

Furfural Synthesis from Mile-a-Minute Weed (*Mikania micrantha*) using Roselle Petal Extract as Catalyst

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Keywords: Hydrolysis, mile-a-minute weed, roselle petal extract, furfural yield

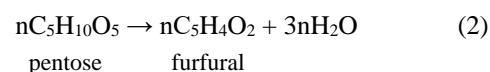
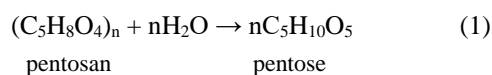
Abstract: Mile-a-minute weed (*Mikania micrantha*) contains a large fraction of pentosan, and thus, is suitable as a precursor of furfural. Generally, furfural production from biomass requires inorganic acids, such as sulfuric acid and hydrochloric acid, as catalyst. However, the use of inorganic acid is not environmentally benign and causes equipment corrosion. In this study, 50 g dry mile-a-minute weed was reduced to 100 meshes and mixed with 50 g sodium chloride. Then, this mixture was added into roselle petal extract at a ratio of 1:6 (w/v) in a three-neck flask. The flask was then connected to a Liebig condenser and an erlenmeyer was placed at the other end of the condenser to collect the furfural. The reaction was carried out at 100-120°C and for 0-330 min. The resulting furfural was separated from water by extraction using chloroform. Two layers of liquid were formed during extraction. The top layer was rich in water and the bottom layer was rich in chloroform and furfural. The lower layer was distilled to purify furfural. The purified furfural was identified by aniline acetate color test, Fourier-Transform Infrared Spectroscopy (FTIR) and Gas Chromatography–Mass Spectrometry (GCMS). The results suggested that organic acids from roselle petal extraction can be used as a catalyst in furfural synthesis.

1 INTRODUCTION

The mile-a-minute weed has been known as one of the most rampant invasive species in the world. This plant has pentosane content reaching 56% and is widespread throughout the Asia-Pacific region, especially in Southeast China since 1980 (Ko et al., 2013). It is listed as introduced, invasive, and noxious plant according to United States Department of Agriculture (USDA). For newly established plantations such as those of tea, coffee, cocoa, coconut, and palm oil, mile-a-minute is a threat to the plant growth (Anderson et al., 2012). Control of mile-a-minute is difficult and time-consuming, the methods are also limited and expensive. It was recommended cutting plants that grow on the ground periodically to control their growth (Kuo, et al., 2003). Thus, this plant needs to be utilized to reduce the loss to many aspects of human life. One of its utilization is as precursor of furfural (Taslim et al., 2018).

Furfural is a furan derivative originating from hemicellulose fraction of lignocellulose, which is considered a promising biochemical based commodity because its use allows production of several products such as antacids, paints, fuel additives, and fertilizers, as well as various other products usually produced from non-renewable resources (Guche et al., 2017).

Furfural is usually produced by hydrolysis with aid of acid catalyst. Pentose dehydration is shown in the following equation.



Furfural production and utilization will be useful for reducing energy and environmental crises, as well as increasing benefits of biorefinery economy (Zhu et al., 2017).

Furfural synthesis from various biomass has been reported in several literature using phosphoric acid (Lenihan et al., 2010), sulfuric acid (Lacerda et al., 2012), and hydrochloric acid (Hernandez-Salas et al., 2009) as catalysts. The use of inorganic acids can cause corrosion in the equipment used, and also not environmentally benign. To overcome these problems, organic catalysts is considered. The use of organic acids derived from bilimbi as a catalyst in furfural production had been carried out, in which the yield reached 7.2% at 100°C (Taslim et al., 2018).

Until now, the use of organic acids from roselle petals has never been reported. In fact, roselle flower extract contains high organic acids including citric acid, hydroxycitric acid, hibiscus acid, malic acid and tartrate acid as the main compound, and oxalic and ascorbic acid as minor compounds (Da-Costa-Rocha et al., 2014). Therefore, this study aimed to investigate the use of organic acids derived from roselle petals as catalysts in furfural synthesis from mile-a-minute weed, and compare it with sulfuric acid catalyst.

