



Short communication

# New role of chromium fluoride: Its catalytic action on the synthesis of hydroxymethylfurfural in ionic liquid using raw plant biomass and characterization of biomass hydrolysis

Young-Byung Yi<sup>a</sup>, Myoung-Gyu Ha<sup>b</sup>, Jin-Woo Lee<sup>a</sup>, Chung-Han Chung<sup>a,\*</sup><sup>a</sup> Department of Biotechnology, Dong-A University, 840, Ha-Dan-Dong, Sa-Ha-Gu, Busan 604-714, South Korea<sup>b</sup> High-Technology Components & Materials Research Center, Korea Basic Science Institute, Busan 618-230, South Korea

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## ABSTRACT

A simple two-step process was conducted to scrutinize new catalytic action of chromium fluoride ( $\text{CrF}_3$ ) by evaluating its effect on the yield of hydroxymethylfurfural (HMF) in ionic liquid (1-octyl-3-methylimidazolium chloride) using raw tapioca root biomass with high starch, and hydrolysis efficiency of the biomass extract was characterized by FT-IR spectrometry and FESEM image analysis. The FT-IR absorbance bands confirmed the presence of starch and other soluble sugars in the acidic biomass extract by presenting its frequency signals in the  $950\text{--}1200\text{ cm}^{-1}$  regions. FESEM image showed that the efficiency of the biomass hydrolysis is time-dependent. The concentration of  $\text{CrF}_3$  significantly affected the yield of HMF. Its highest yield ( $52.6 \pm 4.8\text{ dwt}\%$ ) was achieved at  $1\%$   $\text{CrF}_3$ , but over  $1\%$   $\text{CrF}_3$  its yields began to decline. The combined addition of  $\text{CrF}_3$  and  $\text{CrBr}_3$  showed ca. 1.3-fold higher yield than  $\text{CrF}_3$  alone. The reaction rates of HMF synthesis were considerably influenced by the stoichiometry ratio of  $\text{CrF}_3$  to biomass. The highest reaction rate ( $0.41\text{ g/g biomass/h}$ ) occurred at 0.2 ratio value.

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## 1. Introduction

It is known that fluorinated metal catalysts function as the heterogeneous catalysts in some chemical reactions such as isomerization, alkylation, and dismutation by enhancing their acidic properties (the Brønsted and Lewis acid) [1]. Nonetheless, the use of some fluorinated metal catalysts such as chromium fluoride ( $\text{CrF}_3$ ) is very rare because mainly of a narrow spectrum of their catalytic action and weak coordination activity [1,2]. In recent, some workers [3] demonstrated that lithium fluoride (LiF) showed no catalytic effect on the synthesis of HMF that can be used as a platform feedstock for the syntheses of various important carbon compounds including biofuels such as dimethylfuran (DMF) [4,5]. Contrary to this finding, however, in our study a high catalytic activity was identified with  $\text{CrF}_3$ , indicating its new catalytic action in synthesizing HMF. The addition of this metal catalyst to the reaction mixture containing an ionic liquid and other additives significantly affected the synthesis of HMF. In particular, the use of the raw biomass in chemical syntheses could be conducive to sustainable chemical industry [6,7] and thus in this study, raw tapioca root biomass rich in starch (ca. 70–75% by dry weight) were employed because starch can be more favorable feedstock in the synthesis of HMF due to its

