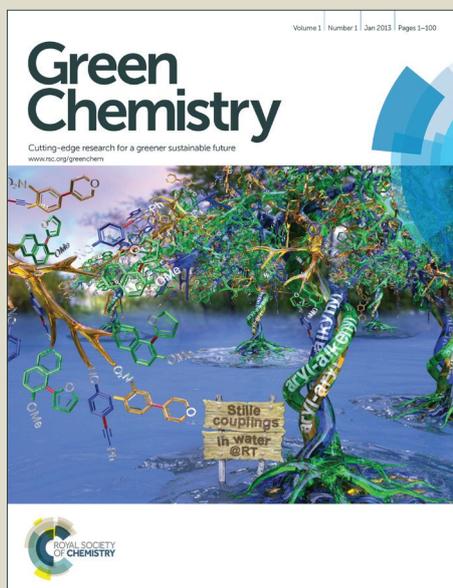


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ARTICLE

CO₂-catalysed conversion of carbohydrates to 5-hydroxymethyl furfural

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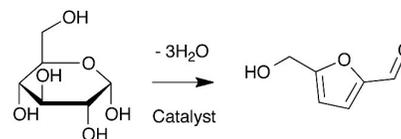
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The conversion of sugars to furans has been gaining attention in recent years as a potential source of renewable chemical building blocks. This work considers the viability of CO₂ as an acid catalyst for the conversion of carbohydrates to 5-hydroxymethyl furfural (5-HMF). In addition, the effects of secondary solvents for the separation of the produced 5-HMF from the aqueous reaction mixtures are explored. The addition of salts as a means of phase separation to improve the 5-HMF yield was also investigated. The yield of 5-HMF for CO₂-catalyzed glucose conversions was increased from 18% to 64% by varying the concentrations of sugar, salt and choice of secondary solvent. This method was also applied to starch, xylan, and cellulose, and was able to achieve 55%, 51% and 22% respectively. This work shows that high yields of 5-HMF could be achieved through the use of CO₂-catalyzed carbohydrate conversions.

Introduction

In recent years there has been an increased interest in chemical products derived from biomass to increase the sustainability of the chemical industry.^{1, 2} A present area of interest includes the use of sugars as a source of furan compounds, which can subsequently be used as a platform for the downstream generation of bio-products, such as bio-fuels,¹⁻⁴ as well as monomers for the production of polymers.^{5, 6} Furfural from pentose sugars and 5-hydroxymethyl furfural (5-HMF) from hexose sugars (Scheme 1) can be readily converted to a range of chemicals, including bio-fuels, through a number of upgrading approaches.³

A wide range of acid catalysis have been reported for this reaction, including organic and inorganic acids,⁶ organic and inorganic salts,^{7, 8} Lewis acids,⁹ ion exchange resins,¹⁰ and zeolites.¹¹ These approaches have been shown to effectively convert C6 sugars and produce high yields of 5-HMF, but suffer from deactivation of the catalyst after several cycles, or loss of the catalyst to the aqueous medium. Studies have shown that the use of CO₂ as a catalyst is possible for the conversion of inulin, a polymer of fructose, to 5-HMF.¹² Wu *et al.*¹² showed that high conversion rates



Scheme 1: Dehydration of glucose to 5-hydroxymethyl furfural

could be achieved with yields of up to 53% using CO₂. Generally, CO₂ is non-toxic and easily recoverable, and thus ideally suited for use as a catalyst. It may also be possible to use CO₂ as a means of extracting the 5-HMF in downstream processing steps.

There are a number of issues associated with the use of traditional acid catalysts in the conversion of pentose and hexose to furan compounds, such as furfural and 5-HMF. One of the most pressing concerns is the formation of undesirable humic compounds, which result from the self-condensation of furan compounds.^{13, 14} In addition, product separation from common solvents such as DMSO has been a challenge, as it potentially requires a substantial energy input for industrial production, greatly increasing process costs.^{15, 16}

The use of secondary non-polar solvents to form a biphasic system with water, to reduce side reactions and improve the purification of furan compounds, using traditional acid catalysts such as solid acid catalysts has been comprehensively reviewed by Saha and Abu-Omar.¹⁶ The secondary phase is capable of sequestering furan compounds as they are produced, leading to a reduction of their concentration in the aqueous phase. This sequestering component limits the opportunity for side reactions, thereby improving both the yield and purity of the final product. Selection of a secondary

