Optimization of Sulfonated Chemi-Mechanical Pulping of Palm Oil Empty Fruit Bunch Using Response Surface Methodology

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In order to optimize the sulfonated chemi-mechanical pulping of palm oil empty fruit bunch, the response surface methodology was employed. It was intended to determine the optimum level of sodium sulfite dosage, sodium hydroxide dosage, maximum cooking temperature, and cooking time at the sulfonation stage, and their influences on paper sheets properties were analyzed. An optimum compromise was obtained, and the sodium sulfite dosage, sodium hydroxide dosage, maximum temperature, and cooking time were 18%, 4%, 155 °C, and 100 min, respectively. The density, bursting strength index, tensile strength index, and tearing strength index were 0.5622 g/cm^3, 2.60 kPa·m^2/g, 45.01 N·m/g, and 7.53 mN·m^2/g, respectively.

Keywords: Oil palm empty fruit bunch; SCMP; Response surface methodology

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INTRODUCTION

Wood shortages, environmental pollution, and high-energy consumption remain major obstacles hindering the development of today's pulp and paper industry (Yue *et al*. 2016). The pulp and paper industry is a resource-intensive industry, and the adequate availability of pulp and paper raw materials, including waste paper and non-wood, are essential to the industry. For a long time, limited wood raw materials have brought the industry difficulty and uncertainty in the supply chain (Hubbe 2014). Therefore, non-wood raw materials including bamboo, rice straw, bagasse, and reed have become important raw material resources for the pulp and paper industry because of their wide sources, abundance, and low prices (Marín *et al.* 2009; Sharma *et al.* 2011; Ferhi *et al.* 2014; Ooi *et al.* 2017; Emmclan *et al.* 2018). Palm oil empty fruit bunches (POEFB), the industrial residue of the palm oil production process, generally have been treated by direct incineration (Colonia *et al.* 2019). This treatment not only fails to fully utilize the value of the biomass itself, but it also causes serious environmental pollution. Additionally, this approach does not comply with the notion of sustainable economy, so it is necessary to find other applications to increase the value of the empty fruit bunch, such as making pulp out of the lignocellulosic-rich POEFB (Colonia *et al.* 2019). According to the statistics, for every ton of palm oil produced, there will be 1.1 tons of POEFB produced (Shinoj *et al.* 2011). Therefore, the advantages of POEFB for the pulp and paper industry include its large stock, low price, and easy accessibility as it is collected in the palm oil factory.

POEFB has been investigated as a raw material for pulp and paper production. The

earliest research into the pulping of POEFB was reported by Muthurajah and Peh (1977), where the researchers used this kind of material for kraft cooking. In terms of chemical composition, POEFB is similar to hardwood, but the pentosan content is higher (Sannigrahi *et al.* 2010; Shinoj *et al.* 2011) and the physical properties of POEFB paper sheets are slightly poorer than the sulphate paper made from hardwood. Daud and Law (2011) pointed out that the palm fruit bunch fiber exhibited an average length of 0.99 mm and a width of 19.1μm in their research, which is consistent with it being a good papermaking raw material. Because of the greater stiffness and thicker walls of POEFB fibers, POEFB pulp could be bleached more easily by hydrogen peroxide than aspen pulp. Furthermore, Jiménez *et al.* (2009) obtained POEFB pulp by soda-anthraquinone pulping under the optimal experimental conditions (15% soda dosage, 170 °C, 70 min, and 2400 numbers of PFI beating revolutions), and the properties of pulp were 59.6 Nm/g tensile strength index, 4.48% stretch, 4.17 kN/g bursting strength index, and 7.20 mNm^2/g tearing strength index.

An environmentally friendly and energy-saving pulping method is needed, especially for non-woody materials. Although palm oil empty fruit bunches have been reported in chemical pulping in recent years, the study of palm empty fruit bunches in high yield pulp has rarely been reported. Sulfonation chemi-mechanical pulping (SCMP) is a kind of high yield pulping method developed in the 1970s. It has attracted attention for its high pulp yield, low pollution, good strength, and low energy consumption (Liu 2007).

SCMP is a multivariate and heterogeneous reaction process. In a multivariable system, the influence of a single variable on the experimental results does not represent the interaction of multiple variables unless all other conditions are kept constant. Therefore, this kind of experimental method does not fully explain the influence of each factor and analyze the interaction between different factors. The response surface method (RSM) is a technique that is particularly well suited for this situation, combining a planned and efficient experimental design approach with a least squares model to determine the optimal conditions for process response (Tan *et al.* 2009).

In the present study, by using the hand sheets properties (density, bursting strength index, tensile strength index, and tearing strength index) as indicators, the effects of sulfonation factors (sodium sulfite dosage, sodium hydroxide dosage, maximum temperature, and cooking time) on the sulfonation results during the sulfonation pretreatment were investigated. As mentioned earlier, the complex effects of the pulping variables on each response are tested and analyzed by a central composite design (CCD) method in a statistical experimental design RSM. For ease of analysis, Design-Expert 11.1.2 software was used to optimize the aforementioned parameters.

