MAKALAH ILMIAH

AN EXPERIMENTAL STUDY ON THERMAL CATALYTIC DECOMPOSITION OF INULIN TO 5-HYDROXYMETHYLFURFURAL AND LEVULINIC ACID AND EFFECT OF C6 ON FURFURAL DURING DECOMPOSITION PROCESS

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An experimental study on thermal catalytic decomposition of inulin to 5 hydroxymethylfurfural and levulinic acid and the effect of C6 on furfural during the decomposition process

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Abstract. The attractive biobased platform chemicals, 5-Hydroxymethylfurfural (HMF) and Levulinic Acid (LA), are commonly produced by the conversion of monomeric sugars. Nevertheless, a polymeric sugar such as inulin shows promising. This work reports the study on the thermal catalytic decomposition of inulin to HMF and LA. This work also investigated the effect of furfural during the process. The decomposition reactions were conducted in a batch reactor in a temperature (153-187)ºC, an inulin loading (0.03- 0.12) g mL^{-1} and reaction times (18 -74 minutes) using a central composite experimental design. Furthermore, to study the effect of fructose and glucose on furfural, some additional experiments were also performed in the batch system. The decomposition process gained 35 wt% yield of HMF and 13 wt % yield of LA. The HMF and the LA model were statistically formulated and showed a good fit to the experimental data. The fructose particularly plays a role in furfural disappearance during the process.

1. Introduction

5-hydroxymethylfurfural (HMF) and levulinic acid (LA), two of biobased chemical products [1], have been associated to the top 12 biobased chemicals from biomass by the US Department of Energy (DOE) [2], [3], [4]. The HMF is generally synthesized from hexoses by the exclusion of three water molecules in the presence of brönsted acids such as hydrochloric acid and sulfuric acid [5],[6]. The decomposition of both monomeric and polymeric sugar to HMF and levulinic acid in the aqueous medium is typically one spot reaction scheme. This scheme leads to low yield and selectivity due to the formation of insoluble polymers and consecutive reactions. To increase the yield, nowadays, some methods using heterogeneous catalyst and organic solvents are proposed and reported in the literature. Nonetheless, related to catalyst lifetime, catalyst deactivation and down-stream processing, using water gives more benefits than a heterogeneous system and organic solvents [7], [8], [9] [10], [11].
Due to the reactivity, It is stated that d-fructose is preferred and selective feedstock to produce HMF than d-glucose [12]. Thus, the biomass polymers enriched in d-fructose units could be an alternative feed. A promising biomass polymer is an inulin which is an oligosaccharide containing fructose-fructose unit or fructose-glucose unit. The advantages of using inulin are abundant and reactive [6], [13]. Inulin can be easily found in plants, such as Jerusalem artichoke, chicory, and dahlia tubers [14].
This work mainly reports a study on the decomposition of inulin to HMF using water as the solvent in the thermal catalytic process in the absence of a catalyst. Water was chosen as the selected solvent, as it is environmentally friendly, a good solvent for many carbohydrates and it is cheap, nontoxic, and nonflammable [15], [16]. This work is also to report the effect of C6 on furfural during the inulin decomposition.

2. Methods

2.1 Decomposition Process

Inulin from Dahlia tubers was purchased from Acros Organic (Geel, Belgium). Amount of inulin was fed into ampoules (5 mm in ID, 15 cm in length and 1.5 mm in thickness) filled with 4 mL of deionized water. The ampoules were sealed with a torch and placed in a rack in a heating oven (Heraeus Instruments Type UT 6060) at a constant temperature. At different reaction times, an ampoule was taken from the oven and quickly quenched in cold water to stop the reaction. All experiments were conducted in triplicate and the average value is taken. After the reaction, the ampoules were opened and the reaction mixture was taken out and centrifuged for about 10–30 min to remove the solids. The liquid product was diluted with demi water before analysis. A liquid sample was taken and analyzed by HPLC.

