



Novel hybrid process for the conversion of microcrystalline cellulose to value-added chemicals: part 3: detailed reaction pathway

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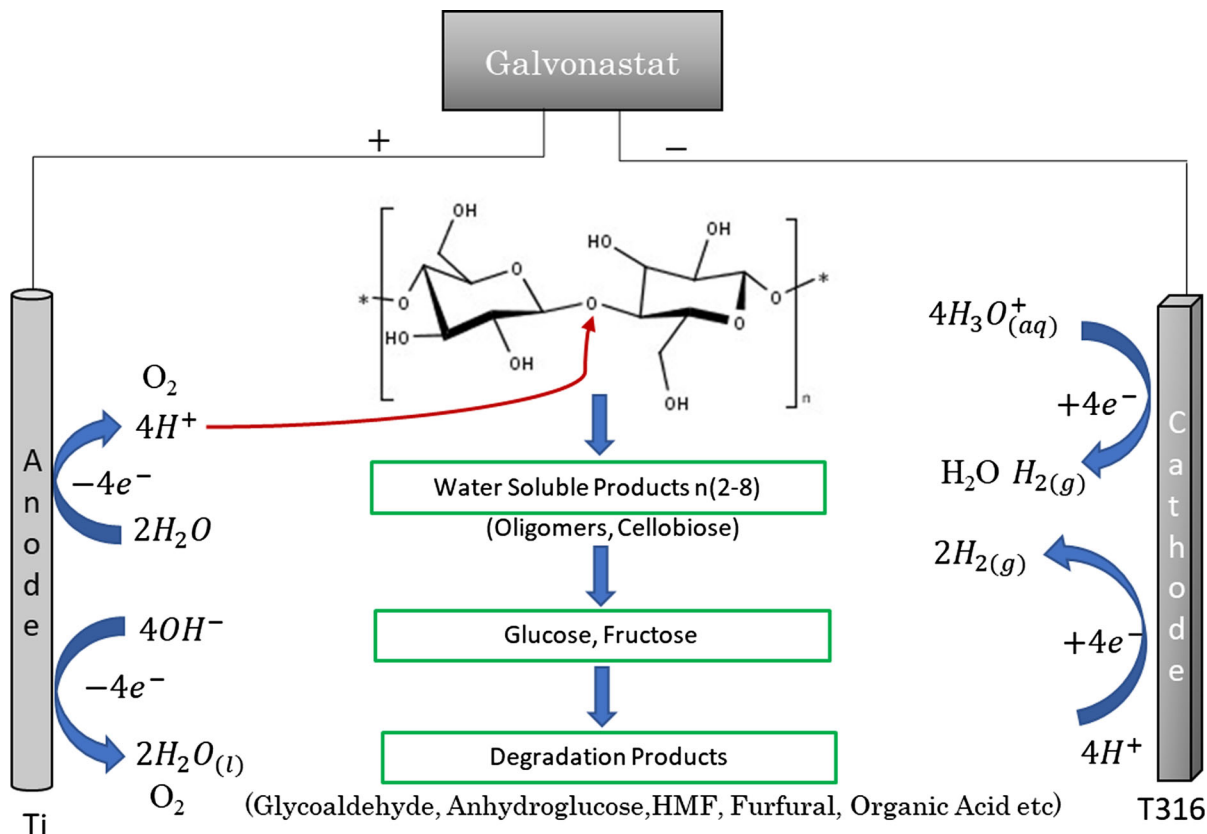
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Abstract In this study, a novel method of hydrothermal electrolysis of microcrystalline cellulose (MCC) under sub-critical water conditions (200 °C) was investigated by applying direct current at constant voltage with the presence of acid catalyst of 5 mM H₂SO₄. Direct current at constant voltage of 2.5 V, 4.0 V and 8.0 V was applied between cylindrical anode (titanium) and cathode (reactor wall). Hydrothermal electrolysis reactions were carried out in a batch reactor (450 mL-T316) for the reaction time of 240 min. Decomposition products of MCC were analyzed by GC–MS and the decomposition pathway of cellulose under applied voltage was postulated.

Levoglucosan and levoglucosenone formations were detected as the first hydrolysis products of MCC and further hydrolysis yielded to formation of glucose and fructose. The major decomposition products of cellulose were detected as levulinic acid (LA), 5-HMF and furfural. Further reactions of LA such as electrochemical decarboxylation, dehydration, hydrogenation, resulted in the formation of 2-butanone, 2-butanone-3-hydroxy, gamma-valerolactone, respectively. Most dramatic results on the product distribution were obtained at applied 2.5 V voltage in which LVA and 5-HMF were selectively produced.

