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Review

Recent Advances in Catalytic Conversion of Biomass to 2,5-Furandicarboxylic Acid

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Abstract: Converting biomass into high value-added compounds has attracted great attention for solving fossil fuel consumption and global warming. 5-Hydroxymethylfurfural (HMF) has been considered as a versatile biomass-derived building block that can be used to synthesize a variety of sustainable fuels and chemicals. Among these derivatives, 2,5-furandicarboxylic acid (FDCA) is a desirable alternative to petroleum-derived terephthalic acid for the synthesis of biodegradable polyesters. Herein, to fully understand the current development of the catalytic conversion of biomass to FDCA, a comprehensive review of the catalytic conversion of cellulose biomass to HMF and the oxidation of HMF to FDCA is presented. Moreover, future research directions and general trends of using biomass for FDCA production are also proposed.

Keywords: biomass; 2,5-furandicarboxylic acid; 5-hydroxymethylfurfural; biocatalysis

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1. Introduction

In the 20th century, non-renewable resources such as petroleum and fossils made important contributions to economic and social development, and currently, people are becoming increasingly dependent on non-renewable resources such as petroleum. At the same time, the contradiction between the reduction in the storage of non-renewable resources and the increasing fuel demand, as well as the environmental pollution caused by the excessive development and use of fossil resources, has become a huge challenge facing humanity [1,2]. Faced with such a dilemma, people have proposed ways to find renewable alternative resources [3]. Lignocellulosic biomass is one of the most attractive alternative raw materials, which is mainly composed of cellulose (40–50%), hemicellulose (16–33%), and lignin (15–30%) [4]. Therefore, the conversion of lignocellulose into valuable chemicals and fuels has aroused great interest among researchers. The first article published in 1951 by Newth et al. on the production of furan from carbohydrates led researchers to gradually increase interest in the production of bio-based chemicals through a catalytic process [5]. Among these bio-derived molecules, 2,5-furandicarboxylic acid (FDCA) has gained increased attention because of its chemical properties as it can produce various polymers (Figure 1). FDCA can perfectly replace the petroleum-based polyester monomer terephthalic acid that is currently used in the production of PEF [6,7]. FDCA is not only used extensively for the synthesis of bio-based polymers but also serves as a versatile synthetic intermediate in organic synthesis, pharmaceuticals, and metal–organic framework materials [8]. In 2025, FDCA is predicted to reach a market value of approximately EUR 770 million, with a compound annual growth rate of about 11% [9].

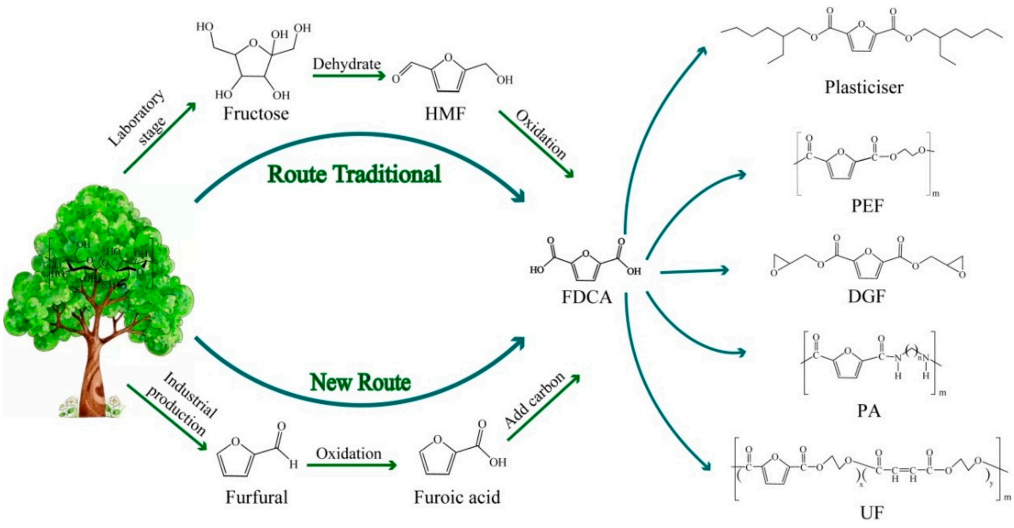

Figure 1. Synthetic pathway of FDCA and its derivatives from biomass.

FDCA can be synthesized from a variety of substrates such as furoic acid [10], furan [11], adipic acid (galactaric acid or glucaric acid), glycolic acid, and 5-hydroxymethyl furfural (HMF) [12] (Figure 2). Among these starting materials, HMF, the dehydration product of C_6-based carbohydrates, is a bridge between biomass and bio-based compounds. Hence, catalytic oxidation of HMF is the most promising route for industrial production of FDCA [13–15]. In addition, FDCA can also be directly synthesized using biomass as a raw material.

