Synthesis of Furfural from Water Hyacinth *(Eichornia croassipes)*

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Abstract. Furfural has been prepared from hydrolysis of dried biomass of water hyacinth *(Eichornia crassipes)* by using diluted hydrochloric acid and sulphuric acid as catalysts. This process involved the conversion of the pentosane fraction in water hyacinth into pentose, and then pentose was cyclodehydrated into furfural. The reaction was conducted in a distillation set with receiving the flask that contains chloroform. Furfural was identified by fehling test which was then characterized using Fourier Transform Infra Red (FTIR) and Proton Nuclear Magnetic Resonance (^{1}H-NMR), followed by Gas Chromatography with Mass Spectroscopy (GC-MS). The yield of furfural obtained using sulphuric acid catalyst was 0.38% and hydrochloric acid catalyst was 0.01% of dried biomass.

1. Introduction

Water hyacinth *(Eichornia crassipes)* is an aquatic plant which can grow fast especially in a rich nutrient water area. 140 millions of water hyacinth can increase every year and these plants cover 140 km^2 water area with a fresh biomass of 28.000 tons [4]. They cause an enormous ecological and economic disaster worldwide, and they must be removed every year [4, 11].

In Indonesia, water hyacinth biomass has been utilized as furniture and handicraft. Also, water hyacinth has been fermented to produce bioethanol [13]. Recently, research on the synthesis of Carboxymethyl Cellulose (CMC) from water hyacinth has been proposed. Carboxymethyl Cellulose (CMC) is a derivated cellulose that is used in food and non-food products for examples as a thickener agent, detergents, and paints [8]. However, thousand tons of this biomass still unutilized properly. A study [3] proven that water hyacinth biomass contains pentosans as much as 23.7%. It's mean that water hyacinth can be used as the promising precursor in the synthesis of furfural.

Furfural is an aldehyde compound that can be derived into furfuryl alcohol and tetrahydrofuran, solvents that widely used in industries. Furfural it self commonly used in the production of plastic resins, metal coatings industry, production of insecticide and food industry [9].

Furfural can be produced by hydrolysis of pentosan with the acid catalyst. Pentosan is one of the important fibre components of non-starch polysaccharides called hemicellulose that can be found in agricultural by products. Hemicellulose is one of the several heteropolymers that present in almost all plant cell walls [12]. The pentosan $(C_5H_8O_4)_n$ fraction of lignocelluloses can be converted into pentose ($C_5H_{10}O_5$) by acid hydrolysis and continued by cyclodehydration process to produce furfural ($C_5H_4O_2$). The reaction of this process is shown in **figure 1** [2].

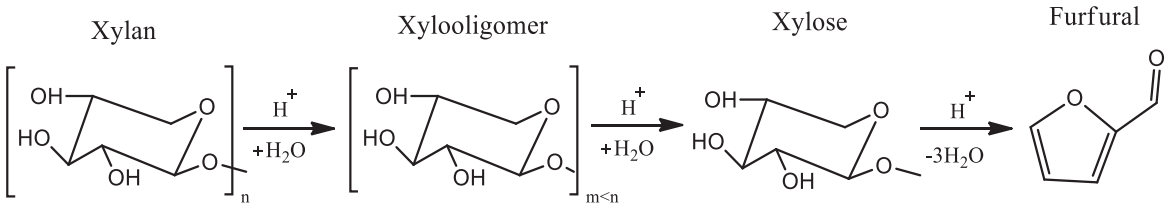


Figure 1. Formation of furfural from pentosan

2. Procedure

2.1 Materials and Instrumentation.

Water Hyacinth *(Eichornia crassipes)* was obtained from Pedalangan village, Sub-district of Banyumanik, Semarang City, Central Java, Indonesia. Freshwater hyacinth was thoroughly washed under tap water to remove sludge and then dried, milled, and stored as dried biomass [6]. The work was carried out in a distillation set as shown in **figure 2**. The apparatus was consisted of eight main parts: 1L round bottom flask as a batch reactor, an oil bath, a connector, thermometers to control the temperature in the round bottom flask and oil bath, a condenser, a receiving flask, and a magnetic stirrer. The condenser was attached to the connector which was also connected to round bottom flask and thermometer. The materials such as 50 g of dried water hyacinth, 700 mL of 1 M HCl, and 0.6 g of NaCl were placed in the round bottom flask and 13 mL chloroform is placed in the receiving flask.

