Engineering the future: Perspectives in the 2,5-furandicarboxylic acid synthesis

Robert Wojcieszak, I. Itabaiana

Engineering the future: perspectives in the 2,5-furandicarboxylic acid synthesis.

R. Wojcieszak, I. Itabaiana*

[a]*Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France*
[b]*Departamento de Engenharia Bioquímica - Escola de Química, Universidade Federal do Rio de Janeiro, Cidade Universitária, Rio de Janeiro - RJ, 21941-909, Brazil.*

**Corresponding author: robert.wojcieszak@univ-lille.fr*

Abstract:

We present a perspective work on the synthesis of *2,5*-furanodicarboxylic acid (FDCA), which is a highly promising building block for resins and polymers. FDCA is presumed as a green replacement for (fossil-based) terephthalate a predominant compound in polymer and resin manufacture today, with a potential market size of several 100 M€. However, the use of FDCA is still limited because of its high price and the various issues linked to its industrial scale production. We discuss herein the synthesis of FDCA from glucose using heterogeneous catalysts and base-free conditions. We discuss also the possibility and the perspectives in an efficient FDCA production process directly from glucaric acid (glucose derivative) using new-engineered nanocatalysts (hybrid catalysts). This process permits to avoid the non-selective and highly expensive step of glucose isomerization to fructose.

Keywords: FDCA, biomass, heterogeneous catalysis, dehydration, hybrid catalysts

1. Introduction

In 2004, the US Department of Energy announced the list of 12 high value-added chemicals obtained from sugars (updated in 2010) [1]). The half of this list constitutes different dicarboxylic acids. Indeed, di-acids are important chemical intermediates from the industrial point of view [2-3]. Some of them, such as maleic or adipic acids, are widely used in industry, with thousands of tons per year, especially in the preparation of polyesters, fibers, plasticizers, food additives and many other applications [2, 4]. Conversion of different molecules to dicarboxylic acids by chemical, enzymatic or heterogeneous catalysis is abundant field of investigation with many possible transformations. Besides the adaptation of the conventional approaches there is a renewed interest towards heterogeneous catalysis due to the so-to-speak reactivation in this field with new concepts and new fundamental approaches. It is therefore a major challenge for the development of selective catalytic materials to selectively transform bio-based molecules to corresponding di-acids. Catalysis plays a crucial role in promoting the feasibility, eco-efficiency and economics of over 90% of chemical processes [2]. However, at the same time, the catalysis is also one of the critical enabling factors that permit the sustainability in the chemical industrial processes. New

innovative catalysts can have a significant impact on the energy, environment and chemicals due to their great industrial potential. Obtaining of highly valuable dicarboxylic acids from bio-based feedstocks is without any doubt of great interest from an industrial viewpoint, as they constitute a very substantial turnover associated with huge quantities of products worldwide for the chemical industry.

Despite a few early pioneering works published at the beginning of XX centaury, the most important progress in the catalytic synthesis of dicarboxylic acid was achieved during last two decades (2000-2018). The development of heterogeneous catalytic processes based on the use of supported nanoparticles (such as Pd, Au and Cu) and mixed oxides (based on Mo, V and P) permitted to achieve high yields and selectivities in the selective oxidation processes. In this period, a huge number of articles were published dealing with the synthesis of various dicarboxylic acids (Figure 1). More then 50% of all publications concerned the synthesis of adipic and glutamic acid. However, since 2006 the number of publications on the synthesis of FDCA (2,5-furanodicarboxylic acid) has increased drastically.

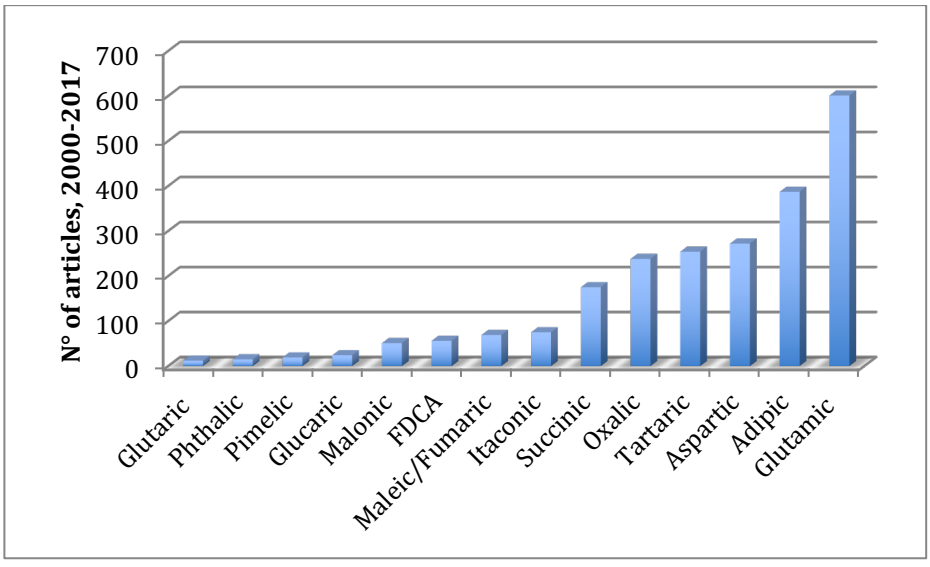

Figure 1. Number of publications in the last 17 years reporting the synthesis of given di-acid (GoogleScholar: as entered "x-acid synthesis", English only)

2,5-furandicarboxylic acid (FDCA) is a highly promising building block for resins and polymers (Figure 2). FDCA is advocated as a green replacement for (fossil-based) terephthalate a predominant compound in polymer and resin manufacture today, with a potential market size of several 100 M€ [5].