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Graphical abstract



Keywords Cellulose · Electrochemical · Sub-critical water · 5-HMF · Levulinic acid · Levoglucosan

Introduction

Biomass utilization to value added chemicals such as fuel additives [levulinate ester, furan dicarboxylic acid (FDCA), gamma-valerolactone etc.] and value-added chemicals (levulinic acid, 5-HMF, furfural) has been investigated widely by both academia (Kilic and Yilmaz 2015; Sasaki et al. 1998, 2000) and industry (Avantium, GF Biochemicals). Different methods have been investigated and reported in literature; solid acid catalysts (Kilic and Yilmaz 2015), biocatalyst (Badgular and Bhanage 2016), ionic liquids (Amarasekara and Wiredu 2015). Sub- and supercritical water as reaction medium exhibited promising result in biomass decomposition and investigated widely by

Sasaki et al. (2000). Water demonstrated significant enhancement in biomass hydrolysis because of its versatile thermophysical properties such as lower dielectric constant ($\epsilon \approx 10$ near critical), high concentration of ionic products 10^{-11} (Marshall and Franck 1981).

In hydrothermal conditions, β -glycosidic bond of cellulose is protonated by ionic products of water as hydroxide OH^- and hydronium ion H_3O^+ which yields to decomposition products. Thus, critical state of water is an effective reaction medium for cellulose hydrolysis. Moreover, as the ionic product concentration increases, the amount of energy required for the migration of electroactive species in electrochemical methods decreases. Thus, current efficiency increases in electrochemical reactions at near critical conditions which makes the hydrothermal electrolysis more economically feasible to be applied for bulk production. Utilization of organic compounds to value added platform chemicals have been investigated by Sasaki and coworkers by using electrochemical methods in

sub-critical water conditions (Sasaki et al. 2007; Yuksel et al. 2011). As hybrid methods, we investigated hydrothermal electrolysis of microcrystalline cellulose (MCC) in sub-critical water conditions via application of constant current (Akin and Yuksel 2016) and constant voltage (Akin and Yuksel 2017). Electrolysis of sulfuric acid–water solution under hydrothermal conditions can alter the reaction medium by the formation of different radical species (SO_4^- , HSO_4^- , OH^-) and ionic products (SO_4^{2-} , H_3O^+ , OH^-) during electrolysis (Davis et al. 2014). The effect of the electrolysis products on decomposition of cellulose was investigated and reported in our previous study (Akin and Yuksel 2017). The research that investigates the effect of applied constant direct current and its relation with other effecting parameters (reaction time, acid concentration, and reaction temperature) revealed that coupled interactions (direct current with reaction temperature or acid concentration) had significant effect on cellulose hydrolysis (Akin and Yuksel 2016). However, selective formation towards platform chemicals was not observed under applied direct current. Moreover, research on constant voltage (Akin and Yuksel 2017) suggested degradation pathway of cellulose under hydrothermal electrolysis and investigated selectivity to main degradation products as levulinic acid, 5-HMF and furfural. We reported that application of 2.5 V of constant voltage resulted in enhanced selectivity toward levulinic acid and 5-HMF. The enhancement in product selectivity towards 5-HMF and LA was due to the fact that applied constant voltage resulted in the formation of functionalization of cellulose or humin particles with sulfur oxide (S=O) and sulfur ester (S–R) functional groups which in terns acts as catalyst Application of voltage in sulfuric acid solution functionalize cellulose particles via oxidation of primary alcohol group to aldehyde (C=O) and then reduction to sulfoxide group or further oxidation to carboxylic acid group. Detailed discussion was investigated via Fourier-transform infrared spectroscopy (FTIR) and reported in our previous study (Akin and Yuksel 2017). However, formation of intermediate products of cellulose decomposition (e.g. LVG, LGO etc.) and the possible electrochemical reactions (e.g. Kolbe reaction) of value-added chemicals under applied constant voltage have not been investigated so far.

The purpose of the study is to investigate the formation of intermediate products of cellulose decomposition under applied voltage by using GC–MS analysis. The study focused on the formation of hydrolysis products such as levoglucosan (LVG), levoglucosenone (LGO) as well as further reactions of levulinic acid (LA) as electrochemical decarboxylation and hydrogenation to 2-butanone, 2-butanone-3-hydroxy and lactones respectively. The objective of the study is to build a detailed decomposition pathway of MCC under applied voltage in sub-critical water condition.

