A Preliminary Study of Catalytic Hydrothermal Conversion of Cellulose to Lactic Acid: Effects of Reaction Temperature and Metal Ion Catalyst

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Abstract. Cellulose biopolymer was converted to lactic acid by catalytic hydrothermal method. The conversion was studied under various temperatures (120 to 190 °C) and types of metal ion catalyst (Pb²⁺ and Al³⁺), while the reaction period remained fixed at 3 h. Following the reaction, the recovery of untreated cellulose and the mass loss were determined by gravimetric means. Meanwhile, the resultant liquid products were analysed by high performance liquid chromatography (HPLC) for detecting the targeted products: lactic acid, glucose, and fructose. The study reveals useful insights; elevating the reaction temperature was found to increase the mass loss, so did the yield of the targeted products. On the other hand, using a metal ion catalyst, possessing stronger Lewis acidity character, further enhanced lactic acid production.

Keywords: cellulose, hydrothermal, metal ion catalyst

1. Introduction

Over the last decade there has been a growing consensus about replacing fossil fuels with other sustainable resources to produce common chemicals. Thus, cellulose has emerged as the most promising resource because the polymer is available abundantly on earth, easily found, renewable and biodegradable [1]. Examples of cellulose feedstocks are crop residues, wood residues, and dedicated energy crops. They must first be subjected to the ‘deconstruction’ process that isolates cellulose from the other biopolymer constituents, hemicellulose and lignin [1]. Currently, deconstruction utilising an ionic solvent, such as the low-cost triethylammonium hydrogen sulfate ionic liquid, [N₂₂₂₀][HSO₄] IL, has actively studied [2-6].

Cellulose can be converted to a variety of platform chemicals, including lactic acid, fructose, and 5-hydroxymethylfurfural (5-HMF) [7-9]. Amongst these, lactic acid has received great interest; it is the monomer of poly(lactic acid) (PLA), a biodegradable polymer widely used as a filament in 3D printing. In 2018, the global market of lactic acid was valued at around $2.9 billion; the value is expected to progressively rise annually in the coming years [7]. The production of lactic acid from cellulose is
achieved through three consecutive steps: (1) hydrolysis of cellulose to glucose, (2) isomerization of glucose to fructose, and (3) conversion of fructose to lactic acid via a retro-aldol reaction. The first step requires the use of a Brønsted acid catalyst to cleave glycosidic bonds in cellulose. Meanwhile, a Lewis acid catalyst is necessitated to favour the retro-aldol reaction in the third step. Examples of metal ion catalysts able to produce a high yield of lactic acid are Pb\(^{2+}\), Zn\(^{2+}\), Mn\(^{2+}\), and Al\(^{3+}\) [7].

In this paper, we present preliminary findings of converting cellulose to lactic acid by means of hydrothermal method. We varied the reaction temperature (consequently the resultant autogenous pressure) (from 120 to 190 °C) besides the type of metal ion catalyst (Pb\(^{2+}\) and Al\(^{3+}\)). The study gives some useful insight into the extent to which the studied parameters influence the conversion process.

2. Methodology

An overall view of the reaction is shown in Fig. 1. A hydrothermal reactor (PTFE Lined, 25 mL and 3 MPa) was loaded with the following chemicals: cellulose particles (2.5 g, sigmacell-cellulose, type 20, 20 μm, Sigma-Aldrich UK), catalyst (0.14 mmol) (lead(II) nitrate, Pb(NO\(_3\))\(_2\) or aluminium(III) nitrate, Al(NO\(_3\))\(_3\)) and distilled water (20 mL) (Fig. 1, Step ①). The reactor was then heated in an oven at a desired temperature (120, 140, 160 or 190 °C) for 3 h (Fig. 1, Step ②). When the heating period had elapsed, the reactor was cooled to room temperature. The resultant suspension was then filtered through a Whatman-filter paper. The recovered solid, composing of unreacted cellulose (Fig. 1, Step ③), was dried at 110 °C and later weighed. Equation 1 was employed to calculate the recovery of unreacted cellulose (wt%).

\[
\text{Unreacted cellulose (\%) = } \frac{W_d}{W_i}
\]  
Equation 1

Here, \(W_i\): mass of unreacted cellulose following the reaction (g), and; \(W_i\): initial mass of cellulose used in the reaction.