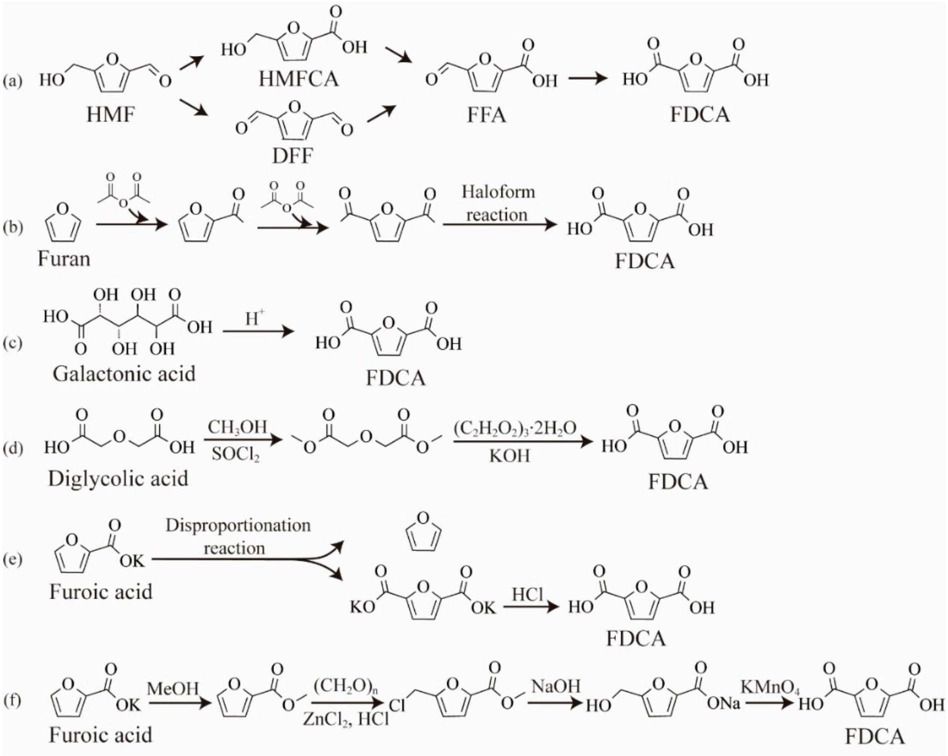

Figure 2. Schematic illustration of FDCA production with different substrates. (**a**) Synthesis of FDCA from HMF via two potential routes; (**b**) production of FDCA from furan by haloform reaction; (**c**) conversion of galactonic acid to FDCA under acidic conditions; (**d**) preparation of FDCA via dimethyl diglycolate from diglycolic acid; (**e**,**f**) production of FDCA from furoic acid through different catalytic pathways.

In this review, we first introduce the progress in the production of HMF from biomass and then summarize the recent developments for FDCA production from HMF. Moreover, the latest achievements in the direct production of FDCA from biomass are also introduced.

2. Catalytic Conversion of Biomass to HMF

HMF, an indispensable member of the furan-based platform compound, known as the "sleeping giant", is a bridge between renewable biomass and industrial bulk chemicals [16,17]. In recent years, the catalytic transformation of biomass to HMF has been widely studied and envisaged to be hopeful in achieving sustainable biorefineries. The synthesis of HMF from biomass requires the acid hydrolysis of biomass to hexose, and then dehydration of hexose, to obtain HMF. In the second step of dehydration, starting from ketohexose (fructose) is more efficient than starting from aldohexose (glucose) [2].

2.1. Synthesis of HMF from Fructose

HMF is mainly converted from natural cellulose, glucose, or fructose. Among these processes, the most studied and generally the easiest is HMF from fructose. When the dehydration reaction starts from ketohexoses (such as fructose), it is more selective and efficient [18]. Although from a stoichiometric point of view, the reaction looks quite simple, that is, the formal elimination of three water molecules from fructose, the design of catalysts that achieve high-yield HMF production is made difficult by the lack of understanding of the mechanistic aspects of fructose conversion to HMF [19,20].

Solid acid catalysts are very effective for the dehydration of fructose to HMF. Hou et al. investigated an efficient reaction system using sulfonated graphene oxide (SGO) as a solid acid catalyst for the production of HMF from fructose, where the HMF yield could reach 94% [21]. Songo et al. investigated the TiO_2C solid acid catalyst for use in the catalytic dehydration of fructose to HMF. It was found that when using TiO_2C as the catalyst, dimethyl sulfoxide (DMSO) as the solvent, and a reaction temperature of 120 °C, the catalyst yield can reach as high as 90% after one hour of catalysis [22]. Wang et al., using a sulfonated carbonaceous material as a solid acid catalyst for the dehydration of fructose to HMF in DMSO, achieved 96.1% conversion of fructose, and an HMF yield of 93.4% [23]. Moreover, several mineral acids such as H_2SO_4, HCl, and H_3PO_4 have been used in the catalyzed dehydration of fructose to yield HMF [24]. Ava-Biochem utilized the simple thermal route, heating fructose in the presence of aqueous H_2SO_4 to produce HMF, although low yields were obtained [25]. Thus far, the selectivity and yield of reactions implemented in aqueous reaction systems are not comparable to those observed in aprotic high-boiling organic solvents such as DMSO, where the solvent also acts as the catalyst. Zhao et al. developed a sulfonated carbon sphere solid acid catalyst that produced 90% of HMF in DMSO as a solvent for 1.5 h at 160 °C with 100% conversion of fructose [26]. Guo et al. investigated a lignin-derived carbonaceous catalyst to convert fructose into HMF under microwave irradiation in a mixture of ionic liquid and DMSO at 110 °C for 10 min with 98% conversion of fructose and an HMF yield of 84% [27]. Hu et al. explored the use of a magnetic lignin-derived carbonaceous acid catalyst for the catalytic conversion of 100% fructose into 81.1% HMF in DMSO as a solvent [28]. Ionic liquids (ILs) are also used as solvents, which are expensive, and it is very troublesome to recover HMF from high-boiling IL systems. Water formed during the dehydration reaction often deactivates ILs, and high-boiling point solvents such as DMF and DMSO are unable to resolve the drawbacks related to the separation issues over different bifunctional acid catalysts [29].

