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A Comprehensive Review on Sustainable Pathways to Synthesize 2, 5-Furandicarboxylic Acid (FDCA) from 5-Hydroxymethylfurfural (HMF) via Oxidative Processes

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Abstract

The increasing global concern over the environmental impact of traditional plastics derived from petroleum and natural gas has spurred a search for more sustainable alternatives. Bioplastics, which are derived from renewable sources and may be biodegradable, have garnered significant interest as eco-friendly materials. Among the promising building blocks for bioplastics, 2,5-Furandicarboxylic Acid (FDCA) has emerged due to its potential to enhance polymer properties. One key precursor for bioplastics, 5-Hydroxymethylfurfural (5-HMF), has been identified, and its oxidation to FDCA represents a significant pathway for bioplastic synthesis. Various oxidation processes, employing homogeneous, heterogeneous catalysis, or even without catalysts, have been explored for the synthesis of FDCA from 5-HMF.This review paper focuses on elucidating the recent advancements in the homogeneous and heterogeneous catalytic synthesis of FDCA from 5-HMF. Homogeneous catalysts, such as metal complexes, and heterogeneous catalysts, including metal oxides and supported metal nanoparticles, have been extensively studied and continue to evolve in terms of design and performance for the conversion of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA). Homogeneous catalysts offer high selectivity, controlled reaction conditions, and mechanistic insights, with examples including Ru-based complexes and Co and Mn salts. Heterogeneous catalysts provide ease of separation, reusability, and stability, with examples including metal oxides like TiO_2 and CeO_2, and supported metal nanoparticles like Pt, Pd, and Au. Recent advances focus on bimetallic and multimetallic systems, nano-structuring, surface fictionalization, and green chemistry approaches to enhance catalytic activity, selectivity, and environmental sustainability. Both types of catalysts are crucial for the efficient and sustainable conversion of HMF to FDCA, with ongoing research aimed at meeting industrial and environmental demands. It provides a comprehensive overview of the methodologies, catalysts, reaction conditions, and outcomes associated with these oxidation processes. By summarizing the state-of-the-art in FDCA synthesis, the review aims to contribute to the understanding and development of sustainable pathways for bioplastic production.

Keywords: HMF, FDCA, Bioplastic, Homogeneous and Heterogeneous catalyst, Oxidation.

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INTRODUCTION

In the today's world of advance technology there is great increment in the modern economy and immeasurable application of plastic in everyday

routines in human life, due to their versatile properties and wide market value with low cost [1]. The production of plastic is extensively increasing due to wide source of origin. The worldwide production of plastic reached over stumble of 400.3 million metric tons in 2022[2]. This incredible growth of versatile plastic materials accounts for continues growth in production with new technology year after year. In collaboration with the production growth the cost of plastic is also increasing [2]. Plastic is polymeric materials derived from fossil fuel which consisting of various complex organic compounds such as carbon and hydrogen with many other components produced by polymerization process. Plastic's diverse range of properties and applications renders it a superior material for a multitude of uses.[3].Polymeric materials are indispensable in our lives, but they are a major source of environmental pollution[4].The major reasons for environmental crisis and adverse effect on it by carbon emission, lead to find the solution with alternative source of plastic which can reduce the environmental pollution[5].Many researcher have conducted the research to find the better solution to overcome the problem related to plastic pollution by finding environmental friendly alternative for the fossil fuel products[6]. Biodegradabale polymer is eco-friendly alternative which has its origin from bio-mass renewable source which easily reduce emission of carbon footprint. Biodegradable plastic has abilities to degrade in environment by large number of microbes including bacteria, fungi and algae [7]. These polymers are broken down by variety of enzymes produced by microorganisms in bio sludge which does not give any adverse effect to environment and climate [8].

For the environmental sustainability and reduction in fossil source, special attention has been made towards the bio renewable polymers [9]. Conversion of biomaterial such as agriculture residue can be processed to convert into bio-based polymers. These bio-mass based polymers are the sustainable substitute to non-degradable plastics. Biomass is distinctive renewable carbon resource, which are origin of plants residues, crops waste and residues from industries. The fruitful usage of biomass results in procedure to overcome the problems of fossil hydrocarbon depletion. Researchers have found numerous platform chemical from the conversion of biomass through catalytic, non-catalytic and bio-catalytic processes [10].

A Building Block Intermediate Chemical: 5-Hydroxymethylfurfural (HMF)

From the wide range of building block chemical converted from the biomass, among the extensively applicable building block chemicals, there are twelve platform chemicals which have been selected by U.S. Department of Energy [11]. 5-hydroxymethylfurfural (HMF) is furan based chemical which serve as bridge between petrochemical resources and biomass resources[11].According to the global industry market there is approximately 1.4% growth of HMF in upcoming years and will grow extensively over 61 million USD in 2024 from 56 million USD in 2019[12].Conversion of C_6 to a various platform chemicals, has gain attention towards the synthesis of 5-Hydroxymethylfurfural (HMF) is heterocyclic furan which consist of C–O bond and C═O bond , this lead to the synthesis of huge derivative chemicals. From Figure 1 structure of 5-HMF shows aldehyde and hydroxide functional group are attached to furan ring [12].

Valuable chemicals such as maleic anhydride, 2,5-furandicarboxylic acid, 3-(hydroxy-methyl) cyclopentanone, 2,5-dihydromethylfuran, 2,5-dihydromethyltetrahydrofuran, 2,5-diformylfuran, 1,6-hexanediol, *p*-xylene, 5-ethoxymethylfurfural, 2,5-dimethylfuran and long-chain alkanes are the platform chemicals shown in Figure 2 has been derived from 5-HMF via hydrogenation, oxidation and ring opening [13].

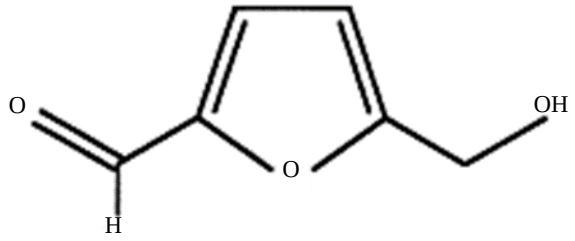

Figure 1. Structure of 5-HMF consists aldehyde and hydroxide functional groups[12]