The filtrate (Fig. 1, Step ④) was filtered through a syringe filter (PTFE, hydrophilic, 13mm x 0.45 μm) and later analysed on Agilent 1200 Series. For the detection of glucose and fructose, the filtrate passed through a Phenomenex Synergi Hydro column (RP80-A, 250mm x 4.6 mm) was employed to detect and quantify lactic acid in the filtrate under the conditions of 0.1% H\(_2\)PO\(_4\) as mobile phase, flowrate of 0.6 mL/min, column oven temperature of 60°C, and injection volume of 20 μL. Meanwhile, a Phenomenex Synergi Hydro column (RP80-A, 250mm x 4.6 mm) was employed to detect and quantify lactic acid in the filtrate under the conditions of 0.1% H\(_2\)PO\(_4\) as mobile phase, flowrate of 1 mL min\(^{-1}\), column oven temperature of 30°C, and injection volume of 20 μL. Standard solutions of glucose, fructose and lactic acid were prepared in distilled water with the following concentrations: 0.1, 1.0, 2.0 and 4.0 mg mL\(^{-1}\). Equation 2 was employed to calculate quantities of the targeted products in wt% (glucose, fructose and lactic acid) (P).

\[
\text{wt\% (P) = } \frac{A_{\text{HPLC}} \times F_D \times V_{\text{PL}} \times F_T(P)}{F_{\text{HPLC}}(P) \times m_{\text{cellulose}}\times F_C}
\]  
Equation 2

Here, \(A_{\text{HPLC}}\): area of HPLC peak; \(F_{\text{HPLC}}\): HPLC calibration factor for the targeted product(s); \(F_D\): dilution factor; \(V_{\text{PL}}\): volume of filtrate in mL; \(m_{\text{cellulose}}\): weight of sigmacell-cellulose (air-dried) in mg; \(F_C\): fraction of glucose sugar in sigmacell-cellulose, and; \(F_T(P)\): transformation factor accounting for molecular mass differences between starting material and products, 0.9 (glucose), 0.9 (fructose) and 0.8 (lactic acid).
3. Results

Table 1 shows how varying reaction temperature and changing metal ion catalyst affect the cellulose conversion. The observed mass loss (Table 1) strongly suggests that cellulose particles might have depolymerised under the applied reaction conditions. This is supported by a visual examination showing the liquid products that looked cloudy (photographs are displayed in Fig. 2). The cloudiness, without any doubts, indicates the presence of small quantities of cellulose particles, which passed through the filter paper during the separation step (Fig. 1). The size of these particles must be smaller (having low degree of polymerisation, DP) than the pore size of filter paper; a thorough investigation to confirm this is pending.

Irrespective of the catalyst type (Pb$^{2+}$ or Al$^{3+}$), the elevating reaction temperature exhibited an increasing-trend in the mass loss. As an example, for Pb$^{2+}$, the mass loss increased by two-fold when reaction temperature was elevated from 120 to 190 °C (Table 1, Entries 1-4). It is worth noting, for Pb$^{2+}$, the targeted products, in particular lactic acid, were formed only at 160 °C and above, with 190 °C generating the highest. In addition, by changing Pb$^{2+}$ to Al$^{3+}$, the production of the targeted products was enhanced. For instance, at 160 °C, the yield of lactic acid produced by Al$^{3+}$ was about nine times higher than that generated by Pb$^{2+}$ (Table 1, Entries 3 vs. 5). A likely reason for this is linked to the difference in Lewis acidity character between the metal ions (further discussion in the next section).