Marullo et al. studied the dehydration of sucrose and fructose to HMF in the presence of Amberlyst 15, using eight deep eutectic solvents (DESs) as solvent media, differing by their hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs). By optimizing the reaction conditions, they obtained a yield of HMF of 78% at 60 °C and 69% at 80 °C for fructose [20].

To further explore the novel and cost-efficient technologies for selective dehydration of fructose to HMF, photocatalysis is a promising candidate for inhibiting the side reactions at high temperature [30]. Fu et al. reported that Brønsted acidic $Ag_{@}ZnFe_2O_4$ NWs exhibit excellent photo-Fenton catalytic activity for the dehydration of fructose to HMF under visible light irradiation [31].

Catalytic reaction systems such as solid acid catalysis, magnetic carbon-based catalysis, and photocatalysis all have problems such as low target product selectivity, difficulty in separating the product from the catalytic system, and many by-products.

2.2. Dehydration of Glucose to HMF

Glucose is the desirable source of HMF, attributed to the lower cost compared to fructose [18]. Glucose is one of the richest monosaccharides in biomass, accessible by chemical or enzymatic hydrolysis from cellulose, starch, or sugar. Moreover, a variety of chemical products can be achieved from glucose which positions it in a critical position as a basic raw material/building block. Aldohexoses (such as glucose) can only enolize to a low degree, which is considered the limiting step in the production of HMF from glucose [18].

Up to now, most studies regarding the acid-catalyzed conversion of fructose and, to lesser extent, glucose to HMF carried out their investigations in aqueous reaction media [18]. Imidazolium-based ILs represent the most extensively studied ones for the dehydration of glucose to HMF. Zhao et al. reported that $CrCl_3^-$ in 1-alkyl-3-methylimidazolium chlorides could be used as an effective catalyst for the dehydration of glucose to HMF. The pivotal role of $CrCl_3^-$ was to affect a formal hydride transfer by forming hydrogen bonds with the hydroxyl groups of glucose, causing glucose to isomerize to fructose which is easily dehydrated to HMF [32]. This can be explained by glucose only being able to enolize to a low degree, which is considered the limiting step in the production of HMF from glucose. Therefore, the challenge for the production of HMF from glucose is to find a catalytic system that can selectively isomerize glucose to fructose in tandem with the dehydration reaction.

Dessbesell proposed converting starch into glucose through enzymatic hydrolysis and then using niobium phosphate to catalyze the dehydration of glucose to produce HMF, which is low cost and high in efficiency [33]. Wang et al. reported a high-yield (62%) reaction system for the catalytic conversion of glucose to HMF. The reaction system is divided into an organic phase and an aqueous phase. The organic phase consists of an alkylphenol compound (2-sec-butylphenol), and the aqueous phase consists of a Lewis acid metal chloride (e.g., $AlCl_3$) and Brønsted acid (e.g., HCl). The conversion of glucose to HMF in this biphasic reactor system in the presence of Lewis acid salts through a tandem reaction involves glucose being isomerized into fructose and the dehydration of fructose [34].

A cost-efficient and convenient method featuring the integration of acid and enzymatic catalysis has been investigated for the selective conversion of glucose into HMF, which provides a new strategy for HMF production from glucose. Huang et al. reported an HMF yield of 63% from glucose in a biphasic system by a two-step process consisting of the isomerization of glucose to fructose using borate ions and glucose isomerase, followed by the acid-catalyzed dehydration of fructose to HMF using HCl as a catalyst [35]. Nikolla et al. reported that the application of Lewis acidic Sn-Beta zeolite along with aqueous HCl could convert glucose to HMF at 180 °C in a biphasic system with about 60% HMF selectivity. However, in the context of green chemical pathways, the corrosivity of HCl is a limiting factor [36]. Recently, Abu-Omar et al. used $AlCl_3{\cdot}6H_2O$ as the catalyst and THF as the extracting solvent for the production of HMF from glucose in a biphasic system with an HMF yield of 61% [27,37]. Feng et al. discovered that a metal catalyst supported by MCM-41 had an excellent performance in converting carbohydrates into HMF [38]. A one-pot/two-step hybrid catalytic pathway was recently reported by Gimbernat et al. for HMF production from glucose in a triphasic compartmentalized reactor [39]. The preparation of HMF from glucose is a complicated process. In order to achieve high yields, future research needs to pay attention to the research on the reaction mechanism and reaction kinetics of HMF from glucose; find low-cost, green, and efficient catalytic systems and solvent systems; and establish high-efficiency and low-energy consumption product separation technology to reduce costs.

2.3. Synthesis of HMF from Cellulose

The cellulosic fraction of biomass is an abundant renewable feedstock and the most widely distributed natural polymeric material on earth. Cellulose is a linear polymer consisting of several units of glucose joined together by β-1,4-glycosidic bonds [7]. In recent years, an increased effort has been conducted to utilize this cellulosic biomass fraction for the production of fuels and chemicals as renewable alternatives to petroleum-based resources [40]. Compared with glucose dehydration, the direct conversion of cellulose to HMF is more attractive and challenging. The production of HMF from cellulose is still not operative at an industrial level [41]. Generally speaking, the conversion of cellulose to HMF requires three steps: the hydrolysis of cellulose into monosaccharides, the isomerization of aldose-type sugars to ketose-type sugars, and the subsequent dehydration of ketose-type sugars to HMF [32] (Figure 3).