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phase that is capable of partitioning furan compounds effectively from water is essential.³ The addition of inorganic salts such as NaCl to the aqueous phase has been shown to improve the partitioning of 5-HMF into the secondary phase, thereby enhancing the selectivity of the reaction.^{3, 17} Yields of 5-HMF as high as 89% have been reported for these biphasic systems through the use of acid ionic liquids or solid acid catalysts.^{17, 18}

The addition of different types of salts can either strengthen or weaken the hydrogen-bonding network of liquid water, resulting in significant changes to the solubility of organic compounds in solution.^{19, 20} Kosmotropic salts strengthen the hydrogen bonding of water, and consequently reduce the solubility of organic compounds. In contrast, chaotropic salts weaken the hydrogen bonding network, thereby increasing the solubility of organics. As such, it is possible to facilitate the formation of a biphasic system of water and a nominally soluble secondary solvent through the addition of a kosmotropic salt. Conversely, the relative concentration of an organic solvent that would normally have very low solubility in water can be increased upon the addition of a chaotropic salt.^{19, 20}

Additionally, the formation of a secondary phase can be achieved through the addition of CO₂ to mixtures of water and an organic solvent.^{3, 17, 21, 22} Morais et al.²¹ recently reported the use of biphasic systems of water/tetrahydrofuran/methyl isobutyl ketone to produce furfural from xylose using CO₂ as a catalyst at temperatures up to 200 °C. It is important to note, however, that the phase behaviour of mixtures of water and non-polar solvents is highly dependent on temperature. For example, while under atmospheric conditions, pentanol will form a biphasic mixture with water, but at higher temperatures the solubility of water in pentanol increases, and will eventually reach an upper critical solution temperature (UCST) at 184.4 °C, at which point the mixture will form a single phase.²³

This work describes the use of CO₂ as a catalyst for the conversion of glucose to 5-HMF in a range of solvent/water/salt mixtures, with a focus on salt selection. Solvent properties, such as logP, as well as the chaotropic/kosmotropic capacity of the salts, are explored with respect to their effects on the yield of 5-HMF produced from glucose. This work shows the capacity for CO₂ to be used as an acid catalyst for the conversion of glucose to 5-HMF, and improves the selection criteria for salts and solvents to be employed in biphasic 5-HMF production systems. The conversion of polysaccharides to 5-HMF is also demonstrated.

Methods and Materials

Reactions were carried out in a Parr 31 mL high pressure vessel (T316SS, Parr no. N4742, modified to 31 mL). Glucose (Ameresco, >99% purity) (1.0 g), salt (NaCl (Fisher scientific, certified ACS grade), Na₂SO₄ (Sigma Aldrich, >99% purity), CaCl₂ (Mallinckrodt chemical works, anhydrous analytical reagent) or CaSO₄ (Sigma Aldrich, >99% purity)), organic

solvent (10 mL, unless otherwise stated) (methanol (ACP, reagent grade), acetone (ACP, reagent grade), ethanol (Fisher scientific, HPLC grade), 2-propanol (Sigma Aldrich, HPLC grade), 1-butanol (Sigma Aldrich, HPLC grade), 2-butanol (Sigma Aldrich, HPLC grade), 1-pentanol (Fisher scientific, HPLC grade), 1-octanol (Fisher scientific, HPLC grade), toluene (Fisher scientific, HPLC grade), hexanes (Fisher scientific, HPLC grade), acetonitrile (Fisher scientific, HPLC grade) or tetrahydrofuran (Fisher scientific, HPLC grade)) and distilled water (10 mL) were added to the vessel along with a stir bar. The vessel was then closed, stirred at 500 RPM and heated in an oil bath to the required temperature (180 or 200 °C, measurement taken in the oil bath) and allowed to equilibrate for 30 min. Following equilibration, the reactor was pressurized with CO₂ (7 or 15 MPa) with a JASCO model PU-980 intelligent HPLC pump, equipped with a pump head chiller set to -5 °C in order to maintain CO₂ in a liquid state. All reactions were conducted in duplicate or triplicate.

Following the reaction, the reaction vessel was cooled on ice for 10 min and then allowed to equilibrate to room temperature and depressurized, the entire sample was collected from the reaction vessel and the reactor was rinsed three times using methanol and twice with water. The sample and solvent used to rinse the reaction vessel (20 mL) were passed through a 0.2 µL filter, and made up to 250 mL with HPLC grade methanol, the resulting 250 mL sample was further diluted by a factor of 10 for the purpose of HPLC analysis. HPLC analysis was performed within 30 minutes of sample collection and preparation to limit the formation of 5-HMF degradation products.