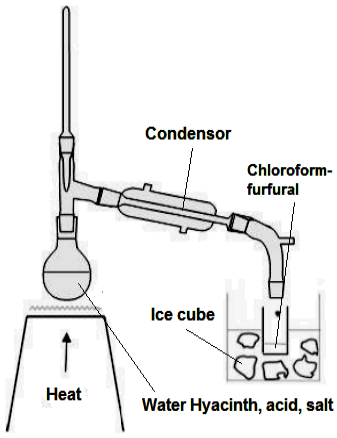


Figure 2. Distillation set up for preparation of furfural

2.2 Experimental procedure

Distillation process was carried out for approximately 7 hours, at 140°-180°C. The distillate containing 50 g of dried water hyacinth, 700 mL of 1 M HCl and 0.6 g of NaCl was set to flow into the receiving flask that containing of 13 mL chloroform. Two layers of aqueous and chloroform would be formed in which the aqueous layer would be at the top and the chloroform-furfural containing layer would be at the bottom of the flask. The chloroform-furfural containing layer was separated by heating in a water bath. The chloroform was recovered at 60°C while the furfural would have remained in the flask. The other experiment was conducted by replacing HCl with 1 M H_2SO_4 in order to compare which one would be more active.

2.3 Identification of furfural

Furfural was identified by Fehling test first before characterized using spectroscopic methods such as Fourier Transform Infra Red (FTIR) model Horizon MB300, ^{1}H-NMR model JEOL ECZ 500R at 500 MHz and Gas Chromatography with Mass Spectrometer (GC-MS) model Perkin Elmer GC Clarus 680 and MS Clarus SQ 8T. Elite- 5 MS Capillary Column (30 m x 0.25 mm I.D.) with 0.25 μm film thickness was used in this work, and Helium at a flow rate of 1 mL/min was used as the carrier gas. The injection port was maintained at 170°C while the column temperature was held at 50°C for 5 minutes to 150°C. The final temperature was held for 25 minutes. Scanning was done from m/z 50 to 300 in one scan. The mass spectral was carried out by comparing with the mass spectra library of National Institute of Standards and Technology (NIST) and Japan AIST/ NIMC Database. This GC-MS method is a modified method from GC-MS analysis furfural from Occupational Safety & Health Administration, US Department of Labor and GC-MS analysis furfural from Malaysian Agricultural Research and Development Institute [9].

3. Result and Discussion

This work is aimed to convert water hyacinth *(Eichornia crassipes)* as an agricultural waste biomass to furfural with diluted acid hydrolysis. The yield of furfural is depending on the percentage of pentosan. Water hyacinth has a composition of 40.71% cellulose, 23.7% pentosan or hemicellulose, and 15.42% lignin [3]. The yield is also affected by acid concentration, reaction time, acid-to-lignocellulosic mass ratio, and temperature of synthesis [7]. The most important parameter affected to sugar yield is acid concentration, while the highest impact on sugar degradation product is temperature [5].

The acid hydrolysis of water hyacinth was carried out using diluted hydrochloric acid and sulphuric acid at a concentration of 1 M. According to a research [1], 1 M is the best concentration to convert furfural from pentosan. The Furfural obtained was in a liquid form. It was colorless to yellowish. The product was confirmed as an aldehyde functional group by the red precipitate that appeared in Fehling test.

The yield of furfural that obtained from acid hydrolysis using 1 M H_2SO_4 and 1 M HCl were 0.19 g (0.38%) and 0.05 g (0.01%) of dried water hyacinth, respectively. It means that H_2SO_4 is more active than HCl in converting furfural from pentosan. As compared to HCl, H_2SO_4 tends to be more selective and stable in the batch reactor. In addition H_2SO_4 have higher boiling point than HCl. Residual sulfates are more easily separable and had less impact than residual chlorides. Besides, H_2SO_4 can reduce corrosiveness, improve selectivity, and has a lower cost [2].

