

# Green Chemistry

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## COMMUNICATION

## CO<sub>2</sub>-catalysed aldol condensation of 5-hydroxymethylfurfural and acetone to a jet fuel precursor

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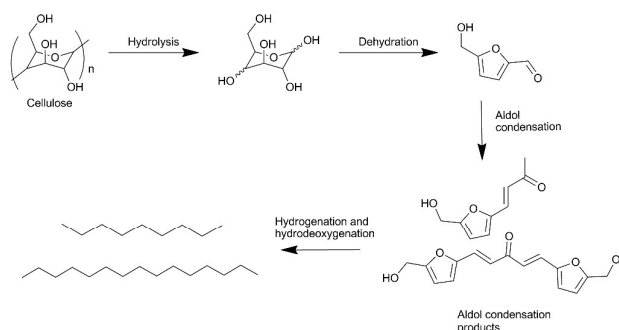
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CO<sub>2</sub> can act as a catalyst for the production of bio-jet fuel precursors through aldol condensation. CO<sub>2</sub>-catalysed aldol condensation of HMF with acetone gives a >95% yield of [4-(5-hydroxymethyl-2-furyl)-3-butenone] mono-aldol condensate, while direct conversion of glucose to the same mono-aldol condensate gave a yield of 11%.

In recent years, the potential for the production of biomass-derived jet fuels has been gaining interest, partially due to increasing concerns over greenhouse gas emissions, fluctuating oil prices, growing environmental stewardship, and a will to move to more renewable fuel sources.<sup>1-4</sup> In recent years, a number of conversion techniques have been developed to produce biomass-derived jet fuels to supplement or replace the use of fossil fuels.<sup>4</sup>

One of the most prominent intermediates derived from biomass is 5-hydroxymethyl furfural (5-HMF).<sup>4-8</sup> Cellulosic material and six carbon sugars (hexoses) can be converted, with the use of acid catalysts, to 5-HMF (Scheme 1). Yields of 5-HMF from glucose and fructose are often greater than 65%. Catalysts that have been reported for the production of 5-HMF include organic and inorganic acids,<sup>9</sup> organic and inorganic salts,<sup>10, 11</sup> Lewis acids,<sup>12</sup> ion exchange resins,<sup>13</sup> zeolites,<sup>14</sup> and CO<sub>2</sub>.<sup>7</sup> The catalysts and associated solvents employed have been shown to affect the yield and the purity of the products formed in the reaction.<sup>15</sup> In many cases, it has been suggested that the 5-HMF produced could be employed in the production of biomass-derived jet fuel (Scheme 1).<sup>1, 2, 8, 16</sup>



Scheme 1: Proposed conversion of cellulose to biomass derived jet fuel.

The envisioned production of biomass-derived jet fuel would involve a 3 to 4 step process, depending on the starting feedstock (cellulosic material/hexoses).<sup>2</sup> In general, following the hydrolysis (acid/enzyme catalysed) of cellulose or hemicellulose to hexoses, as shown in Scheme 1, the sugars (glucose in the current example) undergo an acid catalysed dehydration to 5-HMF followed by a subsequent upgrade to the compounds of interest.<sup>2, 6, 17</sup> For the production of jet fuel precursors, the upgrading is commonly accomplished through base-catalysed aldol condensation with acetone to form both aldol condensation adducts shown in Scheme 1.<sup>17</sup> This is followed by hydrogenation and hydrodeoxygenation to linear alkanes, similar to jet fuel.

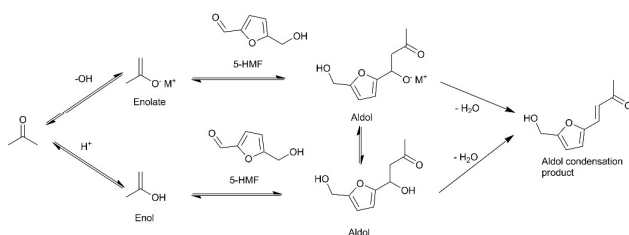
Aldol condensation follows two different mechanisms depending on the catalyst utilised. As shown in Scheme 2, the aldol addition reaction progresses via an enolate mechanism when a base catalyst is used. On the other hand, the acid catalysed aldol addition occurs via an enol intermediate. For both reactions the final step in the process is a dehydration of the resulting intermediate to the condensation product as shown in Scheme 2.<sup>18</sup>

