IOP Conf. Series: Materials Science and Engineering **429** (2018) 012041 doi:10.1088/1757-899X/429/1/012041

Optimization of the product of nanocrystalline cellulose from coconut husks

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Abstract. Coconut husks can increase its value as agricultural wastes by utilizing these wastes to produce nanomaterials. Therefore, in this study prepared nanocrystalline cellulose (NCC) from coconut husks using sulphuric acid hydrolysis. The Box-Behnken Design (BBD) based on the response surface methodology was applied to study the effect of sulphuric acid concentration, reaction time and reaction temperature on the yield of NCc. The result showed that the yield of NCC was 44.94%, under optimum conditions of 64.6% concentration of sulphuric acid, 58.55 minutes and 44.56 ˚C. The X-ray diffraction (XRD) showed the crystallinity index of NCC was 68.3%.

1. Introduction

Cellulose, the most abundant and accessible organic compound in nature, has been increasingly as nanocrystalline cellulose (NCC) in the production of biodegradable materials. NCC are typically rod-shaped cellulose particles, with diameters of 1 to 100 nm and lengths of tens to hundreds nanometers [1]. Their main features include large specific surface area, very high modulus of elasticity and great aspect ratio [2], which determine their utilization as reinforcing agent in polymer composites [3]. For preparing NCC, one of the most commonly used methods is acid hydrolysis, based on the fact that the crystalline regions are insoluble under acid conditions [4]. Such a hydrolysis process can disrupt the disordered and amorphous parts of the cellulose and release ordered and definite crystals .

Over the past decade, several natural fibers such as flax, jute, sisal fibers and cellulosic component have been studied as resources for preparing NCC. However, the use of coconut husks has limited research for its utilization. Coconut husks as agriculture wastes are mostly used as floor mat, doormat and bushes. Coconut husks consists of 38-39% cellulose, 17.33% hemicellulose and 46-53% lignin [5]. Thus, coconut husks are suitable natural cellulose materials to be isolated as NCC because it has high performance to be reinforced with polymer in forming biodegradable film. Preparation of NCC from coconut husks also can greatly increase the economic value of these agricultural wastes.

Response surface methodology as an important experimental design and analysis methodology is to optimize the preparation conditions. The objective of this study is to prepare NCC from coconut husks by sulfuric acid hydrolysis and using Box-Behnken design in response surface methodology to improve the yield of NCC. The crystallinity index of NCC was optimize using X-Ray diffraction (XRD).

2. Materials and Methods

2.1. Materials
Coconut husks were purchased from the local market in Kangar, Perlis, Malaysia. Sodium hydroxide and sodium chlorite were purchased from Sigma-Aldrich and sulfuric acid was purchased from Vectec, PA. Glacial acetic acid was purchased from Fisher, Germany.

2.2. Preparation of coconut husks fibres
The coconut husks were cut and ground until it turned into powder. Then, the powder were sieved to 125 μm for the treatments. The coconut husks were then treated with 4wt% of sodium hydroxide (NaOH) for 2 hours at 80 ˚C with continuous stirring. Then, the fibres were repeatedly filtered with distilled water until the pH turned to neutral. After this alkaline treatment, the fibres were bleached using acetate buffer and 1.7wt% sodium chlorite ($NaClO_2$) at 80 ˚C for 2 hours. The fibres were undergone alkaline and bleaching treatment up to 4 times. The white fibres were then dried in air circulating oven for 24 hours at 50 ˚C.

2.3. Preparation of nanocrystalline cellulose (NCC)
Nanocrystalline cellulose (NCC) were prepared from the coconut husks fibres using acid hydrolysis. The coconut fibres were put into a 100 ml beaker, then the sulphuric acid concentration (60-70 wt%) was added into the beaker with the reaction temperature at (40-50 ˚C) and reaction time for (55-65 min) under continuous stirring. Then, 10-fold of cold water was added to the suspension to stop the hydrolysis process. The suspension was centrifuged for 10 min at 9000 rpm to remove the excessive sulphuric acid. After the suspension was centrifuged repeatedly, the suspension turned into milky suspension and were collected and dried for 24 hours to calculated the yield of coconut husks NCC.

