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OPTIMIZATION OF LIGNIN EXTRACTION FROM RICE HUSK BY ALKALINE HYDROGEN PEROXIDE USING RESPONSE SURFACE METHODOLOGY

Anwar Ma'ruf[1,2], Bambang Pramudono[2,*] and Nita Aryanti[2]

[1]Department of Chemical Engineering, Universitas Muhammadiyah Purwokerto, Jl. Raya Dukuh Waluh, Kembaran, Purwokerto, Indonesia, 53182

[2]Department of Chemical Engineering, Diponegoro University, Jl. Prof. Soedharto, Tembalang, Semarang, Jawa Tengah, Indonesia 50239

*E-mail: pramudonoundip@gmail.com

ABSTRACT

Lignin is a natural polymer consisting of three major phenylpropanoid monomers (coniferyl alcohol (G), sinapyl alcohol (S) and pcoumaryl alcohol (H)). Lignin from biomass can be extracted by several solvents. This research studied the extraction of lignin from rice husk using an alkaline hydrogen peroxide. Three variables of extraction process comprising solvent to solid ratio, hydrogen peroxide concentration and pH of the mixture were studied. Response surface methodology with the central composite design was used to optimize the process variables. The optimum conditions for lignin extraction from rice husk using alkaline hydrogen peroxide were found at the solvent to solid ratio of 8.55, the H_2O_2 concentration of 1.56% and pH of 11.26. At this condition, the amount of lignin extracted was 1.7939%. Rice husk lignin obtained has similar characteristics with the lignin from another biomass source. However, based on FT-IR spectra, the specific characterization of rice husk lignin was found at the band of 2360.78 and 2075.41 cm^{-1}. The band between 2100 and 2360 cm^{-1} is a typical Si-H bond.

Keywords: Rice husk, rice husk lignin, alkaline hydrogen peroxide, response surface methodology

INTRODUCTION

Lignin is an amorphous polyphenolic lignocellulosic material, consists of three major phenylpropanoid monomers (coniferyl alcohol (G), sinapyl alcohol (S) and pcoumaryl alcohol(H)) forming a 3dimensional network inside the cell wall of biomass[1]. Lignin is a raw material for bio-products and bio-fuel. There are several methods for extraction of lignin from biomass. Alkali and acid solvent are the common methods for lignin extraction[2]. Utilization of alkali and acid solvent have disadvantages such as low purity and exhibited the lowest yields. In the recent works, some researchers applied several solvents to increase yield and purity of lignin extracted. There were several categories of solvents for lignin extraction such as organic solvent (organosolv)[3-6], ionic solvent[5,7], oxidative solvent[8,9] and hot water.[10-13] The selection of solvent is an important factor to the process of extraction of lignin from biomass.

Alkaline hydrogen peroxide (AHP) is an oxidative solvent. The AHP solvent is effective enough to raise the yield of lignin[9]. Hydrogen peroxide is a green oxidant that breaks the bond in lignin under alkaline conditions. Hydrogen peroxide is unstable under alkaline conditions and easily decomposes to more active radicals, such as hydroxyl radicals ($OH^{\bullet}$) and superoxide anion radicals ($OO^{\bullet-}$), which influence in the lignin extraction[14]. Many factors such as the solvent to solid ratio, solvent composition, extraction time, extraction temperature and pH of the solution may significantly have an effect on the AHP extraction yield. Optimization of variables is necessary to determine the optimum condition. The common method for variables optimization of the extraction process is Response Surface Methodology (RSM).[15-19]

Rice husk has specific characteristics. Besides its high content of lignin, the rice husk lignin also has high silica content.[20] It means that in the process of lignin extraction, silica will be extracted. Therefore, the purification process of lignin from silica impurities becomes an important factor. In the previous studies,

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the silica extracted in the process of lignin extraction from rice husk has not intensely been investigated.[3-4,21]