2.2 Analysis

HPLC was used to identify and quantify the liquid product from the reactions. The HPLC system consisted of a Hewlett Packard 1050 pump, a Bio-Rad organic acid column Aminex HPX-87H and a Water 410 differential refractive index detector. A sulfuric acid solution (5 mM) was used as the eluent with a constant flow rate of about 0.55 cm3 min-1. The column was operated at 60°C. The HPLC was calibrated with solutions of the pure compounds at a range of concentrations. Using the chromatogram peak area and the external calibration curves, the concentrations of components in the liquid phase were determined.

2.3 Definitions

The yield of HMF and levulinic acid are defined according to equation (1) and (2). Both are reported on a weight basis.

$$y_{HMF} = \frac{C_{HMF} \times M_{HMF} \times V}{W_{in}} \times 100\% \ (wt\%) \tag{1}$$

$$y_{LA} = \frac{C_{LA} \times M_{LA} \times V}{W_{in}} \times 100\% \ (wt\%) \tag{2}$$

Here, C refers to concentration (mol L^{-1}) at a certain time, M is the molecular weight (g mol^{-1}), V refers to reaction volume (L) and W refers to the intake of inulin (g).

3. Results and Discussion

Exploratory experiments on the thermal catalytic conversion of inulin were performed in a range of (153-180°C), using an inulin loading in a range of (0.03- 0.12 g mL^{-1}) and reaction times in a range of (18 -74 minutes). The 24 batch experiments were conducted using a composite design. The data were statistically analyzed and a model was developed to describe the HMF yield versus process conditions like reaction time, inulin intake and reaction temperature.
In this one-spot reactions, since inulin is converted to fructose (94 mol%) and glucose (6 mol%), some compounds are simultaneously produced. HMF, LA, formic acid, acetic acid, and humins were clearly detected during the process. Finally, the possible effects of C6 such as fructose and glucose on furfural during the process were observed.

3.1 Decomposition of Inulin to HMF and LA

During the experiments on the thermal conversion of inulin, some soluble components were detected in the reaction mixtures (HPLC). Three of them, d-fructose, d-glucose and HMF are intermediates in the reaction sequence. The end products are LA, formic acid (FA) and acetic acid (AA). Some brown-black insoluble called humins were identified, which are always formed during the acid catalyzed conversions of carbohydrates in water, either in the monomeric or polymeric form. The typical concentration profile is given in Figure 1 and was performed at 170°C and inulin loading of 0.1 g/mL.

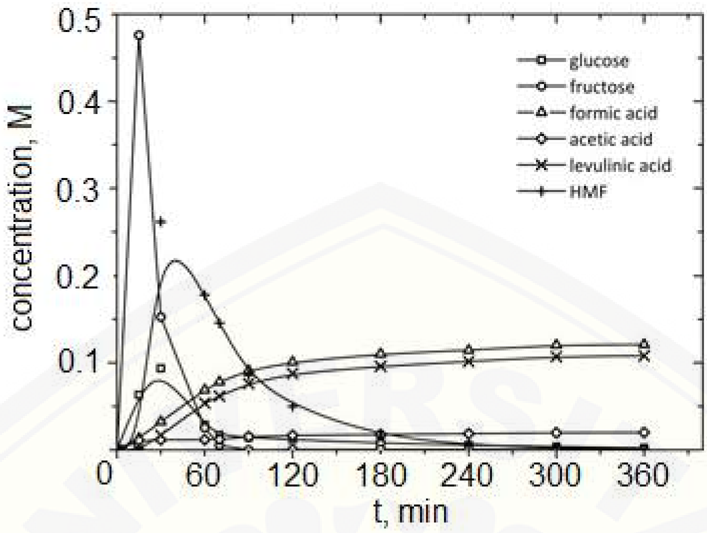

Figure 1. Concentration profile for various compounds during the thermal decomposition of Inulin to HMF

3.2 Effect of Process Condition

To investigate the effect of process variables on HMF, 40 experiments were performed in a batch reactor. Three independent variables which are temperature (150-190°C), inulin intake (0.03-0.12 g /mL) and reaction time (4-74 min) were explored. The yield of HMF was taken as the dependent variable. The results are provided in Table 1.

