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Research Article

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The effect of gamma radiation on 5-hydroxymethylfurfural conversion in water and dimethyl sulfoxide

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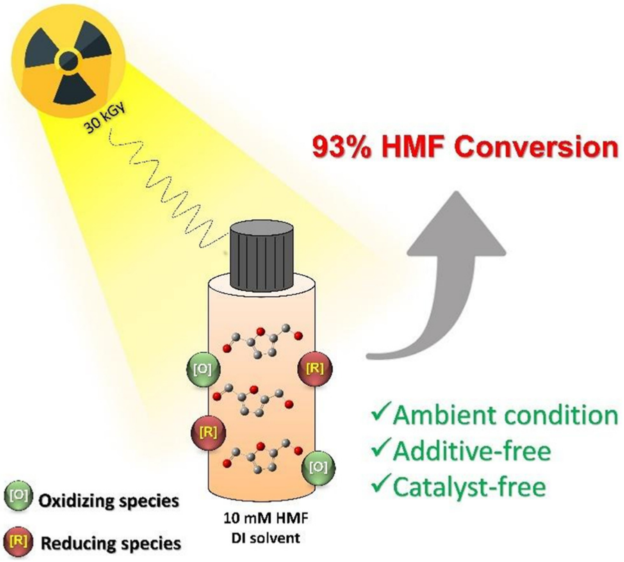
Abstract: 5-Hydroxymethylfurfural (HMF) is a biomass-based chemical platform that can undergo many feasible reactions. One of the most important reactions is the oxidation to 2,5-furandicarboxylic acid (FDCA), which is the monomer for bioplastic production. In this work, the radiation method was used to investigate the conversion of HMF in both aqueous (DI) and dimethyl sulfoxide (DMSO) solutions. The effects of media solvents, atmospheric gases, HMF concentrations, additive bases, and absorbed doses of gamma radiation were studied. The results showed that the media solvent played a crucial role in HMF conversion under gamma irradiation. At 30 kGy, the HMF conversions in DI and DMSO were 92.1 and 24.1%, respectively, and the oxidation products were only found in the irradiated samples under DMSO. The HMF conversion and oxidation product formation increased with the gamma radiation dose. Moreover, it was found that FDCA stability toward gamma irradiation is highly sensitive in aqueous solution but relatively stable in DMSO. The results implied the alternative promising choice of radiation method compared with traditional methods. To join the bridge, the use of a mixture solvent DI/DMSO seems considerable in the future.



Graphical abstract

Keywords: 5-hydroxymethylfurfural, gamma radiation, HMF conversion, 2,5-furandicaboxylic acid, HMF oxidation

Nomenclature

HMF	5-Hydroxymethylfurfural
FDCA	2,5-Furandicaboxylic acid
DFF	2,5-Diformylfuran
HMFCA	5-Hydroxymethyl-2-furancarboxylic acid
FFCA	5-Formyl-2-furancarboxylic acid
LCB	Lignocellulosic biomass
MF	5-Methylfurfural
BHMF	2,5-Bis(hydroxymethyl)furan

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PEF	Polyethylene furanoate
PET	Polyethylene terephthalate
HPLC	High-performance liquid chromatography
DFT	Density-functional theory
LUMO	Least unoccupied molecular orbital
Na_2CO_3	Sodium carbonate
$NaHCO_3$	Sodium bicarbonate
KOH	Potassium hydroxide
K_2CO_3	Potassium carbonate
NaOH	Sodium hydroxide
TFA	Trifluoroacetic acid
DI	Deionized water
LA	Levulinic acid
FA	Formic acid
DMSO	Dimethyl sulfoxide
DMF	Dimethyl formamide
THF	Tetrahydrofuran
ACN	Acetonitrile

