Cellulose Ethers from Banana (*Musa balbisiana* Colla) Blossom Cellulose: Synthesis and Multivariate Optimization

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Abstract: *Cellulose ethers are biocompatible polymers which have attracted considerable attention for various applications due to their physical and mechanical properties. The present work aims to find the optimum condition for synthesizing cellulose ethers from banana blossom cellulose (BBC) such as methylcellulose (MC), carboxymethyl cellulose (CMC) and hydroxypropyl cellulose (HPC). The ultrasonication-assisted method as an energy source is used to shorten the synthesis time at room temperature and obtain high yields. The influences of various parameters (NaOH concentration, etherification agents, and sonication time) were analyzed using a multivariate statistical modeling response surface methodology (RSM). The materials were characterized by FTIR, SEM, and TGA. The cellulose ethers obtained have the potential as food additives with DS values of 2.0, 0.7, and 0.86, respectively. MC was synthesized optimally with a yield of 96.52% using a composition of cellulose (0.4 g), 50% (w/v) NaOH (10 mL) and dichloromethane (6 mL). CMC was synthesized optimally with a yield of 98.26% using a composition of cellulose (0.4 g), 30% (w/v) NaOH (2 mL) and monochloroacetic acid (1 g). HPC was synthesized optimally with a yield of 97.51% using a composition of cellulose (0.4 g), 10% (w/v) NaOH (2 mL) and propylene oxide (1.5 mL).*

Keywords: *banana blossom; cellulose; etherification; response surface methodology*

■ INTRODUCTION

Cellulose can be obtained from various sources, such as plants, bacteria, and algae [1]. It is the most abundant biopolymer, which is the main structural component of plant cell walls [2-3]. Cellulose is a polysaccharide consisting of β-1,4-linked anhydro-D-glucose units [4]. The application of cellulose has been found in many fields, such as construction, paper, textiles, adhesives, coating, pharmaceuticals, cosmetics, and food [5]. Cellulose has recently become a popular natural food additive due to its unique physical and chemical properties. Each glucose monomer has three hydroxyl groups at C-2, C-3 and C-6 that can be modified into cellulose derivatives, such as cellulose esters and cellulose ethers [2].

Several cellulose ethers are approved as food additives in many countries. Methyl cellulose (MC), carboxymethyl cellulose (CMC), hydroxypropyl cellulose (HPC), hydroxypropyl methyl cellulose (HPMC), and

ethyl cellulose (EC) have completely legitimated the identification of the FAO/WHO Joint Expert Committee on Food Additives (JECFA) [6]. They are used as gelling agents in mixing foods, such as MC or HPC in ice cream, as suspending agents in fruit juice and dairy products, and as thickeners in pie fillings. CMC is used in ice cream or juice due to its ability to inhibit crystallization [6]. Bread contains HPMC where gelation occurs in contact with hot oil.

Cellulose ethers have been synthesized using agricultural waste as a starting material, such as MC from the cellulose of jute pulp [7], corn cobs [8], and snakefruit seeds [9]; CMC from the cellulose of corn cobs waste [10], cherry tomatoes and grapes [11] and asparagus stems [12]; and HPC from the cellulose of bagasse [13], oil palm empty fruit bunches [14] and waste paper [15]. The renewable resource of cellulose used in this study is the banana plant. Bananas are

among the most produced, traded and consumed fruits globally. The banana plant (*Musa* spp.) is one of the most important crops, with a global production of 19.6 million tons in 2022 [16]. Due to climatic circumstances (tropical or subtropical), global banana production is centered in Asia, Africa, the Caribbean, and Latin America. The banana blossom is a part of the banana plant that is rarely utilized. It usually becomes agricultural waste. The reddish-purple petals of banana blossom generally consist of 10–13 layers which are ±25–40 cm in size. These reddish-purple petals have a high cellulose content of 57.61% [17]. Banana blossom contains cellulose (57.61%), hemicellulose (12.18%), lignin (15.33%), wax (1.38%), and water (11.37%) [17]. There is no previous research using banana blossom for cellulose ether synthesis.