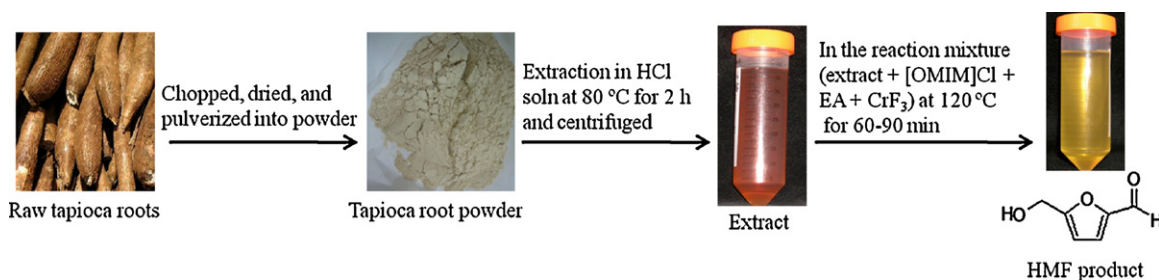
much easier conversion process to HMF than other carbohydrate polymers such as cellulose or lignocellulose [8,9]. Furthermore, because tapioca plant is an annual shrub growing in tropical and subtropical regions, and no systematic farming is required, it could be a good sustainable biomaterial for the industrial production of HMF.

Acid hydrolysis is an essential processing part in the synthetic reaction of HMF from the raw biomass rich in carbohydrate polymers [10]. The hydrolysis efficiency of polysaccharides can be determined by monitoring the physicochemical changes of raw biomass components using FT-IR (Fourier transform-infrared) spectroscopy and SEM (scanning electron microscopy) image analysis because the methods are simpler and more convenient compared with those by chemical analysis [11,12].

The ionic liquid-mediated dehydration of carbohydrates to HMF is another alternative method that has been widely applied by many workers [13]. Because ionic liquids have such properties favorable to chemical reactions as high water miscibility, low vapor pressure, low melting point, thermal stability, etc., they are currently used as solvent in many chemical syntheses [14]. In our study, a disubstituted ionic liquid, 1-octyl-3-methylimidazolium chloride ([OMIM]Cl), was used because it is a more effective ionic liquid for high yield of HMF from some carbohydrate sources [6,8,15–17].

$\text{CrF}_3$  is inexpensive and relatively less harmful, implying that it could be a promising catalyst for the synthesis of HMF from starch-rich raw biomass (Scheme 1). So, our primary research focus

\* Corresponding author. Tel.: +82 51 200 7583; fax: +82 51 200 6536.  
E-mail address: [chchung@donga.ac.kr](mailto:chchung@donga.ac.kr) (C.-H. Chung).



**Scheme 1.** Simple two-step strategy for the synthesis of HMF using raw tapioca root biomass. [OMIM]Cl, 1-octyl-3-methylimidazolium chloride; EA, ethyl acetate.

was to examine the catalytic action of  $\text{CrF}_3$  in association with direct utilization of raw plant biomass for sustainable synthesis of HMF because its high catalytic activity has not been identified in chemical reactions. In addition, some information on hydrolysis efficiency of the biomass was provided by characterizing FT-IR spectroscopy and SEM image analyses because the hydrolysis of the biomass components is a critical parameter in synthesizing HMF from biomass materials [10].

## 2. Experimental

### 2.1. Sample preparation and general reaction procedures

After tapioca roots were dried and pulverized using a sample mill (Cyclotech 1093, Foss), the powder slurries (10%) were prepared in 0.3 M HCl solution. Then they were heated at 80 °C for the given extraction time (60 or 90 min), centrifuged and the supernatants (the biomass extracts) were collected for further uses (Scheme 1).

The reactions were performed on a heating mantle. For the catalytic effect of  $\text{CrF}_3$ , the reactions were undergone at 120 °C for 60 or 90 min using a reaction mixture containing 4 g [OMIM]Cl (98%, Merck), 1 mL ethyl acetate, the given concentration of  $\text{CrF}_3$  catalyst (7 groups of  $\text{CrF}_3$  concentration; 0, 0.5, 1, 1.5, 2, 3, and 4% were applied.), and 5 mL extraction solution with 0.3 M HCl. Before the reaction proceeded, an admix of 4 g [OMIM]Cl and  $\text{CrF}_3$  catalyst was preheated at 120 °C for 15–16 min. Then, 1 mL ethyl acetate and the extraction solution were added and reacted at 120 °C for the given reaction time. For single addition of the catalysts, 1% concentration (0.1 g of the given catalyst in 10 mL reaction mixture) was used. For the combined addition of two catalysts, 2% concentration in total (0.1 g for each catalyst) was used (0.2 g catalyst is contained in 10 mL reaction mixture). The reactions were done as above.

