Formic acid synthesis using CO_2 as raw material: Techno-economic and environmental evaluation and market potential

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ABSTRACT

The future of carbon dioxide utilisation (CDU) processes, depend on (i) the future demand of synthesised products with CO_2, (ii) the availability of captured and anthropogenic CO_2, (iii) the overall CO_2 not emitted because of the use of the CDU process, and (iv) the economics of the plant. The current work analyses the mentioned statements through different technological, economic and environmental key performance indicators to produce formic acid from CO_2, along with their potential use and penetration in the European context. Formic acid is a well-known chemical that has potential as hydrogen carrier and as fuel for fuel cells.

This work utilises process flow modelling, with simulations developed in CHEMCAD, to obtain the energy and mass balances, and the purchase equipment cost of the formic acid plant. Through a financial analysis, with the net present value as selected metric, the price of the tonne of formic acid and of CO_2 are varied to make the CDU project financially feasible. According to our research, the process saves CO_2 emissions when compared to its corresponding conventional process, under specific conditions. The success or effectiveness of the CDU process will also depend on other technologies and/or developments, like the availability of renewable electricity and steam.

Introduction

Carbon capture and utilisation (CCU) stands for the capture of anthropogenic CO_2 and its subsequent use in a synthesis process that utilises CO_2 as a carbon molecule carrier. A carbon dioxide utilisation (CDU) process, in this work, refers to the CO_2 transformation process into another product with commercial value. Note that CDU processes may consume CO_2 not only from power plants or heavy industries, but also CO_2 from the air, generated as by-product or naturally occurring, as from natural gas extraction. Therefore, independently of the development of capture in power plants, the CDU processes can evolve towards a mature market, if CO_2 is

available, i.e. as by-product, or captured from other sources. A variety of industrial synergies (as for CO_2 "management") may be envisioned, yielding win-to-win situations, for example with CO_2 obtained as by-product. CO_2 utilisation processes involve a number of products to be synthesised, and as such, the status of the technology varies according to each synthesised product. CDU should be considered as part of the CO2 abatement options (i) preventing the use of fossil fuel as raw material, and (ii) avoiding net CO2 emissions to the atmosphere, if compared to the benchmark process.

Carbon capture and storage (CCS) and CCU have been acknowledged as important research and development priorities of the European Energy Union, to reach 2050 climate objectives in a cost-effective way [5]. Moreover, it is one of the research priorities of the Strategic Energy Technologies (SET) Plan Action of the European Union (EU) [6] as well as a research theme in the Integrated Road and Action Plan of the SET Plan whose aim is to consolidate the updated technology roadmaps of the SET Plan and to propose research and innovation actions [7]. In this context, CCU is not only relevant to the energy generation or to the heavy industry sectors, but also in a number of areas: greenhouse gas emissions and climate change, emissions of the transport sector, waste disposal, chemical industry and technological development. The potential of CCU is recognized; however, further research is needed to evaluate this potential and to come up with the most suitable strategies or business plans for its implementation.

In CDU processes the CO_2 molecule is chemically changed, in contrast to the use of CO_2 in storage, enhanced oil recovery (EOR), or other uses like in food industry or as supercritical solvent, where the molecule remains unchanged. The attractiveness of CDU stands for the replacement of non-sustainable fossil fuels by CO_2 [1,2]. This is the reason why CDU for the production of fuels, chemicals and materials, has emerged not only as a possible complementary alternative to CO_2 storage (at a much more lower scale), but as a promising competitive advantage for the European industry. These processes may contribute to CO_2 emissions reduction, capped by the demand of the synthesised product. Moreover, CO_2-based products imply a temporary storage of CO_2 (except for mineralisation) [3]. Holistic approaches are therefore crucial to evaluate each CCU or CDU technology contribution to CO_2 emissions abatement, taking into account CO_2 obtaining, transport, transformation and product consumption, so as to guarantee the environmental benefit of using CO_2 as raw material [4]. The current paper evaluates the potential of formic acid (FA) synthesised by CO_2 to decrease CO_2 emissions if compared to the conventional process of FA synthesis, and analyses its competitiveness compared to current market conditions.

Formic acid: overview and future prospects

Formic acid finds its applications in textiles, pharmaceuticals and food chemicals, due to its strong acidic nature and reducing properties. Traditionally, the leather and tanning industry has been the biggest consumer of FA, accounting in 2003 for 25% of its global applications [8]. Since 2006, and due to the total European ban on non-prescribed feed antibiotics,

its main application is as a preservative and antibacterial agent in livestock feed [9,10]. In 2013, the global demand for FA was 579 kt, of which 34% was attributed to animal feed. Leather tanning accounted for 32% and textile dyeing for 13% [11]. Its global production reached 620 kt in 2012 and it is expected to be more than 760 kt in 2019 [12]. The world capacity of FA reached 697 kt in 2013. The global market is expected to grow with an average annual growth rate of 3.8% up to 2019 [12,11]. In Europe, important FA producers are BASF, with sites in Germany; Tamico (ex Kemira Oyj) with sites in Finland; and Perstorp with sites in Sweden. The total installed capacity in Europe is around 350 kt/yr, with about 60% of it located in Germany [13,14] and 30% in Finland [15,16]. Formic acid can be found in the market at concentrations of 85, 90, 95, 98 and 99 wt %, with 85% being the most common [10]. The impurity content depends on the production process and it is a decisive factor for its price. In 2014, FA 85% grade was sold in Europe for 0.51–0.60 €/kg [11]. Formic acid is a high valued product, with a concentrated, small and mature market, with low risk of substitution.

Formic acid synthesis process from CO_2 and H_2 has a technology readiness level (TRL) of 3–5 taking into account homogeneous catalysis and electro-reduction, as summarised in the following lines. Different patents on the synthesis of FA from CO_2 and H_2 using homogeneous catalysts have been granted to companies like BP (see for instance, [17–19]) and BASF (as for example, [20,21]). The most recent patents were granted to BASF. The efforts are focused on decreasing the overall energy consumption of the process. Det Norske Veritas (DNV) [22] and Mantra Venture Group [23,24] have reported their experiences with the electro-reduction of water and CO_2 to obtain FA as main product, with oxygen as by-product. DNV (2007) [22] has a small-scale demonstration electro-reduction plant, of 350 kg FA/yr. Mantra Venture Group (2015) [23] have finished the engineering work on a pilot plant, which produces 35 tFA/yr. Laboratory research on the electro-reduction of CO_2 to FA aims at a continuous synthesis process; materials research is fundamental in the field, as for the electrode and solvent, as studied in Ref. [25,26].

Formic acid and hydrogen

Hydrogen market is growing due to regulations in transport fuel desulphurisation, among others. It is estimated that its global demand will be increasing in the next years [27]. Transport is a key area for hydrogen, and not only for road transportation (as in fuel cell vehicles); see for instance the European project Cryoplane [28], that studied the use of H_2 to replace kerosene in airplanes. Hydrogen is produced in large quantities, both as main product and as by-product. Nearly 96% of all H_2 is derived from fossil fuels: natural gas is the fossil fuel most frequently used to synthesise H_2 through steam reforming (about 48% of the production by fossil fuels), followed by liquid hydrocarbons (30%), coal (18%) and electrolysis and by-product sources, such as gasification (4%) [29,30].

Hydrogen has potential to achieve near-zero CO_2 performances when used [30]; as such, its production must be carbon-free to reduce the life cycle CO_2 emissions. It is therefore imperative to synthesise H_2 from renewable

sources: biomass gasification or electrolysis powered by "zero" emissions sources, i.e. renewables and nuclear. The advantage of nuclear and biomass sources towards intermittent renewable sources, is that the generation of H_2 can take place at a continuous rate. However, for instance, the study by Lee [31] demonstrates the situation in Taiwan, where nuclear results the less favourable source of electricity for the production of H_2. Biomass, wind and solar are currently the most common renewable sources for electricity supply in water electrolysis [33]. Wind and solar need from alternatives to avoid reaching the threshold below which no electricity is produced, and from alternatives to store electricity produced and not used. In electrolysis, H2 may be produced through alkaline or proton exchange membranes (PEM), or by steam electrolysis in a solid oxide electrolyser cell (SOEC). Even if the SOEC is the most efficient option, it is currently less developed than the other types of cell [32]. Carton and Olabi [34] evaluated a system of hydrogen synthesis and fuel cell technology in Ireland, for wind power. The same power-to-gas system, with fuel cells providing electricity when needed, is the subject of study in the work by Gahleitner [35]; a review of worldwide pilot plants points out the interest of Germany in this type of integrated systems. Samsatli et al. [36] performed a mathematical optimisation of the a wind-hydrogen network, to supply the hydrogen demand of Great Britain. The work by Centi et al. [37] pointed out the link between (i) the need for storage of the excess electrical energy, and (ii) the need from the chemical industry to decrease its dependency towards fossil fuel, as both raw material and energy supplier. In this framework, CO_2 use as raw material, combined with H_2, is a mean to introduce renewable energy into the chemical production chain.

The centralised production of H_2 would require the development of infrastructure for delivery to and storage for the end user [38]. In general, H_2 distribution needs to be more energy efficient and reduce costs, reasons why H_2 carriers have a place in the market arena. A number of studies describe the potential of FA for H_2 storage, as a non-toxic and easy-to-store chemical, i.e. as a liquid ([39–41]). As a thermochemical process, FA synthesis from CO_2 and H_2 is an energy-intensive process due to the necessary processes to separate FA from the catalysts and solvents needed to synthesise it. Different laboratory and fundamental research approaches analyse the use of supercritical CO_2, ionic liquids, ruthenium and rhodium based catalysts, in acid or basic media [42–46], to increase the overall reaction efficiency. The dehydrogenation of FA to provide H_2 is similarly studied and needs further R & D [47–50]. The research of the appropriate catalysts is pointed out. Potentially, FA can be used as hydrogen carrier. The so-called "hydrogen economy" aims at increasing the penetration of hydrogen by means of decreasing the use of fossil fuels. Indeed, the use of captured CO2 from power plants and heavy industries to synthesise FA can potentially reduce the emissions from energy and transport sectors.

Formic acid can be directly used in fuel cells. The direct formic acid fuel cell (DFAFC) is an attractive alternative for small portable fuel cell applications [51–53]. In 2006, BASF and Tekion (a developer of micro fuel cell for portable electronic devices) signed a joined agreement to develop and test FA

formulations [54]. However, no further information has been found regarding this project.

The aim of this paper is to evaluate the technological, economic and environmental feasibility of FA synthesis from captured CO_2 and H_2, not only as an individual process, but also as compared to the benchmark conventional FA synthesis plant. The process model is performed in the process modeller CHEMCAD. Based on the simulation results (mass and energy balances), the different key performance indicators (KPIs) are calculated. The CDU plant is compared to the equivalent conventional plant based on the data retrieved from Ecoinvent. Univariate and bivariate sensitivity analyses, implemented in Matlab, are performed to the main problem variables, in order to determine the variables with the most influence on profitability, and the conditions under which the CDU plant becomes profitable. Finally, the market penetration of FA is evaluated through different pathways, used as usual or used as hydrogen carrier, by year 2030.

Methodology

The systematic methodology applied in this paper follows the same general guidelines than in Ref. [92], where methanol (MeOH) synthesis from CO_2 was evaluated.

Process modelling, total purchase cost and variable costs of production

A conceptual design is implemented in the software modeller CHEMCAD, according to an average commercial plant size. The boundaries of the CDU plant, and thus of the model, are set on the utilisation plant itself; CO_2 capture and transport are outside these boundaries. The CDU plant is compared with the benchmark process of synthesis, which uses a fossil fuel instead of CO_2 as its raw material. Fig. 1 represents the boundaries and the main inlet and outlet streams of both, CDU and conventional plants. The analysis performed is gate-to-gate.