Experimental

Microcrystalline cellulose (MCC, Sigma Aldrich, particle size < 20 μm) was used as model compound. Hydrothermal electrolysis of MCC were carried out in a batch reactor with a titanium made cylindrical anode and cathode (T316). The detailed of experimental set-up was given in our previous study (Akin and Yuksel 2016). Reactions were carried out in 5 mM H_2SO_4 solution at 200 °C with application of 0, 2.5, 4.0, and 8.0 V constant voltage for 240 min. Liquid samples were collected 30 min of interval after the desired reaction temperature was reached. Collected samples were filtered with 0.20 μm . Samples were analyzed immediately after collection without further treatment. Cellulose decomposition products were analyzed by GC–MS (Agilent 6890 N/5973 N Network). Stabilwax[®]-DA (Crossbond[®] Carbowax[®] polyethylene glycol, 30-m-long, 1 μm particle size with 0.32 mm inner diameter) column was used. GC–MS analysis was conducted in SCAN mode with the following method; initial oven temperature set as 40 °C and then, first heating (8 °C/min) to 140 °C kept for 5 min, second heating (10 °C/min) to 220 °C and kept for 10 min. Total run time of method is 37.50 min. GC–MS chromatograms were analyzed by using MSD ChemStation E.0202.1431 software and the area of specified chromatogram peaks were calculated accordingly. The effect of applied voltage on product concentration was discussed in comparison of the areas of the chromatogram peaks of products. Moreover, product distribution plots were given as the ratio of peak area of governing species at given reaction to its maximum area obtained throughout the hydrothermal electrolysis reactions (Eq. 1). Analyzed

chromatograms were identified by using National Institute of Standard (NIST) MS search and compounds are tabulated in Table 1.

Relative peak area

$$= \frac{\text{Peak area of species } i \text{ at specified reaction potential}}{\text{Maximum peak area of species } i \text{ among all reactions}} \quad (1)$$

Result and discussion

Decomposition pathway of cellulose

The reaction mechanism of cellulose hydrolysis reaction under sub-critical conditions has been studied extensively and reported (Sasaki et al. 1998). As a result of protonation of β -glycosidic bond of MCC, cellobiose, celotriose and cello-oligomers are produced and further hydrolysis yields to glucose and its isomer to fructose (Sasaki et al. 2007). The formation

Table 1 List of cellulose degradation compounds detected by GC–MS analysis

Compound name	Retention time	Characteristic ions
2-Butanone	4.323	43, 72, 29, 27, 57, 15, 28, 42, 44, 39
Furan, 2-methyl	10.813	82, 53, 81, 39, 27, 54, 51, 50, 28, 52
2-Butanone, 3-hydroxy-	12.217	45, 43, 88, 27, 29, 42, 55, 46, 44, 73
2-Propanone, 1-hydroxy-	12.561	43, 31, 74, 15, 29, 42, 45, 44, 27, 28
2-Cyclopenten-1-one	13.646	82, 39, 54, 53, 28, 27, 55, 26, 81, 51
Angelica lactone	14.8656	55, 98, 43, 27, 70, 39, 26, 42, 15, 99
Acetic acid	15.061	43, 4560, 15, 42, 29, 14, 28, 41, 18
Furfural	15.449	96, 95, 39, 38, 29, 37, 97, 40, 67, 42
Ethanone, 1-(2-furanyl)-	16.353	95, 110, 39, 43, 38, 15, 96, 67, 68, 40
Propanoic acid	16.68	74, 28, 45, 29, 73, 27, 57, 55, 26, 56
Formic acid	16.838	29, 46, 45, 28, 17, 44, 16, 12, 13, 30
2-Furancarboxaldehyde, 5-methyl	18.16	110, 109, 53, 27, 39, 51, 81, 43, 50, 111
2-Butanone, 4-hydroxy	19.917	43, 70, 31, 55, 61, 27, 15, 42, 45, 73
2-Furanmethanol	20.401	98, 41, 8197, 39, 53, 42, 69, 70, 27
Gamma valerolactone	21.442	55, 98, 43, 83, 27, 54, 26, 69, 39, 29
Hexanoic acid	21.599	60, 73, 41, 43, 87, 27, 61, 45, 55, 29
1,4-Pentandiol	22.573	45, 42, 71, 41, 43, 31, 27, 44, 56, 58
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	24.092	112, 69, 55, 41, 43, 83, 56, 84, 27, 39
Heptanoic acid	24.197	60, 73, 43, 41, 87, 55, 29, 27, 71, 70
2-Pentenoic acid	24.232	55, 29, 27, 39, 100, 45, 41, 54, 56, 43
2-Butenoic acid, 2-methyl	24.719	100, 55, 29, 85, 27, 39, 54, 82, 53, 41
5-Hexyl-2-furaldehyde	24.834	109, 81, 110, 53, 180, 123, 95, 97, 96, 52
2-5Furandicarboxaldehyde	26.354	124, 123, 95, 67, 125, 53, 50, 42, 51, 96
Levogluosenone	26.519	98, 96, 39, 53, 68, 97, 42, 41, 70, 29
Formic acid, 2-propenyl ester	28.129	57, 39, 41, 29, 58, 31, 40, 27, 30, 28
Propanoic acid, anhydride	29.052	57, 29, 27, 28, 26, 58, 56, 43, 74, 45
5-Acetoxyethyl-2-furaldehyde	29.127	126, 43, 79, 109, 53, 97, 127, 81, 52, 125
Isopropyl palmitate	29.183	43, 102, 60, 57, 256, 41, 61, 55, 71, 73
Levulinic acid	31.096	43, 56, 45, 55, 73, 29, 27, 15, 28, 42
Levogluosan	31.413	69, 29, 57, 41, 70, 98, 31, 43, 85, 86
5-HMF	33.122	97, 126, 41, 39, 69, 29, 53, 125, 109, 51

