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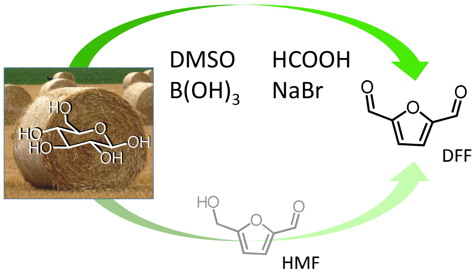

A one pot procedure for the synthesis of DFF starting form mono, di or polysaccharides or from primary biomass has been developed. HMF is formed as intermediate and can also be isolated.

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Simple and efficient one-pot synthesis of 5-hydroxymethylfurfural and 2,5-diformylfuran from carbohydrates.

Quentin Girka,[a,b] Boris Estrine,*[b] Norbert Hoffmann,*[a] Jean Le Bras,[a] Siniša Marinković,[b] and Jacques Muzart[a]

2,5-Diformylfuran (DFF) and 5-hydroxymethylfurfural (HMF) are interesting platform compounds for chemical industry. A sustainable one-pot procedure is reported for the transformation of carbohydrates into DFF. Mono, di and polysaccharides as well as crude biomass (straw and bran) have been transformed. Depolymerisation, glucose isomerisation to fructose, fructose dehydration and finally oxidation of HMF to DFF are involved. The optimized catalytic system contains boric acid in DMSO for HMF synthesis. Addition of sodium bromide and formic acid leads to DFF. Boric acid is mainly involved in depolymerization, isomerisation and dehydration. Larger amounds of boric acid lead to degradation of HMF. NaBr and water are involved in the selective oxidation of HMF. Formic acid is involved in dehydration step and it accelerates the oxidation of HMF.

Introduction

Fossils resources are the main source of carbon based compounds for chemical and energy industry. Taking into account of fossil carbon reserves depletion, biomass appeared as the most reliable source for carbon containing substances.[1-3] The production of biomass by nature is estimated to about $2 \cdot 10^{11}$ tons/year.[4] About 75% of these materials are carbohydrates which are essentially produced by green plants using photosynthesis to transform carbon dioxide back into biomass. In this context, biomass is considered as basis for renewable fuels and chemicals. However, processes in chemical industry are most often optimised for the transformation of compounds obtained from fossil resources, mainly mineral oil. While this material is characterised by low oxygen contain, carbohydrate based biomass generally has a high oxygen content. One strategy for using biomass in chemical industry is to develop new processes for new products with interesting properties. Another or complementary strategy is to develop processes for the transformation of biomass into platform chemicals or intermediates which can be further transformed using established technologies in the chemical industry. In this context, dehydration of carbohydrates is an interesting transformation since furan derivatives are obtained. These compounds are versatile key intermediates not only for industrial chemistry but also for organic synthesis in general. While dehydration of pentose containing biomass leading to furfural is more or less easy[5], dehydration of hexoses such as glucose leading to 5-hydroxymethylfurfural (HMF) is much more difficult.[6-8] During last decades, many efforts have been made in order to improve the production of HMF from biomass.7 It is a versatile key intermediate for organic synthesis[9,10], production of fuels[11,12] and for polymer chemistry.[13]

HMF formation from carbohydrate containing biomass such as cellulose or starch involves three consecutive steps: (1) depolymerisation (2) glucose isomerisation to fructose and (3) fructose dehydration. The second step usually requires the use of metal catalyst such as chromium, tin, vanadium, stain or aluminate based compounds.[14-18]

The efforts in HMF production were strongly affected by the development of ionic liquids (ILs) or deep eutectic solvents[20,21] to dissolve biomass based materials.[22-25] Such media are often called “green solvents” but in order to assess greenness of ILs, synthesis, storage, recycling, and disposal have to be studied more profoundly.[26] The main ionic liquids limitation towards such industrial applications is related to accurately control of purity and moisture.[27] Another well-known solvent for HMF production is dimethylsulfoxide (DMSO). It is very effective for fructose to HMF conversion but it is completely inefficient for glucose or polysaccharides transformation.[28-30] Sustainability or greenness of DMSO is controversially discussed because of its ability to carry almost any substance through skin to more sensitive organs.[31] Anyhow, DMSO is currently used for cystitis