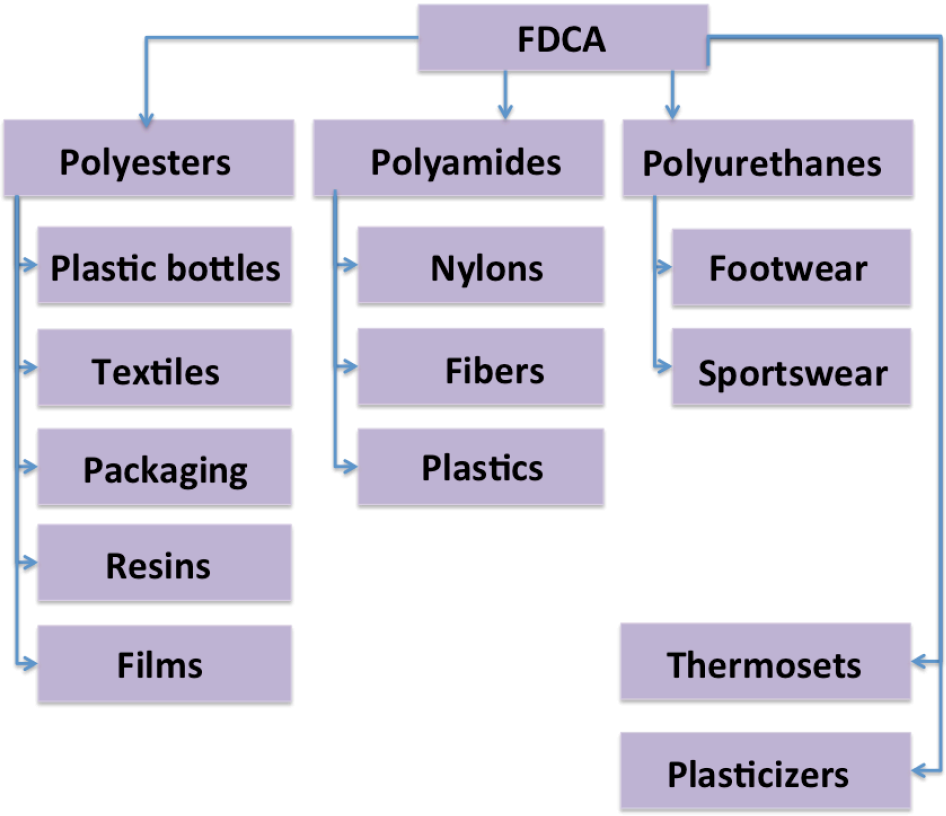

Figure 2. Potential market and application of FDCA. Adapted from [5].

However, the use of FDCA is still limited because of its high price. Indeed, no production on an industrial scale has been carried out so far. Today, it is mostly produced from fructose in some laboratories, but this route of synthesis is quite expensive. Up to now, the best results for the production of FDCA are obtained with the oxidation of HMF (5-hydroxymethylfurfural) even if its stability in acid medium is weak [6-10]. HMF is usually obtained from fructose, which must be very pure. 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 $ 2,300/kg. However, to obtain economically viable production, the FDCA price must be $ 1,000/ton [5]. At the present, the FDCA is thus not commercialized in industrial volumes, its cost price being too high. The production is done only in more or less large laboratories for a sale adapted to each customer and is used to carry out scientific tests. Today, the FDCA produced would be 3.5 to 5 tons for a total estimate of about $ 10 million. In a theoretical scenario of 100% use of FDCA as an alternative to the petrochemical industry, the FDCA market has a total estimate of nearly 50 million tons [5]. Based on new separation technologies and catalysts, Avantium and BASF have announced to create a joint

venture (Synvina) and efficiently produce FDCA economically at $ 1,000/ton. The company is developing a pilot plant in the Netherlands, operating since 2016, with a total capacity of 40 tons for an annual production of 30 to 50,000 tons. Their goal for 2018 was fixed at annual production of 300 000 to 500 000 tons [5]. However, recently the BASF has notified Avantium of its exit from Synvina on January 2019 due to disagree with commercialization of the YXY technology developed by Avantium [11]. This suggests that the fully industrial production of FDCA from HMF is still far from the reality.

2. FDCA synthesis via HMF oxidation in basic media

The oxidation of HMF in basic media permits to obtain very high FDCA yield. However, it is well established that various problems related to the selectivity and the stability or poisoning of the catalysts as well as the stability of starting HMF frequently occur. Indeed, HMF is not stable in basic media and undergoes degradation [12]. Indeed, several tests performed at high pH and in the absence of the catalyst showed that the HMF conversion reach high values but without formation of any oxidation products such as FDCA for example. Moreover, the color change was noticed as the reaction mixture turned off from yellow to brown with the formation of a brown precipitate [13-14]. This precipitate originates from the formation of humic acids and humins. Humins are not soluble in water whatever the pH of the solution is. Contrary to that humic acids could be soluble but only at high pH. Moreover, as pointed our by some works, many different acids such as formic and levulinic acids can form during the degradation of HMF. This confirmed how a high pH is detrimental for the stability of HMF in solution. The increase in both, the NaOH concentration and reaction temperature would enhance the degradation process. However, in the presence of a suitable catalyst, this degradation process can be minimalized [15]. Nevertheless, several papers report good results obtained in HMF oxidation in a basic medium. Accordingly high reaction rates and higher feed concentrations (3%) could be obtained in the presence of a base. The basic media permitted also to avoid the adsorption of the FDCA on the surface of the catalyst [15-16].

