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Parametric Study on Synthesis of Carboxyl Methyl Cellulose from Ozone Pre-Treated Empty Fruit Bunch Using Fractional Factorial Design Study

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Carboxyl methyl cellulose (CMC) is a cellulose derivative that is being used in many industries such as food packaging. This study evaluates the parameter region i.e., NaOH concentration, sodium monochloroacetate (SMCA) ratio, etherification temperature, and time for higher degree of substitution (DS) and viscosity of CMC synthesized from ozone pre-treated empty fruit bunch (EFB), named BiOzCMC. A fractional factorial design (FFD) by using Tibco Statistica software *Ver.* 13 are selected for the study. The cellulose from EFB, named OzyCELL was isolated by using novel ozonolysis technology (OzBiONY 2.0), followed by sodium hydroxide (NaOH) swelling, and hydrogen peroxide (H_2O_2) bleaching. The OzyCELL was then subjected to alkylation and etherification processes for BiOzCMC synthesis. Based on parametric analysis, the parameter region for DS >0.7, purity >90 % and viscosity >20 cP was found to be between 30 - 35 % of NaOH concentration, SMCA ratio 1:1.2 – 1:2.0, time 1.5 – 2.5 h, and temperature of 65 – 75 °C. The scanning electron microscopy (SEM) image of BiOzCMC is comparable to commercial CMC and displayed excellent stability in dispersion based on zeta potential value (-59.67 mV) with a low crystallinity (35.9 %) and particle size of <0.25 mm.

1. Introduction

A flexible polymer, CMC is used in the food industry as an emulsifier, stabilizer, thickener, food packaging and edible coating, also used in the pharmaceutical and cosmetics formulations (Mondal et al., 2015). CMC is produced by reacting cellulose with sodium chloroacetate in the presence of an alkaline reagent, then purifying and neutralizing the product. EFB is a promising alternative raw material as it contains high cellulose fiber. The isolation of cellulose from EFB have used a variety of techniques, such as alkali treatment (Wijaya et al., 2020), acid treatment (Solihat et al., 2020), and enzymatic treatment (Nur-Nazratul et al., 2021). These techniques have a drawback as expensive technology due to the usage of a series of chemicals, fungi, and bacteria. Reducing production cost will be beneficial for technology developers. The high removal of lignin by ozone pre-treatment method of EFB (Shamjuddin et al., 2021) appears as a useful technique for increasing the accessibility of pure cellulose (Wan Omar and Amin, 2021) and reducing production cost because ozone is cheap and can be recycled. Treating EFB with ozone as a precursor for the synthesis of CMC is comparatively new and scarcely reported. Pujokaroni and Ichiura (2022) reported oxidized cellulose from alkaline treatment, they treated EFB with ozone prior to CMC production and discovered that ozonolysis pre-treatment led to a high DS, purity, and solubility of the CMC, but the viscosity was decrease because of 3 h ozonolysis treatment. Therefore, reducing ozonolysis reaction time can eventually lead to better DS and viscosity. Cellulose fibre accessibility and flexibility is shown to be improved by ozone pre-treatment (An et al., 2022), but further research is needed to pinpoint the exact process step that will increase the output and quality of the CMC produced, by minimizing production risks and reducing the cost of production. The objective of this paper is to perform a parametric analysis of CMC production from ozone pre-treated EFB by using the FFD. This research will offer insightful information on the parametric region of sustainable BiOzCMC production for the optimization study.

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2. Materials and Methods

2.1 Materials

The EFB from the palm oil mill at Felda Taib Andak Kulai was collected, desiccated, ground, and sieved. Oxygen gas was supplied by Mega Mount Sdn. Bhd. The chemicals i.e. industrial grade of acetone 100 % (Merck, 1.00014.2511), hydrogen peroxide 50 % (Solvay, INTEROX® ST 50), isopropyl alcohol (99.9 %) (JM0674668-H), ethanol 95 % (VE7043-2500) ,sodium monochloroacetate 98 % (Merck, 291773), methanol 95 % (Merck, 1.06009.2511), sodium hydroxide (Merck, 1.06498.1000) glacial acetic acid 100 % (Merck, 1.00063.2511), and absolute ethanol 100 % pure (Hayman Limited, SIN1170) were used in this study.

