

The Impacts of HCl Concentration and Length of Time to Mesocarp in Producing of Bioethanol

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Abstract

Studies about renewable energy are evolved continuously to decrease the needs of fuel oils that were diminished. One of the alternative energy sources that can be evolved is bioethanol. Mesocarp is farming and trading waste of Cocos Nucifera (Coconut) that contains 40% lignin, 44.4% cellulose, and 15% hemicellulose. Delignification is a process of removing lignin from the materials thus it can produce the high purity of cellulose. Thereby, this study was done for figuring out the impact of HCl concentration and length of time to the decreased lignin content and the quality of bioethanol. The points of impacts that being focused on were 1, 2, and 3M HCl concentration, whereas the points of length of time impacts were about 60, 90, 120, 150, and 180 minutes. The decreased lignin content that was obtained is about 18.5% and the finest bioethanol is 97.38 %, 15°C for flash point, 3.8402 cPs for viscosity, and 0.8252 g/cm³ for density from delignification using 3M HCl for about 150 minutes. The higher of HCl concentration to delignification, the greater quality of bioethanol is produced, therefore can be applied to alternative fuel oils for vehicle.

Keywords: Renewable energy, bioethanol, delignification, HCl, mesocarp

Abstrak (Indonesian)

Penelitian mengenai energi terbarukan terus dikembangkan untuk mengurangi ketergantungan terhadap bahan bakar minyak yang ketersediaannya terus berkurang. Saat ini produk energi alternatif yang berpeluang dikembangkan adalah bioetanol. Sabut kelapa muda merupakan limbah dari perkebunan dan perdagangan buah kelapa muda yang diketahui mengandung senyawa lignin sebesar 40%, selulosa 44,4%, dan hemiselulosa 15%. Proses delignifikasi merupakan proses penghilangan lignin dari bahan, sehingga hasil dari proses ini sudah berupa selulosa dengan kemurnian yang cukup tinggi. Oleh karena itu, penelitian ini dilakukan untuk melihat pengaruh konsentrasi HCl dan pengaruh waktu dalam proses delignifikasi terhadap penurunan kandungan lignin dan kualitas bioetanol yang dihasilkan. Pengaruh konsentasi HCl yang diamati adalah 1, 2, dan 3 M sedangkan pengaruh waktu yang diamati adalah 60, 90, 120, 150, dan 180 menit. Didapatkan penurunan kandungan lignin tebanyak sebesar 18,5% dan karakteristik bioetanol terbaik yang dihasilkan sebesar 97,38%, flash point 15°C, viskositas 3,8402 cPs, dan densitas 0,8252 gr/cm³ dari proses delignifikasi menggunakan larutan HCl 3M dengan lama proses delignifikasi 150 menit. Semakin besar konsentrasi larutan HCl pada proses delignifikasi, maka semakin baik kualitas bioetanol yang dihasilkan sehingga diharapkan dapat diaplikasikan sebagai bahan bakar alternatif kendaraan bermotor.

Kata Kunci: Energi alternatif, bioetanol, proses delignifikasi, HCl, sabut kelapa muda

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INTRODUCTION

Biomass is a renewable organic substance that comes from plants or animals, residues from industrial, agricultural, harvesting, forestry, farming, and fishery. Numerous bioenergy source can be produced from biomass [1]. As a state that has more areas in agricultural, farming, and forestry, there are plenty of nutshell, rice husk, wood sawdust, mesocarp and palm shell that are not utilized (it only burned, discarded, etc.), hence it caused environmental contamination and harmed the ecological balance [2]. One of government approaches is to obligate the uses of biofuels [3]. Currently, the uses of materials that contained crude fiber within its high carbohydrate are being made intensively, which can be cultivated to be bioethanol. For instances, timber root, pineapple peel, banana hump, siwalan peel residues, corn stalks and more.

Bioethanol is one of alternative fuel oils that can be mixed with gasoline to use in combustion engine without any modification. One excess of using bioethanol is that bioethanol is resemble with gasoline in utilizing, storing, and conveying [4]. In addition to that, it also can renew, easily dissolve, and it can be able to use as oxygenating fuel oils, thereby it can reduce the exhaust emission that is environmental-friendly. As is known, the energy needs are more than its increasing population. Increasing population means that enhancement the energy needs. Advanced and utilized technology need its energy, like electricity and fuel oils [5].

