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Research paper

Organosolv Pretreatment Process and Hydrolysis Acid Conversion Oil Palm Frond (OPF) as Bioetanol Raw Material

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Abstract

This research uses a palm frond as a source holoselulosa be converted into raw materials for bioethanol (total sugars). This research aims to study the pretreatment process organosolv with ethanol and acid hydrolysis of the palm frond conversion into sugar. The process of making sugar from palm frond begins with a process of delignification and be followed by a process of hydrolysis. Delignification process takes place in conditions with varying concentrations of ethanol 35%, 55%, 75%, and 90% v/v at 1000C and 1200C and reaction time 60 and 90 minutes. Furthermore, for hydrolysis process using sulfuric acid with variation of concentration 1%, temperature 60, 70, 80, 90 and 1000C and reaction time 15, 30, 45, 60 and 75 minutes. The results showed that in the delignification condition with 75% C 2H5OH concentration, 1200C for 60 minutes and 1% catalyst (H2SO4) and under 1% H2SO4 hydrolysis condition, 30 min and 900C, the highest total sugar yield 93.65 mg/L.

Keywords: *Palm Frond; Lignocellulosic Material; Delignification; Hydrolysis; Bioethanol Feedstock.*

1. Introduction

Lignocellulosic biomass contained in any plant species, and usually obtained from plantations or agricultural waste. Oil palm frond (OPF) is one type of lignocellulosic material produced mostly from a palm plantation and has not been utilized optimally especially as an alternative fuel. In each hectare can produce palm frond dry weight as much as 1,640 kg [1]. The palm frond has a high holocellulose content of 83.5% and the palm fronds can be harvested 1-2 frond / trees throughout the year along with fresh fruit bunch harvest [2]. This makes the OPF strived to be processed into bioethanol.

Various studies have been conducted in the production of bioethanol, whether from the ingredients of liver, molasses, juice or from lignocellulosic biomass. Ishola, et al [3] has succeeded in producing 85% ethanol of raw spruce chips (Swine & Krishnan) [4] has converted rice straw into bioethanol by using Candida Tropicalis as a fermentation medium and yield up to 98%. At the same time, Liu, et al [5] has produced bioethanol feedstock from bagasse baggage known as "bagass" with conversion value up to 99.51%. However, bioethanol production from OPF has not been done yet, so the researcher tries to study by studying approaches with similar material composition.

OPF is a plantation waste which is very rarely used by the public, especially the Acehnese people living around the plantation as in the South West Aceh, Langsa, Aceh Tamiang and North Aceh District as the center of production of oil palm land area total up to 393,000 hectares [6]. OPF in this research is planned to be obtained from plantation area of PT. Fajar Baizuri & Brother and PT. Scofindo in Nagan Raya District, Aceh Province. The bioethanol produced and tested and analyzed according to the standard of use in the supplementary materials in fuel is expected to be applied directly to community mobility in Nagan Raya District.

This research will be carried out the process of pretreatment and hydrolysis of the raw material (palm fronds). Pretreatment process involves a physical process (physical pretreatment) and chemical processes (chemical pretreatment) on raw materials (palm fronds). In this process will be generated holoselulosa from palm fronds which would then be hydrolyzed. The holocellulose hydrolysis process (the result of OPF pretreatment) is performed using dilute sulfuric acid (H_2SO_4) which will produce glucose and other simple sugars (as bioethanol feedstock) and then fermented to produce bioethanol.

2. Research methods

Lignocellulosic waste is the second generation feedstock in bioethanol production. Oil Palm Frond (OPF) is biomass waste generated from oil palm plantations, which are obtained from Nagan Raya. The research activities were conducted at Chemical Engineering Laboratory of Syiah Kuala University and Chemical Engineering Laboratory of Serambi Mekkah University.

2.1. Tools and materials

The tools used in this research are glassware, Thermometer, Analytical Scales, Filter paper, Pipette volume, pH Meter, pH indicator, Autoclave, shaker, incubator, screening, ball mill, Hot Plate, HPLC (Shimadzu) XRD (Shimadzu XRD 600 X-ray diffractometer), SEM (Scanning electron microcope) Philips XL-30 and Oven.

The materials used in this research were OPF, yeast extract, $(NH_4)_2SO_4$, $MgSO_4.7H_2O$, K_2HPO_4, $CaCl_2.2H_2O$, aquadest, Etha-

nol (C_6H_5OH), Glucose ($C_6H_{12}O_6$), Sodium Hydroxide (NaOH), cellulase enzyme, β-glucosidase, saccharomyces cerevisiae, Urea ($CO(NH_2)_2$).