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Electronic Supplementary Information (ESI) available: General methods; typical sugar to HMF or furfural conversion experiment; typical one-pot sugar to DFF experiment; HMF, furfural and DFF analysis; multigram DFF synthesis; synthesis of 5-(bromomethyl)frufural, bromodimethylsulfonium bromide and 5-(formyloxymethyl)furfural; hydrolysis of bromomethylfurfural; ^{1}H and ^{13}C NMR spectra. See DOI: 10.1039/x0xx00000x treatment and studies are in progress on the DMSO effect on arthritis and other diseases.[31]

As already pointed out, pure HMF is difficult to obtain and major problems of HMF large scale production deals with its purification and extraction.[9,30] To overcome those issues, many experimental tools were used such as biphasic systems8 and continuous reactive distillation[32].

Another way to overcome HMF instability is its *in situ* conversion to 2,5-diformylfuran (DFF), which is also a promising platform molecule.[33-35] Actually, DFF production is mainly carried out from pure HMF by metal catalysed oxidation (NaV_2O_3, Ru/hydrotalcite, Pd, etc.) or from fructose after *in situ* dehydration.2’[9,36] Recently, an oxidation of HMF to DFF using heterogeneous photocatalysis with TiO_2 was developed as a particularly sustainable process.[37] Hitherto, no efficient one-pot synthetic method starting from glucose or polysaccharides has been reported.[38,39]

The well-known affinity of boric acid with polyols[40-44] has been successfully used to isomerize glucose to fructose in IL.[45,46,47] To the best of our knowledge, there is only one report on the use of boric acid in more conventional solvent such as water.[48]

Herein we report the use of boric acid, a sustainable non-metal reagent which is involved in many biological structures such as cell walls of green plants[49] in DMSO for efficient and direct HMF synthesis as well as its consecutive transformation into DFF.

Materials and Methods

Chemicals and materials

All sugar reagents and DMSO were provided by Sigma-Aldrich and were used as received. Palatinose hydrate was purchased from TCI-chemicals and dried under vacuum at 40°C for 4 days before use. NaBr and HMF were purchased from TCI Chemicals and use as received.

HPLC experiments were performed on Shimadzu Agilent 1200 series equipped with nucleodur C18 column and a diode array detector. HPLC grade solvents were filtrated and degased before use. Sartorius 20µm filters were purchased from VWR.

Typical experiment for the conversion of sugar to HMF or furfural

A round bottom flask equipped with condenser was charged with carbohydrate (1 g), an appropriate amount of boric acid and DMSO (9 g). The mixture is stirred at 150 °C for an appropriate time.

Typical one-pot sugar to DFF conversion experiment

A round bottom flask equipped with condenser was charged with carbohydrate (1 g), an appropriate amount of boric acid, NaBr (0.3 eq/glucose unit), formic acid (0.3 eq/glucose unit) and DMSO (9 g). The mixture is stirred at 150 °C for an appropriate time. DFF has also been isolated on multigram scale by liquid/liquid extraction (see supporting information).

HMF; furfural and DFF analysis

After the specified time, 0.4 g of reaction mixture were taken and diluted with deionized water (30 mL). This solution was filtrated before HPLC analysis.

HMF and DFF analyses were performed using a AcONa water solution (50 mM) at pH=2.8 (adjusted by addition of AcOH) and acetonitrile (90/10 ratio) at a flow rate of 1 mL.min^{-1} with a column temperature of 55 °C. HMF and furfural analyses were performed with 90/10 water/acetonitrile mixture at a flow rate of 0.6 mL.min^{-1} at 25 °C. HMF, DFF and furfural amounts were determined using standard calibration curves.

Results and Discussion

The influence of boric acid loading on the dehydration process of glucose to HMF (Figure 1) was investigated. In the absence of boric acid, no HMF was formed while in the presence of 0.5, 1 or 2 equivalents of this compound, yields up to 38% of HMF were observed. In the case of 0.5 and 1 equivalent, no decomposition of HMF took place before 8 h and 7 h respectively. However, in the presence of 1 equivalent of boric acid and after 7 h, the yield decreased from 33 to 25% (Figure 1). Another effect of increasing boric acid loading is an increase in total acidity[48] which favoured humins formation. In the case of less than 0.5 equivalents, a very slow conversion occurred. Similar results were obtained with ionic liquids as solvent.[45] Boric acid is essential for the isomerisation of glucose to fructose. A detailed mechanistic study based on DFT calculations has been recently published (Scheme1).[45] This study also involves the dehydration of fructose leading to the formation of HMF. Likewise, it was previously shown that the dehydration of fructose to HMF occurred in DMSO without addition of any catalyst.[28] In this context, it should be mentioned that DMSO at high temperatures may form acidic species which also catalyse the dehydration.[54,56]