2.2 Ozonolysis pre-treatment

Ozonolysis pre-treatment of EFB was carried out using the OzBiONY 2.0 prototype. 500 g EFB with particle size of 0.3 mm was fed into the horizontal reactor. Filtered water was sprayed on the EFB at 3 L/min for 30 s until 20 wt% moisture content was attained. Ozone gas with 60 g/m^3 ozone concentration was continuously supplied at 10 LPM for 90 min during ozonolysis reaction. The sample was then washed with acetone-water with ratio 3:7 for 1 h in the washer unit. The solid fiber was filtered in a filter unit, then it was collected and dried in oven. The dried ozonated EFB, was kept in a plastic bag for analysis and further reaction.

2.3 Cellulose isolation

The dried ozonated EFB was swelled in 10 % NaOH with a ratio of 1:10 (w/v%) at 80 °C for 3 h under vigorous stirring. After three hours, the solution was allowed to cool before being filtered and rinsed to remove excess NaOH. The solid was dried in the oven. The dried sample was weighed and bleached with hydrogen peroxide. A 30 % of hydrogen peroxide (H_2O_2) concentration was mixed with the dried sample at a 1:10 solid to liquid ratio. The sample was bleached for another 3 h to obtain purer and white cellulose fiber. The mixture was then filtered, washed, blended, and dried in the oven overnight at a temperature of 60 °C. The dried sample (OzyCELL) was cooled in the desiccator and weighed. The cellulose content of OzyCELL was determined by using acetic/ nitric reagent method adopted from Tan and Lee (2012) and calculated using the Eq (1) prior to BiOzCMC synthesis. The OzyCELL content with 95% cellulose was proceeded to BiozCMC synthesis. The OzyCELL was sieved and the particle that passed through mesh size 60 (particle size <0.25 mm).

$$\text{Cellulose content (wt\%)} = \frac{\text{Weight of residue (g)}}{\text{Initial weight of sample (g)}} \times 100 \quad (1)$$

2.4 Synthesis of BiOzCMC

A 5 g of OzyCELL sample was weighed and mixed with 150 mL IPA solution while stirring using a magnetic stirrer. The total 16.67 mL NaOH with concentration 20-30 % was added dropwise within 30 min of the alkylation and then continuously stirring for another 1 h. The desired SMCA powder was added to the solution to begin the etherification reaction at desired temperature and time (Table 1). After the reaction, the sample was allowed to cool for 1 to 2 min under atmospheric conditions, then the liquid is drained. Methanol was then added and immediately stirred to prevent the hardiness of the sample and to ensure proper extraction of NaCl, as a byproduct. The neutralization process began by adding dropwise a glacial acetic acid until the mixture reached pH 7. The sample was then filtered using a filter bag (mesh size=100) and washed thoroughly in hot (65 °C) 70 % ethanol three to four times and lastly with absolute ethanol. The BiOzCMC obtained was then dried in the oven at 50 °C overnight, weighed and ground before any further testing.

Table 1: Design of Experiment (DOE) & BiOzCMC Experimental Results

Standard Run	Design: 2**(4-1) design.				BiOzCMC Experimental Results			
	NaOH concentration (%)	SMCA ratio	Etherification Temperature (°C)	Etherification Time (h)	Yield (%)	DS	Viscosity (cP)	Purity (%)
1	20.0	1.1	55.0	1.5	148	0.5	5.74	10
2	30.0	1.1	55.0	3.0	111.2	0.54	9.09	38
3	20.0	1.2	55.0	3.0	110.4	0.11	12.38	5.67
4	30.0	1.2	55.0	1.5	183.4	0.56	6.8	37
5	20.0	1.1	65.0	3.0	165	0.33	7.88	38.67
6	30.0	1.1	65.0	1.5	188	0.7	8.73	40.33
7	20.0	1.2	65.0	1.5	185	0.42	5.58	13
8	30.0	1.2	65.0	3.0	189.8	0.72	9.8	28.33

2.5 Design of experiment (DOE)

This study examines the effect of four independent variables NaOH concentration (X1), SMCA ratio (X2), etherification temperature (X3), and etherification time (X4) on yield, DS (Y1), viscosity (Y2), and purity (Y3) of BiOzCMC. A fractional factorial design in Tibco Statistica Ver. 13 software is employed to design the experiment. The design is suitable to screen the region of parameter condition for desired target response by Response Surface Methodology (RSM) approach for smaller size experiment and limiting background information. Table 1 tabulates the design of the experiment and results obtained from the experiments.