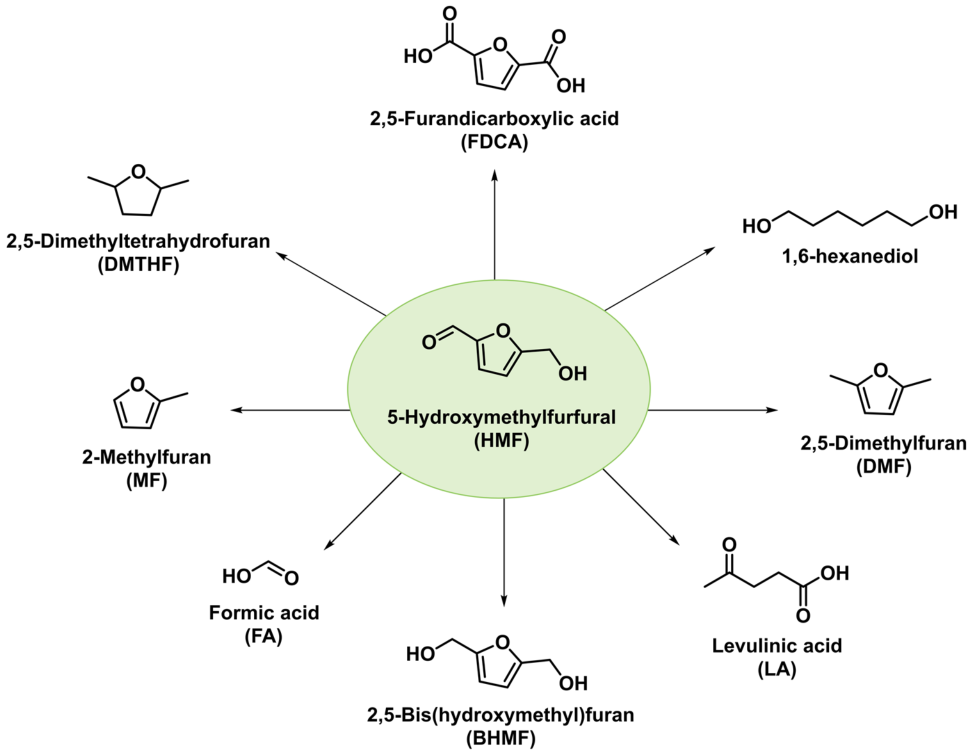
1 Introduction

5-Hydroxymethylfurfural (HMF) was discovered by Düll and Kiermayer [1] in the late eighteenth century. Its versatile applications and great capabilities to replace fossil-fuel utilization allowed it to be denoted a sleeping giant and listed as one of the top ten chemical platforms for sustainable development in the chemical industry by the US Department of Energy since 2004 [2]. It can be synthesized from lignocellulosic biomass (LCB) by hydrolysis of carbohydrates into hexose sugars (i.e., glucose and fructose), followed by dehydration to HMF. Even though the concept of this process seems simple, the formation of side reactions [3], such as hydrolysis to levulinic acid (LA) and formic acid (FA) and cross polymerization to soluble polymer and insoluble humin, sometimes raises the complexity. One of the factors that was considered to improve the selectivity for HMF formation is the media solvent. The integration of a polar aprotic solvent such as dimethyl sulfoxide (DMSO), dimethyl formamide (DMF), tetrahydrofuran (THF), acetonitrile (ACN), and acetone into the synthetic system revealed a better yield of HMF than conducting in a water-only system [4]. DMSO is the most favorable choice among those candidates due to its ability to strongly bind with both substituted groups of HMF, which enhanced its LUMO energy, suppressing the side reactions [5], as reported in Bhaumik and Dhepe [6] and Yu's works [7].

The structure of HMF consists of a furan ring substituted by aldehyde and hydroxymethyl groups at the C_2 and C_5 positions, respectively. HMF is an important platform that can convert into various value-added chemicals, as shown in Scheme 1. By opening the ring or modifying the functional groups, it can undergo many feasible reactions, including rehydration to LA and FA [9], ring-opening oxidation to succinic acid [10], hydrogenation to 5-methylfurfural (MF) [11] or 2,5-bis(hydroxymethyl)furan (BHMF) [12], ring cleavage to hexanediol [13] or hexanedione [14], and condensation and hydrodeoxygenation to alkane [15]. Moreover, oxidation of its substituted groups leads to the formation of various valuable compounds, including 2,5-diformylfuran (DFF) [16], 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) [17], 5-formyl-2-furancarboxylic acid (FFCA) [18], and 2,5-furandicarboxylic acid (FDCA) [19], as shown in Scheme 2 [20]. Interestingly, all compounds can be applied in many applications; DFF is the platform molecule for fine chemicals and pharmaceutical drugs [16], and HMFCA is the monomer to prepare furanic polyesters and is used for anticancer and interleukin inhibitors in the pharmacy industry [17]. FFCA is an important intermediate in the production of FDCA, which is a monomer in bioplastic production. Polymerization of FDCA with ethylene glycol produces polyethylene furanoate (PEF), which can act in a manner similar to a well-known petroleum-based polyethylene terephthalate (PET) [20].