The highest experimental y_{HMF} is about 35 wt % (entry 6 in Table 1) and was achieved at 180 °C, an inulin intake of 0.05 g/mL and a reaction time of 18 min. At different conditions, the highest y_{LA} is about 13.4 wt % (entry 9 in Table 1) and was achieved at 187 °C, an inulin intake of 0.08 g/mL and a reaction time of 39 min.

The HMF yield as a function of temperature, reaction time and inulin loading was statistically formulated using the Design-Expert 10 software package. The appropriate model equation is given in equation (3). The model accommodates both quadratic and interaction terms. It implies process variables affect the HMF yield. The R-squared of the model is 0.9664. An indication of the good fit between the model and experimental data is given in Figure 2.

Table 1. HMF yield on various reaction conditions

Run	C_{in}, g/mL	$T_{reaction}$, °C	t, min	y_{HMF}, wt %	y_{LA}, wt %
1	0.08	170	39	22.8	4.0
2	0.05	160	18	2.7	0.0
3	0.08	170	39	23.1	3.1
4	0.08	170	39	23.9	3.2
5	0.05	180	18	32.1	5.6
6	0.05	180	18	35.0	6.1
7	0.12	170	39	17.6	6.1
8	0.08	170	39	23.1	3.3
9	0.08	187	39	14.6	13.4
10	0.08	170	39	22.5	1.1

Run	$C_{in,}$ g/mL	$T_{reaction}$, °C	t, min	y_{HMF}, wt %	y_{LA}, wt %
11	0.08	170	39	21.8	1.5
12	0.08	170	39	19.4	1.8
13	0.08	170	39	16,6	2.2
14	0.08	170	74	8.9	1.9
15	0.1	180	18	20.9	5.5
16	0.03	170	39	24.8	3.6
17	0.05	160	60	25.7	3.1
18	0.1	160	60	23.3	3.6
19	0.1	160	18	3.2	0.0
20	0.05	180	60	10.1	9.4
21	0.05	180	60	10.4	9.0
22	0.1	180	60	3.1	9.5
23	0.1	180	60	2.2	9.8
24	0.08	153	39	12.4	0.3

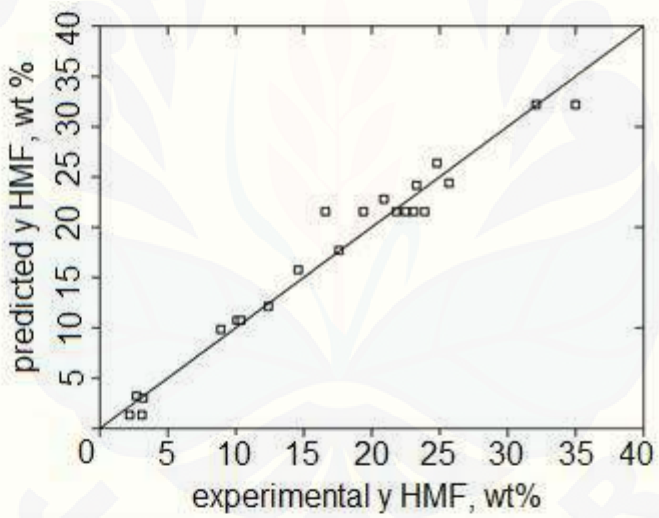

Figure 2. Parity plot between the experimental and modeled HMF yields

$$y_{HMF} = (1466.7)C_{in} + (11.8)T + (9.3)t - (9.2)C_{in}T - (0.05)tT - (0.03)T^2 - (0.009)t^2 - 1223.9 \quad (3)$$

The model predictions at a batch time of 30 min (Figure 3, left), implies that the HMF yield is a function of both the temperature and inulin intakes. Highest yields are obtained at the highest temperature in the range and the lowest inulin intake. The exact temperature dependency of the HMF yield is a function of the inulin intake. At low inulin intakes, the y_{HMF} increases with the temperature, up to a maximum of 35 wt % at 186 °C. At high intakes, a maximum of the y_{HMF} is observed at intermediate temperatures. The reduction of the y_{HMF} at the higher temperatures is likely due to the subsequent reaction of HMF to LA and FA (Scheme 1), leading to a lowering in the y_{HMF}. As expected, this subsequent reaction is occurring to a larger extent at 40 min batch times (Figure 3, right) and the y_{HMF} are considerably lower than for 30 batch times.