3. FDCA synthesis via base-free HMF oxidation

Taking into account the issues mentioned above, development of new base-free oxidation processes using heterogeneous catalysts and green conditions are highly important. These processes would facilitate the FDCA recovery by the elimination of the neutralization

step of the reaction. Recently, various heterogeneous catalysts especially based on supported gold nanoparticles have been developed in order to enhance the rates of the base free oxidation reaction [12]. These catalytic materials are believed to be able to obtain high activity and selectivity without the need of additional base. However, only few works deal with the oxidation of HMF to FDCA in base free conditions using supported metallic nanoparticles. Erbitani *et al.* reported good results obtained in the aerobic oxidation of HMF in water without addition of any base [17]. They studied Au nanoparticles supported on hydrotalcite mixed oxides and observed very high conversions. FDCA was yielded with 99% only after 7 h at 95 °C. Moreover, the activity of Au-hydrotalcite catalyst was compared to various Au based catalysts deposited on different supports. Catalysts based on neutral or acidic supports (such us Au/Al_2O_3 and Au/SiO_2) showed very low conversion with almost any FDCA production. Basic supports (such as MgO, hydrotalcite) provided very high yield and achieved full HMF conversion. However, in the case of Au/MgO catalyst the selectivity to FDCA was quite low (only 21%). These results confirmed that the basicity of the catalyst and metal dispersion have crucial role in the HMF oxidation. However, in case of MgO and hydrotalcite support the serious problems with the stability of the catalysts occurred. Zope *et al.* showed that high Mg^{2+} leaching from hydrotalcite occurred in the oxidation of HMF in water without any base addition [18]. It was concluded that the dissolution of MgO is a result of an acid-base reaction. The acid formed in the oxidation reaction decreases the pH of the mixture and at the end enhances the consumption of the solid base. The local basicity of the gold-based catalysts could be also enhanced by incorporation of a second metal. This was studied by Wang *et al*. [19]. They reported a new carbon nanotubes (CNT) based catalyst with bimetallic AuPd nanoparticles (AuPd/CNT). It was shown that this material could reach 100% of HMF conversion after only 12 h of reaction using O_2 as terminal oxidant. For the best composition very good selectivity to FDCA was obtained (<94%). The authors studied also the influence of the nature of the support comparing various AuPd supported catalysts [19]. In their work the catalytic activity in terms of the HMF conversion and FDCA yield followed similar trend to that reported by other researchers [17]. As expected catalysts based on basic supports were much more active then neutral or acidic supports. If compared, Au-based catalysts supported on carbon materials such as CNT and grapene oxide (GO) highest activity was observed for carbon nanotubes materials. However, the superiority of the carbon materials is based on their stability in acidic medium [19]. Indeed, as reported the catalysts based on basic supports were not stable and presented the decrease in the overall catalytic activity during the recycling tests due to the leaching of basic oxides [12, 19]. Contrary to that

the Au/CNT material remained active for more then 5 catalytic cycles. This phenomenon could be explained taking into account the organic groups present on the support surface. These active groups are formed during the oxidative treatment of the materials at high temperature and can significantly affect the adsorption of the substrate, intermediates and product on the catalyst surface. The characterization of the carbon nanotubes revealed the presence of both, phenol and carbonyl/quinone groups on the surface. These groups are believed to favor the preferential adsorption of HMF instead of FDCA. In the same time the authors emphasized also the synergistic effect observed between both metals as bimetallic Au-Pd sample presented much higher activity than the monometallic Pd or Au based catalyst [19].

Recently we have studied the base free oxidation of HMF on Au supported on MgO-MgF_2 materials in order to elucidate the influence of the support basic sites on the catalytic activity of gold [20]. It is generally admitted that [21] the role of basic support in oxidation reaction is to increase the population of hydroxyl species on the catalyst surface. In our work we have studied the incorporation of a basic MgO oxide into the neutral MgF_2 support. Increasing of the MgO content would permit the increase of the basicity of the catalysts and promote the oxidation of HMF. In the oxidation tests carried out in water MgO will react with water forming basic $Mg(OH)_2$ and in the same time will increase the final pH of the solution. Indeed, the presence of the Mg^{2+} ions in the reactant solution in case of the materials with high MgO content was confirmed by ICP analysis and basic pH after reaction. Moreover, the basicity of the support resulted also in the different reaction pathways [20]. In the case of the absence of basic sites (MgF_2) high selectivity to DFF (*2,5*-diformylfuran) was observed. Contrary to that in the case of the MgF_2-MgO mixtures the presence of DFF was not observed. The increase in the MgO content changed the reaction pathway towards HMFCA (*5*-hydroxymethyl-*2*-furancarboxylic monoacid) further converted to FDCA. In addition, the FFCA (*5*-formyl-*2*-furancaboxylic acid), another reactant intermediate was also detected. In case of the low MgO content (<40 mol%) the pH of the final solution was acid (<3,8). At this pH, the FDCA is totally protonated ($pKa = 3.16$) that favors the direct acid isolation. It was shown that mixing basic MgO with inactive MgF_2 it was possible to ally high conversion and high product recovery at low pH [20].

