

Full Length Research Paper

Enhancement of Rice Straw Biodegradability by Alkaline and Acid Thermochemical Pretreatment Process: Optimization by Response Surface Methodology (RSM)

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The solubility of rice straw in alkali, Sodium Hydroxide (NaOH) and Potassium Hydroxide (KOH), and acid, Sulfuric Acid (H₂SO₄), pretreatment process were optimized by response surface methodology (RSM). Laboratory-scale experiments were carried out in a reflux completely mixed reactor with 500 mL capacity. The reaction temperature, stirring time and chemicals concentration are three chosen parameters for achieving to optimum solubility of rice straw. The experimental data were evaluated statistically by the analysis of variance (ANOVA). The maximum solubility of 82.40% was obtained in 200°C, 180 min and 0.6 g NaOH /g waste. The efficiency of NaOH in rice straw solubilization process is around 35% higher than KOH and around 77% higher than H₂SO₄. As a main result, NaOH pretreatment appears to be the most effective method in hydrolysis of rice straw compared with KOH and H₂SO₄ reagents. Also, the RSM is a reliable tool to the optimization of rice straw solubility process.

Key words: alkali and acid solubilization, Response Surface Methodology, rice straw, thermochemical pretreatment,

Abbreviations: Analysis of Variance (ANOVA), Central Composite Design (CCD), Chemical Oxygen demand (COD), Organic Matter (OM), Total Organic Carbon (TOC), Total Kjeldahl Nitrogen (TKN), Carbon to Nitrogen (C:N), Electrical Conductivity (EC), Response Surface Methodology (RSM), Soluble Chemical Oxygen Demand (SCOD), Volatile Solids (VS).

1. INTRODUCTION

Rice straw is one of the abundant renewable resources in the world. Today, field rice straw burning threatens public health (Binod et al., 2010; Mussatto and Roberto, 2004; Shafie et al., 2012). Usage of rice straw in biological process, such as composting and biogas production, is limited by slow degradation in bio-converting process. Low solubility of organic solid waste is main limiting factor for spreading anaerobic process in solid waste bio-conversion (Fdez.-Güelfo et al., 2011).

Lignocelluloses digestibility is enhanced by the alkali and acid pretreatment process (Alvira et al., 2010; Kootstra et al., 2009; Sumphanwanich et al., 2008).

The chemical composition straw mainly contains lignocellulosic that is made up of a matrix of cellulose and lignin bound by hemicelluloses chains and it composed of (32–47%), hemicellulose (19–27%) and lignin (5–24%) (Drapcho et al., 2008; Garrote et al., 2002; Mussatto and Roberto, 2004; Saha, 2003; Sarkar et al., 2012). The pretreatment process is used to

break the matrix materials to simple structure compounds in order to reduce the degree of crystallinity of the cellulose and increase the fraction of amorphous cellulose. The hydrolyzed compound is most suitable form for enzymatic attack (Sanchez and Cardona, 2008).

Alkali and acid pretreatment involves the application of chemicals solutions like NaOH, KOH or H₂SO₄ to remove lignin and a part of the hemicelluloses. In other word, the main effect of alkali and acid pretreatment on lignocellulosic biomass is delignification by breaking the ester bonds cross-linking lignin and xylan, thus increasing the porosity of biomass and an increase in the accessibility of the enzyme to cellulose (Binod et al., 2010; Chen et al., 2010; Lloyd and Wyman, 2005; Wyman, 1996; Zhang et al., 2011). In alkali pretreatment process, reaction temperature and contact time of 190°C and 5–10 min, respectively, are significant parameters on break down of lignocelluloses complex polymer into simple structure compound (Chen et al., 2011).

Diluted acid pretreatment is one of the most important techniques for production of sugars from

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lignocellulosics also sulfuric acid is widely used for the pretreatment. Acid pretreatment is usually carried out by concentrated or diluted acids (usually between 0.2% and 6% w/w) at temperatures between 130 °C and 210 °C (Cardona et al., 2009; Li et al., 2009).

Some studies indicated that alkali treatment appears to be the most effective method in breaking the ester bonds between lignin, hemicellulose and cellulose, and avoiding fragmentation of the hemicellulose polymers compared with acid or oxidative reagents (Carvalho et al., 2008; Zhang et al., 2011).

Dilute-acid cellulose and hemicellulose hydrolysis kinetics models are both based on a first-order term for reactants with an Arrhenius temperature dependence and an acid concentration raised to a power. All models predict that the end produced yield will increase with increasing acid concentration and temperature (Jacobsen and Wyman, 2000).

The efficiency of chemical pretreatment process on solubility of organic matter was determined based on the value of soluble COD (SCOD) (Cesaro et al., 2012; Chiu et al., 1997; Fdez.-Güelfo et al., 2011). SCOD is frequently used as an index for evaluation of effectiveness of the pretreatment on cellulosic compound such as Beet-pulp, switchgrass, organic fraction of solid waste, lignocellulosic biomass and kitchen waste in several research studies (Eskicioglu et al., 2006; Kim et al., 2003; Ozkan et al., 2011; Valo et al., 2004; Zhang et al., 2011). Also the results other studies indicated that the high concentration of SCOD means more soluble substrates in the hydrolysates are available for anaerobic digestion and eventually resulted in high methane yield. SCOD is a key parameter that represents the extent of solubilization of organic matters (Elbeshbishy et al., 2011; Eskicioglu et al., 2006; Kim et al., 2003; Valo et al., 2004; Zhang et al., 2011).

Alkali pretreatment of shredded rice straw with 2% NaOH with 20% solid loading at 85 °C for 1 h decreased the lignin by 36% (Zhang and Cai, 2008). Saccharification yield 74% was obtained when wheat straw was treated to 0.75% v/v of H₂SO₄ at 121 °C for 1 h (Saha et al., 2005). 76.5% of hydrolysis yields from olive tree biomass were resulted with 1.4% H₂SO₄ at 210 °C (Cara et al., 2008). Also, a high ethanol yield, 0.47 g/g glucose, was obtained in fermentation tests with cashew apple bagasse pretreated with diluted H₂SO₄ at 121 °C for 15 min (Rocha et al., 2009). 40-50% solubilization of VS was resulted from a pretreatment of activated sludge with 0.3 g

NaOH/g VS at 130°C for 5 min (Tanaka et al., 1997). Sun et al. (Sun et al., 1995) studied the effectiveness of different alkaline solutions by analyzing the delignification and dissolution of hemicellulose in wheat straw. They found that the optimal process condition was that using 1.5% NaOH for 144 h at 20 °C, releasing 60% and 80% lignin and hemicellulose respectively.