The reaction rates were measured by calculating the HMF yield (g) per g biomass per hour (g yield/g biomass/h) and expressed as a function of the ratio of  $\text{CrF}_3$  to the biomass. The ratio value was obtained by calculating the ratio of  $\text{CrF}_3$  to the biomass. The same reaction procedures were applied as described above.

All measurements performed were estimated with the mean values of at least 4 independent reactions and expressed with standard deviations.

### 2.2. FT-IR analysis

For the Fourier transform infrared (FT-IR) measurement, the sugar samples were precipitated by ethanol extraction method and treated with KBr pellet and the microscopic FT-IR/Raman spectroscopy equipped with a diamond crystal ATR (attenuated total reflectance) accessory (Vertex 80 V, Bruker) used. The sample powder (approximately 2 mg) was placed on the diamond ATR crystal (Vertex 80 V, Bruker) and analyzed. For the FT-IR spectral record, a spectrometer (Bruker) was used to record its spectral data in the 400–4000  $\text{cm}^{-1}$  frequency ranges by accumulating 128 scans with a

resolution of 4  $\text{cm}^{-1}$ . Other more detailed methods were performed according to the manufacturer's instruction.

### 2.3. FESEM analysis

A field emission scanning electron microscope (JEM-6700F, JEOL) was used for field emission scanning electron microscopy (FESEM). The samples were coated with platinum (20 nm thick) using a vacuum ion sputter (108auto, Cressington). The platinum-coated specimen was then observed with the FESEM microscope at the probe energy level of 5.0 kV and its image was photographed at magnification of 700 or 1000 $\times$ .