Table 1. Outcomes of conversion of cellulose under various reaction temperatures and metal ion catalysts. All reactions were conducted for 3 h.

| Temp (°C) | Catalyst | Untreated Cellulose (wt%) | Mass loss (wt%) | Glucose (wt%) | Fructose (wt%) | Lactic Acid (wt%) |
|----------|----------|---------------------------|----------------|--------------|---------------|------------------|
| 120      | Pb$^{2+}$| 90.6±0.65                 | 9.4±0.65       | -            | -             | -                |
| 140      | Pb$^{2+}$| 85.4±0.95                 | 14.6±0.95      | -            | -             | -                |
| 160      | Pb$^{2+}$| 84.6±0.54                 | 15.4±0.54      | 0.12         | -             | 0.14             |
| 190      | Pb$^{2+}$| 79.8±0.66                 | 20.2±0.66      | 1.48         | 0.57          | 1.33             |
| 160      | Al$^{3+}$| 80.2±0.99                 | 19.7±0.99      | 0.73         | 0.53          | 1.34             |
| 190      | Al$^{3+}$| 60.1±0.90                 | 33.9±0.90      | 2.99         | 0.67          | 5.47             |
Fig. 2. Liquid products obtained following the conversion of cellulose under reaction conditions of (catalyst: Pb$^{2+}$): (a) 120 °C, (b) 140 °C, (c) 160 °C, and (d) 190 °C; (catalyst: Al$^{3+}$): (e) 160 °C and (f) 190 °C. All reactions were conducted for 3 h.

4. Discussion

Effect of Reaction Temperature on Mass Loss. Cellulose can be depolymerised through hydrolysing its glycosidic bonds catalysed by hydroxonium ions, [H$_3$O]$^+$. It can therefore be said that the reaction progress relies upon two factors: the accessibility of glycosidic bonds and the availability of [H$_3$O]$^+$ ions.

Limited accessibility of glycosidic bonds makes cellulose recalcitrance to the hydrolysis reaction. This is because the β-1,4-glucan long chains in the biopolymer are linked by strong complex networks of intra- and intermolecular H-bonds, forming closely-packed microfibrils (likely structures are shown in Fig. 3) [2,10]. A thermal treatment, including the hydrothermal reaction, has been reported to be able to weaken H-bonds networks in cellulose, making glycosidic bonds to be more accessible [10]. Based on this, it was believed that the studied reaction (Fig. 1) might have experienced a similar occurrence to the aforesaid. In this regard, the elevation of reaction temperature (consequently increasing autogeneous pressure) might have increased the weakening effect of H-bond networks, allowing more glycosidic bonds to be exposed.

Fig. 3. Arrangements of β-1,4-glucan chains forming cellulose micro- and macrofibrils (left) and a proposed reaction pathway for lactic acid production from cellulose (right) [7].

Hydrolysis cellulose to glucose typically used a strong acid, like H$_2$SO$_4$ (pK$_a$ -3), for generating [H$_3$O]$^+$ ions, which later serve as Brønsted acid catalysts [1,13]. This study, however, did not employ any acid. It was therefore suspected that [H$_3$O]$^+$ ions could be generated, to a certain extent, via two reactions. The first is autoionisation of water occurring when the molecule is heated in a hydrothermal
vessel at an elevated temperature (reaction shown in Equation 3) [11,12]. The second is protonation of water by \([\text{Fe(H}_2\text{O)}_2]^{2+}\) complexes, as shown in Equation 4.

\[
\text{H}_2\text{O} + \text{H}_2\text{O} \leftrightarrow [\text{H}_2\text{O}]^+ + [\text{OH}^-] \quad \text{Equation 3}
\]

\[
[\text{Fe(H}_2\text{O})_2]^{2+} + \text{H}_2\text{O} \leftrightarrow [\text{Fe(H}_2\text{O})_2(\text{OH}^-)]^+ + [\text{H}_2\text{O}]^+ \quad \text{Equation 4}
\]

The concentration of \([\text{H}_2\text{O}]^+\) ions in the reaction medium (Fig. 1, Step 2) was believed to increase with elevating reaction temperature. This is due to the fact that ionisation constant of water (\(K_w\)) and temperature exhibit a direct relationship: the higher the temperature, the greater the \(K_w\) values (because the reaction in Equation 3 favours forward direction) [10,13,14].