In the last 20 years, over 2,000 studies on HMF-derived FDCA have been published [21], and the most commonly used method reported in the literature is conventional heating with the addition of metal catalysts and oxidizing agents [21,22]. Recently, the microwave irradiation method has also been reported [23,24]. These traditional methods showed favorable outcomes in terms of yield and selectivity. However, they required the chemical additives as well as the operation under high temperatures (100–150°C) and high pressures (>0.3 MPa) with reaction times of 2–24 h [23], which allowed the enlargement of chemical waste and extended cost, risk of explosion, and difficulty to upscale. To the best of our knowledge, there is no report on gamma irradiation methods in this aspect. The use of gamma irradiation was believed to overcome the extreme conditions and chemical addition due to the ability to penetrate radiation and self-generate the active free radicals via excitation and ionization, as well as allow the convenience for large-scale production [25,26]. The reaction can be performed in up-scale size and can be used as the catalytic agent for large chemical production in the industries [25]. For example, radiolysis of water gives rise to both reducing agents (e^-_{eq}, $H^\bullet$, H_2) and oxidizing agents ($HO^\bullet$, H_2O_2, H_3O^+) as shown in equation (1) [27,28]:

$$\begin{aligned} H_2O\ \gamma \rightarrow {} & [2.8]HO^\bullet + [2.7]e^-_{aq} + [0.6]H^\bullet + [0.72]H_2O_2 \\ & + [2.7]H_3O^+ + [0.45]H_2, \end{aligned} \tag{1}$$



Scheme 1: Potential chemical compounds derived from 5-HMF [8].

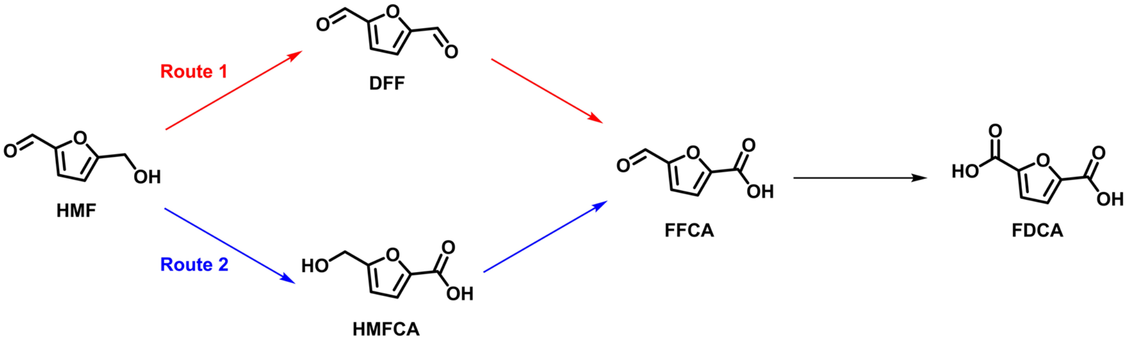
where the values in brackets are the number of each molecule generated per 100 eV (*G*-value). It is worth noticing from the equation that the oxidizing species are generated in higher amounts than the reducing agent. Taking the benefit from these advantages, gamma irradiation was a novel choice for HMF oxidation.

This project provided an important opportunity to advance the understanding of the radiation process for HMF conversion. The effects of solvents (water and DMSO), atmospheric gases (air, N_2, O_2, and N_2O), initial concentration of HMF, additives, and gamma doses were studied. Water was reported as a general solvent for the HMF reaction, which gave a high yield, but there were several by-products; however, DMSO had a few issues. The stability of FDCA and the potential oxidation products of HMF were also studied under gamma irradiation.

2 Experimental

2.1 Materials and instruments

5-Hydroxymethylfurfural (HMF), 2,5-furandicarboxylicaldehyde (DFF), and 2,5-Furandicarboxylic acid (FDCA) were purchased from Sigma-Aldrich. 5-Hydroxymethyl-2-furancarboxylic



Scheme 2: Oxidation pathway of HMF to FDCA.

acid (HMFCA) and 5-formyl-2-furancarboxylic acid (FFCA) were purchased from TCI. The bases used in this work, including sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), potassium hydroxide (KOH), and potassium carbonate (K_2CO_3) were purchased from Merck, ALPHA CHEMIKA, Ajax Finechem, KEMAUS, and Daejung, respectively. Trifluoroacetic acid (TFA) was purchased from Merck, and DMSO was purchased from RCI Labscan. All chemicals were of analytical grade and used as received without further purification. Methanol (HPLC grade) was purchased from Fisher Chemical. Deionized water (DI) was collected from ultra-pure water ASTM Type I, ThermoScientific, with a resistivity > 18.2 MΩ. Gamma radiation was generated from a cobalt-60 irradiator (30366 Ci) coupled with Harwell Amber Perspex dosimeter with a dose rate of 1.7 kGy/h.