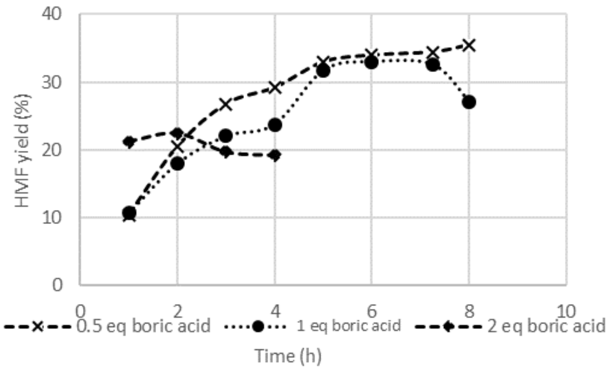
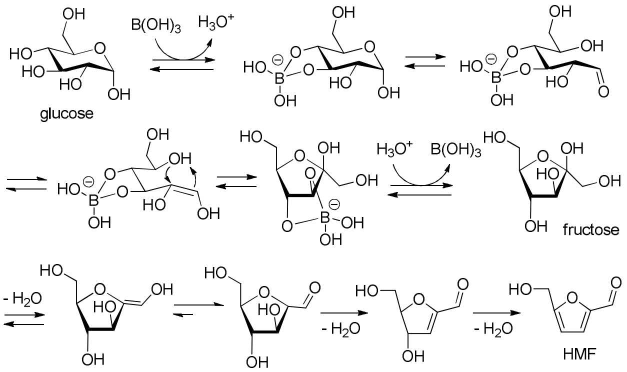


Figure 1. Effect of boric acid loading on HMF yield in the transformation of glucose. Glucose (1 g; 5.6 mmol), boric acid (0.5, 1 or 2 eq), DMSO (9 g), 150 °C.



Scheme 1. Simplified mechanism for the transformation of glucose into HMF.[45]

Carbohydrate concentration is well known to play an important role in HMF synthesis. We observed that best results were obtained with 10% w/w of glucose with respect to DMSO (Figure 2). Higher concentrations lead to lower selectivities, probably because of polycondensation reactions occur which are generally favoured by higher monomer concentrations. Lower concentrations lead to almost the same yield. However, such conditions have no practical interest due to high solvent consumption. It should further be pointed out that after 8.5 h, no glucose has been detected in the reaction mixture (NMR analysis).

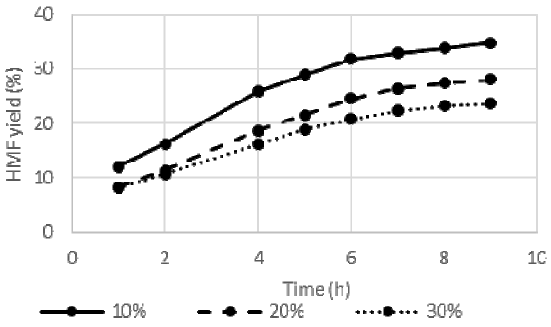


Figure 2. The effect of glucose concentration on HMF yield. Glucose (1 g; 5.6 mmol), boric acid (172 mg, 2.8 mmol), DMSO, 150 °C

We applied the reaction conditions to the transformation of di and polysaccharides as well as to the reaction of two pentoses (Table 1). Under the reaction conditions previously optimised, HMF was obtained with yields in the same order of magnitude from disaccharides (entries 2-5). The transformation of different starches yielded HMF in slightly lower yields (entries 6-8). However, in the case of potatoes and corn starches, the concentration of boric acid needed to be increased to 2 eq/glucose unit (entries 6 and 7). The transformation of pure amylopectin is easier since it was successful under standard conditions, which may be explained by its amorphous structure (entry 8). Crystallinity acts as a physical barrier to chemical transformation. The low reactivity of crystalline areas slows down the depolymerisation step. A reaction can only take place at the surface of the crystals. Reaction centres inside the crystals are not accessible for a reagent. Excess of boric acid is believed to overcome crystallinity effect allowing satisfactory yield of HMF. In these experiments (entries 6 and 7), a larger amount of boric acid does not lead to significant degradation of HMF (compare Table 1 and its discussion). This observation may be explained by the fact that a part of the boric acid is bound to the polysaccharide which leads to its deactivation. These experiments thus highlight that boric acid plays also an important role in depolymerisation and decrystallisation processes. Only low amounts of HMF were formed in the transformation of micro crystalline cellulose under the standard conditions. This result may be explained by the very low solubility and almost complete crystallinity of this polysaccharide.

