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Catalytic Pyrolysis of Impregnated Citronella Biomass Using Boric Acid to Produce Furfural

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Abstract

Citronella oil residue is one of the abundant lignocellulosic biomass wastes which has the potential to be converted into useful products through pyrolysis process. One of the useful products that can be produced from this residue is furfural compounds. Previous research has shown that furfural can be produced through the pyrolysis mechanism of lignocellulosic biomass. However, the amount of furfural compounds obtained is still relatively low. Therefore, in this study a research is carried out regarding catalytic pyrolysis process through impregnation method of biomass using boric acid as catalyst to produce furfural compounds with variation of catalyst ratio (0, 0.1, 0.3) and pyrolysis temperature (450 ºC, 500 ºC, 550 ºC) to determine the optimal conditions for furfural production. Using GC-MS analysis, results were obtained which indicated the role of boric acid impregnation in increasing and maximizing the yield of furfural products. The optimal conditions for furfural production were obtained at a pyrolysis temperature of 550 ºC and the use of a boric acid catalyst with a ratio of 0.1, whereby the yield of furfural compounds by GCMS analysis was 19.17% area.

Keywords: *biomass; catalytic pyrolysis; furfural; boric acid; GC-MS*

Introduction

Currently acid hydrolysis of agro-based biomass is used industrially for producing furfural, but there are some disadvantages, such as environmental problems, low yield, and poor furfural selectivity that caused furfural production plant closure (Dashtban et al., 2012). Alternatively, furfural can be produced from cellulose and hemicellulose by pyrolyzing this biomass with addition of impregnation method.

Cellulose and hemicellulose itself can be found in lignocellulose biomass. One of the potential materials that can be used as the feed is citronella plant. Citronella has a lignin permanganate content of 11% and a holocellulose fraction of 58% (Rolz et al., 1986). Holocellulose itself is the total fraction of polysaccharides that make up plant cell walls consisting of cellulose and hemicellulose (Nugroho et al., 2013). Citronella can be obtained from the residue of citronella essential oil, whereas the growth of citronella oil exports reached quite high values, ranging from 9-10% (Sulaswatty et al., 2019). This value encourages an increase in citronella oil production, on the other hand an increase in citronella oil production causes a high amount of residue which is a by-product of citronella oil production. The high amount residue is a problem because there is no optimal utilization of the residue from the steam distillation of citronella oil. Based on that fact, this research aims to take advantage of citronella oil residue by testing its usability, using citronella as biomass feed, to produce furfural using catalytic pyrolysis mechanism.

In order to produce furfural, this research carried out a catalytic pyrolysis process in the presence of acid catalyst impregnation method, namely boric acid, impregnated on citronella biomass. Impregnation process is a process of completely and thoroughly saturating a solid substance. Impregnation was carried out on citronella biomass using boric acid with the aim of optimizing the cracking process to increase furfural yield.

The pyrolysis process is a biomass conversion process using high temperatures in conditions without using oxygen (Chen et al., 2019). The products that can be produced through the pyrolysis process are carbon-rich solid products, namely char, incondensable gas products (CO_2, CO, H_2, and CH_4), and condensable gas products which become bio-oil containing organic compounds such as aldehydes, ketones, furans, phenols, and others (Collard et al., 2015).

The addition of a catalyst serves to accelerate the reaction rate by reducing the activation energy to obtain the desired product. However, the ratio of the acid catalyst also needs to be considered because it is feared that the furfural compounds formed will break down so that the resulting furfural compounds will be smaller.

The acid catalyst that can be used in this study is boric acid catalyst. The use of boric acid aims to increase the formation of furfural in the pyrolysis process. Boric acid changes the chemical pathway of cellulose pyrolysis, in which hydrogen ions are present, apart from the complexation reaction between boric acid and carboxyl groups, which become catalysts in the depolymerization stage of cellulose (Zhang et al., 2020). Then the complexation of the borate

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structure also has a role in preventing the formation of levoglucosan, where the B-O-C bond replaces the hydroxyl at C6 or carbon in another position which causes limitation of the acetal reaction in the formation of levoglucosan (Zhang et al., 2020). Through this mechanism, the opening and rearrangement of the glucose ring occurs to form a new furan structure in the presence of borate (Zhang et al., 2020).