2.2 Experimental setup

The experiments on HMF conversion under gamma irradiation were conducted in three duplicates. Primarily, liquid HMF was added into a 10 mL amber vial and dissolved with either DI or DMSO. In an aqueous solution, an equivalence of base was mixed into the vial. The mixture was covered and bubbled with gas for 5 min. The solution was then irradiated under gamma radiation to the target absorbed dose. The recovered sample would be worked up and subsequently analyzed by high-performance liquid chromatography (HPLC, Waters 2695) coupled with a UV-visible detector (Waters 2489) at wavelengths of 280 and 254 nm using ZORBAX C18 reverse column and 0.1% TFA/MeOH (80:20) mobile phase. The stabilities of FDCA in both solvents were also determined by a similar process under ambient conditions.

3 Results and discussion

3.1 Effect of atmospheric gases and media solvents

In this work, the conversion of HMF and the subsequent oxidation product formation under gamma irradiation were investigated. First, the experiment was conducted at 30 kGy with varied atmospheric gases and media solvents. According to radiation chemistry, the reaction system filled with oxygen or nitrous gas was assumed to scavenge electrons (e^-_{eq}), rendering the whole system environment to a more oxidized condition after gamma irradiation, as described in the equation (1) [29]. The system filled with nitrogen aimed to reduce the amount of dissolved oxygen in the solvent [30]. The reaction under an ambient atmosphere (without bubbling of gas) was also conducted for comparison. However, the obtained results, depicted in Figure 1, exhibited no significant difference in the HMF conversion regarding the atmospheric gas variation.

On the other hand, media solvent played an important role in the HMF conversion and oxidative products. HMF conversion in aqueous solution is much greater than in DMSO. Unfortunately, conversion up to 92.1% in aqueous solution led to other side reactions, as shown in Table 1, which is suspected to rehydrate back to LA and FA [31]. The HMF rehydration pathway is suggested to consist of the formation of 2,5-dioxo-3-hexenal, followed by the decomposition to LA and FA, as shown in Scheme 3 [9]. According to Zhang and Weitz's report [32], ^{13}C-labeled HMF showed that the breaking at the C_1–C_2 position of HMF led to the transformation of HMF to FA, and the C_6 position of HMF was mapped onto the carbon of LA. The results confirmed the rehydration reaction of HMF to LA and FA (Scheme 3). In addition, the analysis of the products from the conversion of HMF in water was investigated using a liquid chromatography-mass spectrometer (LC-MS), provided in the supporting information as shown in Figure S1. There were peaks at 115 *m*/*z*, corresponding to LA, and at 127 *m*/*z*, corresponding to the remaining HMF. However, FA cannot be detected because its molecular weight is lower than that of a liquid chromatography-mass instrument.

The oxidation beyond FDCA is another possibility of HMF conversion in an aqueous solution, so this assumption would later be proved by investigating FDCA stabilities under gamma irradiation in both solvents. This research

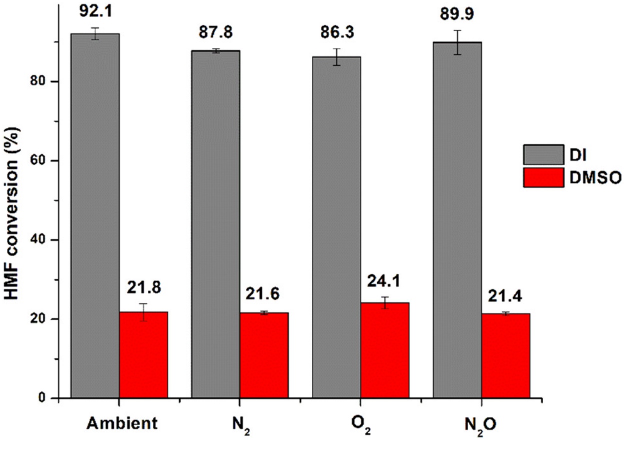


Figure 1: Effect of the atmospheric gas and media solvent variation on the conversion of HMF under gamma irradiation at 30 kGy (reaction conditions: HMF 0.1 mmol, solvent (DI or DMSO) 10.0 mL, bubbled gas: N_2, O_2, or N_2O).