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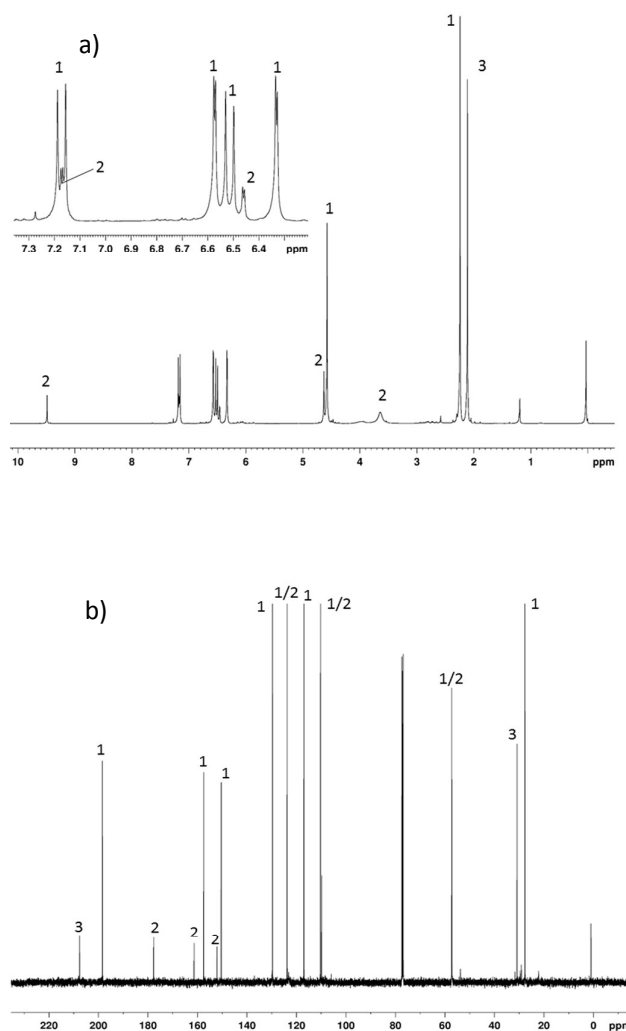


**Scheme 2:** Reaction scheme for acid and base catalysed aldol condensation of 5-HMF and acetone.

The conversion of hexoses to 5-HMF has been shown to be possible using  $\text{CO}_2$  as the acid catalyst.<sup>7, 16</sup> At this time,  $\text{CO}_2$  has not been utilised as an acid catalyst for aldol addition or condensation of any aldehydes. This paper explores the use of  $\text{CO}_2$  as a catalyst for the production of aldol condensation products from 5-HMF, as well as the use of  $\text{CO}_2$  as a catalyst for the one step conversion of glucose to aldol condensation products. The use of  $\text{CO}_2$  rather than conventional acid catalysts could reduce the environmental impact of the production of biomass-derived jet fuels because  $\text{CO}_2$  is less harmful to health and the environment than conventional acid catalysts and is easy to remove from the product.

Reactions were carried out in a 31 mL high pressure stainless steel vessel (T316SS, Parr no. N4742, modified to 31 mL). Glucose, 5-HMF, reaction solvents and stir bar were added to the vessel. The vessel was then closed, stirred at 500 RPM and heated in an oil bath to the targeted temperature (temperature was measurement taken in the oil bath) and allowed to equilibrate for 30 min. Following equilibration, the reactor was pressurized with  $\text{CO}_2$  using a JASCO model PU-980 HPLC pump equipped with a pump head chilled to  $-5^\circ\text{C}$  in order to maintain  $\text{CO}_2$  in a liquid state while inside the pump, during addition of  $\text{CO}_2$  no changes in temperature were noted. All pressures are reported as gauge pressures. After the reaction, the vessel was cooled 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 all rinse solutions were filtered with a 0.2  $\mu\text{L}$  filter and made up to 20 mL with HPLC grade methanol; the resulting sample was further dilution by a factor of 10 in preparation for GC analysis. Reactions were performed in triplicate.