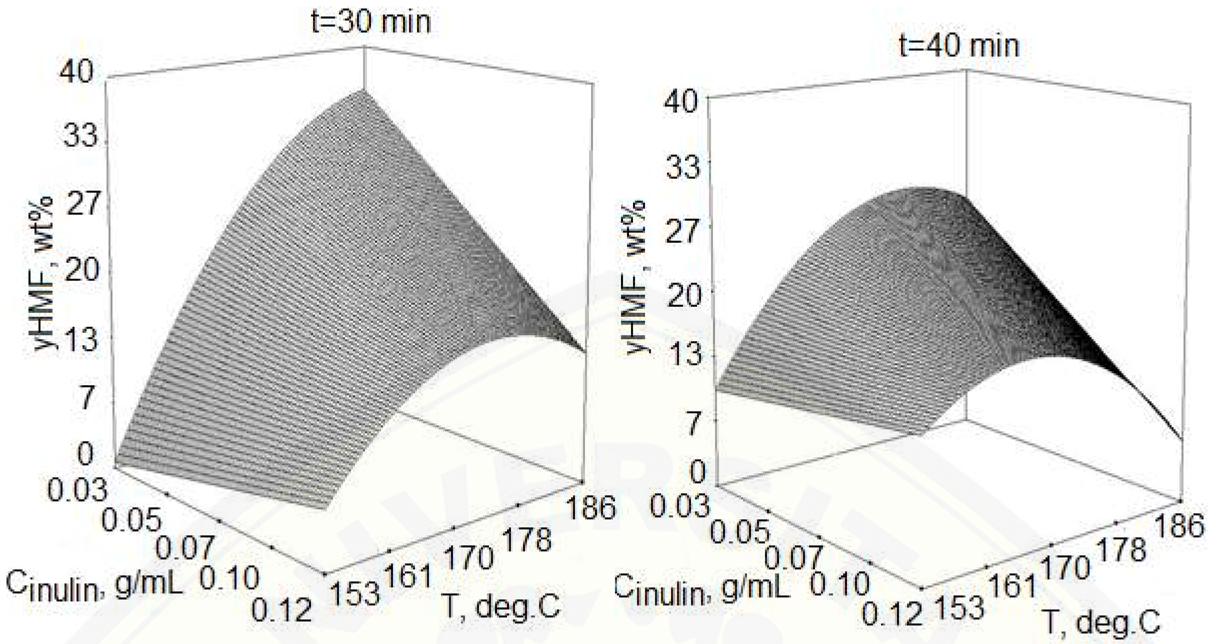

Figure 3. Modeled HMF yield versus temperature and inulin intake at two batch times.

The occurrence and importance of the consecutive reaction are also confirmed by considering the yLA versus the process conditions (Table 1). The y_{LA} was also statistically modeled and is given in equation 4 and Figure 4. The model equation has an R square of 0.9464.

$$y_{LA} = 437.51 - (188.89)C_{in} - (5.41)T + (0.09)t - (0.12)C_{in}T + (0.17)C_{in}t + (5.88.10\text{-}4)Tt + (1422.29)C_{in}^2 + 0.02)T^2 - (1.69.10\text{-}3)t^2 \quad (4)$$