2.4. Experimental design
To obtain the optimum preparation conditions of coconut husks NCC, the response surface method was used in this study. The sulphuric acid concentration (X_1), reaction temperature (X_2) and reaction time (X_3) were chosen as variables and yield (Y) was chosen as response value. The parameters of the test are shown in **Table 1.**

Table 1: The parameters that used for analyse NCC using the Design Expert 7.1.5

	Levels		
Factors	**-1**	**0**	**1**
X_1 (wt%)	60	65	70
X_2 (˚C)	40	45	50
X_3 (min)	55	60	65

2.5. X-ray Diffraction (XRD)
The crystallinity of NCC were characterized using Bruker AXS D8 Advance diffractometer with a scanning rate of 5˚ per min. The range of diffraction angle were 2θ = 10 - 40˚. The crystallinity index of the samples was calculated according to the Segal method as shown in equation below, where I_{002} for crystalline region and I_{am} for amorphous region.

$$CrI\ (\%) = \frac{I_{002} - I_{am}}{I_{002}}$$

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3. Results and Analysis

3.1. Optimum preparation conditions of NCC from coconut husks

To obtain the optimum preparation conditions of NCC from coconut husks, sulphuric acid concentration (60-70 wt%), reaction temperature (40-50 ˚C) and reaction time (55-65 min) were used Box-Behnken design (BBD) and obtain the regression model. Design of Box-Behnken test and results of the yield for NCC obtained shows in **Table 2**.

Table 2: Design of BBD and percentage of yield for test

No	X_1 (wt%)	X_2 (˚C)	X_3 (min)	Y (%)
1	60	40	60	43.67
2	70	40	60	43.26
3	60	50	60	43.28
4	70	50	60	43.37
5	60	45	55	44.08
6	70	45	55	44.06
7	60	45	65	44.11
8	70	45	65	43.54
9	65	40	55	44.22
10	65	50	55	43.42
11	65	40	65	42.91
12	65	50	65	43.58
13	65	45	60	44.76
14	65	45	60	44.84
15	65	45	60	44.93
16	65	45	60	44.92
17	65	45	60	44.89

Based on the design and results of Box-Behnken design in **Table 2**, the Design Expert software was used to fit the regression model and the obtained regression equation was expressed as follows:

$$Y = 44.81 - 0.11X_1 - 0.054X_2 - 0.21X_3 + 0.13X_1X_2 - 0.14X_1X_3 + 0.37X_2X_3 - 0.53X_1^2 - 0.95X_2^2 - 0.39X_3^2$$

The significant analysis was showed in **Table 3**. The significance level of the model was less than 0.0001, which showed that the model and method were reliable. The model determination coefficient R^2 was 0.9881 suggested the fitted model could explain 98.81% of the total variation, which further confirmed that the model could fit well the experimental results.

Table 3: Regression analysis of variance

Source	Sum of Squares	Degree of Freedom	Mean Square	F Value	P value
Model	7.28	9	0.81	64.31	< 0.0001
X_1	0.099	1	0.099	7.87	0.0263
X_2	0.023	1	0.023	1.84	0.2714
X_3	0.34	1	0.34	26.73	0.0013
X_1X_2	0.068	1	0.068	5.37	0.0535
X_1X_3	0.076	1	0.076	6.01	0.0440

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X_2X_3	0.54	1	0.54	42.95	0.0003
X_1^2	1.19	1	1.19	94.56	< 0.0001
X_2^2	3.77	1	3.77	299.86	< 0.0001
X_3^2	0.64	1	0.64	50.65	0.0002
Residual	0.088	7	0.013		
Lack of fit	0.069	3	0.023	4.69	0.0847
Pure Error	0.019	4	4.870E-003		
Cor Total	7.37	16			
R squared	0.9881				