4. Perspectives and challenges in FDCA synthesis

Even if HMF could be directly obtained from sugars using various heterogeneous catalysts still some drawbacks concerning the degradation of HMF and the use of organic solvents (purification and separation issues) exist. The liquid phase oxidation processes using heterogeneous catalysts also still needs to be improved. Especially, when working in base free conditions, the leaching of the active phase should be avoided [12].

For these reasons the development of new methods for the synthesis of FDCA directly from glucose (and its derivatives) is of great interest. One of the possibilities is the catalytic dehydration of glucaric acid obtained from glucose oxidation (Figure 3).

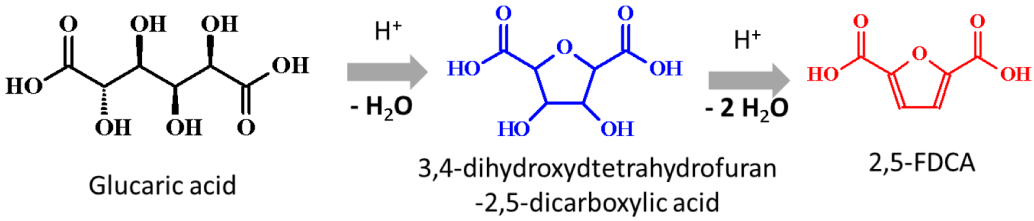

Figure 3. Catalytic process of the synthesis of FDCA from glucaric acid

As it appears from the literature, dehydration processes are carried out using acidic medium. The reaction should involve dehydration of glucaric acid with the formation of 5-members cycle with subsequent dehydration to form furanic ring. This route of FDCA synthesis using heterogeneous catalysts has not been yet reported in the literature. However, four patents are reported but are mostly based on the use of concentrated mineral acids such as HBr [22-25]. This reaction should be similar to the dehydration of C5 (xylose) and C6 (sorbitol, fructose) sugars into furan-based compounds like furfural, isosorbide and HMF, respectively [26-27]. The main difference is the presence of two carboxylic groups instead of carbonyl or -OH groups in the case of sugars. The presence of these functional groups should affect the reaction in two ways. Firstly the carboxylic groups will participate in the reaction of dehydration of glucaric acid and the main side reaction should be decarboxylation and ring opening in comparison with humins formation in the case of sugars. Secondly the side esterification of etherification reactions could occur during the reactions carried out in the presence of solvents.

Different types of homogeneous and heterogeneous acidic catalysts have been found for dehydration of sugars into furan compounds and which might be efficient for dehydration of glucaric acids [26-27]. It has been found that the highest selectivities for the synthesis of furans might be obtained by application of catalysts with the strong Brønsted acid sites like ion exchange resins (Amberlyst-15), sulfonated silica, zeolites and niobium oxide. The first

document published in 1956 shows the possibility to dehydrate glucaric acid to FDCA using concentrated HBr (48%) [28, 29]. In this work the yield obtained was of 50% after 27 hours of reaction. Recently Anarasekara et al. published the new results on mucic acid dehydration using also concentrated HBr [30]. 3 of the patents already reported concern the dehydration of glucaric acid using mineral acids (mostly HBr with 60% yield of FDCA) [22-24]. One of the patent reports [25] the use of heterogeneous catalysts such as Amberlyst 15, MCM-41 and sulphated zirconia. However, the yields to FDCA reached values between 0.1 and 8% depending on the catalyst and glucaric acid/catalyst ratio. In case of Amberlyst 15, 1% yield was obtained with glucaric acid/catalyst weight ratio of 1:2 and only 0.4% of yield in case of glucaric acid/catalyst ratio of 10. No results in solvent free conditions were reported in the literature up to now. This is one of the challenges for this reaction. Two different routes should be studied: solvent free dehydration (especially interesting from the industrial point of view) and classical dehydration with diluted samples. The implementation of the solvent free dehydration reaction is a scientific and technological challenge. The advantages of this approach are the improvement of the stability of the catalysts and the facility of the recovery of the catalyst after the reaction. Concerning the whole glucose to FDCA process two different methods should be explored in the future as discussed below.

4.1. Integrated process

The first step of the FDCA synthesis from glucose is the oxidation of glucose to glucaric acid. The whole process can be schematically carried out as represented on Figure 4. The first step being the base free oxidation of glucose to glucaric acid using supported noble metal nanoparticles catalysts.