In this study, pyrolysis process will be carried out using variations in pyrolysis temperature and the presence of a catalyst for the process carried out to obtain the highest possible conversion of the reaction and the target furfural compound.

Research Methods

Boric acid solution is prepared by dissolving the acid in water at a temperature of around 90 ^oC. Boric acid solution is added into the beaker until all of the biomass is submerged according to the specified catalyst mass ratio. Biomass added catalyst mixture of biomass and sample solution is mixed to make it evenly distributed. The mixture is dried using an oven at a temperature of around 105 °C for approximately 6 hours. The following is a research equipment scheme presented in Figure 1, research conditions presented in Table 1.

Tabel 1. Research Conditions.

Feed Mass	15-50 gram
Temperature	450-550 °C
Nitrogen Pressure	1 bar
Nitrogen Flow Rate	150 ml/minute
Catalyst Mass Ratio	0-0.3

The temperature is set by taking fast pyrolysis conditions into the consideration, whereas the fast pyrolysis temperature is set about 500 ^oC (Bridgwater, 2012).

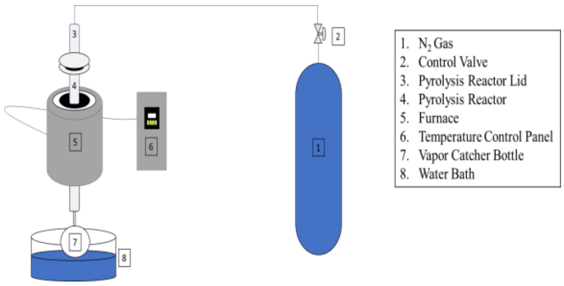

Figure 1. Research Equipment Scheme.

The pyrolysis process begins with the preparations of citronella biomass as the feed, then turning on the furnace to adjust the temperature according to the pyrolysis temperature variations also there is purging process (using nitrogen) to minimize the oxygen. The feed is set about 31.5 grams and the samples are taken after 60 minutes of operation.

Results and Discussion

In the citronella pyrolysis process, steam is produced which can be condensed into bio-oil and the remaining feed char which is present after the pyrolysis process takes place. The results of the pyrolysis are shown in Figure 2.

Figure 2. Pyrolysis Products.

 ISSN 1693-4393

Figure 3. Pyrolysis Bio-oil Products(Temperature in Order: 450 ºC, 500 ºC, 550 ºC).

The optimum temperature can be determined by considering the product to be produced, namely furfural, where furfural is produced through pyrolysis of cellulose and partly through pyrolysis of hemicellulose. To be able to crack the cellulose structure, a temperature greater than 300 °C is needed, while to crack the hemicellulose structure, a temperature greater than 280 °C is required (Wang et al., 2017).

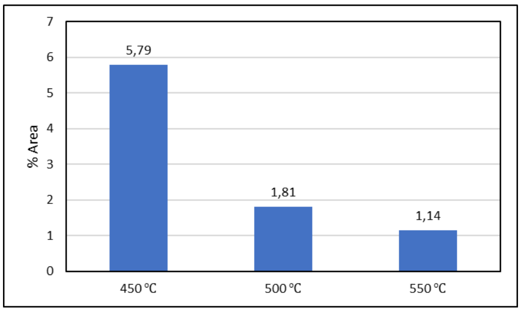

Figure 4. Furfural Yield Graph of Citronella Pyrolysis.

In citronella feed without catalyst, it was found that the furfural compound formed decreased with increasing pyrolysis temperature. Based on visual observations of the results obtained, the resulting bio-oil has a different color whereby lower pyrolysis temperature of citronella resulting browner and more concentrated color of the produced bio-oil. It indicates the presence of more furfural and non-oxygenate compounds, this can occur because furfural has a blackish brown color when exposed to oxygen from the air (Eseyin et al., 2015). This is thought to occur due to an overcracking mechanism which causes the formation of new compounds due to the re-cracking of pyrolysis products after being formed under higher temperature conditions (Hanif et al., 2016).

In the citronella feed in the presence of boric acid catalyst with a mass ratio of 0.1, it was found that the furfural compounds formed increased with increasing pyrolysis temperature.