The factors X_1, X_3, X_1X_3, X_2X_3, X_1^2, X_2^2 and X_3^2 significantly affected the yield of the of NCC ($p \leq 0.05$) and the factor that ($p \geq 0.1$) are not significant. So it was not linear relationship between the effects of different factors on the response value. **Figure 1 (a, b and c)** shows the result for response surface figure under these three factors. Taking the maximum yield as the objective, the 64.61 wt% of sulphuric acid, 44.55 ˚C of reaction temperature and 58.54 min of reaction time, the predicted yield of NCC was 44.84% under these conditions. The results showed that the response surface methodology can be used to optimize the preparation conditions of NCC in order to increase the yield.

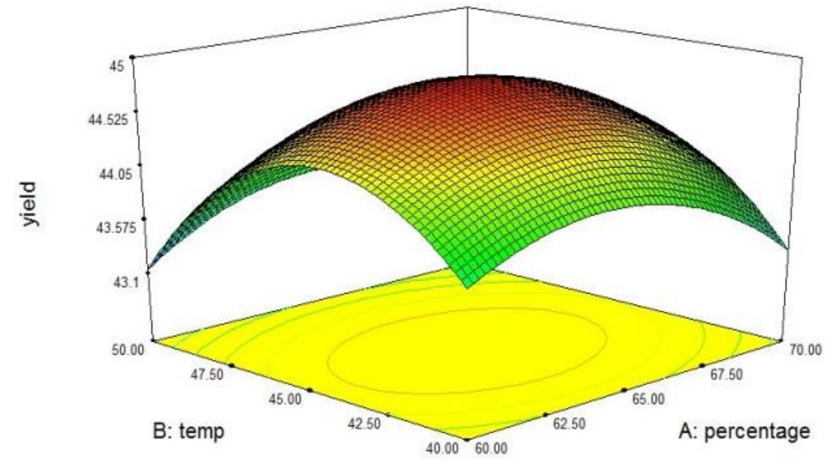

Figure 1(a): Response surface plot of yield of NCC (Factors X_1 and X_2)

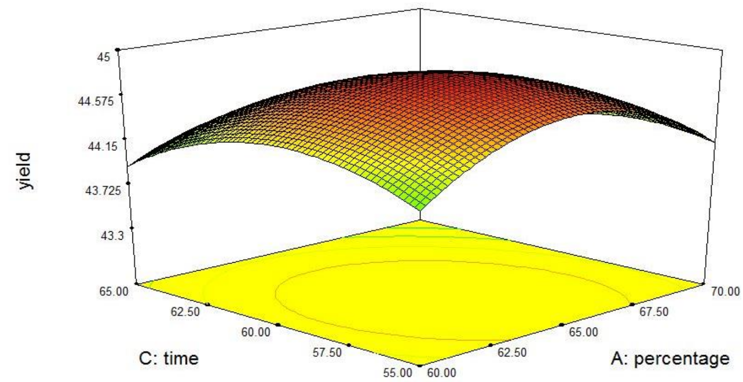

Figure 1(b): Response surface plot of yield of NCC (Factors X_1 and X_3)