Aldol condensation products were further identified using  $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  NMR spectroscopy (Figure 1). Figure 1 shows the NMR spectra of the crude product of entry 5 in Table 1. Following reaction and analysis, the sample was stripped of the bulk of its volatile content by rotary evaporation at  $50^\circ\text{C}$  (with vacuum supplied by a Piab Lab Vac rated for 20 mbar absolute pressure) for 15 min, re-solubilized in dichloromethane and washed with water to remove acetone. Dichloromethane was evaporated using rotary evaporation at  $50^\circ\text{C}$  for 10 min, and the resulting solid was dissolved in NMR solvent. The spectra show the presence of aldol condensation product, 5-HMF, and acetone in the crude product. The peaks



**Figure 1:**  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra (a and b, respectively) of the product mixture from a  $\text{CO}_2$  catalysed aldol condensation of 5-HMF with acetone. The peaks have been assigned: 1) mono-aldol condensate, 2) 5-HMF, and 3) acetone

assigned to the aldol condensation products were comparable to literature data for the mono-aldol product.<sup>19, 20</sup> Peaks associated with the di-aldol product were not observed, the possibility that it was present as a very minor product could not be excluded.

**4-(5-Hydroxymethyl-2-furyl)-3-butenone (mono-aldol condensate)**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.24 (s, 3H), 3.64 (broad, 1H), 4.58 (s, 2H), 6.33 (d,  $J = 3.2$  Hz, 1H), 6.51 (d,  $J = 15.9$  Hz, 1H), 6.57 (d,  $J = 3.2$  Hz, 1H), 7.17 (d,  $J = 15.9$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  27.7, 57.3, 110.3, 117.0, 123.8, 129.7, 150.4, 157.5, 198.4.

In the system, the Brønsted acidity of the combination of water and  $\text{CO}_2$  is likely necessary to obtain significant conversion of 5-HMF to the aldol condensate. Therefore, the amount of water in the system was envisioned to be a major contributing factor in determining the yield of aldol condensation products. Additionally, the use of secondary solvents in the reaction should allow for greater yield through the reduction of secondary side reactions that have been

shown to occur during the formation of 5-HMF from hexoses.<sup>21, 22</sup> The addition of either excess water or secondary solvents such as toluene to the reaction inhibited the formation of the aldol condensation product, as shown in entries 1, 2 and 3 by comparison to entry 4.

**Table 1:** Effect of solvent on the yield of mono adduct aldol condensation product from 5-HMF ( $\approx 2.5$  mmol) and acetone (20 h, 200 °C and 15 MPa). Yields determined from GC-MS.

	Toluene (mL)	Water (mL)	Acetone (mL)	5-HMF conversion (%)	Aldol condensate yield (%)
1	10	5	5	90 $\pm$ 3	6 $\pm$ 2
2	10	0.5	5	57 $\pm$ 4	27 $\pm$ 1
3	0	5	10	50 $\pm$ 2	33 $\pm$ 2
4	0	0.5	10	89 $\pm$ 1	70 $\pm$ 3
5	0	0.05	10	86 $\pm$ 2	39 $\pm$ 2

However, when the toluene-rich phase was not present in the system (entries 3 vs 1 and entries 4 vs 2), there was a significant increase in the yield of aldol condensate. The water content did play an important role in the system, with the yield for the aldol condensation product being greatest when 0.5 mL of water was used (entries 3-5). Increasing or decreasing the amount of water lowers the yield. It appears that 0.05 mL of water is insufficient to generate enough carbonic acid catalyst, while having too much water may decrease the yield by inhibiting the dehydration step of the aldol reaction.

The application of higher pressure and/or higher temperatures would result in greater energy costs, so the use of lower temperatures and pressures was tested. Table 2 presents the effect of different temperatures and pressures on the aldol condensation product yield. Initially, the reaction time was limited to 1 h (Table 2, entry 5). The low yield suggested that little product was formed in the reaction within the first hour of the reaction. To assess the effect of reaction temperature, the reaction was performed over a range of temperatures (Table 2, entries 1-4). As can be seen, no aldol condensation product formation was observed at temperatures below 175 °C. The reaction was performed at 100 °C at an extended reaction time and applying the CO<sub>2</sub> pressure that gave the best result at 200 °C, but without success. Using an intermediate reaction temperature of 175 °C (Table 2, entry 4) did result in the formation of aldol condensation product, although the yield of aldol condensate under these conditions was relatively low.

The effect of lowering the CO<sub>2</sub> pressure on the reaction was also evaluated (entries 6 through 8). The yield of the aldol condensation product increased from 70% at 15 MPa to >95% at 2.5 MPa. Because the HMF conversion barely changed, this increase seems to be due to a decrease in secondary reactions leading to the formation of humic compounds via self-condensation reactions of 5-HMF.<sup>6, 15</sup> However, CO<sub>2</sub> addition played an important role in the reaction as an acid catalyst, given that thermal conversion alone showed lower yields by comparison to CO<sub>2</sub> catalyzed aldol condensation.

