Synthesis and Identification of Furfural from Cocoa Pod Husk (CPH) with Pretreatment Process before Hydrolysis Process

Lisa Aulia Lubis, Amir Husnin, Maulida
Department of Chemical Engineering, Universitas Sumatera Utara, Jl. Almamater Kampus USU, Medan, North Sumatera, Indonesia

Keywords: Biorefinery, Cocoa Pod Husk, Furfural, Pretreatment, Process Optimization

Abstract : Furfural is an organic compound that can be produced from agricultural waste such as oats, corn cobs, rice husks, bagasse, and sawdust. Cocoa pod husk is a renewable raw material for furfural manufacturing. Furfural synthesis from cocoa pod husk is an attempt to create value-added of cocoa pod husk. Furfural synthesis was based on the hydrolysis of pentosan into xylose which was then dehydrated to furfural. Cocoa pod husk waste contains pectin and lignin which can interfere hydolysis process. It make use pretreatment process to reduce pectin and lignin. Percentages pectin, lignin and pentosan before pretreatment were 9.2 ± 0.5, 14.7% and 38.9% and after pretreatment to be 1.7 ± 0.01, 4.13% and 37.5%. In this study used hydrolysis temperature variations (110, 120, 130 and 140) ^{0}C and hydrolysis time (10, 20, 30, 40 and 50) minutes. The optimum conditions obtained at temperature and time of hydrolysis of 130^{0}C and 30 minutes, weight furfural obtained was 6.728 g/7,50g pentosan or 6,728g/20g of cocoa pod husk and yield furfural obtained was 82.2%. This shows that cocoa pod husk has a high potential to be converted into furfural and can be used as a renewable raw material in furfural manufacturing. Furfural identified by color test using aniline acetate 1:1, Gas Cromatographic Mass Spectrometry (GCMS) and infra-spectrophotometer (FTIR).

1 INTRODUCTION

In the last decade there has been climate change and depletion of fossil fuels which were the main reasons humans use renewable raw materials such as lignocellulose residues to produce fuel. In recent years many researchers have devoted themselves to the exploration and development of efficient production for furfural.Many studies using renewable raw materials for furfural production are one of them biomass agricultural wastes (Liu, 2018).

Raw material from biomass has several advantages, They are biomass as renewable source, hemicellulose in biomass is high, furfural production can be produced more than 98%, besides it was easy to obtain, low cost and it was not pollute environment (Machad, 2016).

Cocoa is one of the plants that produce biomass of agricultural waste. Cocoa (Theobroma cacao L) is the nameof fruit fromcocoa tree. Cocoa fruit consists of seeds and shell or test. The biggest waste component in cocoa is cocoa pod husk (CPH). The cocoa pod husk are 70% -75% of the total cocoa fruit (Daud, 2014). The high production made from cocoa beans increases the world's cocoa pod husk waste in almost 700,000 tons in year (Okiyama, 2017).

The reason of this study using cocoa pod husk as a raw material for produce furfural is renewable, high amount of hemicellulose, increase demand for chemicals produce from agricultural waste, and the growing awareness of the environment. It has potential as a raw material for produce furfural. The composition of CPH can be show in Table 1.

Table 1: Chemical Composition of Cocoa Pod Husk (CPH)

Komponen	* Percentage (%)	**(%)	*** (%)
Cellulose	28.78	35.40	44.69
Hemicellulose	8.70	37.00	11.15
Lignin	42.90	14.70	34.82
Ash	1.87	12.30	7.40

Sumber : *(Syam, 2000)
**(Daud, 2014)
***(Nazir, 2016)

Lubis, L., Husin, A. and Maulida, .
Synthesis and Identification of Furfural from Cocoa Pod Husk (CPH) with Pretreatment Process before Hydrolysis Process.
DOI: 10.5220/0008863801600164
In *Proceedings of the 1st International Conference on Chemical Science and Technology Innovation (ICOCSTI 2019)*, pages 160-164
ISBN: 978-989-758-415-2

There were three step to produce furfural. First step waspetreatment, second step was hydrolysis process from pentoseto xylose and last step was dehydrated xylose to furfural. The stoichiometric equation for reaction is as below (Branca, 2012):

$$C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3H_2O \quad (1)$$

Biomass as raw materials in the process of produce chemicals was often carried out pretreatment process to reduce the presence of compounds such as lignin, pectin and other compounds it can disturb hydrolysis process, pretreatment was done first. In study conducted by (Mao, 2012) using raw material corn cobs the pretreatment process was not carried out, so the maximum yield was produced only 67.89% due to the presence of other compounds that inhibited the hydrolysis process, while the study was conducted (Liu, 2018) using a pretreatment process produces a maximum yield of 73%. It shown the pretreatment process can increase yield furfural.