The aims of this research are to determine the optimum condition of lignin extraction and describe silica extracted base on liquor concentration. Three process variables comprising solvent to solid ratio, the concentration of hydrogen peroxide and pH of the solution are evaluated. The RSM with central composite design (CCD) is applied to optimize the process variables of extraction. The CCD was effectively used to optimize the variables process.[22-24]

EXPERIMENTAL

Materials

Rice husk was purchased from a local rice milling factory at Banyumas, Jawa Tengah, Indonesia. Rice husk was crushed to mesh size of 40 – 60 and dried at 60ºC for 6 hours. Hydrogen peroxide solution (30%), sulfuric acid and sodium hydroxide were obtained from Merck. Demineralized water was produced by ELVA-VEOLIA water demineralized.

Isolation Process

Lignin isolation process was performed by using an alkaline hydrogen peroxide solution. A total of 20 grams of rice husk was inserted into the 500 ml flask and then added 180 mL demineralized water containing 1.5% H_2O_2 with the ratio of volume/weight of 9:1. The mixture was added by a 2N NaOH until pH of 11 was achieved. The mixture was then isolated at the temperature of 100°C by using the heating oil bath for 3 hours starting after the temperature reached 100°C. After the isolation process completed, the solution (liquor) was separated from the solids using a filter paper.

Analysis of Lignin and Silica Concentrations of Liquor

Lignin concentration of liquor was analyzed by UV-Vis Spectrophotometer (UV-1800 SHIMADZU) with a resolution of 1 nm. Lignin concentration was done at the wavelength of 280 nm.[25] Silica concentration of liquor was analyzed by AAS (AA-6300 SHIMADZU). The analytical process was done using silica cathode lamp at the wavelength of 251.53 nm. Burning gasses were using nitrous oxide and ethylene.

Purification and Precipitation of Lignin

Purification of lignin was executed by using microfiltration with the ceramic membrane. The ceramic membrane was supplied by Polymer and Membrane Research Center of Chemical Department of Universitas Muhammadiyah Purwokerto. Precipitation of lignin was carried out by adding H_2SO_4 2 N until pH of 2. The liquor was then stirred for 4 hours. The precipitated lignin was dried at the temperature of 60ºC for 6 hours. Rice husk lignin (RHL) obtained was then characterized using Fourier Transform Infrared (FT-IR) spectrophotometer.

Characterization Methods

FT-IR spectrophotometer (SHIMADZU with DRS-8000) was used to analyze Fourier Transform Infrared spectroscopy using a KBr pellets. The KBr pellets consist of 300 mg KBr and 0.1 mg fine powder of lignin sample. Scans were recorded from 400 to 4000 cm^{-1} at a resolution of 16 cm^{-1}.

Design Experiment

The optimization of isolation of lignin from rice husk was using response surface methodology with central composite design (CCD). The range and level of independent process variables are shown in Table-1. The response of each variable and interaction of variables was evaluated using a quadratic polynomial model equation. The equation of quadratic polynomials is described in Equation-1:

$$Y = \beta_o + \sum_{j=1}^{3} \beta_j X_j + \sum_{j=1}^{3} \beta_{jj} \beta_j^2 + \sum_{i<j} \beta_{ij} X_i X_j \quad (1)$$

The significance of each variable and interaction of variables was evaluated by P-value at the significance of 95%. The analysis of variance (ANOVA) using Fisher F-test was used to assess the each model obtained. STATISTICA 6 was used to analysis the models.

Table-1: Range and level of independent process variables

Variables (X)	Range and levels				
	-α	-1	0	+1	+α
Solvent/weight ratio (X_1), ml/gr	7.32	8.00	9.00	10.00	10.68
H_2O_2 Concentration (X_2), %	0.66	1.00	1.50	2.00	2.34
pH (X_3)	10.16	10.50	11.00	11.50	11.84

