5-Hydroxy-2(5H)-furanone: a new platform chemical for bio-based four carbon chemicals

Yayati Naresh Palai[1], Atsushi Fukuoka[1]*, Abhijit Shrotri[1]*

Affiliations:

[1]Institute for Catalysis, Hokkaido University, Kita21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan

*Corresponding author. Email: ashrotri@cat.hokudai.ac.jp, fukuoka@cat.hokudai.ac.jp

Abstract: Industrial chemicals with a four-carbon backbone like maleic acid, 1,4-butanediol, γ-butyrolactone and pyrrolidones are currently obtained from petroleum. Synthesis of these C4 chemicals from biomass is difficult owing to the low abundance of C4 sugars and development of a suitable C4 platform chemical is necessary. We show that 5-hydroxy-2(5H)-furanone (5H5F) is a versatile platform for above mentioned C4 chemicals. 5H5F was synthesized by oxidation of furfural at room temperature in the presence of TS-1 catalyst with 92 % yield and was isolated by extraction. As a platform chemical, 5H5F was reactive under mild conditions owing to electrophilicity of the carbon atom attached to hydroxyl group. Oxidation, reduction and reductive aminolysis of 5H5F using supported metal catalysts produced industrial C4 chemicals in high yield. We propose that 5H5F can serve as multipurpose platform for C4 chemical synthesis from biomass in industry.

One-Sentence Summary: Facile synthesis and the reactive structure of 5-hydroxy-2(5H)-furanone makes it a good platform for C4 chemicals.

Main Text: Chemical synthesis from biomass is an attractive way to reduce the dependence of chemical industry on petroleum resources. Platform chemicals play a pivotal role towards this goal by serving as a bridge between the polymeric composite of biomass and the value-added chemical stream in industry. Owing to the abundance of hexose and pentose sugars in biomass, synthesis and reactions of platform chemicals with six and five carbon atoms, like 5-hydroxymethylfurfural, sorbitol and furfural and their downstream reactions are well documented in literature (*1–9*). However, the chemical industry also has a huge demand for chemicals with a four-carbon backbone (C4 chemicals). For example, more than 2 million tonnes of 1,4-butanediol (BDO) is produced each year for the manufacture of polymers (*10–12*). Similarly, maleic anhydride is used as a precursor for polymers and other C4 derivatives such as γ-butyrolactone (GBL), and 2-pyrrolidone (*12–14*). Catalytic synthesis of these C4 chemical from C5-C6 sugars has remained elusive owing to the low selectivity of C-C bond cleavage step (*15–17*). Microbial fermentation of sugars to succinic acid has had some success, owing to its high selectivity, but the technology has been proven difficult to commercialize (*18*). Therefore, the key scientific challenge is to discover an all-purpose C4 platform chemical which can be catalytically produced from biomass in high yield and serve as a versatile precursor for value added chemicals of the C4 chemical family. In this paper, we propose that 5-hydroxy-2(5H)-furanone can be an effective C4 platform for biomass derived C4 chemical synthesis (Fig. 1).
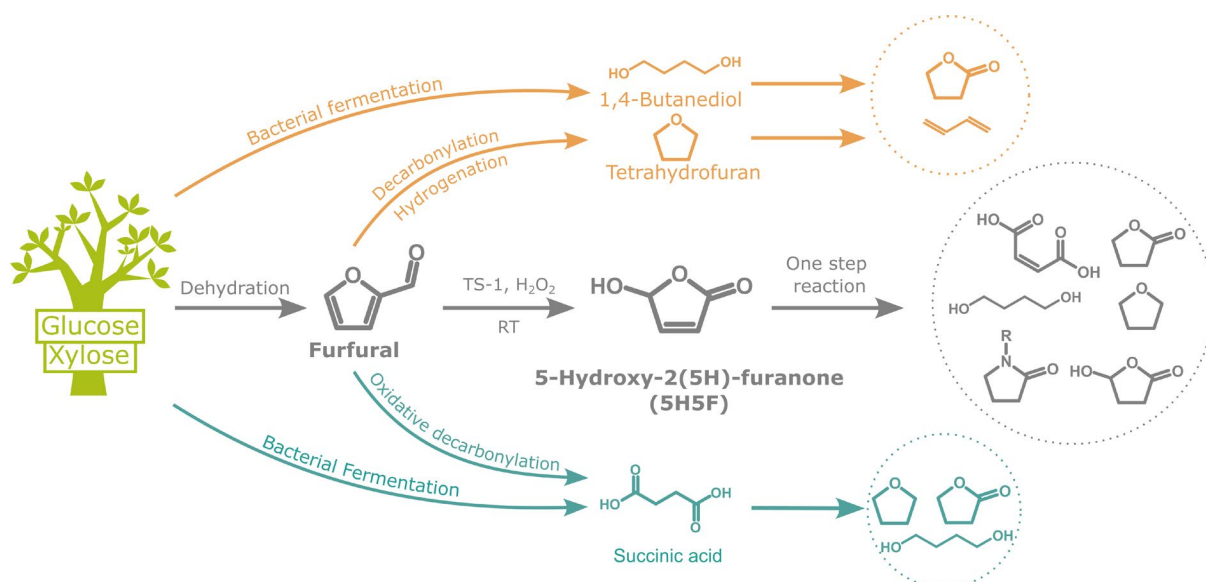

Fig. 1. Illustration showing C4 chemical synthesis pathway through 5-hydroxy-2(5H)-furanone in comparison with existing pathways showing accessibility to a larger C4 chemical pool in case of 5H5F as a platform chemical.

