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Recent advances in carboxylation of furoic acid into *2,5*-furandicarboxylic acid: different chemical pathways towards bio-based polymers

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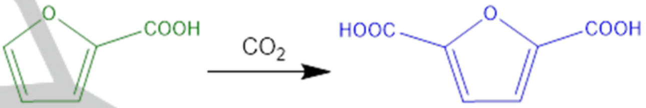
Abstract: 2,5-furandicarboxylic acid (FDCA) is one of the most important biosourced building blocks currently and several routes for its synthesis have been reported. FDCA is presumed to be an ideal green alternative for terephthalate, which is one of the predominant monomer in polymer industry. Herein, we present a review on the synthesis of FDCA using various carboxylation reactions. Thus, we discuss the synthesis of FDCA starting from furoic acid and CO_2 and using different catalytic and stoichiometric processes. This process is of high interest as it allows avoiding the glucose isomerization step and selectivity issues observed during the 5-hydroxymethylfurfural (HMF) oxidation step of the current alternative route to FDCA. We focus on the main parameters that govern the selectivity and activity in the carboxylation processes. Besides, various processes already described in the literature are also discussed such as Henkel reaction, enzymatic, homogeneous and electro-photo catalytic processes.

1. Introduction

The 2,5-furandicarboxylic acid (FDCA) is currently recognized as one of the most important “platform molecules” due to its potential application as a monomer in the synthesis of green polymers.[1–3] It was demonstrated that FDCA could efficiently replace terephthalic acid (TA), one of the most used petroleum-based monomers, in the polyethylene terephthalate (PET) synthesis. Three main methods of FDCA synthesis are described in the literature. The first abundantly described method is the oxidation of 5-hydroxymethylfurfural (HMF).[4–6] A second method concerns the conversion of different furanics compounds such as 5-acetoxymethylfurfural (5-AMF) or furoic acid (FA)[7] and the last and less described method is based on dehydration of sugar acids.[8,9] Until now, the best catalytic results were obtained using the first strategy. However, HMF is generally obtained from fructose, which must be of very high purity. It is also an edible product. Moreover, the current FDCA production process via dehydration of fructose to HMF followed by oxidation of HMF to FDCA is generally nonselective, as several unstable intermediate products could be formed.[10–13] Thus, the production of FDCA from hemicellulose-derived platform molecules issued from non-edible biomass is of high interest. Furfural could play this role as it is already industrially produced from a very long time from non-edible bio based resources. For many years, the hydrogenation of furfural for the production of fuels, such as tetrahydrofuran and 2-methyltetrahydrofuran have been widely studied.[8,14] However, the oxidation of furfural can lead also to very interesting products, such as 2-furoic (FuA)[15,16] or maleic acids[17]. Indeed, 2-furoic acid can undergo the C-H carboxylation with CO_2 to form FDCA[7,18] as represented in Scheme 1.



Scheme 1. Carboxylation of furoic acid with CO_2 to FDCA.

The first step, oxidation of furfural to furoic acid, is generally carried out in the presence of heterogeneous catalysts in a alkaline[19] or base-free solutions[20]. The second step is more complicated and can be performed using various processes. The direct catalytic and sustainable carboxylation of aromatic compounds by “simple” insertion of carbon dioxide into the sp^2 C-H bond is highly desirable. The first direct carboxylation of phenol with CO_2 was reported by Kolbe in 1860 and it is known as a Kolbe-Schmitt synthesis.[21–23] They demonstrated that the presence of the phenol group is essential in this reaction. However, as it could be stoichiometrically deprotonated its industrial application is still limited. Hitherto various carboxylation processes were studied such as: i) Henkel, ii) homogeneous catalysis, iii) molten salts, iv) enzymatic reactions and v) photo-electrocatalytic processes. However, many of these synthetic processes face important drawbacks. The most important are the necessity to use stoichiometric volumes of organometallic reagents and activated substrates. The first issue would be without any doubts the production of significant amounts of hazardous wastes, which is contradictory with the “Green Chemistry” principles. The second drawback is also very important because the activation of substrates (CO2 and furan derivatives) could be very time consuming and financially not acceptable. In the same way, the use of none-activated substrates would increase the overall cost of the process.[24]

In this purpose we discuss herein the various carboxylation processes reported in the literature for the synthesis of FDCA from furoic acid. We discuss the mechanism of the reaction and main drawbacks linked to each process.

Biographical Sketch.

((Author Portrait))

Biographical Sketch.