The carbon utilisation plant includes electrolysis to obtain H_2, CO_2 purification to avoid catalyst poisoning and compression previous to the synthesis process. Electrolysis and CO_2 purification units are modelled as black box units and their investment costs are estimated using available figures in literature: Bolat and Thiel [56] for the electrolyser, and Heyne and Harvey [57] for the purification unit. The total cost of purchase of the equipments is estimated with CHEMCAD and also using the design criteria of Towler and Sinnot for heat exchangers cost estimation [58]. The currency used is €$_{2014}$, and currency conversion is performed using Eurostat data [59]. The purchased equipment costs are estimated for carbon steel, and adapted to consider the utilisation of 304 stainless steel, by means of a material cost factor of 1.3 [58]. The Chemical Engineering Plant Cost Index CEPCI published monthly in the Chemical Engineering Magazine is used to actualise each unit purchase cost, when needed, to July 2014 [60]. The plant is assumed to be built in Western Europe (location factor of 104.3%, to transform the costs from US Gulf Coast basis to Western Europe [61]), and the production time is 8000 h per year.
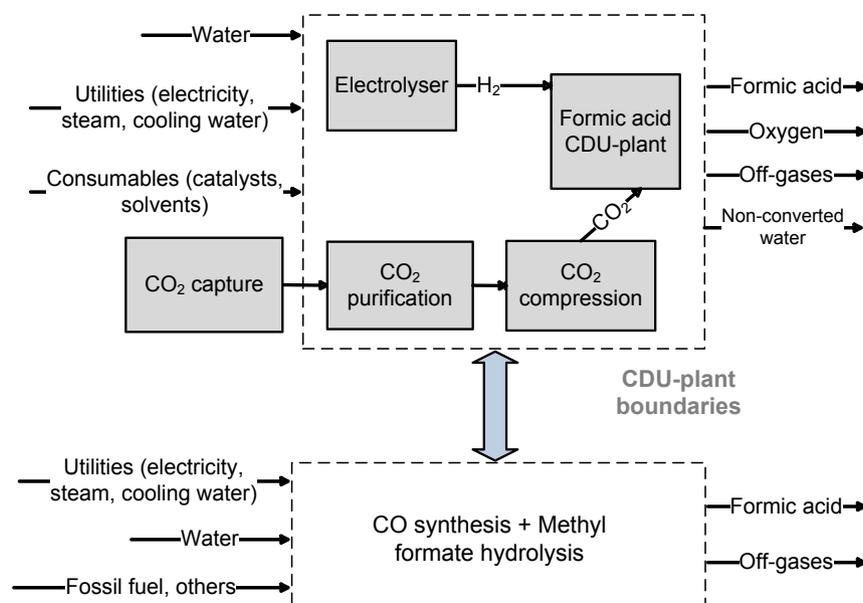
Fig. 1 — Gate-to-gate analysis: Boundaries of the simulated CDU plant towards the boundaries of the most common FA synthesis process in Europe.

It is assumed that the required steam is at saturated conditions for each required temperature, when no heat integration is possible among the cooling and heating needs of the process, and that cooling water is available at 8 bar and 15 °C, with a minimum temperature difference of 10 °C. Constant ambient air temperature of 20 °C, and atmospheric pressure of 1.013 bar, are supposed.

Key performance indicators

The mass and energy balances from the model are the starting point to calculate the following selected metrics or KPIs. These represent different aspects of the process which are relevant to the total CO_2 emissions of the plant. CO_2 equivalent emissions are taken into account. The different indicators are normalised to one tonne of FA.

Technological metrics
These metrics result directly from the model of the process.

- CO_2 and H_2 converted. These metrics evaluate, (i) the CO_2 and H_2 that are transformed in the reactor of the synthesis process (CO_2convR), and (ii) the CO_2 and H_2 that are transformed into product through the whole process (CO_2convP). They are expressed as a percentage of the total amount of CO_2 and H_2 that enters the process as raw material, as in Eq. (1).

$$CO_2conv = \left(\frac{CO_2in - CO_2out}{CO_2in}\right)_{R/P} \qquad (1)$$

where, CO_2in is the inlet flow rate to the reactor (R) or to the whole process (P), and CO_2out is the outlet flow rate from the reactor or from the whole process, in tonnes per tonne of FA. Analogous calculations are performed for the H_2 flow.

- CO_2 used. It is defined as the net amount of CO_2 that is converted into the product, in our gate-to-gate analysis of the CDU process. It takes into account the difference between the amount of CO_2 that enters the process as raw material and the direct and indirect emissions of CO_2, this last due to electricity and steam consumptions, as in Eq. (2).

$$CO_2used = (CO_2in - (CO_2out + CO_2indirect))_P \qquad (2)$$

where, CO_2in is the inlet flow rate of CO_2 (in tonnes per tonne of FA) that enters the whole process, CO_2out is the total outlet flow rate of CO_2 in purge streams and in product/by-product or residual streams, and $CO_2indirect$ are the CO_2 emissions in tonnes per tonne of FA due to electricity and steam consumptions. The metric CO_2used is employed as a design condition: it has to be positive for the CDU process, to emit less CO_2 than the CO_2 that is used as raw material.

The relevant energy and mass balances data from the CDU plant are compared with conventional plant values to discuss the technological features.

Economic metrics
Costs are estimated using a bottom-up approach with input data from the process model. The approach used to calculate the installed costs (ISBL) follows the detailed factorial methodology described in Towler and Sinnott [58]. The calculation of the total capital expenditure (CAPEX), variable costs of production (VCP) and fixed costs of production (FCP) also follow the methodology from Towler and Sinnott [58]. The economic parameters and assumptions are provided in Appendix A.

The gross margin (GM) is calculated as the difference between the revenues (REV), obtained from selling products and by-products, and the cost of raw materials (RM) (as in Eq. (3))

$$GM = REV - RM \tag{3}$$

The benefit/cost ratio (BCR) is defined as the ratio between unitary benefit and unitary cost, as in Eq. (4). This metric reflects how much of the cost to synthesise a unit of product is covered by the benefit of selling it.

$$BCR = \frac{Total\ unitary\ benefit\ of\ selling\ the\ product}{Total\ unitary\ cost\ to\ make\ the\ product} \tag{4}$$

Environmental metrics

Two emission-based metrics are defined to compare the CDU process with the conventional process in our gate-to-gate approach. These compare direct and indirect CO_2 emissions of both plants, expressed in tonnes per tonnes of product, without taking into account the inlet amount of CO_2. In order to evaluate the CO_2 savings due to the non-use of fossil fuels as raw material, the $CO_2 not-emitted$ is calculated as in Eq. (5). The $CO_2 change$, expressed as a percentage, relates the $CO_2 not-emitted$ to the CO_2 emissions of the conventional plant (Eq. (6)).

$$CO_2 not - emitted = (CO_2 out + CO_2 indirect)_{conv}$$
$$- (CO_2 out + CO_2 indirect)_{CDU} \tag{5}$$

$$CO_2 change(\%) = \frac{CO_2 not - emitted}{(CO_2 out + CO_2 indirect)_{conv}} \tag{6}$$

where, CO_2 for conventional and CDU plants take into account direct and indirect emissions. The saving of fossil fuel due to the use of CO_2 as carbon carrier is also evaluated.

Sensitivity analysis

The net present value (NPV) is the metric used to evaluate the profitability of the CDU plant from a private investor viewpoint. The following assumptions are taken into consideration:

- the economic CDU plant life is 20 years. A unique investment takes place at the beginning of the project;
- capital expenses occur during the first three years of the life of the plant (30, 60 and 10% of the total fixed capital cost − TFCC, respectively);
- there are revenues from year 3 of the project onwards. The plant operates at 30, 70 and 100% of its capacity (91.3%, which corresponds to 8000 h of operation per year) during years 3, 4 and 5 and onwards;
- prices are estimated for year 2014, and are considered constant along the 20 years; no inflation is considered;
- pre-taxation rates are of concern (neither taxes nor depreciation are taken into account);
- the real discount rate i_r is 8%.

The market feasibility or competitiveness of the CDU plant is analysed through sensitivity analyses of selected costs and prices, with the aim of determining the variables with the most influence and the conditions under which the NPV of the CDU plant becomes positive. First, univariate sensitivity analyses and second, bivariate sensitivity analyses are performed.

Market perspective

This analysis aims at evaluating (giving ranges of magnitude) (i) the future demand of the product synthesised by CO_2, considering current and possible new uses; (ii) the captured CO_2 required as feedstock for the CDU process to supply the assumed demand, and (iii) the overall CO_2 not-emitted because the product demand is supplied by the CDU process instead of the conventional one. Different penetration pathways are defined up to year 2030. These are assumed for the European market, and take into account the:

- provision of product demand increase by 2018, based on market growth of current applications;
- replacement of product imports in Europe, by year 2018; and
- provision of product demand due to emerging uses, in 2030, in the transport sector.

Note that the forecast of product demand and imports are based on current market predictions, that do not provide estimates beyond 2018. In the current paper we assume that, due to the emerging nature of CDU, it is not realistic to assume that the yearly increase, up to 2030, of the product demand and/or imports will be completely provided by the CDU process. Therefore, we have considered a maximum of five years (as an optimistic point of view), and a minimum of one year (as a pessimistic point of view), of product demand increase provided by the CDU process. The competition with other new, efficient and renewable synthesis processes (as biomass routes, for instance, to produce H_2), market saturation risk and the analysis of the prices evolution, are outside the scope of this section. Therefore, we assume the simplest market case: the CDU process replaces conventional FA, at current price, even in the newest penetration pathways.

Formic acid evaluation

Conventional production of formic acid

Formic acid can be produced via four different chemical processes: (i) methyl formate hydrolysis, (ii) oxidation of hydrocarbons, (iii) hydrolysis of formamide, and (iv) preparation of free FA from formates. In Europe, the methyl formate hydrolysis is the most common route [10]. The hydrolysis of methyl formate is based on a two-stage process, according to Eq. (7) and Eq. (8):

$$CO + CH_3OH \rightarrow HCOOCH_3 \tag{7}$$

$$HCOOCH_3 + H_2O \leftrightarrow CH_3OH + HCOOH \tag{8}$$

In the first reaction, about 95% of the carbon monoxide and 30% of the MeOH are converted. In the second reaction, the methyl formate is hydrolysed to form FA and MeOH,

which is recycled. In order to shift the equilibrium towards FA, excess of one of the reactants is needed. This leads to higher conversions, but also causes a diluted final product. Therefore, FA needs to be separated from the excess of reactant [10]. The two main FA companies in Europe have two different licensed processes, with identical first stage, but with different strategies in the second one. In the Kemira-Leonard process, the excess of methyl formate is considered and FA is dehydrated by distillation, usually in two columns, reaching maximum concentrations of 98 wt % [10]. In the BASF process, excess of water is used, and the separation is done via liquid − liquid extraction with a secondary amide and the extract is separated via distillation [13,10]. During the production of FA from hydrolysis of methyl formate, CO_2 emissions derive from steam and synthesis gas productions. The syngas needed to obtain the CO that reacts with MeOH, may come from steam reforming of light ends, as natural gas, or from partial oxidation of fossil feedstocks or gasification of coal [62,63]. The major energy consumption step in FA synthesis is syngas production, followed by steam needs. The consumption of electricity is the lowest. The production in conventional FA plants may range from 100 to 20 ktFA/yr [10]. The new plant that is currently built in Louisiana (US) by BASF, due to cheap shale gas availability, has a production of 50 ktFA/yr [64].

Synthesis of formic acid using captured CO_2

Chemical catalysis has been selected instead of the electrochemical route taking into account that, in general, chemical catalysis has been performed for more years. The process considered for the production of FA from captured CO_2 is based on a homogeneous catalysis and the layout follows the process described in the patent from Schaub et al. [21], specifically, in Fig. 2 from the mentioned patent. To the best of our knowledge, this is the most detailed source found in public bibliography. It is assumed that the plant, at full market scale, works under the same conditions as the ones reported for the laboratory tests from Ref. [21]. The efficiencies, as calculated from the values stated in the patent, have been used to calibrate and validate the CHEMCAD model. The selected values to perform our process model belong to examples A-12, B-3, D-1a and D-1b. The selected scale for modelling is lower than the average scale for the conventional FA synthesis plant, taking into account also the existence of smaller electrochemical plants, as summarised in the previous section.