Bioethanol is accomplished by delignification, hydrolysis, and distillation. The processes are done for getting glucose. Glucose is done by 2 stages, namely delignification and hydrolysis. Cellulose will be produced in delignification. Following this, cellulose will be in the further process to be glucose namely hydrolysis. Lignin is a part of changing to solid of plants, like corncobs, leatherette paper, seeds, the coarse fiber, root, stem, and leaf. Lignin contains complex substance and a combination two or more different chemical elements, namely carbon, hydrogen, and oxygen. Additionally, another part of peat is cellulose. Cellulose is poly saccharide that contains glucose in it. Lignin separating and removing process out of its cellulose fiber called delignification or pulping. There are three methods of lignin separating process, namely, mechanism means, chemical means, and semi chemical means [6].

There are two methods that is in delignification, acidic and alkaline process. Delignification has three stages i.e., initial, main, and residual [7]. Delignification can be done by thermal, chemical, and biological basis.

Therefore, cellulose and hemicellulose substrate will be convenient to access. Despite every basis can reduce the lignin content, physical and biological are not more effective than chemical [8]. Mechanical, alkaline, and acidic methods are often used in determining lignin content in delignification [9]. Delignification is done for altering or undermining the structure of constituent components in biomass hence facilitating the enzyme to hydrolyze to glucose monomers. Delignification points to dissolving and separating process to one or more components of biomass thus materials bond will have more ranging and facilitates chemical or even biological structure to decompose it. The ideal catalyst sums and range of temperature will produce yield and the quality of hydrocarbon that in accordance to decree of General Directorate Oil and Gas [10].

This research is implied to diminish the waste of *Cocos Nucifera* due to its mesocarp is one of lignocellulose of biomass that contained lignin (35.4%), cellulose (43.44%), pectin (3%), hemicellulose (10.25%) and ash (2.22%). Lignin is a lead content of its fiber that is rigid and prevents the cellulose damaging in degradation. By that metric, mesocarp has the potential to be converted to ethanol [11]. The mesocarp waste is the one that can be used for deriving its lignin. Mesocarp has 33% lignin. Cellulose content in mesocarp can be hydrolyzed enzymatically after the initial treatment. The initial treatment is called delignification thus the hydrolysis process will not be constrained thereby cellulose will be hydrolyses to glucose [12]. Safaria [13] stated that the cellulose in mesocarp can be utilized to produce glucose in hydrolysis. Biomass that contained hemicellulose will be the fine bioethanol without interfering the dietary requirements. The crude fiber of bagasse contains cellulose (21% - 40%), lignin (15% - 47%), and hemicellulose (12% - 27%). The work of Cabral, et al. [14] found that 1gr glucose has 0.511% ethanol in it considered the theory of Gay-Lussac. The finding showed the feasibility to use mesocarp as the raw materials using in bioethanol making.

There were a lot of research that using lignocellulose biomass as the raw materials but less researches were focused on delignification in bio conversion of lignocellulose residues went to bioethanol. For that reason, utilizing mesocarp as the alternative energy source is one probability to do, this study figured out the part of delignification in hydrolysis and fermentation as the sets in producing bioethanol. In using mesocarp as the materials to produce bioethanol, the lignin content that is in mesocarp needs to be removed. Nonetheless,

delignification using mesocarp as the materials are not yet widely done. Therefore, this study was done for figuring out the impacts of length of time, HCl concentration in delignification pre-treatment. Thus, it can produce the fine bioethanol.

MATERIALS AND METHODS

Materials

The materials and instruments that used for this study are:

- The materials: Mesocarp, distilled water, *Saccharomyces cerevisiae*, HCl, NaOH, char, and calcium hydroxide.
- The instruments: Measuring pipette, chemical filter, rubber bulb, beaker glass, analytical balance, spatula, funnel short, pH meter, delignification instrument, fermentation instrument, and distillation instrument.

The instruments manufactured to study delignification. As is shown in Figure 1, below is the instrument for delignification in producing bioethanol.

