

Project Report

The Use of CO₂ in the Production of Bioplastics for an Even Greener Chemistry

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Abstract: The high life expectancy of the world population provokes increase in demand for food and energy. As a result, the intense industrialization and the application of fossil sources is responsible for high levels of CO₂ emission and waste generation. To mitigate the CO₂ emission a practical solution at the very short term is urgently needed. The capture of CO₂ and its application in chemical processes for the valorization of residual biomass are of great importance nowadays. The application of CO₂ in the selective carboxylation of furoic acid for the production of 2,5-furandicarboxylic acid (FDCA), a bio-based monomer, has been an important step towards obtaining biopolymers to replace petroleum-based plastics such as polyethylene terephthalate (PET). In this project report, we discuss on the current challenges for obtaining the 2,5-FDCA precursor from the furfural in two main routes involving oxidation and carboxylation via heterogeneous catalysis. We present the main objectives and discuss the importance of this research for the development of more sustainable processes.

Keywords: CO₂ utilization; carboxylation; bioplastics; 2,5-FDCA; furoic acid



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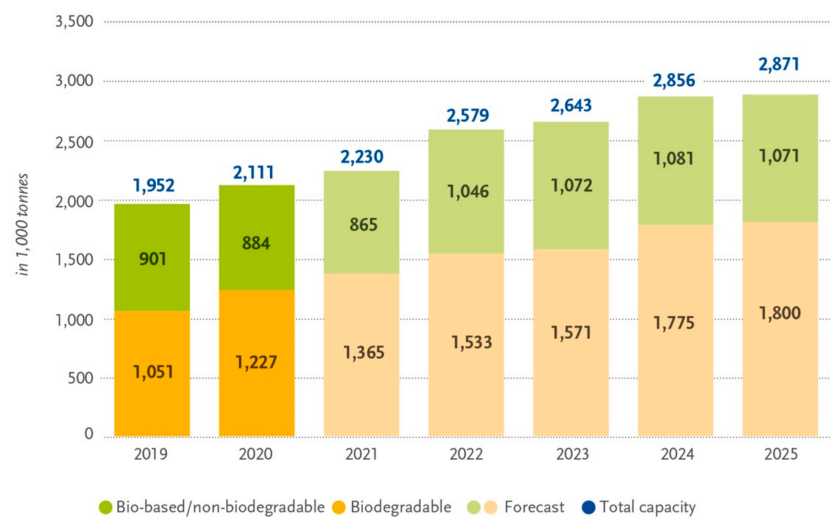


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1. Introduction

Nowadays, looking for alternative renewable bio-resources is urgent and important in order to replace non-bio and non-renewable ones conventionally employed in different industrial areas. The valorization of biomass, currently experiencing a great blooming, constitutes a considerable pathway among the available and proposed solutions [1–3]. Moreover, the intensive exploitation of fossil sources is one of the major causes of the CO₂ emissions, a hazardous greenhouse gas and a major cause of the global warming that is dangerously threatening our existence [4]. In the European Union alone, more than 75% of the greenhouse gas emissions come from the production and consumption of fossil fuels. In order to reduce the amount of CO₂ released, some processes have been suggested to capture the gas and use it for several chemical reactions [4]. The carboxylation of chemical compounds with CO₂ is one of these reactions that can be applied in the valorization of biomass. Part of biomass valorization consists of producing bioplastics from sugars such as xylose or glucose, which are abundantly present in agricultural productions such as wheat or beet, in agricultural residues or even in sawdust. Indeed, scientific research is increasingly concerned with the production of bioplastics, which represent about 1% of the 368 million tons of plastic produced each year in the world. Thus, the demand for the production of biopolymers for bioplastics, more resistant and even more biodegradable ones, is constantly increasing and diversifying (Figure 1). Indeed, the production of bioplastics, especially which are biodegradable, is expected to increase by 50% in the next 25 years.

Global production capacities of bioplastics



Source: European Bioplastics, nova-Institute (2020)
 More information: www.european-bioplastics.org/market and www.bio-based.eu/markets

Figure 1. Global bioplastic production capacity. Reprinted with permission from ref. [5].

It is worth noting that plastic surrounds us wherever we go, whatever we use, and it can be roughly said that currently plastic constitutes an entire portion of our daily life. However, at the same time its excessive consumption and environmental risks and impacts posed by it are very strongly linked. The progressive replacement of plastic with bioplastic allows us to fight against pollution caused by carbon dioxide.