RESULTS AND DISCUSSION

Model Fitting Analysis

Analysis of Response Surface Methodology was done to study the influence of solid ratio, the concentration of hydrogen peroxide and pH of the solution on the concentration of lignin and silica of liquor. The design of experiment (DOE) of lignin extraction process is presented in Table-1. The research data used to assess the effect of process variables on the lignin and silica extracted are shown in Table-2.
Table-2 shows that the concentration of lignin of liquor is in the range from 0.828% to 1.855%. On the other hand, the concentration of silica was found in value from 158.224 ppm to 1946.217 ppm. The multiple regression analysis was applied to the experiment data. The correlation of response variable and the test variables are determined by the second-order polynomial equation according to the coded values as expressed by equation (2) and (3):

$$Y_L = 1.712436 + 0.410846\ X_3 - 0.285710\ X_3^2 \quad (2)$$

$$Y_{Si} = 1155.619 - 585.963\ X_2^2 + 654.454\ X_3 \quad (3)$$

Where Y_L is the lignin concentration of liquor and Y_{Si} is the silica concentration of liquor calculated by the regression model, X_1, X_2, and X_3 are the coded variables.

The observed and predicted value of the lignin concentration of liquor (Y_L) and the silica concentration of liquor (Y_{Si}) were examined and described in Figure-1 and Figure-2. This test was conducted to determine the suitability between the observed values and the predicted value.
The determination coefficients value (R^2) of 0.80178 and 0.79983 for Y_L and Y_{Si} show that the observed and predicted values have a good suitability.
The fit quality of the lignin concentration of liquor (Y_L) and the silica concentration of liquor (Y_{Si}) model was examined with analysis of variance (ANOVA) as described in Table-3 and Table-4. Table-3 presents that the calculated F-value of the lignin concentration of liquor at 30.6121 is indeed higher than that of F distribution table (F-tabel $_{(0,95;7,16)}$ = 3.4944) at 5% level of significance. It shows the relationship between process variables with the lignin concentration of liquor. Table-4 displays that the calculated F-value of the silica concentration of liquor at 25.51346 is indeed higher than that of F distribution table (F-tabel $_{(0,95;7,16)}$ = 3.4944) at 5% level of significance. It shows also that the silica concentration of liquor influenced by the process variables.

Table-2: Lignin and silica concentration of liquor at various process variables

Run	Solvent/solid ratio (X_1), ml/gr	H_2O_2 Concentration (X_2), %	pH (X_3)	Lignin concentration of liquor (Y_L), %	Silica concentration of liquor (Y_{Si}), ppm
1	8.00 (-1)	1.00 (-1)	10.50 (-1)	1.576	907.072
2	8.00 (-1)	1.00 (-1)	11.50 (+1)	1.576	934.457
3	8.00 (-1)	2.00 (+1)	10.50 (-1)	1.524	774.013
4	8.00 (-1)	2.00 (+1)	11.50 (+1)	1.629	1396.217
5	10.00 (+1)	1.00 (-1)	10.50 (-1)	0.828	226.563

6	10.00 (+1)	1.00 (-1)	11.50 (+1)	1.454	991.530
7	10.00 (+1)	2.00 (+1)	10.50 (-1)	0.974	352.385
8	10.00 (+1)	2.00 (+1)	11.50 (+1)	1.454	1209.046
9	7.32 (-α)	1.50 (0)	11.00 (0)	1.629	1089.145
10	10.68 (+α)	1.50 (0)	11.00 (0)	1.629	1799.836
11	9.00 (0)	0.66 (-α)	11.00 (0)	1.454	158.224
12	9.00 (0)	2.34 (+α)	11.00 (0)	1.629	728.125
13	9.00 (0)	1.50 (0)	10.16 (-α)	0.907	639.474
14	9.00 (0)	1.50 (0)	11.84 (+α)	1.855	1946.217
15	9.00 (0)	1.50 (0)	11.00 (0)	1.629	1205.263
16	9.00 (0)	1.50 (0)	11.00 (0)	1.629	882.237
17	9.00 (0)	1.50 (0)	11.00 (0)	1.855	1339.474