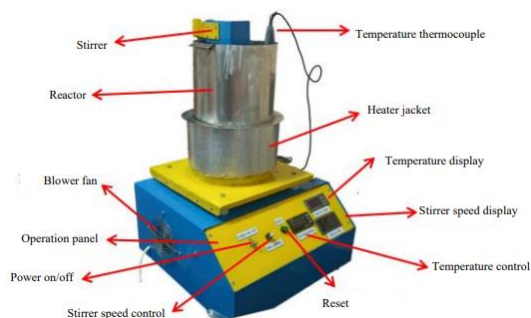


Figure 1. Delignification Instrument

The flowchart of research can be seen in Figure 2:

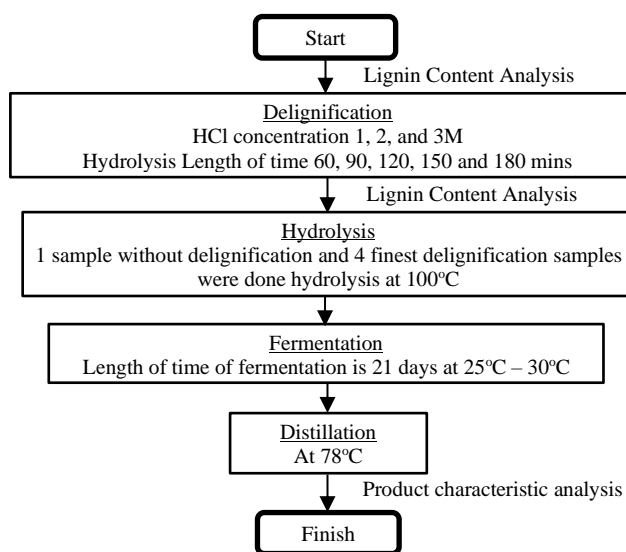


Figure 2. Research Design Flowchart

This part should contain sufficient detail so that all procedures can be repeated. It can be divided into subsections if several methods are described. Heading and sub-headings can be used up to 3 levels. Chemicals grade and specification should be stated. Instruments used in the research should be also described its operational condition.

Methods

According to R. A. Mukti, et al. [15], K. Nadliroh, et al. [16], dan A. M. Jannah, et al. [17], stages that used for this research are raw materials preparation, delignification, hydrolysis, fermentation, distillation, and analysis processes.

- Preparation and Delignification
 - The wastes of mesocarp that are not used were retrieved.
 - The mesocarp separating from its shell was peeled and refined to crumb and dehydrated in oven.
 - The sample was retrieved for lignin content analysis.
 - The crumb was measured for 1000g.
 - HCl 1M was added for 2000 mL.
 - The materials were heated and stirred for 60 minutes at 100°C.
 - The residue was sieved and taken, rinsed with distilled water, and dehydrated in oven.
 - The sample was taken for lignin content analysis.
 - HCl 2 and 3M were conducted with the sort lengths of time 90, 120, 150, and 180 minutes.
- Hydrolysis
 - The sample (mesocarp) was taken after delignification, sieved, and taken the residue and rinsed with distilled water
 - NaOH was added to pH 4 and heated at 100°C with covering the reactor and stirred for 1 hour.
 - It was refrigerated to room temperature (25–30°C).
- Fermentation
 - 300 g *Saccharomyces cerevisiae*, 100 g char, and 100gr slaked lime were added.
 - It was done fermentation for 21 days and was maintained pH 4-5 and temperature 25–30°C.
- Distillation
 - Fermented was put into reactor.
 - Distillation was done for separating bioethanol from the water after fermentation at 78°C.

- Observing was done for 4 times hence getting the finest purity of bioethanol.
- Fermented was taken for doing the characteristic product analysis.

Data Analysis

Lignin content analysis was conducted in Energy Laboratory in Politeknik Negeri Sriwijaya. Delignification of mesocarp wastes was used acidic initial treatment namely HCl using sorts of concentration of 1, 2, and 3M, along with that length of time for 60, 90, 120, 150, and 180 minutes. For figuring out the lignin content, it used Klason method [18]. Klason method is a method of analysing lignin in quantitative basis. Separated lignin in acidic hydrolysis method is called for Klason lignin.