EXPERIMENTAL

Materials

The POEFB was obtained from Heng Huat Group (Pulau pinang, Malaysia) and washed with hot water at 80 °C to remove impurities such as dust, dirt, and grease on the surface of the raw material. The washed empty fruit string was squeezed, centrifuged, air-dried at room temperature, cut to a length of 10 cm, and placed in a plastic bag to balance the moisture content.

Methods

Measurement of fiber dimensions and chemical composition

The representative POEFB fiber raw material sample was selected and cut into a length of about 2 cm. Then, the sample was boiled to remove the air. After the sample sunk to the bottom of the water-filled container, it was taken out and soaked in a 1:1 solution of glacial acetic acid and hydrogen peroxide (30 wt%) at a temperature of 60 °C. It took 30 to 48 h to fully disperse and bleach the fibers. The obtained fibers were washed with distilled water to neutralize the pH and were collected after the water was filtered.

The POEFB fiber dimensions were characterized as follows: fiber length, fiber diameter, and lumen width of 200 randomly selected fibers were measured using a light microscope (DMi8; Leica, WEertzlar, Germany). Average fiber dimensions were calculated and relevant parameters were determined based on the following equations:

$$\textit{Fiber wall thickness} = (\textit{Fiber diameter} - \textit{Lumen width})/2 \quad (1)$$

$$\textit{Runkel ratio} = 2 \times (\textit{Wall thickness}/\textit{Lumen width}) \times 100 \quad (2)$$

$$\textit{Flexibility coefficient} = (\textit{Lumen width}/\textit{Fiber diameter}) \times 100 \quad (3)$$

$$\textit{Slenderness ratio} = (\textit{Fiber length}/\textit{Fiber diameter}) \quad (4)$$

Regarding the chemical composition, the benzene alcohol extraction and ash were measured according to TAPPI T204 CM-97 (1997) and TAPPI T211 om-93 (1993), respectively. The contents of lignin and cellulose were determined according to the method of notional renewable energy laboratory (Sluiter *et al.* 2008). All experiments were carried out twice, and the average values were reported in this paper.

Experimental design

According to the Box-Behnken center combination design principle in the response surface analysis experiment software Design-Expert 11.1.2, the study of SCMP POEFB consisted of 6 central experiments and 24 peripheral experiments. The sodium sulfite dosage, sodium hydroxide dosage, maximum temperature, and cooking time used were 12%, 15%, and 18% (on oven dry raw material); 2%, 3%, and 4% (on dried raw material); and 120 °C, 140 °C, and 160 °C; and 60 min, 80 min, and 100 min, respectively. The operational variables were normalized according to Eq. 5,

$$X_i = 2\frac{X-\overline{X}}{X_{max}-X_{min}} \quad (5)$$

where X_i is the normalized value of sodium sulfite dosage (SS), sodium hydroxide dosage (SH), maximum temperature (MT), and cooking time (CT); X is the absolute experimental value of the variable concerned; $\bar{X}$ is the mean of the extreme values of X; and X_{max} and X_{min} are the maximum and minimum value of X.

Optimization of sulfonated processing conditions for POEFB SCMP was carried out using the following methodology:

Initial design — central composite

Study type — response surface

Design model — quadratic

Independent variables — sodium sulfite dosage, sodium hydroxide dosage, maximum temperature, and cooking time
Response — density, bursting strength index, tensile strength index, and tearing strength index

Pulping

The POEFB SCMP pulping process consists of three different stages. Firstly, the sulfonation pretreatment of POEFB was conducted in a horizontal rotary digester. At this stage, 300 g (o.d.) of treated POEFB were pretreated with sulfonation using a 4 L-horizontal rotary digester (NO. 2611; Kumagai Riki Kogyo Co., Ltd., Tokyo, Japan). The process included 12% to 18% of sodium sulfite, 2% to 4% of sodium hydroxide, a maximum temperature ranging from 120 °C to 160 °C, and cooking time at the maximum temperature for 60 min to 100 min. The liquor-to-solid ratio was 5:1, and the digester temperature was raised to the maximum in 70 min. Then, the pretreated POEFB was defibrated three times under an atmospheric pressure and room temperature using a continuous high-consistency disc refiner (2500-II; Kumagai Riki Kogyo Co., Ltd., Tokyo, Japan) at a high consistency (25% to 30%). The clearance between two refining discs was set at 0.5 mm for the first and second defibrate process. The stock refined twice was screened with a 0.2 mm diaphragm screen, and the rejects were refined another time at a clearance of 0.2 mm and screened again. The accepts from the first screening and the second screening were mixed and stored as POEFB SCMP. Finally, post-refining was conducted on POEFB SCMP to further improve the properties using a PFI refiner under 5000 revolutions according to ISO 5264-2 (2002), and the SCMP refined was stored in a refrigerator for subsequent operation.