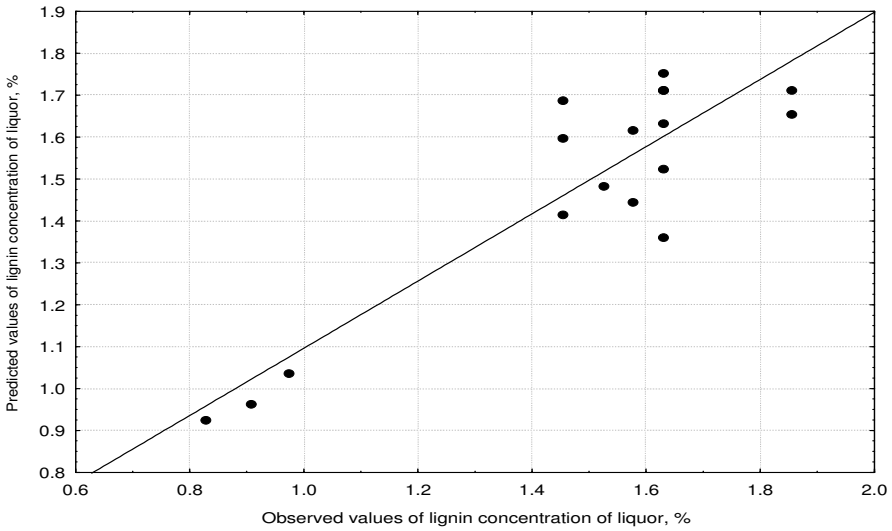


Fig.-1: Model suitability of lignin concentration of liquor (R^2 = 0.80178)

Table-3: ANOVA results for the lignin concentration of liquor model

Source	Sum of square	Degree of freedom	Mean Square	F-value
SS regression	1.2523	9	1.2523	30.6121
SS error	0.2863	7	0.040900	
SS total	1.4447	16		
R^2	0.80178			

Table-4: ANOVA results for silica lignin concentration of liquor model

Source	Sum of square	Degree of freedom	Mean Square	F-value
SS regression	2844461	9	2844461	25.51346
SS error	780420	7	111489	
SS total	3898696.68	16		
R^2	0.79983			

Effect of Process Variables

Tabel-5 and Table-6 illustrate the effect of variables on lignin and silica concentration of liquor. Based on Table-5, it can be seen that the main factor for lignin extraction using AHP is pH of the mixture. The p-value for the linear and quadratic coefficient is below 0.05. While the solvent to solid ratio and H_2O_2 concentration are not significant (p-value > 0.05).

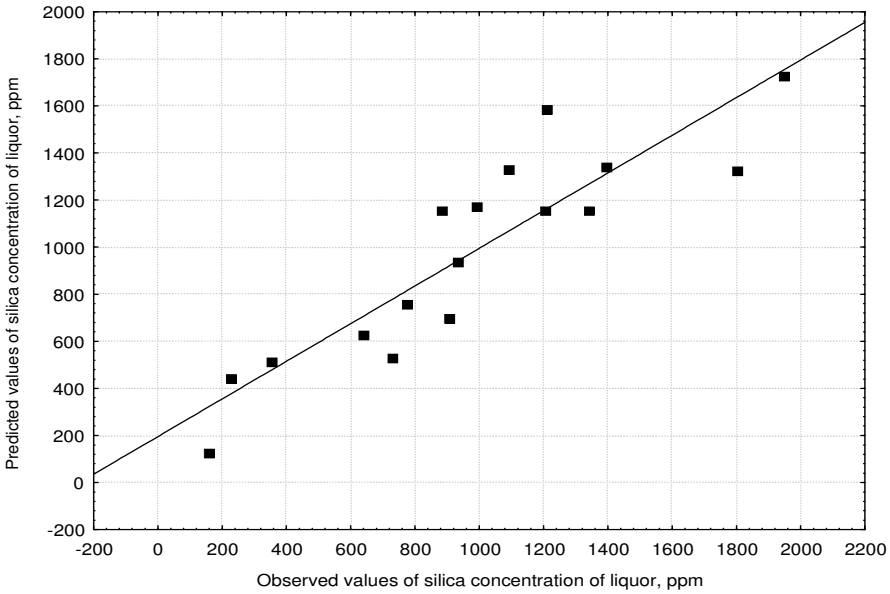


Fig.-2: Model suitability of silica concentration of liquor (R^2 = 0.79983)

