Potential of lime as a green catalyst in the manufacture of furfural from *Mikania micrantha*

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**Abstract.** An attempt to increase the added value of lime has been done. The use of lime extract as a green catalyst in furfural manufacturing is expected to reduce the burden of pollution, and corrosion problems. This study aimed to evaluate the performance of lime extract as an organic acid catalyst in furfural production from *Mikania micrantha* (MM) through hydrolysis and dehydration and compare it with sulfuric acid catalyst. In this work, 50 g MM and 50 g dry NaCl powder were placed into a three neck flask equipped with a long condenser. The lime extract catalyst was added to the mixture at a ratio of 6:1 (v/w). The reaction temperature was varied from 100–120°C, and the condensed furfural was stored in an erlenmeyer as a function of time (0–330 min). Furfural was separated from water done by adding 50 ml chloroform to form two layers. The lower layer rich in furfural and chloroform was distilled at 70°C to evaporate chloroform. Purified furfural was identified using FTIR and GC-MS. The results obtained confirm that lime extract can be used as a green catalyst in furfural synthesis from MM.

1. **Introduction**

*Mikania micrantha* (MM) is one of invasive plants in the world and considered to be one of the 10 worst weeds. MM is a semi-timber plant originating from Central and South America. MM is spread over several topical regions including Asia, Papua New Guinea, the Indian Ocean islands, Pacific Ocean islands and Florida. To control its growth, physical, chemical, biological and ecological methods can be used. However, because of its fast growth and costly control, there is no effective method to deal with MM growth. Therefore, critical thinking is needed to develop innovative and cost-effective strategies in controlling it [1,2]. One of them is the transformation of lignocellulosic biomass from MM to furfural. MM is a biomass source that has high levels of pentosane (> 50%) so that it can be used as an alternative raw material for furfural production [3].

Lignocellulosic biomass is considered a sustainable raw material because it is easily renewable, abundant and available in nature. This biomass is composed of three main components namely hemicellulose, cellulose and lignin and thus is an efficient carbon source for the production of alternative petroleum chemicals and biofuels. One of the chemical products derived from lignocellulosic biomass is furfural, which can be applied as an additive to gasoline, intermediate chemicals in the manufacturing, plastic, pharmaceutical and agrochemical industries. Furfural production generally goes through two stages of reaction: hydrolysis of biomass containing pentosanes
to pentoses, followed by dehydration of pentose to furfural [4,5]. Both stages require a catalyst to speed up the reaction. The use of catalyst is one of the crucial factors in the conversion of biomass to produce furfural with high yield and selectivity. Inorganic acid catalyst is the type of catalyst most often used in converting lignocellulose to furfural. However, the use of inorganic acid catalysts has serious impacts such as the equipment corrosion, and being not environmentally benign [4,6]. To overcome such problems, the use of organic acid catalysts can be considered [4,5,7]. Plant based organic acid catalysts are environmentally benign (green catalysts). On top of that, they are also renewable. However, the use of organic acids derived from lime (Citrus aurantifolia) has never been reported, whereas lime juice contains citric acid, malic acid, and ascorbic acid [8]. Therefore, this study aimed to evaluate lime extract as an organic acid catalyst in furfural production from Mikania micrantha (MM) through hydrolysis and dehydration and compare it with sulfuric acid catalyst.

2. Materials and Methods

2.1. Materials
MM and lime were obtained from Kampung Durian Medan, Indonesia. Chemicals such as acetic acid, sodium chloride, sulfuric acid, chloroform, aniline was purchased from several local suppliers.

2.2. Preparation of catalyst
Lime was washed with running water to dissolve dirt. It was cut into two parts and then squeezed. The juice was filtered with Whatman paper no. 41. This filtrate was stored in refrigerator at 0℃ [4,5]. Before usage, the pH and acid number of filtrate were analyzed. The pH was measured using a pH meter.

2.3. Preparation of MM powder
The mix of MM stems and leaves was washed with water until clean, and cut into pieces of size ± 1 cm using a knife. It was then dried in an oven at 100℃ for 4 h, crushed in a ball mill, sieved to 70 mesh [4,5]. This MM powder was stored in a plastic bottle, and ready to be used as a furfural precursor. It was analyzed for its pentosane level and moisture content.