RSM has been widely used in the empirical study of the relationship between one or more measured responses such as yield on one hand, and a number of input variables such as time, temperature, pressure, and concentration on the other hand (Aziz et al., 2009; Chow and Yap, 2008; Ko et al., 2009; Kumar et al., 1999).

In the present study, was investigated to verify how rice straw solubility was affected by alkaline and acid solutions. RSM was employed to identify the optimum conditions for enhancing rice straw solubility by analyzing the relationships among a number of parameters that affect the overall process. SCOD is considered a suitable indicator for evaluating the solubility of the cellulosic compound of rice straw.

In the present study, was investigated to verify:

1. Rice straw solubility rate after alkali and acid pretreatment
2. How rice straw solubility was affected by influence parameter of alkali and acid pretreatment process
2. Is RSM a useful tool for identification of optimum conditions for enhancing rice straw solubility by analyzing the relationships among a number of parameters that affect the overall process?

2. MATERIALS AND METHODS

2.1. Collection of the sample

Rice straw samples were taken from a local farm of Sungai Dua located in Pulau Penang, Malaysia then it straw was cut nominally to 5–10 cm in length, washed thoroughly with tap water, air-dried for 24 hr and then store. Usually grinding is the initial step of pretreatment of any biomass which reduces the particle size, therefore it was grinded to 2–3 mm size and it was stored in an airtight plastic container at cool room for further treatment.

2.2. RSM

The experimental design for the selected process variables was carried out using CCD. To obtain the required data, the suitable range of values of each

of the three variables was identified as shown in Table 1. The table shows temperature, stirring time and concentration of alkali and acid are in the range of 30-200 °C, 10-120 min and 0-0.6 g/g dry rice straw and 0-10% diluted H₂SO₄ respectively (Chow and Yap, 2008; Drapcho et al., 2008; Garrote et al., 2002; Garrote et al., 2002; Kootstra et al., 2009; Sumphanwanich et al., 2008).

For three variables (n = 3) and five levels [low (-) and high (+)], the total number of experiments was 20, as determined by the expression 2ⁿ (2³ = 8 factorial points), 2n (2 × 3 = 6 axial points), 6

$$Y = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \sum \beta_{ij} x_i x_j \quad (1)$$

Y is the response (solubility value), β₀ is the intercept coefficient, β_i is the linear term, β_{ii} is the squared term, β_{ij} is the interaction term, and x_i and x_j are the un-coded independent variables. The model evaluated the effect of each independent

(center points, six replications) as given in Table 2. SCOD was selected as the response for the combination of independent variables. Experimental runs were randomized to minimize the effects of unexpected variability on the observed responses.

A quadratic polynomial equation was developed to predict the response as a function of the independent variables and their interactions. In general, the response for the quadratic polynomials is described in Eq. (1).

variable to the response. The fit quality of the models was evaluated from their correlation of determination (R²) (Ahmadi et al., 2005; Ghafari et al., 2009; Jo et al., 2008).

Table 1: Independent variables and their levels used for the Central Composite Design

1.a: Alkaline pretreatment						
Factor	variable	Coded levels of variables				
		-1	-0.5	0	0.5	1
Temperature, °C	A	30	72.5	115	157	200
time, min.	B	10	52.5	95	137.5	180
NaOH and KOH Concentration, g/g dry rice straw	C	0	0.15	0.3	0.45	0.6

1.b: Acid pretreatment						
Factor	variable	Coded levels of variables				
		-1	-0.5	0	0.5	1
Temperature, °C	A	30	72.5	115	157.5	200
time, min.	B	10	52.5	95	137.5	180
H ₂ SO ₄ Concentration, %	C	0	2.5	5	7.5	10

2.3. Analytical procedures

The selected physicochemical properties of the raw materials were measured prior to the start of the thermochemical process experiment. The water-soluble extract was prepared using the following procedure: 5 g of the sample was initially mixed with 100 ml of de-ionized water, shaken for 2 h, and left for 30 min. Next, the supernatant was filtered, 0.45μ through a filter paper (Whatman No. 1) (Rice et al., 2005; Zhang et al., 2011). SCOD and TKN of the filtrate were measured using dichromate digestion and the Kjeldahl method, respectively (Abdelhamid et al., 2004;

APHA, 2005; Rice et al., 2005; Strauch and Ballarini, 1994; Zhang et al., 2011). The SCOD of the samples was determined using COD reactor-Hach and DR2800 Spectrophotometer. The solubility of rice straw was calculated as the difference between initial weight of sample and total dissolved solids after hydrolyzation process as a percentage. TOC is oxidized with a mixture of K₂Cr₂O₇ and H₂SO₄. Unused K₂Cr₂O₇ is back-titrated with FeSO₄. TOC content was determined using by Modified Walkley-Black methods manual. The pH values were measured using a pH digital meter (EUTECH, pH 510) (Standard Method:2510-B)and an EC meter (VSI, Model

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30M, 100FT, USA) (USEPA 9045D) in aqueous extract (weight: volume = 1:10) (Rice et al., 2005; Zhang et al., 2011). The moisture content of the raw materials was determined by drying the samples at 105 °C for 24 h. Ash was determined in

a muffle furnace at 550 °C for 24 h, and OM was calculated as the difference between ash and its dry weight as a percentage (ASTM D2974)(Rice et al., 2005; Zhang et al., 2011).

Table 2: Complete experimental conditions tested and corresponding observed and predicted values of solubility of rice straw in alkali and acid pretreatment:

2.a: Alkali pretreatment

Run order	Type	Factors			SCOD _{NaOH} value		SCOD _{KOH} value	
		A	B	C	Observed	Predicted	Observed	Predicted
1	Fact	30	10	0	3.31	8.81	3.35	6.42
2	Fact	200	10	0	4.33	0.75	4.20	8.26
3	Fact	30	180	0	5.08	0.33	5.04	8.71
4	Fact	200	180	0	7.68	11.63	7.69	10.55
5	Fact	30	10	0.6	6.60	2.89	6.13	2.25
6	Fact	200	10	0.6	31.03	36.70	18.83	27.20
7	Fact	30	180	0.6	16.50	21.83	17.00	24.97
8	Fact	200	180	0.6	82.40	77.15	54.00	49.91
9	Axial	72.5	95	0.3	9.23	4.83	10.47	13.94
10	Axial	157.5	95	0.3	15.83	16.27	17.90	20.63
11	Axial	115	52.5	0.3	15.13	14.72	12.00	14.16
12	Axial	115	137.5	0.3	15.43	22.55	15.87	20.41
13	Axial	115	95	0.15	18.47	19.55	21.87	12.88
14	Axial	115	95	0.45	39.50	34.45	20.10	21.68
15	Centre	115	95	0.3	25.00	18.64	17.52	17.28
16	Centre	115	95	0.3	17.70	18.64	13.74	17.28
17	Centre	115	95	0.3	15.20	18.64	26.03	17.28
18	Centre	115	95	0.3	14.87	18.64	19.74	17.28
19	Centre	115	95	0.3	14.60	18.64	27.63	17.28
20	Centre	115	95	0.3	24.20	18.64	26.57	17.28