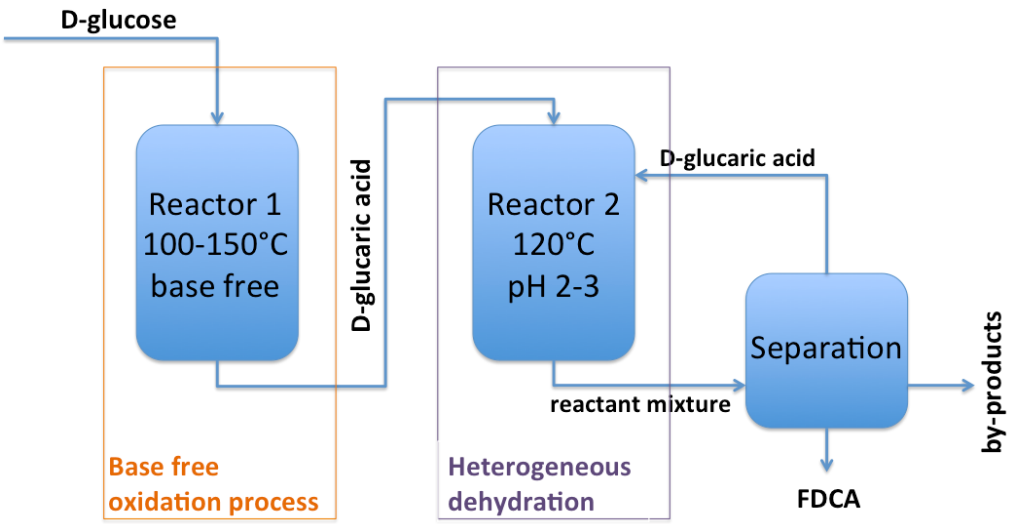

Figure 4. Schematic representation of the FDCA synthesis from glucose using heterogeneous catalysts.

Currently the production methods are based on chemical oxidation of D-glucose using nitric acid. However, this method is not compatible with the principles of green chemistry due to the release of huge quantity of NO_x. Nowadays some modification of this process has been made and the NO_X is recycled but the oxidation of glucose can be much more greener. Catalytic oxidation with oxygen and using heterogeneous catalysts is an ideal alternative to nitric acid oxidation. Catalysts based on Au or Pd (and the mixture of both) have shown good activity in the oxidation of glucose reaction. Pamuk *et al.* [31] obtained a 63% yield of D-glucaric acid directly from the sugar beet molasses using sodium nitrite, nitric and sulfuric acid. Mehltretter [32] attained a selectivity of 54% for D-glucaric acid by the oxidation of D-glucose with Pt/C as catalyst. D- Glucaric acid was prepared also in a yield of 41% by oxidizing dextrose with nitric acid. Matthey [33] oxidized D-glucose with $Hg(OH)_2$ at 40±60°C and reported a yield of 80% in their study. An extensive investigation of the oxidation of aldopentoses to the corresponding aldonic and aldaric acids has been reported [34]. Pt-based catalysts are preferred over palladium in the oxidation of primary hydroxyl groups because platinum is more active. However, the rates of oxidation of primary hydroxyl groups on Pt catalysts are usually low because strongly adsorbed products or byproducts easily poison catalysts. Owing to the low activity, besides the oxidation of primary alcohol groups, secondary alcohol functions are also oxidized along with the formation of more oxidized products such as tartrate and oxalate, leading to very poor selectivity to the desired aldaric acid. Thus, oxidations of D-Gluconic acid on Pt/C catalysts yielded, under optimized conditions, about 40% of D-glucarate [35]. Slightly higher yields (55% at 97.2% conversion) were reported by Besson *et al.* [36] working with more concentrated solutions of D-gluconate and lower amounts of catalyst. Although, the glucaric acid yields remain still low and the price of such as type of catalysts is still high, the first industrial scale example of catalytic glucose oxidation is already being tested in by Rennovia and Johnson Matthey [37].

4.2. Hybrid catalysis

To make the given process economically viable the high selectivities are required. In this respect the use of enzymes will have a crucial role. The oxidation of the glucose can be achieved *via* enzymatic route as schematically represented on Figure 5.

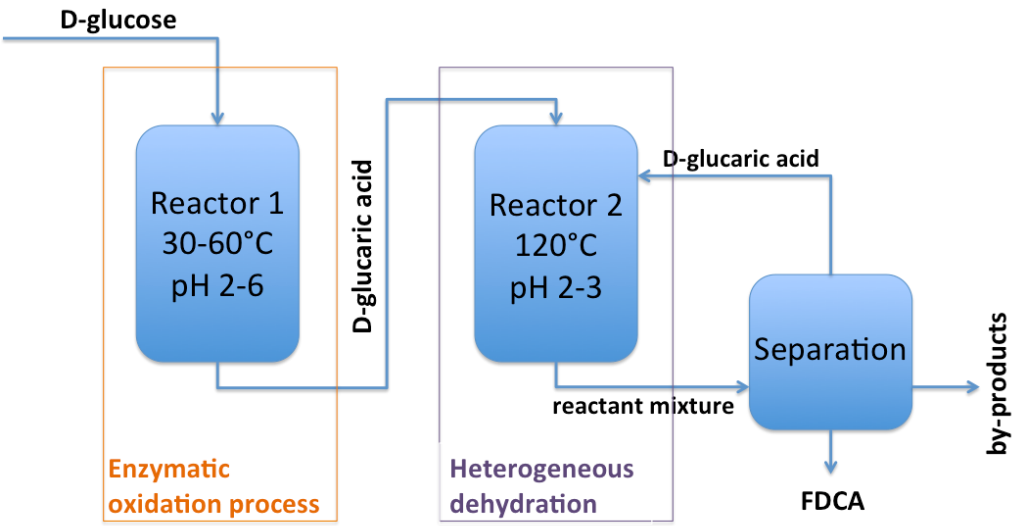

Figure 5. 2-steps synthesis of the FDCA from glucose using enzymatic and heterogeneous processes.