The synthesis process can be divided into five sections: (i) compression stage, (ii) reaction stage, (iii) liquid—liquid separation stage for catalyst recovery, (iv) stripping stage for MeOH recovery, and finally, (v) reactive distillation stage for the formation and purification of the FA product. The plant is designed to produce 1500 kg/h (12 kt/yr) of FA at a purity of 85 wt % diluted in MeOH. Therefore, 1260 kg/h of CO_2 and 90 kg/h of H_2 are required as feed. In the reactor, the two main streams react in the presence of two catalysts (ruthenium- and phosphino-based catalysts), a tertiary amine, and a polar solvent (made by a mixture of MeOH and water); all of them composing the group of consumables, to form a FA-amine adduct, which has to be thermally separated to provide FA in the last distillation step. The two catalysts and the tertiary amine have been introduced into the software based on the information from Sigma−Aldrich and ChemSpider websites [65−67]. The properties of the amine and the adduct (a combination of one mole of FA + one mole of amine) have been estimated in CHEMCAD with the Elliot group contribution method [68].
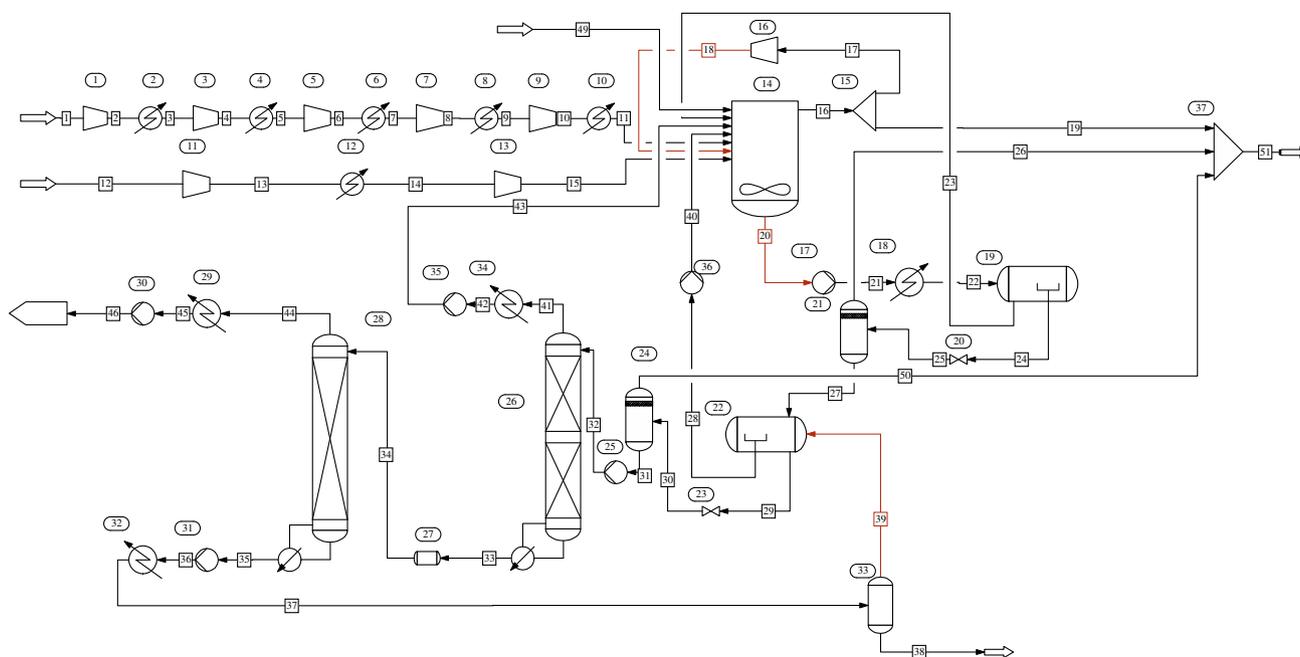

Fig. 2 − Process flow diagram for the synthesis of FA from CO_2 and H_2 from electrolysis.

The process is modelled in CHEMCAD 7 using the Predictive Soave-Redlich-Kwong (PSRK) method for equilibrium and property calculation. The PSRK subgroup parameters have been taken from the UNIFAC consortium parameter set distributed in 2015 [69]. Due to uncertainties in the thermodynamic model at the pressures of the process (up to 105 bar), conversion and consumption figures have been estimated, in addition, from the patent [21]. Fig. 2 shows the process flow diagram of the simulated process, and the different stages are explained in the following lines.

Compression stage (Units 1−13)
As explained in the introduction, captured CO_2 may come from different sources. It is assumed that the captured CO_2 is available at ambient conditions, as a worst case scenario (i.e. the CDU plant takes care of all the stream compression). Therefore, the CO_2 feed stream coming at atmospheric pressure and ambient temperature (stream 1), is compressed in a five-stage compression system up to 105 bar (units 1, 3, 5, 7, 9). It is cooled down to 25 °C in the intermediate cooling stages (units 2, 4, 6, 8) and to 30 °C in the after cooler (unit 10), that is condensing the CO_2 stream going to the reactor. The compressors are assumed to operate at an isentropic efficiency of 75% which leads to an electricity consumption of 130 kW. The H_2 feed stream enters the process at 30 bar and ambient temperature (stream 12), coming from the electrolyser. It is compressed in two steps, up to 105 bar, consuming 35 kW of electricity (units 11 and 13, with intermediate cooling, unit 12). In the electrolyser, a stream of 900 kg/h of water is needed. The electrolyser consumes 5.7 MW of electricity, and produces the required H_2 and 720 kg/h of oxygen as by-product. It is assumed that the oxygen is made available to the market, without any further stream conditioning.

Reaction stage (Units 14−16)
The reactor size has been assumed proportional to the batch reactor considered in the reported laboratory tests, scaled-up based on the inlet CO_2 flow rate; the resulting size is about 18.5 m^3. In the reactor vessel (unit 14), the liquid reaction of CO_2 and H_2 with the amine to form the FA-amine adduct, takes place under the presence of a ruthenium- and phosphino-based catalyst. The simplified reaction is expressed as:

$$CO_2 + H_2 + C_{18}H_{39}N \leftrightarrow C_{18}H_{39}N - HCOOH \qquad (9)$$
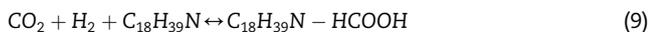
The reactor is designed to reach a conversion of 19% of the incoming H_2. The unconverted H_2 leaves the reactor in the gas phase, together with some unsolved CO_2. The temperature of the reactor is fixed at 93 °C. Even though the reaction is exothermal, a small amount of steam is required to maintain the temperature at 93 °C (around 300 kW at 110 °C). The gas leaving the reactor is recycled back (stream 18) to the inlet with a compressor (unit 16), while a small gas percentage is purged to avoid the accumulation of unreacted (reactive and inert) components (stream 19; splitting fraction 1% in mass basis). The recycle rate is highly dependent on the reactor temperature and the amount of CO_2 solved in the liquid phase. This liquid phase (stream 20) has two well differentiated parts: a heavy phase, enriched with the adduct and the polar solvent, and a light phase, enriched with the tertiary amine (that

is not combined to form the adduct) and the homogeneous catalyst. Free amine is present in both phases. See a diagram of this two phase liquid in Appendix B, Fig. B. 8. The partition coefficients have been estimated based on data from the patent [21], example A-12.

Catalyst recovery (Units 17−22)
After cooling down (unit 18) the reactor liquid product, the amine and catalyst can be recycled back to the reactor after the separation of the light phase in a decanter (unit 19). The pressure of the reactor liquid product is increased up to 130 bar (unit 17) in order to avoid a flashing of CO_2 in the decanter (to ease the downstream liquid−liquid separation), which can thus be operated at a separation efficiency of 85%: this means that 15% of the light phase remains in the heavy phase. This separation factor is based on the operation ranges described in the patent [21], example B-3.

As the catalyst is very expensive (see Appendix C) and to recover as maximum as possible, a second decanter is placed downstream (unit 22). This is operated at 70 bar, after a separation of flashing gases in a flash vessel (unit 21). In order to increase the catalyst recovery, the amount of amine is increased in unit 22 by adding the recycled amine stream from the purification stage (stream 39). In the model, a complete recovery of the catalyst is assumed in order to simplify the recycle calculations. As for costs purposes, it has been assumed that the catalyst is renewed once per year (see Section Results and discussion).

Methanol recovery (Units 23−26, 33 and 34)
Methanol is recovered in a stripping column working at 3 bar (unit 26). Before feeding stream 29 to the column, light gases are separated at atmospheric pressure in a flash vessel (unit 24). This keeps the temperature in the condenser (unit 34) above the cooling water temperature.

The purity of the bottom product from the stripping column (stream 33), is adjusted in order to fit the desired product purity of FA, approximately 85 wt % (stream 43). The top product, which contains MeOH, water and dissolved CO_2, is condensed and recycled back to the reactor (stream 32). The results from this step are checked with the values reported in Ref. [21], example D-1a. In Appendix B, Fig. B.9 shows the boiling point − dew point temperature curve for the binary mixture of MeOH and amine of the separation occurring in the stripping column (unit 26). For costs purposes, it has been assumed that the MeOH-based solvent is renewed once every ten years (see Section Results and discussion).

Formic acid formation and purification (Units 27−33)
By reducing the pressure to 250 mbar and increasing the temperature to 180 °C, the dissociation of the adduct to FA and amine is initiated. This happens in a reactive distillation column where, additionally, the separation of the amine from the FA product is also taking place. For modelling purposes, the reaction and the separation happen in two separated unit operations. In an adiabatic reactor (unit 27), the adduct is decomposed into FA and amine, as follows:

$$C_{18}H_{39}N - HCOOH \leftrightarrow C_{18}H_{39}N + HCOOH \qquad (10)$$

The endothermal reaction leads to a temperature reduction from 175 °C (in stream 33) to 88 °C (in stream 34). This heat is added in the column (unit 28) in order to reach the bottom temperature of 180 °C, since this is where the reaction actually takes place.

The separation of FA from the amine (in unit 28) is complex, as the mixture of FA, amine and MeOH may form two liquid phases. In Appendix B, Fig. B.10 shows the conditions under which the decomposition of the adduct occurs. At the conditions selected in unit 28, the decomposition into two liquids inside the column is avoided. The feeding stream (stream 34) has a FA concentration of 11%, with 1% of MeOH, and 88% of amine in mass basis. It forms two liquid phases. However, as most of the FA flashes at the top of the column, the liquid composition on the first tray is already outside the 3-phase region, with a composition of 3% FA, 0.5% MeOH and 96.5% amine, in mass basis. The column (unit 28) is modelled with four equilibrium stages. This is enough, as the separation of FA and amine is relatively simple due to the large difference in vapour pressures, as shown in Appendix B, Fig. B.11. We assume that the operation of the real column may be more difficult, as the dissociation of FA and amine takes place at the bottom of the column, where most probably two liquid phase would happen. However, this effect is not considered in the current model because the reaction (unit 27) was separated from the separation step (unit 28).

The amine is recycled from the bottom of the column (stream 35) to the secondary decanter (unit 22) to increase the catalyst recovery. For modelling simplification, the remaining fraction of FA (0.3% in mole basis) in stream 37 is separated from the amine stream in unit 33 (which does not represent a real physical unit operation). Different purge streams result from the modelled flowsheet: stream 38 (as a result of the separation in unit 33), stream 19 (as described in the reaction stage section), stream 26 (as a result from the flash unit 21, explained in the catalyst recovery unit) and stream 50 (as the gas phase released in the flash unit 24, explained in the MeOH recovery unit). The amine stream is not explicitly purged in the model. For costs purposes, it has been assumed that the amine is renewed once every ten years (see Section Results and discussion).