Paper sheet making and hand sheet properties measurement

The POEFB SCMP handsheets were produced in accordance with ISO 5269-2 (2004). The prepared handsheets were placed in a constant temperature and humidity (23 °C, 50% RH) laboratory for 24 h, and the relevant properties were measured. Basic paper properties of basis weight, thickness, and brightness were measured. The physical properties, including bursting strength, tensile strength, and tearing strength, were measured in accordance with ISO 2758 (2014), ISO 1924-2 (2008), and ISO 1974 (2012), respectively. Indexes of those properties were calculated to avoid the errors brought by basis weight difference.

RESULTS AND DISCUSSION

Raw Material Characterization

The dimensions of POEFB fibers and the relevant data from the literature are shown in Table 1. The dimensions of POEFB were in accordance with those reported by Law and Jiang (2001). Although the fiber length of POEFB is generally shorter than other non-wood fibers, the composite performances of POEFB are superior. The Runkel classification value was obtained by dividing cell wall thickness by lumen diameter, and it was analyzed to prove whether this raw material is suitable for pulping and papermaking (Xu *et al.* 2006). It is expected that the Runkel proportion is smaller than 1. The obtained value of 0.51 indicates that the cell wall of POEFB is thin and fibers obtained from POEFB are suitable

for the production of paper. The anticipated slenderness ratio value of fibers for papermaking is over 33 (Kiaei *et al.* 2011). The slenderness ratio for POEFB was 52.2, which was higher than 33 and beneficial for papermaking. The higher flexibility coefficient indicates the fiber is more flexible. According to Table 1, it can be concluded that POEFB fibers suits paper production better than bagasse and rice straw for pulping and papermaking.

Table 1. Properties of POEFB and Relevant Data from the Literature

Material	Length (mm)	Diameter (μm)	Lumen width (μm)	Cell wall thickness (μm)	Runkel ratio	Slend. ratio	Flex. Coeff.	Ref.
POEFB	0.96	18.4	12.2	3.10	0.51	52.2	66.3	This study
EFB strand	0.99	19.1	12.4	3.38	0.55	51.8	64.8	Law *et al.* 2001
Canola straw	1.31	31	19.5	5.75	1.25	42.3	62.9	Hosseinpour *et al.* 2010
Bagasse	1.59	20.96	9.72	5.63	1.16	76.0	46.4	Khakifirooz *et al.* 2012
Rice straw	0.83	10.89	4.57	3.16	1.38	76.6	42.0	Kiaei *et al.* 2011
Wheat straw	1.17	15.9	10.2	2.83	0.55	73.6	64.4	Moradian *et al.* 2001

The chemical composition of POEFB fibers is listed in Table 2, and the results are in accordance with Liu *et al.* (2019). The cellulose content of POEFB is slightly lower than canola straw and bagasse, but higher than rice and wheat straw. In previous studies, it has been proven that rice straw (Lam *et al.* 2001; Juwono and Subawi 2014) and wheat straw (Hedjazi *et al.* 2009; Nasser *et al.* 2015) can be used for pulping and papermaking, and ideal physical properties could be obtained. This confirms the feasibility of POEFB being used as feedstock for the production of paper.

Table 2. Chemical Composition of POEFB and Other Non-Wood Raw Materials

Material	Cellulose (%)	Lignin (%)	Benzene alcohol extraction (%)	Ash (%)	Ref.
POEFB	44.5	22.8	4.1	1.4	This study
EFB strand	42.7	17.2	0.9	0.7	Khoo and Lee 1991
Canola straw	48.5	20	-	6.6	Hosseinpour *et al.* 2010
Bagasse	55.57	20.50	3.25	1.85	Khakifirooz *et al.* 2012
Rice straw	41.20	21.9	0.56	9.2	Sannigrahi *et al.* 2008
Wheat straw	34.9	18.5	7.62	7.56	Tozluoğlu *et al.* 1990

Analysis of Optimized POEFB SCMP Pulping Process by RSM

Table 3 summaries the experimental results for the physical properties of paper sheets made of POEFB SCMP pulps with the normalized and real values of the operational

variables. Based on the statistical analyses provided, the quadratic model was selected. Experimental data were modelled using the following second-order polynomial Eq. 6,

$$Y = A_0 + \sum_i^k \beta_i X_i + \sum_i^k \beta_{ii} X_i^2 + \sum_{i<j}^k \beta_{ij} X_i X_j \quad (6)$$

where Y is the estimate for a response variable pulp bulk, bursting strength index, tensile strength index, and tearing strength index; k is 4, the total number of operational variables (X_i); β_s is the estimate of a regression parameter computed by the least-squares method or named as least squares coefficients; and Xi, X_i^2, and X_iX_j are the linear effects, the quadratic effects, and the two-variable interaction effects, respectively.