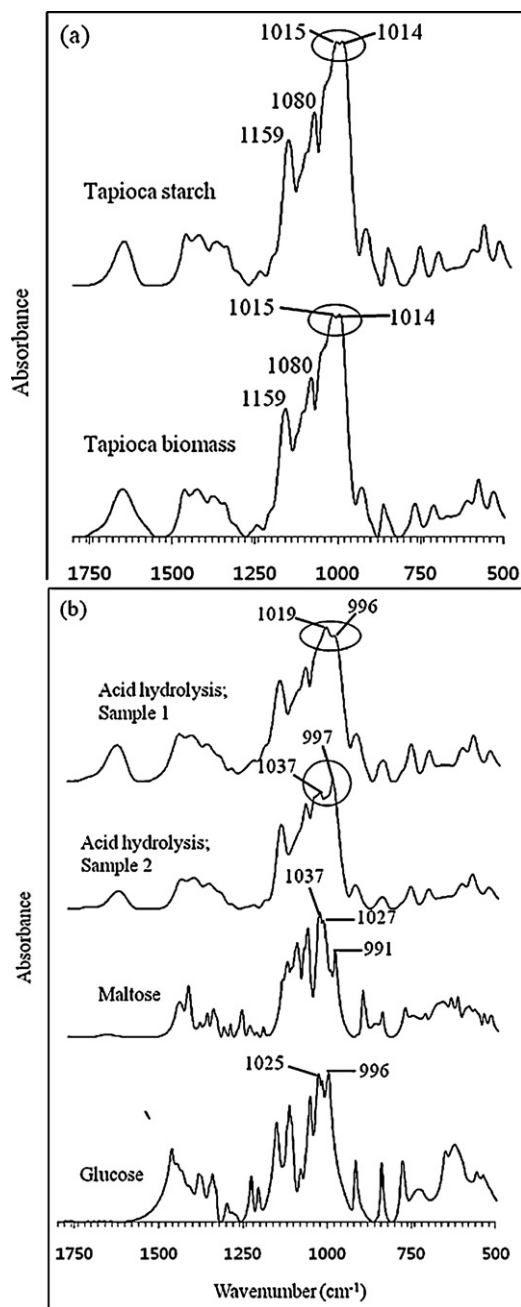
### 2.4. HPLC analysis

High performance liquid chromatography (HPLC, Waters) equipped with an absorbance detector (Waters) was used. For quantification of HMF, a Waters XBridge  $\text{C}_{18}$  reversed-phase column (4.6 mm  $\times$  150 mm, 5  $\mu\text{m}$ ) was used. HPLC analysis was operated using a gradient mobile phase at a flow rate of 0.7 mL/min (UV at 320 nm). The gradient condition was as follows: 100% water phase for 2 min, transition and gradient phase in the ratio of 80% water and 20% methanol for 8 min, and 100% water for 20 min including transition time.

## 3. Results and discussion

### 3.1. Characterization of biomass hydrolysis by FT-IR and FESEM

The physicochemical changes of the extractant derived from the tapioca root biomass were characterized using FT-IR and field emission scanning electron microscopy (FESEM) by measuring their chemical and morphological behaviors. Fig. 1 shows the FT-IR spectral profiles of the biomass material and its acid hydrolysate. The absorption bands of the raw biomass by the C–O–C and C–OH stretching modes that is typically observed in carbohydrates such as starch [17,18] were identified in the 900–1200  $\text{cm}^{-1}$  regions (Fig. 1a). The banding pattern of the raw biomass was very similar with that of starch derived from the native tapioca roots (Fig. 1a), implying that the main composition of the biomass would be starch. The absorbance bands around 1010 and 1150  $\text{cm}^{-1}$  regions also confirm that the biomass is comprised of starch because the vibration modes by  $\text{C}_1\text{–O–C}_4/\text{C}_1\text{–O–C}_6$  stretching in the  $\alpha$ -1,4-/1,6-glycosidic bonds, and C–O/C–C stretching modes in the pyranose rings are frequently detected in these regions [18,19]. The FT-IR spectral profiles were changed by the addition of HCl. The absorption band shifts were observed in the 950–1200  $\text{cm}^{-1}$  regions (Fig. 1b). After acid hydrolysis, some absorbance signals (1014 and 1015  $\text{cm}^{-1}$ ) were not detected in the biomass and some new ones (996, 997, 1019, and 1037  $\text{cm}^{-1}$ ) occurred in its hydrolysate (Fig. 1b and Table 1). This shift in the absorbance signals (Fig. 1b, the circled regions) may be due to the change of chemical conformation of the biomass starch caused presumably by its depolymerization



**Fig. 1.** FT-IR spectra of raw tapioca biomass and its sugar products by acid hydrolysis. (a) FT-IR absorbance signals of raw tapioca biomass and its starch. (b) FT-IR absorbance signals of the hydrolysis product of the biomass: Sample 1, hydrolysate in 0.3 M HCl; Sample 2, hydrolysate in 0.5 M HCl.

reaction into smaller molecules such as glucose or maltose and thus results in the formation of new vibration modes contributing to the depolymerization products (Table 1). Based on the above results, it is thought the FT-IR spectral shift in the 995–1040  $\text{cm}^{-1}$  regions could be a critical indicator for determination of starch depolymerization into its products (mainly glucose and maltose) because some new bands contributing to monosaccharides and other oligosaccharides appeared (Table 1), which are frequently found from glucose and maltose standards (Fig. 1b).

The SEM observation of the native tapioca powder sample shows the presence of globular starch granules with irregular shapes (from ca. 5 to 15  $\mu\text{m}$ ) and biomass debris (Fig. 2, 0 min). However, as the extraction time elapsed, the number of starch granules gradually decreased, implying that the destruction degree of the starch

**Table 1**

Spectral shifts by acid hydrolysis of raw tapioca biomass in the 950–1200  $\text{cm}^{-1}$  frequency regions.