2 MATERIAL AND METHOD

Mile-a-minute weed and roselle petals were obtained from Medan Tuntungan, Indonesia. Chemicals used such as sodium chloride, sulfuric acid, aniline, acetic acid, and chloroform were purchased from Rudang Jaya, Medan.

2.1 Sample Preparation

Sample preparation was carried out using a procedure reported in the literature (Taslim et al., 2018). A mix of mile-a-minute weed stems and leaves were washed with water until free of dirt. They were cut to ± 1 cm using a knife. Then, they were dried in the oven for 2 h at 100°C. After drying, mile-a-minute weed was milled in a ball mill, and sieved to 100 meshes. Afterwards, the sample was stored in a sealed plastic box at room temperature and ready to be used for furfural synthesis.

2.2 Extraction of Roselle Petals

Roselle extraction followed a procedure reported by Taslim et al., (2008). Roselle petals were cleaned using water to a constant pH, then grounded using a commercial blender to get roselle extract. The extract was filtered using Whatman paper number

41. Roselle filtrate was analyzed for its pH, normality, acid number, and stored in a refrigerator at 0°C.

2.3 Synthesis of Furfural

Furfural synthesis followed a procedure reported by Taslim et al., (2018) with modifications. As much as 50 g mile-a-minute weed powder, 600 ml roselle extract and 50 g sodium chloride were placed in a three neck flask. The volume of the reaction mixture was adjusted to 750 ml by adding distilled water. The mixture was heated on a hot plate and stirred using a magnetic stirrer. The flask was connected to a long vertical pipe to provide sufficient length for furfural steam passages. The long tube was connected to a condenser to condense furfural vapor. The reaction was carried out at 100, 110 and 120°C for 30, 60, 90, 120, 150, 180, 210, 240, 270, 300 and 330 min. The collected furfural-water mixture were then extracted by adding 50 ml chloroform. After extraction, two layers were formed, the top layer was rich in water and the bottom layer was rich in furfural and chloroform. The lower layer was distilled at 60-70°C to separate furfural from chloroform. The purified furfural was collected and its volume was recorded.

For comparison, the same procedure was carried out using a 20% sulfuric acid catalyst. The furfural obtained from these two types of catalyst were identified by color assessment, FTIR, and GCMS.

3 RESULTS AND DISCUSSION

3.1. Preliminary Analysis

3.1.1. Preliminary Analysis of Mile-a-Minute Weed

Preliminary analysis of mile-a-minute weed included water content and pentosan content analysis. From the results, mile-a-minute weed has an average moisture of 80% and average pentosan content of 46%. These pentosan level is very close to the levels reported in the literature (Ko et al., 2013; Taslim et al., 2018).

3.1.2. Preliminary Analysis of Roselle Petal Extract

Initial analysis of petal roselle catalyst extract included pH, normality, and acid number. From the

results, the pH was 2.4, normality was 0.15 N, and acid number was 6.93 g/g. For comparison, the 20% sulfuric acid catalyst has pH of 0.2, normality of 2.27 N, and acid number of 222.83 g/g.

3.2. Effect of Reaction Temperature and Reaction Time on Furfural Yield

The effect of reaction temperature and reaction time on furfural yield is shown in Figure 1. In Figure 1, furfural formation catalyzed by roselle petal extract was first observed at 30 min for reaction temperature of 110 and 120°C. While for reaction temperature of 100°C, furfural formation occurred at reaction times above 90 min. However, after 300 min, the furfural yield at 100°C rivaled those of the other temperatures. At 110 and 120°C, evaporation rate of water was greater than furfural formation. Pentosan in mile-a-minute weed was hydrolyzed to pentose under acidic condition by the help of H^+ from roselle petal extract, then pentose dehydration produced furfural as shown in equations (1) and (2). Pentosan hydrolysis requires water while pentose dehydration releases water. If water was evaporated too quickly, hydrolysis will be incomplete and pentose yield decreased. As a result, the furfural yield may also decrease with increasing reaction time and temperature. This causes furfural yield to decrease at 330 min reaction time and reaction temperatures of 110 and 120°C. Thus temperature control is very necessary in this reaction to ensure that these two stages of reaction take place well.