Table 3. Experimental Conditions in Normalized Values According to Central Composite Design and the Results of Four Responses for POEFB SCMP

No.	Pulping variables Normalized values				Response			
	SS	SH	MT	CT	Density (g /cm^3)	Bursting strength index (kPa·m^2/g)	Tensile strength index (N·m/g)	Tearing strength index (mN·m^2/g)
1	1	1	1	-1	0.5682	2.29	45.9	7.88
2	-1	1	1	-1	0.5685	2.36	39.3	8.04
3	-1	1	1	1	0.5321	2.48	42.7	8.08
4	1	-1	-1	1	0.4462	1.42	28.4	6.22
5	0	0	0	1	0.5290	2.29	44.8	6.79
6	0	0	-1	0	0.4629	1.55	32.2	6.19
7	-1	-1	-1	1	0.4066	0.87	18.8	3.86
8	0	-1	0	0	0.5096	1.88	36.3	6.8
9	0	1	0	0	0.5546	2.37	43.8	7.08
10	1	1	-1	-1	0.4793	1.83	36.9	5.92
11	1	0	0	0	0.5435	2.30	41.9	6.75
12	1	-1	-1	-1	0.4170	0.97	19.3	3.99
13	0	0	0	-1	0.5101	2.06	40.7	6.76
14	1	1	1	1	0.5723	2.85	43.2	8.28
15	-1	1	-1	1	0.4592	1.46	30.8	6.01
16	-1	0	0	0	0.5154	2.14	37.9	6.82
17	-1	1	-1	-1	0.4788	1.66	30.4	5.78
18	0	0	1	0	0.5632	2.29	41.1	6.59
19	1	-1	1	-1	0.5649	2.43	41.8	6.49
20	-1	-1	1	1	0.5549	2.32	37.6	6.55
21	-1	-1	-1	-1	0.4194	1.18	20.9	4.9
22	0	0	0	0	0.5063	2.12	39.6	6.64
23	-1	-1	1	-1	0.5272	2.37	41.0	7.04
24	1	-1	1	1	0.5886	2.72	43.9	7.08
25	1	1	-1	1	0.4951	1.87	39.1	6.38
26	0	0	0	0	0.5192	2.22	40.6	6.42
27	0	0	0	0	0.4984	2.09	38.7	6.35
28	0	0	0	0	0.5146	2.10	39.2	6.72
29	0	0	0	0	0.5198	2.15	41.0	6.81
30	0	0	0	0	0.4935	2.05	38.2	6.05

Note: SS is sodium sulfite; SH is sodium hydroxide dosage; MT is maximum temperature; and CT is cooking time.

Table 4. Pulp Yield during Mechanical Pulping Process and the CSF and Energy Consumption during PFI Refining

No	Total yield (%)	Screened yield (%)	Initial CSF (mL)	Energy consumption (kW·h)	Final CSF (mL)
1	75.50	67.13	700	49	320
2	78.83	63.43	655	48	325
3	77.74	69.28	700	56	270
4	80.03	52.76	685	62	395
5	78.31	62.83	655	54	215
6	78.02	53.99	665	60	335
7	78.29	54.62	765	64	640
8	82.88	58.05	665	57	315
9	77.87	60.30	655	50	310
10	79.76	53.65	635	46	360
11	81.42	66.51	620	53	255
12	78.68	50.07	735	65	550
13	76.71	65.61	635	55	260
14	73.84	61.48	705	45	385
15	80.63	55.53	680	58	345
16	77.28	57.23	645	56	255
17	75.66	55.78	670	59	300
18	72.75	66.56	720	49	395
19	70.46	65.57	675	49	365
20	67.25	61.03	700	50	395
21	82.89	55.30	735	62	485
22	90.34	61.01	670	58	270
23	77.58	64.81	665	54	305
24	73.62	65.15	715	49	390
25	84.45	59.66	645	57	220
26	89.26	61.15	670	58	270
27	89.54	60.66	675	58	275
28	90.71	60.98	665	57	275
29	91.02	62.17	665	58	265
30	90.04	60.39	675	58	275

To establish a perspicuous model with minimum equation coefficients and also prevent over-fitting, the insignificant coefficients, which had values nearest to 0, were deleted from the models (Leh *et al.* 2008). The significant coefficients and statistical data of each response are given in Table 5. The quadratic multiple regression equation estimated by CCD was used and is shown by Eq. 7,

$$Y_n = A + BX_{SS} + CX_{Sh} + DX_{MT} + EX_{CT} + FX_{SS}X_{SH} + GX_{SS}X_{MT} + HX_{SS}X_{CT} + IX_{SH}X_{MT} + JX_{SH}X_{MT} + KX_{MT}X_{CT} + LX_{SS}^2 + MX_{SH}^2 + NX_{MT}^2 + OX_{CT}^2 \quad (7)$$

The standard deviation is expected to be as low as possible and R^2 is expected to be near 1. All models were significant at a level of less than 0.0001 with satisfactory values of R^2, thus confirming the sufficiency of the fitted models. The Lack of Fit indicates the probability that the predicted values of the models do not fit the actual values, and the proximity of the models obtained by the reaction fitting to the experimental data. The P-values (Prob.>|t|) for the Lack of Fit of each model were higher than 0.05, which indicates

that the Lack of Fit was not significant. Therefore, it was not necessary to adjust the regression equation. Apart from the tearing strength index, the values of R^2_{Adj} subtracting R^2_{Pred} were less than 0.2, further indicating that the models had high credibility. A_{deq} precision is the reproducibility of the experimental results, generally greater than 4. It can be seen from Table 5 that the precision corresponding to the four response values were 20.854, 25.298, 18.978, and 12.433, respectively. All of these values were greater than 4, indicating that the experimental results were repeatable. Therefore, it is possible to predict the responses with sufficient adequacy under any given experimental requirements within the limits of the variables studied by using these models.