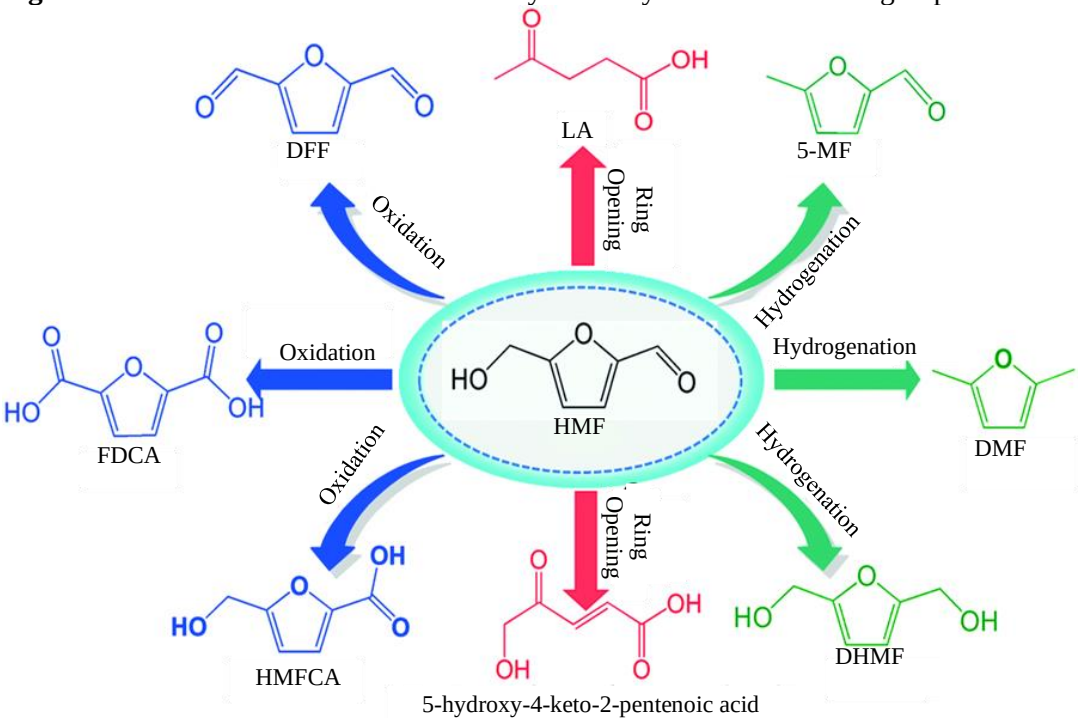

Figure 2. Platform Chemicals from HMF[13].

Biomass feed stocks are classified into three generation from which agricultural waste comes under first generation which is the main source of production of FDCA and HMF. Biomass consist of lignocellulosic which is not applicable in edible sources, so its major and crucial source of HMF [14,15]. Hemicelluloses, cellulose and lignin are the main components in biomass which are the contributor of carbohydrates in abundant [14]. Dehydration of C_6 carbohydrates produce 5-HMF with polymeric and monomeric carbohydrate contents, which includes sucrose, glucose, fructose, starch, inulin, and cellulose.5-HMF is precursor for wide range of application in bio-chemicals which lead to sustainable solution to non-renewable source such as fossil fuel chemicals. Since 19thcentury there is vast growth in research in conversion and application of 5-HMF.Its is most important building block for various value added chemicals [13].

Alternative to conventional polymers: 2, 5-Furandicarboxylic acid (FDCA):

2.5-Furan dicarboxylic acid is predominant building block which consists of furan ring and it produces from the oxidation dehydration of glucose. Its appearance is white powder which has two carboxylic groups as show in Figure 3. It is chemically stable and insoluble in water, ethanol, acetone, or hexane; and in same polar solvent such as n-methyl pyrrolidone (NMP), dimethylformamide (DMF), and dimethyl sulfoxide (DMSO) are soluble.

The presence of two carboxylic acid groups in 2, 5-FDCA leads to the chemical reaction patterns of carboxylic acid [14]. It has higher boiling point 420 °C and melting point 342 °C. It has the potential to

substitute various petrochemicals feed stocks such as terephthalic acid and adipic acid, which plays the main role as a precursor in feedstock of many polymers such as poly (ethylene terephthalate) and poly (butylene terephthalate) [15-17]. The replacement of terephthalic acid with bio-based FDCA marks a significant stride towards sustainability. FDCA holds promise for various applications including polyesters, polyurethanes, and polyamides, as well as the production of eco-friendly polymers like Polyethylene Furanoate (PEF). Polyethylene furanoate, derived from FDCA, is hailed as the "biopolymer of the future," capable of substituting polyethylene terephthalate and Almost 51% to 43% there is reduction in non-renewable energy (NREU) requirements and 54% to 46% in greenhouse gas (GHG) emissions [18-20].

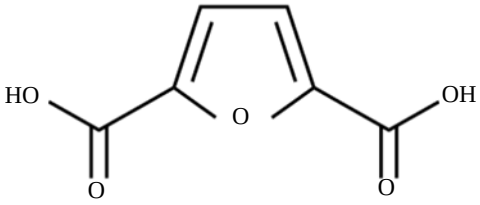

Figure 3. Structure of 2, 5-Furandicarboxylic acid [14].

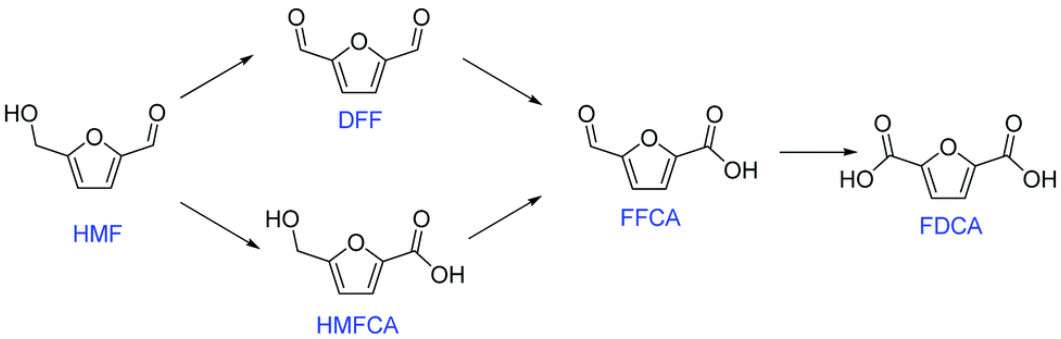

Figure 4. Oxidation of HMF to FDCA with two different pathway via DDF and HMFCA [23]