of glucose and fructose under applied voltage has been studied in our previous study and discussed in detail (Akin and Yuksel 2017) Based on the detected decomposition products via GC/MS analysis (Table 1), cellulose decomposition pathway under hydrothermal electrolysis was postulated (Fig. 1).

The hydroxyl groups located at the end of cellulose chain (C-1 and C-4) are reactive for decomposition

reactions due to the reducing and non-reducing properties (Klemm et al. 2004). Levoglucosan (LVG) can form either ionic based and radical based mechanisms (Zhang et al. 2013). Further hydrogenation and dehydration of LVG forms levoglucosanone (LGO). The effect of applied voltage on formation of LVG and LGO is given in Fig. 2a, b, respectively. LVG was formed under hydrothermal conditions

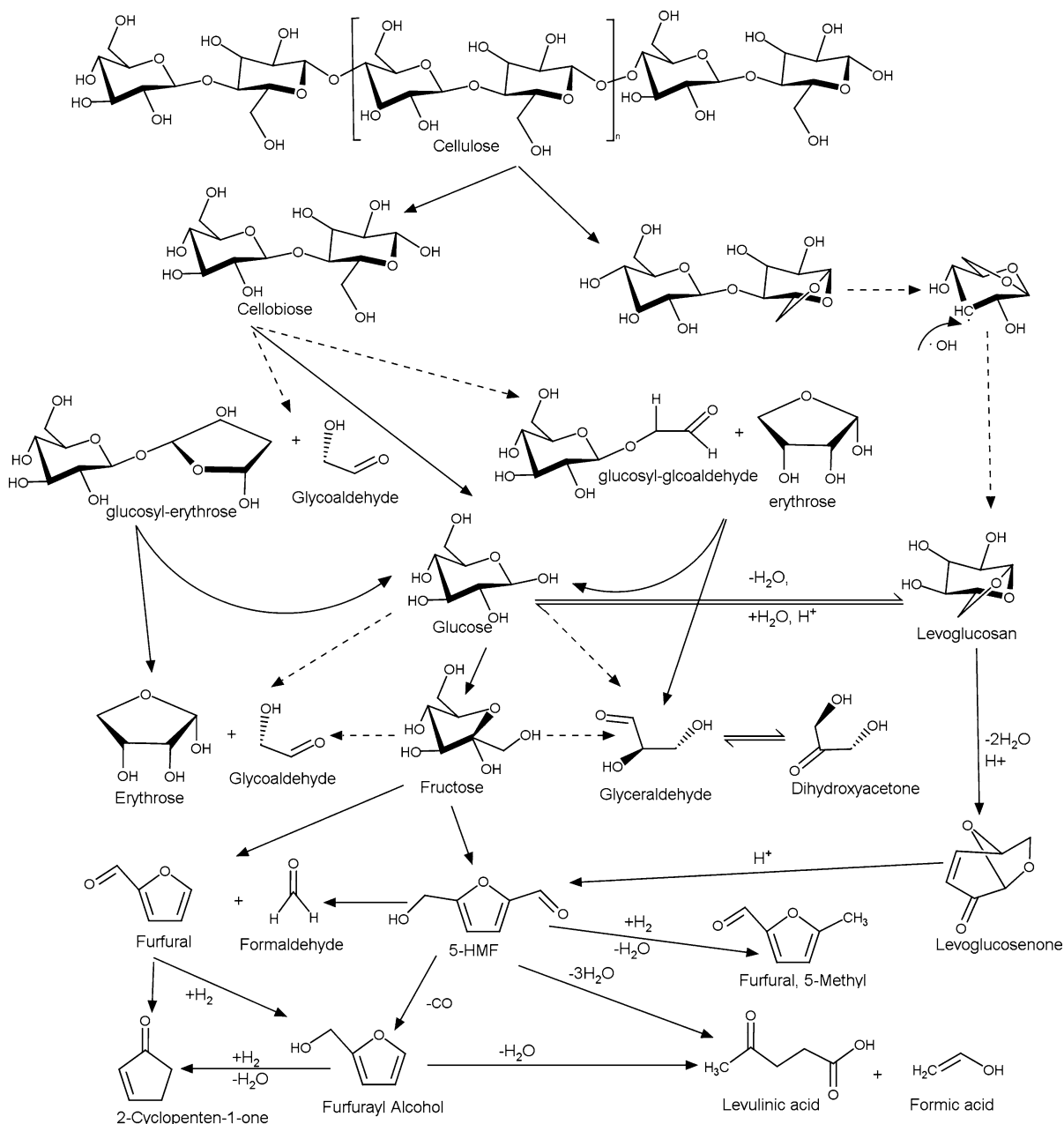
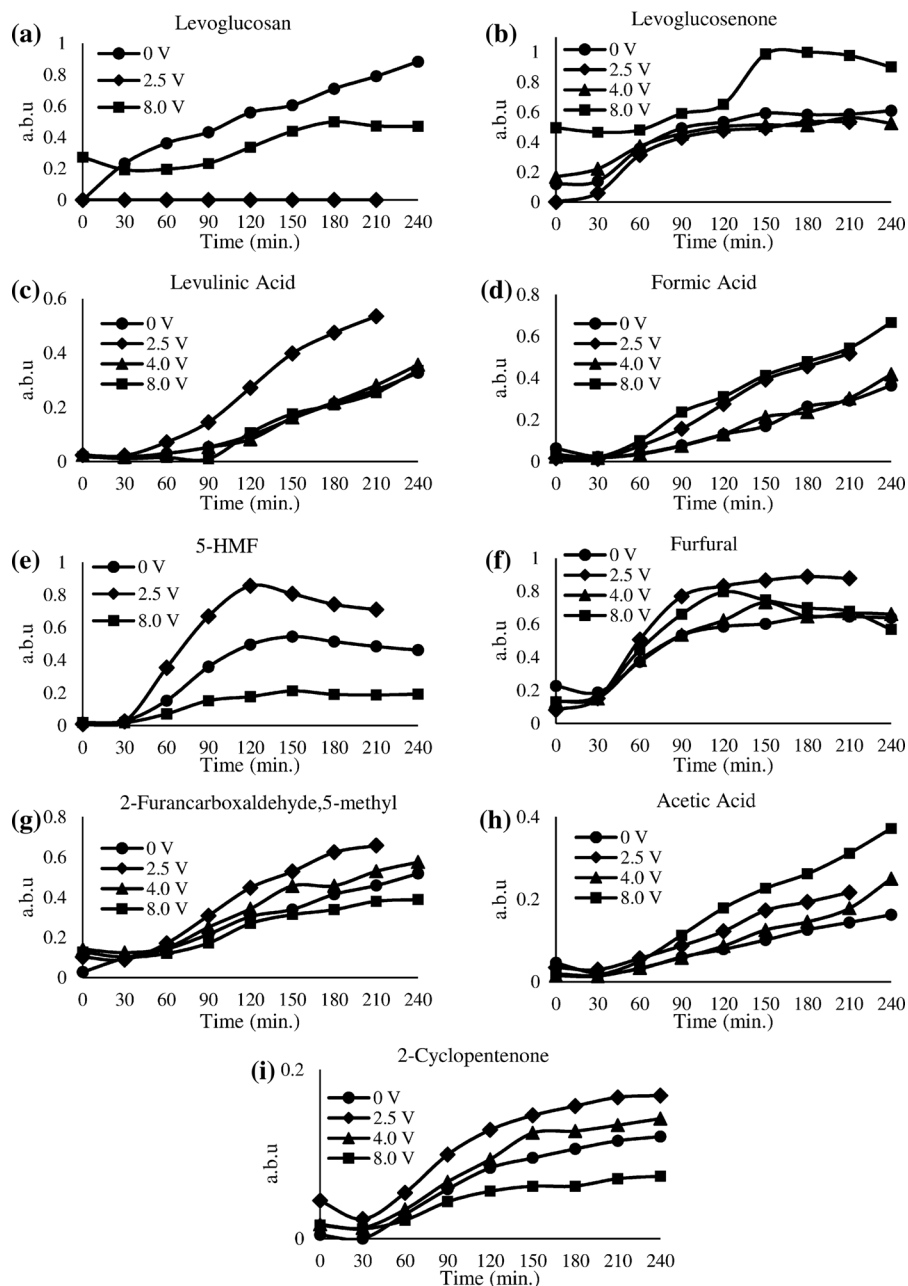


Fig. 1 Postulated decomposition pathway of cellulose under hydrothermal electrolysis