Table 5. Statistical Analysis of Reduced Models and Coefficient of Density, Bursting Strength Index, Tensile Strength Index, and Tearing Strength Index

Factor	Density (cm^3/g)		Bursting strength index ($kPa·m^2/g$)		Tensile strength index ($N·m/g$)		Tearing strength index ($mN·m^2/g$)	
	CE	Prob.>|t|	CE	Prob.>|t|	CE	Prob.>|t|	CE	Prob.>|t|
Intercept	0.52	-	2.14	-	40.35	-	6.64	-
X_{SS}	0.012	0.0011	0.13	0.0001	2.45	0.0001	0.21	<0.0001
X_{SH}	0.015	0.0001	0.17	<0.0001	3.56	<0.0001	0.58	0.0783
X_{MT}	0.054	<0.0001	0.52	<0.0001	6.65	<0.0001	0.93	<0.0001
X_{CT}	0.004-	0.2066	0.074	0.0084	0.80	0.1099	0.15	0.1899
$X_{SS}X_{SH}$	-	-	-0.021	0.4237	-	-	-0.17	0.1674
$X_{SS}X_{MT}$	-	-	-0.036	0.1810	-0.74	0.1602	-0.23	0.0616
$X_{SS}X_{CT}$	0.006	0.1040	0.073	0.0133	0.52	0.3187	0.18	0.1452
$X_{SH}X_{MT}$	-0.014	0.0007	-0.14	<0.0001	-2.68	<0.0001	-	-
$X_{SH}X_{MT}$	-0.008	0.0271	-	-	-	-	-	-
$X_{MT}X_{CT}$	-	-	0.046	0.0937	-0.70	0.1855	-0.10	0.4034
X^2_{SS}	-	-	0.061	0.3561	-1.26	0.3274	-	-
X^2_{SH}	-	-	-	-	-1.08	0.3990	0.16	0.5786
X^2_{MT}	-0.013	0.1116	-0.24	0.0021	-4.49	0.0026	-0.39	0.2018
X^2_{CT}	-	-	-	-	1.59	0.2223	-	-
R^2	0.9643		0.9758		0.9607		0.8874	
R^2_{Adj}	0.9309		0.9533		0.9240		0.7823	
R^2_{Pred}	0.8699		0.8614		0.7693		0.4599	
Model Prod.>F	<0.0001		<0.0001		<0.0001		<0.0001	
Lack of Fit Prod.>F	0.3458		0.0637		0.0547		0.0848	
Adeq Precisior	20.854		25.298		18.978		12.443	
Standard Deviation	0.013		0.10		2.01		0.47	

Note: CE is coefficient estimate.

Process Variable Effect on Physical Properties

The sulfonation of lignin and the dissolution of lignin sulfonate were carried out simultaneously during the sulfonation treatment. The SCMP process uses a higher concentration of sulfite solution for pretreatment, which causes lignin to undergo deeper sulfonation. As a result, the fibers softened and were easier to separate, which helped improve their quality. Therefore, the concentration of sulfite solution is important in sulfonation chemical mechanical pulping.

Figure 1 shows the effects of SS on the physical properties of the paper sheets at SH = 3%, MT = 140 °C, and CT = 80 min. As shown in Fig. 1, the physical properties of the paper sheets increased slightly as SS increased. The purpose of the pretreatment is to acquire maximum sulfonated lignin. With the SS increasing, the degree of sulfonation of POEFB increases (Zhang 2011), which facilitates fiber separation during refining and increases the content of long fibers, thereby improving the physical properties of the paper. These conclusions could be also supported by the data of pulp yield in Table 4. Density has a noticeable impact on the physical properties of the paper, so it is also used as a basic parameter for comparing physical properties of paper (Liu *et al.* 2019). As the SS is increased, the degree of sulfonation of lignin is increased, improving the hydrophilicity, flexibility, and adaptability of the fiber. Therefore, the bonding force between the fibers is increased, and other physical properties are improved as well.