Analysis

Following reaction and dilution, the samples were analyzed using a Jasco HSS-2000 HPLC system, equipped with a quaternary gradient HPLC with an auto sampler, and a UV-visible (PDA) detector. Separation was achieved using a Zobax extended-C18 column (rapid resolution, 4.6 × 150 mm, 3.5 µm) at a constant injection volume of 2 µL. Throughout the HPLC method, the flow was held at a constant rate of 0.5 mL/min using a solution of 10% methanol, 0.1% formic acid and 90% H₂O. Between each injection, the column was washed with methanol to reduce sample carryover. Calibration of the 5-HMF was performed using pure 5-hydroxymethyl furfural (Sigma Aldrich, ≥99% purity) in water. Chromatograms and data were collected using asco-Borwin 1.5 chromatography software. Reported yields are averages and given with standard deviation values.

Results and discussion

Substrate and Solvent Selection

The conversion of glucose in water, under 15 MPa of CO₂ at 200 °C, resulted in a 5-HMF yield of 19.7 ± 0.14%, which was comparable to the results reported (5-HMF yield ≈ 20% under similar reaction conditions) by Wu *et al.*¹² for the conversion of

fructose to 5-HMF under similar conditions. Thus glucose, like fructose, can be dehydrated using CO₂ as a catalyst and the starting material does not appear to significantly affect the yield. This was somewhat surprising because Qi *et al.*²⁴ had demonstrated that the H₂SO₄ catalysed conversion of fructose is faster than glucose, in addition to increased yield of 5-HMF.

The use of a biphasic solvent system have been previously shown to improve the yield of 5-HMF from glucose using various solid acid and sulfuric acid catalyzed dehydrations.¹⁶ In most systems, this would involve the use of a secondary solvent, such as toluene or a similar low polarity solvent, to improve the extraction and separation of 5-HMF from water. However, it has recently been shown that similar results could be achieved with a salt-induced biphasic,^{3, 17} where solvents that are traditionally miscible with water can be used as secondary solvents, because phase separation can be induced by the addition of a salt to the solution. The requirements of the secondary solvent are; negligible effects on conversion, reduction of secondary reactions, ability to extract HMF from water. We therefore evaluated several secondary solvents in batch reactions with CO₂ as the catalyst, to assess the effects of these solvents on the yield of 5-HMF.

A series of short chain alcohols was used to see if there is a correlation between the octanol/water partition coefficient (logP) used as a measure of the hydrophobicity of the organic solvent and the yield of 5-HMF, while maintaining a constant functional group in the solvent molecule. For comparison, other solvents were tested to assess the effects of the alcohol group on the yield, and to explore a greater range of logP values. The choice of the secondary solvent was found to affect the 5-HMF yield, as shown in Figure 1, where the yield of 5-HMF is presented as a function of the logP of the secondary solvent. While short chain alcohols and solvents with logP values below 1 do not form aqueous/organic biphasic mixtures, a number of studies have shown that the addition of either salts, or pressurized CO₂, can induce phase separation at room temperature or at moderately higher temperatures.^{3, 21} These solvents are alternatives to traditional secondary solvents that are more expensive and less environmentally friendly (e.g. 1-pentanol, toluene, etc.).

Figure 1 shows that the yield of 5-HMF in pure water is 19.7 ± 0.14%, and the addition of relatively hydrophilic secondary solvents (logP < 1) substantially decreases the yield. The addition of comparatively hydrophobic alcohols resulted in an increase in the yield of 5-HMF to above the levels observed for water. For hydrophobic non-alcohols (toluene and hexane), the yield of 5-HMF was similar to that in just water. The increase in yield with the hydrophobic alcohols may potentially be due to the separation of 5-HMF product from the aqueous phase, reducing the exposure of the HMF product to acid, and therefore slowing the unwanted secondary reactions (i.e. formation of humins).²¹ However, the UCST for pentanol and water is 184.4 °C,²³ which increases with the addition of CO₂ to the system.²¹ Thus the presence of pressurized CO₂ could cause the solvent system to be biphasic at 200 °C. At this time no data for the phase behaviour of a mixture of water/pentanol/CO₂ has been reported for the temperatures

and pressures employed in this study. Because we lack vessels with windows that can withstand these temperatures, we can not be certain whether there are one or two liquid phases at the reaction conditions. The decrease in yield with the use of toluene and hexane, although at higher logP values, was likely due to the solubility of 5-HMF in the secondary solvent. The maximum yield of 5-HMF for the solvents investigated was found to occur above a logP value of 1.5. This would suggest that in order to improve 5-HMF yield, the solvents selected for the secondary phase should produce a biphasic system with water under atmospheric conditions and should be soluble in, but not completely miscible with, water, allowing increased water to solvent mixing than would be observed with very hydrophobic solvents.