In this study used a renewable raw materials. It was cocoa pod husk with pretreatment process for removal of pectin and lignin. Cocoa pod husk was a renewable raw material, therefor researchers also do variation of temperature and reaction time in the hydrolysis process, to find out the optimum conditions and the highest furfural yield that can be produced by cocoa pod husk.

2 MATERIALS AND METHODS

2.1 Raw Material

The raw material for cocoa pod husk was obtained from cocoa fruit trees in Naga Timbul Village, Indonesia.

The cocoa pod husk from farm was collected, washed, dried at 110^0C until the water content is ± 10%, after dried CPH was cut into sizes up to 1cm (Nazir, 2016).

2.2 Process Pretreatment

2.2.1 Pectin Extraction

Extraction of pectin done for elimination of pectin in cocoa pod husk. It used a citric acid. 100g of sample were added 1:25 citric acid solvent, extraction time of 3 hours, pH 2.5 at 95^{o}C (Nazir, 2016).

2.2.2 Reduction of Lignin

Samples from the pectin extraction process added 4% NaOH solution with a solid-liquid ratio of 1:25 was autoclaved at 121^{o}C for 100 minutes, filtered and washed until netral pH, dried at 105^{o}C for 6 hours (Nazir, 2016).

2.3 Furfural Production

As 20g of sample was added H_2SO_4 3M (Stein, 2011) with a ratio of 1:15 (Kaur, 2011), added NaCl 20g reacted to batch reactor with variationsreaction temperature (110, 120, 130 and 140)^{o}C (Peleteir, 2016) and reaction time (10, 20, 30, 40 and 50) minutes. Hydrolysis and dehydration results of vapor phase-shaped samples contained in furfural compounds. The reactions that occur can be show in Figure 1 (Branca, 2012).

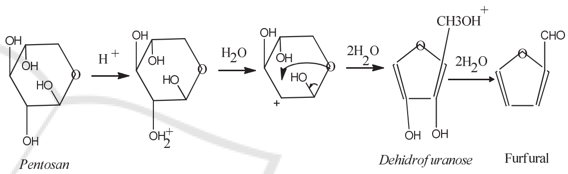

Figure 1: Hydrolysis reaction of Pentosan to Xylose and Dehydration to Furfural (Branca, 2012)

2.4 Analysis

Analysis of the composition of cellulosa, hemicellulose and lignin with chesson methode and pentosan in cocoa pod husk before and after pretreatment was carried out by gravimetri (Griffin, 1972). Furfural analysis obtained by color test of aniline acetate 1:1, GC-2010 Serial No. 020504702444 Shimidzu Corp) and FTIR Boil SHIMIDZU at laboratorium. Department Chemical Engineering. Lhoksumawe State Polytechnic.

3 RESULTS AND DISCUSSION

3.1 Raw Material Composition

The composition of lignin, cellulose, hemicellulose, pentose and pectin, before and after pretreatment show in Table 2: In these results it show that the composition of lignin was reduced to 10.57% after the pretreatment process. Pentosan also reduction of 1.4%. This is because a little pentosan bond also reacts.

Table 2: Results of Analysis Composition Cocoa Pod Husk

Component	Before Pretreatment	After Pretreatment
Lignin	14.81%	4.13%
Hemicellulose	42.10%	40.30%
- Pentosan	38.91%	37.50%
Cellulose	40.00%	37.31%
Pectin	9.2 ± 0.5	1.7 ± 0.01

Result of composition CPH in this study was different with other researcher. It was show in Tabel 1. This is due to differences in nutrients in the soil in each region.

3.2 Effect of Time and Temperature to Yield of Furfural.

In the process of produced furfural reaction time and temperature greatly affect furfural yield. The effect of the reaction time and temperature on furfural yield show in Figure 2.

$$\text{Yield of Furfural} = \frac{\text{Mass of Furfural (g)}}{\text{Mass of pentosan}} \times \%\text{area} \qquad (1)$$

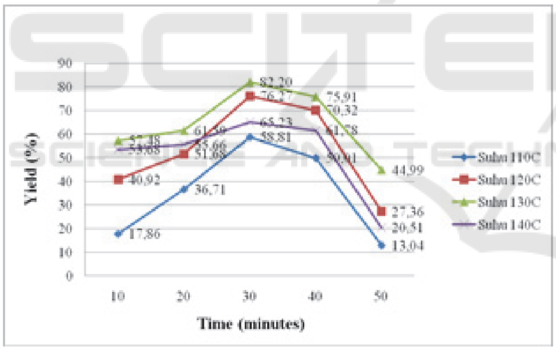

Figure 2: Effect of Time and Temperature to Yield of Furfural.