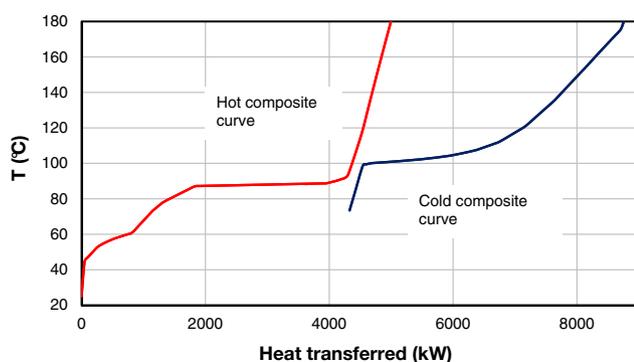Finally, the FA produced (stream 44), coming from the condenser of the column, is cooled down (unit 29) and sent to a product tank. The results from this step are checked with the values reported in Ref. [21], example D-1b.

Fig. 3 depicts the composite curves of the overall process. It is seen that heat integration can save up to 800 kW of external provision. The only heat sinks of the process are the reboilers of the two stripping columns, and thus integration would require hybrid reboilers. This option is not considered here, and therefore, all heating and cooling needs in the CDU plant are provided by external supplies of cooling water and steam (high pressure − HP and medium pressure − MP steam), which are assumed to be available at the gate of the plant.

Black-box units

There are two units which are evaluated but that are not modelled in CHEMCAD: the CO_2 purification unit and the electrolyser, as depicted in Fig. 1. The unit selected to clean up the CO_2 is a membrane. It is assumed that the use of electricity or steam of this purification unit is negligible in relation to the needs of the rest of the plant. It is also assumed that the unit can treat any type of inlet composition, under any conditions of pressure and temperature. The total purchase cost of the equipment is 434.6 €/m^2, and it is sized according to a ratio of 3.9 m^3/s, treated in 3335 m^2 of membrane [57]. The FCP are included in the costs of the plant estimation, as a percentage of the investment costs.

The device selected to produce hydrogen is an alkaline electrolyser (AE), as it is the most commercialised one to date [56]. A small scale electrolyser (0.6 MW) is considered for the CDU plant. It consumes 1.62 kWe/kWH$_2$ and the investment cost is 1980 €/kW [56]. A power law formula that takes into account economies of scale, with a scale factor of 0.5, is considered to calculate the cost of this equipment. The FCP are included in the costs of the plant estimate as a percentage of the investment costs. VCP are calculated according to its electricity consumption.

Results and discussion

KPIs evaluation

Table 1 summarises FA CDU plant technological, economic and environmental KPIs. For the consumption of catalysts, solvent and amine it is assumed that the catalysts are renewed once a year [70] and that solvent and amine are completely renewed once every 10 years. The amount of catalysts used in the reactor is 30 kg/yr for the ruthenium-based catalyst, and 15 kg/yr for the phosphino-based catalyst based on the reaction time and the turnover frequency of the catalyst, reported in Ref. [21]. Appendix C shows the prices considered for the estimation of operating costs. For the evaluation of indirect CO_2 emissions, the factors used are 0.508 tCO_2/MWh for electricity consumption [71], and 0.072 tCO_2/GJ of steam needed [72]. The steam needed results in HP and MP steam (taking into account saturated steam), with reboilers from units 26 and 28 as main consumers: 2 tMP_{steam}/tFA and almost 4 tHP_{steam}/tFA.

From the mass balance in Table 1, feed streams are H_2O to the electrolyser and CO_2. There is an amount of O_2

Fig. 3 − Composite curves of the FA synthesis process plotted for a minimum temperature difference of 20 K.

Table 1 – KPIs results for the FA CDU plant. * As resulted in the model and including CO_2, H_2, water, solvent and amine; however, for costs estimation, we have taken into account the assumptions referred along the text, regarding renewal periods and catalyst, solvent and amine consumptions.

Technological Metrics	
Mass balance (t/tFA)	
Inlet CO_2	0.834
Inlet H_2O	0.595
Make-ups*	0.266
Outlet FA	1
Outlet H_2O	0.060
Outlet O_2	0.477
Off-gases	0.158
Energy balance (MWh/tFA)	
Electricity consumption	4.054
Electricity consumption (w/o electrolyser)	0.296
Heating needs	2.783
Cooling needs	2.962
CO_2 convR (%)	81
CO_2 convP (%)	96
H_2 convR (%)	19
H_2 convP (%)	62
CO_2 used (tCO₂/tFA) (renewable electrolyser and steam)	0.668
Economic Metrics	
ISBL (M€)	6.7
CAPEX (M€)	16.2
VCP (M€/yr)	14.8
FCP (M€/yr)	3.5
GM (M€/yr)	7.7
BCR (−)	0.43
Environmental Metrics	
CO_2 not-emitted (tCO₂/tFA)	2
CO_2 change (%)	92

Table 2 – Variation of CO_2 used, combining zero emissions allocated to electricity and/or steam, and emissions derived from 0.508 tCO₂/MWh electricity [71], and 0.072 tCO₂/GJ steam [72].

	tCO₂/tFA
Indirect CO_2 emissions are allocated to steam and electricity needs of the electrolyser	−1.970
Indirect CO_2 emissions are only allocated to electricity needs of the electrolyser	−1.249
Indirect CO_2 emissions are only allocated to steam needs	−0.054
Indirect CO_2 emissions are zero	0.668

process generates more CO_2 emissions than the ones utilised as feedstock. From now on, the emissions related to the FA CDU process will consider zero emission sources for the electricity needed for electrolysis and for the generation of steam.

Fig. 4 depicts the breakdown of costs. Among the investment needed, in Fig. 4 (a), the electrolyser represents 43% of the total ISBL. It is followed by the contributions from the compression system and the separation processes. Fig. 4 (b) points out that consumables and utilities (electricity and steam) are the main contributors to the production costs. As shown in Table 1, the calculated BCR, at 0.43, underlines the need to compensate the high variable costs (production costs are more than twice the benefits obtained). The GM is 7.7 M€/yr, which means that revenues and by-product benefits are larger than raw materials cost.

(a) Total installed cost (ISBL) breakdown.

(b) Operating costs breakdown. FCP in grey bars, VCP in grey striped bars and FA and oxygen revenues in orange striped bars.

Fig. 4 – Estimated installed costs and operating costs for the FA CDU plant.
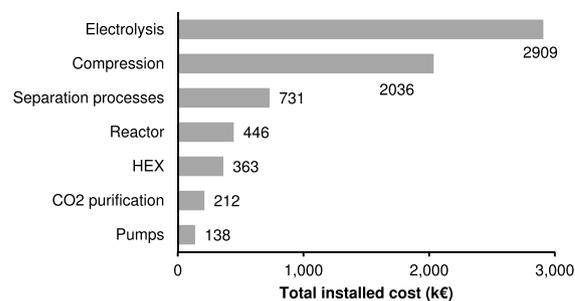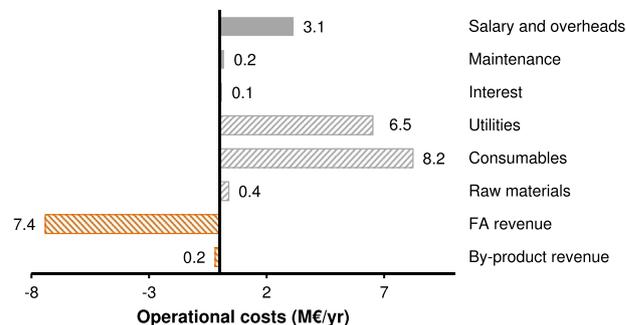
produced from the electrolysis process, sold as a by-product, a certain amount of unreacted water which is considered a by-product for disposal, and off-gases or purge gases resulting from the FA separation processes. The energy needs outlined in Table 1, indicate that the FA CDU plant requires electricity, cooling water and steam. The total electricity consumption for compression (CO_2, H_2 and recycled gas streams) and pumping, and the requirement of the electrolysis process is about 4 MWh/tFA. The cooling water needed is 252 t/tFA, while steam needs are 3.7 t/tFA for HP steam, and 2 t/tFA for MP steam. The reactor conversion is 19% for H_2 and 81% for CO_2; while the whole process converts 98% of inlet CO_2 and 63% of inlet H_2. From this is derived an amount of CO_2 used of 0.668 t/tFA, only if renewable steam and electrolysis are considered (as described in the methodology, the metric CO_2 used is employed as a design condition of the CDU process, and it has to be positive). The current work assumes as a simplifying hypothesis that electricity and steam coming from renewable sources, contributes with zero CO_2 emissions to the overall emissions balance. This hypothesis will be further discussed in Section Discussion. Table 2 summarises the value of the CO_2 used if steam and/or electricity do not come from renewable sources. Note that "zero emissions" sources are crucial to achieve an FA CDU process with net CO_2 emissions reduction. Otherwise, the

The final balance of CO_2 emissions is positive for the FA CDU plant if compared to the conventional plant, with electrolysis and steam using zero emissions sources (see the environmental metrics in Table 1). Note that the reference values for the conventional plant do not take into account renewable sources, but European averages for electricity and steam emissions [73,63]. This leads into an optimistic comparison for the CDU plant, towards the conventional plant. Table 3 compares the FA CDU plant and the methyl formate hydrolysis process to produce FA, including generation of CO. Whereas the CDU plant consumes less steam than the conventional plant and the final balance of CO_2 emissions shows a clear advantage for the CDU plant (mainly because of the use of zero emissions sources for electricity and steam production), the production costs are notably higher than for the conventional plant. This is mainly due to the contribution of consumables (mainly catalysts), the higher consumption of electricity due to the electrolyser needs, and steam, due to process heating needs. An emission change (reduction) of almost 92% exists when producing FA with a CDU process, corresponding to 2 tCO_2/tFA not emitted. The production of 12 ktFA/yr with a CDU plant saves almost 5 kt/yr of heavy fuel oil.

As main differences with the conventional FA synthesis configuration, (i) the electrolyser is the main responsible of electricity consumption, (ii) the expensive catalyst, solvent and amine, impact operating costs, and (ii) electricity for electrolysis and steam needs have to be supplied by zero emissions sources in order to have a positive CO_2 used. Overall, it is important to point out the uncertainty linked to the layout of the FA CDU process, and to the relatively new catalyst use, due to its current low TRL. This may lead to under or over estimations of the KPIs in the current analysis.

Sensitivity analysis

The NPV for the FA plant is evaluated in −91 M€, under the hypotheses outlined in Section Methodology. In order to know the situations in which the project could become profitable, different sensitivity analyses have been performed.

The selected variables: prices of FA, O_2 and CO_2, are widely varied in order to obtain a NPV equal to zero. Electricity price, HP steam price, ISBL and consumables contribution have upper bounds (current values or plus 10% in the case of consumables) and lower bounds (zero for electricity and steam prices, down to 12 and 45% of current values for consumables and ISBL) and are depicted in orange in Fig. 5. It can be seen that the most important influence on NPV comes from consumables contribution and FA price. These are followed by the price of electricity and ISBL. Contributions from O_2, steam and CO_2 prices seem to have less impact on the NPV. Table 4 summarises the values that make NPV equal to zero; electricity price, HP steam price, ISBL and consumables cannot reach alone a NPV equal to zero. Based on these results, different circumstances may result in the FA plant becoming profitable. For FA, the breakeven price is 2.5 times the reference price. However, the numbers in Table 4 depicts unrealistic prices for the tonne of O_2 and CO_2.