The dehydration of pentoses leading to furfural is well established[5] and we also tested our reaction conditions for this transformation. Thus, the reaction of xylose and arabinose was performed with similar yields (entries 10 and 11). It should further be pointed out that in these cases, the sugar concentration can be doubled without diminishing the efficiency. This observation and the ease of the dehydration of pentoses are explained by the predominance of the furanose form in the equilibrium with the pyranose form in the case of these sugars.[50]

Table 1. The transformation of various carbohydrates into HMF or furfural.

Entry	Carbohydrate[a]		Reaction time (h)	HMF yield (%)[b]	Furfural yield (%)[b]
1	Glucose		8	35	-
2	Maltose		8	31	-
3	Sucrose		8	42	-
4	Palatinose		5	37%	-
5	Cellobiose		6	38%	-
6	Starch	Potatoes	7	15[a] , 33[c]	-
7		Corn	6	30 [c]	-
8		Amylopectin	7.5	29	-
9	Cellulose (MCC)		7.5	7[c]	-
10	Xylose[d]		8	-	35
11	Arabinose[d]		8	-	29

[a]sugar (1 g), boric acid (172 mg, 2.8 mmol, 0.5 eq/glucose unit), DMSO (9 g), 150 °C [b]yields were determined by HPLC [c]sugar (1 g), boric acid (762 mg, 12.3 mmol, 2 eq/glucose unit), DMSO (9 g), 150 °C [d]sugar (2 g, 13.3 mmol), boric acid (412 mg, 6.6 mmol, 0.5 eq) and DMSO (8 g) were used.

Application to primary biomass feedstock

We then applied our method to straw and bran as representative primary feedstock (Table 2). In order to lower mixture viscosity, concentration of biomass had to be adjusted to 5% w/w instead of 10% w/w. Despite the large amounts of carbohydrates in straw, this material was completely unreactive and neither HMF nor furfural was detected. This may be explained by the high crystallinity index of straw cellulose.[51] On the other hand, bran gave good yield of HMF and furfural. When starch was previously removed from bran, HMF yield decreased probably because of the presence of more crystalline areas mainly attributed to remaining cellulose.

Our system provides a simple and versatile method for HMF and furfural synthesis in satisfactory yield from carbohydrates. It allows one-pot deconstruction, isomerisation and dehydration without transition metal catalyst under standard conditions in DMSO.

Table 2: The transformation of primary biomass composition and conversion

	Glucose (%)	Arabinose (%)	Xylose (%)	HMF yield (%)[b]	Furfural yield (%)[b]
Wheat straw	39,3	30,4	3,6	Nd[c]	Nd[c]
Wheat bran	26,5	9	17	25	19
Bran without starch	19	15,8	29,1	10	22

[a]biomass (1 g), DMSO (19 g), boric acid (2 eq/sugar unit), 150 °C [b]yields with respect to the initial composition were determined by HPLC. [c]not detected.

One-pot DFF synthesis

DFF is usually synthesized form pure HMF with the use of metal catalyst in quantitative yield.[52] However, those procedures do not consider effect of impurities such as humins owing of HMF synthesis. It has been proven that insoluble humins could inhibit HMF to furandicarboxylic acid (FDCA) oxidation.[53] They have to be filtered off before further transformation. This result emphasised heterogeneous catalysis limitation since humins completely inactivated the catalyst. Recently, a new and efficient procedure to synthesize DFF from fructose has been reported. Sodium bromide as a halide donor and DMSO as both solvent and oxidant are involved.[54] Under these conditions, HMF is easily oxidized to DFF. This procedure is expected to be also efficient even in presence of humins or other contaminant formed during sugar transformation.