<sup>a</sup> Glucose concentration reported as a wt% of total solvent (water + acetone) (20 h, 0.5 mL water and 10 mL acetone).

**Table 2:** Effect of physiochemical reaction conditions on the yield of mono adduct aldol condensation product from 5-HMF and acetone (0.5 mL water and 10 mL acetone).

	Temperature (°C)	Time (h)	Pressure (MPa)	5-HMF conversion (%)	Aldol condensate yield (%)
1	100	20	15	7 $\pm$ 2	0
2	100	71	2.5	6 $\pm$ 3	0
3	150	20	15	29 $\pm$ 2	0
4	175	20	15	38 $\pm$ 2	5 $\pm$ 0.5
5	200	1	15	50 $\pm$ 3	3 $\pm$ 0.5
6	200	20	15	89 $\pm$ 1	70 $\pm$ 3
7	200	20	2.5	>95 $\pm$ 3	>95 $\pm$ 4
8	200	20	0	49 $\pm$ 4	32 $\pm$ 5

It has been shown previously by Lee *et al.*<sup>21</sup> that CO<sub>2</sub> is an effective catalyst for the conversion of glucose to 5-HMF. Additionally, CO<sub>2</sub> catalyzed conversion of polysaccharides of hexoses has been reported.<sup>7, 16</sup> Combining those CO<sub>2</sub>-catalyzed reactions with our CO<sub>2</sub>-catalyzed aldol condensation, it should be possible to directly convert glucose to the aldol condensation product directly. This one-pot reaction would reduce the number of process steps for the conversion of glucose to the biomass-derived jet fuel precursor. As an exploratory study to assess the viability of direct CO<sub>2</sub> catalyzed conversion of glucose to aldol condensate, a number of reactions were performed at conditions relevant to the aldol condensation reaction. Table 3 shows the direct CO<sub>2</sub> catalyzed conversion of glucose to the aldol condensation product. Our preliminary tests show that this is indeed possible, with a yield of 11%.

To assess the effect of reactant concentration, the mass of glucose added to the reactor was varied between 1 and 27 wt%. At higher glucose concentrations (Table 3, entry 7), the aldol condensation product was not detected following the reaction. Instead, large amounts of dark solid residue, typically associated with side reactions and the formation of humic compounds, was formed in the reactor. This dark solid is associated with the side reactions and the formation of humic compounds. It was noted by Wu *et al.*<sup>7</sup> that the concentration of inulin in the water greatly affected the yield of 5-HMF from CO<sub>2</sub>-catalyzed conversion of inulin, with lower inulin concentrations resulting in increased yields. Consistent with Wu *et al.*<sup>7</sup> and Lee *et al.*,<sup>21</sup> reducing the concentration of glucose in the reaction also resulted in an increased aldol condensate yield and a corresponding reduction in the formation of dark solid residue (humic compounds). Following the addition of 3 wt% (Table 3, entry 3) glucose to the reactor, a yield of 8% aldol condensation product was observed. Further reduction of glucose concentration to 1 wt%, at 15 MPa (Table 3, entry 2) yielded 3% aldol condensation product.

**Table 3:** Direct CO<sub>2</sub> catalyzed conversion of glucose to aldol condensation product at 200 °C.<sup>a</sup>

	Glucose (wt%)	Pressure (MPa)	Aldol condensate yield (%)
1	1.0	2.5	1 $\pm$ 1

2	1.0	15	3 ±1
3	2.6	15	8 ±0.5
4	2.9	2.5	11 ±2
5	3.5	5.5	8 ±1
6	5.0	15	6 ±5
7	27	15	0

The concentration of glucose had a strong effect on yield of the aldol condensation product. High concentrations resulted in side reactions that reduced the aldol condensate yield. Conversely, reduced yields were observed when the concentration was too low. An intermediate concentration of glucose produced the highest yields. As can be seen from Table 3 entry 4 at a concentration of 3 wt% glucose and pressure of 2.5 MPa, a yield of 11% aldol condensation product was obtained.