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2. Heterogeneous catalysts

2.1. Generality from Benzoic to Furoic acid

The Reacke/Henkel process (also called Henkel reaction), firstly reported in 1952[25,26], is one of the approaches to synthesize symmetrical diacids from an aromatic acid. This reaction takes place as a result of the thermal rearrangement or disproportionation of alkaline salts derived from aromatic acids, which gives rise to both the symmetrical diacids and the unsubstituted aromatic compound. This process has been applied for the production of potassium terephthalate and benzene from potassium benzoate in the presence of a metallic salt (e.g. cadmium, zinc…) in carbon dioxide or nitrogen atmosphere at high pressure and temperatures between 350 °C and 550 °C.[27–31] Once acidified; potassium terephthalate gives terephthalic acid which is the monomer used for the production of poly(ethylene terephthalate) (also called PET).

Although the main products in the Henkel reaction are the symmetrical diacids and the unsubstituted aromatic compounds, the formation of co-products in minor amounts such as benzophenone, diphenylmethane, triphenylmethane and phenylfluorene is possible.[32]

In this context, several catalysts have been studied and among them, cadmium[28,32,33] and zinc salts[34] have shown great performances. Indeed, Ogata *et al.* investigated a wide range of metal catalysts and claimed that Cd presented the best catalytic performances, followed by Zn for the phthalate rearrangement, achieving yields up to 80% when Ba, Ca, Cu and Sr showed poor catalytic performances.[31] Furthermore, the anionic portion of catalysts influenced largely the yield, following the order $I^- > Br^- > Cl^- > CO_3^-$ [31,35] whereas nitrates and sulfates were ineffective[36].

Regarding the reaction conditions, applying pressure between 3 and 68 bar of carbon dioxide seemed to favor the reaction, while using nitrogen or a lower pressure decrease the yield.[28] Revankar *et al.* performed a kinetic study on the thermal conversion of potassium benzoate, pointing out an optimal pressure of 11 bars.[35] Moreover, the presence of water, oxygen, hydrogen and acids could limit the Henkel reaction favouring side reaction as the cycle-opening or the decarboxylation of the diacids.[28]

Analogous to the Henkel process for terephthalic acid synthesis, the alkaline salts of furoic acid disproportionate in a similar way to produce FDCA.[37–41] Nevertheless, the Henkel reaction produced also furan as side product which can be hydrogenated to 1,4-butanediol.[42] A polycondensation could occur between the latter and FDCA to yield poly(1,4-butylene 2,5-furandicarboxylate) (PBF), a renewable alternative to PET.[43]

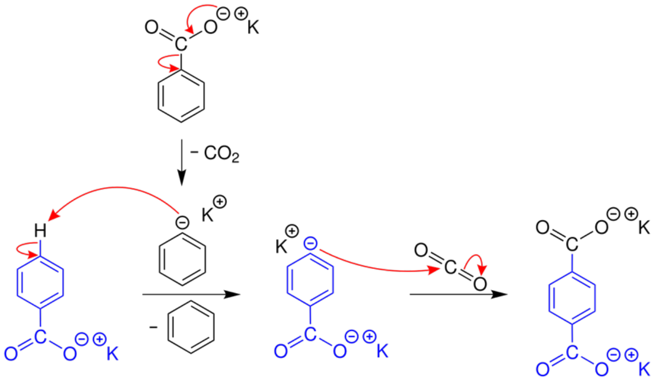
Recently, Pan *et al.* have reported a selectivity of 86% to FDCA with 61% conversion when the reaction is performed from potassium furoate using $ZnCl_2$ as catalyst, under 38 bars of CO_2 at 250 °C for 3 hours.[41] However, the 2,5-FDCA purity was not reported. The authors tested different Cd and Zn salts and Lewis acid catalysts (nickel salts). It was shown that the he anion of the catalyst has a significant impact on the furoate conversion. Both ZnO and Zn acetate gave any positive results while ZnCl2 was the most active with very good yield of FDCA (53%). The authors showed also that the presence of dry ice was beneficial for the reaction as the CO2 may be involved in the reaction mechanism.

Even if the reaction is selective to the formation of symmetrical diacids, Thiyagarajan *et al.* showed that asymmetrical diacids, as 2,4-FDCA, are also formed.[37,40] They performed the disproportionation of potassium 2-furoate at different temperatures and using several catalysts. Results showed selectivities towards FDCAs formation up to 91% using CdI_2 at 260 °C for 5.5 h under a low flow of N_2.[37] However, after performing the esterification of the crude reaction mixture with a methanolic HCl solution at 75 °C for 6 h, they concluded that the reaction products were a mixture of 2,4-FDCA and 2,5-FDCA (30:70, selectivity ratio of FDCAs) with traces of the 3,4-isomer.[37]

2.2. Mechanism of Henkel reaction

The Henkel reaction mechanism has been investigated by several authors.[29,44–47] Two mechanisms have been proposed for the disproportion of potassium benzoate.