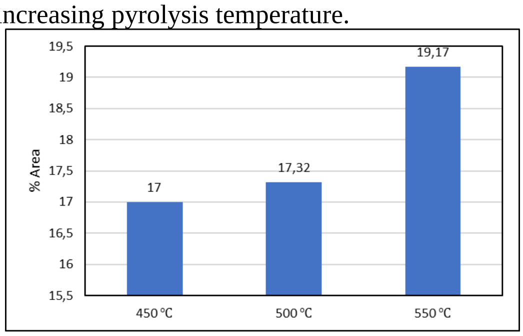

Figure 5. Furfural Yield Graph of Citronella Catalytic Pyrolysis.

It can be seen that there are differences in the effect of temperature on the feed with a catalyst and without a boric acid catalyst. With the addition of boric acid, there is an increase in the temperature of the thermal degradation of lignocellulosic materials because it is believed that boric acid turns into a B_2O_3 film which isolates oxygen and heat where the mechanism is believed to be a way of boric acid in its role of inducing fire inhibition (Zhang et al., 2020).

With the addition of a catalyst to the biomass feed, a different color is obtained from the bio-oil produced. Based on visual observations of the results obtained, the resulting bio-oil has a different color whereby higher catalyst ratio

ISSN 1693-4393

in pyrolysis of citronella resulting browner and more concentrated color of the produced bio-oil. This indicates the presence of more furfural and non-oxygenate compounds, this can occur because furfural has a blackish brown color when exposed to oxygen from the air (Eseyin et al., 2015).

Figure 6. Catalytic Pyrolysis Bio-oil Products.

In citronella feed with various catalyst ratios, it can be seen that the furfural content is highest in the variation ratio of 0.1. Based on these results it can be seen that the greater the amount of boric acid catalyst added does not guarantee an increase in furfural yield.

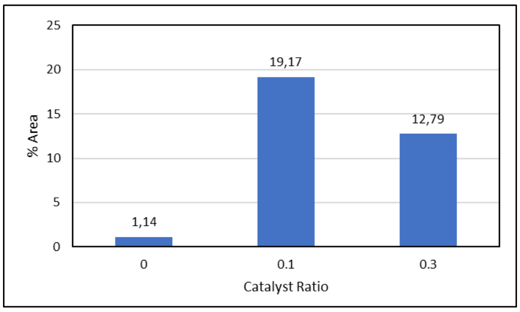

Figure 7. Furfural Yield Graph of Citronella Catalytic Pyrolysis at The Optimum Temperature of 550 ^oC.

It is suspected that the factor affecting the decrease in furfural yield at a higher boric acid catalyst ratio is competition between the formation of furfural compounds and other compounds, such as heptane and acetic acid whose content increases with the addition of boric acid catalyst.

By using microcrystalline avicel ph102 or pure cellulose as a reference material in the pyrolysis process, the role of cellulose pyrolysis in furfural recovery can be determined. The comparison between pure cellulose and citronella furfural yield can be seen in Figure 8.

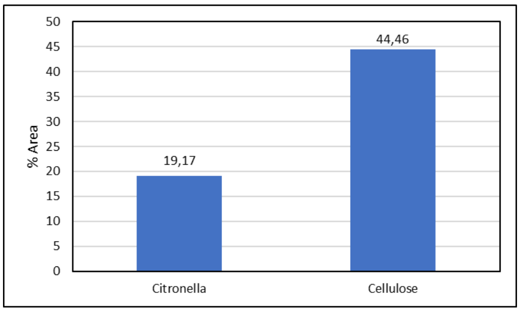

Figure 8. Furfural Yield Graph of Citronella and Cellulose Catalytic Pyrolysis at The Optimum Temperature of 550 ^oC.

Based on the results obtained in Figure 8, it can be seen that the yield of furfural obtained from pure cellulose is greater than that obtained from citronella, so it can be concluded that most of the furfural is produced from the pyrolysis of cellulose while the rest is produced from the pyrolysis of other components such as hemicellulose.

ISSN 1693-4393

Conclusion

It is proven that citronella biomass can be utilized to produce furfural compounds through the mechanism of cracking lignocellulosic biomass by means of a pyrolysis process, this is evidenced by the production of furfural compounds in citronella pyrolysis products. The optimum condition for pyrolysis of citronella to produce furfural compounds is at a temperature of 550 ^{o}C with a boric acid catalyst ratio of 0.1, where the gain of furfural compounds detected on the GCMS chromatogram is 19.17% area. This proves the role of acid catalyst impregnation in increasing the recovery furfural compounds.

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