A good platform chemical should be an intermediate in the value chain with the ability to transform into diverse products. This provides flexibility in the manufacturing process and reinforces commercial applicability. Such a platform chemical would feature multiple functional groups that can be targeted for different reactions. Moreover, the synthesis of the platform should be facile with high selectivity, and it should not be prone to degradation during downstream reactions.

Succinic acid was the first well recognized bio-based C4 platform chemical (*19*). In a catalytic pathway, succinic acid is produced by oxidation of furfural using sulfonated carbons (*20*) or Lewis acid zeolites (*21*). The catalytic reaction has several steps and achieving high selectivity is difficult owing to multiple intermediates. As a platform chemical succinic acid can be converted in a single step to BDO, tetrahydrofuran (THF) and GBL via hydrogenation (*22–24*). However, succinic acid has two carboxylic acids as functional groups which limits

2

its reactive versatility. Moreover, harsh conditions are needed for its reaction owing to the formation of inter and intramolecular hydrogen bonds among the carboxylic acid groups in succinic acid (*25*). This issue, coupled with the corrosiveness of succinic acid under hydrothermal conditions, limits its use as an ideal C4 platform chemical (*26–28*).

Biomass derived BDO has also been proposed as a platform chemical in C4 chemistry. BDO synthesis from biomass is particularly attractive because it can be dehydrated to 1,3-butadine or THF. In a catalytic pathway, THF is obtained first instead of BDO by decarbonylation of furfural to furan followed by its hydrogenation. The decarbonylation of furfural has long been known to occur over Pd catalyst (*29*, *30*). However, in the subsequent hydrogenation reaction, adsorption of furan over catalyst surface is difficult owing to the lack of functional groups (*31*, *32*) and C-O bond breaking product like n-butanol and cracking products like propylene are formed along with BDO (*33*, *34*). Similar to succinic acid, BDO and THF also lack multiple functional groups necessary for flexibility in manufacture of diverse products.

Erythrose and erythritol are other potential C4 platforms, however the challenges in synthesizing C4 sugar in high yield has hampered their application (*15*). Considering the lack of a suitable C4 platform chemical, discovery of a new C4 platform is necessary to develop catalytic pathways for C4 chemical synthesis from biomass.

In this study, we introduce 5-hydroxy-2(5H)-furanone (5H5F) as a versatile C4 platform chemical for several industrially important products. Currently, 5H5F find use as a niche precursor for biologically active compounds and it is reportedly synthesized from furfural using photo or electrochemically activated oxygen radicals (*35–37*). In our study, 5H5F was obtained by oxidation of furfural at room temperature using titanium silicalite-1 (TS-1) with 92 % yield and isolated using extraction. The downstream reactions of 5H5F to C4 chemicals were facile and a variety of value-added chemicals were produced in a single step under mild conditions. In addition to oxygenates, nitrogen containing heterocyclic compounds were also obtained directly from 5H5F by reductive aminolysis.

Oxidation of furfural to 5H5F

5H5F was synthesized by oxidation of furfural at room temperature with Lewis acid zeolites in the presence of H_2O_2. See supporting information (SI) section 1.1, Fig. S1-S2 for details of reaction procedure and analysis of reaction mixture. TS-1 catalyst was much more active at room temperature when compared with Ti-Beta, Nb-Beta and Zr-Beta zeolite catalysts prepared by post-synthetic incorporation of metal ions in the Beta zeolite (See SI section 1.2 and Fig. S3-S8 for synthesis and characterization of catalysts). 5H5F yield of 92 % was obtained in 8 h when TS-1 was used as catalyst along with 93 % yield of formic acid (Table 1). Ti-Beta and Nb-Beta zeolites produced 15 % and 8 % yield of 5H5F at room temperature, respectively. The 5H5F yield was correlated with the activation of H_2O_2 over the metal sites as observed in the diffused reflectance UV-Vis spectrum of the H_2O_2 treated catalyst (Fig. 2a). Bands were observed in Ti-Beta, Nb-Beta and TS-1 catalyst, associated with charge transfer transition of metal peroxo or hydroperoxo species (Fig S9 shows models of different chemisorption modes of H_2O_2) (*38*, *39*), which are known to catalyze the epoxidation reaction. Unlike the band for H_2O_2 treated Ti-Beta and Nb-Beta, the band for H_2O_2 treated TS-1 catalyst was centered around 395 nm, suggesting a different structure of chemisorbed H_2O_2 in case of TS-1. Formation of bridging peroxo species in the presence of dinuclear Ti^{4+} site has been reported in literature, which is predicted to have a lower energy pathway for epoxidation reactions (*40*). In line with the UV-Vis peak positions and catalytic activity we propose TS-1 catalyst possesses such bridged peroxy species, which are responsible for high activity for furfural oxidation to 5H5F.

We have previously shown that 5H5F is formed as an intermediate in maleic acid synthesis from furfural with H_2O_2 and the rate of formation of 5H5F was 37 times faster than its conversion to maleic acid at 80 °C in presence of TS-1 (*21*). Therefore, in this study 5H5F was selectively produced at room temperature with H_2O_2 because its further oxidation to maleic acid would require higher activation energy. In the presence of stoichiometric H_2O_2 amount (2 eq.), the reaction was slower and 80 % yield of 5H5F was obtained after 24 h (Table 1 entry 9). Formation and accumulation of (Z)-4-oxopent-2-enedial (4O2EL), a C5 intermediate, was observed at lower H_2O_2 concentrations (see LC-MS of 4O2EL in Fig. S10). Epoxidation of the double bond away from carbonyl group in furfural would yield 4O2EL as shown in Fig. 2 b. When furfural-α-^2H was used as reactant only deuterated formic acid was obtained after reaction, originating from the cleavage of aldehyde group (Fig. S11). Hence, we propose that the conversion of 4O2EL occurs through non-catalytic Baeyer-Villiger oxidation to produce 5H5F because the terminal aldehyde group is highly electrophilic due to the presence of acyl substituent and susceptible to reaction with H_2O_2 (Fig. 2b). At low H_2O_2 concentration, accumulation of 4O2EL would slow the reaction, as it would be in equilibrium with its hydrated structures in water as evidenced by NMR analysis of mixture after reaction with sub-stoichiometric H_2O_2 amount (Fig. S12). Furthermore, it is likely that formation of polymeric products by condensation reaction of hydrated aldehyde groups in 4O2EL would reduce the 5H5F selectivity as shown in Fig S13. Therefore, increasing the H_2O_2/furfural ratio accelerated the oxidation of 4O2EL and 5H5F yield increased (Fig. S14, S15).