2.2. Research variables

2.2.1. Fixed variables

1) Drying conditions OPF (105ºC, ± 36 hours, constant water content)
2) Particle size OPF (250 mesh)
3) 1% Sulfuric Acid Concentration (Organosolv pretreatment catalyst)

2.2.2. Changed variables

1) Organosolv pretreatment
a) Operation Time (60, 120, 180, 240 minutes)
b) Concentration of Ethanol (35.55, 75, 90% v / v)
c) Temperature (100, 120, 150 and 180ºC)
2) Simultaneous Saccharification and Fermentation (SSF), Fermentation Time (24, 36, 72 and 96 hours)

2.3. Research procedures

2.3.1. Pretreatment

Phase physical pretreatment OPF that has been dried, then destroyed with blender to get the size of raw material 250 mesh. OPF sieved to get a particle size of 250 mesh. The OPF has been stored in the desiccator to maintain the moisture level. Chemical pretreatment stage: Weighed OPF by a certain gram mass, then delignified in cooking liquid (ethanol) with variation in ethanol concentration, time and temperature specified. Further solid (holocellulose) is separated from the cooking liquid by means of filter paper. The resulting solid (holocellulose) is washed with hot water (Liquid hot water) until the filtrate is clear. Pulp (holoselulosa) which had been washed and then dried in the oven at a temperature of 105ºC to constant weight (± 24 hours).

2.3.2. Enzymatic and hydrolysis

OPF which have been pretreated or without pretreatment then hydrolyzed. A total of 3 grams of substrate and 60 ml of 0.05 M sodium citrate as buffer (pH 4.8) were mixed. Then 0.5 g/l of antibacterial agent and hydrolytic enzyme were added to the mixture. The enzyme contains 30 FPU cellulase and 60 IU β-glucosidase per gram of substrate. Furthermore, the flask or Erlenmeyer was covered with butyl rubber stoppers and aluminum lids and incubated for 72 hours at the incubator shaker at 45^0C and 120 rpm. The liquid samples were taken at any time during the hydrolysis and supernatant processes separated from the residue of the solid material by centrifugation (3000 rpm for 15 min) and stored at -20°C before analyzing the sugar composition.

2.3.3. Process of simultaneous saccharification and fermentation (SSF)

Ethanol is produced by SSF at 37ºC and 130 rpm in anaerobic conditions during fermentation time was varied. The medium contains 5 g/l of yeast extract, 7.5 g/l $(NH_4)_2SO_4$, 0.75 g/l $MgSO_4.7H_2O$, 3.5 g/l K_2HPO_4, 1 g/l $CaCl_2$. $2H_2O$ and 50 g/l OPF pretreatment and without pretreatment prepared in 0.05M citrate buffer. The pH of the media is adjusted at 5.5 with 1M NaOH. Then diautoclave at 121ºC for 20 minutes. After cooling at room temperature, 1 g/l of microorganisms were prepared along with 20 FPU celulase and 30 IU β-glucosidase per gram subtract and added 2.5 g/l Tween 20. Fermented products analyzed ethanol yield obtained.

3. Results and discussion

3.1. Preparation of biomass oil palm frond (OPF)

Preparation of raw materials aims to facilitate the treatment process, small particle size will facilitate the process because it has a large surface area. Pengukilan pengukur done by using the destroyer which then done sifting. Sifting is the separation of various mixtures of solid particles having different sizes of materials using mesh-sized sieves. The particle size of Oil Palm Frond (OPF) used in this study was 250 mesh.

3.2. Moisture content analysis

Determination of water content in oil palm frond done by drying method or methods oven for 3 hours at a temperature of 105° C. While the determination of ash content is done by using the furnace is done at a temperature of 210ºC. Moisture content and ash content of the chemical composition of which should be known within the material frond palm oil, because of the water content and higher ash levels will affect the high presence of cellulose contained dibahan oil palm frond, a reduction in moisture content and ash content on a wide variety of treatment as shown in Figure 1 below:

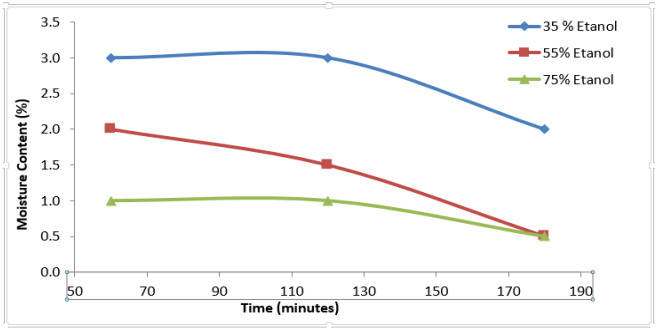

Fig. 1: Determination of Moisture Content in Various Treatment Variations.

Based on research that has been done for water content analysis where the examination variable is done at 60, 120 and 180 minutes with variation of ethanol concentration used as solvent which is 35%, 55% and 75%. Treatment conditions where the water content produced in accordance with the time variation decreases. The best results were obtained at 180 minutes and 75% ethanol content.

3.3. Analysis of ash content

The result of the analysis of ash content where the best result was also obtained at 75% ethanol solvent condition. The effect of ethanol used as a solvent is very well obtained at the highest conditions.