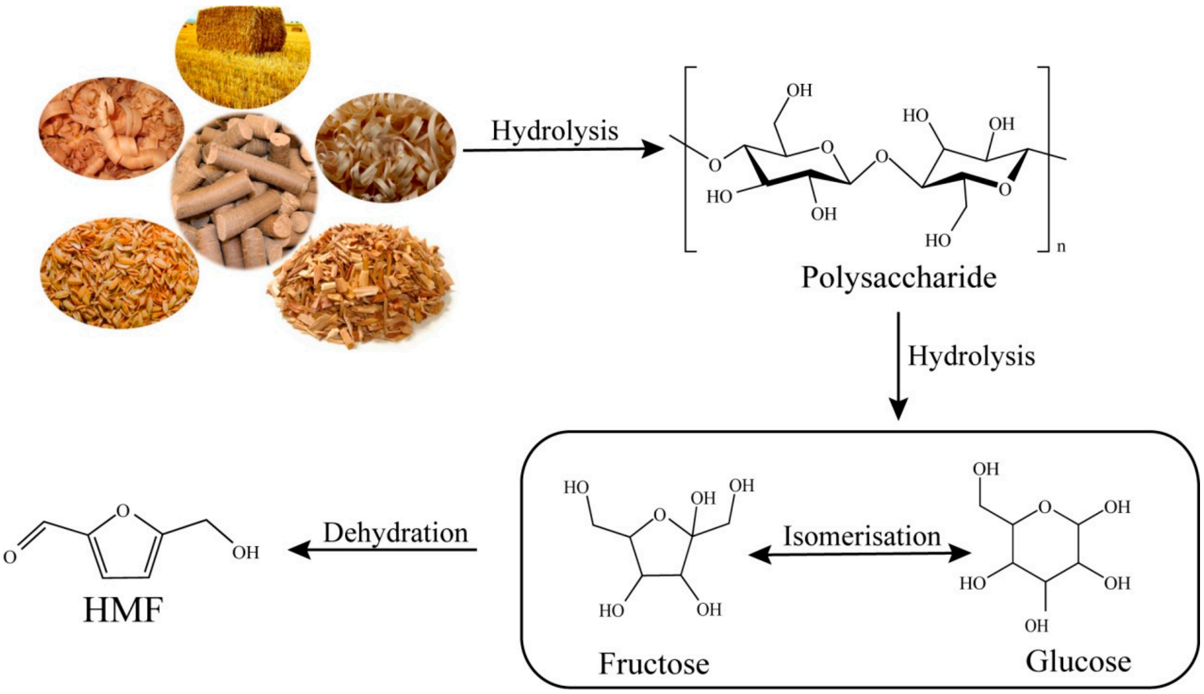

Figure 3. Catalytic conversion of cellulose into HMF.

The production of HMF from cellulose catalyzed by a series of transition metal chlorides (i.e., $FeCl_3$, $RuCl_3$, VCl_3, $TiCl_3$, $MoCl_3$, and $CrCl_3$) was studied in a biphasic system. $RuCl_3$ was the most efficient catalyst among these transition metal chlorides for HMF production and resulted in both the highest yield of 83.3% and selectivity of 87.5% in a NaCl-aqueous/butanol biphasic system [42]. Zhang et al. reported the $CuCl_2$- and $CrCl_2$-catalyzed transformation of cellulose, and 58% HMF was achieved in IL([EMIM]Cl) [43]. Kim et al. also reported the formation of 58% HMF from cellulose using $CrCl_2$ and $RuCl_3$ as the catalyst in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) [44]. It was reported that using *N*,*N*-dimethylacetamide containing lithium chloride (DMA-LiCl) as the solvent and 10% $CrCl_3$ and 10% HCl with 60% [EMIM]Cl as the catalyst produced HMF and furfural with a yield of 48% and 34%, respectively, at 160 °C after 2 h from corn stover [45]. Due to the complex structure of lignocellulose, its conversion is difficult. Researchers are seeking efficient methods to allow cellulose to develop in the direction of mild conditions, easy operation, low cost, fast speed, environmental protection, and green production, and to realize the organic connection between the cellulose preparation platform compound and the existing energy chemical industry.

3. Synthesis of FDCA from HMF

The chemical conversion of HMF into furanic derivatives is challenging because both the formyl and the hydroxymethyl groups can undergo oxidation to various extents, leading to several possible products with variable stabilities [46]. Due to the great potential of FDCA, its production via the oxidation of HMF has received increased attention in recent years.

3.1. Synthesis of FDCA from HMF Using Heterogeneous Metal Catalyst

Precious metal catalysts have been widely studied because of their high catalytic activity, high-temperature resistance, corrosion resistance, and oxidation resistance. In most of the traditional synthesis approaches for the oxidation of HMF to prepare FDCA, noble metals and oxygen (or air) were essentially employed as the catalyst and oxidant, respectively [47].

The Pt catalyst is one of the most important varieties of precious metal catalysts. The use of Pt for efficient catalysis and oxidation of HMF has been extensively investigated (Table 1). Verdeguer reported that Pt-Pb/C catalysts and oxygen catalyze the oxidation of HMF to produce FDCA. The reaction needs to be carried out in a strongly alkaline aqueous medium. The reaction time is less than 2 h, the recovery rate of FDCA can reach 81%, and the purity can reach 99% [48]. Liguori et al. reported the synthesis and characterization of a heterogeneous, resin-supported Pt catalyst and its use in the one-pot oxidation of HMF to FDCA in neat water under continuous flow conditions [49].

