IDENTIFICATION OF FUNCTIONAL GROUPS ORGANIC COMPOUNDS FROM RICE STRAW PULP BASED SPECTRA FTIR

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ABSTRACT. The purpose of research is conducted in the order to would have known determine of functional groups organic compounds contained by rice straw pulp treatment of the experimental results rice straw pulping. By identifying the functional groups of organic compounds through rice straw pulp FTIR spectrum of research results and then compare it with the image of standard cellulose FTIR spectra. And analyze with the framework of functional groups of organic compounds builder cellulose structure.
Based on the experimental results pulp cooking rice straw treated with solution of cooked 2 % NaOH, 3 % NaOH and 4 % NaOH obtained average yields rice straw pulp is 49,28 %, 27,62 % and 24,39 %.
Based on test results FTIR spectra of rice straw pulp known as much as 18 peaks the wavelength of functional groups of organic compounds, as shown in Table – 5.
From the identification of the peak wavelength of functional groups organic compounds and compare it with the image of standard cellulose FTIR spectra, as shown in Table – 5 there were 11 peaks of functional groups of organic compounds which has a wavelength closes the wavelength approaches value of functional groups organics compound cellulose standard FTIR spectrum image.
Of the 11 peaks of functional group organic compounds,there are as many 6 functional group of the organic compound cellulose structure of the skeleton builder wavelengths 2889,37 cm^{-1} ; 1667,28 cm^{-1} ; 1431,18 cm^{-1} ; 1327,03 cm^{-1} ; 1249,87 cm^{-1} and 898,83 cm^{-1}
Keywords : effectiveness delignification,rice straw pulp, organic compounds and functional groups builder skeleton structure of cellulose.

1. INTRODUCTION

Rice straw is a waste of rice plants. The cultivation of rice plants will yield rice straw around 5 ton / ha, whenever the harvest. Having a sun-dried ingredients are 10% to 70%, equivalent to 3.0 ton of to 3.5 ton of sun-dried rice straw per hectare. Or comparable with fiber production 1.5 ton to 2.0 ton of dry matter fibers based on the calculation of air dried (Haryanto in Antonious, 2010).
The great potential of this rice straw, making it an agricultural waste which is very likely to be a source of fiber raw materials. A lignocellulose rice straw fiber, means a material containing fiber and lignin. Rice straw instead of wood as biomass (non-wood), consisting of a mixture of carbohydrate polymers, namely cellulose, hemicellulose and lignin.

According Nurhayati, 2014, cellulose is a linear polymer compound comprising repeat units β - D - glucopyranose. One process for separating cellulose from cellulosic feedstocks is the pulping techniques, namely cooking with NaOH alkaline solution. NaOH solution can reduce

the degree of polymer, crystallinity index and break the bonds between lignin and carbohydrates. Cellulose is widely used as raw materials / auxiliary materials for the industry either still in the form of fiber, and that has been converted into its derivatives (cellulose derivatives).

Table – 1. Analysis of Chemical Composition of Rice Straw.

No.	Parameter	Composition (%)
1.	Extractive	4.1
2.	Ash	14.1
3.	Lignin	17.8
4.	Pentosan	12.5
5.	Holoselulosa	71.4
6.	α-cellulose	45
7.	β and γ - cellulose	13.9

Source : Mohamed, 2015

Based on the degree of polymerization and solubility in 17.5% NaOH solution, the cellulose can be distinguished:

1. Cellulose - α (alpha cellulose), is a long-chain cellulose, not dissolved in a solution of 17, 5% NaOH. Alpha cellulose is used as a probe or a determinant of the degree of purity cellulose.
2. Cellulose - β (beta cellulose), is a short-chain cellulose, dissolved in a solution of 17.5% NaOH, with a degree of polymerization of 15 to 90, can precipitate when neutralized.
3. Cellulose - γ (gamma cellulose), is the same as the beta cellulose with a degree of polymerization of less than 15.