We wonder whether these conditions may be combined with the improved isomerisation of glucose involving boric acid. First, we investigated the influence of halogen source on DFF yield (Table 3). In the case of NaCl (entry 1), only low quantities of DFF were formed while high amounts of HMF were detected. In the presence of NaBr (entry 2) substantial amounts of DFF were formed and no HMF was detected. It seems that this salt accelerates the oxidation of HMF to DFF. The better results obtained with NaBr may be explained by the higher nucleophilicity of the Br^- ion when compared to Cl^- (vide infra). The addition of NaI (entry 3) did not lead to an efficient formation of neither HMF nor DFF. It is believed that active iodide compounds are generated and further oxidation or degradation may take place.[54] As it was previously observed, formic acid is capable of catalysing the fructose dehydration[55], we decided to study the influence of this acid in our reaction mixtures. Formic acid as a reductant also stabilises DMSO with respect to oxidative degradation at high temperature.[56]

In order to improve comparability, we stopped the reaction after 17 h instead of heating for 24 h (Table 3, entries 4-6). Under these conditions and in the presence of NaBr, DFF was obtained in 16% yield from glucose (entry 4). In the presence of formic acid, DFF was formed in relatively high yield (entry 5). When compared to the result in the absence of formic acid (entry 4), the formation of DFF was significantly accelerated. Since no HMF was detected at the end of the transformation after 17 h in the presence of formic acid (entry 5), we may suppose that formic acid also promote the oxidation of HMF to DFF (vide infra). It must further be pointed out that formic acid in absence of NaBr was not able to promote this oxidation (entry 6).

Table 3. The halogen effect on the formation of DFF.

Entry	Additives [a]	Reaction Time (h)	DFF yield (%)[b]	HMF yield (%)[b]
1	NaCl	24	8	38
2	NaBr	24	26	nd[c]
3	NaI	24	5	nd[c]
4	NaBr	17	16	7
5	NaBr, formic acid[b]	17	28	nd[c]
6	formic acid[c]	17	4	30

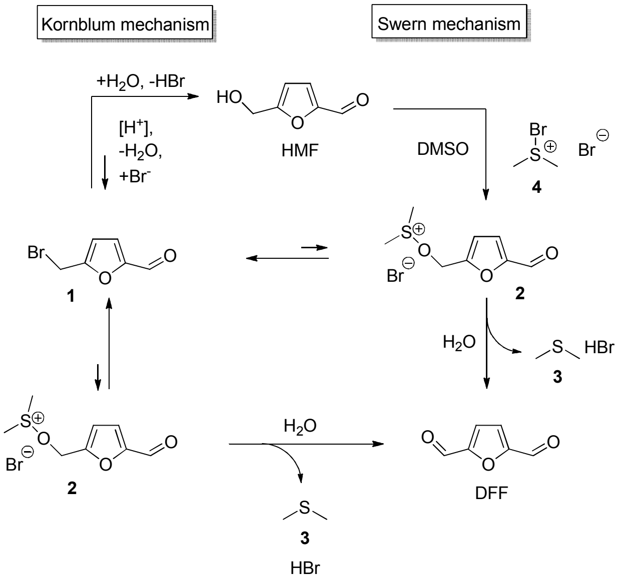
[a]glucose (1 g, 5.6 mmol), boric acid (172 mg, 2.8 mmol), DMSO (9 g), NaX (0.3 eq) and/or formic acid (63 µL, 1.7 mmol, 0.3 eq), 150 °C [b]yields were determined by HPLC.[c] not detected

Discussion of DFF formation mechanisms

Recently, it was discussed that the DMSO/NaBr system induces bromation of HMF and subsequent oxidation to DFF according to a Kornblum-like mechanism (Scheme 2, left part).[54,57-59] Thus HMF is transformed into the bromoderivative **1**. Addition of DMSO should lead to the intermediate **2**. Deprotonation and elimination of dimethylsulfide **3** then lead to DFF.

In order to check whether such a transformation may occur under our conditions, which involve the formation of 3 molecules of H_2O resulting from the dehydration steps, **1** was prepared[60] It is known that the corresponding chloroderivative (5-chloromethylfurfural) rapidly undergo hydrolysis.[61] Indeed, when the bromoderivative **1** was dissolved in DMSO containing 3 equivalents of water and heated at 60°C for 2 hours, we observed fast and complete hydrolysis leading to the formation of HMF. At higher temperature, the hydrolysis is almost instantaneous. Under those conditions, HBr is obviously formed but the equilibrium between HMF and **1** is completely displaced to HMF formation. We then explored a Swern-like reaction mechanism (Scheme 2, right part). The first step of Swern reaction is DMSO activation usually through chlorosulfonium chloride synthesis. We synthesized[62] its bromo analogue (bromosulfonium bromide **4**) and compared its reactivity with the NaBr/DMSO system. When HMF is reacted with **4** in presence of water at 150 °C, DFF is obtained.