Considering the aforesaid information, it seems very likely that the increasing-trend in mass loss (Table 1, Entries 1-4) occurs due to the intensified hydrolysis of glycosidic bonds. The intensification, a consequence of rising the temperature from 120 to 190 \(^\circ\)C, is driven by the aforementioned factors: the increased accessibility of glycosidic bonds as well as concentration of \([\text{H}_2\text{O}]^+\) ions. This in turn produces more cellulose particles having much lower DP values, and possibly oligomers that are soluble in water. These particles and oligomers might then pass through the filter paper during the separation step (Fig. 1).  

**Effect of Reaction Temperature on Targeted Products.** A plausible flow describing the production of targeted products, in particular lactic acid, from cellulose is shown in Fig. 3. In the case of \(\text{Pb}^{2+}\), the products were recorded only at 160 \(^\circ\)C and above (Table 1, Entries 1-4).

As proposed in Fig. 3, glucose is the intermediate precursor that leads to the production of platform chemicals, in particular lactic acid (Fig. 3, Step 3). In theory, hydrolysis of cellulose to glucose proceeds via two consecutive steps. The first is called ‘primary’ hydrolysis that produces cellulose particles having much shorter chains (lower DP values). These particles then undergo so-called ‘secondary’ hydrolysis yielding glucose [10].

From Table 1, it can be seen that the targeted products are undetected for 120 and 140 \(^\circ\)C (Table 1, Entries 1-2). The resultant liquid products, however, looked cloudy (Fig. 2 (a) and (b)), which strongly implies cellulose particles (having lower DP values) that escaped during the filtration step (Fig. 1). Based on this, it seems very likely that the applied conditions promoted the primary hydrolysis, but unable to produce water-soluble oligomers. As a result, the secondary hydrolysis to yield glucose did not occur, preventing subsequent conversions (Fig. 3, Step 2-4).

At 160 \(^\circ\)C, the detection of glucose, even at a relatively low yield, strongly indicates that the applied condition produced water-soluble oligomers, which later hydrolysed to glucose (Table 1, Entry 3). It should be borne in mind that the glucose yield of 0.12 wt% is not an absolute quantity. Some of glucose molecules were converted to lactic acid catalysed by \(\text{Pb}^{2+}\) (Fig. 3, Steps 2 and 3). At 190 \(^\circ\)C, yields of glucose and lactic acid were far higher than those produced at 160 \(^\circ\)C (Table 1, Entries 3 vs. 4). Such an observation was believed to reflect the enhanced production of soluble cellulose oligomers, eventually generating a higher glucose concentration under the applied condition. Besides converting to lactic acid in the presence of \(\text{Pb}^{2+}\) (Fig. 3, Steps 2 and 3), the applied condition also dehydrated glucose to 5-HMF (Fig. 3, Steps 2 and 4). This is evidenced by the colour of the liquid product that looked brownish (Fig. 2 (d)), a strong indicator of the presence of 5-HMF.

**Effect of Type of Catalyst on Targeted Products.** Table 1 also shows that, under similar reaction conditions, yield of lactic acid generated by \(\text{Al}^{3+}\) was much higher than that recorded when using \(\text{Pb}^{2+}\) (Table 1, Entries 3 vs. 5). A reason for this is straightforward: \(\text{Al}^{3+}\) is a stronger Lewis acid species than \(\text{Pb}^{2+}\). This appears to be in a good agreement with a previous study [7].
5. Conclusion

This study investigates the extent to which the reaction temperature and the type of metal ion catalyst influence the catalytic hydrothermal conversion of cellulose to lactic acid. To accomplish this, the conversion was studied under various temperatures (120 to 190 °C) and types of metal ion catalyst (Pb²⁺ and Al³⁺), while the reaction period remained fixed at 3 h. It was found that increasing the reaction temperature enhanced the mass loss significantly; an indicator of the hydrolysis of glycosidic bonds in cellulose by [H₃O]⁺ ions intensifying. Despite exhibiting an increasing-trend with raising reaction temperature, lactic acid (and other intermediate products) was only produced at 160 °C and above. Expectedly, changing the type of metal cation from Pb²⁺ to Al³⁺ further enhanced yields of the targeted products, especially lactic acid.

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