Taking into account the importance of the FA and electricity prices, Fig. 6 (a) summarises a bivariate sensitivity analysis, with the price of electricity as independent variable and the price of FA that make NPV equal to zero (at the given electricity price), as the dependent variable. Considering the reference price of FA, 650 €/t (Table 4), even at low electricity prices, the prices needed to make the plant profitable are far from market conditions. As outlined in Fig. 5, the price of consumables has an important bearing on the NPV. If this price is decreased by a factor of 6 (Fig. 6 (b)), the prices of FA that make NPV equal to zero, at lower electricity prices, are closer to the market reference value. A combination of favourable conditions will be thus needed for FA from CO_2 to become competitive. Particularly important is R & D, to achieving a decrease in catalysts costs.

Market perspective

The following market penetration possibilities assume that the FA CDU plant is fully commercial and available for implementation (in year 2015). The depicted penetration
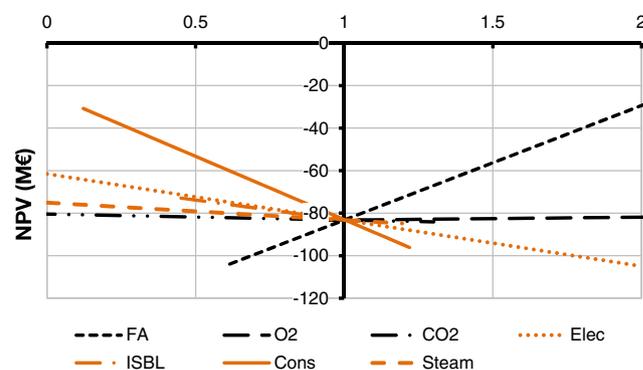

Table 3 – Main metrics comparison between the FA CDU plant and the conventional methyl formate hydrolysis process. The conventional pathway includes (i) CO synthesis and (ii) FA production [73,63]. The conventional production costs have been estimated assuming a 27% of benefits.

	CDU plant	Conventional plant
Electricity needs (MWh/tFA)	4.07	1.55
Steam needs (MJ/kg FA)	10.03	19.25
Cooling water needs (tH_2O/tFA)	251.53	375.50
Process water needs (tH_2O/tFA)	0.59	0.60
Production costs (€/tFA)	1524	475
Total CO_2 emissions (tCO_2/tFA)	0.166	2.18
Inlet CO_2 (tCO_2/tFA)	0.834	
Heavy fuel oil savings (t/yr)	4863	

Fig. 5 – **NPV variation with prices of FA, oxygen, CO_2, electricity, steam and consumables and ISBL. These are represented by relative increments/decrements towards the original values considered.**

Table 4 – Breakeven prices for NPV = 0.

	Breakeven price (€/t)	Reference price (€/t)
FA	1656	650
O_2	3322	54
CO_2	−1100	38
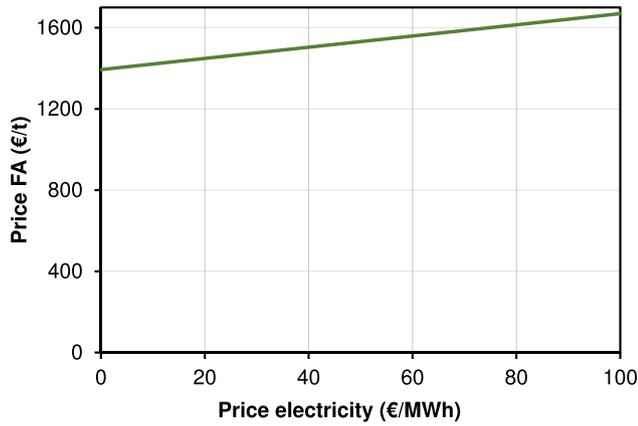
(a)
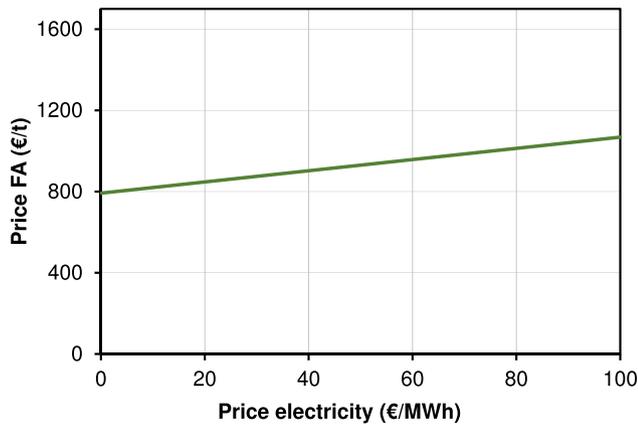
(b)

Fig. 6 – Prices of FA that make NPV equal to zero, for a range of electricity prices (x axis) (a) taking into account the FA plant as studied, and (b) considering that the price of consumables is decreased by a factor of 6.

pathways of FA (PF) are inspired by current legislation in Europe and state-of-the-art research. These are defined to complement each other. As a hydrogen carrier, once FA is converted back to H_2, the CO_2 spent to synthesise the molecule of FA is released. This CO_2 can be used again to synthesise FA with new inlet H_2, in the so-called circular approach. The current paper does not consider this circular approach, and as a result, when calculating the PFs as hydrogen carrier, a "net" CO_2 demand is assumed. Therefore, the following results remain optimistic on the side of CO_2 demand. Seven PFs have been identified:

- yearly increase of FA demand (PF1);
- use as hydrogen carrier, in gas and fuel cell vehicles (FCV) (PF2-3);
- use as hydrogen carrier, to supply part of an assumed growing demand of MeOH (PF4);
- use as hydrogen carrier, to cover the increase of merchant H_2 demand (PF5);
- stationary applications, in fuel cells (PF6-7).

The assumptions taken in each PF are described in Appendix D, according to a conservative and an optimistic point of view. In order to estimate PF1, the predictions of Section Formic acid: overview and future prospects for the FA market are used. For the stationary sector (PF6-7), the information is from the EC Roadmap 2050 [74]. In order to evaluate the potential of H_2 as transport fuel, the in-house Powertrain Technology Transition Market Agent Model (PTT-MAM) is used to depict the 2030 panorama [75,76]. This is a comprehensive system dynamics model of the EU-28 light duty vehicle sector which accounts for interactions and feedback between manufacturers, infrastructure providers, authorities and users. The model includes a realistic share of fuels (i.e. gasoline, diesel, electricity, liquefied petroleum gas, compressed natural gas (CNG), hydrogen, biodiesel and bioethanol) for passenger and light commercial fleet and different powertrains according to the Council Regulation (EU) number 630/2012 amending Regulation (EC) No 692/2008, Directive 2009/30/EC and Directive 2014/94/EU, and takes into account the EC Clean Power for Transport package from the EC Roadmap 2050 [74]. Input data are obtained from numerous sources and expert judgements, mainly Eurostat and the EU Reference Scenario 2013 TRACCS.

Taking into account representative current policies and techno-economic trends, BASE scenario is obtained, as depicted in Fig. 7, left column. This scenario, for passenger and light commercial vehicles by 2030, highlights a dominance of gasoline and diesel vehicles. This is not unexpected, as turnover of stock is limited by the reactively long lifespan
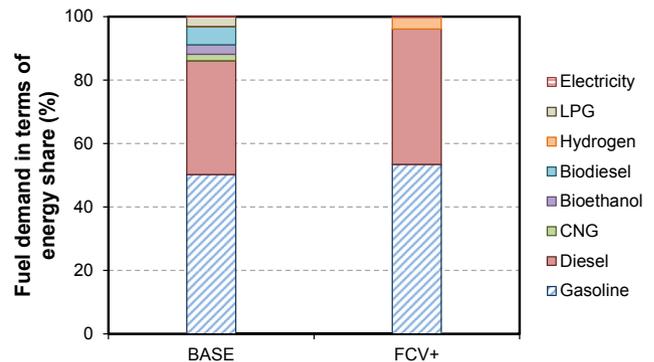

Fig. 7 – Fuel's share for private and light commercial vehicles by 2030 in Europe for the two considered scenarios, BASE and FCV+, in the PTT-MAM model. Hybrid vehicles are also included.

of vehicles, and the alternative powertrain market is still in its infancy. In order to have a contribution from FCV to motivate FA penetration, an ad-hoc scenario has been performed. The scenario FCV+ (Fig. 7, right column) motivates FCV deriving from the BASE scenario premises. In order to achieve this, the scenario is highly optimistic, including early introduction of FCV models, high infrastructure and FCV purchase subsidies with no electric vehicles subsidies, and the removal of alternative fuel options for conventional powertrains to prevent competition. See Appendix D for further detail.

Table 5 summarises the total amount of FA needed, the corresponding tonnes of CO_2 required as inlet raw materials and the amount of CO_2 not-emitted. FA has a current demand of 0.62 Mt/yr. According to the results obtained for year 2030, the overall demand of FA may be in the range of 5–24 Mt/yr (embracing both scenarios and points of view). To satisfy this demand, CO_2 provision is in the range of 4–21 Mt/yr. The amount of CO_2 not-emitted is between 10 and 47 Mt/yr. These numbers underline that the proposed PFs are overall optimistic, if compared with the current demand of FA worldwide, and that it would depend on the explicit stimulation of the hydrogen economy.

Discussion

FA is a candidate to be used as a hydrogen carrier, thus hydrogen demand could lead to a notable increase in the demand for FA. The modelled process is composed by a catalytic reactor that combines H_2 and CO_2, and the following product separation steps; liquid–liquid separation and two distillation columns. The technology is at TRL 3–5. The assumed plant scale used is 12 ktFA/yr. The electrolyser and the steam generator have to be powered by renewables to have a net amount of CO_2 used, as a design condition in this work. The simulated process is highly efficient in terms of CO_2 conversion, and less efficient for H_2 conversion. It entails less CO_2 emissions when compared to the benchmark conventional process considered (i.e. methyl formate hydrolysis with CO synthesis using heavy fuel oil), about 92% of CO_2 change (reduction), where the use of renewables have an important role. Operating costs are higher than benefits, with the variable costs of consumables (mainly catalysts) and electricity, followed by steam, as main contributors. In order to have a positive NPV, the sensitivity of the NPV to variations of the prices of FA, O_2, CO_2, electricity, steam, consumables and to

the variation of the ISBL have been evaluated. The most important variables are consumables (particularly, the specialised catalysts), FA and electricity prices. Prices of FA higher than 1700 €/t (reference price, 650 €/t), or an income from CO_2 higher than 1100 €/t, would allow positive NPVs. The bivariate analysis demonstrates that the price of electricity by itself, cannot make the CDU plant competitive. A lower price of consumables is crucial, and this may be only achieved by sustained R & D. FA has a current global production of 0.62 Mt/yr (2012). The estimate of different PFs, as in the fuel cells market for stationary applications and its use as a hydrogen carrier in the transportation sector (in FCV and combined with CNG) results in a total European demand for FA of a minimum of 5 Mt/yr of FA, entailing a demand of 4 $MtCO_2$/yr, or a maximum of 24 Mt/yr of FA, involving 21 $MtCO_2$/yr. This means that there are 10–47 $MtCO_2$/yr that would not be emitted because of the hypothetical use of the CDU process, instead of the conventional one. This would also imply savings in heavy fuel oil consumption: a total amount of 2–10 Mt/yr.

As order of magnitude comparisons, a project like ROAD (in The Netherlands) aims at storing 1.1 $MtCO_2$/yr, and the newer White Rose (in UK) has as objective to store 2 $MtCO_2$/yr. A conventional coal power plant of 750 MW of net power, emits about 6 $MtCO_2$/yr [77]. Urea is the most important product synthesised from CO_2, using it as carbon carrier; about 112 $MtCO_2$/yr were used in 2011 as feedstock [78]. FA CDU process would demand 4–21 $MtCO_2$/yr in Europe. Note that 1 to 4 coal plants (with partial capture) would supply the corresponding CO_2 for FA synthesis.