The synthetization of those cellulose ethers was conducted by conventional methods that have limitations such as requiring a high temperature, a long-time reaction, and a large amount of solvent [18]. Therefore, it is necessary to control the reaction through green chemistry processes, which can reduce or eliminate the use or generation of hazardous substances. Applications of ultrasound methods in green chemistry processes establish benefits such as low cost, short time, saving energy, reduced number of steps in a reaction, allowing on-site treatment, and environmentally friendly [19-20].

In this study, cellulose ethers, such as MC, CMC, and HPC are synthesized from the cellulose of banana (*Musa balbisiana* Colla) blossoms with ultrasonication method. Cellulose from banana blossom is a promising starting material for synthesizing cellulose ethers. Optimization of cellulose ethers synthesized was used Box Behnken design (BBD) design, which was developed by the response surface methodology (RSM) and was analyzed using Design Expert v.13 software with BBD design. RSM is a statistical technique used to design experiments, build models, evaluate the effects of variables, identify optimal conditions for variables, and predict responses reliably, quickly, and straightforwardly [20-21]. The three-level factorial setting on the optimization using BBD allows this design to be more efficient and economical. The independent variable consisted of NaOH concentration, etherification agents, and sonication time, while the dependent variable was the yield (%).

■ EXPERIMENTAL SECTION

Materials

The materials used in this study were banana blossom (*Musa balbisiana* Colla) obtained from the local area (Klaten, Indonesia). The chemicals such as NaOH (Merck, Germany), NaOCl (Merck, Germany), 2-propanol (Merck, Germany), acetone (Merck, Germany), monochloroacetic acid (Sigma-Aldrich, USA), dichloromethane (Merck, Germany), propylene oxide (Sigma-Aldrich, USA), acetic acid glacial (Merck, Germany), methanol (Merck, Germany), and ethanol (Merck, Germany).

Instrumentation

The reaction of synthesis cellulose ethers was explored using ultrasonic equipment from a DSA50-GL1 ultrasound cleaner operating at a power of 50 W (constant frequency) for 20–40 min at room temperature. The characterization used an FTIR spectrophotometer (Shimadzu FTIR Prestige-21), SEM (JEOL Benchtop JCM 7000), and TGA (Linseis PT–1600).

Procedure

Cellulose isolation from banana blossom

BB (325 g) was cut into small pieces in 2–3 cm size and dried sun. Dried samples were immersed in water for 3×24 h, where water was replaced daily. BB was filtered and then dried by sun. The final dried BB was ground by blender to obtain BB powder (270 g) [22].

Isolation of cellulose from BB was carried out in two stages, i.e., alkalization and bleaching [1]. BB powder (100 g) was added by 10% NaOH with a ratio of 1:20 (w/v) between BB powder and NaOH solution, and the mixture was stirred for 2 h. The mixture was neutralized with water and filtered, and the residue was dried at 60 °C for 3 h to obtain alkalized BB powder. In the bleaching stage, 4% NaOCl was used with a ratio of 1:20 (w/v) between alkalized BB powder and NaOCl solution. The mixture was stirred at 80 °C for 20 min. The mixture was then neutralized with water, filtered, and dried at 60 °C for 3 h. The obtained cellulose was crushed and sieved for 100 mesh.

Synthesis of MC

Cellulose (0.4 g) was added to 50% NaOH (w/v) in variations of 6, 8, and 10 mL. The mixtures were stirred for 1 h at room temperature. The mixtures were then added acetone (8 mL) as a solvent and CH_2Cl_2 as an etherification agent in variations of 2, 4, and 6 mL. Ultrasonic waves were applied to the mixture with ultrasonication time variations of 20, 30, and 40 min [20]. The mixtures were then neutralized using acetic acid 10% (v/v) and washed with acetone to remove by-products. Suspension was then filtered and dried at room temperature to obtain MC [8].