In order to investigate the role of water in this system, we conducted anhydrous experiments. Interestingly, in the absence of water, 5-bromomethylfurfural **1** remained unreactive at 150 °C in DMSO. Furthermore, HMF reacts with NaBr/DMSO at 150 °C and leads to the formation of the bromo compound **1** without DFF formation. When HMF is heated at 150 °C in anhydrous DMSO in presence of **4**, no DFF is formed and only **1** is detected. These results emphasised that in absence of water, the equilibrium between **1** and **2** is displaced to the formation of **1**. Since Kornblum and Swern reactions occurred only in presence of bases,[58,63,64] we may conclude that water acts as a base in the oxidation step.



Scheme 2. Mechanism of the oxidation of HMF to DFF.

The very fast hydrolysis of compound **1** and the similarity between NaBr/DMSO and the bromosulfonium **4** lead us to suggest that Swern reaction is the preferred pathway for DFF formation. We therefore suggest the following mechanism (Scheme 1, right part). HBr is formed from DMSO In presence of sodium bromide under acidic condition. HBr is then involved in the formation of bromosulfonium **4**[65] which reacts with HMF to form the oxosulfonium **2**. In the presence of water, oxosulfonium **2** is deprotonated. The elimination of dimethylsulfide leads to DFF and HBr.

As already mentioned, the presence of formic acid has also a positive impact on the oxidation of HMF to DFF. Indeed, the presence of formic acid in the reaction mixture accelerates this oxidation and a quantitative yield of DFF is rapidly detected (Figure 3). In order to check whether formic ester of HMF undergoes transformation to DFF, this ester was synthesized[66] and subjected to the reaction conditions. However, this HMF derivative was stable under these conditions. Furthermore, in the absence of formic acid, the transformation starts after an induction period. This period is shorter when formic acid is present in the reaction mixture. Since conversion of **2** to DFF takes place in presence of water as base, formic acid is believed to be involved at the beginning of the reaction. We suggest that formic acid promotes the formation of bromodimethylsulfonium **4**.

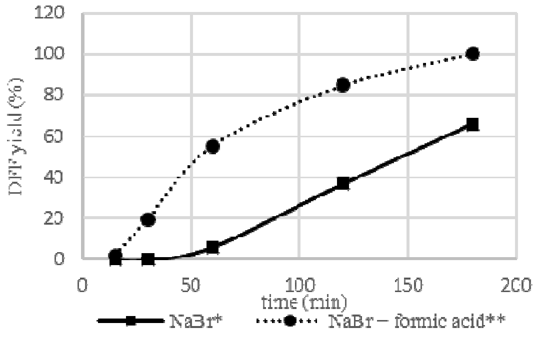


Figure 3. The effect of formic acid on direct conversion of HMF to DFF. *HMF (240 mg, 1.9 mmol), H_2O (102 µL, 5.3 mmol), boric acid (118 mg, 1.9 mmol), NaBr (196 mg, 1.9 mmol), DMSO (9 g) 150 °C **HMF (240 mg, 1.9 mmol), H_2O (102 µL, 5.3 mmol), boric acid (118 mg, 1.9 mmol), NaBr (196 mg, 1.9 mmol), formic acid (72 µL, 1.9 mmol), DMSO (9 g) 150 °C

Conclusions

We have developed the first one-pot production of 2,5-diformylfuran (DFF) from mono and polysaccharides. The process has also been applied to the transformation of primary feedstock such as straw and bran. It involves monomerization, isomerisation of glucose to fructose, dehydration leading to 5-hydroxymethylfurfural (HMF) and finally selective oxidation to DFF. The process is efficient and environmentally friendly. Boric acid, sodium bromide and formic acid are used as reagents. The reactions have been carried out on multigram scale in the laboratory (see SI). In order to further improve the degree of sustainability, the extraction and purification process needs to be optimised.

Acknowledgements

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