Effect of Temperature and CO₂

Wu *et al.*¹² previously demonstrated that it was possible to increase the yield of 5-HMF by decreasing reaction temperature, which consequently reduces secondary reactions that can lead to the formation of humins in the system.¹² However, in this study (Figure 1), decreasing the temperature from 200 °C to 180 °C reduced the 5-HMF yield. As noted for 200 °C, the choice of secondary solvent influences the yield of 5-HMF in the reaction at 180 °C. However, no secondary solvent produced yields of 5-HMF significantly greater than water at 180 °C.

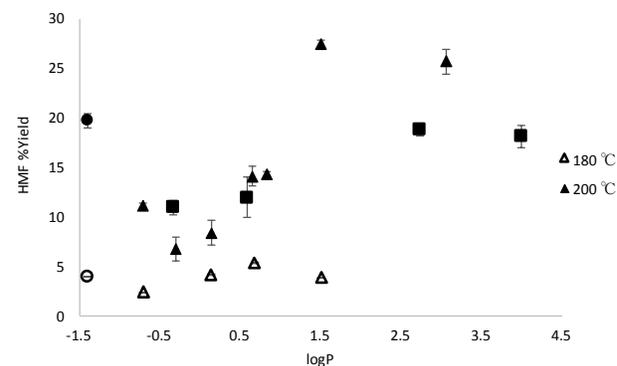


Figure 1: Effect of secondary solvent partitioning coefficient on the yield of 5-HMF at 180 or 200 °C, 2 h, 15 MPa CO₂, ≈ 1 g glucose, 10 mL of water, and 10 mL of solvent (water (180 °C, ○; 200 °C, ●), methanol, ethanol, 2-propanol, 1-butanol, 2-butanol, 1-pentanol, 1-octanol (180 °C, △; 200 °C, ▲), toluene, hexane, acetonitrile and tetrahydrofuran (200 °C, □)). Error bars show are standard deviations.

Performing the reaction without CO₂ lowered the yield more than four-fold (Table 1, entries 3 and 4).

Kosmotropic vs. Chaotropic Salt Effects

As previously noted, the purpose of the secondary solvent in this experiment was to effectively separate the 5-HMF from water, consequently reducing the formation of humins as secondary reaction products, by limiting interactions between the HMF product and acid (e.g. carbonic acid) in the aqueous phase. Nevertheless, a number of other factors could play a role in the observed in 5-HMF yields with different secondary

solvents. These factors include the isomerization of glucose to fructose,²⁴ the hardness of water, and any changes in the hydrogen-bonding network.^{19, 20} Chaotropic and/or kosmotropic agents have been shown to influence the solubility of both the 5-HMF and the secondary solvent, as a result of “salting in” (increasing solubility of organic layer in water) and “salting out” (pushing the produced 5-HMF into the organic layer) effects.^{3, 17} In an attempt to understand the factors that affect 5-HMF yield with different secondary solvents, and in order to identify the roles played by the factors noted above, a number of tests were performed with different salts and reaction conditions as shown in Table 1.

It has been suggested that, in a biphasic system, the 5-HMF can be found in the secondary (organic) phase and is, therefore, separated from the acid, leading to a reduction in the formation of humins.^{3, 17} As can be seen from Table 1, a change in the volume of the secondary solvent appeared to result in a change in the 5-HMF yield (entries 2 and 3). Under the same experimental conditions, changing the solvent ratio of H₂O:pentanol from 1:1 (entry 2) to 1:1.5 (entry 3) decreased the yield from 27% to 18%, which would suggest that partitioning of the product into the secondary phase plays a role in the reaction. However, partitioning to another phase does not explain these results, as increase of the yields of 5-HMF would be expected with increases in the volume of the secondary phase. This decreased yield of 5-HMF may be the result of increased apparent glucose concentration in the aqueous phase due to loss of water to the pentanol thought solubilisation.

Román-Leshkov and Dumesic¹⁷ demonstrated that sodium chloride could be employed to encourage “salting out” of 5-HMF to a secondary phase in order to get a greater 5-HMF yield. Varying the salt used in the reaction makes it possible to study effect and role of the salt.