Table 1. Yield of products after furfural oxidation with aq. H_2O_2 in the presence of different catalysts. Reaction conditions: Furfural 1 mmol, aq. H_2O_2 1-16 mmol, catalyst 100 mg, water 5 mL, 8 h, room temperature.

Entry	Catalyst	H_2O_2 (mmol)	Conversion (%)[a]	Product yield (%)				
				5H5F[a]	Maleic acid[a]	2(3H)-Furanone[a]	Succinic acid[a]	Formic acid[b]
1	TS-1	16	>99	92	5	0	0	93
2	Ti-Beta	16	>99	15	2	0	0	96
3	Nb-Beta	16	27	8	<1	13	5	25
4	Ti/SBA15	16	14	0	0	3	1	9
5	Zr-Beta	16	11	<1	0	<1	1	8
6	Zr/SBA15	16	5	<1	<1	<1	<1	5
7	TS-1	1	>99	29	<1	0	0	37
8	TS-1	2	>99	55	<1	0	0	73
9	TS-1	2[c]	>99	80	<1	0	0	95
10	TS-1	3	>99	69	<1	0	0	97
11	TS-1	4	>99	75	1	0	0	96

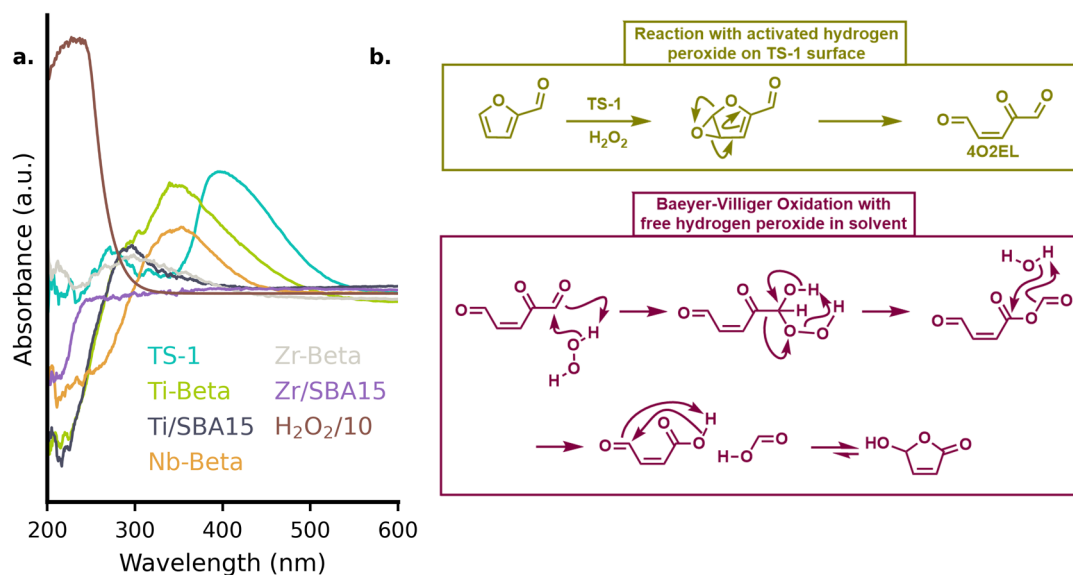[a]Determined by HPLC, [b]Determined by NMR (See Fig. S2), [c]reaction time was 24 h.

Fig. 2. a. DRUV-Vis spectrum of catalysts treated with H_2O_2, showing activation of H_2O_2. The spectrum of H_2O_2 was recorded in transmission mode in liquid phase for comparison and the absorbance was divided by 10 to make the intensities comparable to the solid samples. b. Proposed reaction mechanism for catalyst furfural oxidation to 4O2EL followed by oxidation of 4O2EL to 5H5F.

After oxidation 5H5F was extracted from the reaction mixture with ethyl acetate as a yellowish compound with more than 99 % purity (See SI Section 1.4 for detailed procedure). Formic acid and by-products like dicarboxylic acids were easily separated because they were retained in the aqueous phase during extraction. NMR analysis and mass fragmentation pattern of the purified product confirmed the 5H5F structure (Fig. S16 and S17). Melting point of the purified 5H5F was determined to be 50 – 55 °C (Fig. S18), which was in good agreement with literature (*41*, *42*). Elemental analysis of 5H5F revealed the composition to be 47.2 % C, 48.9 % O and 3.9 % H by weight, which gives the molecular formula of $C_4H_4O_3$.

5H5F was stable under ambient conditions without degradation for at least four months as determined by NMR. Thermal and hydrothermal stability of 5H5F was tested by heating 5H5F in acetonitrile and water, respectively. In the absence of any reactive environment 91 % of original 5H5F was recovered after 1 h in acetonitrile at 200 °C (Table S1). In water 5H5F was stable at 100 °C and 95 % was recovered after 1 h. At higher temperature, β-formyl acrylic acid (BFA) was formed by hydrolysis of 5H5F along with some undetected products.

