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Lignocellulosic Conversion of Oil Palm Frond for Bio-ethanol

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Abstract

Alternatives for energy resources such as petroleum are highly in demand nowadays. One of the more appealing substitutes for fossil fuels are ethanol, which is produced through the fermentation of sugars that could be fragmented from lignocellulosic materials of any plants. Being one of the biggest producers of palm oil in the world, Malaysia are a natural candidate to provide alternative fuels from the conversion of palm oil agricultural waste to bio-ethanol. As for this study, the waste material from the palm oil industry, which is the oil palm frond (OPF), were converted into ethanol via fragmentation and fermentation. Through a sequential two-stage pre-treatment process, the mechanically pulverized lignocellulosic materials underwent two different chemical pre-treatments which includes an alkaline and acidic hydrolysis to break the fragmented cellulose into glucose. The glucose is the final form of monosaccharide that can readily be converted to alcohol via fermentation using Saccharomyces cerevisiae or yeast. The presence of alcohol was determined via infrared absorption frequency using the Fourier Transform Infrared (FTIR) Spectroscopy to identify the functional group, meanwhile the alcohol yield were determined through the specific gravity of the solution. The result shows that the fragmented fermentation process successfully produces alcohol through the analysis of the infrared absorption frequency via FTIR which indicates the presence of peak at 3200 - 3600 cm⁻¹, confirming the presence of alcohol. The specific gravity of the samples determined the alcohol by volume percentage of 6.9%, indicating the agricultural residue OPF as a viable renewable resource for the production of the equally renewable fossil fuel alternative, which is bio-ethanol.

Keywords: ethanol, fermentation, biomass, oil palm frond, lignocellulose

Introduction

Biofuel is a renewable energy source obtained from natural resources, which is a highly recommended alternative for fossil fuel. Contrary to gasoline production that requirese derivation from crude fossil fuel, bio-ethanol can be synthesized from plants through fermentation process (Phalan, 2009). According to Nigam (2010), starchy plants such as corn and sugar cane can be converted into ethanol through a one-stage conversion process of sugar, whereas, for the lignocellulosic residues which uses agricultural waste,

a two-stage procedure is required, consists of the conversion of cellulose to sugar and sugar to ethanol.

The efficacy of lignocellulosic biomass conversion into bio-ethanol has increased due to the highly-abundant residues, consequently preserving the price of food commodity. Numerous research has been done on the conversion of bio-ethanol from biomass, such as water hyacinth (Das *et al.*, 2016), empty fruit bunch (EFB) (Cheng *et al.*, 2007), corn cobs (Lima *et al.*, 2002) and oil palm trunk (OPT) (Lim, 1992).

The abundance sources of oil palm-based biomass provide an impulsion for the bioethanol industry. In Malaysia, there are over 4.3 million hectares of oil palm plantation which generates an approximately 90 million MT of renewable biomass (i.e. trunks, fronds, shells, and empty fruit bunch) in each and every single year (Wan *et al.*, 2010). A great example for the production of bio-ethanol from oil palm biomass is the production from EFB. Although yielding only a small significant volume of ethanol, it shows a promising future for the biofuel production as it utilizes residues (Cheng *et al.*, 2007). Development and research should also be done to the other abundant oil palm biomass, especially oil palm frond, in which, has a higher potential due to the higher holocellulose content.

Oil palm fronds (OPF) meanwhile proves to be one of the more reliable agricultural biomass due to the estimated availability of fronds during every pruning of about 10.4 tonnes, giving an average of 6.97 million tonnes per year, which represents about 7.7% of the total 90 million MT of renewable biomass generated from the oil palm industry. Moreover, it was estimated an average of 54.43 million tonnes per year of oil palm fronds will be available during the replanting process in the years of 2007 – 2020, giving a more stable proof of the continuous supply (Anon, 2009). Content-wise, OPT are potentially one of the best holocellulose source, with an estimated of 80% from the overall composition (Hamid, 2008). As for this study, the OPT were chosen to be the raw material for the two-stage bio-conversion to obtain bio-ethanol.

Materials and Methods

Preparation of Raw Material

Oil palm frond (OPF) was freshly obtained from surrounding oil palm plantation in Kota Kinabalu, Sabah. The samples were divided to two; with the bast removed and not. The frond underwent a series of mechanical comminution that includes chipping, flaking and grinding, followed by a screening process to obtain finer particles in the form of powder. Smaller sizes ensures better chemical penetration due to the higher exposed surface

area. Chemicals such as sulfuric acid and sodium hydroxide, as well as the yeast (*Saccharomyces cerevisae*) were purchased from Gainchem Enterprise.

Alkaline hydrolysis

The alkaline hydrolysis is one out of the three stages of hydrolysis process to breakdown the lignocellulose to obtain glucose for fermentation. This process requires the usage of sodium hydroxide 1% as the reacting mixture, with high temperature (100 °C) for two hours. The ratio of fiber to solution is 1:50. This process is important as a preparation step in producing better fiber forms before undergoing the harsher acid hydrolysis, as well as removing the lignin from the samples.

Concentrated Acid Hydrolysis

The second type of hydrolysis is the concentrated acid hydrolysis which allows the breakdown of the long-chained linear cellulose and branched hemicellulose. This step requires using a high concentration sulfuric acid of 75% concentration immersed in medium temperature of 50 °C with fiber-solution ratio of 1:15 for an hour.