Au shows good catalytic performance in the selective oxidation of hydrocarbons. It is a type of “green” selective oxidation catalyst with great potential. The Au catalyst can catalyze the oxidation of HMF to FDCA. Casanova et al. investigated the effect of Au/TiO_2, Au/CeO_2, Au/C, and Au/FeO_2 catalysts on the oxidation of HMF in the air [50]. For heterogeneous metal-catalyzed aerobic oxidations, the high manufacturing cost of noble-based or bimetallic catalysts, the potential leaching of metal ions, and the employment of an excessive inorganic base severely hamper their industrial applications [8]. Danielli et al. used a trickle-bed reactor in the presence of the Ru/Al_2O_3 catalyst. Oxidation of HMF to FDCA was carried out over Ru/Al_2O_3 using O_2 aqueous alkaline solutions in a trickle-bed reactor. HMF was completely converted at 30 bar O_2, 140 °C, resulting in 98% FDCA selectivity [51].

A novel hierarchical porous nitrogen-doped carbon (NC)-supported bimetallic Au/Pd catalyst was synthesized by the Pickering high-internal phase emulsion (Pickering HIPE) templating method, subsequent carbonization, and the sol-curing technique, and the highest yield of FDCA at 96.7% was achieved under the optimal reaction conditions [52]. Pt NPs supported by NC-800 (Pt/NC-800) proved to be an efficient catalyst in the aerobic oxidation of HMF to FDCA [53]. Partenheimer reported the production of FDCA from HMF using the Co/Mn/Br catalyst in an acetic acid solvent via aerobic oxidation, with a 60.9% FDCA yield [54]. Chen et al. studied the homogeneous aerobic oxidation process of HMF to FDCA with detailed side reactions and proposed a general reaction network for HMF oxidation over the Co/Mn/Br catalyst. After investigating the influence rule of the reaction variables on both the main reactions and side reactions, they found that purified FDCA with a high selectivity can be successfully obtained under optimized conditions [55]. Generally, most heterogeneous catalysts can achieve higher FDCA yields. However, noble metal nanoparticles have a high cost and poor stability, and catalyst deactivation is still the main obstacle to the large-scale use of FDCA.

3.2. Synthesis of FDCA from HMF Using Homogeneous Metal Catalysts

Most of the homogeneous catalyzed oxidations of HMF took place in copious amounts of organic solvents or corrosive acids. The aerobic oxidation of HMF with heterogeneous

Au–TiO_2 and Au–CeO_2 and homogeneous $Co(OAc)_2/Zn(OAc)_2/Br^-$ nanoparticulate catalysts was carried out in acetic acid with and without a trifluoroacetic acid (HTFA) additive. The homogeneous oxidation catalyst showed a higher selectivity for FDCA (60% yield) under 1 atm of O_2 at 90 °C, while Au–TiO_2 afforded 80% FFCA under the same conditions [56]. However, homogenous catalysis has faced problems in processing and recycling [57]. Au/$Mg(OH)_2$ is a metal–solid base catalyst used in the oxidation of HMF. Under optimal reaction conditions, the yield of FDCA can reach 92.6% [45]. A novel composite catalyst, $Ru_xCoO_y(OH)$, was prepared by the simple one-pot hydrolysis of Ru and Co salts at room temperature in the presence of $NaBH_4$. This catalyst showed promise for the aerobic oxidation of HMF to FDCA under environmentally benign conditions, using O_2 as the oxidant, water as the solvent, and no soluble base additives. It was shown that the $Ru_4CoO_y(OH)$ catalyst with an enhanced Ru−Co metal interaction was the most active, providing a 99.9% yield of FDCA at 10 bar of O_2 and 140 °C after 18 h, corresponding to high productivity (3.3 mol FDCA mol Ru^{-1} h^{-1}) compared to that of the Ru-based benchmark catalysts in the literature [58]. A Co_3O_4 NP-decorated Mn-Co-O solid solution, donated as Co_3O_4/Mn_XCo, was prepared by the co-precipitation method and used as a non-precious metal catalyst for the base-free oxidation of HMF to FDCA in the presence of O_2 and water [59].

Homogeneous catalysts act independently of molecules or ions, with uniform active centers, high activity, and high selectivity, but usually have problems related to catalyst recyclability, low yield, high energy costs, by-product formation, and environmental pollution.

3.3. Electrocatalytic Oxidation of HMF into FDCA

Electrocatalytic refinement of bio-derived raw materials is becoming a sustainable and environmentally friendly method of producing high-value chemicals. Compared with the thermal catalytic process that usually collects energy from oxidizers and reducing agents at elevated temperatures and pressure, electrochemical oxidation is carried out at normal temperatures and pressure, and the electrochemical reaction driven by the applied potential can proceed without a chemical oxidizer. As it eliminates the impact of using chemical oxidants harmful to the environment, it is considered a clean synthetic method. The electrochemical oxidation of HMF is a good choice for FDCA production [60].

Barwe et al. prepared FDCA using a high-surface area Ni foam modified with a high-surface area nickel boride as the electrode, with a yield of 98% [61]. In this study, nickel borides (NiB_x) doped with different amounts of phosphorus were prepared by a simple method and applied to the electrocatalytic oxidation of HMF. It was found that the FDCA yield on P-doped NiB_x (NiB_x-P_y) gradually improved first and then decreased with the increase in the phosphorus content [62]. Zhang et al. showed that NiB_x displayed excellent selectivity, conversion, and faradaic efficiency values at both the cathode and the anode simultaneously using water as the oxygen and hydrogen source. A conversion efficiency and selectivity of ≥99% were observed during the oxygenation of HMF to FDCA and the simultaneous hydrogenation of p-nitrophenol to p-aminophenol [60].