Conversion of biomass to FDCA, which derives sugars, or platform chemicals typically encompasses from processes such as chemical, biological, and electrochemical processes [20]. FDCA has wide application in bio-based polymers and flexible synthetic intermediate [21]. The predominant approach to produce FDCA from lignocellulosic biomass involves catalytically oxidizing HMF [22]. Figure 4 represents two pathway route for synthesis of 2, 5-FDCA from 5-HMF as precursor [23]. Through the oxidation reaction of 5-Hydroxymethylfurfural (5-HMF) to 2,5-furandicarboxylic acid (FDCA) follows two primary pathways, each exhibiting a distinct bias towards the preferential oxidation of either the hydroxyl or aldehyde group. Pathway 1 involves diformylfuran (DFF), is produced by the oxidation of HMF, primarily targeting the aldehyde group, followed by subsequent oxidation of DFF to yield 2, 5-furfurancarboxylic acid (FFCA). Ultimately, oxidation of FFCA derives FDCA at elevated potential conditions. Conversely, Pathway 2 prioritizes the oxidation of HMF to hydroxymethylfuroic acid (HMFCA), predominantly focusing on the hydroxyl group. Subsequent oxidation of HMFCA leads to the formation of FFCA, which undergoes deep oxidation to yield FDCA under higher potential conditions. These pathways involve sequential oxidation steps that selectively target specific functional groups present in HMF. Optimization of these pathways is crucial for maximizing FDCA yield while minimizing the formation of undesirable by-products and enhancing overall process efficiency. By studying the pathways for the development of strategies to control lied and enhance FDCA from the oxidation of HMF, which is pivotal for the production of sustainable and renewable bio-plastics and other valuable chemicals.

Synthesis of 2, 5-FDCA from 5-HMF

From the last few decades, conversion of HMF to FDCA through oxidation reaction has been conducted through various methods including homogeneous catalysis, electro-catalysis, and heterogeneous catalysis [24-26]. Currently, there is a growing interest in employing bio-catalysis for the conversion of HMF into FDCA [27]. From the homogeneous catalysis, metals such as palladium, platinum, or ruthenium-based catalysts are often employed the addition of a base is necessary, leading to increased operating costs for FDCA separation and the need for acid to dispose of resulting waste salt [28,29]. Heterogeneous catalytic systems may utilize metal oxides or supported metal catalysts with good selectivity and stability, along with ease of catalyst separation and recycling [30]. Bio-catalysis, which involves the use of enzymes or whole cells as catalysts, has also gained attention for its potential to perform this conversion under mild conditions with high selectivity and offers high selectivity and compatibility with aqueous environments, but may require optimization for stability and activity of the biocatalyst[31].Electrocatalysis can offer precise control over reaction kinetics and selectivity, with potential for continuous processing and integration into electrochemical systems. Consequently, there is significant enthusiasm for exploring environmentally friendly and cost-effective methods HMF oxidation to FDCA [26]. The oxidation of HMF into Furanic derivatives is difficult due to the presence of two groups such as the formyl and the hydroxymethyl which undergoes oxidation to the extents, which leads to various possible products with its stabilities. The synthesis process of FDCA by conversion of HMF using oxidation reaction, which have the great potential to received increased attention in recent years.

Synthesis of FDCA via Oxidation of HMF using Homogeneous and Heterogeneous Catalyst

Efficient FDCA synthesis is crucial for PEF development, and the 5-hydroxymethylfurfural (HMF) route appears promising. However, challenges arise due to HMF's some properties such as its highest boiling point, hydro-scopicity in nature, and instability, making its separation, purification, and transport a persistent obstacle in achieving efficient FDCA synthesis from sugar. Addressing these challenges remains a key focus for advancing sustainable and effective FDCA production [32].

From the literature review, researchers have focused on environmentally friendly catalytic processes for synthesizing 2, 5-FDCA from 5-HMF. Using magnetic Nanoparticles $MnFe_2O_4$ and an oxidant as tert-butyl hydroperoxide, the researchers achieved an efficient 85% yield of FDCA in just 5 hours at 100 °C. $MnFe_2O_4$'s variable oxidation state enhances its catalytic activity, and the process is more time and energy-efficient than other reported methods. Importantly, the avoidance of a homogeneous base adds to its green credentials. The catalyst is easily recyclable, maintaining its effectiveness over multiple cycles. Overall, this method shows promise for sustainable and economically viable FDCA production [33]. Adopting catalyst such as nickel, cobalt, iron which are examples of non-noble metal can be used as catalyst, from the literature mixed oxides of $MnOx–CeO_2$were used. By the precipitation method catalysts were prepared, and characterized by their Mn/Ce ratios, and the Manganese Oxides-Cerium oxide-6 catalyst (Mn/Ce = 6) demonstrated exceptional performance. The Manganese Oxides-Cerium oxide-6 catalyst exhibited a high FDCA yield of 91% and maintained its catalytic activity through five reuse cycles, highlighting its reusability. 5-HMF oxidation is due to active sites which were identified as surface Mn4+ ions, showcasing the catalyst's effectiveness without the need for noble metals [34]. An ionic liquid prompts the use of Fe–Zr–O catalysts in base-free reaction system. The $Fe_{0.6}Zr_{0.4}O_2$ catalyst exhibited exceptional performance, by yielding FDCA around 60.6% yield and HMF conversion was 99.9% under 2 MPa O_2 pressure for 24 hours. The catalyst's success is attributed to its abundant acidic and basic sites, high reducibility, and oxygen mobility. The study investigated production of by product humin and reaction pathways in ionic liquids, proposing a plausible mechanism. Notably, the catalyst-maintained activity over five cycles, marking a significant advancement in the base-free oxidation of HMF to FDCA in the presence non-noble metal-catalyzed using molecular oxygen. This research contributes a vital step towards sustainable and efficient FDCA production [35]. Researchers addressing challenges in HMF synthesis and isolation, emphasized the use of crude HMF due to cost considerations. Non-precious metal catalysts, particularly Cu–Mn, are demonstrated for efficient FDCA synthesis, comparable to the widely studied Ru/C catalyst. The study