Table-5: Effect estimates of variables on lignin concentration of liquor

Factors	Effect	P-value	Assignment
Intercept	1.712436	0.000002	
Solvent/solid ratio, X_1 (L)	-0.233351	0.070485	ns
Solvent/solid ratio, X_1 (Q)	-0.110450	0.389766	ns
H_2O_2 concentration, X_2 (L)	0.064303	0.575358	ns
H_2O_2 concentration, X_2 (Q)	-0.172121	0.196177	ns
pH, X_3 (L)	0.410846	0.007137	s
pH, X_3 (Q)	-0.285710	0.049503	s
X_1 by X_2	0.036433	0.806247	ns
X_1 by X_3	0.250207	0.123693	ns
X_2 by X_3	-0.010150	0.945410	ns
R-sqr	0.80178		
Adj.	0.5439		

s = (significant); ns = (not significant)

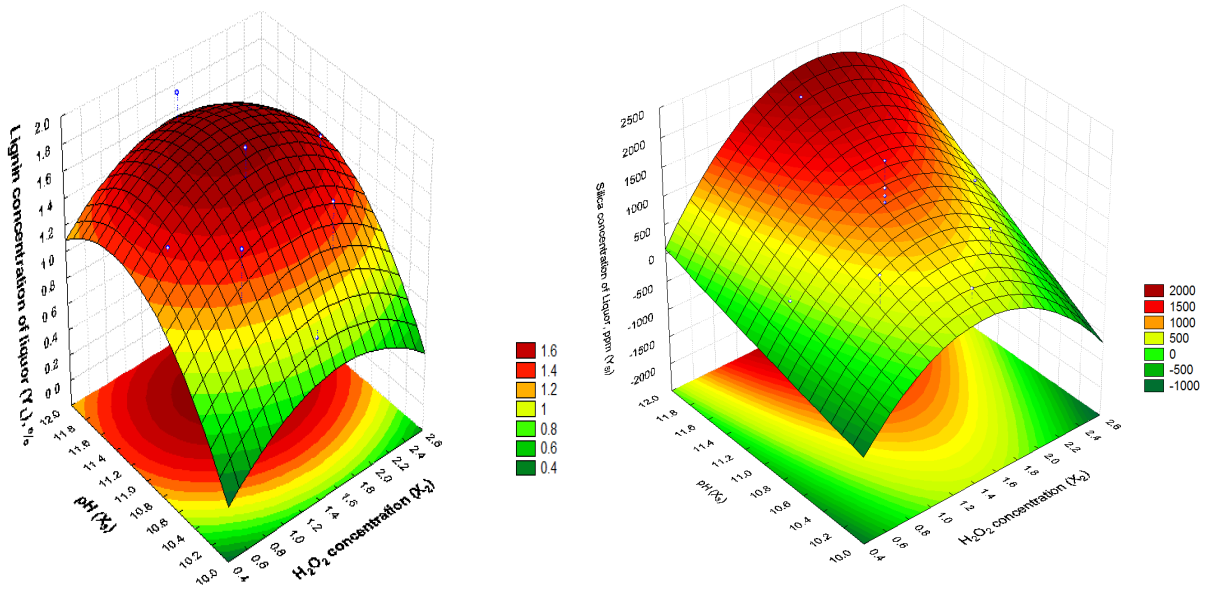
Table-6 shows that the two factors affecting the silica extracted on the lignin extraction of rice husk using AHP that are the H_2O_2 concentration and pH of the mixture. The p-value for quadratic coefficient of H_2O_2 concentration is 0.02279 (p-value < 0.05). And, p-value for linear coefficient of pH is 0.00849 (p-value < 0.05).