Table 1: Effect on 5-HMF yield due to changes in the reaction conditions. 10 wt% glucose, 10 mL water, and 15 MPa of CO₂.

	Salt	Temp. (°C)	Salt (wt%)	Time (h)	Pentanol (mL)	% Yield	Standard dev.
1	-	180	-	2	10	4	2.2
2	-	200	-	2	10	27	1.1
3	-	200	-	2	15	18	1.1
4 ^a	-	200	-	2	15	4	0.5
5 ^{bc}	CaCl ₂	180	10	0.75	15	10	0.7
6 ^{bc}	CaCl ₂	200	10	1.5	15	64	0.8
7 ^d	CaCl ₂	200	10	2	15	46	1.4
8	CaCl ₂	200	10	2	15	44	0.2
9 ^b	CaCl ₂	200	10	2	15	53	1
10	CaCl ₂	200	50	2	15	23	0.4
11	CaSO ₄	200	10	2	15	16	0.8
12	Na ₂ SO ₄	200	10	2	15	40	0.8
13	NaCl	180	5	2	10	11	1.4
14	NaCl	180	10	2	10	16	0.5
15	NaCl	180	20	2	10	8	1.8
16	NaCl	200	10	2	10	37	0.3
17	NaCl	200	10	2	15	23	1.8
18	NaCl	200	50	2	15	41	1.3

^a No CO₂ added. ^b Concentration of glucose added to the reactor reduced to 1 wt%. ^c CO₂ pressure reduced to 7 MPa. ^d 10 wt% fructose instead of glucose.

The introduction of sodium chloride resulted in an increase in 5-HMF yield from 27% (entry 2, Table 1) to 37% (entry 16), at 200 °C, with constant concentration of glucose and solvent volumes. Additionally, the increase in yield at 180 °C (entries 1 and 14) suggests that the addition of NaCl may aid in the separation of the 5-HMF into the organic phase (“salting out”). However, there is no apparent direct link between the salt concentration and the yield of 5-HMF (0 wt%_(NaCl) = 4% yield (entry 1), 5 wt%_(NaCl) = 11% yield (entry 13), 10 wt%_(NaCl) = 16% yield (entry 14) and 20 wt%_(NaCl) = 8% yield (entry 15)). It is likely that the optimal concentration of salt varies with the selection of co-solvent, salt, and catalyst. If the increase in 5-HMF yield is the result of salting out, then the yield should depend on the relative ability of the salt to salt out 5-HMF from solution.²⁵

Based on the Hofmeister series²⁵ and relative ionic strengths, where SO₄²⁻ > Cl⁻ and Na⁺ > Ca²⁺,²⁵ the most effective salt would be expected to be Na₂SO₄. The addition of NaCl did increase the 5-HMF yield from 18% to 23% (entry 3 compared to entry 17). As expected, keeping Na⁺ but changing the anion from Cl⁻ to SO₄²⁻ increased the yield further to 40% (entry 12). Again, a decrease in the yield was anticipated with a change in the cation from sodium to calcium, while using sulfate as the anion, due to their relative position on the Hofmeister series.²⁵ This decrease in yield was observed when the results using Na₂SO₄ to CaSO₄ (40% to 16% respectively for entry 12 and entry 11) are compared. For the chlorine salts however, this trend was reversed. For calcium, a change in the anion from Cl⁻ to SO₄²⁻ resulted in a decrease in the 5-HMF yield from of 44% for CaCl₂ (entry 8) to 16% for CaSO₄ (entry 11) contrary to the Hofmeister series. The trend cannot be explained by the Hofmeister series and “salting out”, so other mass transfer considerations may be important.

Modifying the best method (entry 8) by reducing the glucose concentration causes an increase in the yield (entry 9) while additionally lowering the pressure of CO₂ to 7 MPa increases the yield further to 64 % (entry 6). These conditions were also applied to starch, xylan and cellulose to assess their capacity for converting polysaccharides. These experiments achieved a yield of 55%, 51% and 22% respectively. These results are shown in Figure 2. Future work will include optimizing reaction conditions for a variety of polysaccharides.