systematically explores factors like purity of HMF, oxidant such as air, and reaction conditions. Formation pathways and confirmation techniques for isolated FDCA are also discussed. The study demonstrates the use of catalyst like transition metal oxide which are low-cost mixed metal oxides also known as non-precious-metal oxides catalysts in the aqueous medium in the presence of oxygen/air. The Cu–Mn catalyst at 120 °C within 8 hours in the presence of oxygen at 10 bar is highlighted, achieving a 90% yield of FDCA. This activity is comparable to the commercially available Ru/C (5 wt%) catalyst, which yields 93% FDCA [36]. Using bio-mass based catalysts which were composed of a core-shell structure with a magnetic nano-particle core and a shell comprising Nb-MCM-41 and Mn, Co, or Fe oxides. The composite catalysts demonstrated high selectivity, with 96.5% selectivity achieved for FDCA from HMF by using composite catalyst 10Co@22Nb@MNP. This research finds a synergistic effect between the metal oxides and Nb species in the activation of t-butyl hydroperoxide and the oxidation of HMF. This synergy likely contributes to the enhanced performance of the catalysts in promoting the desired oxidation reactions. The developed catalysts do not require the presence of a base in the homogeneous phase, which simplifies the reaction conditions. Subsequently, the magnetic properties of the catalysts offer advantages over the separation and recovery processes [37]. For production of FDCA, specific steps are followed according to chemical reaction system which involves the acetalization of HMF with 1, 3-propanediol to stabilize the reactive formyl group, followed by aerobic oxidation using a highly active catalyst supported on Au catalyst in water with the base additive. 5-(Hydroxymethyl) furfural has been used in large-scale chemical production processes, both in batch and continuous operations. It has been hindered by the formation of by-product humin. To address this challenge, researchers have developed a method involving the reaction of 1, 3-propanediol with HMF to produce a stable HMF acetal derivative with excellent thermal stability. This acetal derivative can be aerobically oxidized using a Na_2CO_3 in and water CeO_2-supported Au catalyst, resulting yield around 95% of furan 2, 5-dicarboxylic acid, an crucial chemical as the bio-renewable material in industry, without the formation of humin [38]. The study focused on highlights of the potentially application of alkaline-earth metal bearing heteroatomic zeolites as the multi-functional supports of noble metal NPs in biomass conversion field. The oxidation of HMF into FDCA carried out by the Au/MgSi-ZSM-12 catalyst which shows better stability and activity. Liquid base is not required in the presence of atmospheric dioxygen still results in excellent yield around 87 % with optimum reaction condition, molar ratio = 20:1 of HMF/metal, 4 mL of distilled water, under 90 ^oC temperature for 24 h with O_2 balloon [39]. FDCA was synthesised in presence of air and homogenous catalyst of cobalt, Manganese and bromide composite and in acetic acid under reaction condition at 130 to 170 ^0C temperation [40]. An advanced technology was developed which can increase the efficiency and selective of FDCA from oxidation of HMF by utilizing the liquid oxygen source as hydrogen peroxide and graphene oxide which is derived from biomass feed-stocks and was given the support of metal catalyst. This works shows high yield of 98.8% with less quantity of catalyst in 5 hours implementing catalyst Ru@S-GO which exhibited a high activity and selectivity for production of furan dicarboxylic acid under optimum condition [41]. Conversion of HMF via oxidation to FDCA using ZSM-5 catalyst from natural sources has been demonstrated. ZSM-5 was modified with CuO and NiO oxide metals which results in increase in it's acidity and oxidizing ability. The best result in conversion of HMF was seen by NiO/ZSM-5 catalyst with 99.2% HMF conversion and 88.9 % FDCA yield. At relevant temperature of about at T = 130 ◦C, considerable conversion of HMF and yield of FDCA were obtained for NiO/ ZSM-5 (98.9 %, 81.6 %), ZSM-5 (67.8 %, 52.79 %), and CuO/ZSM-5 (82.1 %, 70.7 %) [42]. From the literature it was found that the conversion of HMF using nano-particle catatlyst as Ru nano-particles which was impregnated on the Cr-Fe-O support i.e. (Ru/Cr-Fe-O) was prepared. The particle-supported the resulted in Ru/Cr-Fe-O catalysts deliver better at less-temperature reducibility and hold various weak acid sites. The optimal reaction conditions were 100 ^oC temperature with 1 MP pressure with the reaction time 16 h. Maximum conversion was achieved with highest yield 99.9%. Characterizations were carried out to reveal the activities associated with the surface chemistry states catalyst. This research offers some insights into the rational selection of support type catalysts for selective oxidization reactions [43]. Table 1 describes the summary of the literature review on various homogeneous and heterogeneous catalysts used to convert of HMF to 2,5-FDCA with notable findings [46,47].

Other Novel Techniques for Synthesis of FDCA via Oxidation:

Electrochemical Oxidation

In electrochemical oxidation, HMF is directly oxidized at the electrode surface, where electrons are transferred from HMF to the electrode. This electron transfer process leads to the formation of intermediate species, which subsequently undergo further oxidation to yield FDCA or other desired products. The electrochemical oxidation of hydroxymethylfurfural (HMF) presents a promising avenue for its conversion to valuable products like 2,5-furandicarboxylic acid (FDCA) under ambient conditions, circumventing the need for external oxidants. This process involves the migration of electrons at the electrode interface, facilitating direct oxidation of HMF without requiring harsh reaction conditions or additional chemical agents [48-53] Through electron transfer, HMF is oxidized to intermediate species, which further react to yield FDCA or other desired products. Electrochemical oxidation offers several advantages, including mild reaction conditions, selective product formation, reduced environmental impact, and versatility in reaction design. Nonetheless, challenges such as electrode fouling and product selectivity need to be addressed for scalable and efficient implementation of electrochemical oxidation processes. Very few researches have been found on conversion of HMF to FDCA through electrochemical oxidation which has been summarized in Table 2 [54-57].

Table 1. The literature review on homogeneous and heterogeneous catalysts.

Sr.no.	Catalyst	Oxidant	Solvent	Conversion of HMF	Yield % of FDCA	Tempº C	Time	Catalyst recycle	RPM	Reference
1	$MnFe_2O_4$	tert-butyl hydroperoxide	acetonitrile	NA	85	100	5h	4	1000	**33**
2	MnOx–CeO2(molar ratio 6)	NA	NA	NA	91	75+110	15+6h	5	NA	34
3	Fe0.6Zr0.4O2	NA	[Bmim]Cl ILs	NA	60.6	160	24	NA	NA	36
4	NiO/ZSM-5	H_2O_2	K_2CO_3, a weak base	99.2	88.9	130	NA	NA	NA	43
5	Ru/Cr_2-Fe-O	NA	$KHCO_2$	100	99.9	80-120	12-24	5	NA	44
6	10Co@22Nb@MNP	NA	water	96.6	96.5	110-180	NA	NA	NA	45
7	CeO_2 /Au	Na_2CO_3	water	99	90	158	15	NA	NA	46
8	Pt/C	NA	GVL/H_2O	97	95	110		NA	NA	47
9	Au/Si-ZSM	O_2	NA	99	98	90	24	NA	NA	40
10	RuHcl(CO)AcrPNP	NaOH	NA	99	95	160		NA	NA	48
11	Pt/C	NA	NA	100	89.5	75	6	NA	NA	49
12	$[EMIM]_4MOgO_{26}$	Acetic acid	KOH	NA	95	50	26	6	NA	50
13	Pd-BI-Te/C	H2O-methanol	K_2CO3	NA	85	140	30	NA	NA	51
14	Pd/CC	water	NA	NA	91	90	20	NA	NA	52
15	Pt/SiO2	Water/dioxane	NaBr	NA	68.6	80	12	NA	NA	53
16	Fe3O4-CoOx	DMSO		NA	60.6	160	24	NA	NA	54

17	Fe0.6Zr0.4O2	[Bmim]Cl	KOH	NA	95	50	6	NA	NA	55

NA: Not Applicable

Table 2. Conversion of HMF to FDCA by Electrochemical Oxidation.