Synthesis of CMC

Cellulose (0.4 g) was added by 30% (w/v) NaOH with variations of 1.2, 1.6, and 2.0 mL. The mixtures were then added isopropanol (8 mL) as a solvent and then stirred for 1 h at room temperature. $ClCH_2COOH$, as an etherifying agent with variations of 0.5, 1.0, and 1.5 g was added slowly into the mixture. Ultrasonic waves were applied to the mixture with ultrasonication time variations of 20, 30, and 40 min [20]. The mixtures were neutralized using glacial acetic acid and washed with 80% ethanol and methanol to remove by-products. The mixtures were filtered and dried at room temperature to obtain CMC.

Synthesis of HPC

Cellulose (0.4 g) was added by 10% (w/v) NaOH with variations of 1.2, 1.6, and 2.0 mL. The mixtures were added isopropanol (8 mL) as a solvent and stirred for 1 h at room temperature. The mixtures were then added C_3H_6O slowly as an etherifying agent with variations of 0.5, 1.0, and 1.5 mL [13]. Ultrasonic waves were applied to the mixture with ultrasonication time variations of 20, 30, and 40 min [20]. The mixtures were then neutralized using 10% acetic acid (v/v) and washed with 80% ethanol to remove by-products. The mixtures were filtered and dried at room temperature to obtain HPC.

Physicochemical characteristics of cellulose ethers

The physicochemical characteristics of cellulose ethers, such as color, shape, smell, solubility, degree of substitution (DS), and pH, were evaluated.

FTIR analysis

Characterization of BBC, MC, CMC, and HPC was done using FTIR to determine the absorption of the resulting functional groups. Infrared absorbance was observed in the wavelength range of 4000–400 cm^{-1}.

SEM analysis

Characterization using SEM was done to determine the surface morphology of BBC, MC, CMC, and HPC with 2,500× magnification.

TGA analysis

Characterization using TGA was done to determine the thermal stability and temperature degradation that occurs in BBC, MC, CMC, and HPC. Sample (0.01 g) was heated from 10 to 900 °C at 10 °C/min under a nitrogen atmosphere.

Statistical analysis of cellulose ethers

Statistical analysis was carried out to determine the optimum prediction of cellulose ether synthesis (MC, CMC, HPC). The optimization process used RSM using Design Expert v.13 software, Stat-Ease Inc., with BBD simulation. Study's independent variables included NaOH, etherification agent, and sonication time. Meanwhile, yield is the dependent or response variable (Eq. (1)). Synthesis of cellulose ethers uses three central points in 15 runs for each synthesis.

$$\text{yield}(\%) = \frac{\text{Dried of cellulose ethers}}{\text{Dried of cellulose}} \times 100 \qquad (1)$$

ANOVA was performed based on the proposed model to determine the influence between factors and responses. The value of the coefficient of determination (R^2 and R^2 adj) was used to determine the model's suitability. The p-value approach ($p < 0.05$) was used to determine the significance of the variables to the model. The system's behavior was described as a quadratic polynomial Eq. (2) as a function of the independent variables involving the interaction of the squares and the quadratic terms.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{i<j}^{k} \beta_{ij} X_i X_i + \varepsilon \quad (2)$$

The value of Y is a response (dependent variable, which for this study was % yield), k is the amount of the independent variables (k = 3), X_i and X_j are variables (i

and j are the index numbers for the pattern range from 1 to k), β_0 is the model interception coefficient; β_j, β_{jj} and β_{ij} are successively the interaction coefficients of linear, square and second-order tribes, and ε is a random error for uncertainty between measured and predicted values [23-24].

■ RESULTS AND DISCUSSION

Synthesis of Cellulose Ethers

White powder cellulose was successfully isolated from BB in 83% yield, as confirmed by FTIR spectra and SEM images. Cellulose ethers were synthesized based on the green chemistry principle using ultrasonication methods. The synthesis of MC, CMC and HPC was carried out by Williamson-type etherification, namely, nucleophilic substitution of the corresponding alkyl halide (Scheme 1).