2.b: Acid pretreatment

Run order	Type	Factors			SCOD _{H2SO4} value	
		A	B	C	Observed	Predicted
1	Fact	30	10	0	4.50	4.98
2	Fact	200	10	0	5.70	5.72
3	Fact	30	180	0	5.52	5.23
4	Fact	200	180	0	8.73	9.21
5	Fact	30	10	10	7.95	7.40
6	Fact	200	10	10	10.95	11.17
7	Fact	30	180	10	11.58	11.49
8	Fact	200	180	10	19.04	18.49
9	Axial	72.5	95	5	10.27	10.32

10	Axial	157.5	95	5	13.45	12.25
11	Axial	115	52.5	5	9.90	9.82
12	Axial	115	137.5	5	10.56	11.71
13	Axial	115	95	2.5	11.68	9.82
14	Axial	115	95	7.5	11.31	12.75
15	Centre	115	95	5	11.01	11.28
16	Centre	115	95	5	10.07	11.28
17	Centre	115	95	5	11.80	11.28
18	Centre	115	95	5	11.13	11.28
19	Centre	115	95	5	10.61	11.28
20	Centre	115	95	5	12.32	11.28

2.3.1. Alkali and Acid pretreatment

To ensure low moisture content prior to treatment rice straw was dried at 105 °C for 24 h. Pretreatment process was carried out in a reflux completely mixed reactors with 500 ml capacity. Temperature and agitation speed during the pretreatment was controlled and monitored with a digital controller. A typical hydrolysis mixture consisted of 5 g of dry mass of rice straw and this mixed with 0-50 mL of de-ionized water at room temperature. Calculated amount of 98% (w/w) sulfuric acid was just about 0–5 mL, however the calculated concentration of sodium hydroxide and potassium hydroxide were 0-0.6 g/g mass. After

the mixed solution was introduced to the reflux reactor, it was heated to the designated temperature with the agitation rate set at 200 rpm. The pretreatment process time began with this introduced. The alkali and dilute acid pretreatment conditions are summarized in Table 1. The temperatures of pretreatment process were designed within the range of 30–200 °C with a reaction time from 10 to 180 min. When the pretreatment was finished, the pretreated solution was then separated by filtration. The liquid fraction was analyzed by COD method to determine the concentration of SCOD and calculation of solubility rate based on difference of initial weight of sample and final weight after solubilization.

Table 3: Selected physiochemical properties of rice straw

NO	Parameters	Rice Straw
1	OM (%)	88.4
2	TOC (% dw)	43.17
3	TKN (% dw)	0.653
4	C:N	66.11
5	PH	7.15
6	EC (μSm^{-1})	2381
7	MC (%)	9.76

*All analysis was reported on a dry weight (dw) basis

2.4. Analysis of Variance (ANOVA)

ANOVA was applied to estimate the effects of the main variables and their potential interaction on the solubility value. The ANOVA table can also be used to test for the statistical significance of the ratio of the mean square due to regression and the mean square due to residual error. Fisher F-test was used to check the adequacy of the model, whereas the p-value and Student's test were used to check for the significance of the equation parameters for the response. Three-dimensional response surfaces were used for facilitating a

straight forward examination of the effect of the experimental variables on the responses (Jo et al., 2008). The analysis of the experimental design and the calculation of the predicted data were carried out using Design Expert Software (Version 6.0.6, Stat Ease Inc., Minneapolis, USA) to estimate the response of the independent variables.

3. RESULTS AND DISCUSSION

3.1. Physicochemical property of rice straw

Physicochemical parameters were selected based on the effective parameters of the methane production and composting processes (Table 3). Analysis of selected physicochemical properties of rice straw residues are found to be rich in OM (88.4%) and TOC (43.17%), and they have a low TKN (0.652%) and high C:N ratio (66.11). These properties make rice straw a suitable carbon source for biogas production or the composting process. The results of other studies (Abdelhamid et al., 2004; Rashad et al., 2010) are slightly different because the climate and soil characteristics of the rice field in Malaysia are different.

$$Solubility_{NaOH} = 18.64 + 11.44 A + 7.83B + 14.9 C - 32.35 A^2 + 33.45 B^2 + 5.38 AB + 10.84 AC + 7.02 BC \quad (2)$$

$$Solubility_{KOH} = 17.2842 + 6.67 A + 6.25 B + 14.9 C + 5.78 AC + 5.12 BC \quad (3)$$

$$Solubility_{H_2SO_4} = 11.28 + 1.94 A + 1.90 B + 2.93 C - 2.07 B^2 + 0.81 AB + 0.755 AC + 0.96 BC \quad (4)$$

Table 2 and 4 show the predicted values for NaOH, KOH and H₂SO₄ analysis match the observed values reasonably well within the ranges of experimental conditions, with an R² value of 0.928, 0.746 and 0.930 respectively. This result suggests the applicability and reliability of the equation in representing the reaction over a range of experimental conditions with sufficient degree of accuracy. Thus, it can be used to simulate the thermochemical hydrolysis process.

The statistical analysis obtained from ANOVA for the three response surface quadratic models are shown in Table 4. The values of “PNF” for the models are less than 0.05, indicating that it is significant and desirable because it indicates that the terms in the model have a significant effect on the response. The values P < 0.0001 for solubility_{NaOH}, P = 0.0008 for solubility_{KOH} and the values P < 0.0001 for solubility_{H₂SO₄} indicate that there are only 0.01%, 0.08% and 0.01% chances, respectively, that a “model F-value” this large can occur due to noise in the experiment. Generally, P-values lower than 0.01 indicate that these models are statistically significant at 99% confidence level (Ravikumar et al., 2005). Values greater than 0.1000 indicates that the model terms are not significant. The “Lack of Fit F-value” of 2.18026, 1.60005 and 2.099079 implies that Lack of Fit is not significant relative to the pure error. Therefore,

3.2. Model fitting and statistical analysis

The obtained and predicted results are summarized in Table 2. The solubility values of rice straw in NaOH and KOH pretreatment ranged from 3.31 to 82.40% and 3.35 to 54% depending on the experimental conditions, respectively. While efficiency of H₂SO₄ in solubility of rice straw ranged from 4.5 to 19.04 %.