2.4. Synthesis of furfural
As much as 50 g MM powder, 50 g NaCl, and 600 ml lime extract were put into a three-neck flask equipped with stirrer, condenser, heater, and thermometer. The initial total volume was set 750 ml by adding distilled water [5]. The reaction was carried out from 0-330 min at 100-120℃. Vapor formed during the reaction was condensed as crude furfural and collected. This crude furfural was extracted with 50 ml chloroform to form 2 layers. The upper layer was rich in water and the lower layer was rich in furfural and chloroform. Furfural and chloroform were separated by distillation at 70℃. The bottom distillation product (furfural) was collected and ready for analysis. The same procedure was repeated, for H₂SO₄ 20 % catalyst as comparison.

3. Results and Discussion

3.1. Preliminary analysis
On initial analysis, average pentosane content in the MM stem and leaf mixture was 53.58%. This result is close to the results in the literature of 56.04% [3]. The mix average water content was 84%. The pH and acid number of lime extract which would be used as an organic acid catalyst was 2.1 and 15.8 mg/g respectively. For the sulfuric acid catalyst, the pH value was 0.21 and the acid number was 200.2 mg/g.
3.2. Effect of reaction time on furfural yield

The reaction time greatly influences furfural formation as in Figure 1. For sulfuric acid catalyst at constant reaction temperature, furfural yield increased with time up to 180 min, then decrease. Increased reaction time allows more contact between reactant molecules and catalyst, leading to higher furfural yield. However, after a certain time, yield decreased due to further reactions such as humin formation [9]. Furfural formation using sulfuric acid catalyst occurred faster than that using lime extract catalyst. In addition, the furfural yield obtained was also higher. This is due to sulfuric acid having lower pH than lime extract as shown in Table 1. Lower pH or higher acid number indicates greater acidity. Sulfuric acid is a stronger acid compared to lime extract. For sulfuric acid catalyst and reaction temperature of 120℃, furfural was detected in 30 min and reached the highest yield of 13.5% in 190 min. For lime extract catalyst and reaction temperature of 120℃ furfural began to be detected after 60 min and reached the highest yield of 9.8% at 300 min then decreased. This decrease in yield is due to furfural degradation to form smaller molecular products and furfural resinification [4].

| Catalyst           | pH   | Acid number (mg/g) | Yield (%) | Operating condition |
|--------------------|------|--------------------|-----------|---------------------|
| Sulfuric acid 20%  | 0.78 | 144.6              | 13.5      | 120℃, 180 min       |
| Lime               | 2.10 | 15.8               | 9.8       | 120℃, 300 min       |

At 80 and 100℃ furfural yield obtained using lime extract catalyst were lower than that at 120℃. In general, the rise in temperature can accelerate collisions between reactant molecules, so that furfural yield increases. At 80℃, collisions between reactant particles are weak, and furfural formation is slow thus the yield reached only 3.3%. At 100℃, collisions between reactant particles are stronger, as a result the yield increased up to 8.1%. The yield obtained from this study is greater than the yield reported by known researchers where they used bilimbi extract and tamarind extract as catalysts with yields around 7.2% [4,5].

3.3. FTIR analysis

The results of furfural IR spectra using either lime extract or sulfuric acid as catalyst are presented in figure 2. Based on FTIR analysis, the aldehyde functional group in furfural is characterized by the presence of C-H stretching vibrations (2900-2700 cm⁻¹) and C=O (1740-1620 cm⁻¹) at peaks of 2862 cm⁻¹ and 1680 cm⁻¹ for both lime extract catalyst and sulfuric acid catalyst. The presence of stretching vibrations of the aromatic C=C group (1620-1560 cm⁻¹) is shown in the area around 1566 cm⁻¹.
For the aromatic C-H group (3060-3010 cm\(^{-1}\)), absorption occurs at 3020 cm\(^{-1}\) and the C=O-C group (1140-1070 cm\(^{-1}\)) is evidenced at vibration peak of 1077 cm\(^{-1}\). These vibration values are very close to those reported by previous researchers [4,5,10]. The standard furfural vibration values are in Table 2.