Optimization for Synthesizing MC

MC synthesis is carried out through two stages, namely alkalization and etherification. Cellulose is activated with concentrated alkali to break hydrogen bonds and promote swelling. The ring-opening reaction of cellulose took place and was ready for the methylation process to obtain methylcellulose (Scheme 1(a)) [8]. Etherification of cellulose was carried out by dichloromethane in acetone using an ultrasonic batch. DS of commercial MC is 1.7–2.2, producing a semi-flexible

polymer that dissolves in water at low temperatures [25]. MC has several purposes as a food ingredient, including stabilization, thickening, and emulsification in the production of ice cream and sauces [7,25]. The properties of MC products meet the standards for the use of cellulose ether in food additives (Table 1). MC was obtained as a white and odorless powder and soluble in water with a pH of 7.59. Synthetic MC had a DS value of 2.00, whereas food grade MC has a DS value of 1.7 to 2.2 [4].

Synthesis of MC was optimized using RSM with BBD. Parameters of NaOH (x_1), etherification agent (x_2), and sonication time (x_3) were examined. The response used to achieve the optimum value is the yield (%). Eq. (3) shows the second-order squared polynomial of MC and the value of the probability change in response (Y) per unit change in factor when the independent variable is maintained constant.

$$\begin{aligned}
Y_{MC} =\ &133.2388 - 6.4971x_1 - 1.1617x_2 - 0.7417x_3 \\
&+ 0.5305x_1^2 + 0.4680x_2^2 + 0.0175x_3^2 \qquad (3) \\
&- 0.2944x_1x_2 - 0.0281x_1x_3 - 0.0159x_2x_3
\end{aligned}$$

As shown in Eq. (3), NaOH (x_1) and etherification agent (x_2) have a significant effect on the yield response. The yield tends to increase with an increasing amount of NaOH and etherifying agent, as shown in the 3D surface plot (Fig. 1). The p-value also confirmed that NaOH and the etherifying agent had a significant effect, where the p-value was less than 0.05 (Table 2). The optimum value
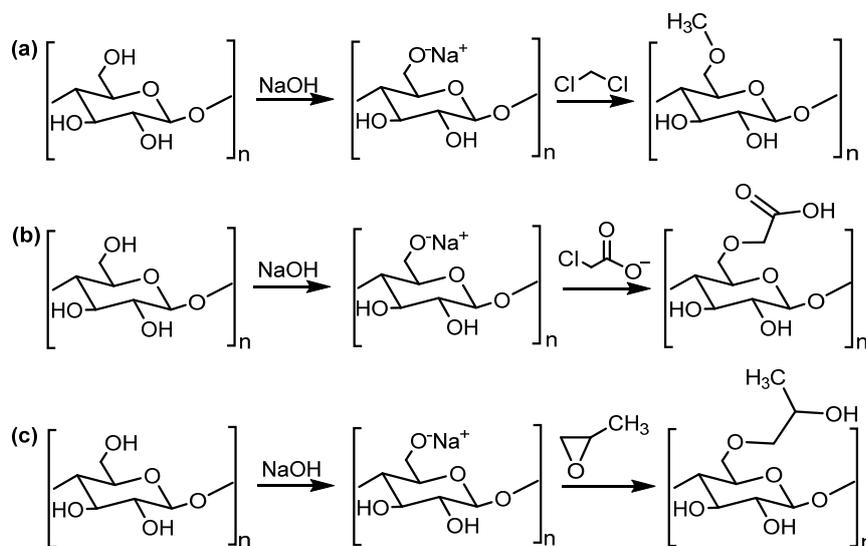

Scheme 1. Etherification reaction of (a) MC, (b) CMC, and (c) HPC

Table 1. Characteristics of MC according to the standard of cellulose ether in food additives

Parameters	MC standard food additives [26]	MC (In this work)
Form	Powder	Powder
Color	White	White
Odor	Odorless	Odorless
Solubility	Water	Water
pH (1%)	3.0–11.0	7.59
DS	1.7–2.2	2.0