Table 1: HMF conversion, the oxidation product yield, and selectivity induced by gamma irradiation in aqueous and DMSO solution with various atmospheric gases (reaction conditions: HMF, 0.1 mmol; solvent: 10.0 mL DI or DMSO; bubbled gas: N_2, O_2, or N_2O, at 30 kGy)

Entry	Solvent	Gas	HMF conversion (%)	HMFCA yield (%)	HMFCA selectivity (%)	FFCA yield (%)	FFCA selectivity (%)
1	DI	Ambient	92.1 ± 1.5	ND	ND	ND	ND
2		N_2	87.8 ± 0.6	ND	ND	ND	ND
3		O_2	86.3 ± 2.1	ND	ND	ND	ND
4		N_2O	89.9 ± 3.0	ND	ND	ND	ND
5	DMSO	Ambient	21.8 ± 2.2	3.3	14.9	9.3	43.0
6		N_2	21.6 ± 0.4	3.0	13.9	8.4	38.7
7		O_2	24.1 ± 1.6	3.2	13.1	9.1	37.6
8		N_2O	21.4 ± 0.5	3.5	16.4	8.1	37.9

Note: ND: not determined.

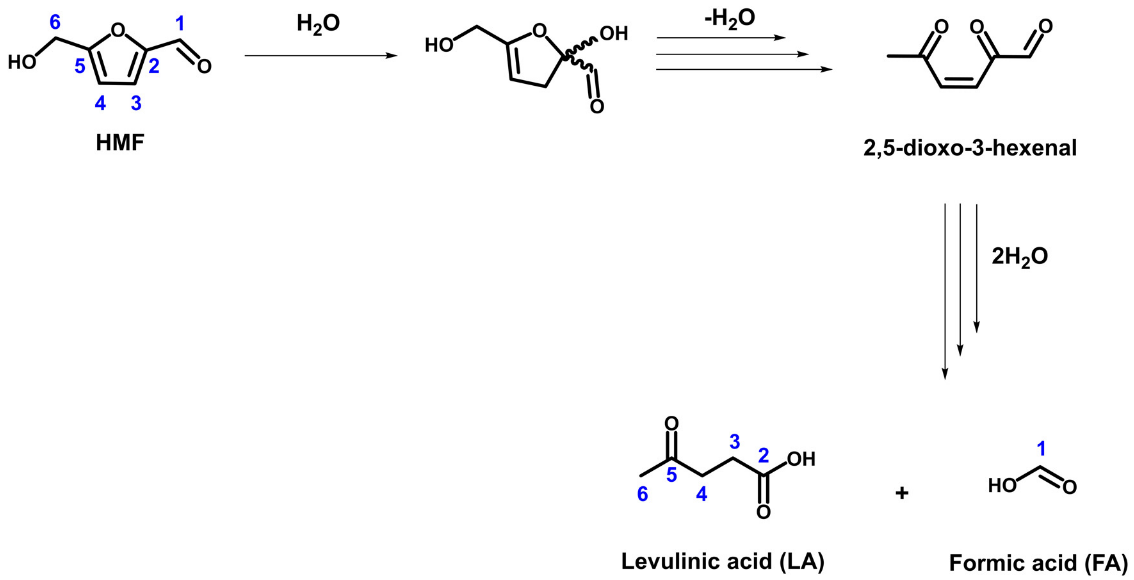
focused on the investigation of the radiation effect on HMF conversion; therefore, no catalysts were used in this experiment, resulting in low selectivity of the oxidative products.

For DMSO, some HMFCA (3.0–3.5% yield) and FFCA (8.1–9.3% yield) are detected in the reaction in DMSO even when HMF conversion was only 21.4–24.1%. The relatively low conversion confirmed the tolerance of HMF in this polar aprotic solvent (DMSO). Low HMF conversion may result from the formation of reducing agents (H_2, CH_4, and C_2H_6) during gamma irradiation, as shown in equation (2) [33]. However, better selective oxidative products in HMF were oxidized to HMFCA, FFCA, and FDCA. Therefore, the further experiments were focused on using DMSO as a solvent:

$$\begin{aligned} CH_3SOCH_3\gamma \rightarrow [0.2]H_2 + [3.3]CH_4 + [0.49]C_2H_6 \\ + [1.2](CH_3)_2S. \end{aligned} \tag{2}$$

3.2 Effect of initial HMF concentration on HMF conversion at different gamma doses

As mentioned previously, HMF is more stable in DMSO and also more selective to oxidative products to the FDCA production pathway because DMSO can suppress the rehydration and polycondensation of HMF, which are the side reactions that occur in the water system [34]. Therefore, the insight experiment was then carried out in DMSO with the variation of HMF concentration to further investigate the conversion trend and the dependency of the oxidation product formation at gamma irradiations of 0, 10, 20, and 30 kGy. The HMF conversion and oxidative products increased significantly as the gamma dose increased, as shown in Figure 2. Approximately 5% of HMF conversion was found



Scheme 3: Rehydration pathway of HMF to LA and FA [9].

