product price further, as the conventional process would significantly increase its costs. Increasing the plant size by 50–100 % (which is within the current range of FA plant capacities) would also result in better performance.

Although this design has been assessed as an independent process, if it is integrated into a larger chemical plant complex, it can benefit from the synergies of various processes, potentially reducing working capital, labour, and utilities costs. Further improvements in the cost, energy and material efficiency could be achieved by incorporating a membrane reactor for simultaneous reaction and selective CO separation. This would promote continuous product removal and shift the equilibrium towards higher CO yield. Additionally, electrifying the rWGS reactor heater could further contribute to achieving net-zero emissions.

CRedit authorship contribution statement

Savvas Staikos: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Investigation, Data curation, Conceptualization. **Amsalia Barus:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Investigation, Data curation, Conceptualization. **Maximiliano Taube:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Investigation, Data curation, Conceptualization. **Nikolaos Kalmoukidis:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Data curation, Conceptualization. **Anton A. Kiss:** Writing – review & editing, Writing – original draft, Validation, Supervision, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Farzad Mousazadeh:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Formal analysis, Conceptualization.

Declaration of Competing Interest

The corresponding author, Anton Kiss, is an editor for the journal Chemical Engineering Research and Design, but has had no access to, or involvement in, the peer review process for this paper or its handling by the journal at any point

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Notation	
ACC	Annualized Capital Cost
BEC	Bare Equipment Cost
CAPE	Capital Expenditure
CCUS	Carbon Capture, Utilisation and Storage
CEPCI	Chemical Engineering Plant Cost Index
DWC	Dividing-Wall Column
FA	Formic Acid
FCI	Fixed Capital Investment
KPI	Key Performance Index
MF	Methyl Formate
NRTL	Non-Random Two-Liquid model
OPEX	Operational Expenditure
PI	Process Intensification
PFR	Plug Flow Reactor

(continued on next column)

(continued)

RD	Reactive Distillation
rWGS	reverse Water Gas Shift
TRL	Technological Readiness Level
UNIQUAC	Universal Quasichemical model
C_A	MF concentration in mol L ⁻¹
C_B	water concentration in mol L ⁻¹
C_C	FA concentration in mol L ⁻¹
C_D	methanol concentration in mol L ⁻¹
E_a	activation energy of the uncatalyzed reaction in kJ/mol
E_a'	activation energy of the autocatalyzed reaction in kJ/mol
$\bar{k}$	rate constant for the uncatalyzed reaction in L ² mol ⁻² s ⁻¹
$\bar{k}'$	rate constant for the autocatalyzed reaction in L ² mol ⁻² s ⁻¹
K_c	equilibrium constant (dimensionless)
r	reaction rate in mol L ⁻¹ s ⁻¹
R	gas constant in kJ mol ⁻¹ K ⁻¹
T_R	reference temperature, 368.15 K
T	reaction temperature in K
ΔG°	Gibbs free energy

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.cherd.2024.09.001](https://doi.org/10.1016/j.cherd.2024.09.001).

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