Table 2. ANOVA test result of MC

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	44.930	9	4.990	6.410	0.027	Significant
x_1-NaOH	0.029	1	0.029	0.037	0.855	
x_2-Etherification agent	1.980	1	1.980	2.540	0.172	
x_3-Sonication time	0.259	1	0.259	0.333	0.589	
x_1x_2	5.550	1	5.550	7.120	0.044	
x_1x_3	1.270	1	1.270	1.630	0.258	
x_2x_3	0.403	1	0.403	0.518	0.504	
x_1^2	16.630	1	16.630	21.350	0.006	
x_2^2	12.940	1	12.940	16.620	0.009	
x_3^2	11.270	1	11.270	14.470	0.013	
Residual	3.890	5	0.779			
Lack of fit	3.860	3	1.290	72.950	0.014	Significant
Pure error	0.035	2	0.018			
Cor total	48.830	14				
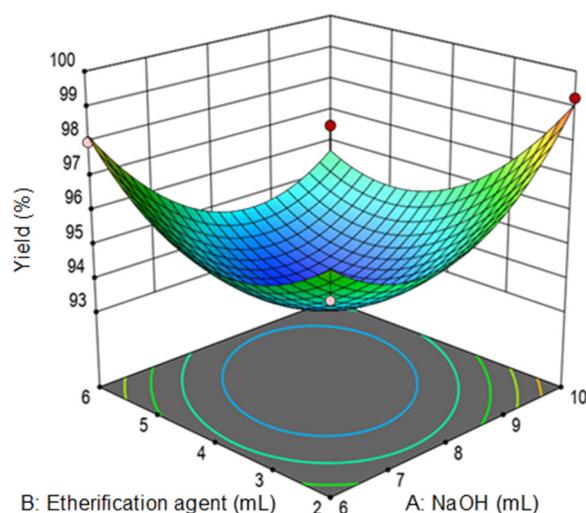
Fig 1. Plot surface 3D synthesis of MC

for MC synthesis was 0.4 g cellulose, 10 mL NaOH 50%, 6 mL dichloromethane, and 30 min of sonication time, resulting in 96.52% yield.

The ultrasonication-assisted method of MC synthesis shows efficiency compared to conventional methods. In the conventional method, MC is synthesized for 5 h at 50 °C in 36.60% yield with a DS value of 2.29 [7]. In the ultrasonication-assisted method, MC synthesis was carried out for 30 min at room temperature in 96.52% yield with a DS value of 2.0. The higher the DS value, the more substituted ether groups.

Optimization for Synthesizing CMC

Synthesis of CMC was carried out through two steps, namely the alkalization and etherification stage. The alkalization stage was carried out by adding 30% NaOH (w/v) and isopropanol. Sodium hydroxide activates the ring opening of epoxide and facilitates the methylation process (Scheme 1(b)) [8]. In this step, the color of the mixture changed from white to yellow-brown and coagulated. The next step was esterified with

monochloroacetic acid ($ClCH_2COOH$) in an ultrasonic batch. CMC is the most frequently produced and utilized cellulose ether in the food business due to its capabilities as an emulsifying agent, thickening agent, suspending agent, and stabilizing agent in food additives [27]. The average number of substituted hydroxyl groups per monomer is represented by DS. CMC's DS value commercially ranges from 0.4 to 1.5 [28]. The CMC product developed in this investigation meets the criteria for cellulose ethers in food additives (Table 3). CMC was obtained as a white powder, which was soluble in water with a pH of 7.4. DS value of synthesized CMC was 0.71, which was in the range of 0.2–1.5 for food additives [29].