The structure of 5H5F is of a γ-lactone with a hydroxyl group and a double bond. Although, the reaction of γ-lactones at the carbonyl center is difficult due to steric hindrance, in case of 5H5F the presence of hydroxyl group at the C4 carbon enhances its electrophilicity making it a reactive center for nucleophilic addition. The double bond in 5H5F is an effective dienophile for Diels-Alder reaction and 5H5F can be used as an alternative to maleic anhydride for synthesis of phthalic anhydride (*43*). In this study, we tested the versatility of 5H5F as a platform chemical for C4 chemicals via oxidation, hydrogenation and reductive aminolysis reactions.

Oxidation of 5H5F

Oxidation of 5H5F with H_2O_2 in the presence of TS-1 catalyst at 80 °C produced maleic anhydride and maleic acid (quantified together and referred as maleic acid) with a

total yield of 93 % (Fig. 3a-b). Other Lewis acid zeolites like Nb-Beta, Ti-Beta and Zr-Beta also oxidized 5H5F with reasonable yield of maleic acid. In this reaction, the hydroxyl group of 5H5F was oxidized by peroxo species formed on metal sites. Net maleic acid yield of 86 % was obtained from furfural after the two-step reaction, in comparison to 56 % in a single step reaction (*21, 44*).

Unlike the epoxidation reaction, the oxidation of 5H5F was not specific to the structure of metal peroxo species. Therefore, 5H5F oxidation also proceeded under typical oxidation conditions using molecular oxygen. In the presence of Pt supported on carbon black (Pt/C) catalyst at 100 °C and 0.9 MPa O_2, 81 % yield of maleic acid was obtained after 12 h (Fig. 3c). Therefore, oxidation of 5H5F was facile with high yield of maleic acid under mild conditions.
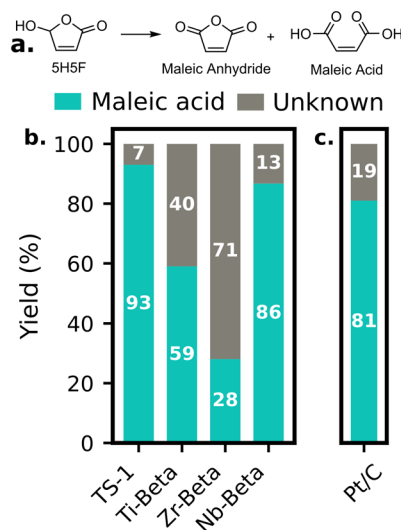

Fig. 3. a. Reaction scheme of 5H5F oxidation to maleic acid and maleic anhydride (quantified together as maleic acid), b. Product yield after 5H5F oxidation over zeolite catalysts in presence of H_2O_2. Reaction conditions: 5H5F 1 mmol, catalyst 50 mg, water 5 mL, 30 % aq. H_2O_2 2 mL, 80 °C, 2 h., c. Product yield after 5H5F oxidation over Pt/C catalyst in presence of O_2. Reaction conditions: 5H5F 1 mmol, catalyst 50 mg, water 5 mL, O_2 0.9 Mpa, 100 °C, 12 h. Unknown represent the difference between 5H5F conversion and yield of maleic acid.

Hydrogenation of 5H5F

Hydrogenation of 5H5F was carried out in the presence of different metal catalysts supported on carbon black (catalyst characterization Fig. S19-23). Pt/C catalyst selectively hydrogenated the double bond in 5H5F to yield 5-hydroxy-γ-butyrolactone (HGBL) as shown in Fig. 4a-b (HPLC profile and NMR of reaction mixture is given in Fig. S24-25). At 100 °C the yield of HGBL was 89 % in the presence of Pt/C catalyst. Rh/C produced 72 % yield of HGBL along with small amount of GBL, BDO, succinic acid (SA) and propionic acid (PA). GBL yield increased to 12 % over Pd/C catalyst with 75 % of HGBL. Ru/C catalyst on the other hand produced GBL in 93 % yield, and there was no HGBL present after reaction. Hydrogenation of HGBL as reactant with Ru/C produced GBL with >95 % selectivity (Table S2), which shows the ability of Ru to open the ring. When 5H5F was treated in the absence of H_2 under same condition, β-formyl acrylic acid (BFA) was produced in 5 %, and 0 % yield over Ru, and Pt catalyst respectively (Table S2), which further confirms that Ru could catalyze the ring opening of both 5H5F and HGBL. 5H5F hydrogenation can proceed via one of the two pathways shown in Fig. S26. In the first pathway, the double bond is hydrogenated

to form HGBL followed by ring opening, hydrogenation and dehydration to GBL. In the second pathway, 5H5F is converted to its open chain isomer BFA via hydrolysis and dehydration. BFA is then further hydrogenated to form GBL. Based on our results we propose that double bond hydrogenation of 5H5F to HGBL followed by ring opening is the major pathway.