One of the most important steps in the manufacturing process of these bioplastics is achieved using CO₂. This step consists of the selective production of 2,5-furandicarboxylic acid (2,5-FDCA) from a bio-sourced compound, furoic acid. 2,5-FDCA is one of the most important components for the production of biopolymers, such as polyethylene furoate (PEF), which is a natural replacement for polyethylene terephthalate (PET) derived from terephthalic acid (TA), an unsustainable molecule derived from petrochemistry (Figure 2). PEF is used for the manufacture of rigid and flexible packaging. Moreover, this biopolymer is totally recyclable and biodegradable. The properties of this biopolymer are also very interesting, offering the possibility of obtaining highly stable materials, while improving the barrier protection against oxygen and CO₂ of the packaged products. In addition to packaging, other applications could be possible, including in textiles.

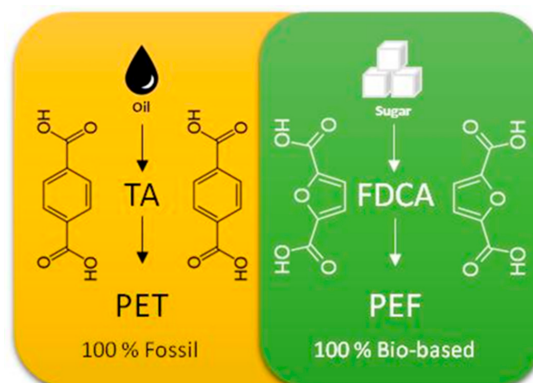


Figure 2. Diagram of the manufacturing process of PET (100% fossil) and PEF (100% bio-based).

2. Project Objectives

Currently, two main routes are being studied by scientists for the synthesis of the biopolymer, 2,5-FDCA. The first route consists of the oxidation of 5-hydroxymethylfurfural (HMF) with oxygen using heterogeneous or chemical catalysts. This route allows attainment of the best catalytic performances, but some problems concerning the purity of 2,5-FDCA are encountered due to the formation of unstable intermediates. Moreover, the HMF generally obtained from fructose must also be of very high purity [6]. Recently, studies have shown that the dehydration and then the oxidation processes for obtaining FDCA are not always very selective, which creates more stable by-products. According to several reports, the current cost of FDCA is on average USD 2300/kg [6]. However, to obtain economically viable production, the FDCA price must be USD 1000/ton. At the present, FDCA is thus not commercialized in industrial volumes, its cost price being too high. Production only is carried out in laboratories of various sizes for sales adapted to each customer and is used to carry out scientific tests [6].

The second method consists of using furfural, which is industrially produced from non-edible bio-sourced resources (agricultural residues, wood...). Furfural undergoes an oxidation step to obtain furoic acid. Then, the carboxylation of furoic acid with CO₂ allows the formation of 2,5-FDCA (Figure 3). This reaction pathway was found to be more selective than the one with HMF and therefore yields the desired product with higher purity.

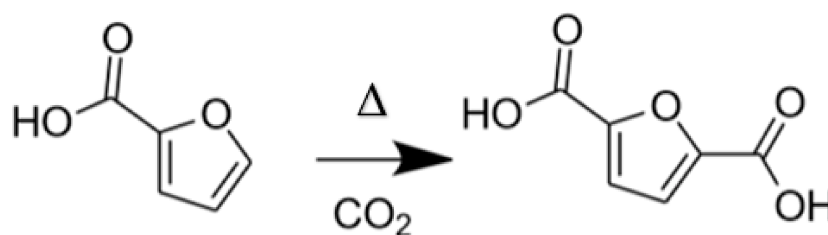


Figure 3. Reaction scheme for the CO₂ carboxylation of furoic acid to 2,5-furandicarboxylic acid (2,5-FDCA). Conditions used: substrate/M = 9, FCO₂ = 45 mL min⁻¹, 20 rpm, T = 200 °C, t = 20 h, STY_{FDCA} = 1260 μmol kg⁻¹ h⁻¹).