The analysis conducted by Fourier Transform Infra Red (FTIR) is a non-destructive technique to determine qualitatively and quantitatively from functional groups of organic compounds in a material based on the image expressed by the FTIR spectrum of wavelengths (cm^{-1}) and transmittance (%). Which occurred in the region of 4000 cm^{-1} to 200 cm^{-1}. From the wavelength and transmittance, happens can be learned crystallinity and hydrogen bonding of the formation of a material lignocellulose. Apart from that also can be used to learn the system fiber or fiber orientation distribution in a material that has lignocellulose. Hemicelluloses is a polysaccharide that has a complicated structure and is linked to the cellulose. Hemicellulose is naturally connected with micro fibril cellulose is non-covalent and generally consist of more than one type of mono saccharide units. Depending upon the type of material lignocellulosic, that hemicellulose may be Xylo glucan, xylan, glucomannan, galactoglucomanan and others. Infrared absorption information, given in the form of the spectrum is expressed in the cross axis to the wavelength (cm^{-1}) as abscissa - X and the intensity of the absorption or transmittance (%) as ordinate - Y. Transmittance is the ratio between the fraction of light transmitted by the sample (I) and the amount of light received by the sample (Io).

Table - 2. Structural and Chemical Composition Of Cellulose, Hemicellulose and Lignin Of Plants.

No.	Parameter	Lignin	Hemiseluosa	Cellulose
1.	sub unit	• Guaiacylpropane (G) • Syringilpropane (S) • Hydroxyphenilpropane (H)	• D - xylose • Mannose • L - Arabinose • Galactose • Glucuranic acid	• D – Pyran glucose
2.	Bond between sub unit	• C - C Bond • β- O - 4 ether	• β - 1, 4 - Glycosidic • β - 1.2 -, β - 1.3 - β - 1.6 Glycosidic	• β - 1, 4 – Glycosidic bond
3.	Polymerization	4000	<200	s / d 10 000
4.	Polymer	• G lignin • GS lignin • GSH lignin	• Polixylosa • Galactoglucomanan (Gal - Glu - Man) • Glucomannan (Glu - Man)	• β - Glucan

Source : Chen, 2014

According to Abbakar, 2015, in his research to isolate alpha cellulose hydrolyzing local rice straw with 18% NaOH solution. The results obtained were identified by FTIR spectrum as shown in Table - 3.

Table – 3. Wavelength And Transmittance Of The FTIR Spectrum From Rice Straw Pulp Abbakar (As Comparison).

No.	Wavelength (cm^{-1})	Transmittance (%)
1.	3421,48	51,20
2.	2914,24	61,60
3.	2382,54	61,40
4.	1637,45	64,70
5.	1510,16	66,80
6.	1421,44	62,60
7.	1371,29	61,40
8.	1334,56	61,10
9.	1158,14	57,60
10.	1066,56	53,10
11.	895,84	65,20
12.	798,66	68,80
13.	667,32	63,00
14.	595,86	62,90
15.	561,00	63,00
16.	470,00	62,10

Source : Abbakar,2015.

The purpose of this study is :

1. To determine the effectiveness of the delignification of straw into pulp cooking process of rice straw.

2. Identify the content of the groups of organic compounds based on the image of rice straw pulp FTIR spectrum of research results and compare it with the image of the FTIR spectrum of straw pulp other research.
3. Analyze the character of cellulose contained by the image of rice straw pulp FTIR spectrum of research results and compare them with the patterns FTIR spectrum of standard cellulose and organic compound cellulose structure of the skeleton builder.

2. METHODOLOGY.

2.1 Preparation of Materials

The raw material used is rice straw obtained from the rest of the rice harvest paddy fields. As a raw material for pulping of rice straw, rice straw which then still green, dried beforehand to dry sunshine.

Other materials necessary for making pulp of rice straw is a technical caustic soda, sodium hydroxide, chlorine water CaOCl and clean water. Then as fuel, used rubber wood (ie wood waste rubber from rubber wood processing factory), which are widely sold in the community.

2.2 Tools

The equipment used to make rice straw pulp is the pot (cooking vessel), plastic containers (buckets, plastic scoop and others), plastic gauze sieve, wood moldings (net size of 30 x 15 x 2 cm), scales and more.

2.3 Trial Preparation Rice Straw Pulp.

In the experimental rice straw pulping, which is cooked with a dry weight basis conditioning 500 gr where the treatment is the solution cooker respectively 2% NaOH, 3% NaOH and 4% NaOH. After boiling solution, rice straw was added to the cooking vessel, and boiled for 30 minutes, after which the cooking process is stopped.

According to Nasution, 2010, the concoction of rice straw was complete, when the straw that has been discussed earlier, drawn stick and pulled by hand so easily have dropped.