The results of this study indicate the highest yield value at 130°C with a time of 30 minutes of 82.20%. From these data it show at the reaction time of 10 to 30 minutes the resulting furfural yield increases, while at the reaction time of 40-50 minutes the resulting furfural yield decreases. This was because the longer reaction was carried out, the more side products are formed and can degrade furfural (Peleteiro, 2016). The by-products formed are 2-Furancarboxaldehyde, 5-methyl, the side product data obtained from the results of analysis with Gas Cromatographic Mass Spectrometry (GCMS) conducted by researchers. Furfural yield also increased from 110°C - 130°C and decreased at 140°C. Further demonstrating that thereaction selectivity can be conveniently tuned by adjusting thetemperature of the reaction. Reversely, an increase of the reaction temperature to 140°C lowered the yield of furfural, mostly due to its degradation or condensation (Liu, 2014).

3.3 Analysis of Aniline Acetate

In this study the color test of the product by using aniline acetate (1:1) to identify the presence or absence of furfural compounds in the products. The results of this color test showed a positive presence of furfural compounds in the product of hydrolysis, color was change to be red when aniline acetate added to product.

3.4 Analysis with FTIR and GCMS

After testing with aniline acetate which stated the presence of furfural, furfural test was carried out using Fourier Transform Infra Red (FTIR) and GCMS. FTIR test can be show in Figure 3.

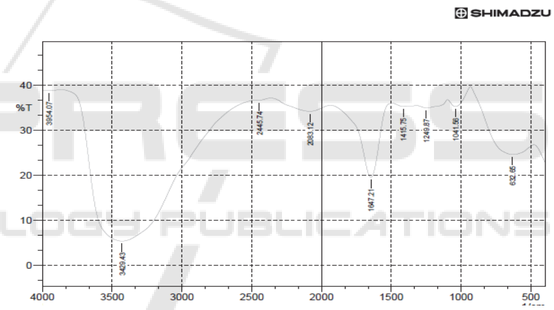

Figure 3: Furfural Results by Using FTIR Simidzu.

The IR spectrum (Figure: 3) shows a very strong absorptionC = O (1600 - 1700 cm^{-1}). sample obtained a very strong wave number absorption peak that is equal to 1647.21 cm^{-1}. This absorption shows a very significant functional group (C = O). Internal hydrogen bonding which occurs in conjugated unsaturated aldehydes (Ambalkar et al, 2017).

Absorption peak of 2445.74 cm^{-1} approaching the presence of C-H aldehyde (2800 - 2860cm^{-1}). The presence of an aromatic C = C bond is shown by the appearance of stretching vibrations C = C aromatic (1475 - 1600cm^{-1}) in the area of about 1415.75cm^{-1} nearing the presence of the cluster. The broad peaks observed at vibrations of 3400 to 2400 cm^{-1} from the sample showed wave absorption peaks of 3429.43 cm^{-1} and 2445.74 cm^{-1}, which indicated that the aldehyde bond of the absorption complex showed aldehyde stretching. If the sample has an ester - O - peak, C = C peak will be observed at

1685 cm^{-1} to 1660 cm^{-1} (Ong, 2007), but the sample does not show the same absorption. can be show in Table 3.

Table 3: Furfural Vibration

No .	Vibration	Furfural Standard
1.	*Streching* aldehyde complex	3429.43
2.	*Stretching* C-H aldehyde	2445.74
3.	*Stretching* C=O aldehyde	1647.21
4.	*Stretching* C=C aromatic	1415.75
5.	*Stretching* C- aldehyde	1249.87
6.	*Stretching C-O-C*	1041.56

Based on the furfural standard vibration value it can be concluded that the compound produced from the hydrolysis of cocoa pod huskwas furfural because it shows spectra which are almost identical to the standard furfural vibration. Based on the furfural standard vibration value it can be concluded that the compound produced from the hydrolysis of cocoa fruit skin is furfural because it shows spectra that are identificationof furfural. Further furfural can be identified with GCMS. The results of GCMS identification can be show in Figure 3.