Table-6: Effect estimates of variables on silica concentration of liquor

Factors	Effect	P-value	Assignment
Intercept	1155.619	0.000539	
Solvent/solid ratio, X_1 (L)	-5.419	0.976914	ns
Solvent/solid ratio, X_1 (Q)	122.075	0.558775	ns
H_2O_2 concentration, X_2 (L)	238.781	0.227924	ns
H_2O_2 concentration, X_2 (Q)	-585.963	0.021525	s
pH, X_3 (L)	654.454	0.008491	s
pH, X_3 (Q)	14.846	0.942588	ns
X_1 by X_2	3.660	0.988066	ns
X_1 by X_3	243.010	0.337604	ns

X_2 by X_3	171.628	0.490862	ns
R-sqr	0.79983		
Adj.	0.54246		

s = (significant); ns = (not significant)



(a) (b)

Fig.-3: Three-dimensional response surface: (a) silica concentration of liquor; (b) silica concentration of liquor

Table-7 shows that the optimum conditions for lignin extraction from rice husk using AHP are at the solvent to solid ratio of 8.55, the H_2O_2 concentration of 1.56% and pH of 11.26. At optimum condition, the amount of lignin extraction is 1.7939%. Figure-3 shows the lignin and silica concentration of liquor at various pH and H_2O_2 concentration. At the optimum condition, the amount of silica extracted is 1,631.80 ppm.

Table-7: Critical value of lignin extraction using AHP

Factors	Observed minimum	Critical value	Observed maximum
Solvent/solid ratio, X_1	7.31821	8.55564	10.68179
H_2O_2 concentration, X_2	0.65910	1.56219	2.34090
pH, X_3	10.15910	11.26111	11.84090

FT-IR Characteristics of Pure Lignin

Figure-4 shows the spectra of pure rice husk lignin obtained. The band between 3330-3400 cm^{-1} is a typical of hydroxyl groups (O - H stretch) in phenolic and aliphatic structures. The peak at 2924.09 and 2854.65 cm^{-1} indicated a sp^3 C-H stretching in methyl (-CH_3), methylene (=CH_2/-CH_2-) and methoxy (-OCH_3) groups.[21] In the carbonyl/carboxyl region, a weak band is found at 1720.50 cm^{-1}, originating from unconjugated carbonyl/carboxyl stretching[26]. The band at 1635.64 cm^{-1} confirms a C=O stretching in conjugated p-substituted aryl ketones[21]. The range band of p-substituted aryl ketones is found at 1670–1640 cm^{-1}. An Aromatic skeleton vibration is showed at the band of 1512.19 cm^{-1}.

The band at 1396.48 cm^{-1} is a typical aromatic skeleton vibration combined with C-H in plane deformations, while 1365.80 cm^{-1} is of aliphatic C-H stretching in CH_3 (not -OCH_3) and phenolic –O-H. The band at 1211.00 cm^{-1} shows C-C plus C-O plus C=O stretching (G condensed > G etherified, typical of G units).[21] FT-IR spectra indicate the spectral features of GSH type lignin that are the band at 1134 and 864.11 cm^{-1} [27]. The aromatic C–H deformation at 1064.71 cm^{-1} appears as aromatic C-H in plane deformation (G > S) plus C-O deformation in primary alcohols plus C=O stretching (unconjugated).[21]

Commonly, the RHL obtained has similar characteristics with lignin from another biomass source. However, based on FT-IR spectra, the RHL was found having specific characteristics at the band of 2360.78 and 2075.41 cm^{-1}. The band between 2100 – 2360 cm^{-1} is a typical Si-H bond.[28-30] It means that the lignin still containing Silica. Singh and Dhepe[21] reported the FT-IR characteristics of RHL extracted by the organosolv process. Their report showed no peak at the band of 2360.78 and 2075.41 cm^{-1}