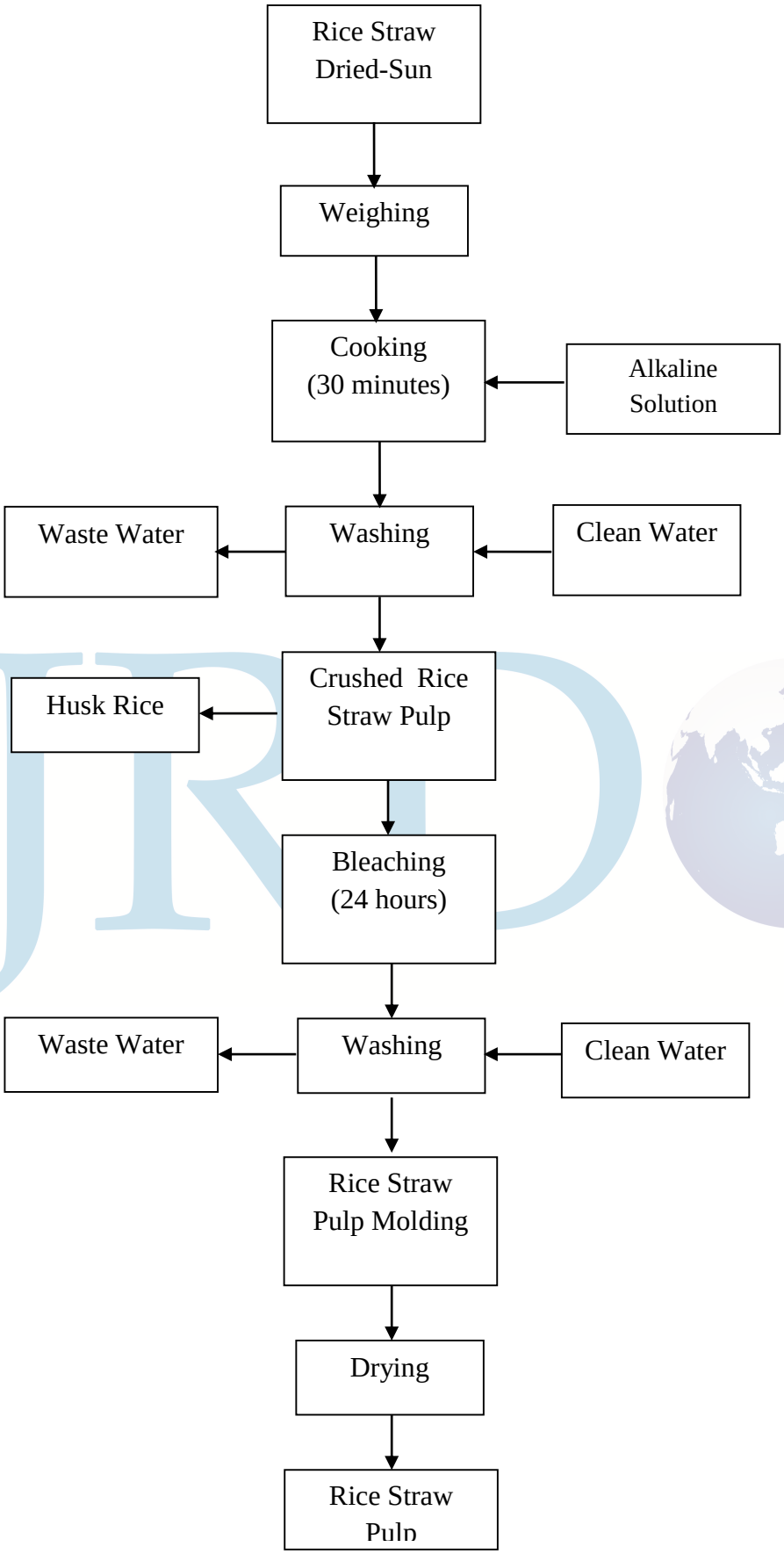

Diagram 1 .Flowchart Preparation of Rice Straw Pulp.

Rice straw pulp samples to be tested are sun-dried in the form of plates with a size of 30 x 15 x 2 cm. Testing is done with Shimadzu FTIR instrument at 8400 S Research Laboratory University of North Sumatra in the City of Medan.