2.6 Degree of substitution (DS), viscosity and purity of BiOzCMC determination

The ASTM-D1439-03 method of Kannel (1976) was adopted for determination of DS and Golbaghi et al. (2017) for purity determination of BiOzCMC. The DS determination involved the purification of BiOzCMC, charred sample to ash at 650 ºC in the furnace, and titration of ash using H_2SO_4 and methyl red as an indicator. Meanwhile, the purity is determined by dissolving the BiOzCMC in hot distilled water, followed by the centrifugation process to separate all byproducts, and then regenerating the pure BiOzCMC using acetone before filtration and drying processes. The viscosity of 2 wt% CMC solution was measured at 25 +/- 0.5 °C with Brookfield viscometer, spindle CPE41 (Batelaan et al., 1992).

2.7 Physico-chemical characterization (XRD, SEM, PSA and Zeta potential)

The XRD characterization was performed to determine the crystallinity and amorphosity of BiOzCMC at 2θ between 0 º-120 º. SEM analysis using a voltage of 5 KV and magnification of 1500x was used to determine the morphology and structure of BiOzCMC. Zeta potential analysis was used to determine the particle size range and the zeta potential values. The sample was sonicated at a frequency of 35 kHz for 20 min to stabilize the suspension before the zeta potential analysis (Bahreini, 2022).

3. Results and discussion

3.1 Model validation

The synthesis of CMC is a very delicate procedure that requires a careful understanding of the process. The parametric study of the response surface model is an analysis tool that helps to understand the effect of process parameters by small design of experiments. The experimental data was verified by using analysis of variance (ANOVA) and regression analysis. The predicted model is significant at R^2 83.06 %. The model is validated at suggestion conditions of NaOH concentration of 30 %, SMCA ratio of 1:1.15, etherification temperature 65 ºC, and etherification time of 3 h to reach DS 0.63, purity 41 %, and viscosity 10 cP. Based on the profile for predicted values and desirability in Figure 1a, the display is somehow in line with Wan Omar and Amin (2016) by assigning the predicted values with scoring range between 0 (very undesirable) and 1 (very desirable). The error between predicted and experimental after validation of data is 10 %.

3.2 Parametric interaction

Figure 1b describes the desirability surface/contour plot of the parameter responses to achieve a high DS, purity, and viscosity for BiOzCMC. Plot I-III observes the relationship between NaOH concentration and other parameters. The figure indicates that the concentration of NaOH needs to be above 32 % when in relation to SMCA ratio >1:1.2, temperature above 66 ºC, and time between 2.2 - 2.6 h to improve the amorphous structure of CMC and achieve a high DS (Tasaso, 2015). The plot IV &V illustrates the relationship between SMCA vs temperature and time. DS above 0.7 can be reached at the SMCA ratio higher than 1:1.22 since a high availability of carboxyl group is provided. The solubility and stability of the CMC can be improved (Rahman et al., 2021) when the 2.2 h etherification time, and temperature more than 66 ℃ is applied. The relationship between time and temperature as plot VI demonstrates a shorter reaction time of 1.8 h and higher temperatures should give a DS above 0.7. Hence, the relationship between the parameter performed by RSM analysis can be predicted using a simulation trial by Tibco Statistica Ver 13 software.

3.3 Parametric estimation of region for highest quality of BiOzCMC

Figure 2 illustrates the parametric prediction of DS, viscosity, and purity of CMC for reaction parameters of NaOH, SMCA, temperature, and time based on region of study. From the figure, a high DS above 0.7 needs a high NaOH concentration loading, and the etherification temperature while using a low SMCA ratio and a short etherification time. For viscosity, only the etherification temperature must be low, and the other parameters like NaOH, SMCA and etherification time are needed to be used at a higher value. Since purity is one of the important parameters to consider in CMC, obtaining a high purity BiOzCMC would be of utmost benefit. To achieve a high purity BiOzCMC, the SMCA loading ratio should be low while all other parameters are high especially for NaOH

concentration and etherification temperature. Taking into consideration all these behaviors and limitation of experiment, a parametric analysis predicts a range in parameters for optimization study to synthesize high quality BiOzCMC for DS of about 1.2 is 30 - 35 % of NaOH concentration, SMCA ratio 1:1.2 – 1:2.0, etherification time 1.5 – 2.5 h, and etherification temperature of 65 – 75 ºC.