Cai, MK researched the possibility of HMF electrooxidation into FDCA by Ni-based two-dimensional metal–organic frameworks (2D MOFs) as electrocatalysts [63]. Liu et al. developed earth-abundant bimetallic NiFe-layered double-hydroxide nanosheets on carbon fiber paper as the anode for the electrochemical oxidation of a highly concentrated solution of HMF to FDCA, with a 99% faradaic efficiency [61]. Gao et al. reported a TiO_x@MnO_x electrocatalyst which can obtain FDCA precipitation in one step in acidic media. The TiO_x@MnO_x catalyst with the active MnO_x species was confined in the acid-resistant TiO_x nanowires and obtained a consistent yield of FDCA precipitation in the continuous conversion of 100 mM HMF (similar to 24% under the stoichiometric charge). TiO_x@MnO_x is a practical and inexpensive catalyst for the sustainable synthesis of FDCA in an acidic electrocatalysis system [64]. Zhang et al. developed a facile and scalable synthetic immersion approach to grow ultrathin nickel hydroxide nanosheets in situ on commercial nickel foam (Ni(OH)(2)/NF) as an anode for the electrocatalytic oxidation of HMF to FDCA with complete HMF conversion, 100% FDCA yield, and >99% faradaic efficiency at 1.39 V (vs. RHE) within 90 min [65].

In recent years, research efforts have been devoted to exploring different electrocatalysts and processes, which have led to fundamental mechanistic understandings of ECH (electrocatalytic hydrogenation) and ECO (electrochemical oxidation).

3.4. Biocatalytic Oxidation of HMF into FDCA

Biocatalysis is preferred owing to the fact that it can be conducted under mild reaction conditions (ambient temperature and pressure), in an aqueous environment, and using benign oxidants (O_2) and biodegradable catalysts (enzymes or cells) [2,66,67]. In addition, biocatalysis also has the advantages of being a simple process and having high selectivity. Although there is less current research on the synthesis of FDCA by biocatalytic oxidation of HMF than that of chemical catalysis, the biocatalysis method has become increasingly more popular in recent years due to its unique advantages.

3.4.1. Enzymatic Oxidation

Bio-enzyme catalysts are green catalysts that meet environmental protection requirements and are non-toxic, harmless, and pollution-free. Therefore, it is greener to convert HMF to FDCA using a biological enzyme catalyst. The advantage of enzymes which work under mild conditions (at room temperature, in aqueous solution, and under atmospheric pressure), for the production of FDCA, has gained increased attention, and several studies on the enzymatic oxidation of HMF to FDCA are available [68] (Table 2). HMF contains an aldehyde group and an alcohol group, and the conversion of HMF to FDCA requires three consecutive oxidation steps. To the best of our knowledge, only a few enzymes have been found to be active toward HMF [47,69].

In 2014, Dijkman et al. discovered a new enzyme that can efficiently convert HMF to FDCA at room temperature and pressure, with a yield of 90%. Examination of the underlying mechanism showed that the oxidase acts on the alcohol groups only and depends on the hydration of the aldehydes for the required oxidation reaction to form FDCA. They studied the catalytic conversion effect of this invertase, and the results showed that HMF oxidation is divided into two routes (Figure 4), with route B being the main route [70].

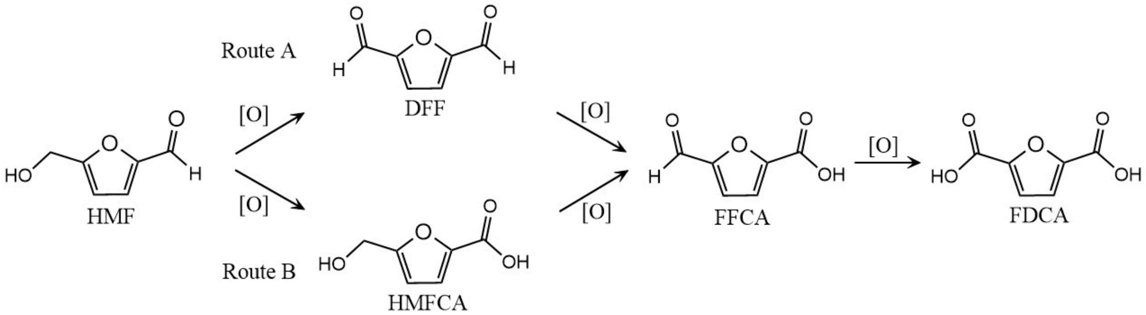

Figure 4. The potential pathway for FDCA production from HMF.

McKenna et al. realized the enzymatic oxidation of HMF to FDCA using galactose oxidase M_{3-5} (GO M_{3-5}) and aldehyde oxidase PaoABC through a one-pot reaction, with a 74% isolated yield of FDCA [71]. Zou et al. developed a method of coupling reactions to produce FDCA from HMF. The main features of this approach are the oxidation of the hydroxymethyl group through a TEMPO/laccase system and the oxidation of the aldehyde moiety via *P. putida* KT2440 cells [72]. To further improve the synthesis efficiency of FDCA, the enzymatic oxidation of HMF to FDCA was obtained by McKenna et al. using GO M_{3-5}, PaoABC, catalase, and horse radish peroxidase (HRP) via a one-pot reaction [73].