3 RESULTS AND DISCUSSION

Table - 4. Yield of Rice Straw Pulp Cooking Results

No.	Cooking NaOH Solution Concentration (%)	Average Yield of Rice Straw Pulp Cooking Results (%)
1.	2	40.28
2.	3	27.62
3.	4	24.30

Table - 5. Wavelength And Transmittance of the FTIR Spectrum Rice Straw Pulp Research Results.

No.	Wavelength (cm^{-1})			Transmittance (%)		
	Cooking			Cooking		
	I	II	III	I	II	III
1.	3930,93	3930,93	3930,93	1,91	20,39	28,08
2.	3410,15	3421,72	3414,00	0,17	2,42	2,94
3.	2889,37	2889,37	2889,37	0,45	6,30	8,47
4.	2542,14	2546,04	2542,18	1,07	13,11	18,48
5.	2345,44	2341,58	2341,58	1,30	15,02	20,75
6.	2314,58	2314,58	2314,58	1,30	14,72	20,59
7.	2129,41	2129,41	2129,41	1,14	13,22	18,09
8.	2056,12	2052,26	2052,56	1,19	13,56	19,15
9.	1631,78	1631,78	1635,64	0,54	6,85	10,16
10.	1431,18	1431,18	1431,18	0,27	3,60	4,99
11.	1365,60	1369,46	1365,60	0,21	2,94	3,95
12.	1323,17	1327,03	1323,17	0,20	2,86	3,80
13.	1253,73	1249,87	1249,87	0,27	3,56	5,04
14.	1114,86	1122,57	1118,71	0,08	1,30	1,46
15.	898,83	898,83	898,83	0,30	4,07	5,38
16.	574,79	617,22	613,36	0,11	1,52	1,89
17.	509,21	578,64	578,64	0,13	1,58	1,97
18.	424,34	451,34	451,34	0,17	1,66	2,20

3.1 Cooking Rice Straw Pulp.

Cooking rice straw implemented using pot / container open the cooker 2% NaOH solution, 3% NaOH and 3% NaOH. While the solution is boiling cookers, air-dried rice straw inserted after being weighed first. Cooked / boiled each time for 30 minutes while stirring occasionally so that cooking evenly. After process cooking is complete, then cooled and washed until free of the black liquor. Then soak it in water and add water with chlorine, for a process of bleaching. After it was washed and will obtain rice straw pulp, white and clean. To enable the development of fiber (swelling), then soaking it in water for 24 hours. So next day washed again, and do

blending for that rice straw pulp obtained in the form of porridge and ready to be rice straw pulp molding.

From cooking experiments with varying concentrations of 2% NaOH solution cookers, 3% NaOH and 4% NaOH yields gained an average of 40.28%, 27.62% and 24.30%.

3.2 Identification of Clusters Function Organic Compounds From Rice Straw Pulp.

Table - 6. Wavelength Spectrum Of Cellulose Standard, Rice Straw Pulp Abbakar (For Comparison) And Rice Straw Pulp Research Results

No.	Wavelength (cm^{-1})				
	Cellulose Standard (cm^{-1})	Rice Straw Pulp Abbakar (cm^{-1})	Cooking		
			I	II	III
1.	3350,70	-	-	-	-
2.	2901,34	2914,24	2889,37	2889,37	2889,37
3.	2366,40	2382,24	-	-	-
4.	2346,40	-	2345,44	2341,58	2341,58
5.	2129,90	-	2129,41	2129,41	2129,41
6.	1640,09	1637,45	1631,78	1631,78	1635,64
7.	1430,00	1421,44	1431,18	1431,18	1431,18
8.	1372,30	1371,29	1365,60	1369,46	1365,60
9.	1337,00	1334,56	-	-	-
10.	1318,10	-	1323,17	1327,03	1323,17
11.	1282,10	-	-	-	-
12.	1235,90	-	1253,73	1249,87	1249,87
13.	1202,90	-	-	-	-
14.	1163,30	1158,14	-	-	-
15.	1112,20	-	1114,86	1122,57	1118,71
16.	1059,60	1066,56	-	-	-
17.	1035,80	-	-	-	-
18.	898,50	895,84	898,83	898,83	898,83
19.	670,20	-	-	-	-
20.	663,40	667,32	-	-	-
21.	617,00	-	-	617,22	613,36
22.	561,00	561,00	-	-	-