The first mechanism, proposed by Ratusky *et al.*[46], for the synthesis of potassium terephthalate from potassium benzoate in the presence of CdI_2 is presented in Scheme 2.

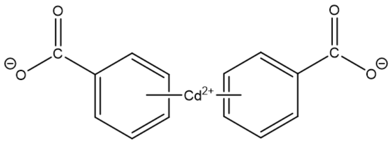


1 2 3

Scheme 2. Mechanism of Henkel reaction with of potassium benzoate.[27]

The disproportionation of potassium benzoate starts by a decarboxylation of the reactant giving a phenyl anion. According to the literature, the removal of the carboxylate group is considered as the rate-determining step in this reaction.[35,45] The phenyl anion, through a nucleophilic attack, deprotonates a second molecule of potassium benzoate (1) producing benzene and the carbanion of potassium benzoate (2). The negative charge is often located at the para- position of the carboxylate function due to a highest acidic character of the hydrogen on that position.[7,45,48] However, recent articles suggest that the negative charge is located in ortho- position, giving rise to the 1,4-isomer.[37] Then, (2) react with carbon dioxide through a nucleophilic attack leading to the dipotassium terephthalate (3). The latter is then protonated in the presence of HCl to obtain terephthalic acid.

The role of the catalyst during the reaction is not considered in the first mechanism. However, the second mechanism proposed by Ogata *et al.* suggests the formation of sandwich type complexes (Scheme 3) with two molecules of potassium benzoate and cadmium, when using a catalyst salt like CdI_2.[31,44,45] Furthermore, the use of a catalyst promotes the proton extraction and the decarboxylation step.[28,34,38] Indeed, the absence of catalyst in this reaction, provokes a decrease of the selectivity towards the thermodynamically favored symmetrical diacid, pointing out the pivotal role of the catalyst.[32]



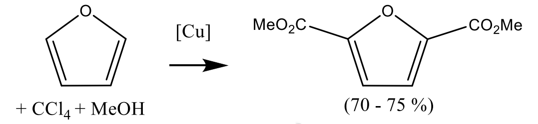
Scheme 3. Representation of the Cd^{2+} complex with two reactants as intermediate in the Henkel reaction.[31,44,49]

Regarding the disproportionation of potassium furoate to potassium FDCA, no mechanism has been yet proposed. Nevertheless, results of few studies have shown that the reaction favours the production of the symmetrical diacid (2,5-FDCA), suggesting that the mechanism could be similar to that observed for potassium benzoate.[37,40,41,50,51]

3. Homogeneous catalysts

There are only few papers dealing with the carboxylation of furan and furan derivatives using homogeneous catalysis. In 1943, Morton and Patterson, studied the methyl furoate synthesis from furan, n-amyl chloride and sodium sand.[52] They observed that after the carbonation at 140°C, dimethyl furan 2,5-dicarboxylate was obtained with 19% yield, which indicated that the formation of intermediate dianion occurred.

The direct carboxylation of furoic acid or methalation followed by carboxylation of furan derivatives was also reported. Khusnutdinov *et al.*[53] studied the direct synthesis of dimethyl furan 2,5-dicarboxylate with Cu salts and CCl_4. Using $Cu(acac)_2$, CuI, $CuBr_2$, and $Cu(OAc)_2$ as catalysts they succeeded to get 75% yield to dimethyl furan 2,5 dicarboxylate as represented in Scheme 4.

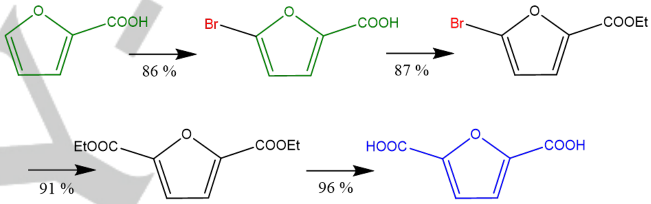


Reagents and conditions: [Cu] : [furan] : $[CCl_4]$: [MeOH] = 1 : 100 : 750 : 6500; [Cu] = $Cu(acac)_2$, CuI, $CuBr_2$, $Cu(Oac)_2$; 150 °C, 6 h.

Scheme 4. Carbonylation of furan. Adapted from Khusnutdinov *et al.*[53].

Moreover, they observed that this yield could reach 95% when furoic acid was used as starting material. No significant differences in the catalytic activity were observed for all the Cu salts tested with which the yield to diester always stayed in the 75-83% range.