From figure 1, furfural yield produced using roselle petal extract catalyst is still lower than that using sulfuric acid catalyst. This is because the acid number of sulfuric acid is 32 times greater than the acid number of roselle petal extract, which means that H^+ ions in sulfuric acid are more concentrated than H^+ ions in roselle petal extract. The highest furfural yield of 4.8% was obtained at reaction time of 330 min, and reaction temperature of 100°C. The optimum temperature reported by previous researchers was 100°C, both for furfural formation from pentose sugar using formic acid (Kim et al., 2016) and for furfural formation from mile-a-minute weed using organic acid catalysts from bilimbi Taslim et al., 2018).

At constant temperatures, increasing reaction time increases furfural yield due to longer contact times. The use of roselle petal extract in furfural production does not require high temperatures, but requires a long time of around 300 min.

In this study, furfural yield obtained using a 20% sulfuric acid catalyst was up to 6.4%. This yield is

lower than the yield reported by other researcher at 8.3% under similar condition, but using corn cobs as precursor (Shaffeeq et al., 2015).

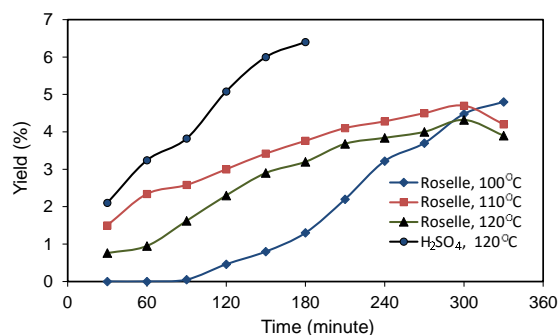


Figure 1: Effect of reaction time on furfural yield at various temperatures

3.3. Furfural Analysis

3.3.1. Identification of Furfural by Colour Assessment

In this study, the qualitative identification of furfural was done using aniline acetate reagent at aniline and acetate ratio of 1:1 (v/v). The change in sample color from clear to red indicates the presence of furfural. In figure 2, the red color is still pale, indicating that furfural formed using a roselle petal extract catalyst was not much.

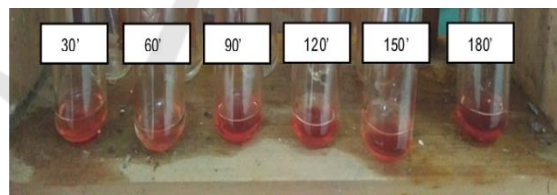


Figure 2: Colour assessment of furfural produced using roselle petal extract catalyst at 120°C, at different reaction time

In figure 3, the darker red color indicates that more furfural was formed using sulfuric acid catalysts. Sample at 180 min (3 h) appears darker, indicating more formation of furfural. As shown in figure 3, all samples became dark red after reaction time of 30 min. This suggests that for sulfuric acid catalyst, a long reaction time is not required. Similar result was also reported in the literature (Taslim et al., 2018).

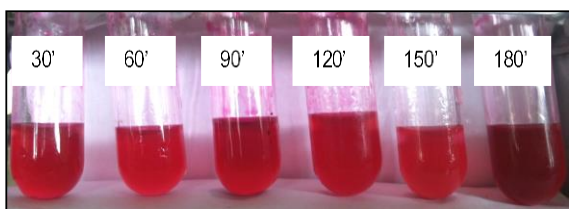


Figure 3: Colour assessment of furfural produced using sulfuric acid catalyst at 120°C, at different reaction time.