However, the main problem in the synthesis of 2,5-FDCA from furoic acid is the insertion of carboxylate groups at the C-H bonds of the hydrocarbons [7]. As a C1 feedstock, CO₂ has thermodynamic and kinetic limitations [8]. Indeed, in the esterification of aromatic hydrocarbons with CO₂, low equilibrium conversion is obtained at several temperatures [8]. Therefore, several solutions have been investigated to, aiming achieve the direct carboxylation of C-H, such as the use of a base, developed by Kolbe and Schmitt [9–11], a Lewis acid [12], transition metal catalysts [13], and enzymes [14] as reagents. In terms of mechanism, these reagents could influence the mode of C-H cleavage, which could be an electrophilic aromatic substitution, C-H deprotonation by a base, or C-H oxidation and subsequent insertion. This reaction can take place under both basic and acidic conditions. Under basic conditions, the use of a strong base deprotonates the C-H group with the most acidic proton, which is at position 5 in the FA [15] to form a strong nucleophilic carbon atom that could react with the weakly electrophilic CO₂. In an acidic environment, CO₂ is activated by coordination with a Lewis acid, resulting in a reaction between the reactant and the activated CO₂ [16].

Generally, this reaction is carried out using homogeneous catalysts (Henkel reaction [17–20]) which are very complicated to separate from the obtained products. This is the same for melted salt [19]. This reaction involves the thermal rearrangement or dismutation of alkali salts derived from aromatic acids into unsubstituted and symmetrical aromatic diacids known in particular for the production of TA. The selectivity in desired products cannot exceed 50%.

One of the main objectives of this project is to design heterogeneous catalysts easy to separate from the reaction medium with simple filtration. For this purpose, researchers were first interested in designing heterogeneous catalysts to activate CO₂ at relatively mild

conditions of temperature and pressure, known to be weakly active, in order to perform the direct carboxylation of furoic acid.

Silver nanoparticle catalysts have been shown to interact with CO₂, giving the possibility of carboxylation of furoic acid to 2,5-FDCA [21]. This reaction can occur at relatively low temperatures but requires high CO₂ pressure in a closed reactor. Under these conditions, the catalysts were able to obtain interesting yields of 2,5-FDCA suggesting an avenue of research for the replacement of the use of homogeneous catalysts on a laboratory scale. In addition, the use of undesirable reagents such as sodium hydroxide, a strong base, was eliminated. These results suggest the feasibility of this process at laboratory scale. However, the catalytic performances remain to be improved upon by working for example on the type of used catalyst. In order to apply a such process on an industrial scale, it will be necessary to improve the yield of 2,5-FDCA.

3. Methodology

Currently, one of the most important bio-sourced platform molecules is 2,5-furandicarboxylic acid (FDCA) due to its potential application as a building block for green polymers, which could replace petro-sourced polyethylene terephthalate (PET). Our team developed a very efficient, innovative and green process to oxidize furfural (FUR) to furoic acid (FA) with a 95% yield [22]. Recent work from our group has also shown that FA could undergo a C-H carboxylation with CO₂ to form FDCA [21]. We have combined our respective processes to gain access to FDCA from FUR via FA using only O₂ and CO₂ as the main reactants. At this stage, we have demonstrated the feasibility of this very exciting concept. This is very encouraging and places us at the cutting-edge of innovation in the area of FDCA production. In this context, the main objectives of the project are: (i) to study the catalytic process of furoic acid transformation to FDCA via Henkel reaction (TRL 3); (ii) to design new heterogeneous catalysts to obtain a minimum yield of 90% in Henkel reaction and (iii) to assess the validity and acceptance of the technical solutions retained from the environmental, economic and societal points of view. FDCA synthesis was performed in a Glass Oven B-585 Kugelrohr (Büchi) at 200 °C, under a continuous flow of CO₂ (45 mL min⁻¹), over 20 h.

At the end of this project, we should be able to conclude on the possibility of transferring our academic research results to the socio-economic world by patenting and/or licensing our whole process to an industrial partner and, hence, on the necessity to invest in a more ambitious maturation program.

4. Conclusions

The valorization of lignocellulosic biomass and CO₂ capture have been very important processes for the reduction of the greenhouse effect and the implementation of more sustainable processes. 2,5-FDCA is a promising bio-based building block used to produce bioplastics and other biopolymers in order to replace petroleum-based molecules. Recent work from our group has also shown that FA could undergo a direct C-H carboxylation with CO₂ to form FDCA using only O₂ (first step oxidation of furfural) and CO₂ as the main reactants, where high yield in FDCA can be obtained from a raw FA (un-published data) but using molten salts instead of heterogeneous catalyst. These data, as well as the several publications of our group are very encouraging and place us at the cutting-edge of innovation in the area of FDCA production.

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Conflicts of Interest: The authors declare no conflict of interest.

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