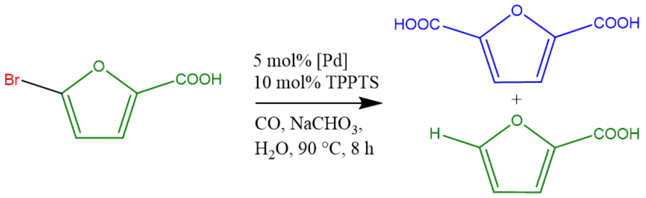
Furoic acid was also used for FDCA synthesis through multistep process involving cascade reactions: bromination, esterification, carbonylation, and hydrolysis. This four steps process can reach 65% total yield. Moreover, it was showed that the crucial step, namely the palladium-catalyzed carbonylation of ethyl 5-bromo-furan-2-carboxylate can reach 90% of isolated yield in the scaled-up process (Scheme 5).



Scheme 5. Carbonylation of ethyl 5-bromo-furan-2-carboxylate pathways. Adapted from Zhang *et al.*[54].

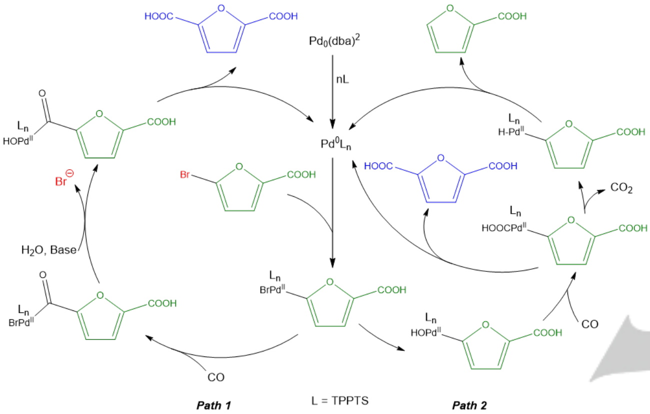
Taking into account the high yield obtained, the authors studied various palladium complexes. In the reaction, carried out in N-methyl-2- pyrrolidone (NMP) solvent using a CO source, and tri-n-butylamine (TNBA) as a base, different Pd catalysts were studied. 5 mol% $Pd(OAc)_2$ with 10 mol% PPh_3 as the ligand gave 48.2% yield with 99.6% conversion in 12 h at 100 °C. However, in the absence of PPh_3 ligand and using $Pd(OAc)_2$ as catalyst only 15.3% yield was obtained. Moreover, a significant amount of black palladium powder was observed indicating the metal reduction. When using other phosphine ligands such as dppb (1,4-bis(diphenylphosphino)butane) and dppp (1,3-bis-(diphenylphosphino)propane), a much lower activity compared to the one reached on Pd(OAc)2 was observed. However, the authors observed that using $PdCl_2$ as catalyst and dppf as ligand a higher yield of diethyl furan-2,5-dicarboxylate can be obtained as compared to the PPh3 ligand (47.2% and 43.2%, respectively). It is worth noting also that using a freshly synthetized $Pd(PPh_3)_2Cl_2$ complex as the catalyst even higher yield of desired diester can be obtained (52.7%). These results strongly indicate that the nature of ligation of phosphine ligand to Pd is the crucial parameter in the efficient furoic acid carbonylation reaction.[54]

The same group published also a second article on this subject using 5-bromo furoic acid as a starting substrate. Using various palladium catalysts and TPPTS (tris(3-sulfophenyl)phosphine trisodium salt) as the ligand very good yields of FDCA were obtained.



Scheme 6. Carbonylation of ethyl 5-bromo-furan-2-carboxylate using Pd catalyst. Adapted from Zhang *et al.*[55].

Simple Pd salts such as $PdCl_2$ and $Pd(OAc)_2$ gave more than 80% yield to FDCA with full 5-bromo-furoic acid conversion. In their study the $Pd(dba)_2$ catalyst and TPPTS ligand exhibited the best carbonylation efficiency providing FDCA with 93% yield and giving also 2% yield to furoic acid.

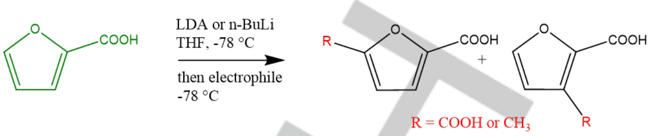


Scheme 7. Mechanism of the carbonylation using homogenous Pd based catalyst. Adapted from Zhang *et al.*[55].