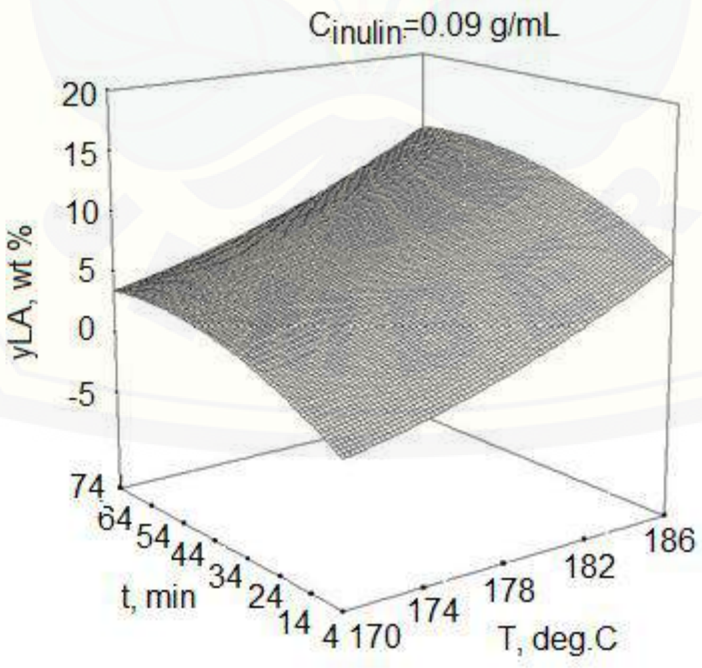

Figure 4. Modeled LA yield versus temperature and reaction time at selected inulin loading

3.3 Effect of C6 on Furfural

Some research has reported furfural as one of the decomposition product of carbohydrate [14], [17], [18], [19]. Conversely, herein this work, furfural is unidentified in the reaction condition window. To check the possible reason, some additional experiments were performed involving fructose, glucose and formic acid. The fructose-furfural and the glucose-furfural interaction were checked as the molecule structure of inulin containing both fructose and glucose. The interaction formic acid-furfural were also checked as the formic acid is able to present the autocatalytic process [20]. All interaction was described in Figure 5. As a result, the interaction between fructose- furfural shows a tremendous effect on the furfural disappearance compared to glucose-furfural and formic acid-furfural (Figure 5 left). To gain insight into the effect of fructose to furfural, the various fructose concentration (0.1-0.4) M was applied in this study. As fructose concentration increases, the furfural concentration dramatically decreases (Figure 5 right). This indicates that the reactivity of fructose may be playing a role in furfural disappearance.

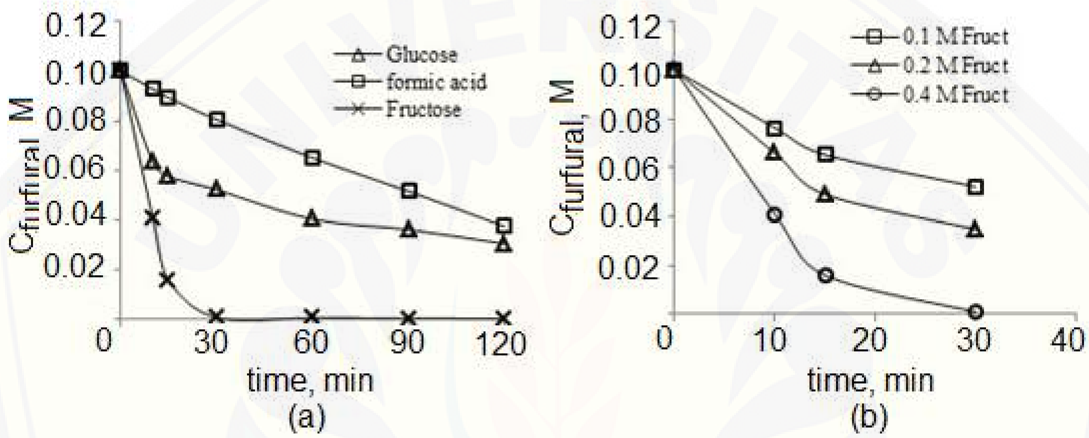

Figure 5. The relationship between furfural and reaction time in the presence of glucose, fructose and formic acid (a) and the relationship between furfural and reaction time on the different fructose concentration (b)

4. Conclusion

This work concludes that the thermal catalytic decomposition of inulin to HMF in water was studied in a wide range of reaction conditions, including variations in temperature, inulin loading and reaction time. The highest HMF yield was 35 wt % (180 °C, inulin intake of 0.05 g mL^{-1} and a reaction time of 18 min). The experimental data were modeled using a statistical approach. The model shows a good fit with the experimental data and allows estimation of the HMF yield as a function of temperature, inulin intake and reaction time.

The C6 such as fructose formed in the reaction strongly indicates playing a role in furfural disappearance during the inulin decomposition.

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