Catalyst	Solvent	Temperature ºC	Time(hr)	Yield %	Selectivity%	Reference
NiO(OH)	NaOH	Room Temp.	4.00	71.0	NA	56
Pt	$NaClO_4$,	50.00	4.00	7.27	26.0	57
$Pd1Au_2/C$	KOH	25.00	1.00	83.0	83.0	58
MnO	H_2SO_4,	60.00	NA	53.80	53.80	59
NixB/Ni foam	KOH	NA	0.50	98.50	98.50	60

NA: Not Applicable

Photo Catalysis

Photo catalysis has emerged as a promising strategy to convert HMF to FDCA, offering efficient and environmentally friendly pathways. Photo catalysts, typically semiconducting materials, harness light energy to drive chemical reactions, followed by the oxidation reaction of HMF to FDCA under optimum mild conditions. Various photo catalysts, including metal oxides (e.g., TiO2, ZnO), metal-organic frameworks (MOFs), and carbon-based materials (e.g., graphene, carbon nitride), have been explored for this purpose. These materials exhibit unique properties such as tunable band gaps, high surface areas, and excellent charge carrier mobility, which are conducive to photo catalytic reactions. There reactive oxygen species (ROS) was generated in the photocatalytic conversion of HMF to FDCA till upon illumination, which react with HMF to initiate oxidation reactions leading to the formation of FDCA. Key factors influencing the efficiency of photo catalytic conversion include the choice of photo catalyst, light intensity, reaction conditions, and catalyst morphology. While photo catalytic systems offer several benefits such as good selectivity, potential for solar-driven processes and mild reaction conditions, challenges remain in achieving high conversion yields, catalyst stability, and scalability for industrial applications. Continued research efforts aimed at designing novel photo catalysts, optimizing reaction conditions, and understanding reaction mechanisms are essential for realizing the full potential of photo catalysis in the conversion of HMF to FDCA and other valuable chemicals. Conversion of HMF to FDCA through photo catalytic oxidation using different catalysts has been summarized in Table 3 [58-64].

Biocatalysis

Biocatalysis presents an intriguing avenue for synthesis of FDCA from HMF, offering sustainable and selective routes under mild reaction conditions. Various biocatalysts, including enzymes and whole cells, have been explored for this purpose. One notable enzyme is oxidoreductase, which catalyses the oxidation of HMF to FDCA using molecular oxygen as the oxidizing agent. Other enzymes such as dehydrogenases and oxidases have also shown potential for catalysing specific steps in the conversion pathway. Whole cells of microorganisms, including bacteria and fungi, have been engineered to express enzymes capable of converting HMF to FDCA. Biocatalytic processes offer several advantages, including high selectivity, mild reaction conditions, and compatibility with renewable feed stocks. However, challenges such as enzyme stability, substrate inhibition, and scalability need to be addressed for industrial-scale applications. Continued research efforts focused on enzyme engineering, immobilization techniques, and process optimization are essential for harnessing the full potential of biocatalysis in the conversion of HMF to FDCA and other valuable chemicals in a sustainable manner. Synthesis of FDCA by conversion of HMF through biocatalysis oxidation has been summarized in Table 4 [65-68].

Table 3. Synthesis of FDCA from HMF through photo catalyst oxidation at room temperature.

Catalyst	Solvent/pH	Time(hr)	Yield %	Selectivity %	Reference
$CoPz/gC_3N_4$	$Na_2B_4O_7$ buffer, 9.18	14.00	96.1	96	61
Ni/CdS nanosheets	NaOH	2.00	100	100	62
$BiVO_4$ þ TEMPO	borate buffer, 9.2	1.00	99	99	63

Table 4. Conversion of HMF to FDCA through biocatalyst oxidation.

Biocatalyst	Buffer	Temperature ºC	Time hr.	Yield %	Reference
HMF H in Pseudomonas putida S12	NH_4OH	30	144	97	64
HMF oxidase	Potassium phosphate buffer	24	25	95	65
Aryl-alcohol oxidase, peroxygenase	Aryl-alcohol oxidase, peroxygenase	Room Temp.	116	91	66
Galactose oxidase $M_{3\text{-}5}$, PaoABC, catalase	Aryl-alcohol oxidase, peroxygenase	37	16	74	67

CONCLUSION

The conversion of HMF to FDCA represents a significant improvement in the sustainable process, offering a renewable route to important industrial chemicals. Oxidative synthesis of 2,5-furandicarboxylic acid (FDCA), utilizing both homogeneous and heterogeneous catalysts presents a promising avenue towards sustainable chemical production. Significant efforts have been directed towards designing and optimizing catalysts to enhance reaction rates, selectivity, and stability. Homogeneous catalysts such as metal complexes have been extensively studied, while heterogeneous catalysts including metal oxides and supported metal nanoparticles continue to evolve in terms of design and performance.

Utilizing catalysts such as ruthenium, iridium, palladium, and other metal complexes, as well as non-noble metals like nickel, cobalt, and iron, in homogeneous form is the key for achieving optimal conditions for converting 5-HMF to 2,5-FDCA, resulting in high yields through tailored modifications. However, despite their ability to enhance catalyst properties, challenges arise in their separation and recycling due to dissolution in the reaction mixture, posing environmental concerns and increasing process costs.

Heterogeneous catalysts, such as palladium, gold, and silver supported with carbon or zeolites substrates, demonstrate superior performance compared to homogeneous catalysts. They ensure maximum yield under stable reaction conditions and facilitate easy separation for multiple recycling, thus rendering the process cost-effective. However, recurrent recycling may potentially diminish reactivity alongside selectivity.

Alternative Approaches for FDCA Synthesis via Oxidation, Including Electrochemical, Photocatalytic, and Biocatalytic Methods, Present Promising Avenues for Sustainable Production Despite Some Limitations. Electrochemical oxidation offers high selectivity and efficiency; however, it requires the substantial power inputs and leads to electrode degradation, maintenance and increasing costs. With photocatalysis process which offers a promising avenue for sustainable production, catalyst reusability and compatibility with renewable energy sources. But catalyst sensitivity, complex reactor design, separation of product, ensuring efficient and environmentally friendly processes are of concern. Sustainable approach was also fulfilled by biocatalysis in many ways such as high selectivity, stable reaction conditions, and compatibility with aqueous systems, making it promising for green chemistry applications with few disadvantages such as substrate and product inhibition, enzyme stability, specificity, and scale-up issues require careful consideration and optimization for industrial implementation.

From the study it reveals that the catalysts play vital role in the synthesis of 2,5-FDCA from 5-HMF with some advantages and disadvantages. However, the selection of catalyst depends on the major factors such as selectivity, economy of process, environments impact. Crucial research is needed to optimize the good efficiency for the production of 2,5-FDCA from the biomass sources such as 5-HMF.