The presence of furfural (aldehyde) was proven by IR spectrum (**Figure 3**) with the existence of four peaks gained at 3132.17 cm^{-1} (sp^2C-H), 2812.01 cm^{-1} and 2842.87 cm^{-1} (C-H aldehyde), 1670.25 cm^{-1} (-C=O, carbonyl) and 1461,1 cm^{-1} (-C=C-).

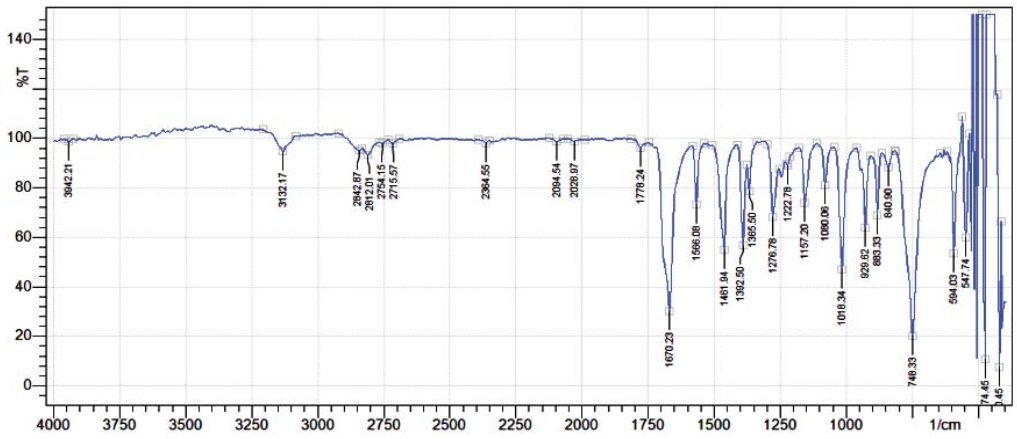


Figure 3. FTIR spectrum of furfural

A typical ^{1}H-NMR spectrum of furfural can be seen in **figure 4**. The aldehyde proton signal appears in the normal low-field position at δ 9.633 (1H). The ring protons appear due to the asymmetry as three groups of signals in a region 6.57 - 7.67 ppm (3H).