Fig. 2 GC–MS results of main decomposition products of cellulose under applied voltage



(0 V) with an increasing concentration. LVG was not detected when 2.5 V was applied. This could be due to further reactions of LVG such as isomerization to glucose and dehydration to LGO (Fig. 2b). Moreover, when 8.0 V of potential difference was applied, higher concentration of LGO obtained throughout the reaction time. In order to understand the effect of application of direct current at constant voltage on

product distribution further reaction of LVG and LGO should be considered simultaneously. Under acidic conditions, 5-HMF is produced from both fructose via dehydration reaction and isomerization reaction of LGO (Krishna et al. 2017). Most dramatic results were obtained at applied voltage of 2.5 V. At 2.5 V value, LA (Fig. 2c) and 5-HMF (Fig. 2e) was produced in higher concentration. The selectivity values of LA and

5-HMF were reported in our previous study as 20% and 30% respectively (Akin and Yuksel 2016). Applied 8.0 V resulted in lower concentration of 5-HMF and LA. However, formic acid concentration was similar to that of 2.5 V. As, formic acid is formed along with the LA, it is an evident that LA selectively goes further reactions at applied 8.0 V. Moreover, total organic carbon (TOC) yields were reported as 60% (8.0 V) and 50% (2.5 V) (Akin and Yuksel 2017), indicating that decline in LA concentrate is due to further reactions involved. For instance, oxidation of LA yields to acetic acid and applied 8.0 V was dramatically changed its concentration (Fig. 2h) throughout the reaction. Further reactions of LA under

applied voltage are discussed in following sections. 5-HFM involves series of reactions; decarbonation to furfuryl alcohol (Li et al. 2016), hydrogenation to furfural, 5-methyl and rehydration to LA. Furfural 5-methyl (Fig. 2g) and 2-cyclohexanone (Fig. 2i) were also detected compounds in cellulose decomposition. Application of 2.5 V resulted in higher concentration and applied 8.0 V resulted in lowest concentration in comparison to that of 4.0 V of potential difference and voltage free reactions.