Wavenumber ( $\text{cm}^{-1}$ )	Vibration group and mode		
	Biomass	Sample 2	
996	998	C–C stretch in pyranose ring	
1014	–	C–O (in starch), C–O–C stretch in glycosidic bonds	
1015	–	C–O (in starch), C–O–C stretch in glycosidic bonds	
–	1019	C–OH bending in mono- and disaccharides	
–	–	1037	C–OH bending in oligosaccharides
1045	–	–	C–OH stretch in granular starch

–, no presence of absorbance signal.

granules may depend on the reaction time (Fig. 2). This SEM observation also displays that after 90 min extraction, the starch granules were almost destroyed, indicating that the optimal extraction time would be 90 min (Fig. 2, 90 min, and 120 min). Fig. 2 illustrates that the starch released from starch granules by the acidic extraction was depolymerized into the sugars with a crystalline form (Fig. 2, sugar products), which were produced by HCl hydrolysis [20]. The sugars obtained could be then utilized as the feed substrates for the synthesis of HMF.

### 3.2. Catalytic activity of $\text{CrF}_3$ on the biomass conversion to HMF

Fluorinated metal catalysts have been used as the heterogeneous catalysts in chemical reactions by changing their acidity, but their use is very rare due to low catalytic activity [1,2]. However, in our study, a notable result was obtained in the synthetic process of HMF. As shown in Fig. 3, the concentration of  $\text{CrF}_3$  significantly affected the yields of HMF. At 1% of  $\text{CrF}_3$ , the highest yields of HMF ( $52.6 \pm 4.8$  dwt% at 90 min reaction) were determined, whereas above 1% of  $\text{CrF}_3$ , its yields began to rapidly decline. This unexpected finding evidently contrasted with the report that other fluorinated metal catalysts such as LiF exerted no effect on HMF synthesis [3]. Furthermore, higher HMF yield was identified by  $\text{CrF}_3$  catalysis rather than  $\text{CrCl}_2$  and  $\text{CrCl}_3$ , which were known as most effective catalysts [21]. Compared with other chromium halides ( $\text{CrBr}_3$ ,  $\text{CrCl}_2$ , and  $\text{CrCl}_3$ ), their HMF productivity was 27.4% lower on the average than that of  $\text{CrF}_3$  (Fig. 4). At 90 min reaction time, its yield exhibited first order dependence with respect to  $\text{CrF}_3$  concentration until its concentration reached 1%, but as the concentration was increased, the yield began to decline and finally little catalytic effect was examined (Fig. 3). Fig. 3 also shows higher yield of HMF at 90 min reaction time than 60 min, indicating that the former is more effective in synthesizing HMF. In addition, we observed that the combined addition of  $\text{CrF}_3$  and other chromium halides ( $\text{CrBr}_3$ ,  $\text{CrCl}_2$ , and  $\text{CrCl}_3$ ) appeared more effective for HMF yield than single addition. The most effective combination was achieved in the reaction mixture of  $\text{CrF}_3$  and  $\text{CrBr}_3$  with ca. 1.3-fold higher HMF yield, and the other reaction mixtures revealed slightly higher yields (Fig. 4). The enhancement in HMF yield by the combined addition of two catalysts could be due to the synergistic interaction between the two catalysts.