The authors proposed also the mechanism of the carbonylation reaction (Scheme 7). Two main pathways were proposed depending on the pH of the reaction. Pathway A was dominant at a pH below 8, while pathway B could have a significant contribution at higher pH. In addition, both paths may competitively exist in the carbonylation reaction.

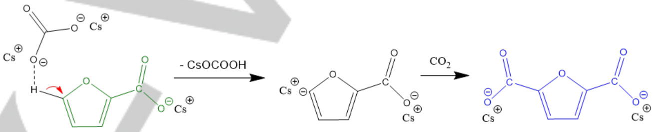
Carbonylation of 5-bromofuroic acid was also studied by Yin et al.[56-57] Common palladium based catalyst ($PdCl_2$) was used in DMF solvent and 99% yield of FDCA was obtained (90% isolated yield). The influences of the palladium precursor, phosphine ligands and different bases were studied and reported in details.[56-57]

The first study on dianions formation directly from furoic acid and using lithium di-isopropylamide (LDA) was reported by Knight and Nott.[48] They examined also the reaction of the lithium 5-lithiofuran-2-carboxylate formed with a wide range of electrophiles compounds such as CO_2. The authors observed the formation of dianion by the regioselective deprotonization of 5-furoic acid with LDA and its high reactivity with more or less reactive electrophiles. This regioselectivity was claimed to be strongly dependent on the type of lithium species used.[56] Contrary to that Fischer and Fišerová[58] observed the inversion of regioselectivity in favor of 2,3-regioisomer. They studied the one step carboxylation of furoic acid using CO_2 and n-butyllithium or LDA (lithiumdiisopropylamide). The reaction yielded a mixture of both regioisomers, namely 5-methylfuran-2-carboxylic acid and 3-methylfuran-2-carboxylic acid in a 35:65 ratio, together with a total yield of 83%.



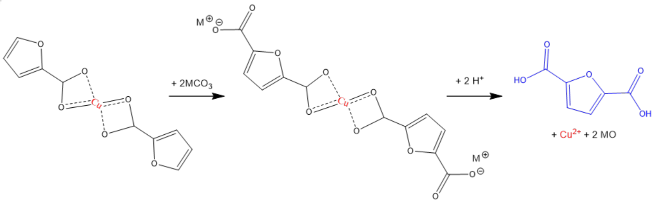
Scheme 8. Carbonylation using lithium di-isopropylamide as catalyst. Adapted from Fischer *et al.*[58].

The carboxylation reaction of furan derivatives compounds is generally favored by lowering the charge density on the cation.[50] This is why the inorganic carbonates with monovalent cations are efficient in the synthesis of FDCA from furoic acid by carboxylation at high pH following the mechanism proposed on Scheme 9:



Scheme 9. Mechanism of the stoichiometric carboxylation. Adapted from Kanan *et al.*[7,18]

Nocito *et al.*[50] studied the direct carboxylation of furoic acid with a Cu difuroate complex ($Cu(FC)_2$). They demonstrated that the coordination to Cu significantly increased the acidity of the hydrogen in position 5 on the ring. This strongly increases the efficiency of the decarboxylation reaction. It was showed that the carboxylation occurs more efficiently with $Cu(FC)_2$ than with FCA. The mechanism proposed by authors is given on Scheme 10.



Scheme 10. Formation of the Cu complexes during the direct carboxylation reaction. Adapted from Nocito *et al.*[50]

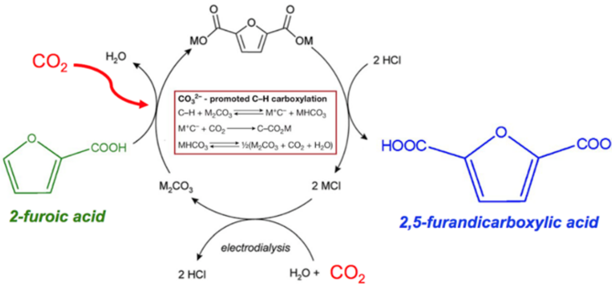
Moreover, studying the carboxylation reaction with and without CO_2 they stated that CO_2 does not play a direct role in the mechanism of the reaction. It serves only in the *in-situ* regeneration of carbonate species, as already observed by Kanan *et al.*[7,18,59]

4. Non-catalytic reactions

In parallel to the catalytic processes evoked in the above sections, non-catalytic ones have also proved to be highly efficient and considerably efficient for the conversion of furoic acid into 2,5-furan dicarboxylic acid.

In 2016, Banerjee and co-workers[7] have shown the possibility to promote the carboxylation of the very weakly acidic C-H bond using carbonate anion under a flow of carbon dioxide. The attractiveness of that pathway comes from a strong interest in the synthesis of polymer units from biomass sources and in the replacement of petroleum-originated units. Additionally, the employment of CO_2 as a feedstock in the transformation of non-edible biomass processes will help reducing the greenhouse gas emissions.