The purpose of this paper was to provide an overview and rough values for the FA CDU process. The main questions to answer were about technological feasibility, economic viability and possible environmental impact. As for the technological feasibility, the modelling work has demonstrated its feasibility, however, with some uncertainty, due to the low TRL of the process and the low publicly available information. The consumption of electricity and steam is important in the process (note that electrolysis and steam are also dominant in the electrochemical synthesis of FA [79]). In the current work we proposed as a design condition the positive value of the metric CO_2 used; this made integrating renewables in the FA CDU process. Regarding the economic viability, a price of FA 2.5 times the current market price, would allow revenues for such an investment. Moreover, this price increase would not be that important if catalysts are available at lower price, and if electricity is also available at a lower price. CO_2 emissions available for CDU processes are not limited to power plant flue gases. A variety of synergies (as for captured CO_2 "management") may be envisioned, yielding win-to-win situations, not only for power plants or industrial plants, but also for renewable plants that would like to store electricity as part of their strategy. Under the depicted conditions, the use of the FA CDU plant instead of the conventional plant, emits less CO_2 and saves heavy fuel oil.

Overall, this study remains an optimistic evaluation of the situation, since different simplifications were taken into account:

Table 5 – Main values calculated for all PFs, BASE and FCV+ scenario, and conservative and optimistic points of view in Europe.

Points of view for BASE/ FCV+ scenarios	FA demand (Mt/yr)	CO_2 needed (Mt/yr)	CO_2 not-emitted (Mt/yr)	Heavy fuel oil savings (Mt/yr)
Conservative	5/8	4/7	10/16	2/3
Optimistic	14/24	13/21	29/47	6/10

- The emissions allocated to renewable sources are zero. These are different from zero, if taking into account a complete life cycle approach.
- The study is a gate-to-gate study. For a holistic and accurate view, an LCA has to be taken into account, to consider upstream (for instance, environmental impact allocation to the captured CO_2, becoming feedstock CO_2), and downstream echelons (as the CO_2 storage duration, and the specific circular approach for FA as an hydrogen carrier) [80,81]. Note that different CDU products, will have different environmental impact [82].
- Market simplification. The CO_2-based FA will have to compete in the market with already existing products, synthesised from fossil fuel at lower production cost. The introduction of CO_2-based FA, assuming that this is completely equivalent to the one that has been synthesised through the conventional process, could saturate the market, and could increase the price of CO_2 as product. Moreover, for the calculation of CO_2 not-emitted, only one conventional process has been considered, as benchmark. As H_2 demand increases, also alternative processes to synthesise it will proliferate and could be also contrasted with the CDU process.

These points will be addressed in future works.

Conclusions

Based on the FA case study, it can be concluded that CDU has potential to be part of the CO_2 abatement options of the future, entailing less fossil fuel consumption and a way of electricity storage. Overall, carbon utilisation processes can provide a net contribution to CO_2 emissions reduction, at plant level (i.e. other echelons of the supply chain are not taken into account). There is a need of R & D for electrolysers to become more mature (and thus, less expensive), and there is a need to link CDU with renewable energies. In general, CO_2 utilisation processes consuming H_2 as raw material will be favoured from specific renewable/energy storage advancements. Under the hypotheses of this study, currently, the FA CDU plant is technically feasible but it is not economically sustainable. Different favourable conditions may help the FA CDU plant to reach its profitability, and a combination of them is desirable: lower electricity and steam prices and higher prices for the tonne of FA are needed. R & D is also crucial to decrease the operating costs, especially linked to the use of catalysts.

Acknowledgements

Acronyms

AE	alkaline electrolyser
BCR	benefit/cost ratio
CAPEX	capital expenditure
CCS	carbon capture and storage
CCU	carbon capture and utilisation
CDU	carbon dioxide utilisation
CEPCI	Chemical Engineering Plant Cost Index
CNG	compressed natural gas
DNV	Det Norske Veritas
DFAFC	direct formic acid fuel cell
EOR	enhanced oil recovery
EU	European Union
FA	formic acid
FCP	fixed costs of production
FCV	fuel cell vehicle
GM	gross margin
HP	high pressure (steam)
ICE	internal combustion engine
i_r	interest rate
ISBL	inside battery limits investment
KPI	key performance indicator
MeOH	methanol
MP	medium pressure (steam)
NPV	net present value
OSBL	offsite battery limits investment
P	process
PEM	proton exchange membrane electrolysis
PEMFC	proton exchange membrane fuel cell
PF	penetration pathway for FA market analysis
PTT-MAM	Powertrain Technology Transition Market Agent Model
R	reactor
REV	revenues
RM	raw materials
SET	Strategic Energy Technologies
SOEC	solid oxide electrolyser cell (SOEC)
t	tonne (metric tonne)
TFCC	total fixed capital cost
TRL	technology readiness level
VCP	variable costs of production
wt	weight
yr	year

Appendix A. Economic evaluation parameters

Table A.7 – Costs breakdown and assumed parameters, taking into account a process with a low TRL [58].		
Total fixed capital cost (TFCC)	ISBL capital costs	Factorial methodology
	OSBL capital costs	35% of ISBL
	Engineering costs	30% of ISBL and OSBL
	Contingency	30% of ISBL and OSBL
	Working capital	20% of ISBL and OSBL
CAPEX	TFCC + Working capital	
Variable costs of production (VCP)	Raw materials costs	Market prices (Appendix C) and model results
	By-products disposal	
	Catalyst consumption [21]	
	Utilities consumption	
Fixed costs of production (FCP)	Salaries and overheads	4 operators [70], 3 shift positions
		78 000 €/yr [83]
		Supervision is 25% of operating labour
		Overhead is 45% of labour and supervision
		Plant overhead is 65% of labour and maintenance
		Tax and insurance are 2% of TFCC
	Maintenance	3% of ISBL
	Interest	6% of working capital
	Royalties	None

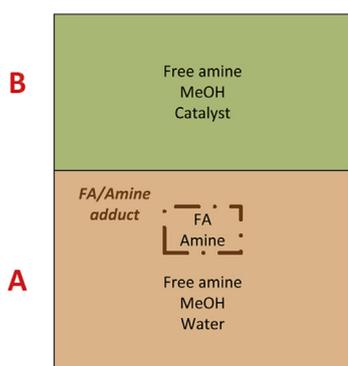## Appendix B. Further modelling information

Fig. B.8 – Diagram representing the product from the hydrogenation reactor: a two phase liquid, with a lower phase that is heavier than the upper phase.
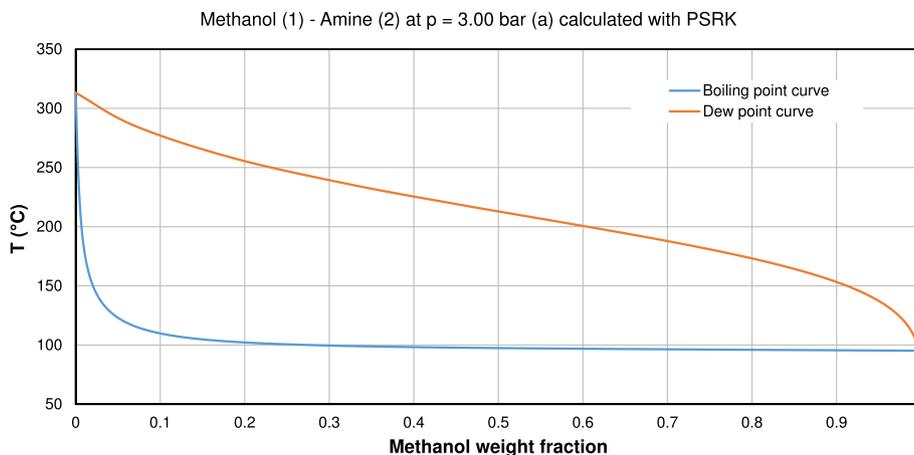

Fig. B.9 – Phase diagram for the separation of methanol and amine in column 26.
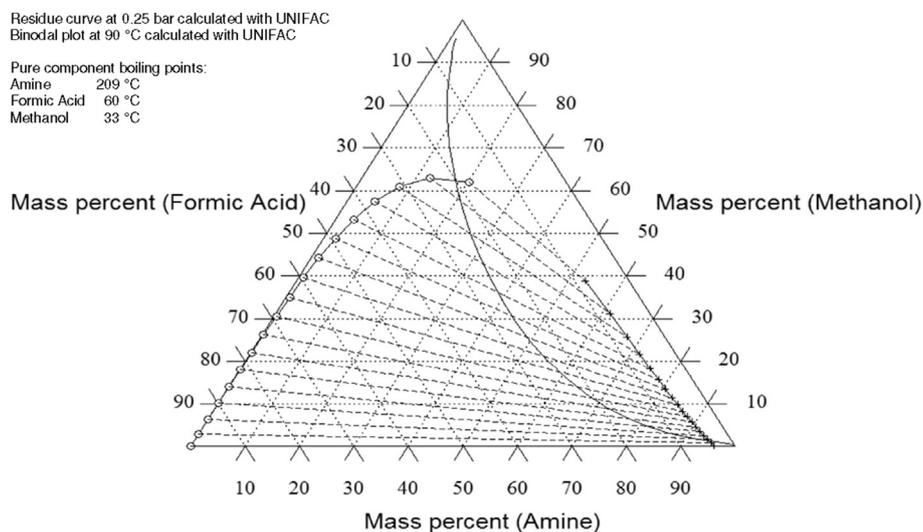
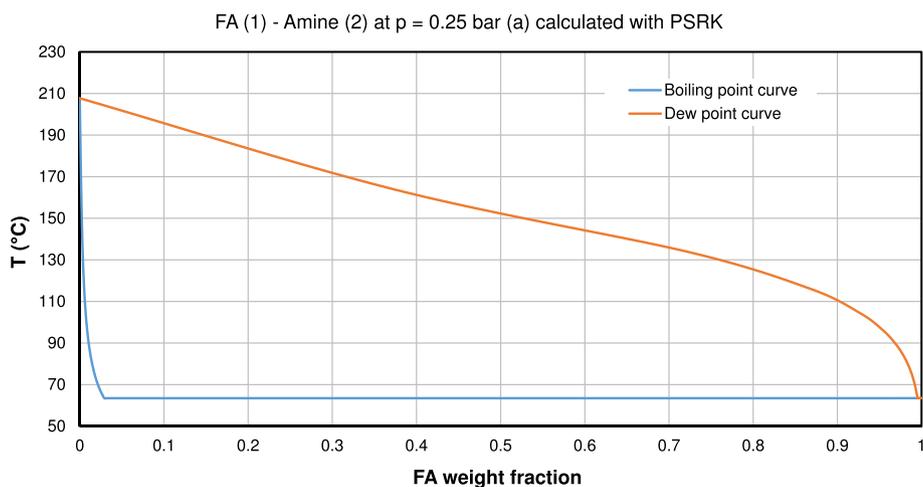Fig. B.10 — Residue curve plot with binodal plot separation of methanol and FA from the amine in column 28.

Fig. B.11 — Phase diagram for the separation of FA and amine in column 28.

Appendix C. Production costs and revenues — prices

Table C.8 — Prices, in €2014.	
Item	Price
CO_2 captured	38.4 €/tCO_2 [84]
Water	1 €/tH_2O [58,61]
Cooling water	0.025 €/tH_2O [58,61]
HP steam	25.12 €/tH_2O [58,61]
MP steam	22.83 €/tH_2O [58,61]
Electricity	95.09 €/MWh [61,38]
Oxygen	54.2 €/tO_2 [85]
Formic acid	650 €/tFA [11,86]
Ruthenium-based catalyst	210 000 €/kg$_{cat}$ [87]
Phosphino-based catalyst	84 900 €/kg$_{cat}$ [88]
Methanol	350 €/tMeOH [89]
Amine	724 €/kg [90]

Appendix D. Market analysis and penetration pathways

Table D.9 – Description of each penetration pathway for FA synthesis from CO_2. Conservative and realistic points of view differ in the percentages of energy demand replaced by the product synthesised by CO_2, and in the years of accumulated growing demand. PF2 considers the mixture H_2/CNG proposed in Ref. [91]. PF5 considers the market bounds for MeOH depicted in Ref. [92].