The waste crumbs of mesocarp that done for the process were computed to find out the lignocellulose content using the following equation:

$$\text{Lignin (\%)} = \frac{(b-c)}{a} \times 100\% \quad (1)$$

Where:

a = Initial dry weight of mesocarp waste

b = Dry weight of residue heated to heated water

c = Dry weight of final residue

There were numerous of analyses done for this research:

a. Fermented Analysis

This analysis was done for figuring out the lignin content prior and after delignification. This analysis was done by using Klason SNI-0492:2008 Method.

b. Characteristic Product Analysis

One sample of raw materials and four finest samples of materials using the sorts of HCl concentration and length of time of delignification were used for this analysis. Analyses that were implemented to the products were bioethanol content, flash point, viscosity, and density.

RESULTS AND DISCUSSION

As shown in Figure 3, there are the decreasing lignin content in mesocarp after delignification for 1M HCl concentration and sorts of lengths of time (60, 90, 120, 150, and 180 minutes). There is a sharp reduction of lignin content hence delignification pre-treatment using HCl. The length of time of delignification it was computed by Klason Method. The higher HCl concentration used, the more molecules were able to split the lignin. Permatasari, et al. [19] and Anggorowati, et al. [20], stated that the decreasing the lignin content could have more reactive cellulose than hydrolyze.

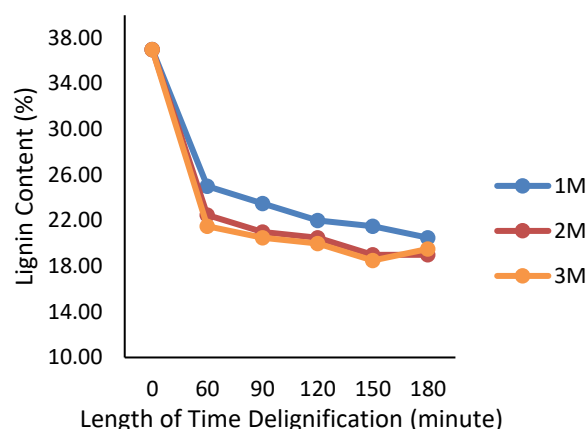


Figure 3. The Decrease of lignin content after delignification

Pre-treatment was done for conditioning the lignocellulose both in its structure and in size. Damaged structural of crystal facilitate cellulose to biodegrade to glucose [20]. There is a visually change having in this process, the amount of the sample was diminished and there is a physically change, the shade of mesocarp was turned to another. This occurred because the lignin content has vanished thus obtained the cellulose that used for saccharification and fermentation.

In this process, it was used mesocarp as the raw materials to produce bioethanol by utilizing the delignification process. Bioethanol that was in distillation before, has analyzed to figure out the ethanol content. Ethanol content was affected by HCl concentration and length of time of delignification that as can be seen in Figure 4.

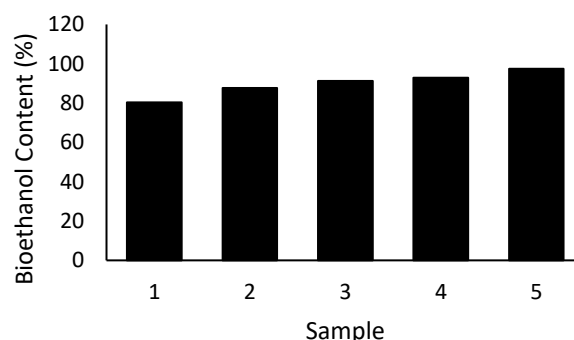


Figure 4. Ethanol Content

The highest ethanol content is 97.38% in sample 5, it is the delignification yield using HCl 3 M for 150 minutes. Whereas the lowest ethanol content is 80.34% in sample 1, it is the raw materials without having delignification. It claimed that delignification was affected to the purity of bioethanol because of the

decreased lignin that can interfere the fermentation. R. A. Mukti, et al. [15] has drawn attention to the fact that the one bioethanol that was produced is 95% because of having only the fermentation without having delignification. The previous research was not complied with the standard of bioethanol content, which was still under 99.5% for the grade of fuel oils based on Indonesian National Standard (SNI).