It was previously found that an increase in aldol condensation product could be promoted by reducing the reaction pressure, as shown in Table 2. Additionally it was reported by Lee *et al.*<sup>21</sup> that reducing the CO<sub>2</sub> pressure could also increase the 5-HMF yield from glucose. However, the effect of CO<sub>2</sub> pressure on the aldol reaction of glucose is unclear; at 1 wt% glucose, the yields are all very low and, within error, are the same for 2.5 and 15 MPa. Similarly, at about 3 wt% glucose, the yields are independent of CO<sub>2</sub> pressure, within error.

## Conclusions

The use of CO<sub>2</sub> as a catalyst for the aldol condensation of 5-HMF with acetone was explored. Yields of >95% were obtained, with the mono-aldol condensate as the only detected product. Different reaction conditions were explored and the best results for the conversion of 5-HMF to the aldol condensation product were obtained at high temperatures (200 °C), 20 h and moderate pressure of CO<sub>2</sub> (2.5 MPa). The reaction did not occur at temperatures below ~175 °C, for the conditions tested. To our knowledge, this is the first report of an aldol condensation catalyzed by CO<sub>2</sub>, which could have larger implications for green organic synthesis.

When this reaction is used in conjunction with a previously reported CO<sub>2</sub>-catalyzed conversion of glucose to 5-HMF, it was possible to convert glucose to 5-HMF using only CO<sub>2</sub> as a catalyst. One-pot conversions of glucose to the aldol condensate were performed and preliminary results produced yields of 11%. Future work will focus on increasing this yield and gaining an understanding of the effects of process conditions.

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## References

1. S. Dutta, S. De, B. Saha and M. I. Alam, *Catalysis Science & Technology Issue*, 2012, **2**, 2025-2036.
2. J. Lange, E. V. D. Heide, J. V. Buijtenen and R. Price, *Chem. Sus. Chem.*, 2012, **5**, 150-166.
3. R. Lee and J. Lavoie, *Animal Frontiers*, 2013, **3**, 6-11.
4. J. J. Roylance and K.-S. Choi, *Green Chemistry*, 2016.
5. H. v. Dam, A. Kieboom and H. V. Bekkum, *Starch/Starke*, 1986, **38**, 95-101.
6. B. Saha and M. Abu-Omar, *Green Chem.*, 2014, **16**, 24-38.
7. S. Wu, H. Fan, Y. Xie, Y. Cheng, Q. Wang, Z. Zhang and B. Han, *Green Chem.*, 2010, **12**, 1215-1219.
8. K. Pupovac, PhD Dissertation, Solid Acid-Catalyzed Dehydration of Sugars to 5-Hydroxymethylfurfural, subsequent Aldol Condensation and Hydrogenation over Bifunctional Spinel Oxides, Max-Planck-Institut für Kohlenforschung, 2013.
9. A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411-2502.
10. S. Tyrlik, D. Szerszeń, M. Olejnik and W. Danikiewicz, *Carb. Res.*, 1999, **315**, 268-272.
11. H. Zhao, J. Holladay, H. Brown and Z. Zhang, *Science.*, 2007, **316**, 1597-1600.
12. T. Deng, X. Cui, Y. Qi, X. Hou and Y. Zhu, *Chem. Commun.*, 2012, **48**, 5494-5496.
13. Y. Nakamura and S. Morikawa, *Bull. Chem. Soc. Jpn.*, 1980, **53**, 3705-3706.
14. E. Nikolla, Y. Román-Leshkov, M. Moliner and M. Davis, *ACS Catal.*, 2011, **1**, 408-410.
15. Y. Román-Leshkov and J. Dumesic, *Top. Catal.*, 2009, **52**, 297-303.
16. A. Morais, M. Matuchak, J. Andreasc and R. Bogel-Lukasik, *Green Chem.*, 2016.
17. W. Shen, G. Tompsett, K. Hammond, R. Xing, F. Dogan, C. Grey, C. Conner, S. Auerbach and G. Huber, *Applied Catalysis A: General*, 2011, **392**, 57-68.
18. A. Nielsen and W. Houlihan, *Organic Reactions*, 2011, **16**, 1-438.
19. J. Julis, M. Hölscher and W. Leitner, *Green Chem.*, 2010, **12**, 1634-1639.
20. A. Bohre, B. Saha and M. Abu-Omar, *ChemSusChem*, 2015, **8**, 4022-4029.
21. R. Lee, J. Harris, P. Champagne and P. Jessop, Submitted, 2016.
22. S. Siankevich, Z. Fei, R. Scopelliti, P. Jessop, N. Yanc, and P. Dyson, In Press.