Further analysis of the results showed that they developed the highest order polynomial equation (in coded units) that can relate the solubility rate to the parameters studied. The quadratic models are given in Eq. (2, 3, 4).

there are 20.50%, 31.44% and 21.58% chances, respectively, that a “Lack of Fit F-value” this large can occur due to noise. An insignificant lack of fit is good because the primary objective is to have a model that fits the experimental data.

3.3. Process analysis

The response surface plots for NaOH, KOH and H₂SO₄ are shown in Figures 1, 2 and 3 respectively. The two-dimensional representation of the responses on the stirring time-temperature, stirring time-reagent concentration, and temperature- reagent concentration planes shows concentrically closed curves whose centers represent the optimum conditions.

In alkali and acid hydrolysis process an increase in solubility of rice straw was noticed with an increase in reagent concentration, stirring time and reaction temperature. Interaction of stirring time with temperature of reaction is presented in Figure 1.a. The optimum points occur at a temperature of 146 °C, time of 180 min, and dosage of 0.6 g NaOH/g mass. Likewise, Figure 3.a shows that the optimum sulfuric acid solubility occurs at around a temperature of 200 °C, time of 170.18 min, and concentration of 10 % for H₂SO₄.

Table 4: ANOVA for the quadratic model

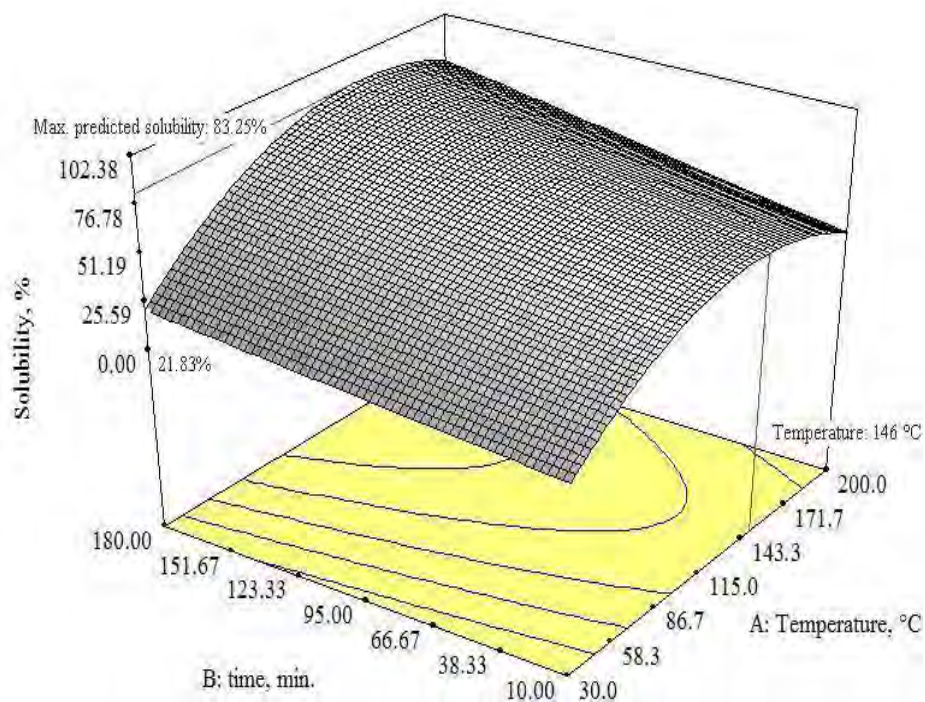
Response	Source	Sum of Squares	Degree of Freedom	Mean Square	F- Value	Prob > F	Remark
SCOD _{NaOH}	Model	5362.126	8	670.2658	17.78626	< 0.0001	significant
	A	1112.654	1	1112.654	29.52554	0.0002	significant
	B	520.7862	1	520.7862	13.81965	0.0034	significant
	C	1887.085	1	1887.085	50.07591	< 0.0001	significant
	A ²	257.9618	1	257.9618	6.845306	0.0240	significant
	B ²	275.8973	1	275.8973	7.321246	0.0204	significant
	AB	231.4833	1	231.4833	6.14267	0.0307	significant
	AC	939.9728	1	939.9728	24.94324	0.0004	significant
	BC	394.1028	1	394.1028	10.45796	0.0080	significant
	Residual	414.5293	11	37.68448			
	Lack of Fit	299.9016	6	49.9836	2.18026	0.2050	not significant
	Pure Error	114.6276	5	22.92553			
	Cor Total	5776.655	19				
	Std. Dev.	6.138769		R-Squared	0.928241		
Mean	19.105		Adjusted R-Squared	0.876052			
C.V.	32.13173		Predicted R-Squared	0.66227			
PRESS	9602.339		Adequate Precision	18.91505			
SCOD _{KOH}	Model	1847.1	5	369.42	8.21961	0.0008	significant
	A	381.118	1	381.118	8.47992	0.0114	significant
	B	332.343	1	332.343	7.39467	0.0166	significant
	C	658.241	1	658.241	14.6459	0.0018	significant
	AC	266.805	1	266.805	5.93643	0.0288	significant
	BC	208.59	1	208.59	4.64115	0.0491	significant
	Residual	629.211	14	44.9437			
	Lack of Fit	467.047	9	51.8941	1.60005	0.3144	not significant
	Pure Error	162.164	5	32.4329			
	Cor Total	2476.31	19				
	Std. Dev.	6.704		R-Squared	0.74591		
	Mean	17.2842		Adj. R-Squared	0.65516		
	C.V.	38.787		Pred. R-Squared	0.09667		
	PRESS	2236.92		Adeq. Precision	12.9797		
SCOD _{H2SO4}	Model	171.7501	7	24.53572	22.84883	< 0.0001	significant
	A	31.87431	1	31.87431	29.68286	0.0001	significant
	B	30.45742	1	30.45742	28.36339	0.0002	significant
	C	72.86426	1	72.86426	67.85464	< 0.0001	significant
	B ²	19.38308	1	19.38308	18.05044	0.0011	significant
	AB	5.238006	1	5.238006	4.877878	0.0474	significant
	AC	4.5602	1	4.5602	4.246674	0.0417	significant
	BC	7.3728	1	7.3728	6.8659	0.0224	significant
	Residual	12.88594	12	1.073829			
	Lack of Fit	9.614329	7	1.373476	2.099079	0.2158	not significant
	Pure Error	3.271615	5	0.654323			
	Cor Total	184.636	19				
	Std. Dev.	1.036257		R-Squared	0.930209		
	Mean	10.404		Adj. R-Squared	0.889497		
C.V.	9.960179		Pred. R-Squared	0.626404			
PRESS	68.97926		Adeq. Precision	20.62067			

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DESIGN-EXPERT Plot

Solubility, %
 X = A: Temperature, °C
 Y = B: time, min.