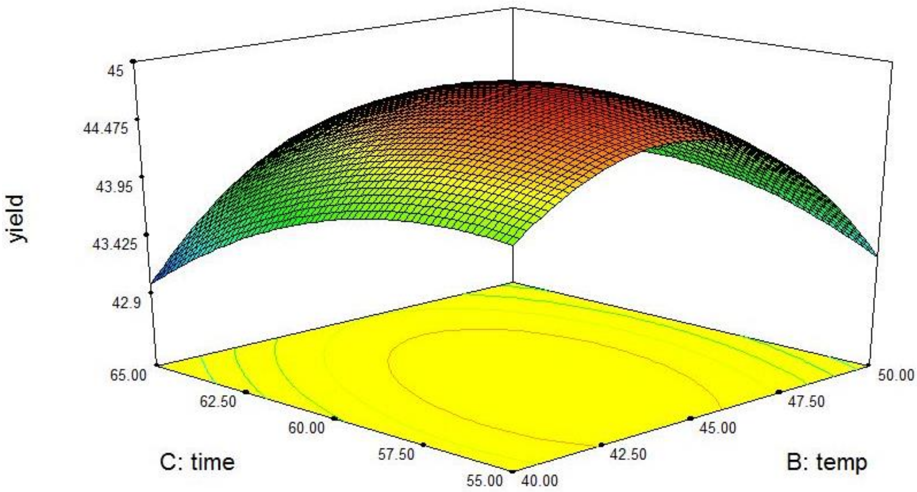

Figure 1(c): Response surface plot of yield of NCC (Factors X_2 and X_3)

3.2. XRD Analysis

Figure 2 shows the XRD pattern of NCC. In the diffraction pattern, there were crystalline peaks around 2θ= 16˚, 22˚ and 35˚, which presented the type of cellulose I pattern [6]. In this study, the crystallinity index of NCC for coconut husks was found about 68.3%, which indicating good crystallinity. This study also have a good agreement with Liu and his co-workers in 2015 stated that the angle of diffraction of NCC for peanut shells obtained were same with this study [7]. The intensity for NCC shows it is higher and indicates good crystallinity obtained for NCC.

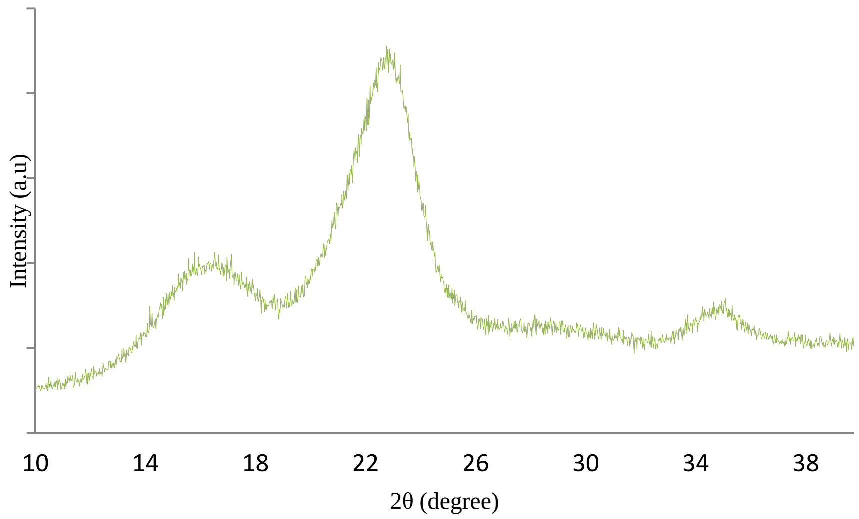

Figure 2: XRD pattern of NCC for coconut husks

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4. Conclusion

This study investigated the optimisation of preparation of NCC from coconut husks using response surface methodology. It was found that the sulphuric acid concentration, reaction temperature and reaction time all affected the yield of NCC. The Box-Behnken design based on the response surface methodology can be used to establish the regression model of the yield of NCC. Based on the variance analysis, the regression equation can fit well the changes in the emulsifying properties. According to the regression equation, the optimum preparation conditions of NCC were 64.61 wt% of sulphuric acid, 44.55 ˚C of reaction temperature, 58.54 min of reaction time and the yield of NCC obtained was 44.84%. The crystallinity of NCC was 68.3% and it shows that the crystal type of NCC was cellulose I pattern.

Acknowledgments
The authors would like to acknowledge the support from the Fundamental Research Grant Scheme (FRGS) under a grant number of FRGS/1/2015/TK10/UNIMAP/03/5 from the Ministry of Higher Education of Malaysia.

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