### 3.3. Proposed catalytic action of $\text{CrF}_3$

The catalytic mechanism of  $\text{CrF}_3$  in HMF synthesis is not yet known. However, some research groups [3,21] have proposed the mechanistic pathways for sugar conversion to HMF by chlorinated metal catalysts such as  $\text{CrCl}_2$  and LiCl. Based on their reports and other published data [1,2], the key catalytic mechanism of  $\text{CrF}_3$  in



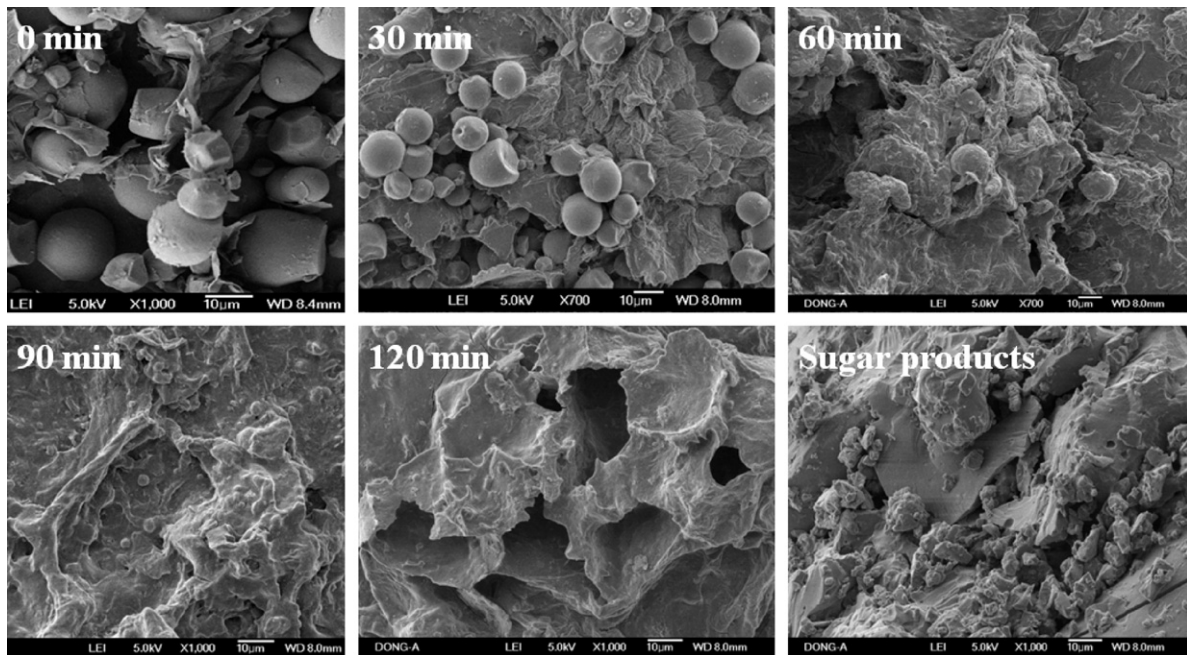


Fig. 2. FESEM image of raw tapioca biomass during its extraction and acid hydrolysis.

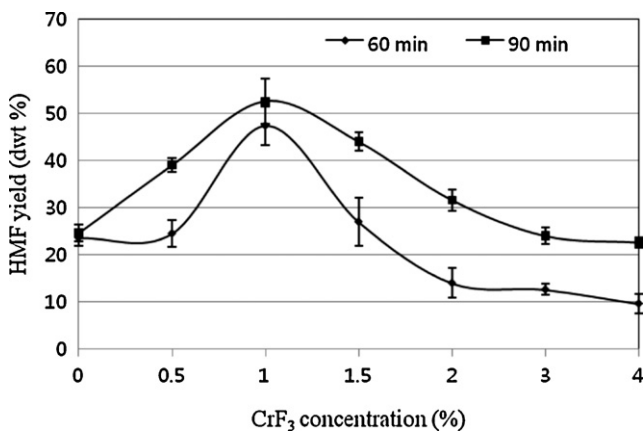


Fig. 3. Catalytic effect of CrF<sub>3</sub> on the HMF yields synthesized from the raw tapioca biomass.

synthesizing HMF from sugars would be attributed to the presence of weak coordination of fluorine–chromium and sugar–chromium metal in the acidic ionic liquid [21], probably caused by low coordination ability of the ligands (fluorine and sugar hydroxyl groups)