Actual Factor
 C: NaOH, g/g waste = 0.60

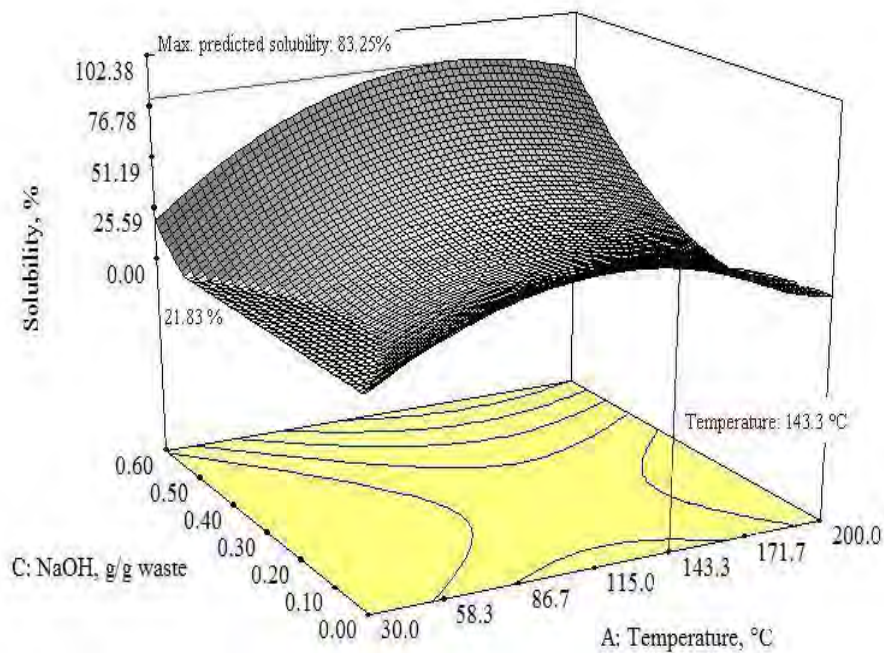


(1.a)

DESIGN-EXPERT Plot

Solubility, %
 X = A: Temperature, °C
 Y = C: NaOH, g/g waste

Actual Factor
 B: time, min. = 159.96



(1.b)

DESIGN-EXPERT Plot

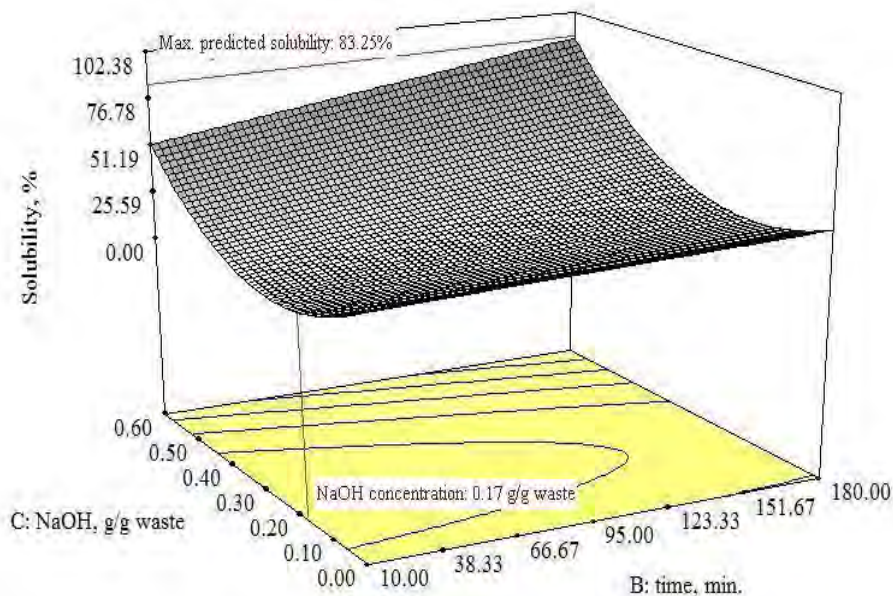
Solubility, %

X = B: time, min.

Y = C: NaOH, g/g waste

Actual Factor

A: Temperature, °C = 159.1



(1.c)

Fig. 1: Expert plot; response surface plot for influencing of NaOH concentration and temperature (1.a) and NaOH concentration and stirring time (1.b) on SCOD

From the plot in Figures 1.a and 3.a at a higher alkali and acid concentration, the increase in reaction temperature up to 146 and 200 °C for NaOH and H₂SO₄ respectively, corresponds to an increase in the solubility of rice straw. For example, at a NaOH concentration of 0.6 g/g mass, the solubility of rice straw increased from 21.83 to 83.25% when the temperature was increased from 30 to 146 °C, whereas at a H₂SO₄ concentration of 10 %, the solubility increased from 9.21 to 18.49% when the temperature was increased from

30 to 200 °C. From another perspective, by making the chemical concentration constant, the solubility also varies with the reaction temperature and stirring time depending on the extremity of the used operating conditions. Therefore, in order to obtain the optimum solubility by making the chemical concentration constant, there is a need to analyze the relationships of factors A and B. This is due to the indefinite trend observed in examining such variation in the current study, as observed in Figures 1.a and 3.a.