Based on the data in the Table - 6, can be discussed as follows:

With increasing concentration of the solution cookers, it will generate an average yields rice straw pulp has declined. But it does reduce the peak number of functional groups of organic compounds contained by rice straw pulp, which is still a total of 18 functional groups of organic compounds. Then the wavelength of each peak groups of organic compounds cooker result of the treatment solution (as seen in the Table - 6), can be expressed not happen wavelength difference (change in the structure of functional groups of organic compounds) which was

based on the variation significant. Treatment solution cooker intensity difference absorption occurs, ie the more concentrated solution of the cooker, the more soluble chemical compounds that are in the rice straw into black liquor. So the percentage of absorption intensity (transmittance) of rice straw pulp to be increasing.

According to Mohadi, 2014, FTIR spectrum of standard cellulose showed absorption at 3350.7 cm^{-1} wavelength which is a hydroxyl group (OH) vibration strain. Next peak at 2901.3 cm^{-1} wavelengyh indicates vibration strain (CH) of the alkyl group is a frame builder cellulose structure. Wavelength 1640 cm^{-1} and 1430 cm^{-1} represents an alkyl group (CH). Strengthened by the ether group (CO), which is located in the vibrational strain fingerprint region at wavelength 1282 cm^{-1} and 1035 cm^{-1}, which is the liaison carbon chains in the compound wave cellulose. Wavelength 898.50 cm^{-1} is a ring cellulose of deformation and strain (C - O - C), (C - C - O) and (C - C - H).

According to Purwanto, 2014, the functional groups of organic compounds were identified as a constituent of cellulosic namely functional groups of organic compounds (- CH_2) at a wavelength of 903 cm^{-1}, the functional groups of organic compounds (C - H) at a wavelength of 2924 cm^{-1}, group function organic compounds (C - O) at a wavelength of 1065 cm^{-1}; 1327 cm^{-1} and 1242 cm^{-1} and functional groups of organic compounds (O - H) at a wavelength of 3441 cm^{-1}.

According to Stuart, 2004, p-179, functional groups of organic compounds from cellulose FTIR spectrum consists of a group (OH) vibration strain with a range of 3300 cm^{-1} wavelength, group of organic compounds with the strain vibration wavelength 3000 cm^{-1} - 2900 cm^{-1}, group organic compound (C - H) vibration bends with wavelength 1500 cm^{-1} - 1300 cm^{-1} and a cluster of ether (C - O) vibrational stretch at 1030 cm^{-1} wavelength. Referring to the explanation Mohadi, 2014, Purwanto, 2014 and Stuart, 2004 can be described as follows:

That rice straw pulp research results with the treatment of the above mentioned cooking as much as 18 peak functional groups of organic compounds.

Based on Table - 6 of the wavelength spectrum rice straw pulp results were obtained 11 the peak of functional groups of organic compounds that follow the pattern of standard cellulose FTIR spectrum of 22 peaks functional groups of organic compounds owned cellulose standard. Then from 11 functional groups of organic compounds that follow the pattern of standard cellulose FTIR spectrum there are 6 functional groups of organic compounds is the builder skeleton structure of cellulose with a wavelength of 2889.37 cm^{-1} 1631.78 cm^{-1}; 1431.18 cm^{-1}; 1327.03 cm^{-1}; 1249.82 cm^{-1} and 898.83 cm^{-1}

To see more clearly the skeleton structure of cellulose pulp raw materials other research results, then try than the functional groups of organic compounds from other raw materials such as the following:

Susana, 2011, the research on the extraction of cellulose waste crown of the pineapple, then based spectrum FTIR gained as much as 8 peaks of functional groups of organic compounds that follow the pattern of FTIR spectrum of cellulosic standard of the number 15 peak of functional groups of organic compounds contained in the pulp waste crown of the pineapple.

From 8 functional groups of compounds organic follows the pattern of standard cellulose FTIR spectrum, there are 5 functional groups of the organic compound cellulose structure of the skeleton builder.

According to Nasution, 2015,on research in cellulose oil palm trunk vascular network , then based FTIR spectrum obtained by 14 peaks of functional groups of organic compound that follow the pattern FTIR spectrum of standard cellulose from number 17 peak of functional groups of organic compounds contained in oil palm trunk vascular network pulp. From 14 functional groups of organic compounds that follow the standard cellulose FTIR spectrum, there are 8 functional groups of the organic compound cellulose structure of the skeleton builder.