Direct conversion of 5H5F to BDO and THF was achieved over bimetallic Ru-Re/C catalyst as shown in Fig. 4c (See HPLC profile and GC-MS, Fig. S27-29). At 150 ° C, 60 % of BDO was obtained from 5H5F in 24 h. BDO was formed by hydrogenation of GBL, and it underwent dehydration to THF. Monometallic Re catalyst produced HGBL (42 %) and GBL (27 %) and BDO was formed only in the presence of bimetallic catalyst. H_2 TPR of Ru-Re/C suggested that Ru helps in reduction of rhenium oxide (Fig. S30). Reduced Re species are known to promote hydrogenation of GBL and succinic acid to BDO due to its acidity, oxophilicity and ability to dissociate hydrogen heterolytically (45–47). THF was formed by dehydration of BDO and performing the reaction in the presence of ethanol as solvent instead of water produced THF in 64 % yield. Small quantities of diethyl and monoethyl ether of BDO were also obtained (Fig S29).
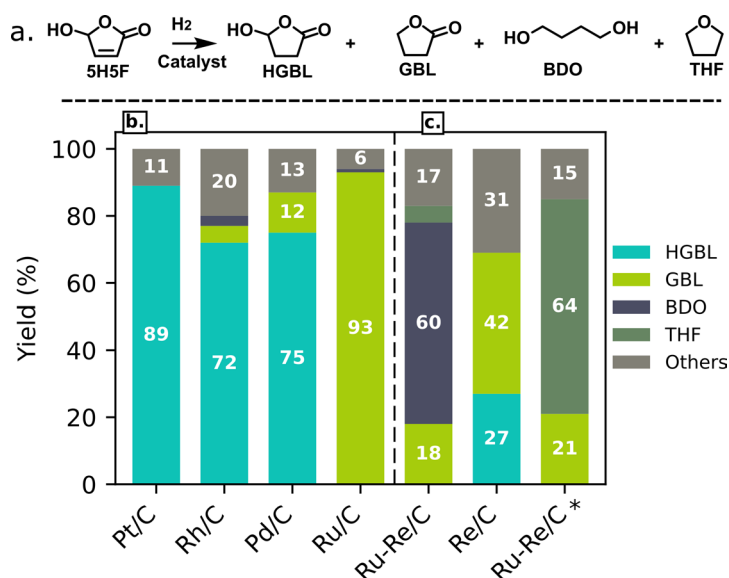

Fig. 4. a. Reaction scheme showing possible products from hydrogenation of 5H5F. b. 5H5F hydrogenation to HGBL and GBL, reaction conditions – 5H5F 1 mmol, catalyst 50 mg, water 5 mL, H_2 2 MPa, 100 °C 1 h. c. 5H5F hydrogenation to BDO and THF. Reaction conditions – 5H5F 1 mmol, catalyst 50 mg, water 5 mL, H_2 4 MPa, 150 °C, 12 h. Others represent butanol, succinic acid, propionic acid and undetected products. *The reaction was carried out with ethanol as solvent instead of water.

Reductive aminolysis of 5H5F

In addition to opening the ring of 5H5F by nucleophilic addition of water, it is possible to use other nucleophiles to directly produce nitrogen containing heterocyclic C4 compounds. In the presence of H_2 and NH_3, 5H5F produced γ-aminobutanoic (GABA) and 2-pyrrolidone via reductive aminolysis over Ru/C catalyst (Fig. 5a). After 1 h at 110 °C, GABA was obtained in 71 % yield (Fig. 5b). Increasing the temperature to 130 °C caused the cyclization of GABA to 2-pyrrolidone and over the course of 18 h, 2-pyrrolidone yield increased to 67 % (LC-MS profile and NMR of reaction mixture Fig. S31 and Fig. S32).

We propose that 5H5F undergoes aminolysis to form a hemiaminal structure as shown in Fig. S33. The hemiaminal would undergo dehydration to form an imine, which will then undergo hydrogenation to produce GABA followed by its cyclization to 2-pyrrolidone.
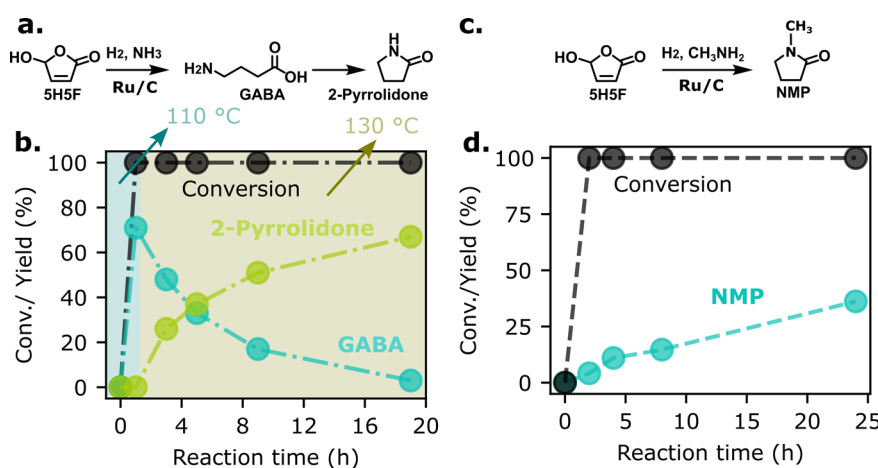
7

Fig. 5. a. Reaction scheme showing formation of 2-pyrrolidone from reductive aminolysis of 5H5F via GABA. b. Time course of 5H5F to 2-pyrrolidonereaction in the presence of Ru/C catalyst. Reaction conditions – 5H5F 5.56 mmol, Ru/C catalyst 200 mg, aq. NH$_3$ (27 %) 7.5 mL, H$_2$ 2 MPa, 110 °C for 1 h and 130 °C for 18 h. c. Reaction scheme showing formation of NMP from reductive aminolysis of 5H5F. d. Time course of 5H5F reductive aminolysis reaction with methylamine as amine source. Reaction conditions – 5H5F 1 mmol, Ru/C catalyst 50 mg, CH$_3$NH$_2$ 4 mmol, water 2 mL, H$_2$ 2 MPa, 130 °C.