Penetration pathways for FA for year 2030, except for PF1 and PF5	Conservative point of view	Optimistic point of view
PF1. Current demand (2013); the yearly increase of demand in Europe is provided by CDU-plants, up to 2018.	1 year	5 years
PF2. Passenger and light commercial vehicles; H_2 (FA as H_2 carrier) is blended with CNG in an internal combustion engine (ICE). As a CNG flex-fuel vehicle, 20 % H_2 and 80 % CNG in mass basis is allowed. The percentages in the different points of view correspond to the provision of H_2 in the replacement of the energy needs of the CNG fleet, predicted by PTT-MAM.	10 %	30 %
PF3. Passenger and light commercial vehicles; H_2 (FA as H_2 carrier) is used in FCV. The percentages correspond to the provision of H_2 in the FCV fleet predicted by PTT-MAM.	10 %	30 %
PF4. Synthesis of MeOH from captured CO_2; FA as H_2 carrier is used to satisfy the growing demand of MeOH.	0.5 MtMeOH/yr	1 MtMeOH/yr
PF5. Current demand (2013) of merchant H_2; FA as H_2 carrier is used to satisfy the growing demand of merchant H_2.	1 year	5 years
PF6. Fuel cells for electricity supply in the residential sector; FA is used as H_2 carrier in proton exchange membrane fuel cells (PEMFC). The percentages in the different points of view correspond to the contribution of FA in the PEMFC share.	10 %	30 %
PF7. Fuel cells for electricity supply in the industrial sector; FA is used as H_2 carrier in PEMFC. The percentages in the different points of view correspond to the contribution of FA in the PEMFC share.	10 %	30 %
PF8. Micro fuel cells for portable devices; FA is used as hydrogen carrier.	Not realistic for 2030	
PF9. H_2 as combustible in airplanes; replacing kerosene. FA is used as hydrogen carrier.	Not realistic for 2030	

Table D.10 – Hypotheses and parameters assumed for each penetration pathway for FA, based in Europe. For PF5, H_2 production is estimated in Ref. [93]. Penetration percentages of fuel cells in stationary markets are from Ref. [74]. The conversion of the fuel cell for PF6 and PF7 is from Ref. [94].

Penetration pathway for FA	Hypotheses and parameters
PF1	The demand of FA is growing at 2.6 % per year.
PF2	The conversion factor results in 25.6 kg FA/kg H_2, assuming a molar conversion efficiency of 90 % in the process FA to H_2. The mixture H_2-CNG does not modify the efficiency of the gas engine.
PF3	The conversion factor results in 25.6 kg FA/kg H_2, assuming a conversion efficiency of 95 % in the process FA to H_2.
PF4	According to our modelling work, 0.2 tH_2/tMeOH are needed. The conversion factor results in 25.6 kg FA/kg H_2, assuming a conversion efficiency of 95 % in the process FA to H_2.
PF5	The overall global demand of H_2 is growing at an average of 5.5 % per year. It is extrapolated to the specific demand of merchant H_2, which corresponds to 9 % of the total H_2 demand. It is assumed that the EU demand is equal to its production, of 92 billion m^3. The conversion factor results in 25.6 kg FA/kg H_2, assuming a conversion efficiency of 95 % in the process FA to H_2.
PF6	The penetration of fuel cells is of 0.018 % of the total electricity needs in the residential sector. The contribution of PEMFC to the total fuel cell penetration is 90 %. The efficiency of the PEMFC, as conversion of the inlet H_2 into electricity, is 45 %. The conversion factor results in 25.6 kg FA/kg H_2, assuming a conversion efficiency of 95 % in the process FA to H_2.
PF7	The penetration of fuel cells is of 0.013 % of the total electricity needs in the industrial sector. The contribution of PEMFC to the total fuel cell penetration is 90 %. The efficiency of the PEMFC, as conversion of the inlet H_2 into electricity, is 45 %. The conversion factor results in 25.6 kg FA/kg H_2, assuming a conversion efficiency of 95 % in the process FA to H_2.

REFERENCES

[1] Aresta M, Dibenedetto A, Angelini A. The changing paradigm in CO_2 utilization. J CO_2 Util 2013;3—4:65—73.

[2] Styring P, Quadrelli E, Armstrong K. Carbon dioxide utilisation: closing the carbon cycle. 1st ed. Elsevier; 2015.

[3] Bruhn T, Naims H, Olfe-Krautlein B. Separating the debate on CO_2 utilisation from carbon capture and storage. Environ Sci Policy 2016;60:38—43.

[4] von der Assen N, Voll P, Peters M, Bardow A. Life cycle assessment of CO_2 capture and utilisation: a tutorial review. Chem Soc Rev 2014;43:7982—94.

[5] European Commission. Energy union package — a framework strategy for a resilient energy union with a forward-looking climate change policy, Communication. Brussels: European Commission (EC); February 2015. available at: http://ec. europa.eu/priorities/energy-union/docs/energyunion_en.pdf [last accessed September 2015].

[6] European Commission. Towards an integrated strategic energy technology (SET) plan: Accelerating the European energy system transformation, Communication. European Commission (EC); 2015. available at: https://ec.europa.eu/ energy/sites/ener/files/documents/1_EN_ACT_part1_v8_0. pdf [last accessed November 2015].

[7] European Commission. Towards an integrated strategic energy technology (SET) plan: research and innovation challenges and needs of the EU energy system, Communication. European Commission (EC); 2013. available at: https://setis.ec.europa.eu/set-plan-process/ integrated-roadmap-and-action-plan [last accessed November 2015].

[8] ICIS Chemical Business. Kemira to expand Finnish formic acid capacity. Webpage summary, available at:. July 2006. http://www.icis.com/resources/news/2003/07/04/500868/ product-profile-formic-acid/ [last accessed November 2015].

[9] European Commission. European Commission Regulation (EC) No 1831/2003 of the European Parliament and the Council of 22nd September 2003 on additives for use in animal nutrition. Off J Eur Union 2003. L268 18.10.2003, http://eur-lex.europa.eu/legal-content/en/ALL/?uri=CELEX: 32003R1831.

[10] Reutemann W, Kieczka H. Formic acid. In: Ullmann's encyclopedia of industrial chemistry. 7th ed. Wiley-VCH; 2012.

[11] TranTech Consultants Inc. Chemical profile: formic acid. July 2014. Webpage summary, available at: http://chemplan.biz/ chemplan_demo/sample_reports/Formic_Acid_Profile.pdf [last accessed November 2015].

[12] Markets and Markets. Formic acid market by types (grades of 85%, 94%, 99% and others), by applications (agriculture, leather and textile, rubber, chemicals, pharmaceuticals and others) and by geography. Global trends, forecasts to 2019. May 2014. Webpage summary, available at: http://www. marketsandmarkets.com/Market-Reports/formic-acid-Market-69868960.html [last accessed November 2015].

[13] BASF. Tradition of ideas: formic acid. December 2012. Online news, available at: http://www.intermediates.basf.com/ chemicals/topstory/ideen_tradition [last accessed November 2015].

[14] Chemicals-Technology.com. BASF-YPC integrated petrochemical complex, Nanjing China. 2015. Online news, available at: http://www.chemicals-technology.com/ projects/basf/ [last accessed November 2015].

[15] ICIS Chemical Business. Product profile: formic acid. 2003. Online news, available at: http://www.icis.com/resources/ news/2003/07/04/500868/product-profile-formic-acid/ [last accessed November 2015].

[16] Kemira. Kemira Oyj sells ChemSolutions' formic acid business to Taminco Corporation, Stock exchange release. December 2013. available at: http://www.kemira.com/en/ newsroom/whats-new/Pages/1751415_20131223080045.aspx [last accessed November 2015].

[17] Drury D. Production of formate salts. European patent publication number 0 095 321 A2. 1983.

[18] Anderson J, Hamlin J. Process for the preparation of formic acid. European patent publication number 0 126 524 B2. 1984.

[19] Anderson J, Drury D, Hamlin J, Kent A. Process for the preparation of formic acid, United States patent number 4855496 (1989).

[20] Hladiy S, Starchevskyy M, Pazderskyy Y, Lastovyak Y. Method for production of formic acid, United States patent number 6713649 B1 (2004).

[21] Schaub T, Fries D, Paciello R, Mohl K. Process for preparing formic acid by reaction of carbon dioxide with hydrogen, United States patent number 8791297 B2 (2014).

[22] Det Norske Veritas (DNV). Carbon dioxide utilisation: electrochemical conversion of CO_2 — opportunities and challenges. 2007. Position Paper 07, available at: http://www. dnv.com/binaries/DNV-position_paper_CO2_Utilization_ tcm4-445820.pdf [last accessed November 2015].

[23] Mantra. Mantra releases update on demonstration projects. February 2015. Online news, available at: http:// mantraenergy.com/mantra-releases-update-on-demonstration-projects/ [last accessed November 2015].

[24] Robledo-Díez A. Life cycle assessment on the conversion of CO_2 to formic acid [Master thesis]. Norwegian University of Science and Technology; 2012. available at:, http://brage. bibsys.no/xmlui/handle/11250/234844 [last accessed November 2015].

[25] Álvarez-Guerra M, Del Castillo A, Irabien A. Continuous electrochemical reduction of carbon dioxide into formate using a tin cathode: comparison with lead cathode. Chem Eng Res Des 2014;92:692—701.

[26] Del Castillo A, Álvarez-Guerra M, Solla-Gullón J, Sáez A, Montiel V, Irabien A. Electrocatalytic reduction of CO_2 to formate using particles sn electrodes: effect of metal loading and particle size. Appl Energy 2015;157:165—73.

[27] IHS Chemical. Hydrogen — abstract from the report. August 2013. Online news, available at: http://www.ihs.com/ products/chemical/planning/ceh/hydrogen.aspx [last accessed August 2014].

[28] European Commission. H2Aircraft — CRYOPLANE and the future of flight, research and innovation projects. August 2013. available at: http://ec.europa.eu/research/transport/ projects/items/h2aircraft___cryoplane_and_the_future_of_ flight_en.htm [last accessed November 2015].

[29] Kothari R, Buddhi D, Sawhney R. Comparison of environmental and economic aspects of various hydrogen production methods. Renew Sustain Energy Rev 2008;12:553—63.

[30] International Energy Agency (IEA). Energy technology perspectives 2012: pathways to a clean energy system. France: IEA Publications, International Energy Agency (IEA); 2012.

[31] Lee D-H. Toward the clean production of hydrogen: competition among renewable energy sources and nuclear power. Int J Hydrogen Energy 2012;37:15726—35.

[32] Redissi Y, Bouallou C. Valorization of carbon dioxide by co-electrolysis of $CO_2/H_2 O$ at high temperature for syngas production. Energy Proced 2013;37:6667—78.

[33] Langè S, Pellegrini L. Sustainable combined production of hydrogen and energy from biomass in Malaysia. Chem Eng Trans 2013;32:607—12.

[34] Carton J, Olabi A. Wind/hydrogen hybrid systems: opportunity for Ireland's wind resource to provide consistent sustainable energy supply. Energy 2010;35:4536–44.

[35] Gahleitner G. Hydrogen from renewable electricity: an international review for power-to-gas pilot plants for stationary applications. Int J Hydrogen Energy 2013;38:2039–61.

[36] Samsatli S, Staffell I, Samsatli N. Optimal design and operation of integrated wind-hydrogen-electricity networks for decarbonising the domestic transport sector in Great Britain. Int J Hydrogen Energy 2016;41:447–75.