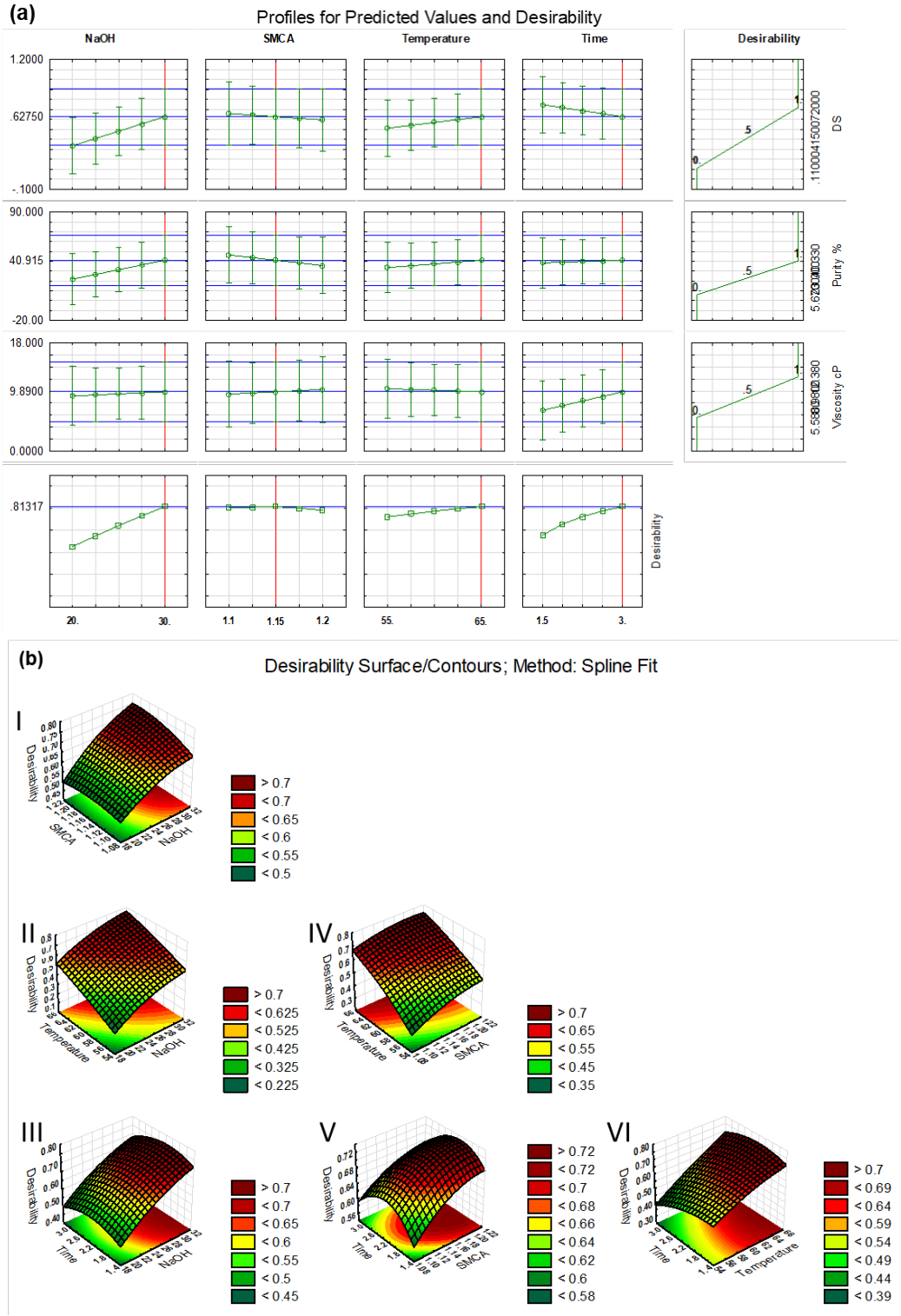

Figure 1: Illustration of (a) Desirability plot and (b) Surface/contour response

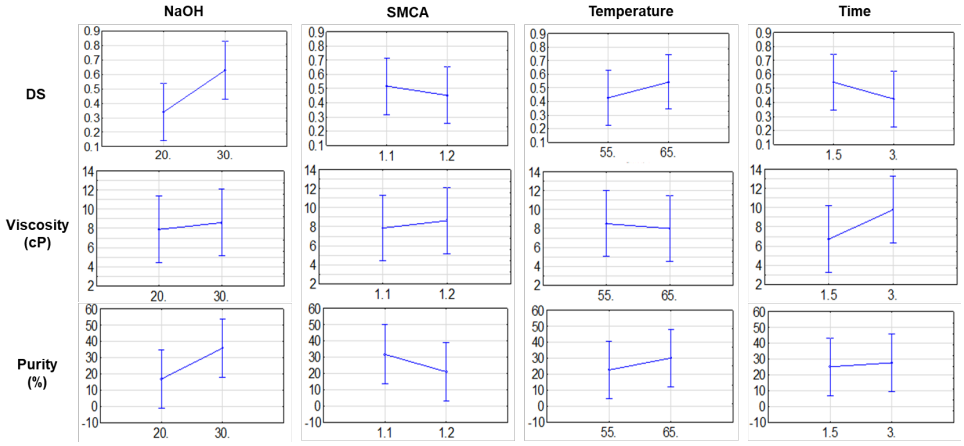

Figure 2: Parametric prediction for DS, Viscosity, and Purity of BiOzCMC

3.4 Physico-chemical characterization of BiOzCMC

The diffraction of XRD for BiOzCMC is illustrated in Figure 3a. The peak shows that BiOzCMC structure is semi-crystalline with crystallinity index of 35.9 %. A similar trend has been found by Rasid et al. (2021). Figure 3b illustrates the surface morphology of BiOzCMC which has a clear, compact, and smooth surface like pure commercial CMC in Figure 3d (Rasid et al., 2021). This indicates that the etherifying agent provides better access to the cellulose molecules during CMC production, while the alkaline solution weakens the structure, stabilizes the molecular orientation, and causes the cellulose to lose some of its crystallinity (Rahaman et al., 2022) making the BiOzCMC amorphous in the XRD analysis with SEM image of a smooth surface structure.
The particle size distribution curve for BiOzCMC is shown in Figure 3c. Based on the polydispersity of the distribution, BiOzCMC has a particle size of 7.5 d. nm with a narrow size distribution of 98.9 %. The