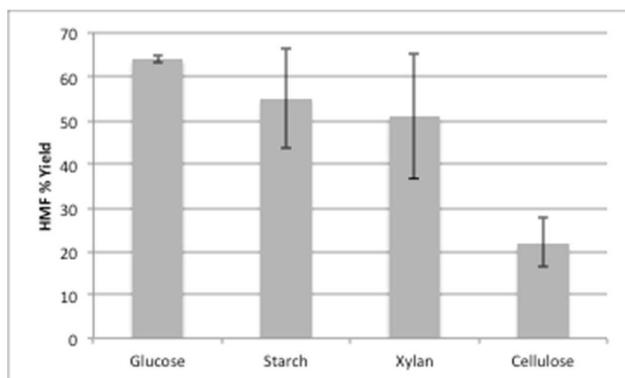


Figure 2: Yield of 5-HMF production reaction performed on 1 wt% carbohydrate, at 200 °C, 7 MPa of CO₂, 1.5 hr, 15 mL of pentanol, and 10 mL or 10% wt CaCl₂ deionized water. Standard deviation of results is shown using error bars.

The 64% yield of 5-HMF from glucose is comparable to the yields for the same reaction in the literature, but the literature studies generally used more environmentally damaging solvents or acid catalysts. Li et al.²⁵ obtained 60% yield using Hf(OTf)₄ acid catalyst in water. Págan-Torres et al.²⁶ obtained 62% using a combination of AlCl₃ and HCl in a brine/2-sec-butylphenol mixture, at 170 °C. Tong et al.²⁷ obtained 42-54% yields using Amberlyst-15 and Mg-Al hydrotalcite as catalysts in DMF.⁵ Zhou et al.²⁸ obtained 61% yield using chromium-exchanged bentonite as the catalyst in ionic liquid 1-butyl-3-methylimidazolium chloride ([Bmim]⁺Cl⁻) and dimethyl sulfoxide (DMSO) mixtures. Zhao et al.²⁹ reported a 5-HMF yield of 68-70% using CrCl₂ in 1-alkyl-3-methylimidazolium chloride. While these literature studies used lower temperatures than the present study, their use of metal and halide-containing catalysts and more harmful solvents would contribute to the environmental and economic costs.

In an effort to address potential concerns related to environmental impact, water-recycling experiments were carried by repeating the experimental procedure without replacing the aqueous phase. No significant lowering of the yield was found after 3 cycles.

Conclusions

The use of CO₂ as a catalyst for the conversion of carbohydrates to 5-HMF was shown to be highly effective, allowing 5-HMF yields of up to 64%, and is effective on a range of polysaccharides. As CO₂ is non-toxic and produces higher yields of 5-HMF, it is an effective and non-toxic alternative to other acid catalysts. The use of a secondary solvent in the reaction did appear to greatly affect the yield of 5-HMF, while the partitioning coefficient plays a potential role in the effect of the solvent on the yield. The use of sodium chloride has been previously shown to increase 5-HMF yield and allow the use of miscible solvents as the secondary phase in the reaction, due to its ability to “salt out” organic compounds

from the aqueous phase. In this study, it was found that it is possible to use both kosmotropes and chaotropes to increase the yield of 5-HMF through their use in the formation of a secondary phase. The choice of both solvent and salt needs to be assessed in order to determine the best combination for their use in the dehydration of glucose to 5-HMF, as effective mass transfer of the product to the secondary phase is necessary.

Acknowledgments

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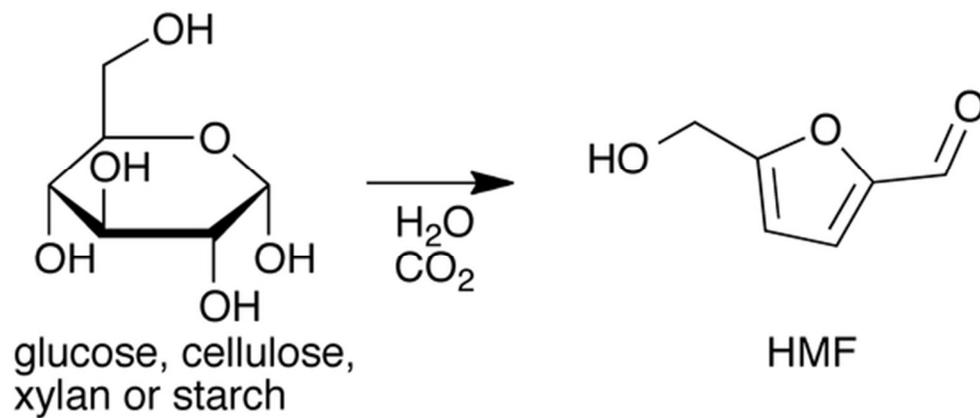
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