### Table 2. Vibration of furfural standard

| Functional groups   | Absorption range (cm\(^{-1}\)) |
|---------------------|---------------------------------|
| Aromatic C-H        | 3060-3010                       |
| Aldehyde C-H        | 2900-2700                       |
| Aldehyde C=O        | 1740-1620                       |
| Aromatic C=C        | 1620-1560                       |
| C-O-C               | 1140-1070                       |

3.4. GCMS analysis

The GCMS results on furfural using lime extract catalyst is in figure 3 and table 3, while for sulfuric acid catalyst is in figure 4 and table 4. It is observable that furfural compounds were formed from MM hydrolysis.

![Figure 2. FTIR analysis of furfural using lime extract and sulfuric acid as catalyst](image)

**Figure 2.** FTIR analysis of furfural using lime extract and sulfuric acid as catalyst

By comparing the vibrational values obtained from this study with the standard vibrational values of furfural in the literature [11], it can be confirmed that the compound obtained was furfural compound.

![Figure 3. GCMS analysis of furfural produced using lime extract as catalyst](image)

**Figure 3.** GCMS analysis of furfural produced using lime extract as catalyst
Table 3. GCMS data of furfural produced using lime extract as catalyst

| Peak | Retention time | Area    | Area % | Name                          |
|------|----------------|---------|--------|-------------------------------|
| 1    | 3.193          | 2346198 | 1.63   | Methanamine                   |
| 2    | 3.267          | 10636864| 7.40   | -                             |
| 3    | 4.275          | 2426121 | 1.69   | -                             |
| 4    | 4.961          | 8159137 | 5.68   | Benzene                       |
| 5    | 5.810          | 3498380 | 2.43   | Benzene                       |
| 6    | 7.397          | 3224521 | 2.24   | 2-Furancarboxaldehyde (furfural) |
| 7    | 7.553          | 30983732| 21.55  | 2-Furancarboxaldehyde (furfural) |
| 8    | 7.757          | 3772300 | 2.62   | 2-Furancarboxaldehyde (furfural) |
| 9    | 7.902          | 2186357 | 1.52   | Cyclohexene                   |
| 10   | 8.099          | 3985781 | 2.77   | Calarene                      |
| 11   | 8.253          | 3235287 | 2.25   | Ethanone,                     |
| 12   | 8.393          | 15893182| 11.05  | Benzyl chloride               |
| 13   | 9.344          | 2149649 | 1.50   | (R)-(−)-14-Methyl-8-hexadecyn-1-ol |
| 14   | 9.450          | 4692728 | 32.64  | 2-Furancarboxaldehyde (furfural) |
| 15   | 11.498         | 2282514 | 1.59   | beta-Maaliene                 |
| 16   | 16.102         | 2062797 | 1.43   | Cyclohexane                   |
| Total|                | 143770098| 100.00 |                               |

In table 3, the percentage of area for furfural (2-furancarboxaldehyde) compounds is 59.05%. This is the furfural concentration obtained by MM hydrolysis using lime extract catalyst. Furfural compounds are identified each at peak 6, 7, 8 and 14 at retention time of 7.397; 7.533; 7.757 and 9.450 min respectively. Meanwhile, furfural obtained using sulfuric acid catalyst is identified at peak 1 in figure 4 at 8.975 min retention time.

![Figure 4](image)

Figure 4. GCMS analysis of furfural produced using sulfuric acid as catalyst

In table 4, furfural obtained using sulfuric acid catalyst reached 100%. This result is higher than furfural concentration using lime extract catalyst. However, from an environmental perspective, the use of lime extract as a green catalyst is very promising.

Table 4. GCMS data of furfural produced using sulfuric acid as catalyst

| Peak | Retention Time | Area    | Area % | Name       |
|------|----------------|---------|--------|------------|
| 1    | 8.975          | 34964012| 100    | Furfural   |
4. Conclusion
Evaluation of lime extract as a green catalyst in furfural synthesis from MM have been successfully carried out. The best furfural yield of 9.8% was achieved at reaction time of 300 min and reaction temperature of 120°C. Analysis by FTIR indicated the presence of C-H and C = O aldehyde functional groups at wavenumber of 2862 and 1680 cm\(^{-1}\). GCMS analysis further confirmed the presence of furfural compounds, observed at 7.397; 7.544; 7.757 and 7.584 min retention times with 59.05% area for lime extract catalyst, and 8.975 min retention time with 100% area for sulfuric acid catalyst. The results obtained from this study confirm that lime extract can be used as a green catalyst in furfural production from MM.

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