3.3.2. FTIR Analysis

The result of furfural analysis using FTIR is shown in figure 4. Based on IR spectra (Figure 4) aldehyde group in furfural was observed as evidenced by C=O stretching vibration (1700-1600 cm^{-1}) and CH aldehydes (2860-2800 cm^{-1}) reflected by the peak at 1674.52 cm^{-1} and 2851.07 cm^{-1} respectively for sulfuric acid catalyst and roselle petal extract catalyst. The appearance of C=C aromatic stretching vibration (1600-1475 cm^{-1}) was evidenced in the area around 1521.45 cm^{-1} . Stretching vibration peak at around 1166.00 on sample using roselle petal extract catalyst indicated C-O-C bonds (1200-1100 cm^{-1}) within the molecular structure of furfural, while for sulfuric acid catalyst, same occurrence was observed at vibration peak of 1176 cm^{-1} . The spectra of the compound produced from mile-a-minute weed hydrolysis was virtually identical to standard vibrations of furfural (Ong and Sashikala, 2007). Therefore, it can be stated that the compound was furfural.

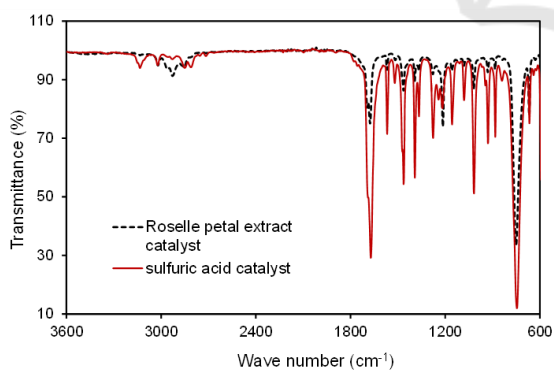


Figure 4: FTIR spectra of furfural produced using roselle petal extract and sulfuric acid catalyst

3.3.3. GCMS Analysis

Figure 5 shows the results of analysis using GCMS. These results confirm that furfural has been formed as a result of mile-a-minute weed ahydrolysis. For the roselle petal extract catalyst, furfural compound

was identified at peak 2 (retention time of 3.37 min) as 2,5 furandione, 3-ethyl-4-methyl. For sulfuric acid catalyst, furfural compound was identified at peak 3 (retention time of 3.28 min) as 2,5 furandione. Furandione belongs to the furfural group, which proves that the samples contained furfural.

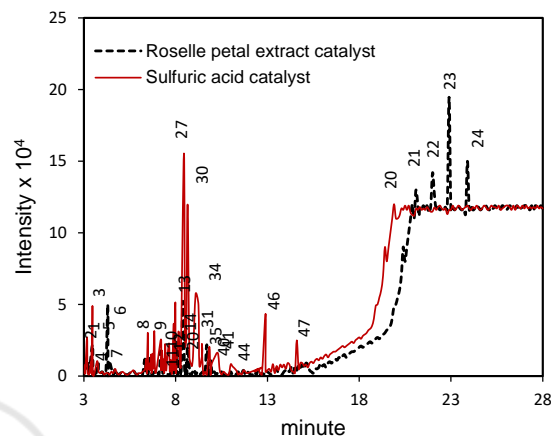


Figure 5: GCMS analysis of furfural produced using roselle petal extract and sulfuric catalyst

4 CONCLUSIONS

Roselle petal extract can be used as a catalyst in furfural synthesis from mile-a-minute weed. The highest furfural yield of 4.8% using the roselle petal extract was obtained at reaction temperature of 100°C and, reaction time of 330 min. This yield is still lower than that using a sulfuric acid catalyst which reached 6.4% in 150 min. Colour assessment, FTIR, and GCMS analysis indicated the presence of furfural as a result of mile-a-minute weed hydrolysis.

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