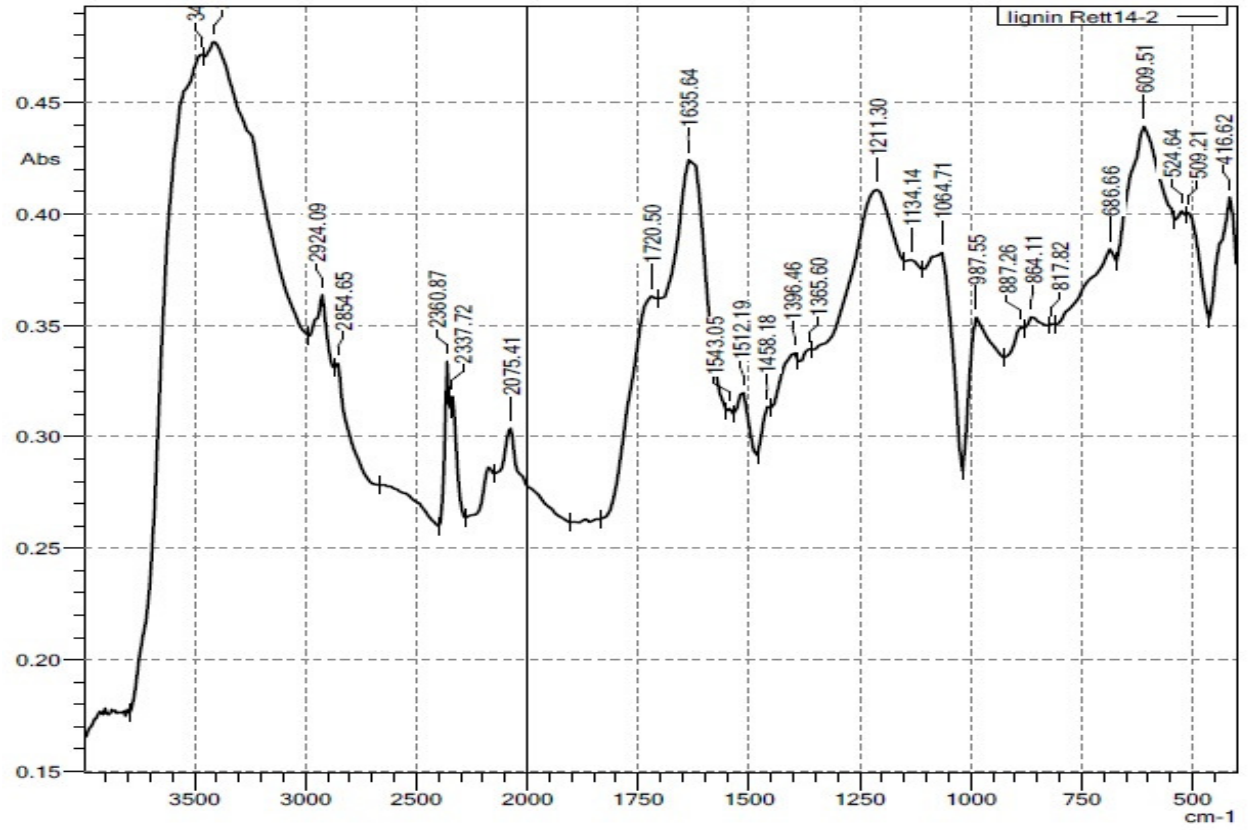


Fig.-4: FT-IR spectra of pure rice husk lignin (RHL)

CONCLUSION

Alkaline hydrogen peroxide (AHP) is of oxidative solvents. AHP solvent is effective enough to raise the yield of lignin obtained from rice husk. Optimization of process variables was success done by response surface methodology with the central composite design. The optimum conditions for lignin extraction from rice husk using AHP are at the solvent to solid ratio of 8.55, the H_2O_2 concentration of 1.56% and pH of 11.26. At optimum condition, the amount of lignin extraction is 1.7939%. RHL obtained has similar characteristics with lignin from another biomass source. However, based on FT-IR spectra, RHL has specific characteristics that are at the band of 2360.78 and 2075.41 cm^{-1}. The band between 2100 and 2360 cm^{-1} is a typical Si-H bond.

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