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Author Contributions

Aditi Vetal, Dr. Jharna Gupta, Piyush Shrivastava, Rushil Bhatt has help to collect the data and written the manuscript. and Dr. Anand Metre has given valuable suggestions for finalizing the manuscript.

Competing Contributions

The authors declare that they have no conflict of interest regarding this publication.

REFERENCE

1. Rahman, M. H., & Bhoi, P. R. (2021). An overview of non-biodegradable bioplastics. *J. Clean. Prod.*, 294, 126218.
2. Madhumitha Jaganmohan. Annual production of plastics worldwide from 1950 to 2022 (in million metric tons). https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950 . 22/02/2024.
3. Shrivastava, A. (2018). Plastic properties and testing. *Int. Plast. Eng.* 49.
4. Mishra, R. K., Maria, H. J., Joseph, K., & Thomas, S. (2017). Basic structural and properties relationship of recyclable microfibrillar composite materials from immiscible plastics blends: An introduction, In Micro and nano fibrillar composites (MFCs and NFCs) from polymer blends. Woodhead Publishing. pp. 1-25. 978-0-08-101991-7
5. Ahsan Ali, Ali Bahadar, Afrasyab Khan, Khairuddin Sanaullah,,(2022), Role of agricultural waste in recycled plastic bio composites, Recycled Plastic Biocomposites, Woodhead Publishing Series in Composites Science and Engineering, PP.165-194. 978-0-323-88653-6
6. Venkatachalam, H., & Palaniswamy, R. (2020). Bioplastic world: A review. *J. Adv. Sci. Res*.,11(03), 43-53.
7. Alshehrei, F. (2017). Biodegradation of synthetic and natural plastic by microorganisms. J. App. & Env. Microbiol., 5(1), 8-19.
8. Wei, R., & Zimmermann, W. (2017). Microbial enzymes for the recycling of recalcitrant petroleum-based plastics: how far are we? *Microb. biotechnol*., 10(6), 1308-1322.
9. Shashi Kant Bhatia, Sachin V. Otari, Jong-Min Jeon, Ranjit Gurav, Yong-Keun Choi, Ravi Kant Bhatia, Arivalagan Pugazhendhi, Vinod Kumar, J. Rajesh Banu, Jeong-Jun Yoon, Kwon-Young Choi, Yung-Hun Yang, Biowaste-to-bioplastic (polyhydroxyalkanoates): Conversion technologies, strategies, challenges, and perspective, *Bioresour. Technol*.,326-124733.
10. Jae Bok Heo, Yong-Suk Lee, Chung-Han Chung (2020), Toward Sustainable Hydroxymethylfurfural Production Using Seaweeds, *Trends Biotechnol*.,38(5), 487-496.
11. Xiao Kong, Yifeng Zhu Zhen Fang, Janusz A. Kozinski, Ian S. Butler, Lujiang Xu, He Song and Xiaojie Wei(2018), Catalytic conversion of 5-hydroxymethylfurfural to some value-added derivatives. Green Chem.,20, 3657-3682.
12. Qing-Shan Kong, Xing-Long Li, Hua-Jian Xu, Yao Fu (2020). Conversion of 5-hydroxymethylfurfural to chemicals: A review of catalytic routes and product applications, *Fuel Process Technol.*, 209, 06528.
13. 13.Bao Chen, Xin Li, Peng Rui , Yuewen Ye , Tongqi Ye , Rulong Zhou , Dongdong Li, James H. Carter and Graham J. Hutchings(2022), The reaction pathways of 5-hydroxymethylfurfural conversion in a continuous flow reactor using copper catalysts, *Catal. Sci. Technol.*,12, 3016-3027.
14. Wang, Y., Wang, H., Kong, X., & Zhu, Y. (2022). Catalytic Conversion of 5-Hydroxymethylfurfural to High-Value Derivatives by Selective Activation of C− O, C= O, and C= C Bonds. *ChemSusChem*, 15(13), e202200421.
15. Parshetti, G.K, Suryadharma, M.S, Pham, T.P.T, Mahmood, R, Balasubramanian, R. (2015). Heterogeneous catalyst,assisted thermochemical conversion of food waste biomass into 5,hydroxymethylfurfural. *Bioresour. Technol*.,178, 19–27.