Ring opening of 5H5F by reductive aminolysis was not limited to 2-pyrrolidone formation. N-methyl pyrrolidone (NMP) was also directly produced from 5H5F as shown in Fig. 5 (LC-MS of product, Fig S34). Replacing NH$_3$ with methyl amine the reaction proceeded in a similar manner. All the 5H5F was consumed in the initial 30 minutes, with only 4 % NMP. N-methyl pyrrolidone yield increased to 36 % after 24 h reaction. However, an intermediate was not identified even after rigorous analysis of reaction mixture. It is likely that oligomeric imines are formed by aminolysis and dehydration of 5H5F with methyl amine, which would slowly convert to NMP under the reaction condition.

Discussion

A major limiting factor in implementation of biomass as a chemical resource has been the energy consumption in synthesis and reaction of platform chemical. Synthesis of 5H5F from furfural was feasible at room temperature owing to the ability of TS-1 to catalyze the epoxidation reaction at low temperature. Epoxidation of furan has also been reported to produce 5H5F in a similar way (*48*). Considering that furan is obtained by decarbonylation of furfural, a single step reaction at room temperature is more efficient. Separation of 5H5F was also energy efficient because extraction was sufficient to obtain a product with 99 % purity.

5H5F was stable enough to avoid rapid degradation and at the same time it was reactive under oxidation, hydrogenation and aminolysis conditions at 100–150 °C. The fourth carbon of 5H5F was reactive towards nucleophilic addition leading to formation of oxygen and nitrogen containing value added C4 chemicals. Furfural is currently produced directly from biomass in a single step. Therefore, by using 5H5F as a platform chemical, it is feasible to synthesize most of the C4 chemicals in three steps from raw biomass, which would reduce the energy required for C4 chemical synthesis.

Currently, industrial processes and much of the literature in C4 chemistry are focused on conversion of succinic acid or GBL to products like BDO and pyrrolidones. For example, 2-pyrrolidone is produced industrially by reaction of GBL with ammonia in vapor phase (*14*). The reaction is generally carried out at 250 – 300 °C. GBL itself is derived from petroleum by energy intensive reaction steps. Similarly, NMP is industrially made by reacting GBL with methyl amine at 250–400 °C and 6 – 12 MPa (*14*). In contrast, the reaction conditions for

direct aminolysis of 5H5F to 2-pyrrolidone and NMP were significantly milder. Consequently, owing to the simple synthesis and high reactivity of 5H5F it has the potential to be a wide application as a C4 platform chemical.

Conclusion

Synthesis of value-added chemicals from biomass relies on platform chemicals that serve as precursors for different classes of chemicals. While platform chemicals for C6 and C5 chemical are well established a suitable platform for C4 chemical synthesis is lacking. In this study, we have shown that 5-hydroxy-2(5H)-furanone (5H5F) can function as a biomass derived platform for C4 chemical synthesis. 5H5F was produced by oxidation of furfural at room temperature with 92 % yield and it was isolated from the reaction mixture by extraction. Epoxidation of furfural by H_2O_2 activated on TS-1 catalyst produced an intermediate which underwent Baeyer-Villiger oxidation to form 5H5F. Oxidation of 5H5F to maleic acid proceeded with both H_2O_2 and molecular oxygen. Nucleophilic addition of water and amines under hydrogenation environment produced GBL, BDO, THF, 2-pyrrolidone and NMP over Ru/C or Ru-Re/C catalyst in a single step. In comparison to other biomass derived C4 platforms like succinic acid, 5H5F is easier to synthesize, isolate and it is susceptible to catalytic transformation under milder conditions. Owing to these traits we believe 5H5F is a good platform chemical for C4 synthesis and this work will open new avenues for research in C4 chemical synthesis from biomass.

References and Notes

1. H. Kobayashi, Y. Yamakoshi, Y. Hosaka, M. Yabushita, A. Fukuoka, Production of sugar alcohols from real biomass by supported platinum catalyst. *Catal. Today*. **226**, 204–209 (2014).

2. A. Corma, S. Iborra, A. Velty, Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **107**, 2411–2502 (2007).

3. A. Fukuoka, P. L. Dhepe, Catalytic Conversion of Cellulose into Sugar Alcohols. *Angew. Chem. Int. Ed.* **45**, 5161–5163 (2006).

4. M. Zangiabadi, Y. Zhao, Synergistic Hydrolysis of Cellulose by a Blend of Cellulase-Mimicking Polymeric Nanoparticle Catalysts. *J. Am. Chem. Soc.* **144**, 17110–17119 (2022).

5. V. Choudhary, S. H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N. S. Marinkovic, A. I. Frenkel, S. I. Sandler, D. G. Vlachos, Insights into the Interplay of Lewis and Brønsted Acid Catalysts in Glucose and Fructose Conversion to 5-(Hydroxymethyl)furfural and Levulinic Acid in Aqueous Media. *J. Am. Chem. Soc.* **135**, 3997–4006 (2013).

6. W. Xu, Y. Zhang, J. Wang, Y. Xu, L. Bian, Q. Ju, Y. Wang, Z. Fang, Defects engineering simultaneously enhances activity and recyclability of MOFs in selective hydrogenation of biomass. *Nat. Commun.* **13**, 2068 (2022).

7. Y. M. Questell-Santiago, R. Zambrano-Varela, M. Talebi Amiri, J. S. Luterbacher, Carbohydrate stabilization extends the kinetic limits of chemical polysaccharide depolymerization. *Nat. Chem.* **10**, 1222–1228 (2018).

8. C. O. Tuck, E. Pérez, I. T. Horváth, R. A. Sheldon, M. Poliakoff, Valorization of Biomass: Deriving More Value from Waste. *Science*. **337**, 695–699 (2012).