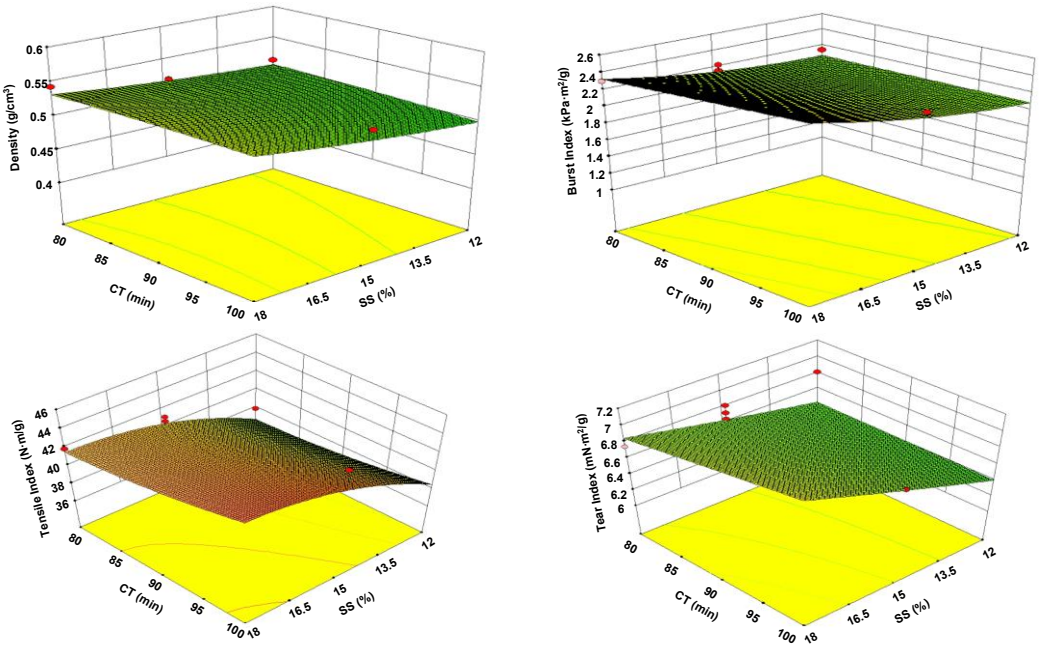

Fig. 1. 3D response surface plots of physical properties as a function of sodium sulfite dosage, at sodium hydroxide dosage = 3%, maximum temperature = 140 °C, and cooking time = 80 min

The effects of SH on the physical properties of the paper sheets at SS = 15%, MT = 140 °C, and CT = 80 min is shown in Fig. 2. The physical properties of the paper sheets increase gradually as the SH increased. During the pretreatment, one of the main effects of sodium hydroxide is the softening of fibers. Sodium hydroxide is an ideal swelling agent and softener (Bengtsson and Simonson 1990). Sodium hydroxide make the fibers swell, then the fibers are separated and fibrillated during mechanical pulping, which enhances the flexibility of the SCMP fibers compared with mechanical pulp. When the SH is increased, the nucleophilic hydroxide ions are increased. As a result, the degradation and dissolution of lignin and carbohydrate are increased. Although excessive NaOH will cause a decrease in the sulfonic acid content in the slurry, the sulfonic acid group content is not the only factor determining the strength of the pulp. NaOH is beneficial for the penetration of chemicals, dissolution of lignin, and softening of fibers, which makes fibers separate more easily and reduces fiber cutting during refining. So, the content of long fiber was increased in the pulp, enhancing the paper sheet's strength.

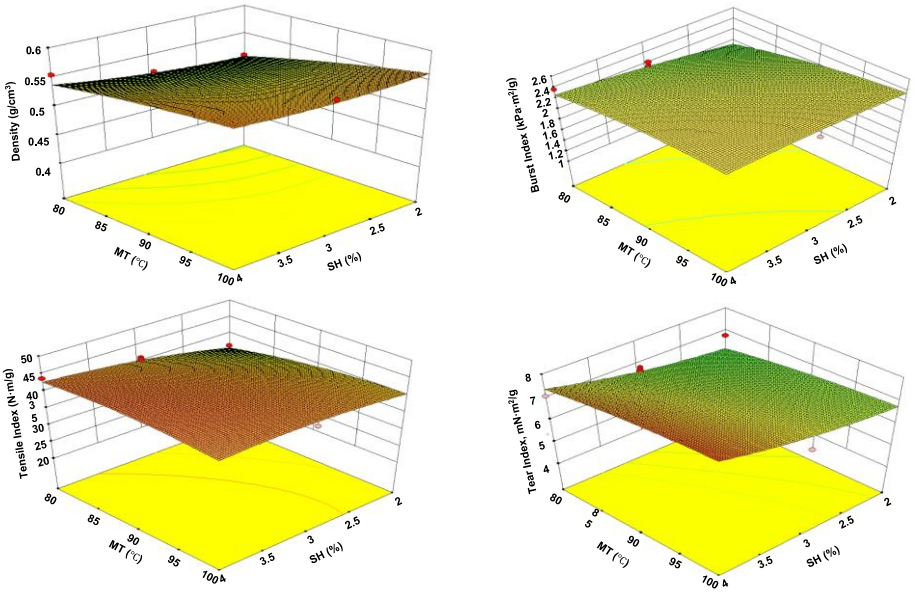

Fig. 2. 3D response surface plots of physical properties as a function of sodium hydroxide dosage, at odium sulfite dosage = 15%, maximum temperature = 140 °C and cooking time = 80 min

Figure 3 shows the effects of MT on the physical properties of the paper sheets at SS = 15%, SH = 3%, and CT = 80 min. When the MT was raised from 120 °C to 160 °C, the density, bursting strength index, tensile strength index, and tearing strength index of the paper sheets increased by 24.4%, 86.8%, 49.1%, and 36.5%, respectively. With the MT rising, it seems that the dissolution of sulfonated lignin was accelerated, and the degradation and dissolution of carbohydrates were also increased. During the sulfonation pretreatment, the sulfonation of lignin mainly takes place at lower temperatures, while the dissolution of lignin sulfonate is the major reaction at higher temperature, and an appropriate MT is necessary in balancing the sulfonation of lignin between cost (Irvine 1985). As for the paper properties, higher MT leads to higher paper density. The rise of MT is beneficial to the SCMP because it is helpful in the sulfonation of lignin and softening the fibers.