16. Chen, H. (2014). Chemical composition and structure of natural lignocellulose. Chapter 2. In: Biotechnology of Lignocellulose: Theory and Practice. Springer, The Netherlands. pp. 25–71.
17. Wang, J., Liu, X., Zhu, J., & Jiang, Y. (2017). Copolyesters based on 2, 5-furandicarboxylic acid (FDCA): effect of 2, 2, 4, 4-tetramethyl-1, 3-cyclobutanediol units on their properties. *Polymers*, 9(9), 305.
18. Dedes, G., Karnaouri, A., & Topakas, E. (2020). Novel routes in transformation of lignocellulosic biomass to furan platform chemicals: from pretreatment to enzyme catalysis. *Catalysts*, 10(7), 743-767.
19. Papageorgiou, G. Z., Papageorgiou, D. G., Terzopoulou, Z., & Bikiaris, D. N. (2016). Production of bio-based 2, 5-furan dicarboxylate polyesters: Recent progress and critical aspects in their synthesis and thermal properties. *Eur. Polym. J.*, 83, 202-229.
20. Eerhart, A.J.J.E, Faaij, A.P.C, Patel, M.K. (2012) Replacing fossil-based PET with biobased PEF; process analysis, energy and GHG balance. Energy Environ. Sci., 5(4),6407–6422.
21. Liu, K. J., Zeng, T. Y., Zeng, J. L., Gong, S. F., He, J. Y., Lin, Y. W., ... & He, W. M. (2019). Solvent-dependent selective oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid under neat conditions. *Chin. Chem. Lett.*, 30(12), 2304-2308.
22. Shen, G., Andrioletti, B., & Queneau, Y. (2020). Furfural and 5-(hydroxymethyl) furfural: Two pivotal intermediates for bio-based chemistry. *Curr opin. Green Sustain chem.*, 26, 100384.
23. Zou, L., Zheng, Z., Tan, H., Xu, Q., & Ouyang, J. (2020). Synthesis of 2, 5-furandicarboxylic acid by a TEMPO/laccase system coupled with Pseudomonas putida KT2440. *RSC advances*, 10(37), 21781-21788.
24. Sajid, M., Zhao, X., & Liu, D. (2018). Production of 2, 5-furandicarboxylic acid (FDCA) from 5-hydroxymethylfurfural (HMF): recent progress focusing on the chemical-catalytic routes. *Green chemistry*, 20(24), 5427-5453.
25. Kubota, S. R., & Choi, K. S. (2018). Electrochemical oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid (FDCA) in acidic media enabling spontaneous FDCA separation. *ChemSusChem.*, 11(13), 2138-2145.
26. Zhu, B., Chen, C., Huai, L., Zhou, Z., Wang, L., & Zhang, J. (2021). 2, 5-Bis (hydroxymethyl) furan: a new alternative to HMF for simultaneously electrocatalytic production of FDCA and H2 over CoOOH/Ni electrodes. *Appl. Catal. B: Environ.* 297, 120396.
27. Sheng, Y., Tan, X., Zhou, X., & Xu, Y. (2020). Bioconversion of 5-hydroxymethylfurfural (hmf) to 2, 5-furandicarboxylic acid (fdca) by a native obligate aerobic bacterium, Acinetobacter calcoaceticus NL14. *Appl. Biochem. Biotechnol.*, 192, 455-465.
28. Messori, A., Fasolini, A., & Mazzoni, R. (2022). Advances in Catalytic Routes for the Homogeneous Green Conversion of the Bio-Based Platform 5-Hydroxymethylfurfural. *Chem. Sus. Chem*, 15(13), e202200228.
29. Wei, Z., Li, W., Yuan, F., Sun, W., & Zhao, L. (2022). Kinetic Modeling of Homogenous Catalytic Oxidation of 5-Hydroxymethylfurfural to 2, 5-Furandicarboxylic Acid. *Ind. Eng. Chem. Res.*, 61(50), 18352-18361.
30. Davis, M. E. (2015). Heterogeneous catalysis for the conversion of sugars into polymers. *Top. Catal.*, 58, 405-409.
31. Yuan, H., Liu, H., Du, J., Liu, K., Wang, T., & Liu, L. (2020). Biocatalytic production of 2, 5-furandicarboxylic acid: recent advances and future perspectives. *Appl. Microbiol. Biotechnol.*, 104, 527-543.
32. Chen, G., Wu, L., Fan, H., & Li, B. G. (2018). Highly efficient two-step synthesis of 2, 5-furandicarboxylic acid from fructose without 5-hydroxymethylfurfural (HMF) separation: in situ oxidation of HMF in alkaline aqueous H2O/DMSO mixed solvent under mild conditions. *Ind. Eng. Chem. Res.*, 57(48), 16172-16181.
33. Gawade, A. B., Nakhate, A. V., & Yadav, G. D. (2018). Selective synthesis of 2, 5-furandicarboxylic acid by oxidation of 5-hydroxymethylfurfural over MnFe2O4 catalyst. *Catal. Today*, 309, 119-125.

34. Han, X., Li, C., Liu, X., Xia, Q., & Wang, Y. (2017). Selective oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid over MnO x–CeO 2 composite catalysts. *Green Chem.*, 19(4), 996-1004.
35. Chen, G., Wu, L., Fan, H., & Li, B. G. (2018). Highly efficient two-step synthesis of 2, 5-furandicarboxylic acid from fructose without 5-hydroxymethylfurfural (HMF) separation: in situ oxidation of HMF in alkaline aqueous H2O/DMSO mixed solvent under mild conditions. *Ind. Eng. Chem. Res.*, 57(48), 16172-16181.
36. Yan, D., Xin, J., Zhao, Q., Gao, K., Lu, X., Wang, G., & Zhang, S. (2018). Fe–Zr–O catalyzed base-free aerobic oxidation of 5-HMF to 2, 5-FDCA as a bio-based polyester monomer. *Catal. Sci. Technol.*, 8(1), 164-175.
37. Lokhande, P., Sonone, K., & Dhepe, P. L. (2023). Industry-oriented method for the aqueous phase oxidation of crude 5-hydroxymethyl furfural (HMF) to 2, 5-furandicarboxylic acid (FDCA). *New J Chem.*, 47(32), 15325-15335.
38. Tirsoaga, A., El Fergani, M., Nuns, N., Simon, P., Granger, P., Parvulescu, V. I., & Coman, S. M. (2020). Multifunctional nanocomposites with non-precious metals and magnetic core for 5-HMF oxidation to FDCA. *Appl. Catal. B: Environ.*, 278, 119309.
39. Kim, M., Su, Y., Fukuoka, A., Hensen, E. J., & Nakajima, K. (2018). Aerobic Oxidation of 5-(Hydroxymethyl) furfural Cyclic Acetal Enables Selective Furan-2, 5-dicarboxylic Acid Formation with CeO2-Supported Gold Catalyst. *Angew. Chem., Int. Ed.*, 57(27), 8235-8239.
40. Chen, L., Zhuang, W., Lan, J., Liu, X., Jiang, S., Wang, L., ... & Wang, J. (2021). Base-free atmospheric O2-mediated oxidation of 5-Hydroxymethylfurfural to 2, 5-Furandicarboxylic acid triggered by Mg-bearing MTW zeolite supported Au nanoparticles. *Appl. Catal. A Gen*, 616, 118106.
41. Ban, H., Zhang, Y., Chen, S., Cheng, Y., Pan, T., Wang, L., & Li, X. (2020). Production of 2, 5-furandicarboxylic acid by optimization of oxidation of 5-methyl furfural over homogeneous Co/Mn/Br catalysts. *ACS Sustain Chem. Eng*., 8(21), 8011-8023.
42. Mittal, N., Kaur, M., & Singh, V. (2023). Mild and selective catalytic oxidation of 5-HMF to 2, 5-FDCA over metal loaded biomass derived graphene oxide using hydrogen peroxide in aqueous media. *Mol. Catal.*, 546, 113223.
43. Herlina, I., Krisnandi, Y. K., & Ridwan, M. (2024). Oxidation of 5-hydroxymethylfurfural into 2, 5-furandicarboxylic acid over CuO and NiO modified natural sourced hierarchical ZSM-5. *S. Afr. J. Chem. Eng.*, 47(1), 75-82.
44. Zhang, S., Yang, Y., Chu, G., Wang, S., Wang, C., Zhang, Y & Mei, J. (2023). Surface chemistry regulation on particle-support interaction of ruthenium and Cr-Fe oxides for selective oxidation of 5-hydroxymethylfurfural. *J. Chem. Eng.*, 474, 145670.
45. Tirsoaga, A., El Fergani, M., Nuns, N., Simon, P., Granger, P., Parvulescu, V. I., & Coman, S. M. (2020). Multifunctional nanocomposites with non-precious metals and magnetic core for 5-HMF oxidation to FDCA. *Appl. Catal. B-Environ.*, 278, 119309.
46. Kim, M., Su, Y., Fukuoka, A., Hensen, E. J., & Nakajima, K. (2018). Aerobic oxidation of 5-(hydroxymethyl) furfural cyclic acetal enables selective furan-2, 5-dicarboxylic acid formation with CeO2-supported gold catalyst. *Angew. Chem., Int. Ed.*, 57(27), 8235-8239.
47. Motagamwala, A. H., Won, W., Sener, C., Alonso, D. M., Maravelias, C. T., & Dumesic, J. A. (2018). Toward biomass-derived renewable plastics: Production of 2, 5-furandicarboxylic acid from fructose. *Sci. Adv.*, 4(1), eaap9722.
48. Kar, S., Zhou, Q. Q., Ben-David, Y., & Milstein, D. (2022). Catalytic furfural/5-hydroxymethyl furfural oxidation to furoic acid/furan-2, 5-dicarboxylic acid with H2 production using alkaline water as the formal oxidant. *J. Am. Chem. Soc.*, 144(3), 1288-1295.
49. Chen, G., Wu, L., Fan, H., & Li, B. G. (2018). Highly efficient two-step synthesis of 2, 5-furandicarboxylic acid from fructose without 5-hydroxymethylfurfural (HMF) separation: in situ oxidation of HMF in alkaline aqueous H2O/DMSO mixed solvent under mild conditions. *Ind. Eng. Chem. Res.*, 57(48), 16172-16181.