New catalytic processes using enzymatic systems may lead to higher yields and selectivities. This results from the relatively mild operating conditions of such processes and the specificity of enzymes, which minimizes by-product formation [38]. Concerning the synthesis of D-glucaric acid, it is reasonable to start with an examination of the naturally existing mammalian pathway, which has been elucidated [39]. D-Glucaric acid is the end product of the D-glucuronic acid pathway [40]. This pathway is a cycle that is initiated with D-glucose and interacts with the pentose phosphate pathway. D- glucuronic acid is converted to D-glucaric acid in three successive steps through the intermediates D-glucurono-γ-lactone and D-glucaro-γ-lactone. Therefore, there is a known route for the production of D-glucaric acid from D-glucose [41]. Moon *et al.* [41] reported the construction of a synthetic pathway in *E. coli* for the production of D- glucaric acid by combining 5 enzymatic steps whose uronate dehydrogenase which is the final enzyme catalyzing the conversion of D-glucuronic acid to D-glucaric acid where NAD cofactor is necessary.

Combination of glucose-fructose oxidoreductase (GFOR) and gluconolactonase (GL) has been also used for the conversion of D-glucose to D-glucuronic acid. These enzymes are provided from *Zymomonas mobilis*, bacteria known for sorbitol production. The GFOR enzyme contains tightly bound NAD as the hydrogen carrier and does not require any added cofactor for activity [42]. This combination could be an alternative pathway to those reported by Moon *et al.* in replacement of the first 3 enzymes [41].

A patent [43] describing compositions and methods for producing chemicals, such as glucaric acid, by enzymatic pathways has been published. In general the conversion of D-glucose to 1,5-gluconolactone can be performed with enzymes of the family oxygen dependent glucose oxidases (EC 1.1.3.4) or NAD(P)-dependent glucose dehydrogenases (EC 1.1.1.118, EC 1.1.1.119). *Gluconobacter oxydans, Zymomonas mobilis* have been shown to efficiently oxidize glucose to gluconic acid. Concerning the conversion of 1,5-gluconolactone to gluconic acid, many microorganisms contain specific 1,5-glucololactone hydrolases (or lactonases), and a few of them have been cloned and characterized, such as *Zymomonas mobilis, Pseudomonas syringae, Pseudomonas fluorescens, Gluconobacter oxydans* (example of enzyme EC 3.1.1.17 [44]). Conversion of gluconic acid to guluronic/glucuronic acid can be performed by the following families: aldehyde oxidase EC1.2.3.1, aldehyde ferredoxin oxidoreduactase EC1.2.7.5, and in all the families of EC1.2.1.-XX, enzymes of the family of urinate dehydrogenases (EC1.1.1.203). Oxidative bacteria such as *Acetobacter* and *Gluconobacter* can be used for screening [45]. Conversion of guluronic/glucuronic to glucaric acid can be performed by enzymes of the family of uronate dehydrogenases (EC1.1.1.203) or the oxidases described in the previous step. Enzymes previously mentioned are NAD(H) co-factor dependent. These co-factors are costly and hydrolytically unstable, and therefore represent a major barrier for preparative biotransformations. The development of efficient methods for their regeneration with cheap reducing equivalents has been an area of intense research in the last decades [38]. Methods explored include chemical, electrochemical and photochemical approaches. None of the methods to regenerate NADH has reached efficiency comparable with enzymatic regeneration that remains the method of choice for most applications. Organometallic-based approaches for NADH regeneration methods represent an alternative solution [38]. However, the frequent problem is the mutual inactivation between the organometallic catalyst for co-factor regeneration and the corresponding NADH dependent enzyme. Compartmentalization of the organometallic complex (Figure 6) can represent a potential remedy [38, 46].

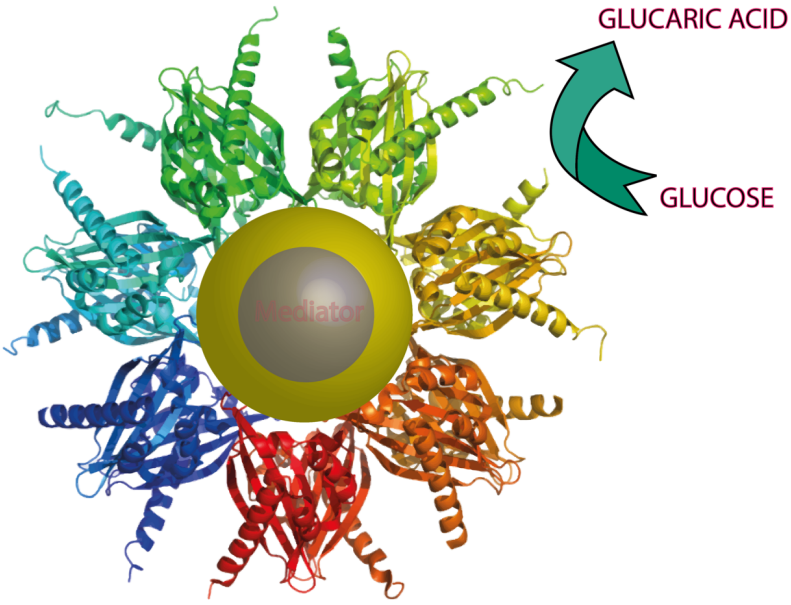

Figure 6. Schematic representation of the hybrid catalysts with compartmentalization of the mediator and the enzymes.

