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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

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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

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