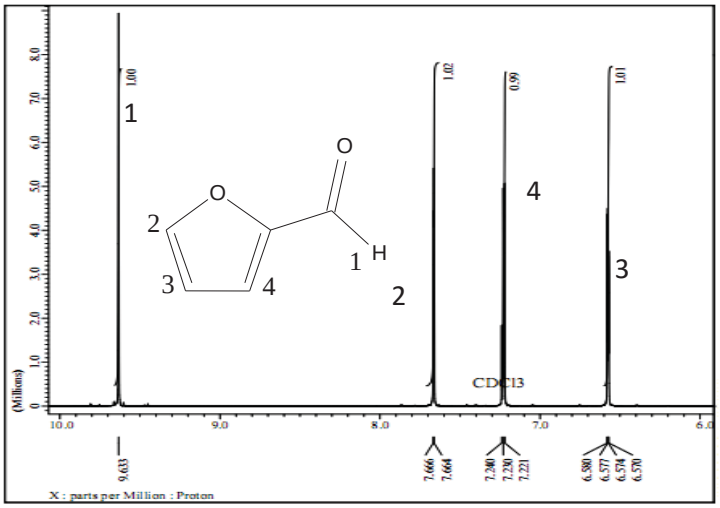
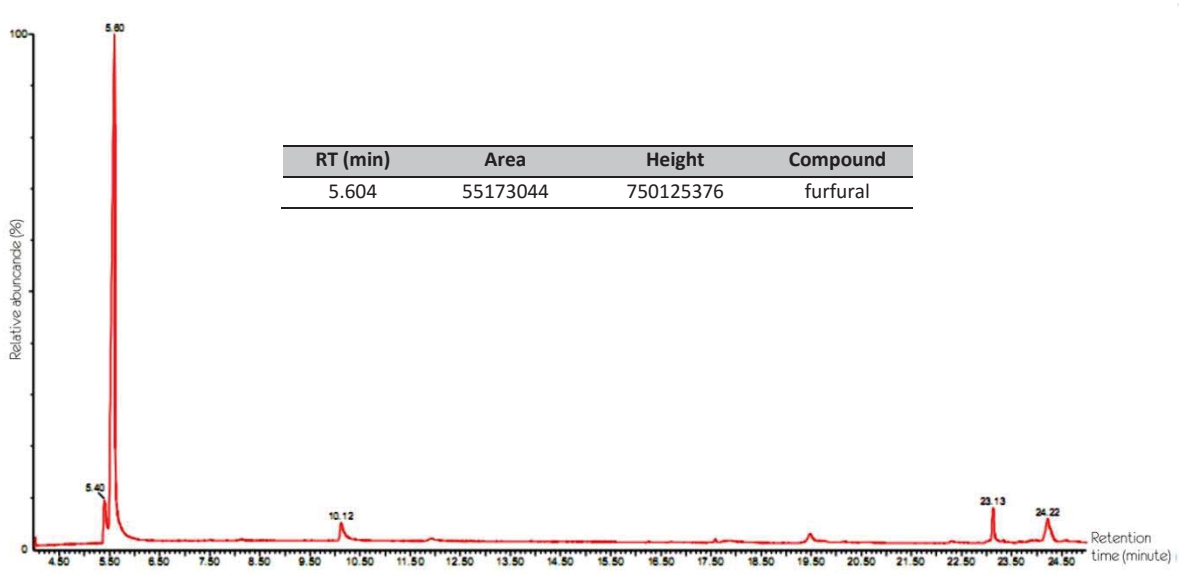


Figure 4. ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of furfural

Chromatogram in **Figure 5** showed a dominant peak which was indicating the presence of only one constituent. Furfural has a retention time of 5.604 minutes with probability or relative abundance of 100%. On comparison with the mass spectra of the constituent with NIST and Japan AIST/ NIMC, that constituent was characterized and identified as Furfural.



RT (min)	Area	Height	Compound
5.604	55173044	750125376	furfural

Figure 5. Chromatogram of furfural

In comparison with the mass spectra of the constituent with NIST and Japan AIST/ NIMC, that constituent was characterized and identified as Furfural (**Figure 6**). The mass spectrum (**Figure 6**) showed a molecular ion peak at m/z 96 which correlates to a molecular formula of Furfural ($C_5H_4O_2$).

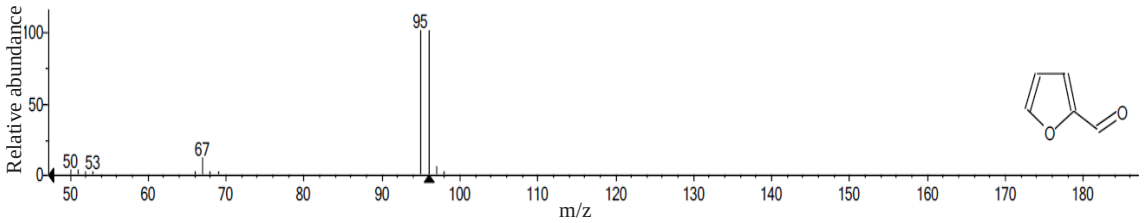


Figure 6. Mass spectrum of furfural (on 5.604 min)

4. Conclusion

Furfural has been successfully synthesized from water hyacinth *(Eichornia crassipes)* by acid hydrolysis method. The yield of furfural obtained using sulphuric acid catalyst was 0.19 g (0.38%) and hydrochloric acid catalyst was 0.05 g (0.01%) of dried biomass. The furfural was colorless to yellowish, with the chemical formula of $C_5H_4O_2$ and molecular weight of 96.

Acknowledgments

We are grateful to the financial support from Diponegoro University (No: SP DIPA-042.01.2.400898/2016, December, 7th 2015).

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