3.4.2. Whole Cell Biotransformation of HMF into FDCA

Generally, whole cells are more preferable for FDCA production due to the fact they do not require complicated cofactor regeneration processes and tedious enzyme purification [74]. Compared with enzyme catalysis, enzymes in whole cell catalysis are more stable in the cell and are less susceptible to toxic substrates. The synthesis of FDCA from HMF has been previously demonstrated using a recombinant whole cell biotransformation [71]. Whole cells also contain endogenous catalases which could catabolize H_2O_2 (common inhibitory by-product of enzymatic oxidation). Furthermore, whole cells also provide a protective barrier against the stress of aeration and reactive toxic substrates or products [75].

However, up to now, there have only been a few studies on the whole cell-catalyzed oxidation of HMF to FDCA. Recently, a novel HMF/furfural oxidoreductase (HmfH) was identified from *C. basilensis* HMF14 that can convert HMF into FDCA. Then, the *hmfH* gene encoding HmfH was introduced into *Pseudomonas putida* S12, and the recombinant whole cell biocatalyst was used to produce FDCA from HMF [12]. Zou et al. developed an efficient and highly selective biocatalytic approach using a TEMPO/laccase system coupled with *P. putida* KT2440 for the production of FDCA from HMF. TEMPO/laccase was used for the selective oxidation of the hydroxymethyl group of HMF to form 5-formyl-2-furoic acid (FFA), which was subsequently oxidized to FDCA by *P. putida* KT2440. By optimizing the reaction conditions, a good HMF conversion (100%) and an excellent selectivity of FDCA (100%) were obtained within 50 h at HMF concentrations up to 150 mM. The cascade catalytic process established in this work offers a promising approach for the green production of FDCA [72]. In order to improve the whole cell catalytic efficiency, an engineered *P. putida* S12 strain expressing HMFO was constructed for the bioconversion of HMF to FDCA. This whole cell biocatalyst produced 35.7 mM FDCA from 50 mM HMF in 24 h without notable inhibition. However, when using 100 mM HMF as the substrate, remarkable inhibition on FDCA production was observed, with an FDCA yield of 42% [76]. Chen et al. developed two stable *P. putida* S12 strains expressing HmfH and HMFO, both being able to convert 50 mM HMF to 43 mM FDCA in 24 h. Co-supplementation of $CaCO_3$ and MnO_2 in the reaction system drastically improved the cell tolerance to HMF and enhanced FDCA production. To strengthen the catalytic efficiency, the HmfH and HMFT1 (HMF transporter) genes were cointegrated, and the recombinant strain enabled converting 250 mM HMF to 196 mM (30.6 g/L) FDCA in 24 h [77].

Yang et al. developed an oxidative cascade for the one-pot synthesis of FDCA from HMF by exploiting *Comamonas testosteroni* SC1588 cells and the laccase-2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) system. HMF was oxidized to HMFCA by the cells at neutral pH. The HMFCA formation shifted the pH of the reaction mixture to the acidic range, which favored laccase-TEMPO catalytic oxidation. FFA derived from HMFCA via laccase-TEMPO catalysis was converted to FDCA by the cells. FDCA was obtained in an 87% yield within 36 h, providing productivity of around 0.4 g/L [78].

Yuan et al. developed a whole cell biotransformation process for the production of FDCA from HMF by a newly isolated *Raoultella ornithinolytica* BF60 strain. First, the maximal FDCA titer of the original strain was 7.9 g/L, and the maximal molar conversion ratio of HMF to FDCA was 51.0% (mol/mol) under optimal conditions. Next, the *dcaD* gene, which encodes dicarboxylic acid decarboxylase, was knocked out to block FDCA degradation, thus increasing FDCA production to 9.2 g/L. To improve FDCA production, two genes, HMFO and HmfH, were introduced into *R. ornithinolytica* BF60. The molar conversion ratio of HMF to FDCA increased from 51.0 to 93.6% [79]. To further improve the FDCA synthesis efficiency, various expression cassettes of key genes hmfH and hmfo were designed and constructed for fine-tuning FDCA synthesis from HMF. The FDCA titer reached 108.9 mM, with a yield of 73%, when 150 mM HMF was used as the substrate. Additionally, to strengthen HmfH expression, ribosomal binding site (RBS) mutants were assembled into HmfH expression cassettes. The HmfH expression was significantly enhanced, and the FDCA titer was increased to 139.6 mM, with a yield of 93% [80]. A novel whole cell biocatalyst was developed by co-expressing HmfH and vanillin dehydrogenase (VDH1) in *Escherichia coli* for the tandem catalytic oxidation of HMF to FDCA under sacrificial substrate-free conditions. HMF was rapidly converted to HMFCA by VDH1, followed by oxidation to FFA by HmfH, and finally, FFA was transformed to FDCA by VDH1 and/or HmfH. Under pH-controlled conditions, the biocatalyst enabled the efficient synthesis of FDCA from 150 mM HMF in a 96% yield [81]. Yang and Huang isolated a *Burkholderia cepacia* H-2 strain that was able to transform 2 g/L of HMF to 1.3 g/L FDCA under a pH of 7 and 28 °C, with a yield of approximately 50% [82].

4. Direct Production of FDCA from Biomass

Biomass is the richest renewable resource. In recent years, some researchers have attempted to directly convert fructose into FDCA. The direct conversion of fructose into FDCA can reduce the cost of raw materials and catalysts. As it can be referred to, the earliest research can be traced to 2000, where Kroger first reported a system that converts fructose directly into FDCA, using PTEF membranes to separate the thermostatic glass reactor from it. Two reaction chambers were, respectively, filled with a water/solid acid catalyst and an MIBK/oxidation catalyst. The solid acid converted fructose into HMF in the water phase, and then HMF entered the MIBK (methyl isobutyl ketone) organic phase through the PTFE membrane to obtain FDCA in MIBK, and an FDCA yield of 25% was achieved [83].