Table 5: Constraints of each variable for the numerical optimization of the SCOD

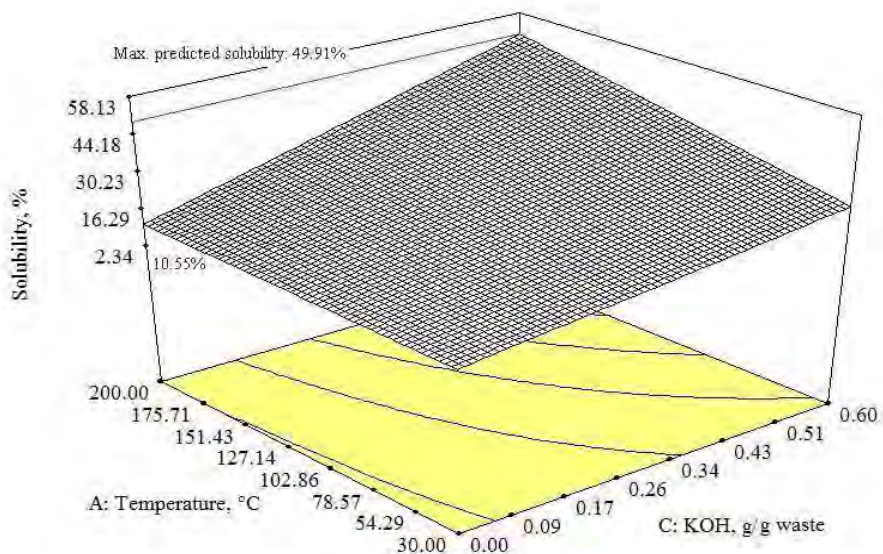
Type of variable	Goal	Lower Limit	Upper Limit
NaOH Concentration, g/g mass	is in range	0	0.6
KOH Concentration, g/g mass	is in range	0	0.6
H ₂ SO ₄ Concentration, %	is in range	0	10
Process temperature, °C	is in range	30	200
contact time, min.	is in range	10	180
Specific capacitance- NaOH	maximize	3.31	82.40
Specific capacitance- KOH	maximize	3.35	54.00
Specific capacitance- H ₂ SO ₄	maximize	4.5	19.04

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DESIGN-EXPERT Plot

Solubility, %
 X = C: KOH, g/g waste
 Y = A: Temperature, °C

Actual Factor
 B: time, min. = 180.00

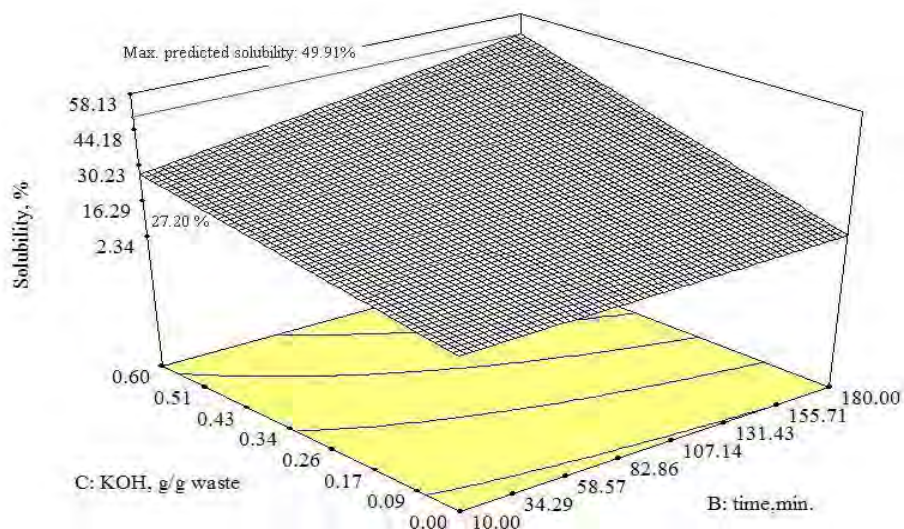


(2.a)

DESIGN-EXPERT Plot

Solubility, %
 X = B: time, min.
 Y = C: KOH, g/g waste

Actual Factor
 A: Temperature, °C = 199.97



(2.b)

Fig. 2: Expert plot; response surface plot for influencing of KOH concentration and temperature (2.a) and KOH concentration and stirring time (2.b) on SCOD

In alkali and acid hydrolysis an increase in solubility of rice straw was noticed with an increase in chemicals concentration and reaction temperature (Figures 1.b, 2.a and 3.b). These figures show that chemicals concentration and temperature interact in affecting the solubility of rice straw in hydrolysis process. Another word, temperature and chemicals concentration have a positive effect on the solubility when stirring time is relatively high. For instance, in Figure 1.b, an increase in solubility from 21.83 to 83.25 % was noticed with an increase in the temperature from 30 to 146 °C and NaOH concentration from 0 to 0.6 g/g mass in stirring time 159.96 min. Likewise,

in Figure 2.a, an increase in the solubility from 10.55 to 49.91% was noticed with an increase in temperature from 30 to 200°C and with an increase in KOH concentration from 0 to 0.6 g/g mass in stirring time of 180 min. In Figure 3.b, at stirring time of 170.18 min., an increase in solubility from 9.21 to 18.49 % was noticed with an increase in acid concentration from 0 to 10% and with an increase in temperature from 30 to 200 °C. As shown in Figures 1.b and 2.a, solubility of rice straw increases as the concentration of sodium hydroxide or potassium hydroxide increases from 0 to 0.6 g/g mass. An increase in solubility indicates that after alkali pretreatment properties of rice

straw is improved for the biogas generation and composting processes (Fernandes et al., 2009; López Torres and Lloréns, 2008). Figure 3.b

indicated that the maximum solubility is obtained at 10% of H₂SO₄ concentration and reaction temperature of 200 °C.

Table 6: Optimum conditions for maximum SCOD production by NaOH, KOH and H₂SO₄

Type of chemicals	No.	Temperature , °C	Time, min	Alkaline con. g/g mass Acid con. %	COD, mg/L	Desirability
NaOH	1	147.7	166.6	0.59	83.3574	1
	2	145.1	179.5	0.59	83.084	1
	3	160.3	164.2	0.60	83.0239	1
	4	155.7	176.6	0.59	83.8162	1
	5	147.0	173.3	0.59	82.4253	1
	6	122.9	180.0	0.00	38.3421	0.443
	7	121.2	156.2	0.00	37.9936	0.439
	8	118.1	126.9	0.00	37.614	0.434
	9	111.8	41.2	0.00	36.806	0.424
KOH	1	199.97	180.00	0.60	49.91	0.91926
	2	200.00	176.30	0.60	49.40	0.909092
	3	200.00	180.00	0.59	49.24	0.906095
	4	200.00	174.49	0.60	49.18	0.904802
	5	200.00	180.00	0.59	49.02	0.901717
	6	179.51	180.00	0.60	46.91	0.859983
	7	200.00	150.98	0.60	46.04	0.842778
	8	142.31	180.00	0.60	41.45	0.752231
H ₂ SO ₄	1	200.00	170.03	10.00	18.52	0.964363
	2	200.00	169.36	10.00	18.52	0.964352
	3	199.89	171.05	10.00	18.52	0.964036
	4	200.00	175.94	10.00	18.51	0.963689
	5	200.00	179.69	10.00	18.50	0.962546
	6	200.00	158.07	10.00	18.48	0.961508
	7	200.00	129.38	10.00	18.05	0.931652