CONCLUSION

Based on the identification of patterns of rice straw pulp FTIR spectra obtained 11 peak of functional groups of organic compounds that follow the pattern of a standard cellulose FTIR spectrum peaks 18 functional groups of organic compounds from rice straw pulp research results.

Of the 11 functional groups of organic compounds that follow the pattern of standard cellulose FTIR spectrum, there are as many as 6 functional groups of the organic compound cellulose builder skeleton structure that is on the wavelength, 2889.27 cm $^{-1}$; 1631.78 cm $^{-1}$; 1431.18 cm $^{-1}$; 1327 cm $^{-1}$; 1249.78 cm $^{-1}$ and 898.83 cm $^{-1}$.

BIBLIOGRAPHY

1. Abbakar, MA and MT Elsheikh, 2015 Investigation of - Cellulose Local Source for the Production of Nitro Cellulose, International Journal of Science: Basic and Applied Research (IJSBAR), vol.19, No.2, p.35 - 50.
2. Antonious, 2010, Effect of Rice Straw Against Palatabilitay Fermented Fiber Digestibility and Energy Digestibel Ra nsum Cattle, Scientific Proceedings of the National Animal Husbandry and Veterinary Technology in City of Medan, p.224 - 228.
3. Chen, H, 2014, Biotechnology of Lignocellulose: Theory and Practice (Chemical Composition and Structure of Natural Lignocellulose), Chemical Industry Press, Beijing.
4. Coates, J, 2000 Interpretation of Infrared Spectra, A Practical Approach, Encyclopedia of Analytical Chemistry by RA Meyer (Ed), pp.10815 - 10837.
5. Ilindra, A and J D Dhale, 2008, Microcrystalline Cellulose from Bagasse and Rice Straw, Indian Journal of Chemical Technology, Vol.15, pp. 497 – 499.
6. Issa, R, M, M M Abou-Sekkina, A M Khedr, Alam El-Deen M, Bastawisy and W A El-Helece, 2011, Trace the Exploitation of Egyptian Rice Straw Through Spectral and Thermal, Arabian Journal of Chemistry, King Saud University.
7. Mohadi, R A Saputra, N Hidayati and A Lestari, 2014, Ion Interaction Studies Cellulose Powder Metal $^{2+}$ With Wood, Journal of Chemistry, Vol.8 No.1, p. 1-8

8. Mohamed, El-Sakhawy, El Samaky M A, Abdel Hakem A A and Amal H Abdelhaer, 2015, Test Liner Paper and Folding Carton From Some Lignocellulosic Materials, IOSR Jurnal of Applied Chemistry, Vol.8.Issued 1 Ver.3, pp. 41 - 46
9. Nasution, ZA, 2010, Preparation and Characterization of Rice Straw From Waste Paper To Print Tray Glassware Hand, News Cellulosa, Vol.45 No. 1, pp. 16-21
10. Nasution, ZA, 2015 Characterization of Cellulose Oil Palm Trunk Vascular Network Based on XRD Diffraction and FTIR Spectra Patterns, Journal of Industrial Crops, Vol.10 No.1. pp.49- 56.
11. Nurhayati and R Kusumawati, 2014, Synthesis of Cellulose Acetate of Waste Gelatin Processing, Post-Harvested and Biotechnology Marine and Fisheries Journals, Vol.9 No.2, pp. 97-107.
12. Purwanto, W Astuti D, H and K Triyana Sosiati, 2014, Characteristics of Morphology and Microstructure Fiber Kenaf (Hibiscus Cannabinus L) Due Treatment Chemicals, Scientific Proceedings of the XXVIII HFI Central Java and Yogyakarta, Yogyakarta, ISSN.0853 - 0822, pp. 66-69.
13. Stuart,B,2004,Infrared Spectroscopy : Fundamentals and Applications,John Willet & Sons Ltd,New York.
14. Susana, 2011, Extraction of Cellulose Waste Crown Pineapple, Journals Vokasi, Vol.7 No.1, p. 87-94.
15. Xu Feng, Jianming Yu, T Tesso, Floyed Cowell and D Hai, 2013, Qualitative and Quantitative Analysis of Lignocellulosic Biomass Using Infrared