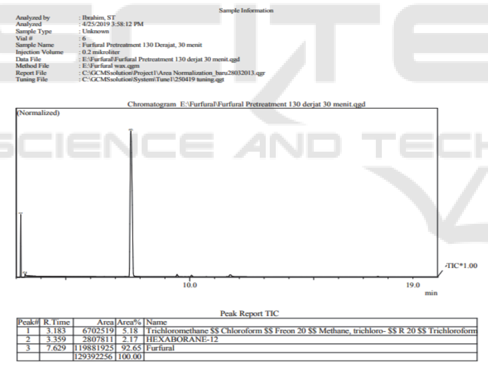

Figure 3: Furfural Results using GCMS Simidzu.

The analysis use GC-2010 Serial No. 020504702444 Shimidzu Corp) strengthens that hydrolysis compounds are furfural. The furfural compound for the process with pretreatment was shown at peak 3, retention time 7,629, area 119881925% area 92.65%.

4 CONCLUSIONS

The conclusion of this study is furfural can be produced using renewable raw materials. It is cocoa pod husk. The pretreatment process can reduce lignin until 10.57% and pentosan until 1.4%. Pentosan and lignin found in cocoa pod husk after pretreatment process was 4.13% and 37.5%. The optimum conditions obtained in the hydrolysis process of cocoa pod husk with a pretreatment process and dehydration process attemperature 130ºC and reaction time of 30 minutes produced a yield of 82.02% obtained from 6.725g / 7.05g pentose.

REFERENCES

Ambalkar, V. U and Talib, M., 2017. *Synthesis and Identification of Furfural from Sunflower Husk*.International Advanced Research Journal in Science, Engineering and Technology. Vol 4

Branca, C., Blasi, C. D. and Galgano, A., 2012.,*Catalyst Screening for the Production of Furfural from Corncob Pyrolysis*. Energy and Fuels. 26: 1520-1530

Daud, Z., Awang, H., Kassim, A.S.M, Hatta, M.Z.M. and Aripin, A.S., 2014. *Cocoa Pod Husk and Corn Stalk:Alternative Paper Fibres Study on Chemical Characterization and Morphological Structures.*Advanced Materials Research. 911: 331-335.

Griffin., Castle, R., Little, A.D., 1972. *Technical Methods of Analysis*. McGraw-Hill Book. 298

Kaur, Ramandeep., 2011.,*Hemicellulosic Furfural Production from Sugarcane Bagasse Using Different Acids*.Sugar Tech. 13: 166-169.

Liu, F., Boissou, F., Vignault, A., Lemee, L., Marinkovic, L., Estrine, B., Vigier, K. D. O. And Jerome, F.*Conversion of Wheat Straw to Furfural and Levulinic Acid in a Concentrated Aqueous Solution of Betaıne Hydrochloride*.Royal Society of Chemistry (RSC) Adv. 4, 28836.

Liu, L., Chang, H., Jameel, H. and Park, S., 2018. *Furfural production from a Pre-hydrolysate Generated using Aspen and Maple Chip*.Biomass and Bioenergy. 104: 1-16

Machado, G., Leon, S., Santos, F., Lourega , R., Dullius, J., Mollmann, M.E. and Eichler, P., 2015. *Literature Review on Furfural Production from Lignocellulosic Biomass*.Natural Resources. 7: 115-129.

Nazir, N., Novelina., Juita, E., Amelia, C. And Fatli, R., 2016. *Optimization of Pretreatment Process of Cocoa Pod Husk Using Various Chemical Solvents.* Advanced Science Engineering Information Technology. 6: 2088-5334

Ong, H.K and Sashikala, M., 2007.*Indentification of furfural synthesized from pentosan in rice husk*. J.Trop. Agric. Nd Fd. Sc. Vol 35, 2007:305-312.

Okiyama, D.C.G., Navarro, S. L.B. and Rodrigues, C.E.C.,2017. *Cocoa shell and its compounds Applications in the Food Industry*.Trends in Food Science & Technology. S0924-2244.

Peleteiro, S., Santos, V., Garotte, G. And Parajo, J.C., 2016. *Furfural Production from Eucalyptus Wood using an Acidic Ionic Liquid*.Carbohydrate Polymers. 146: 20-25.

Stein, T.V., Grande, P. M., Leitner, W. and Maria, P. D. D., 2011. *Iron Catalyzed Furfural Production in Biobased Biphasic Systems: From Pure Sugars to Direct Use of Crude Xylose Effluentsas Feedstock*.ChemSusChem. 4: 1592-1594