9. J. S. Luterbacher, J. M. Rand, D. M. Alonso, J. Han, J. T. Youngquist, C. T. Maravelias, B. F. Pfleger, J. A. Dumesic, Nonenzymatic Sugar Production from Biomass Using Biomass-Derived γ-Valerolactone. *Science*. **343**, 277–280 (2014).

10. A. Kumar, S. Mohanty, V. K. Gupta, Butadiene Rubber: Synthesis, Microstructure, And Role of Catalysts. *Rubber Chem. Technol.* **94**, 393–409 (2021).

11. "Chemicals from the C4 Stream" in *Industrial Organic Chemicals* (John Wiley & Sons, Inc., Hoboken, NJ, USA, 2013), pp. 273–307.

12. M. J. Biddy, C. Scarlata, C. Kinchin, "Chemicals from Biomass: A Market Assessment of Bioproducts with Near-Term Potential" (NREL/TP--5100-65509, 1244312, 2016), (available at http://www.osti.gov/servlets/purl/1244312/).

13. W. Schwarz, J. Schossig, R. Rossbacher, R. Pinkos, H. Höke, "Butyrolactone" in *Ullmann's Encyclopedia of Industrial Chemistry* (Wiley-VCH, Weinheim, 2019; https://onlinelibrary.wiley.com/doi/full/10.1002/14356007.a04_495.pub2), pp. 1–7.

14. A. L. Harreus, R. Backes, J.-O. Eichler, R. Feuerhake, C. Jäkel, U. Mahn, R. Pinkos, R. Vogelsang, 2-Pyrrolidone. *Ullmanns Encycl. Ind. Chem.* (2011).

15. J. Zhang, B. Hou, A. Wang, Z. Li, H. Wang, T. Zhang, Kinetic study of retro-aldol condensation of glucose to glycolaldehyde with ammonium metatungstate as the catalyst. *AIChE J.* **60**, 3804–3813 (2014).

16. S. Lin, X. Guo, K. Qin, L. Feng, Y. Zhang, Y. Tang, Efficient Production of Biomass-Derived C4 Chiral Synthons in Aqueous Solution. *ChemCatChem.* **9**, 4179–4184 (2017).

17. T. Flannelly, M. Lopes, L. Kupiainen, S. Dooley, J. J. Leahy, Non-stoichiometric formation of formic and levulinic acids from the hydrolysis of biomass derived hexose carbohydrates. *RSC Adv.* **6**, 5797–5804 (2016).

18. X. Li, E. Mupondwa, Empirical analysis of large-scale bio-succinic acid commercialization from a technoeconomic and innovation value chain perspective: BioAmber biorefinery case study in Canada. *Renew. Sustain. Energy Rev.* **137**, 110587 (2021).

19. I. Bechthold, K. Bretz, S. Kabasci, R. Kopitzky, A. Springer, Succinic acid: a new platform chemical for biobased polymers from renewable resources. *Chem. Eng. Technol. Ind. Chem.-Plant Equip.-Process Eng.-Biotechnol.* **31**, 647–654 (2008).

20. H. Choudhary, S. Nishimura, K. Ebitani, Metal-free oxidative synthesis of succinic acid from biomass-derived furan compounds using a solid acid catalyst with hydrogen peroxide. *Appl. Catal. Gen.* **458**, 55–62 (2013).

21. Y. N. Palai, A. Shrotri, A. Fukuoka, Selective Oxidation of Furfural to Succinic Acid over Lewis Acidic Sn-Beta. *ACS Catal.* **12**, 3534–3542 (2022).

22. K. Yakabi, A. Jones, A. Buchard, A. Roldan, C. Hammond, Chemoselective Lactonization of Renewable Succinic Acid with Heterogeneous Nanoparticle Catalysts. *ACS Sustain. Chem. Eng.* **6**, 16341–16351 (2018).

23. D. P. Minh, M. Besson, C. Pinel, P. Fuertes, C. Petitjean, Aqueous-phase hydrogenation of biomass-based succinic acid to 1, 4-butanediol over supported bimetallic catalysts. *Top. Catal.* **53**, 1270–1273 (2010).

24. U. G. Hong, H. W. Park, J. Lee, S. Hwang, J. Yi, I. Kyu. Song, Hydrogenation of succinic acid to tetrahydrofuran (THF) over rhenium catalyst supported on H2SO4-treated mesoporous carbon. *Appl. Catal. Gen.* **415–416**, 141–148 (2012).

25. T. H. Nguyen, D. E. Hibbs, S. T. Howard, Conformations, energies, and intramolecular hydrogen bonds in dicarboxylic acids: Implications for the design of synthetic dicarboxylic acid receptors. *J. Comput. Chem.* **26**, 1233–1241 (2005).

26. J. C. Serrano-Ruiz, D. Wang, J. A. Dumesic, Catalytic upgrading of levulinic acid to 5-nonanone. *Green Chem.* **12**, 574–577 (2010).

27. W. R. H. Wright, R. Palkovits, Development of Heterogeneous Catalysts for the Conversion of Levulinic Acid to γ-Valerolactone. *ChemSusChem*. **5**, 1657–1667 (2012).

28. J.-M. Lee, P. P. Upare, J.-S. Chang, Y. K. Hwang, J. H. Lee, D. W. Hwang, D.-Y. Hong, S. H. Lee, M.-G. Jeong, Y. D. Kim, Y.-U. Kwon, Direct Hydrogenation of Biomass-Derived Butyric Acid to n-Butanol over a Ruthenium–Tin Bimetallic Catalyst. *ChemSusChem*. **7**, 2998–3001 (2014).

29. R. Ozer, Vapor Phase Decarbonylation Process (2010).

30. C. Wang, Z. Liu, L. Wang, X. Dong, J. Zhang, G. Wang, S. Han, X. Meng, A. Zheng, F. S. Xiao, Importance of Zeolite Wettability for Selective Hydrogenation of Furfural over Pd@Zeolite Catalysts. *ACS Catal.* **8**, 474–481 (2018).