CMC synthesized was optimized with parameters of NaOH (x_1), etherification agent (x_2), and sonication time (x_3). The response used to achieve the optimum value is the yield (%). Eq. (4) shows the second-order squared polynomial of CMC and the value of the probability change in response (Y) per unit change in factor when the independent variable is held constant.

$$Y_{CMC} = 195.9488 - 64.9635x_1 - 33.2367x_2 - 2.3851x_3$$
$$+ 19.6146x_1^2 + 16.5433x_2^2 + 0.0376x_3^2 \qquad (4)$$
$$- 0.2875x_1x_2 + 0.0775x_1x_3 - 0.0125x_2x_3$$

As shown in Eq. (4), NaOH (x_1) and sonication time (x_3) have a significant effect on the yield response. The yield tends to increase with an increasing amount of NaOH and sonication time, as shown in the 3D surface plot (Fig. 2). The *p*-value also confirmed that NaOH and the sonication time had a significant effect, where the *p*-value was less than 0.05 (Table 4). The optimum value for CMC synthesis was 0.4 g cellulose, 2 mL 30% NaOH, 1 g monochloroacetic acid, and 40 min of sonication time with a yield of 98.26%.

In comparison to conventional methods, an ultrasonication-assisted method for synthesizing CMC shows efficiency. In conventional methods, CMC is synthesized for 3 h at 50 °C in 80% yield with a DS value of 0.2–0.3 [30]. In the ultrasonication method, CMC synthesis was carried out at room temperature for 40 min in 98.26% yield with a DS value of 0.77. In this case, the higher the DS value, the more substituted ether groups.

Optimization for Synthesizing HPC

HPC was synthesized through two steps, i.e., alkalization and etherification. In alkalization, the BBC was activated to more nucleophilicity by NaOH and isopropyl alcohol, giving cellulose alkali ions [8]. Cellulose alkali ion was reacted with propylene oxide (Scheme 1(c)). In the food industries, HPC is used as thickeners, binding agents, stabilizers, and emulsifiers [15]. The average number of hydroxyl groups per repeating unit is referred to as DS. HPC is a commercially
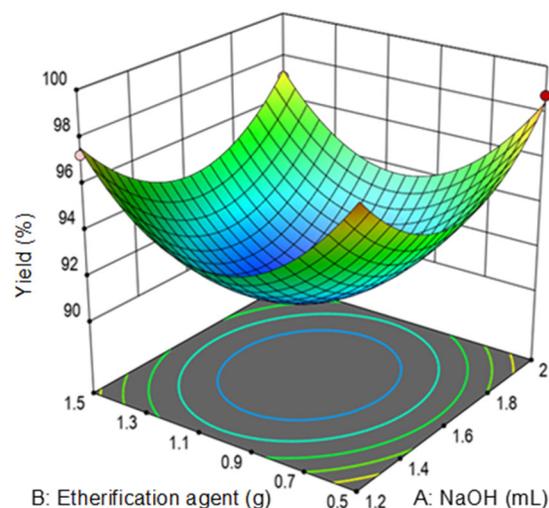

Fig 2. Plot surface 3D synthesis of CMC

Table 3. Characteristics of CMC according to the standard of cellulose ether in food additives

Parameters	CMC standard food additives [29]	CMC (In this work)
Form	Powder	Powder
Color	White	White
Odor	Odorless	Odorless
Solubility	Water	Water
pH (1%)	6.0–8.5	7.4
DS	0.2–1.5	0.71

Table 4. ANOVA test result of CMC

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	134.520	9	14.950	19.250	0.002	Significant
x_1-NaOH	0.032	1	0.032	0.042	0.846	
x_2-Etherification agent	1.940	1	1.940	2.500	0.175	
x_3-Sonication time	0.278	1	0.278	0.357	0.576	
$x_1 x_2$	0.013	1	0.013	0.017	0.901	
$x_1 x_3$	0.384	1	0.384	0.495	0.513	
$x_2 x_3$	0.016	1	0.016	0.020	0.893	
x_1^2	36.370	1	36.370	46.830	0.001	
x_2^2	63.160	1	63.160	81.330	0.000	
x_3^2	52.150	1	52.150	67.160	0.000	
Residual	3.880	5	0.777			
Lack of fit	3.830	3	1.280	50.220	0.010	Significant
Pure error	0.051	2	0.025			
Cor total	138.410	14				

available water-soluble cellulose ether derivative with a DS value of 1.42 [31]. The HPC product obtained in this study meets the criteria for cellulose ether in food additives (Table 5). HPC was obtained as a white powder and soluble in water with a pH of 7.05. The DS value of HPC was 0.86, which was in accordance with the food additive DS value of < 1.42 [32].