The development of strategies towards advanced complex hybrid architectures using pre-organized or self-assembled molecular structures appears as a main challenge for the next years. In the conception of advanced nanoreactor several drawbacks should be solved. Nature has developed an ingenious way to perform cascade reactions in the environment of the cells over enzymes. In the future the research should be focused on the realization of chemo-enzymatic cascade systems to mimic natural cells and at the same time provide synergetic effect of enzymatic and chemical processes. In this case enzymes might be attached to the surface of nanoparticles for oxidation of glucose to glucaric acid. Mediator will be localized inside of nanoparticles for subsequent regeneration of enzymes. The physical contact between mediator and the enzyme should be avoided. However, the use of advanced architectures should permit the easy exchange of the electrons between them. By choosing a chemically inert material as matrix, such as polymers, gold, silica, enzymes could retain the activity of the native enzymes. The matrix also has been used as a platform for the attachment of other compounds inhibitors of enzymatic pathways, antibodies and site directing units [47]. Silica is one of the most convenient materials for the synthesis of such kind of nanoreactors. It might be prepared by hydrolysis of silanes using mild acidic and basic conditions. Typically enzymes are mixed directly with the polymerization solution with minimal use of denaturing solvents. It leads to encapsulation or adsorption of enzymes in the silica structures. Thus, Tsang *et al.* [48] used silica coated magnetic nanoreactors prepared in water-oil emulsion where silica was functionalized with aminopropyltriethoxysilane to attach ß-lactamase. The

catalyst exhibited activity as good as those for free enzymes. Thus, it would be possible to encapsulate first mediator (mandatory for the regeneration of enzymes) inside of the silica shell with subsequent grafting of enzymes (for the glucose oxidation) on the surface for the synthesis of glucaric acid (Figure 6). Polymeric nanoreactors are another important materials suitable for mediator encapsulation due to the high flexibility for functionalization. Herdt [49] used polystyrene-block-polyacrylate copolymer for encapsulation of enzymes with preservation of catalytic activity. Metallic nanoreactors might be also used for encapsulation. Li and coworkers [50] used gold nanoparticles for immobilization of glucose oxidase, which demonstrated higher thermal stability, compared to free enzyme. Thus, different materials might be used for encapsulation of mediator inside of the nanoreactor. In these cases the interior or exterior surface of nanoreactor might be used for grafting/encapsulation of acid sites.

5. Conclusions

The implementation of new processes for biorefineries must be evaluated within the context of green chemistry due to the environmental requirements. For example the selection of adequate organic solvents, reactants and catalytic materials is essential to ensure sustainable processing methods as well as using sustainable resources. In case of FDCA the actually semi-industrial process relay on expensive and low selective process of HMF oxidation. It is clear that new technology and improved catalytic methods are required to produce high valued FDCA directly from glucose with the elimination of isomerization step. We have described a process based on the dehydration of glucose derivatives (glucaric acid). Only few works deal with this method of FDCA synthesis. The main challenge is to obtain high purity glucaric acid using heterogeneous or enzymatic catalysts. Concerning the dehydration reaction, it could be carried out using solvent free conditions. This permits to minimalize the cost of the whole process. However, the challenges are still present. The most interesting from the scientific point of view is the use of hybrid (chemo-enzymatic) catalysts.

6. Acknowledgments

Chevreul Institute (FR 2638), Ministère de l'Enseignement Supérieur, de la Recherche et de l'Innovation, Région Hauts-de-France and FEDER are acknowledged for supporting and funding partially this work. Centrale Lille, CNRS, and the University of Lille, as well as the

Centrale Initiatives Foundation, are thanked for their financial contributions. This work was done in the frame of the LIA “Energy&Environment” funded by CNRS.