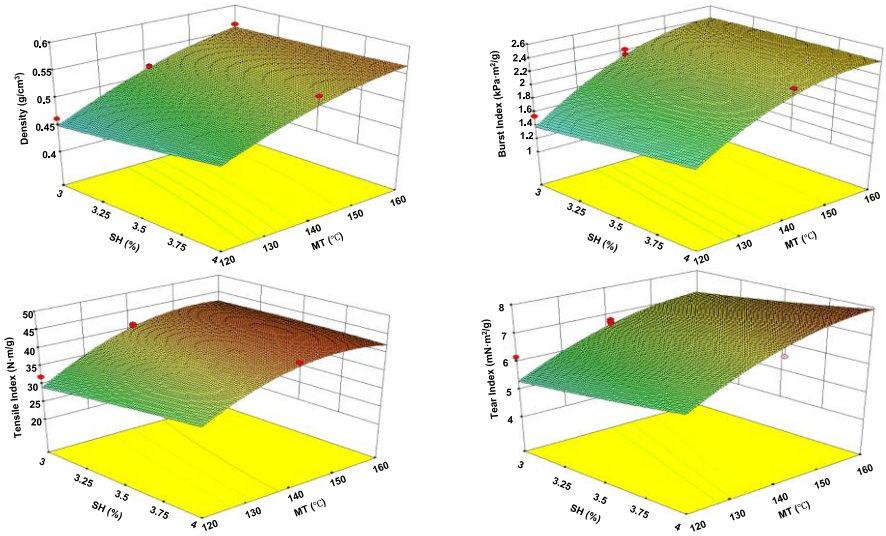

Fig. 3. 3D response surface plots of physical properties as a function of maximum temperature, at odium sulfite dosage = 15%, sodium hydroxide dosage = 3% and cooking time = 80 min

Figure 4 shows the effects of CT on the physical properties of the paper sheets at SS = 15%, SH = 3%, and MT = 140 °C. The effect of CT on the physical properties of paper sheets is small and the increase in physical properties is less than 10%. Properly extending the CT would increase the sulfonation degree and long fiber content of POEFB, which could enhance the paper sheets tearing strength index and increase the paper density. Prolonging the CT is beneficial to the sulfonation reaction and fiber swelling of POEFB. With extended sulfonation reaction from longer CT, it seems that the POEFB fiber is better separated and fiber cut is reduced during refining. However, excessively prolonging the CT seems to reduce the total acid group content in the pulp, and the bonding force between the fibers seems to decrease.

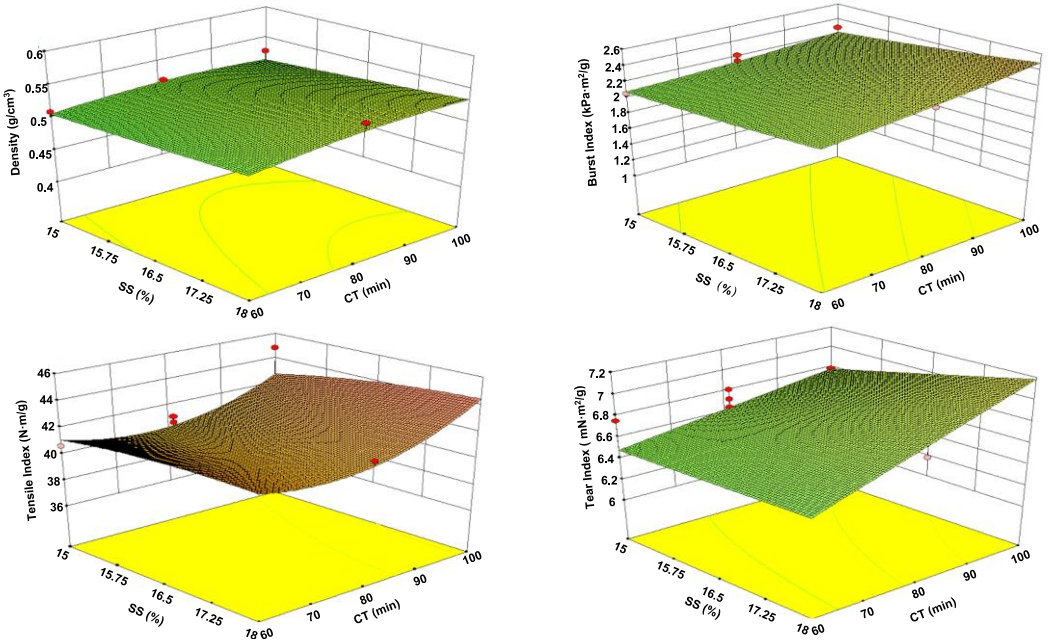

Fig. 4. 3D response surface plots of physical properties as a function of cooking time, at odium sulfite dosage = 15%, sodium hydroxide dosage = 3%, and maximum temperature = 140 °C