HPC synthesizing was optimized using RSM with BBD. Parameters of NaOH (x_1), etherification agent (x_2), and sonication time (x_3) were studied. The response used to achieve the optimum value is the yield (%). Eq. (5) shows the second-order squared polynomial of HPC and the value of the probability change in response (Y) per unit change in factor when the independent variable is held constant.

$$
\begin{aligned}
Y_{HPC} = &\, 173.8088 - 40.5083x_1 - 25.5108x_2 - 2.5459x_3 \\
&+ 11.1823x_1^2 + 12.1267x_2^2 + 0.0372x_3^2 \\
&+ 0.3625x_1x_2 + 0.1531x_1x_3 + 0.0740x_2x_3
\end{aligned} \tag{5}
$$

As shown in Eq. (5), NaOH (x_1) and etherification agent (x_2) have a significant effect on the yield response. The yield tends to increase with an increasing amount of NaOH and etherifying agent, as shown in the 3D surface plot (Fig. 3). The p-value also confirmed that NaOH and the etherifying agent had a significant effect, where the p-value was less than 0.05 (Table 6). The optimum value for MC synthesis was 0.4 g cellulose, 2 mL NaOH 10%, 1.5 mL propylene oxide, and 30 min of sonication time with a yield of 97.51%.

The ultrasonication-assisted method of HPC synthesis shows efficiency compared to conventional methods. In the conventional method, HPC is synthesized for 6 h at 60 °C in 48% yield with DS value of 1.87 [13]. In the ultrasonication method, HPC was synthesized for 30 min at room temperature in 97.51% yield with a DS value of 0.86.

Table 5. Characteristics of HPC according to the standard of cellulose ether in food additives

Parameters	HPC standard food additives [33]	HPC (In this work)
Form	Powder	Powder
Color	White	White
Odor	Odorless	Odorless
Solubility	Water	Water
pH (1%)	5.0–8.0	7.05
DS	< 1.42	0.86

Table 6. ANOVA test result of HPC

Source	Sum of squares	df	Mean square	F-value	p-value	
Model	92.440	9	10.270	8.920	0.013	Significant
x_1-NaOH	0.068	1	0.068	0.059	0.817	
x_2-Etherification agent	4.760	1	4.760	4.130	0.098	
x_3-Sonication time	0.030	1	0.030	0.026	0.878	
x_1x_2	0.021	1	0.021	0.018	0.898	
x_1x_3	1.500	1	1.500	1.300	0.305	
x_2x_3	0.548	1	0.548	0.476	0.521	
x_1^2	11.820	1	11.820	10.260	0.024	
x_2^2	33.940	1	33.940	29.470	0.003	
x_3^2	51.140	1	51.140	44.410	0.001	
Residual	5.760	5	1.150			
Lack of fit	5.460	3	1.820	12.260	0.076	
Pure error	0.297	2	0.148			
Cor total	98.200	14				
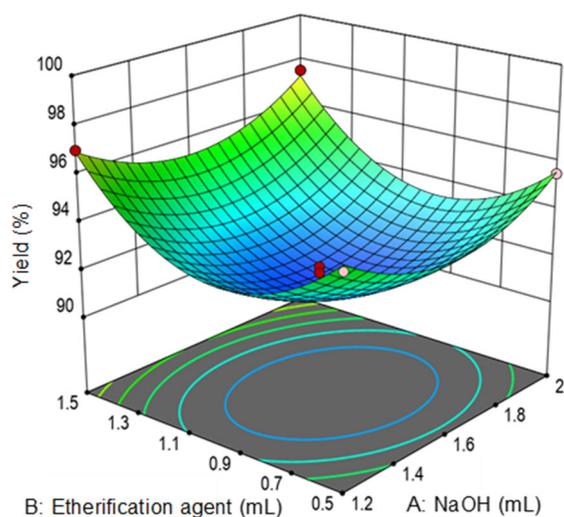
Fig 3. Plot surface 3D synthesis of HPC