The proposed route overcame the constraints of inefficiency, and selectivity in the conventional hexose-based method of FDCA production. A route that was performed through a two-step mechanism, firstly CO_3^{2-} deprotonates the C-H bond to generate nucleophile centered-carbon that will secondly react with CO_2 to form the carboxylate function. The general scheme is illustrated in Scheme 11.



Scheme 11. Schematic illustration of the CO_3^{2-} promoted conversion of 2-furoic acid into 2,5-furandicarboxylic acid.[7,18]

Kanan's group[7] have started their study from the hypothesis that realizing the reaction in a molten salt would allow the deprotonation of furan-2-carboxylate by CO_3^{2-} in the presence of an alkali cation at a high concentration. The latter tends to stabilize the conjugate base by ion pairing.

The caesium furan-2-carboxylate and caesium carbonate have been used as the Cs^+ ion was found to be the most efficient when proceeding.

Concisely described, the experiment consisted in the heating of 1 mmol of caesium furan-2-carboxylate and 0.55 mmol Cs_2CO_3 at 260 °C under a 40 mL.min^{-1} carbon dioxide flow, the experiment was realized in a tube furnace. The FDCA^{2-} yield was 76% after 12 h. The starting material and the decomposition products have completed the carbon balance. It is worth noting that performing reactions in a batch reactor has improved yields and avoided decomposition.

A series of reaction have been also performed with the aim of gaining more insights into the mechanism and studying the parameters that control the FDCA^{2-} yield.

The study of the reaction scale effect has suggested that the reaction takes place at the interface salt-CO_2. It has been also proved that increasing the scale slows down the reaction and decreases the yield because of an induced decrease of the surface area-to-volume ratio. Besides, it is worth mentioning that reactors supplying better dispersion of the salt are very recommended for a better yield. The reaction time has not a significant effect on the yield. On the contrary, an increase of the temperature decreases the yield favouring decomposition.

Other alkali cation-based salts have been tested, no FDCA^{2-} has been produced after mixing furan-2-carboxylate and CO_3^{2-}. In that case, the mixture will require a higher temperature to melt, higher than 200 °C, a condition that provokes the decomposition. The limitation to Cs+ has been overcome by the obtention of a semi-molten mixture using potassium furan-2-carboxylate, K_2CO_3 and potassium isobutyrate. Similarly, it was found possible to produce FDCA^{2-} with addition of potassium acetate. C-H carboxylation is not restricted to caesium salts as already observed but these salts are still having the advantage of the lower melting points. Although all results were in agreement with the mechanism proposed in Scheme 11, other mechanisms where the carbanion intermediate is not involved are possible too. The realization of an isotope exchange experiment has revealed that the five positions of furan-2-carboxylate can be deprotonated and not exceptionally the fifth one.

This conclusion allowed explaining the origin of the selectivity of the adopted process, which is the very high abundance of the carbanion leading to the formation of FDCA^{2-}.

An immediate precipitation of FDCA can be carried out by an acidic treatment (3N HCl) of the crude caesium salt of FDCA^{2-}. CsCl will be left in the aqueous solution with a Cs^+ recovery percentage of 99%. The conversion of CsCl into HCl and caesium hydroxide solution can be performed via a bipolar membrane electrodialysis.[60,61] The acid is employed for the protonation step and the hydroxide is used to generate the starting material after reacting with 2-furoic acid and under CO_2 flow. The developed strategy is finally a free-organic solvent one that does not necessitate a costly extra distillation step of the product.

Along the same lines and a year later, in 2017, Dick *et al.*[18] have proved that the carboxylation of the C-H bond may take place efficaciously in the presence of alkali furoate and carbonates salts containing cation blends (K^+/Cs^+) with a high content of K^+ (K^+:Cs^+ 4:1). To avoid decomposition routes, they have also proved crucial the elimination of H_2O present as a by-product of the reaction.

The main objective of Dick and co-workers was to set a new approach and explore conditions, which are applicable for a very large-scale production. Without by-products, the approach is of high interest as it does not require a complicated and costly final step of purification.

The involvement of other cations was motivated by the relative scarcity of the annually mined Cs^+ salts. More crucially, alkali furoate/M_2CO_3 salts with K^+/Cs^+ preserves mixtures from undergoing a bulk phase transition to a molten phase. Using a fixed bed reactor, furoate was carboxylated with K^+/Cs^+ salts on a 1 mol scale (1000-fold higher than in Banerjee *et al.*[7] procedure) to obtain 89% of FDCA after protonation.

