Characteristics of Liquid Products Derived from Lignocellulosic Biomass via CO_2-Assisted Hydrothermal Treatment

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ABSTRACT

Empty Fruit Bunches (EFBs) are an underutilized lignocellulosic residue with high cellulose content and potential as a feedstock for bio-based platform chemicals. However, the influence of a CO_2 atmosphere on HMF formation and degradation from EFB under hydrothermal conditions remains insufficiently clarified. In this study, the potential for HMF production from EFB through hydrothermal reaction under CO_2 conditions was evaluated, and the effects of reaction temperature and time on HMF formation were investigated. Hydrothermal reactions were conducted at 180-300 °C for 1 h. To evaluate the effect of reaction time, additional experiments were performed at 200-240 °C with reaction times ranging from 1 to 24 h. The results showed that the highest HMF production was obtained at 240 °C, with an optimal reaction time of 2 h. However, HMF production under CO_2 conditions was lower than that under N_2 conditions. This was attributed to the mildly acidic environment formed by CO_2, which may have promoted the further degradation of HMF into by-products such as organic acids and humins. These findings indicate that HMF production from EFB requires careful control of reaction se verity and gas atmosphere, and that CO_2 -assisted acidity does not necessarily enhance HMF accumulation under the investigated conditions.

Keywords: HMF/ Hydrothermal reaction/ Lignocellulosic biomass/ CO_2

1. INTRODUCTION

Among various biomass resources, Empty Fruit Bunches (EFBs) are major by-products generated in large quantities during palm oil production. Due to their limited utilization, a substantial amount of EFBs is often left untreated, which can cause environmental problems such as methane emissions and odor[1, 2]. Cellulose contained in EFB can be converted into 5-hydroxymethylfurfural (HMF), a high-value platform chemical, through hydrolysis and dehydration reactions[3]. HMF is an important platform compound for the production of various bio-based chemicals and can be used as a precursor for 2,5-furandicarboxylic acid (FDCA), a bio-based monomer for bioplastic production. FDCA has attracted considerable attention as a potential alternative to petroleum-derived terephthalic acid (TPA)[4]. In addition, the application of CO_2 in hydrothermal reactions can create a mildly acidic reaction environment, which may affect the hydrolysis of cellulose and subsequent dehydration reactions[5]. However, HMF formation and degradation from actual EFB under CO_2 -assisted hydrothermal conditions, particularly across reaction temperature and residence time and in direct comparison with N_2, remain insufficiently understood. The novelty of this study is the systematic evaluation of temperature, residence time, and gas atmosphere for EFB-derived HMF formation. Therefore, this study aimed to evaluate the feasibility of HMF production from EFB through hydrothermal reaction under CO_2 conditions and to investigate the effects of reaction temperature and time on HMF formation and yield.

2. METHODOLOGY

2.1 Materials

EFBs collected from Indonesia were used as the biomass feedstock for hydrothermal reaction. Their basic characteristics are presented in Table 1.

Table 1. Basic characteristics of EFBs used in this study

Sample	Ultimate Analysis (wt.%)				Proximate Analysis (wt.%)			Calorific Value (MJ/kg)	Moisuture Content (%MC)
EFBs	Carbon	Hydrogen	Oxygen	Nitrogen	Fixed carbon	Volatile matter	Ash		
	42.89	5.24	45.65	1.00	10.26	86.31	3.41	13.77	4.90

2.2 Methods

Hydrothermal reactions were conducted under CO_2 conditions to investigate the effects of reaction temperature and residence time on HMF conversion yield, while N_2 conditions were used as a comparison. Additional experiments with extended reaction times(1-24h) were conducted at 200-240°C. The resulting liquid products were analyzed using HPLC. The experimental conditions are summarized in Table 2.

Table 2. Experimental conditions

Parameter	Condition
Temperature	180-300°C
Reaction time	1 h
Extended reaction time	1-24 h(200-240°C)
Feedstock to solvent ratio	1:20(w/w)
Purging gas	CO_2 / N_2

3. RESULTS AND DISCUSSION

3.1 Biomass Composition of EFB

The analysis of the major components of EFBs showed that cellulose accounted for the highest proportion at 46.22%, indicating its high potential as a feedstock for HMF production. The hemicellulose and lignin contents were 21.81% and 19.55%, respectively, confirming that EFBs are a typical lignocellulosic biomass rich in cellulose.