zeta potential of BiOzCMC from the analysis gave -59.67 mV which is in line with literature stating that zeta potential values between -46 and -60 mV indicates a colloidal stability of negatively charged particles (Kim et al., 2021). This suggests that the BiOzCMC has a greater nanoparticle dispersion inferring that the ozonolysis could improve the BiOzCMC properties.

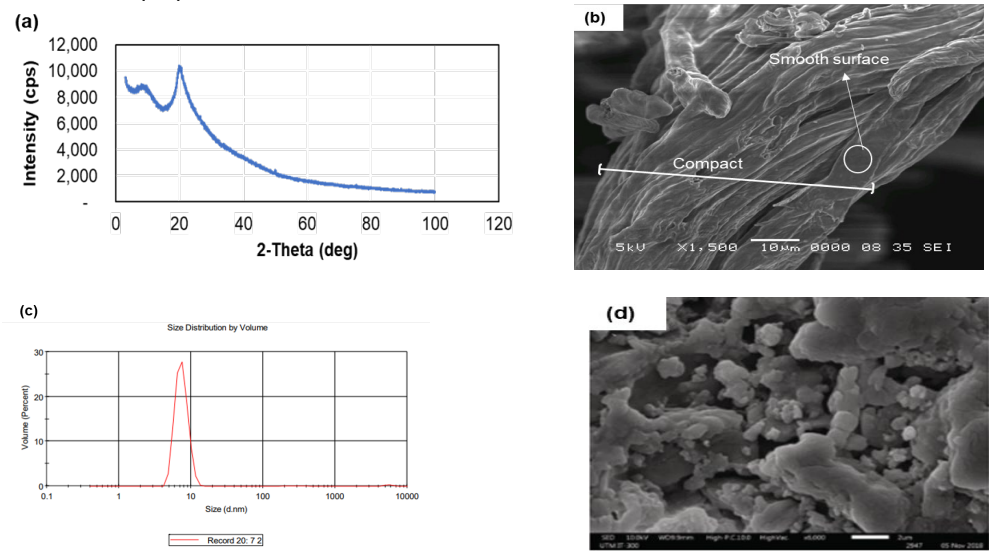

Figure 3: Illustration of (a) XRD diffraction pattern (b) SEM image of BiOzCMC (1500x) (c) PSA distribution of BiOzCMC and (d) SEM image of CMC (6000x) (Rasid et al., 2021)

4. Conclusions

The parametric analysis of the synthesis of BiOzCMC found that the highest DS value of 0.63, purity 41 %, viscosity 10 cP are within the region of the study. The range of process parameters for increasing DS, viscosity,

and purity of the synthesis of BiOzCMC is recommended between 30 - 35 % of NaOH concentration, SMCA ratio 1:1.2 – 1:2.0, time 1.5 – 2.5 h, and temperature of 65– 75 °C. This parametric region can be used to obtain the optimum process condition for BiOzCMC synthesis using the RSM approach. The ozonolysis treatment using OzBiONY 2.0 improves the properties of the BiOzCMC.

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