For more insights, small-scale and preparative-scale reactions using the conditions monitored on a fixed-bed flow reactor have been run as well.

To assess the effect of changing the salt composition, reactions on analytical scale (0.5 mmol) have been firstly surveyed. 2-fruoic acid and K_2CO_3/$CsCO_3$ aqueous solution have been mixed in a glass vial then dried to obtain a solid phase. With a continuous purge of carbon dioxide the generated solid was heated in a vial block during 17 h. Thereafter, the composition was assessed by NMR. In the presence of only Cs^+, a maximum yield of 71% has been reached at 260 °C. No FDCA^{2-} has been observed using only K^+. On the other hand, the yield of FDCA^{2-} was within the 60-70% range with K^+/Cs^+ blends containing a K^+ proportions going from 1 to 4 (1:1 to 4:1 K^+:Cs^+). It is obvious that the yields are not thoroughly optimal using the vial block reactor but the process allows a quick analysis of the impact of the salt composition. The temperatures coinciding with the optimal yields increased concomitantly with the K$^+$ proportion to reach 295 °C when K$^+$:Cs$^+$ equals 4. Unreacted furoate, insoluble char and smaller amounts of acetate and malonate completed the mass balance.

To investigate the origin of that products, furoate and carbonate were heated from 265 to 295 °C under N$_2$ flow for 6 h. The same composition was obtained. Decomposition was found to increase with temperature and Cs$^+$ content. K$^+$ cation was found to lead to a better thermal stability.

It has been shown that decomposition under nitrogen was in some cases higher than under carbon dioxide and comparable in other atmospheres. At 285 °C as an example, a 63% of FDCA^{2-} yield was obtained with K$^+$:Cs$^+$ 2:1 blend under CO$_2$ for 17 h, however more than 90% of the furoate has decomposed after only 6 h under nitrogen. Contrary to that and regardless the cation compositions, FDCA^{2-} showed a good thermal stability under N$_2$ at the same temperature. Carbon dioxide serves for both quenching the decomposition and the carboxylation reaction.

Water as a by-product of the carbonate promoted C-H bond carboxylation and source of hydroxide ions was expected to be at the origin of the furoate decomposition via a nucleophilic attack. To check the availability of that hypothesis, water pre-saturated CO$_2$ has been employed maintaining optimal other conditions of K$^+$:Cs$^+$ ratio (2:1) and temperature (290 °C). FDCA^{2-} decreased from 70 to 31%. Water has been confirmed to slow down FDCA^{2-} synthesis without continuously promoting decomposition when only Cs$^+$ cation is used. The decomposition of products was very remarkably increased with the 2:1 K$^+$:Cs$^+$ blend. A fixed-bed flow reactor has been used in order to overcome the poor carbon dioxide transport in the vial block reactor where it can be only flowed through the headspace above the solid phase. Besides, static and flowing CO$_2$ effects have been studied. The results revealed that under flowing carbon dioxide, FDCA^{2-} yields were noticeably better, generated water being removed away and decomposition being eliminated.

Moreover, forcing CO$_2$ through the solid matter may permit the exposition of salt particles to the gas. Interestingly, fixed-bed experiment proved the possibility of producing FDCA^{2-} with cation blend where the Cs$^+$ content is very low, a yield of 56% has been reached with 20:1 K$^+$:Cs$^+$ ratio. The conditions that have been set with the fixed-bed reactor were used to test the carboxylation on preparative scales. A lower FDCA^{2-} yield has been obtained on a 100 mmol scale, only 66% in comparison to 78% reached on the 10 mmol scale using the fixed-bed reactor (under flowing CO$_2$). The decomposition was more pronounced. It has been supposed that the change of solid powder (fine powder) into compact large mass reduces the solid-gas contact. This may hinder water removal, slow down the carboxylation process and enhance decomposition. Performing tests under temperature gradient permitted to improve yield and attenuate decomposition. It may slow down the compaction of the powder and hence provide a better accessibility for the carbon dioxide.

To sum up, high yield of isolated FDCA have been obtained on a preparative scale (> 100g) with a free solvent and catalytic process. It has been shown that Cs$^+$ is required for the carboxylation but also that cation blends K$^+$/Cs$^+$ with the 1:2 and 1:4 ratios are efficient. For example, 89% of isolated FDCA yield has been reached with 1:2 K$^+$:Cs$^+$ ratio using a fixed-bed reactor. It must be emphasized that the proposed production strategy was not cesium consuming because of a possible cation recovery via a bipolar membrane electrodialysis after the FDCA^{2-} protonation.