Figures 1.c, 2.b and 3.c show the 3D surface plot and the contour plot of the interaction between the chemical concentration and stirring time, as well as their effects on the solubility of rice straw. In these figures, the variation in solubility is highly indefinite and relies solely on the operating conditions such as the stirring time and chemicals concentrations. Analysis of Figure 1.c shows that at a fixed temperature and a high NaOH concentration of 0.6 g/g waste, the solubility increases proportionally with the stirring time. For example, at NaOH of 0.6 g/g waste, when the stirring time was increased from 10 to 180 min, the solubility increased proportionally to 83.25%. Hence, solubility is affected indefinitely by the concentrations of NaOH, the stirring time, and the temperature of the reactants and interaction between themes. This result is confirmed by the obtained results for KOH and H₂SO₄ (Figure 2.b and 3.c).

As mentioned in model 2, 3 and 4, the variable of A, B and C and interaction of AB, AC, BC were

significant model terms for NaOH, KOH and H₂SO₄ hydrolyzation process, however AB was insignificant in model 3 and in order to increasing of accuracy and reliability of model the model was improved by reduction of model. The efficiency of NaOH in rice straw solubilization process is 1.53 times higher than KOH and around 4.33 times higher than H₂SO₄.

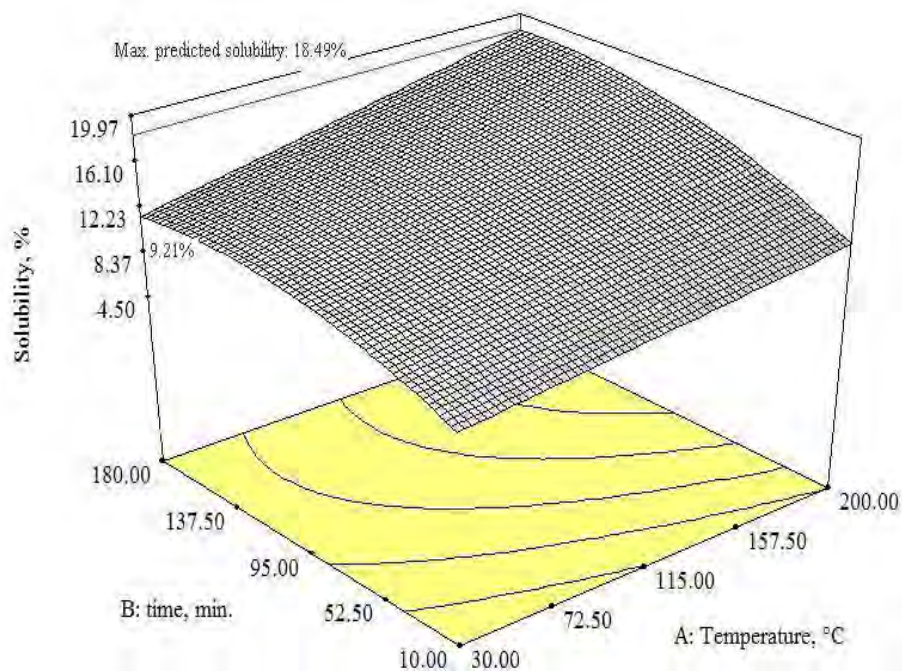
As a main result of these experiments, generally the solubility of rice straw was growth with increasing of reaction temperature, contact time and chemical concentration. This results are confirmed by the obtained result with previously study (Fdez.-Güelfo et al., 2011). In a study conducted at detention times 2.5–6.5 h, the solubility of solid waste increased from 8.5% to 12.5% after alkali hydrolysis (Zhang et al., 2011). In experiments involving fixed temperatures, the effect of temperature on solubility has not been evaluated (Ong et al., 2010; Sun et al., 2000; Zhang et al., 2011).

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DESIGN-EXPERT Plot

Solubility, %
 X = A: Temperature, °C
 Y = B: time, min.

Actual Factor
 C: H2SO4, % = 10.00

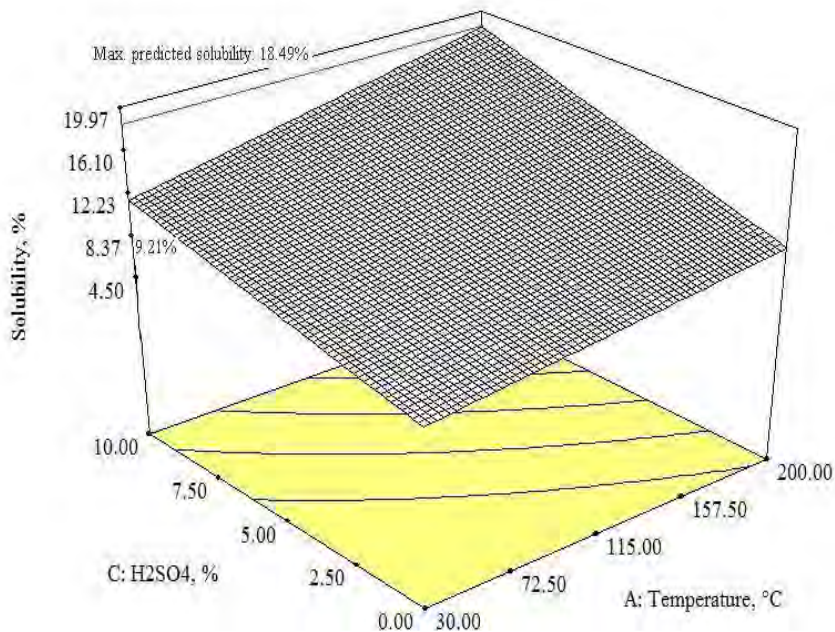


(3.a)