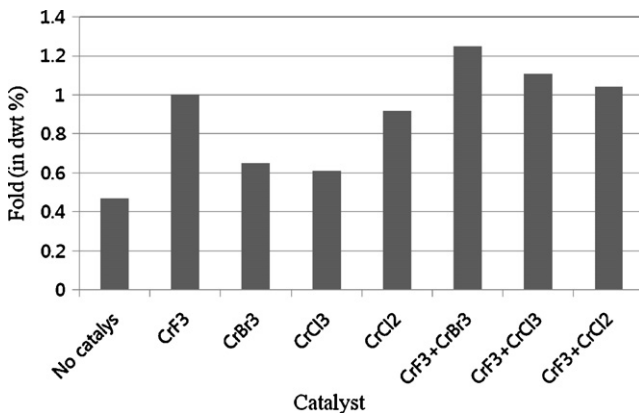


Fig. 4. Comparison of catalytic action of CrF<sub>3</sub> and the other catalysts tested.

with chromium center [22–24]. The proposed mechanistic pathway is outlined in Fig. 5. The  $\alpha$ -form of glucopyranose, which is released from the raw biomass starch by  $\alpha$ -1,4- or  $\alpha$ -1,6-glycosidic bond cleavage that results from the protonation reaction between the glucose oxygen groups and H<sup>+</sup> from HCl (as a Brønsted acid) in association with the help of chromium metal acting as the Lewis acid, is first mutarotated via an acyclic enediol intermediate to  $\beta$ -form (Fig. 5). The  $\beta$ -glucopyranose is then isomerized into fructofuranose, which in turn CrF<sub>3</sub> acting as a nucleophilic catalyst facilitates the formation of an enol intermediate by stabilizing the negative charge developing on the oxygen atom of the furanose ring. In subsequent, the enol intermediate formed is further dehydrated and finally synthesized into HMF [3,21,25–27]. In addition, the presence of dual cation/anion properties of [OMIM]Cl in the reaction mixture may contribute to accelerating the catalytic rates of CrF<sub>3</sub> by stabilizing the reactive intermediates and transition state occurring during the synthetic reaction process of HMF [28]. The decrease in the yields of HMF above 1% CrF<sub>3</sub> or its little effect at 4% may be due to excess CrF<sub>3</sub> because the surplus catalyst may induce the changes in the coordination stability between chromium center and sugar ligand. These changes would affect the catalytic action of CrF<sub>3</sub>, thus resulting in little or no catalytic promotion in the synthesis of HMF [23,27].

### 3.4. Stoichiometry effect of CrF<sub>3</sub> to biomass on the reaction rates

The optimal concentrations of catalyst and feed material are a pivotal parameter in synthesizing HMF from raw biomass for its industrial production. In particular, the ratio of catalyst to feed substrate significantly affects product selectivity and yield. In this experiment, we have examined their influence on the HMF synthesis from raw tapioca biomass. First, we performed the stoichiometry effect between CrF<sub>3</sub> catalyst and the feed biomass on the reaction rates of HMF. As shown in Fig. 6, the highest reaction rate (0.41 g product/g biomass/h) was detected at 0.2 ratio value, while the lowest (0.15 g product/g biomass/h) was at 1.2 value. This finding suggests that its maximum reaction capacity would occur at 0.2 ratio value and most effective reaction process of HMF could be possible at this value. At the ratio values from 0.05 to 0.2, as the value