[37] Centi G, Quadrelli E, Perathoner S. Catalysis for CO_2 conversion: a key technology for rapid introduction of renewable energy in the value chain of chemical industries. Energy Environ Sci 2013;6:1711–31.

[38] Simoes S, Nijs W, Ruiz P, Sgobbi A, Radu D, Bolat P, et al. The JRC-EU-TIMES model. Assessing the long-term role of the SET plan energy technologies, scientific and policy report by the joint research Centre of the European Commission, European Union. 2014. available at: http://publications.jrc.ec.europa.eu/repository/handle/JRC85804 [last accessed December 2014].

[39] Dalebrook A, Gan W, Grasemann M, Moret S, Laurency G. Hydrogen storage: beyond conventional methods. Chem Commun 2013;49:8735–51.

[40] Yadav M, Xu Q. Liquid-phase chemical hydrogen storage materials. Energy Environ Sci 2012;5:9698–725.

[41] Enthaler S, von Langermann J, Schmidt T. Carbon dioxide and formic acid – the couple for environmental-friendly hydrogen storage? Energy Environ Sci 2010;3:1207–17.

[42] Leitner W. Carbon dioxide as a raw material: the synthesis of formic acid and its derivatives from CO_2. Angew Chem Int Ed 1995;34:2207–21.

[43] Dinjus E. Organometallic reactions with CO_2/catalyst design and mechanisms. Advances in Chemical Conversions for Mitigating Carbon Dioxide, 114; 1995. p. 127–40.

[44] Jessop P, Joó F, Tai C. Recent advances in the homogeneous hydrogenation of carbon dioxide. Coord Chem Rev 2004;248:2425–42.

[45] Wesselbaum S, Hintermair U, Leitner W. Continuous-flow hydrogentation of carbon dioxide to pure formic acid using an integrated scCO_2 process with immobilized catalyst and base. Angew Chem Int Ed 2012;51:8585–8.

[46] Moret S, Dyson P, Laurenczy G. Direct synthesis of formic acid from carbon dioxide by hydrogenation in acidic media. Nat Commun 2014;5. http://dx.doi.org/10.1038/ncomms5017.

[47] Laurenczy G, Cyson P. Homogeneous catalytic dehydrogenation of formic acid: progress towards a hydrogen-based economy. J Braz Chem Soc 2014;25:2157–63.

[48] Wang Z-L, Ping Y, Yan J-M, Wang H-L, Jiang Q. Hydrogen generation from formic acid decomposition at room temperature using a NiAuPd alloy nanocatalyst. Int J Hydrogen Energy 2014;39:4850–6.

[49] Guo W, Li L, Li L, Tian S, Liu S, Wu Y. Hydrogen production via electrolysis of aqueous formic acid solutions. Int J Hydrogen Energy 2011;36:9415–9.

[50] Boddien A, Loges B, Junge H, Beller M. Hydrogen generation at ambient conditions: application in fuel cells. ChemSusChem 2008;1:751–8.

[51] Rejal SZ, Masdar MS, Kamarudin SK. A parametric study of the direct formic acid fuel cell (DFAFC) performance and fuel crossover. Int J Hydrogen Energy 2014;39(19):10267–74.

[52] Rice C, Ha S, Masel R, Waszczuk P, Wieckowski A, Barnard T. Direct formic acid fuel cells. J Power Sources 2002;111:83–9.

[53] Kim H, Morgan R, Guray B, Masel R. A miniature direct formic acid fuel cell battery. J Power Sources 2009;188:118–21.

[54] BASF. Basf, tekion collaborate on formic acid fuel cells. Fuel Cells Bull 2006;5. http://www.sciencedirect.com/science/article/pii/S1464285906710410.

[56] Bolat P, Thiel C. Hydrogen supply chain architecture for bottom-up energy systems models. part 2: techno-economic inputs for hydrogen production pathways. Int J Hydrogen Energy 2014;39:8898–925.

[57] Heyne S, Harvey S. Impact of choice of CO_2 separation technology on thermo-economic performance of bio-sng production processes. Int J Energy Res 2014;38:299–318.

[58] Towler G, Sinnott R. Chemical engineering design: principles, practice and economics of plant and process design. 2nd ed. Butterworth-Heinemann, Elsevier; 2013.

[59] Eurostat, ECU/EUR exchange rates versus national currencies, On-line table, available at: http://ec.europa.eu/eurostat/tgm/table.do?tab=table&init=1&language=en&pcode=tec00033&plugin=1 [last accessed December 2014] [Last updated December 2014].

[60] Chemical Engineering Magazine. Chemical Engineering Plant Cost Index CEPCI, July 2014. 2014.

[61] IHS Chemical. Information provided by IHS Chemical in the form of a Chemical Plant Database. 2014.

[62] Arvola J. Reducing industrial use of fossil raw materials: techno-economic assessment of relevant cases in Northern Finland [Academic dissertation]. University of Oulu; 2011. available at:, http://herkules.oulu.fi/isbn9789514296895/isbn9789514296895.pdf [last accessed November 2015].

[63] Althaus H, Hischier R, Osses M, Primas A, Hellweg S, Jungbluth N, et al. Life cycle inventories of chemicals, Ecoinvent report no. 8. Swiss Centre for Life Cycle Inventories; December 2007.

[64] BASF. New formic acid plant in the US in mid-2015. 2012. Online news, available at: http://www.intermediates.basf.com/chemicals/web/en/function/conversions:/publish/content/products-and-industries/formic_acid/pop_up.html [last accessed November 2015].

[65] Sigma-Aldrich. Ru catalysts. 2015. Online information, available at: http://www.sigmaaldrich.com/chemistry/chemistry-products.html?TablePage=16252983 [last accessed November 2015].

[66] Sigma-Aldrich. 1,2-bis(dicyclohexylphosphino)ethane. 2015. Online information, available at: http://www.sigmaaldrich.com/catalog/product/aldrich/479500?lang=en&region=NL [last accessed November 2015].

[67] ChemSpider. N-methyl-n-octyl-1-nonanamine. 2015. Online information, available at: http://www.chemspider.com/Chemical-Structure.516106.html?rid=1bf02744-b817-48e4-8175-d7876d15769a&page_num=0 [last accessed November 2015].

[68] CHEMCAD 7.0.1. Users guide: physical properties version 5.3. Help topics in CHEMCAD software. 2016.

[69] Dortmund Data Bank Software & Separation Technology GmbH (DDBST). The unifac consortium. 2015. Online information, available at: http://www.ddbst.com/unifac-consortium.html#PSRK [last accessed November 2015].

[70] Ulrich GD, Vasudevan PT. Chemical engineering process design and economics. A pratical guide. Sheridan Books, Process Publishing; 2004.

[71] European Commission. JRC technical reports, Well-to-wheels report, Version 4.a. Well-to-wheel analysis of future automotive fuels and powertrains in the European context, Tech. rep.. European Commission; 2014.

[72] Fraunhoffer Institute for Systems and Innovation Research and Oko-Institut. Methodology for the free allocation of emission allowances in the EU ETS post 2012-Sector report for the chemical industry. November 2009.

[73] Sutter J. Life cycle inventories of petrochemical solvents. Ecoinvent report no. 22. Swiss Centre for Life Cycle Inventories; December 2007.

[74] European Commission (EC). DG energy, DG climate and DG for mobility and transport, EU energy, transport and GHG emissions: trends to 2050-reference scenario 2013, technology brief. 2013. European Commission (EC), available at: https://ec.europa.eu/energy/sites/ener/files/documents/trends_to_2050_update_2013.pdf [last accessed November 2015].

[75] Harrison G, Thiel C, Jones L. Powertrain technology transition market agent model (PTTMAM): an introduction, Tech. rep.. 2016. Publications Office of the European Union, available at: http://publications.jrc.ec.europa.eu/repository/handle/JRC100418.

[76] Pasaoglu G, Harrison G, Jones L, Hill N, Beaudet A, Thiel C. A systems dynamics based market agent model simulating future powertrain technology transition: scenarios in the EU light duty vehicle road transport sector. Technol Forecast Soc Change 2016;104:133—46.

[77] Carlsson J. ETRI 2014-Energy technology reference indicator projections for 2010-2050, Tech. rep.. 2014. Publications Office of the European Union, available at: http://publications.jrc.ec.europa.eu/repository/handle/JRC92496.

[78] Peters M, Köhler B, Kuckshinrichs W, Leitner W, Markewitz P, Müller T. Design and simulation of a methanol production plant from CO_2 hydrogenation. ChemSusChem 2011;4:1216—40.

[79] Dominguez-Ramos A, Singh B, Zhang X, Hertwich E, Irabien A. Global warming footprint of the electrochemical reduction of carbon dioxide to formate. J Clean Prod 2015;104:148—55.

[80] Sternberg A, Bardow A. Power-to-what? — environmental assessment of energy storage systems. Energy Environ Sci 2015;8:389—99.

[81] von der Assen N, Jung J, Bardow A. Life-cycle assessment of carbon dioxide capture and utilization: avoiding the pitfalls. Energy Environ Sci 2013;6:2721—34.

[82] Cuéllar-Franca R, Azapagic A. Carbon capture, storage and utilisation technologies: a critical analysis and comparison of their life cycle environmental impacts. J CO_2 Util 2015;9:82—102.

[83] Eurostat, Annual detailed enterprise statistics for industry (NACE Rev. 2, B-E), Wages and salaries for the manufacturing sector, Overall value, On-line table, available at: http://ec.europa.eu/eurostat/en/web/products-datasets/-/SBS_NA_IND_R2 [last accessed October 2015].

[84] Zero Emissions Platform (ZEP). The costs of CO_2 capture, Tech. rep.. 2011. European Commission, available at: http://www.zeroemissionsplatform.eu/library/publication/166-zep-cost-report-capture.html [last accessed November 2015].

[85] Kirschner M. Oxygen. In: Ullmann's encyclopedia of industrial chemistry. Wiley-VCH; 2012.

[86] World Textile. BASF raises prices for formic acid in Europe. 2015. Online news, available at: http://www.textileworld.com/Articles/2015/March/BASF_Raises_Prices_For_Formic_Acid_In_Europe [last accessed November 2015].

[87] Sigma-Aldrich. Bis(cyclopentadienyl)ruthenium(ii). 2015. Online information, available at: http://www.sigmaaldrich.com/catalog/product/aldrich/262455?lang=en&region=NL [last accessed April 2015].

[88] Sigma-Aldrich. 1,2-bis(dicyclohexylphosphino)ethane. 2015. Online information, available at: http://www.sigmaaldrich.com/catalog/product/aldrich/479500?lang=en&region=NL [last accessed April 2015].

[89] Methanex Corporation, Methanex monthly average regional posted contract price history, available at: https://www.methanex.com/sites/default/files/methanol-price/MxAvgPrice_Nov.

[90] Sigma-Aldrich. Trihexylamine. 2015. Online information, available at: http://www.sigmaaldrich.com/catalog/product/aldrich/183997?lang=en&region=NL [last accessed April 2015].

[91] US Department of Energy (DOE). ALternative fuels data center. 2014. Online information, available at: http://www.afdc.energy.gov/fuels/blends.html [last accessed August 2015].

[92] Pérez-Fortes M, Schöneberger J, Boulamanti A, Tzimas E. Methanol synthesis using captured CO_2 as raw material: techno-economic and environmental assessment. Appl Energy 2016;161:718—32.

[93] Steinberger-Wilckens MGR. Deliverable 2.1 and 2.1.a "European hydrogen infrastructure Atlas" and "industrial excess hydrogen analysis"—part II: industrial surplus hydrogen and markets and production. March 2007. Online information, available at: www.roads2hy.com [last accessed August 2014].

[94] Energy Technology Systems Analysis Programme (ETSAP). Fuel cells for stationary applications, technology brief. International Energy Agency (IEA); 2013. www.etsap.org.