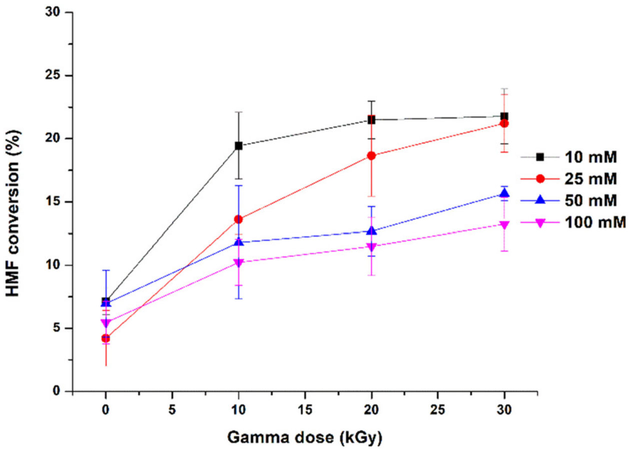


Figure 2: Effect of the initial HMF concentration and absorbed dose of gamma radiation variation on the conversion of HMF under gamma irradiation (reaction conditions: various HMF concentrations: 10, 25, 50, and 100 mM; DMSO, 10.0 mL; ambient gas: at 0, 10, 20, and 30 kGy).

without gamma irradiation [35]. DMSO was initially associated with the hydroxyl group of HMF to form a DMSO-mediated reaction, followed by the free hydroxyl group of another HMF replacing the DMSO associated by the S_N2 reaction to provide oxo-bis(5-methyl-2-furaldehyde) [35]. However, no oxidation products were found in all non-irradiated samples (0 kGy).

The effect of the initial HMF concentration was investigated. The HMF conversion increased as the initial concentration of HMF decreased; that is, the formation of these oxidation products required sufficient radiation energy for each concentration. The reaction may occur via the radical pathway involving bond breaking, crosslinking, or mixing. This would relate to the proposed mechanism of HMF conversion, as mentioned previously. Ramírez-Cahero and Valdivia-López [36] reported the effect of gamma radiation on furanoids, where HMF is sensitive to radiation and can decompose to a greater extent. Their results indicated that the aldehyde functional group of HMF is more favorable to oxidation than its hydroxymethyl group, leading to the high formation of HMFCA. Thus, the oxidation pathway of HMF by gamma radiation might undergo HMFCA (Scheme 1, Route 2). According to our results, the best HMF conversion was at an HMF concentration of 10 mM at 30 kGy, in which HMFCA and FFCA yields were 3.3 and 9.3%, respectively (Table 2). Notably, the yield obtained from the oxidation products is around half of the calculated conversion of HMF (Table 2). The remaining conversion may reduce to BHMF or other reduced products due to the generation of a reducing agent (H_2) from radiolysis of DMSO, as shown in equation (2). There are many reports that the hydrogenation of HMF requires H_2 in the reaction [37,38]

These preliminary results show the possibility of gamma irradiation for HMF oxidation to FFCA without the addition of catalyst and base. Although this system exhibited low HMF conversion, the selectivity is approximately 50% without the catalyst and base. This shows that it is possible to increase conversion by using suitable catalysts.

Table 2: HMF conversion, yield of the oxidation product, and selectivity induced by gamma irradiation with initial HMF concentration variation in DMSO solution (reaction conditions: various HMF concentrations: 10, 25, 50, and 100 mM; DMSO, 10.0 mL; ambient gas, at 0, 10, 20, and 30 kGy)

Entry	HMF concentration (mM)	Gamma dose (kGy)	HMF conversion (%)	HMFCA yield (%)	HMFCA selectivity (%)	FFCA yield (%)	FFCA selectivity (%)
1	10	0	7.1 ± 1.0	ND	ND	ND	ND
2		10	19.4 ± 2.6	1.5	7.8	ND	ND
3		20	21.5 ± 1.5	2.6	12.0	7.5	34.9
4		30	21.8 ± 2.2	3.3	14.9	9.3	43.0
5	25	0	4.2 ± 2.2	ND	ND	ND	ND
6		10	13.6 ± 1.2	ND	ND	ND	ND
7		20	18.7 ± 3.2	2.9	15.5	3.3	17.6
8		30	21.2 ± 2.3	3.5	16.7	3.6	17.2
9	50	0	7.0 ± 2.7	ND	ND	ND	ND
10		10	11.8 ± 4.5	ND	ND	ND	ND
11		20	12.7 ± 2.0	0.3	2.1	2.3	18.4
12		30	15.7 ± 0.5	0.6	4.0	2.8	18.2
13	100	0	5.5 ± 1.7	ND	ND	ND	ND
14		10	10.2 ± 1.8	ND	ND	ND	ND
15		20	11.5 ± 2.3	0.6	5.2	3.2	27.7
16		30	13.2 ± 2.1	0.7	5.7	3.8	29.0

Note: ND: not determined.