31. J.-P. Lange, S. H. Wadman, Furfural to 1,4-Butanediol/Tetrahydrofuran – A Detailed Catalyst and Process Design. *ChemSusChem*. **13**, 5329–5337 (2020).

32. S. H. Wadman, J.-P. Lange, Process for the production of 1,4-butanediol and tetrahydrofuran from furan (2017).

33. C. Sun, Z. Cao, J. Wang, L. Lin, X. Xie, Shape and ligand effect of palladium nanocrystals on furan hydrogenation. *New J. Chem.* **43**, 2567–2574 (2019).

34. C. J. Kliewer, C. Aliaga, M. Bieri, W. Huang, C. K. Tsung, J. B. Wood, K. Komvopoulos, G. A. Somorjai, Furan hydrogenation over Pt(111) and Pt(100) single-crystal surfaces and Pt nanoparticles from 1 to 7 nm: A kinetic and sum frequency generation vibrational spectroscopy study. *J. Am. Chem. Soc.* **132**, 13088–13095 (2010).

35. Y. Morita, H. Tokuyama, T. Fukuyama, Stereocontrolled Total Synthesis of (−)-Kainic Acid. Regio- and Stereoselective Lithiation of Pyrrolidine Ring with the (+)-Sparteine Surrogate. *Org. Lett.* **7**, 4337–4340 (2005).

36. B. M. Trost, F. D. Toste, Palladium Catalyzed Kinetic and Dynamic Kinetic Asymmetric Transformations of γ-Acyloxybutenolides. Enantioselective Total Synthesis of (+)-Aflatoxin B1 and B2a. *J. Am. Chem. Soc.* **125**, 3090–3100 (2003).

37. H. Wu, J. Song, H. Liu, Z. Xie, C. Xie, Y. Hu, X. Huang, M. Hua, B. Han, An electrocatalytic route for transformation of biomass-derived furfural into 5-hydroxy-2(5H)-furanone. *Chem. Sci.* **10**, 4692–4698 (2019).

38. W. Lin, H. Frei, Photochemical and FT-IR Probing of the Active Site of Hydrogen Peroxide in Ti Silicalite Sieve. *J. Am. Chem. Soc.* **124**, 9292–9298 (2002).

39. S. Bordiga, A. Damin, F. Bonino, G. Ricchiardi, C. Lamberti, A. Zecchina, The Structure of the Peroxo Species in the TS-1 Catalyst as Investigated by Resonant Raman Spectroscopy. *Angew. Chem. Int. Ed.* **41**, 4734–4737 (2002).

40. C. P. Gordon, H. Engler, A. S. Tragl, M. Plodinec, T. Lunkenbein, A. Berkessel, J. H. Teles, A.-N. Parvulescu, C. Copéret, Efficient epoxidation over dinuclear sites in titanium silicalite-1. *Nature*. **586**, 708–713 (2020).

41. J. M. Carney, R. J. Hammer, M. Hulce, C. M. Lomas, D. Miyashiro, Microphotochemistry Using 5-mm Light-Emitting Diodes: Energy-Efficient Photooxidations. *Synthesis*. **44**, 2560–2566 (2012).

42. S. P. Chavan, A. L. Kadam, S. S. Shinde, R. G. Gonnade, Furan-Derived Chiral Bicycloaziridino Lactone Synthon: Collective Syntheses of Oseltamivir Phosphate (Tamiflu), (S)-Pipecolic acid and its 3-Hydroxy Derivatives. *Chem. – Asian J.* **15**, 415–424 (2020).

43. E. Mahmoud, D. A. Watson, R. F. Lobo, Renewable production of phthalic anhydride from biomass-derived furan and maleic anhydride. *Green Chem.* **16**, 167–175 (2013).

44. N. Alonso-Fagúndez, I. Agirrezabal-Telleria, P. L. Arias, J. L. G. Fierro, R. Mariscal, M. L. Granados, Aqueous-phase catalytic oxidation of furfural with H2O2: High yield of maleic acid by using titanium silicalite-1. *RSC Adv.* **4**, 54960–54972 (2014).

45. D. Hibbitts, Q. Tan, M. Neurock, Acid strength and bifunctional catalytic behavior of alloys comprised of noble metals and oxophilic metal promoters. *J. Catal.* **315**, 48–58 (2014).

46. S. Liu, Y. Amada, M. Tamura, Y. Nakagawa, K. Tomishige, Performance and characterization of rhenium-modified Rh–Ir alloy catalyst for one-pot conversion of furfural into 1,5-pentanediol. *Catal. Sci. Technol.* **4**, 2535–2549 (2014).

47. K. Tomishige, M. Tamura, Y. Nakagawa, Role of Re Species and Acid Cocatalyst on Ir-ReOx/SiO2 in the C–O Hydrogenolysis of Biomass-Derived Substrates. *Chem. Rec.* **14**, 1041–1054 (2014).

48. P. Kumar, R. Kumar Pandey, An efficient synthesis of 5-hydroxy-2(5H)-furanone using a titanium silicate molecular sieve catalyst. *Green Chem.* **2**, 29–32 (2000).

Acknowledgments:

Author contributions:

Conceptualization: YNP, AS

Methodology: YNP, AS

Investigation: YNP

Visualization: YNP

Funding acquisition: AS, AF

Project administration: YNP, AS, AF

Supervision: AS, AF

Writing – original draft: YNP

Writing – review & editing: YNP, AS, AF

Supplementary Materials

Materials and Methods

Figs. S1 to S34

Table S1 to S2