DESIGN-EXPERT Plot

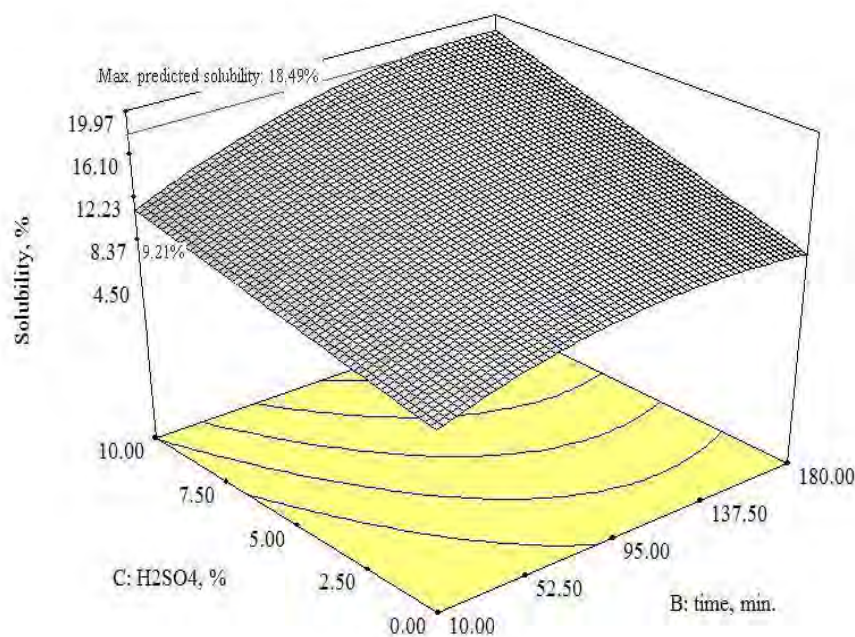
Solubility, %
 X = A: Temperature, °C
 Y = C: H2SO4, %

Actual Factor
 B: time, min. = 170.18



(3.b)

DESIGN-EXPERT Plot

Solubility, %
X = B: time, min.
Y = C: H₂SO₄, %Actual Factor
A: Temperature, °C = 200.00

(3.c)

Fig. 3: Expert plot; response surface plot for influencing of H₂SO₄ concentration and temperature (3.a), H₂SO₄ concentration and stirring time (3.b) and stirring time and temperature (3.c) on SCOD

As already mentioned, delignification by breaking the ester bonds is main effect of alkaline and acid hydrolysis (Lloyd and Wyman, 2005; Wyman, 1996; Zhang et al., 2011). Results of this study are indicated increasing of solubility is resulted of increasing in transforming of lignocelluloses into soluble compound. Soluble compound will be readily biodegradable in composting or methane production process. Also, the results show rising in solubility value is a direct correlation with reagent concentration, stirring time and temperature of reaction. These results are confirmed by cellulose and hemicelluloses hydrolysis kinetic model (Jacobsen and Wyman, 2000).

4. PROCESS OPTIMIZATION

In the alkali and acid hydrolysis of rice straw, the yield can be increased by manipulating parameters such as the chemicals concentration, the reaction temperature, and the contact time. However, optimization of the response is difficult because the variation in each parameter with the hydrolysis of rice straw is highly indefinite as discussed in the previous section. Therefore, in order to optimize the response, the function of desirability was applied using Design Expert software version 6.0.6. In the present study, numerical optimization was chosen. This process presents a

comprehensive and up-to-date description of the most effective methods in continuous optimization (Nocedal and Wright, 2006). To do so, the upper and lower limits of each variable (NaOH, KOH and H₂SO₄ concentration, temperature, and stirring time) and its response as predicted by the model were provided based on the contour and surface plot obtained previously. The ultimate goal of optimization is to obtain the maximum response that simultaneously satisfies all variables' properties and the relationships among them. Table 5 shows the constraints of each variable and the desired response.

Table 6 shows the nine, eight and seven possible solutions that satisfy all the specified conditions for NaOH, KOH and H₂SO₄, respectively. The solutions that gave a desirability value of 1 represent those that can be ideal solutions. Therefore, the optimum conditions in any of the selected solutions can be chosen for further validation. In the current study, the solution number 1 for NaOH (147 °C, 166.6 min. and 0.59 g NaOH /g mass), KOH (199.97 °C, 180 min and 0.6 g KOH /g mass) and for H₂SO₄ (200 °C, 170.03 min, and 10% H₂SO₄) are selected due to their highest prediction of responses (83.35, 49.91 and 18.52% for NaOH, KOH and H₂SO₄ respectively). For validation purpose, comparisons were made between the predicted optimum condition and its subsequent response with the

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results obtained from an earlier experimental work. The observed and predicted result in Table 1 indicates that the percentage difference between both experimental and predicted values for NaOH was 6.4%. The low percentage difference and insignificant of “lack of fit” proved that the model was significant in predicting the response. The percentage difference between the experimental and predicted values for KOH and H₂SO₄ are 7.57 and 2.9%, respectively.

The solubility extracted from the optimum condition of the present work is comparable with those obtained from other studies. For example, the optimum solubilization condition for the organic fraction of solid waste was 2.3 g Ca(OH)₂/L at 6.0 h (Zhang et al., 2011). Under these conditions, the solubility reached levels up to 11.5%. Moreover, in the optimum concentration, the solubility increased from 14664 to 19359 mg/L, a finding that also supports the above results (Zhang et al., 2011). Another study developed an alkali pretreatment process prior to anaerobic digestion of pulp and paper sludge to enhance methane productivity. A maximum SCOD of 83% was achieved in 8 g NaOH/100 g TS sludge (Zhang et al., 2011).

5. CONCLUSION

Analysis of selected physiochemical properties of rice straw residues indicated that rice straw a suitable carbon source for biogas production or the composting process. Thermochemical pretreatment significantly causes a deep delignification and conversion of non-soluble lignocelluloses of rice straw to soluble compounds.

A comparison between the effectiveness of NaOH, KOH and H₂SO₄ in terms of the hydrolysis of non-soluble complex cellulosic compounds in rice straw shows that the NaOH causes a deep delignification and convert the complex polymer of lignocelluloses compound to soluble phase. Influences of NaOH in solubility of rice straw were significantly more than KOH and H₂SO₄. The use of RSM based on CCD is practical for the simultaneous study of the effects of process variables on the solubility value and the possible interaction between them. Further, based on the results it will be predictable that a process for the enhanced production of biogas or compost from rice straw entails two stages: (1) alkaline pretreatment followed by (2) anaerobic digestion or the composting process.

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