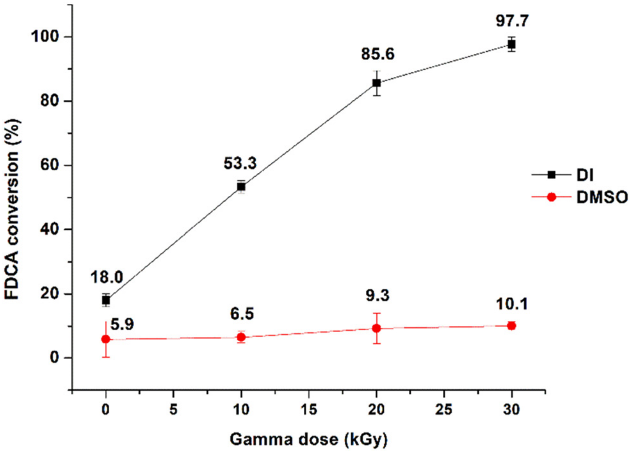


Figure 3: The stability of FDCA in both aqueous and DMSO solutions under gamma irradiation (reaction conditions: FDCA, 0.1 mmol; solvent: 10.0 mL DI or DMSO; ambient gas: at 0, 10, 20, and 30 kGy).

3.3 Stability of FDCA under gamma irradiation

Finally, the stability of FDCA under gamma irradiation in aqueous and DMSO was determined under an ambient atmosphere at 0, 10, 20, and 30 kGy. As shown in Figure 3, FDCA is relatively stable in DMSO under gamma irradiation with the conversion in the range of 5.9–10.1%. However, in an aqueous solution, FDCA almost completely degraded at an absorbed dose of 30 kGy, where no oxidative products were detected (Table 3). The report of Pal and Saravanamurugan [39] revealed some possible conversion products of FDCA, including 2,5-dihydroxymethyl tetrahydrofuran, furoic acid, and succinic acid. Table 4 compares the conversion of HMF and FDCA conversion in DMSO at 0, 10, 20, and 30 kGy. The results demonstrated that FDCA is more stable than HMF under gamma irradiation, where FDCA conversion was 5.9–10.1%, but HMF conversion was 7.1–21.8%. The high HMF conversion was obtained after gamma irradiation due to unstable molecules of HMF [40]. Furthermore, HMF can transform to other products in H_2O more than in DMSO because DMSO binds HMF stronger than H_2O, leading to inhibition of side reactions of HMF. DFT calculations showed that the LUMO energy of HMF was increased in DMSO, which prevented the nucleophilic attack and reduced undesirable hydration and polycondensation reactions [41]. Likewise, FDCA is also stable in DMSO under gamma irradiation.

Table 3: FDCA conversion induced by gamma irradiation in aqueous and DMSO solutions (reaction conditions: 0.1 mmol FDCA; solvent, 10.0 mL DI or DMSO; ambient gas, at 0, 10, 20, and 30 kGy)

Entry	Solvent	Gamma dose (kGy)	FDCA conversion (%)
1	DI	0	18.0 ± 2.0
2		10	53.3 ± 1.9
3		20	85.6 ± 3.8
4		30	97.7 ± 2.3
5	DMSO	0	5.9 ± 5.6
6		10	6.5 ± 1.8
7		20	9.3 ± 4.8
8		30	10.1 ± 1.2

3.4 Comparison with other reports

In this scientific evaluation, various methodologies for the conversion of hydroxymethylfurfural (HMF) to valuable products, particularly FDCA, are examined as shown in Table 5. Among these, the radiation method, a novel approach implemented in this work, demonstrates significant potential. This method shows high HMF conversion efficiency in aqueous conditions, and when applied in DMSO solvent under base- and catalyst-free conditions it exhibits favorable selectivity for oxidation products.