6. References

[1] J.J. Bozell, G.R. Peterson, Green Chem. 12 (2010) 525
[2] G. Centi, S. Perathoner, (2009) in Sustainable Industrial Chemistry (eds F. Cavani, G. Centi, S. Perathoner and F. Trifiró), Wiley, Weinheim, Germany. doi: 10.1002/9783527629114.ch2
[3] F. Dumeignil, M. Capron, B. Katryniok, R. Wojcieszak, A. Löfberg, J.S. Giradon, S. Desset, M. Araque Marin, L. Jalowiecki Duhamel, S. Paul. 58(5) (2015) 257-273
[4] R. Wojcieszak, F. Santarelli, S. Paul, F. Dumeignil, F. Cavani, R.V. Gonçalves. Sustain. Chem. Proces. 3 (2015) 9-20
[5] From Avantium website: https://www.avantium.com/yxy/ (accessed on 28.12.2018)
[6] O. Casanova, S. Iborra, A. Corma, A. ChemSusChem 2 (2009) 1138−1144.
[7] S. Albonetti, A. Lolli, V. Morandi, A. Migliori, C. Lucarelli, F. Cavani. Appl. Catal., B 163 (2015) 520−530.
[8] Z. Miao, Y. Zhang, X. Pan, T. Wu, B. Zhang, J. Li, T. Yi, Z. Zhang, X. Yang. Catal. Sci. Technol. 5 (2015) 1314−1322.
[9] J.Y. Cai, H. Ma, J.J. Zhang, Q. Song, Z.T. Du, Y.Z. Huang, J. Xu, Chem. - Eur. J. 19 (2013) 14215−14223.
[10] S.E. Davis, L.R. Houk, E.C. Tamargo, A.K. Datye, R.J. Davis. Catal. Today 160 (2011) 55−60.
[11] From https://www.avantium.com/wp-content/uploads/2018/12/20181218-Press-release-Avantium-18-December-2018.pdf, accessed on 28.12.2018
[12] R. Wojcieszak, C.P. Ferraz, J. Sha, S. Houda, L. M. Rossi, S. Paul, Catalysts 7 (2017) 352-375.
[13] K.R. Vuyyuru, P. Strasser. Catal. Today 195 (2012) 144–154.
[14] A. Piccolo, P. Conte, A. Cozzolino. Eur. J. Soil Sci. 50 (1999) 687–694.
[15] T. Pasini, M. Piccinini, M. Blosi, R. Bonelli, S. Albonetti, N. Dimitratos, J.A. Lopez-Sanchez, M. Sankar, Q. He, J.L. Kiely, Green Chem. 13 (2011) 2091–2099.
[16] Z. Zhang, K. Deng, ACS Catal. 5 (2015) 6529–6544.
[17] N.K. Gupta, S. Nishimura, A. Takagaki, K. Ebitani, Green Chem. 13 (2011) 824–827.
[18] B.N. Zope, S.E. Davis, R.J. Davis, Top. Catal. 55 (2012) 24–32.
[19] X. Wan, C. Zhou, J. Chen, W. Deng, Q. Zhang, Y. Yang, Y. Wang, ACS Catal. 4 (2014) 2175–2185.
[20] C.P. Ferraz, M. Zieliński, M. Pietrowski, S. Heyte, F. Dumeignil, L. M. Rossi, R. Wojcieszak, ACS Sustainable Chem. Eng., 6(12) (2018) 16332–16340
[21] B.N. Zope, D.D. Hibbitts, N. Neurock, R.J. Davis, Science, 330 (2010) 74-78
[22] A. Gaset, L. Rigal, B. Sene, R. Ralainirina, AIR ARD, 1994 FR2723945A1
[23] M. Asikainen, D. Thoams, A. Harlin, 2015, WO2016166421A1
[24] N. Guo, 2016, WO2017083297A1
[25] D. Miller, L. Peereboom, E. Wegener, M. Gattinger, 2015, US20170144982A1
[26] Y. Román-Leshkov, J.N. Chheda, J.A. Dumesic, Science 312 (2006) 1933.
[27] V.V. Ordomsky, J. van der Schaaf, J.C. Schouten, T. Nijhuis ChemSusChem 5 (2012) 1812-1819
[28] A.C. Cope, R.T. Keller, J. Org. Chem., 21 (1956) 141
[29] G. Gonis, E.D. Amstutz, J. Org. Chem. 27 (1962) 2946-2947.

[30] A.S. Amarasekara, A. Razzaq, P. Bonham ISRN Polymer Science Vol 2013, Article ID 645169 Hindawi Publishing Corporation, 2013, ID 645169.
[31] V. Pamuk, M. Yilmaz, A. Alicilar, J Chem Technol Biotechnol 76 (2001) 186
[32] C.L., Mehltretter, United States Patent 1949, 2 472 168
[33] J. Matthey, Dutch Patent 1968, 6713 718
[34] A. Corma, S. Iborra, A. Velty, Chem. Rev. 107 (2007) 2411
[35] P. C. C. Smits, B. F. M. Kuster, K. Van der Wiele, et al. Appl. Catal. 33 (1987) 83
[36] M. Besson, G. Fleche, P. Fuertes, P. Gallezot, F. Lahmer, Recl. Trav. Chim. 115 (1996) 217
[37] From : http://www.rennovia.com/wp-content/uploads/2017/02/Johnson-Matthey-and-Rennovia-Announce-License-Agreement-with-ADM-for-Glucaric-Acid-Production-Technology-Press-Release-2-21-2017-1.pdf, accessed on 28.12.2018
[38] F. Dumeignil, M. Guehl, A. Gimbernat, M. Capron, N. Lopes Ferreira, R. Froidevaux, JS. Girardon, R. Wojcieszak, P. Dhulster, D. Delcroix. Catal. Sci. Technol. 8 (2018) 5708-5734
[39] V. Kuellmer, April 2001, posting date. Ascorbic acid. In Kirk-Othmer encyclopedia of chemical technology, 4th ed. John Wiley & Sons, NJ.
[40] F. Eisenberg, P. Dayton, J. Burns, J. Biol. Chem. 234 (1959) 250
[41] T.S. Moon, S.H. Yoon, A.M. Lanza, J. D. Roy-Mayhew, K.L. Jones-Prater, Appl. Envi. Microbio. 75 (2009) 589
[42] M. Zachariou, R.K. Scopes, J. Bacteriol. 167 (1986) 863
[43] S. Kambourakis, K. Martin, US 2014/0106414 A1
[44] E. Shiganawa, Y. Ano, T. Yakushi, O. Adachi, K. Matsushita, Biosc. Biotechnol. Biochem. 73 (2009) 241
[45] F. Hollmann, I.W. Arends, K. Buehler, et al. Green Chem. 13 (2011) 226
[46] T. Quinto, V. Köhler, T. R. Ward, Top Catal. 57 (2014) 321
[47] J. Gaitzsch, X. Huang, B. Voit, Chem Rev 116 (3) (2016) 1053–1093
[48] S.C. Tsang, C.H. Yu, X. Gao, K. Tam, J Phys Chem B. 110 (2006) 16914
[49] A.R. Herdt, B.S. Kim, T.A. Taton, Bioconjug Chem. 18 (2007) 183
[50] D. Li, Q. He, Y. Cui, L. Duan, J. Li, Bioch. Biophys Res Comm. 355 (2007) 488