Kim et al. reported a process from cellulose to FDCA, where FDCA is produced from cellulose using a bio-based green solvent composed of gamma-valerolactone (GVL) and H_2O via three-step conversion involving cellulose hydrolysis, glucose dehydration, and HMF oxidation [84]. In particular, Ribeiro and Schuchardt reported the one-pot conversion of fructose into FDCA. Cobalt acetylacetonate encapsulated in sol–gel silica was shown to be an efficient bifunctional catalyst. Fructose was dehydrated to HMF on a silica catalyst, and then HMF was oxidized to FDCA by the metal active site [85].

Yan et al. developed a new method that uses [Bmim]Cl as a solvent and a non-noble metal (Fe-Zr-O) catalyst to directly convert fructose into FDCA. In the same reactor, fructose is dehydrated to HMF under the action of Amberlyst-15 and [Bmim]Cl, and then Fe-Zr-O is used to further oxidize the formed HMF without separating the acid catalyst from the reaction system. Under the base-free conditions, an FDCA yield of 46.4% was achieved, with a fructose conversion of 100% [86].

Zhang and co-workers developed a one-pot conversion of sugars into FDCA in a triphasic system, which is composed of tetraethylammonium bromide (TEAB) or water−methyl isobutyl ketone (MIBK)−water. In this reaction, sugars are first transformed into HMF in TEAB or water (Phase I). The HMF in Phase I is then extracted to MIBK (Phase II) and transferred to water (Phase III), where HMF is converted into FDCA. In this reaction system, HMF was first formed in the TEAB or water phase using the Amberlyst-15 solid acid.catalyst and then transferred to the water phase through the bridge phase of MIBK, where HMF was further oxidized to FDCA over the Au_8Pd_2/HT catalyst in the presence of Na_2CO_3 [87].

In order to reduce the cost of the catalyst and facilitate catalyst recycling, Wang, Zhang, and Liu reported the one-pot conversion of fructose into FDCA. Reasonable routes for the conversion of HMF into FDCA via the Fe_3O_4–Co catalyst were developed, and production of FDCA from fructose by a one-pot reaction method was applied, in which $Fe_3O_4@SiO_2$–SO_3H catalyzed the dehydration reaction, and the nano-Fe_3O_4–CoO_x catalyst promoted the oxidation reaction [14,88]. Chen et al. developed an ionic liquid–heteropolyacid system leading to FDCA at a 48% overall yield from glucose. Various starting materials were studied, and a moderate FDCA yield was obtained from glucose [89].

Table 1. The oxidation of HMF to FDCA via Pt catalysts.

Catalysts	Conv. HMF (%)	Select. FDCA (%)	T (°C)	Time (h)	O_2 (bar)	Reference
Pt/CNT	100	98	95	14	5	[90]
Pt/PVP-ACS	100	100	110	5	10	[91]
Pt/C-EDA	100	96	110	12	10	[92]
Pt/C-MgO	100	97	110	12	10	[58]
Pt/NC-CeO_2	100	100	110	8	4	[93]
Pt−ZrO_2	100	97.3	100	12	4	[92]

Table 2. Enzymatic oxidization of HMF into FDCA.

Enzymes	Oxidant	Reaction System	pH	T (°C)	HMF (mM)	Time (h)	HMF Conversion (%)	FDCA Yield (%)	Reference
Laccase + TEMPO	O_2	50 mM sodium acetate buffer	5.5	35	30	96	100	90.2	[94]
GO + AAO + UPO	O_2	50 mM phosphate buffer	6.0	25	10	24	100	80	[95]
GO $M_{3–5}$ + HRP + CAL + PaoABC	O_2	200 mM phosphate buffer	7.0	37	100	6	100	100	[73]
GO + HRP/CAL-B	O_2/ H_2O_2	Deionized water/EtOAct-butan-ol	-	25/40	30	48/24	-	88	[96]
GO $M_{3–5}$/PaoABC	O_2	400 mM potassium phosphate	7.0	37	100	10/5	100	>99	[71]
AAO/UPO	O_2	50 mM sodium phosphate	6.0/7.0	25	3	4/120	100	91	[47]
HMFO	O_2	100 mM potassium phosphate buffer	7.0	25	4	24	100	95	[70]

5. Summary and Prospect

In summary, the synthesis of FDCA from biomass via HMF, using precious metals, homogeneous metal salts, electrocatalysts, and biocatalysts, was summarized. Despite the significant progress in the production of FDCA from biomass-based HMF, there is still a long way to go before the commercial production of FDCA can be achieved. Further improvements in selectivity and productivity are still necessary in many cases for achieving the goal of industrial production of those processes. The noble metal catalysts, especially bimetallic catalysts, have shown excellent catalytic performances in FDCA production. However, the development of efficient, low-cost, multi-functional green catalysts or rational reaction systems is also in great need of further commercialization. Both electrocatalysis and biocatalysis are green and clean synthetic methods. In contrast, biocatalysis has attracted increasingly more attention due to its simple process and high selectivity. Of the two catalytic methods of biocatalysis, enzyme catalysis and whole cell catalysis, whole cell catalysis has more advantages since it does not require the purification of enzymes. During the catalysis process, various enzymes are less toxic to the substrate, the enzyme activity can be maintained sufficiently, and the catalytic efficiency is higher inside the cell. Simple operation and other advantages have been successfully applied to the industrial synthesis process. Furthermore, research on the commercial application of FDCA should be further strengthened.

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