Comparatively, Chen et al.'s approach [42], utilizing a heat method at 75°C with $NaHCO_3$ and H_2O_2 in H_2O, achieved a 93–100% HMF conversion rate, with an enhancement upon the addition of a Ru/AC catalyst. Zhao et al.'s methodology [23] employed microwave irradiation with a Ru/AC catalyst and Na_2CO_3 base in water, resulting in complete HMF conversion and high FDCA yield. Other studied methods, including the use of Mn/Fe mixed oxides [43], Pt/γ-Al_2O_3 [44], and γ-Fe_2O_3@HAP-Pd(0) [45], required additional O_2 pressure and base additives to achieve conversion rates of 93–97%. In DMSO solvents, catalysts like Ru/C [46], Pt/C [34], and Fe_3O_4-CoO_x [47] reached conversion efficiencies of 97.2–100% and FDCA yields of 59.8–93%, depending on base additives or oxidants. Moreover, Pt/C–O–Mg [48] resulted in 21.5% HMF conversion under heating without

Table 4: HMF and FDCA conversion induced by gamma irradiation in DMSO solution (reaction conditions: 0.1 mmol HMF or FDCA; DMSO, 10.0 mL; ambient gas, at 0, 10, 20, and 30 kGy)

Entry	Solvent	Gamma dose (kGy)	HMF conversion (%)	FDCA conversion (%)
1	DMSO	0	7.1 ± 1.0	5.9 ± 5.6
2		10	19.4 ± 2.6	6.5 ± 1.8
3		20	21.5 ± 1.5	9.3 ± 4.8
4		30	21.8 ± 2.2	10.1 ± 1.2

Table 5: Comparison of the other reported catalysts for HMF conversion and product yield

Catalyst	Additives	Method	Reaction conditions	HMF conversion (%)	Reference
—	—	Gamma irradiation (30 kGy)	Solvent: H_2O Under air conditions Time: 51 h	92.1	This work
—	—		Solvent: DMSO Under air condition Time: 51 h	21.8	
Ru/AC	H_2O_2, Na_2CO_3, NaOH	Microwave heating (continuous flow)	Solvent: H_2O Under air conditions Time: 0.5 h, 80°C	100	Zhao et al. [23]
Ru/AC	H_2O_2, Na_2CO_3	Heating	Solvent: H_2O Under air conditions Time: 1 h, 75°C	100	Chen et al. [42]
Mn/Fe mixed oxides	NaOH	Hydrothermal	Solvent: H_2O Under O_2 (8 bar) Time: 24 h, 90°C	93	Neațu et al. [43]
Pt/γ-Al_2O_3	Na_2CO_3	Hydrothermal	Solvent: H_2O Under O_2 (1 bar) Time: 12 h, 140°C	96	Sahu et al. [44]
γ-Fe_2O_3@HAP-Pd(0)	K_2CO_3	Heating	Solvent: H_2O Under O_2 (1 bar) Time: 6 h, 100°C	97	Zhang et al. [45]
Ru/C	$NaHCO_3$	Hydrothermal	Solvent: DMSO/H_2O Under O_2 (40 bar) Time: 12 h, 130°C	100	Liu et al. [46]
Pt/C	K_2CO_3	Heating	Solvent: DMSO/H_2O (3:1) Under O_2 Time: 10 h, 100°C	100	Chen et al. [34]
Fe_3O_4–CoO_x	—	Heating	Solvent: DMSO Oxidant: *t*-BuOOH Time: 15 h, 80°C	97.2	Wang et al. [47]
Pt/C–O–Mg	—	Hydrothermal	Solvent: DMSO Under O_2 (10 bar) Time: 12 h, 110°C	21.5	Han et al. [48]

base additives. In this study, the radiation method applied in DMSO solvent resulted in 21.8% HMF conversion, with selectivities of 14.9 and 43% for HMFCA and FFCA, respectively. This method demonstrated high efficiency in HMF conversion under aqueous conditions and effective selectivity for oxidative products in DMSO under base- and catalyst-free conditions. The potential of the radiation method for converting HMF into high-value products is evident, and future work may explore the use of additives to further enhance selectivity for specific oxidation products.

4 Conclusions

In this research, the impact of atmospheric gas on the conversion of HMF was found to be minimal. However, the choice of the solvent, specifically DI and DMSO, played a significant role. Using gamma irradiation at a dose of 30 kGy in an aqueous solution, we achieved an impressive 92% conversion of HMF. However, in DI, this process led to side reactions rather than the desired oxidation to FDCA. In contrast, when using DMSO as the solvent, we observed a 24.1% conversion of HMF, leading to the formation of HMFCA and FFCA, without any additional chemicals, as DMSO itself acted as a base. No oxidation products were detected in samples that were not irradiated. Interestingly, FDCA remains stable under gamma irradiation in DMSO but is highly sensitive in an aqueous solution.

The findings of this study highlight that using an aqueous solution is effective for HMF conversion, while DMSO is advantageous for yielding oxidation products. This inspires considering the use of a mixed solvent of DI/DMSO in future experiments. However, challenges remain in enhancing the product yield and selectivity, as well as in designing suitable catalysts for these processes.

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