3.2 Effect of Reaction Temperature on HMF Conversion

The HMF concentration increased with temperature and reached a maximum at 240 °C, but decreased sharply at higher temperatures and became nearly undetectable at 300 °C. This behavior is consistent with previous studies showing that CO_2 -derived carbonic acid can enhance cellulose conversion [5], whereas excessive reaction severity promotes HMF degradation [6]. Thus, 240 °C was identified as a favorable temperature for HMF formation. (Figure 1)

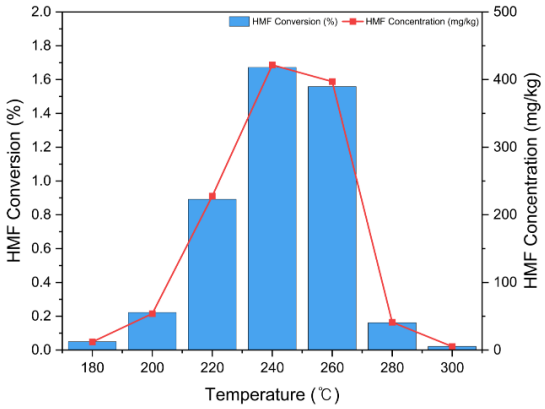

Figure 1. HMF concentration analysis results

3.3 Effect of Reaction Time on HMF Convesion

The effect of reaction time on HMF conversion at 240 °C was investigated under CO_2 and N_2 conditions. Under both gas atmospheres, HMF conversion initially increased with reaction time and reached its highest value at 2 h. At 240 °C for 2 h, the N_2 (without CO_2) condition showed a higher HMF conversion than the CO_2 condition. However, HMF conversion gradually decreased with prolonged reaction time, and HMF was barely detected after 16 h. Girisuta et al. [6] reported acid-catalyzed HMF conversion to levulinic acid and humins, consistent with the decrease observed at prolonged residence times. Jing et al. [5] reported enhanced cellulose-to-HMF conversion using CO_2 -derived carbonic acid with metal oxides; in contrast, HMF formation was lower under CO_2 than N_2 in the present EFB system, suggesting that CO_2 -assisted acidity may also promote secondary degradation. As shown in Figure 2, HMF decreased substantially after the initial maximum at 2 h.

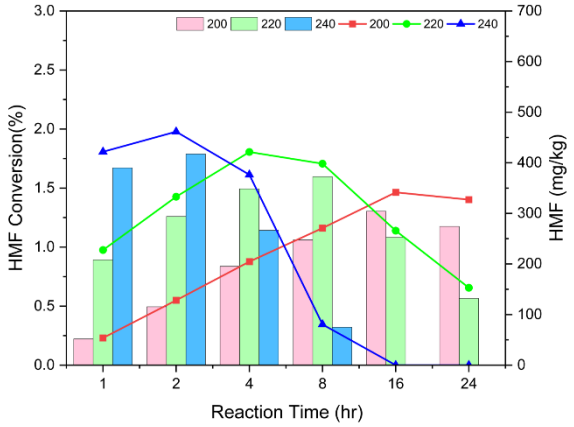

Figure 2. HMF concentaration analysis results.

4. CONCLUSIONS

Based on the laboratory experiments and data analysis conducted in this study, the following conclusions were drawn. EFB contained 46.22% cellulose, indicating its potential as a lignocellulosic feedstock for HMF production. The highest HMF concentration was observed at 240 °C, whereas further increases in temperature promoted HMF degradation. At 240 °C, the highest HMF formation under both CO_2 and N_2 conditions was achieved after 2 h of reaction, while HMF was barely detected after 16 h due to prolonged degradation. In addition, the N_2 condition resulted in higher HMF production than the CO_2 -assisted condition at 240 °C for 2 h. These results demonstrate that reaction temperature, reaction time, and gas atmosphere are important factors controlling HMF formation and degradation during the hydrothermal conversion of EFB. Overall, a reaction temperature of 240 °C and a reaction time of 2 h were identified as favorable conditions for HMF production from EFB. Under the present conditions, CO_2 -assisted acidity did not increase HMF production relative to N_2, indicating that its effect depends on reaction severity. These findings provide a basis for balancing HMF formation and secondary degradation during EFB hydrothermal conversion.

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