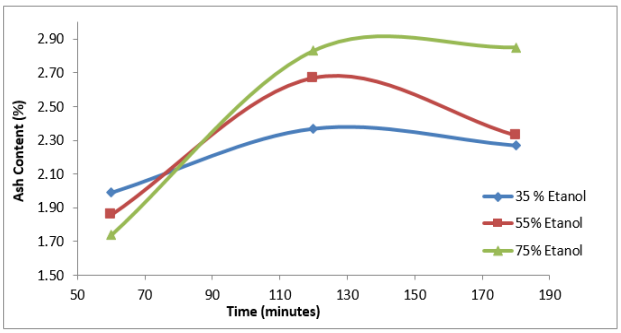

Fig. 2: Determination of Ash Content in Various Treatments Variations.

3.4. Acquisition of total sugar in the delignification process review

Lignocellulosic materials generally consist of cellulose, hemicellulose and lignin. The three components are strongly bonded due to the amorphous structure and 1, 4-β bonding in cellulose, and the presence of lignin compounds that act as compounds that protect cellulose and hemicellulose, this compound that causes the difficulty of degrading cellulose and hemicellulose to monomernya on the occurrence of hydrolysis, for it takes pretreatment to reduce the lignin compound [7].

From the result of pretreatment process (delignification) seen the influence of concentration of cooking solution (ethanol) to the total sugar gain, as shown in Figure 3.3. The highest total sugar gain was 34, 09 mg/L, obtained at 75% ethanol concentration condition. Increased concentration of cooking solution (ethanol) increases the total sugar gain. From Figure 3.3 it can be seen an increase in concentration of the solution cookers (ethanol) from 35% to 75% increase in total yield of sugar [8].

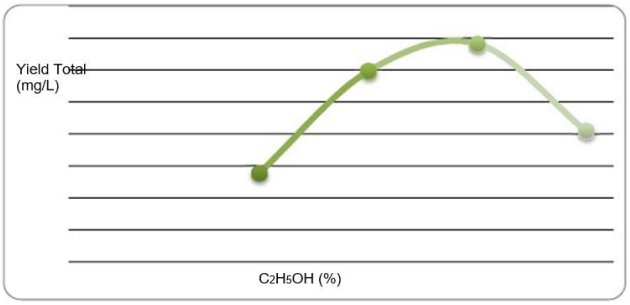

Fig. 3: Graph of the Relation Between Total Sugar Total and C 2H5OH Concentration (%) at 60minutes.

The increase in the total sugar yield is also related to the kappa number, as shown in Figure 3.4, the kappa number decreases as the ethanol concentration increases. A significant decrease in kappa number occurred at ethanol concentrations greater than 35%. The decrease in Kappa numbers indicates more and more of the lignin being decomposed, thus facilitating the degradation of holocellulose into sugars in the hydrolysis process [9].

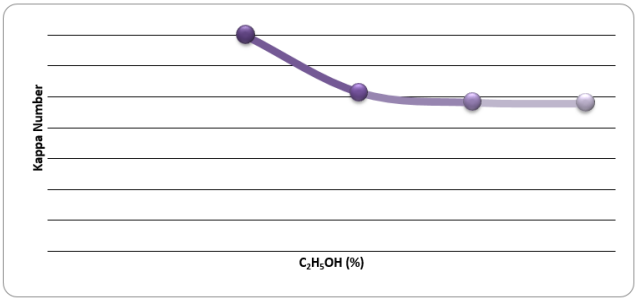

Fig. 4: The Relationship Graph of Kappa Number to the Effect of C2H5OH Concentration (%) at 60 Minutes, 1% H2SO4 Catalyst and Temperature 1000C.

Figure 3.4 also shows a decrease in total sugar yields at ethanol concentrations of more than 75%. This is because at too high ethanol concentration can cause estherification reaction between cellulose with ethanol to form ether, thereby reducing the cellulose content to be hydrolyzed [10].

Meanwhile, according Maurya et al [11], the concentration of ethanol cookers are high on the pretreatment process can also outline some of the hemicellulose in the solution, thereby reducing the hemicellulose content of hydrolyzed, resulting in the acquisition of the total sugar yield decreased.

4. Conclusions

From the results of research that has been done with the process conditions that have been applied in the research can be taken some conclusions as follows:

1) Maximum Condition pretreatment process C_2H_5OH obtained at a concentration of 75%, a temperature of 120^0C for 60 minutes without using NaOH catalyst.
2) The maximum conditions in the hydrolysis process is obtained at a concentration of 0.5% H_2SO_4, temperature of 100^0C for 45 minutes.
3) The highest total sugar yield was obtained at delignification condition with 75% C_2H_5OH concentration, temperature 120^0C for 60 min without using NaOH catalyst and hydrolysis condition of H_2SO_4 1%, temperature 90^0C for 30 minutes ie 93,25 mg/L.

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