In this process, it was used mesocarp as the raw materials to produce bioethanol by utilizing the delignification process. Bioethanol that was in distillation before analyzed to figure out flash point value. Flash point was affected by HCl concentration and length of time of delignification that as can be seen in Figure 5.

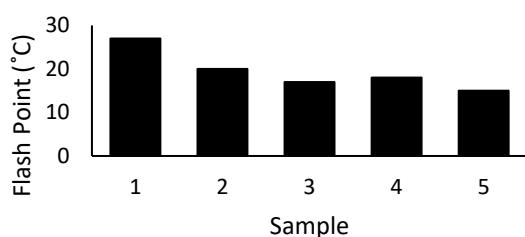


Figure 5. Flash Point

The highest flash point is at 27°C in sample 1 and the lowest flash point is at 15°C in sample 5. It claimed that delignification was affected to the yield of bioethanol that is flammable than the one that was not having delignification. Flash point will be less because of the increased bioethanol content thus the density will be less led to the fuel oils vaporized.

In this process, it was used mesocarp as the raw materials to produce bioethanol by utilizing the delignification process. Bioethanol that was in distillation before analyzed to figure out viscosity value. Viscosity was affected by HCl concentration and length of time of delignification that as can be seen in Figure 6.

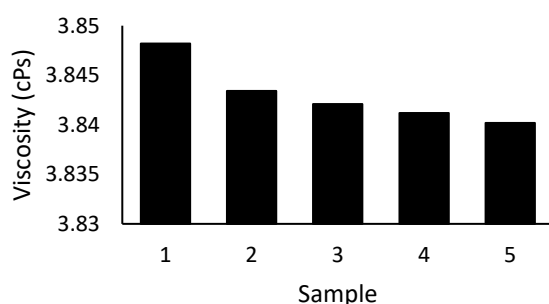


Figure 6. Viscosity of Bioethanol

The highest viscosity is 3.8482 cPs in sample 1 and the lowest viscosity is at 3.8402 cPs in sample 5.

The highest viscosity was affected by the density of bioethanol thus it was affected to the injection pressure of bioethanol [21]. It claimed that delignification can affect to viscosity of bioethanol due to lower viscosity, greater the quality of bioethanol.

In this process, it was used mesocarp as the raw materials to produce bioethanol by utilizing the delignification process. Bioethanol that was in distillation before analyzed to figure out density value. Density was affected by HCl concentration and length of time of delignification that as can be seen in Figure 7.

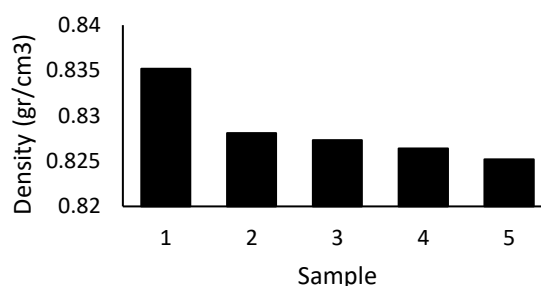


Figure 7. Density of Bioethanol

The highest density is 0.8352 gr/cm³ in sample 1 and the lowest density is 0.8252 gr/cm³ in sample 5. While this was still relatively high above the standard of the density of purity bioethanol, it claimed that delignification affects the mesocarp. This can be inferred that yield of bioethanol of mesocarp can be in flames and can be used as fuel oils and mixed with other fuel oils namely premium/pertalite.

CONCLUSION

From the results, it may be concluded that delignification was implemented to decrease the lignin of mesocarp as the raw materials using HCl as the acidic pre-treatment. The highest lignin content is 18.5% can be degraded because of delignification using 3M HCl for 150 minutes. Delignification is necessary to do in this process due to greater materials can be obtained than the materials without having delignification. The bioethanol characteristic using mesocarp are 97.38% for the content, 15°C for flash point, 3.8402 cPs for viscosity, and 0.8252 gr/cm³ for density. There is continuing need for the research. Further testing should be focused on dewatering process in the oven due to other materials that were still in the same oven at that moment, thereby the greater quality of the result will be obtained. It may contaminate other materials. Following this, calculations, and studies of the yield of bioethanol should be considered due to the yield that remained the least and has not yet fulfilled the standard (SNI).

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