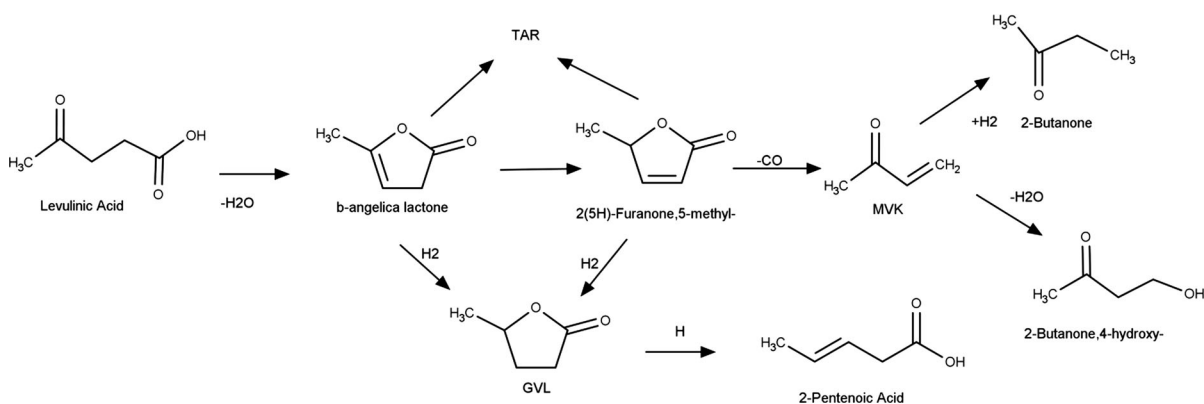


Fig. 3 Reaction pathway of LA dehydration reaction under hydrothermal conditions

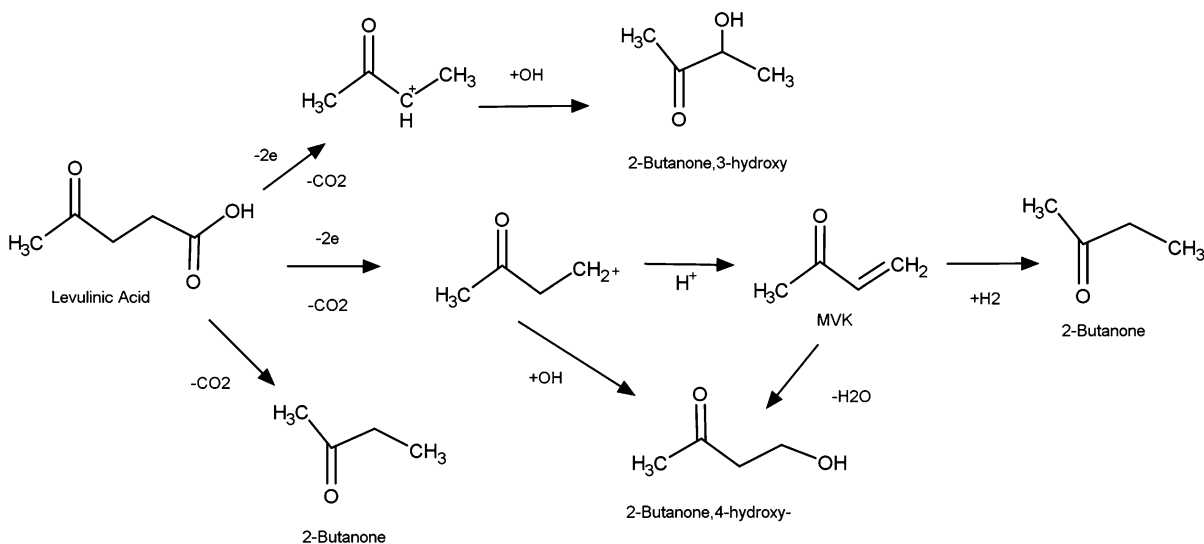


Fig. 4 Decarboxylation reaction of LA via electrochemical pathway

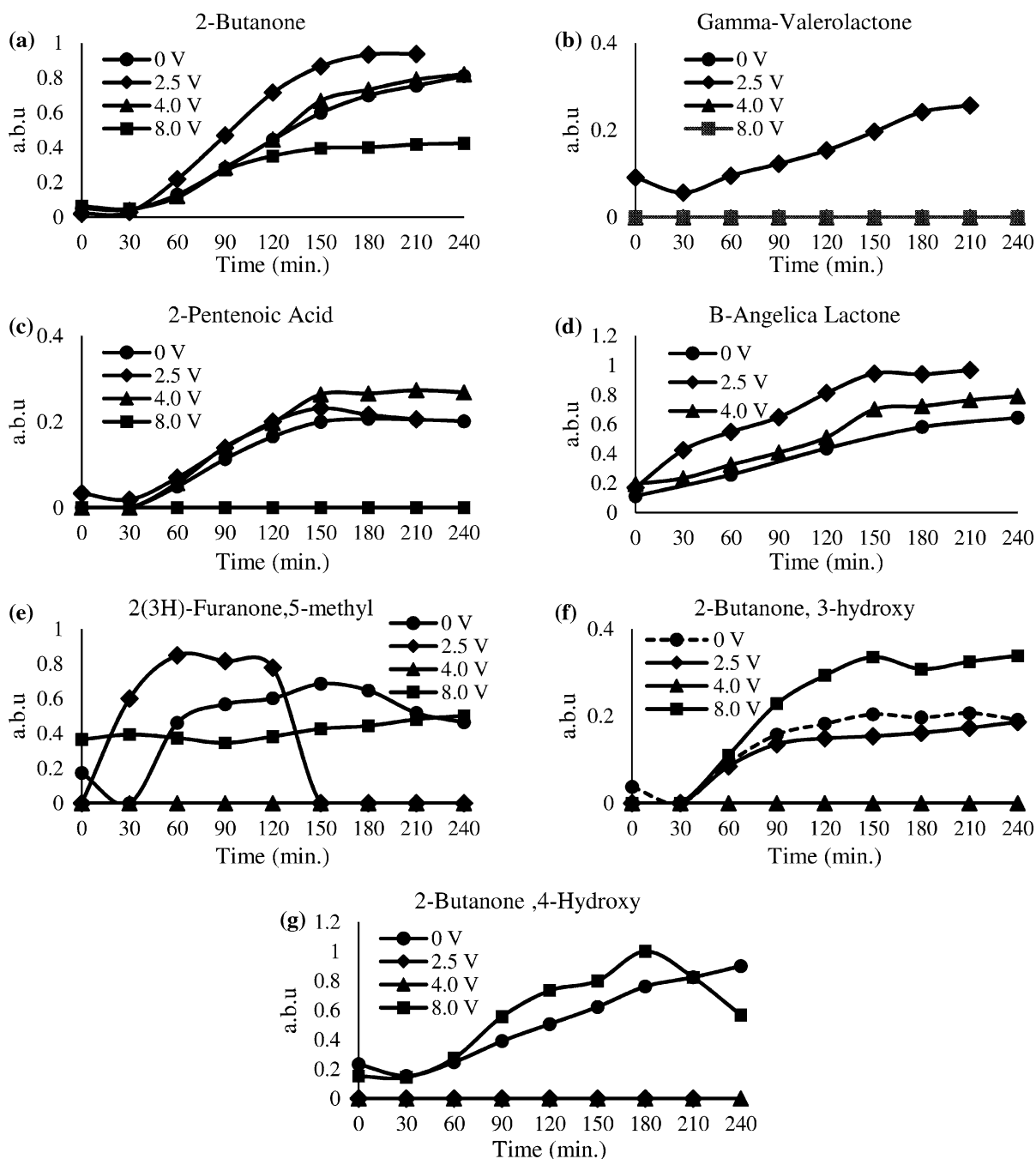


Fig. 5 Hydrolysis and decarboxylation products of levulinic acid under hydrothermal electrolysis conditions