50. Jensen, M. H., & Riisager, A. (2020). Advances in the synthesis and application of 2, 5-furandicarboxylic acid. *Biomass, Biofuels, Biochemicals*, (1)135-170.
51. S.S. Stahl, A.B. Powell, T.W. Root, D.S. Mannel, M.S. Ahmed (2017). Conversion of Alcohols to Alkyl Esters and Carboxylic Acids Using Heterogeneous Palladium based Catalysts. U.S. Patent 9,593,064.
52. Rathod, P. V., & Jadhav, V. H. (2018). Efficient method for synthesis of 2, 5-furandicarboxylic acid from 5-hydroxymethylfurfural and fructose using Pd/CC catalyst under aqueous conditions. *ACS Sustain Chem Eng.*, *6*(5), 5766-5771.
53. Gupta, K., Rai, R. K., Dwivedi, A. D., & Singh, S. K. (2017). Catalytic Aerial Oxidation of Biomass-Derived Furans to Furan Carboxylic Acids in Water over Bimetallic Nickel–Palladium Alloy Nanoparticles. *Chem. Ca.t Chem*., 9(14), 2760-2767.
54. Wang, S., Zhang, Z., & Liu, B. (2015). Catalytic conversion of fructose and 5-hydroxymethylfurfural into 2, 5-furandicarboxylic acid over a recyclable Fe3O4–CoO x magnetite nanocatalyst. *ACS Sustain Chem Eng.* 3(3), 406-412.
55. Yan, D., Xin, J., Zhao, Q., Gao, K., Lu, X., Wang, G., & Zhang, S. (2018). Fe–Zr–O catalyzed base-free aerobic oxidation of 5-HMF to 2, 5-FDCA as a bio-based polyester monomer. *Catal. Sci. Technol.*, 8(1), 164-175.
56. G. Grabowski, G., Lewkowski, J., & Skowroński, R. (1991). The electrochemical oxidation of 5-hydroxymethylfurfural with the nickel oxide/hydroxide electrode. *Electrochim. Acta*, 36(13), 1995.
57. Vuyyuru, K. R., & Strasser, P. (2012). Oxidation of biomass derived 5-hydroxymethylfurfural using heterogeneous and electrochemical catalysis. *Catal. Today*, 195(1), 144-154.
58. Chadderdon, D. J., Xin, L., Qi, J., Qiu, Y., Krishna, P., More, K. L., & Li, W. (2014). Electrocatalytic oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid on supported Au and Pd bimetallic nanoparticles. *Green Chem.*, 16(8), 3778-3786.
59. Kubota, S. R., & Choi, K. S. (2018). Electrochemical oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid (FDCA) in acidic media enabling spontaneous FDCA separation. *ChemSusChem*, 11(13), 2138-2145.
60. Barwe, S., Weidner, J., Cychy, S., Morales, D. M., Dieckhöfer, S., Hiltrop, D., ... & Schuhmann, W. (2018). Electrocatalytic oxidation of 5-(hydroxymethyl) furfural using high-surface-area nickel boride. *Angew. Chem. Int. Ed*., 57(35), 11460-11464.
61. Xu, S., Zhou, P., Zhang, Z., Yang, C., Zhang, B., Deng, K., ... & Zhu, H. (2017). Selective oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid using O2 and a photocatalyst of Co-thioporphyrazine bonded to g-C3N4. *J. Am. Chem. Soc.*, 139(41), 14775-14782.
62. Han, G., Jin, Y. H., Burgess, R. A., Dickenson, N. E., Cao, X. M., & Sun, Y. (2017). Visible-light-driven valorization of biomass intermediates integrated with H2 production catalyzed by ultrathin Ni/CdS nanosheets. *J. Am. Chem. Soc.*, 139(44), 15584-15587.
63. Cha, H. G., & Choi, K. S. (2015). Combined biomass valorization and hydrogen production in a photoelectrochemical cell. *Nat. Chem.*, 7(4), 328-333.
64. F. Koopman, F., Wierckx, N., de Winde, J. H., & Ruijssenaars, H. J. (2010). Efficient whole-cell biotransformation of 5-(hydroxymethyl) furfural into FDCA, 2, 5-furandicarboxylic acid. *Bioresour. Technol.*, 101(16), 6291-6296.
65. Dijkman, W. P., Groothuis, D. E., & Fraaije, M. W. (2014). Enzyme-catalyzed oxidation of 5-hydroxymethylfurfural to furan, 2, 5-dicarboxylic acid. *Angew. Chem. Int. Ed*., *53*(25), 6515-6518.
66. Carro, J., Ferreira, P., Rodríguez, L., Prieto, A., Serrano, A., Balcells, B., ... & Martínez, A. T. (2015). 5-hydroxymethylfurfural conversion by fungal aryl-alcohol oxidase and unspecific peroxygenase. *Febs. J.*, 282(16), 3218-3229.
67. Qin, Y. Z., Li, Y. M., Zong, M. H., Wu, H., & Li, N. (2015). Enzyme-catalyzed selective oxidation of 5-hydroxymethylfurfural (HMF) and separation of HMF and 2, 5-diformylfuran using deep eutectic solvents. *Green Chem.*, 17(7), 3718-3722.
68. Wang, K. F., Liu, C. L., Sui, K. Y., Guo, C., & Liu, C. Z. (2018). Efficient catalytic oxidation of 5-hydroxymethylfurfural to 2, 5-furandicarboxylic acid by magnetic laccase catalyst. *Chem. Bi.o Chem.*, 19(7), 654-659.