Diluted Acid Hydrolysis

This process further allows residual chains of cellulose and branched hemicellulose to be broken to simple sugars. The step requires a diluted sulfuric acid of 6% reacted with a high temperature of 80 °C, with a fiber-solution ratio of 1:15 for two hours.

Fermentation

Saccharomyces cerevisiae were used for the fermentation process to convert glucose into ethanol. The yeast solution was measured by 1 g of yeast to 40cm³ of warm water to react with a 10 g of substrate. The samples were left at room temperature of 28-30 °C for approximately 96 hours to ferment.

Distillation

Since the hydrolysis and fermentation process yields other by-product other than the theoretical by-product, which is carbon dioxide and water, distillation process is necessary to purify the ethanol, by boiling and condensation process. The sample solution are poured into the boiling flask and undergo the distillation process (Figure 20). The boiling flask will then be heated to enable the solution to reach the boiling point of ethanol, which is 78.1°C.

Identification of Bio-ethanol

Infrared Absorption Frequency

The identification of the infrared absorption frequency was done to identify the functional group present in the liquid solution. This process was run using the Fourier Transform Infrared (FTIR) Spectroscopy by obtaining the infrared spectrum of absorption and

emission, among others, for solid, liquid and gas for the main purpose of identifying the functional group present.

Alcohol by volume through specific gravity

The estimation of alcohol content in the end product were identified using specific gravity (SG) of the solution that is taken using refractometer. The specific gravity needed to be identified is the wort's SG, which is the Original Gravity (OG), and the SG reading when the fermentation is completely finished, which is known as Final Gravity (FG). SG is the amount of sugar in water. Basically, the SG of water is 1000 and if there is any sugar added, the SG will increase. However when fermentation occurs, it will decrease the SG due to the presence of alcohol that is naturally less dense to water. To count the alcohol by volume (ABV) of the solution, the formula used is such as in equation 1, in which includes the amount of carbon dioxide produced (1.05) for every gram of ethanol produced (in grams) and the density of ethanol alcohol (0.79).

% Alcohol =
$$\left(\frac{1.05 \text{ x} (\text{OG}-\text{FG})}{\text{FG}}\right) \div 0.79$$
 [equation 1]

Results and Discussion

Infrared Absorption Frequency

There are three or more significant points of frequency for the samples such as alcohol $(3400 - 3600 \text{ cm}^{-1})$ and amides $(1600 - 1640 \text{ cm}^{-1})$, that represents the transmittance percentage of each compound class present. The spectrum graphs of compound class obtained are shown in Figure 1 and Figure 2 for the samples with and without bast, respectively. After obtaining the readings of the compound class that existed in the samples, both bio-ethanol samples has nearly identical readings. The strong absorption between $3400 - 3600 \text{ cm}^{-1}$ frequency in the infrared spectra is caused by the hydroxyl functional group, showing the presence of alcohol. Meanwhile, the absorption frequency of $1600 - 1640 \text{ cm}^{-1}$ show the presence of functional group amides, an organic compound that consists of carbonyl group linked to a nitrogen atom. However, a slight difference can be observed based on the percentage of transmittance for the compound group of benzene (680 - 860 cm^{-1}), where the percentage is higher in the sample of bio-ethanol using oil palm frond with bast, compared to the sample of bio-ethanol using oil palm frond with bast provides higher lignin content, indirectly yielding lower sugar conversion.



Figure 1



Figure 2

Alcohol by volume through specific gravity

The estimation of percentage of alcohol by volume is very important for the estimation of alcohol content in the product. The differences of value of alcohol by volume of the bioethanol produced from the oil palm frond with and without bast are significant based on the data analysis shown in Table 1. About 6.9% and 7.2% of mean ABV percentage were obtained from the bio-ethanol made from oil palm frond with and without bast, showing a slightly higher content for the latter.

Oil Palm Frond	Alcohol by Volume (%)
With Bast (WB)	6.9000 ^{1a}
	(0.1296) ²
Without Bast (WOB)	7.2260 ^b
	(0.1211)

Table 1: The mean value of alcohol by volume from the production of bio-ethanol from Oil Palm Frond

Notes: ¹ Mean Value.

² Value of Standard Deviation.

The differences of alcohol by volume of the bio-ethanol produced from the oil palm frond with and without bast shows a statistical significant difference with p-value > 0.05. Based on the readings, in order to set a higher yield of bio-ethanol and to reduce the difference of alcohol yield in future industrial-scale production, the process of removing the bast is highly recommended. The benzene content, which is known to be hazardous to human, are further reduced by the removal of bast, producing a safer product for human utilization.

Conclusion

The production of bio-ethanol from the lignocellulosic material, which is the oil palm frond, requires the two-stage bio-conversion in order to release the simple sugars densely packed in the structure. A series of hydrolysis were necessary to enable the process, with each chemical components targeting specific polysaccharide to unleash. This study indicates that the presence of bast for the production of bio-ethanol from oil palm frond has a significant effect on the alcohol yield, in which the oil palm frond with the bast removed yielding higher alcohol by volume than those with it. The infrared spectra also shows the extra production of benzene from the bio-ethanol samples produced with bast, which could possibly agitate the safety of the surroundings.

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