Plotting the previously established polynomial equations allowed the most and least influential variables to be identified (Jiménez *et al.* 2009). A small P-value reflects greater influence of physical properties on the paper sheets. As shown in Table 5, the P-value of MT was the smallest, and the P-value for CT was the biggest; thus it can be concluded that the MT was more influential than the CT. This can also be confirmed from Figs. 1 through 4 according to the physical property variations. Moreover, the effect of SS on the physical properties of paper sheets was greater than that of SH. Therefore, the order (from significant to insignificant) of the effect of the operating variables on paper sheets performance was MT, SS, SH, and CT.

Optimization of SCMP Pulping Condition

Table 6 shows the maximum value of each response value under different operating variables. As can be seen from these data, there was no specific set of operating variables conditions that allow response values to reach the maximum (González *et al.* 2013). Therefore, to meet the particular requirement, different conditions for sulfonation are needed. That is, if the paper sheets must have a high density, the pulp should be obtained

with low SH. However, the bursting strength index needs a medium SH and the tensile strength index requires a medium-high MT. On the other hand, the maximum tearing strength index is obtained with low SS and CT.

Table 6. Maximum Value of Each Response Value Under Different Operating Variables

Response	Maximum	Normalized				Desirability
		SS	SH	MT	CT	
Density (g/cm^3)	0.5915	1	-1	1	1	0.982
Bursting strength index (kPa·m^2/g)	2.78	1	0.02	1	1	0.990
Tensile strength index (N·m/g)	47.31	1	1	0.29	1	0.994
Tearing strength index (mN·m^2/g)	8.29	-1	1	1	-1	0.998

In sum, the optimal compromised operating conditions for preparing POEFB SCMP obtained by response surface analysis were SS = 18%, SH = 4%, MT = 155 °C, and CT = 100 min, respectively. According to the above equation (Table 5), the physical properties of the paper can be predicted to be 0.5701 g/ cm^3 of density, 2.75 kPa·m^2/g of bursting strength index, 46.3 N·m/g of tensile strength index, and 7.97 mN·m^2/g of tearing strength index, respectively. Table 7 shows the predicted and measured values under the optimal compromised operating conditions. These values deviate 3.76%, 1.09%, 2.25%, and 4.02%, respectively, from their maximum values (Table 6). The measured paper physical properties obtained by experiment under these operating conditions were 0.562 g/cm^3 of density, 2.60 kPa·m^2/g of bursting strength index, 45.0 N·m/g of tensile strength index, and 7.53 mN·m^2/g of tearing strength index, respectively. The deviation between the experimental results and the predicted values is within 10%, which strongly prove that this model is reliable.

Table 7. Predicted and Measured Values Under the Optimal Compromised Operating Conditions and Deviations

Response	Predicted values	Experimental results	Deviation
Density (g/cm^3)	0.5701	0.5622	1.39%
Bursting strength index (kPa·m^2/g)	2.75	2.60	5.45%
Tensile strength index (N·m/g)	46.27	45.01	2.72%
Tearing strength index (mN·m^2/g)	7.97	7.53	5.52%

CONCLUSIONS

1. Palm oil empty fruit bunch is an ideal non-woody raw material for pulping and papermaking in terms of fiber dimensions and chemical composition.
2. The results of an experimental design applied to the SCMP pulping from POEFB were subjected to multiple regressions in order to obtain polynomial equations that reproduced the properties of the paper sheets. Additionally, the order (from significant to insignificant) of the effect of the operating variables on paper sheets performance was MT, SS, SH, then CT.
3. The optimal compromised conditions for preparing POEFB SCMP pulping by response

surface analysis method was as follows: SS = 18%, SH = 4%, MT = 155 °C, and CT = 100 min. The pulp physical properties obtained by experiment under these operating conditions were 0.5622 g/ cm^3 of density, 2.60 kPa·m^2/g of bursting strength index, 45.01 N·m/g of tensile strength index, and 7.53 mN·m^2/g of tearing strength index, respectively.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the Guangzhou Science and Technology Plan Projects (201707020011), the Special Support Plan for High-Level Talent Cultivation of Guangdong Province (No. 2014TQ01N603), the State Key Laboratory of Pulp and Paper Engineering (201831), and the Guangdong Province Science Foundation for Cultivating National Engineering Research Center for Efficient Utilization of Plant Fibers (2017B090903003).

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Article submitted: December 3, 2019; Peer review completed: January 27, 2020;
Revisions accepted: February 10, 2020; Published: February 25, 2020.
DOI: 10.15376/biores.15.2.2630-2644