LA decarboxylation and dehydration reactions

LA involves further reactions such as dehydration and decarboxylation under hydrothermal conditions (Fig. 3). Dehydration of LA yields to formation of lactones such as β -angelica lactone and α -angelica

lactone. As the lactones are unstable in hydrothermal conditions, they are polymerized to tarry material. Moreover, hydrogenation of lactones results in the formation of gamma-valerolactone (GVL) and further protonation of GVL yields to 2-pentenoic acid.

Methylvinylketone (MVK), 2-butanone are also formed by hydrogenation and dehydration reactions, respectively. Electrochemical decarboxylation of LA to 2-butanone was reported by Nilges et al. (2012). Kolbe reaction of LA resulted in the decarboxylation via electrochemical reaction pathway and yields to formation of 2-butanone (Fig. 4). dos Santos et al. (2015) reported electrochemical reduction and oxidation of levulinic acid to n-octane and 1-butanol. They also found that two-electron decarboxylation yield methyl vinyl ketone that can yield 2-butanone via hydrogenation reaction. However, under hydrothermal conditions LA can form 2-butanone via direct decarboxylation reaction.

Figure 5 indicates the formation of products of LA as a result of dehydration and decarboxylation under hydrothermal electrolysis conditions. GVL (Fig. 5b) was selectively produced by the application of 2.5 V of constant voltage into reaction medium. There was no formation of GVL under hydrothermal and applied voltage values of 4.0 and 8.0. However, degradation product of GVL which is 2-pentanoic acid was formed by applied voltage at 4.0 and 8.0 V. Application of 8.0 V resulted in higher LVG and LVO concentration while the 5-HMF and LA acid yielded lower values. It was found that applied 8.0 V resulted in further electrochemical decarboxylation reactions that formed 2-Butanone, 3-hydroxy (Fig. 5f) and 2-Butanone, 4-hydroxy (Fig. 5g). Moreover, potential difference of 2.5 V was resulted in the formation of 2-pentonic acid. However, GVL was also formed and its degradation to 2-pentonic acid was hindered by applied voltage at 2.5 V. Increase in the product concentration was mainly due to the high total organic carbon values (Akin and Yuksel 2017). Therefore, enhancement in the reaction pathway cannot be conducted clearly, however, formation of GVL at 2.5 V of applied constant voltage supports the idea of enhancement in reaction pathway selectively to the production of both GVL and LA.

Conclusion

In this study, decomposition product of MCC under applied constant voltage of 2.5–8.0 V in subcritical water conditions were investigated by using GC–MS analysis. Decomposition product formations were analyzed in the presence and absence of electrolyte

solution (5 mM H₂SO₄). Reaction pathway of cellulose decomposition under sub-critical water conditions by applying constant voltage was postulated by investigating intermediate and further decomposition products. In our previous study we reported that application of constant voltage (2.5 V) altered the reaction mechanism selectively to 5-HMF (30%) and levulinic acid (20%). The change in the selectivity was found as the catalytic effect of formation of functionalized (sulfoxide and sulfur ester) hummin particles. However, at different voltage values (4.0 V and 8.0 V) the decrease in the selectivity have not been answered yet. In this study, further decomposition of products was revealed by GC–MS analysis. As the end groups of cellulose is most reactive group, decomposition products as levoglucosone (LVG) and levoglucosanone (LVO) were found to be the starting point of degradation pathway along with the hydrolysis products of cellulose as glucose. Application of 2.5 V had significant effect on concentration of LVG and LVO in which there was no formation due to the further reactions that yielded to levulinic acid (LA) and 5-HMF. Most dramatic results were obtained at 2.5 V of applied voltage in which degradation pathway selectively altered towards LA and 5-HMF. Electrochemical oxidation of LA was reported and found that LA involves one-electron decarboxylation to carbonyl radical that ends up in polymerization to octane and two-electron decarboxylation to carbonyl ion which yields to formation of MVK. Possible reaction of MVK are hydrogenation to 2-butanone and dehydration to 2-butanone, 4-hydroxy. The decrease in LA concentration at 8.0 V of applied potential was due to the further reactions in which LA was involved.

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