5. Enzymatic carboxylation

In recent years, biocatalysis was shown to be an important tool for obtaining FDCA. With the advent of recombinant DNA and metabolic engineering techniques, several microorganisms became able to better oxidize or reduce furfural to the corresponding carboxylic acid or alcohol.[62] Some of them are also capable of utilizing HMF or furfural as the sole carbon source for growth.[62] However, the enzymatic carboxylation of furoic acid is still scarcely reported in the literature, being a promising field for further studies.

The degradation for both furfural and HMF pathways involves the decarboxylation of 2,5-furandicarboxylic acid (FDCA) to furoic acid. Previous authors found that in *E. coli* strains this step occur due the presence of UbiD and UbiX genes that codificate a prenylated flavin (prFMN) dependent UbiD family of reversible (de)carboxylases.[63,64] Some enzymes of this family decarboxylases have been demonstrated be able to catalyze carboxylation under excess of CO$_2$.[62-64]

Recently, Payne *et al.* published a detailed characterization of homolog UbiD genes HmfF HmfF from thermophilic *Pelotomaculum thermopropionicum*, revealing that the active site located above the prFMN cofactor contains a furoic acid/FDCA binding site composed of residues H296-R304-R331 specific to the HmfF branch of UbiD enzymes. Besides, it was also demonstrated that HmfF was able to produce FDCA by furoic acid carboxylation at elevated CO$_2$ levels *in vitro*. [65]

6. Summary and Outlook

The Henkel reaction has been scarcely studied in the last decade. The disproportionation of biobased C$_5$ compounds such as furoate has shown high efficiency in conversion and selectivity while information on the mechanism and kinetics are still missing. Thus, the interactions solid-solid in this reaction between reactant and catalyst are still to be more studied to improve catalytic performances.

It is worth noting that for a larger industrial scale, the kinetics of the non-catalytic route of 2-furoic acid conversion into FDCA must be improved. Some parameters have to be controlled, namely the mass transport and the compaction of the mixture as observed in fixed-bed reactors. A device supplying a better gas-solid contact would considerably boost the production of isolated FDCA at a large scale.

It has been demonstrated through this article that enzymatic catalysis represents a challenging discipline that can offer many advantages for the catalytic valorization of furan derivatives and permits to produce FDCA. The great versatility of enzyme catalysts makes theoretically possible to develop an efficient process, while offering substantial atomic and energy savings, particularly with regard to the biorefineries of tomorrow. However, the enzymatic carboxylation of cyclic compounds is still in its infancy, and many challenges remain to be met, both in terms of biological catalysts and in the field of materials and reactors and the development of innovative processes to achieve the effective combination of the latter. In addition, the engineering of thermostable enzymes is of high importance to permit to increase the productivity and possibility to use cooperative chemo-enzymatic catalysts. In addition, cofactor regeneration methods are currently being studied. The first studies report the efficiency of organometallic complexes for cofactor regeneration and in respect of green chemistry principles to reduce separation energy costs and meet the sustainability requirements. However, more efficient and selective complexes as well as a more in-depth study of compatibility with the enzymes are still required in this field.

Carboxylation of furoic acid was studied using homogeneous catalysis. However, this topic still remains a challenge especially for industrial applications. State-of-the-art data revealed substantial limitations, such as stability of the metal complexes. This is especially important with regard to tandem processes: carboxylation and esterification to FDCA esters. In this case the development of recyclables systems and new materials for the carboxylation is highly desirable. Moreover, no clear insights on the mechanism of the reaction are provided, which also hinders concrete progress in this field. In particular, there is a clear lack of understanding of the correlations between the catalyst design and the activation of the furoic acid molecule. In addition, in parallel of experimental works, theoretical studies should be performed to better understand the crucial parameters to develop more efficient homogeneous catalysts. The effects of the electronic properties that govern the ability of the catalysts to efficiently carboxylate have not yet been explored.

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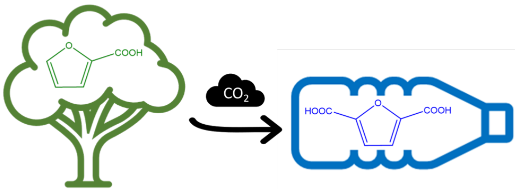
Entry for the Table of Contents



Getting greener with the polymers: The production of new sustainable polymers is of high importance. As discussed in this review, several chemicals and catalytic pathways are possible using furoic acid as a starting molecule to get FDCA. However, this topic still suffers from a lack of systematic studies. Herein, we critically discussed various routes to FDCA using non-chemical catalytic and catalytic carboxylation processes.