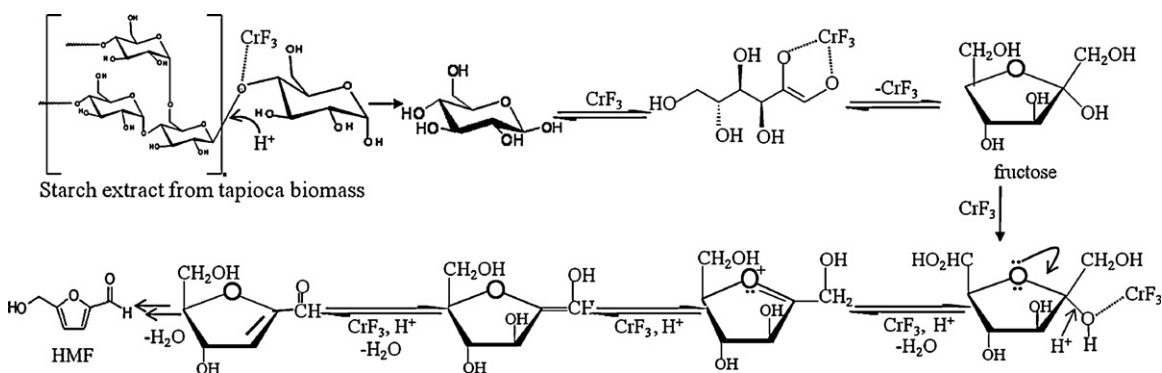


Fig. 5. Scheme for the putative mechanism of direct conversion of the raw tapioca biomass to HMF by chromium fluoride.

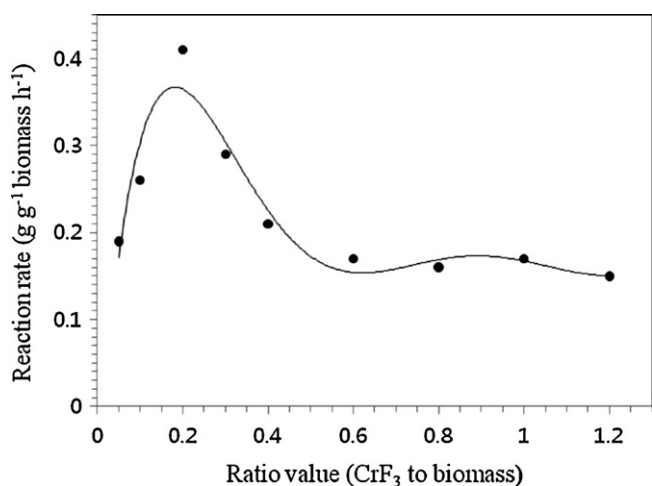


Fig. 6. Stoichiometry effect of CrF<sub>3</sub> to biomass on the reaction rates of HMF synthesis.

was increased, the rates increased, showing the first order relationship between the ratio value and the reaction rate within those ratio values. Above 0.2 ratio value, there was an abrupt decrease in the reaction rates until the value reached 0.4 and then the rates were constantly maintained (Fig. 6), signifying that the catalytic activity of CrF<sub>3</sub> on the reaction process of HMF was considerably affected by the ratio value. The above results account for the importance of CrF<sub>3</sub> concentration optimum in the synthesis of HMF. This stoichiometric relationship between CrF<sub>3</sub> and the biomass could be a rate determining factor in the synthetic process of HMF from the raw tapioca biomaterial. Some workers also reported that fluorinated metal catalysts such as AlF<sub>3</sub> varied in their catalytic action by their concentration present in the reactants [2].

#### 4. Conclusions

To our knowledge, CrF<sub>3</sub> is classified as a seldom used catalyst due to its low catalytic action. However, in this study, we demonstrated that CrF<sub>3</sub> is an excellent catalyst in synthesizing HMF. The addition of CrF<sub>3</sub> catalyst was higher in HMF yield than other halide catalysts including CrCl<sub>2</sub> that is known as the most effective catalyst in HMF synthesis [21], reilluminating the catalytic value of CrF<sub>3</sub>. We also provided some information about hydrolysis efficiency of the tapioca biomass by analyzing physicochemical changes of the biomass hydrolysates using FT-IR spectroscopy and FESEM image. Our work could be not only conducive to the sustainable production of HMF by using renewable biofeedstock such as raw tapioca roots but also valuable to the industrial application.

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