Fig 4. FTIR spectra of (a) BBC, (b) MC, (c) CMC, and (d) HPC

FTIR Analysis

FTIR spectra of BBC (Fig. 4) showed the absence of characteristic peaks of lignin and hemicellulose, such as peaks at 1740 cm^{-1} (C=O), 1515 cm^{-1} (C=C), and 1240 cm^{-1} (C–O) [34]. A peak at 3417 cm^{-1} indicates the stretching of the hydroxyl groups of cellulose. Typical peaks of cellulose were observed at 2918 cm^{-1} (CH stretching), 1623 cm^{-1} (OH bending), 1376 cm^{-1} (CH$_2$ bending), 1058 cm^{-1} (C–O stretching), and 894 cm^{-1} (β-1→4 glycosidic bond). These peaks are similar to FTIR spectra of cellulose of banana blossom [17], peanut shells [35], and seaweed waste [36].

All FTIR spectra of cellulose ethers (Fig. 4) show the characteristic peaks for the COO$^-$ ether group of the carboxyl group and typical peaks of cellulose, indicating the success of etherification reactions. Characteristic peaks for the COO$^-$ ether group of the carboxyl group are presented at 1631, 1606 and 1628 cm^{-1} for MC, CMC and HPC, respectively. Typical peaks for cellulose of MC appeared at 3418 cm^{-1} for OH stretching, 2926 cm^{-1} for stretching CH, 1436 cm^{-1} for bending CH, 1060 cm^{-1} for stretching CO, and 871 cm^{-1} for stretching CH group β-

(1→4) glycosidic cellulose bond [37]. Adsorption of CMC cellulose occurs at 3414 cm^{-1} for OH stretching, 2924 cm^{-1} for stretching the CH, 1327 cm^{-1} for bending the CH, 1060 cm^{-1} for stretching CO, and 904 cm^{-1} for stretching the CH group β-(1→4) glycosidic cellulosic bond [20]. Typical cellulose peaks of HPC are shown at 3442 cm^{-1} for OH stretching, 2905 cm^{-1} for stretching the CH, 1416 cm^{-1} for bending the CH, 1060 cm^{-1} for stretching the CO, and 890 cm^{-1} for stretching CH, β-(1→4) glycosidic cellulose [13].

SEM Analysis

SEM analysis of BBC (Fig. 5) shows a rough and independent fiber surface morphology. Non-cellulose components such as hemicellulose, lignin, and other non-cellulose organic substances have been successfully removed (Fig. 5(a)) [17]. SEM image of MC (Fig. 5(b)) shows the presence of uneven (rough) and non-smooth fibers due to methylation of cellulose [38]. The surface image of CMC (Fig. 5(c)) shows a smooth and uneven

fiber structure because alkaline solution reduces the structure and facilitates etherification [10]. Surface morphology of HPC (Fig. 5(d)) shows the presence of uneven (rough) and corrugated fibers due to hydroxypropylation of cellulose [15].

TGA Analysis

TGA is an analysis that can be used to determine the thermal stability of a material that is decomposed by heat and can break bonds in molecules. TGA analysis of BBC shows three stages of degradation (Fig. 6(a)). The first stage started at a temperature of less than 214.3 °C, a 4.40% weight loss caused by the evaporation of moisture content in the banana blossom [10]. The degradation of the major weight loss of 72.74% occurred at a temperature of 224–398 °C caused by the decomposition of the macromolecular chain (lignin, hemicellulose, and cellulose), which consists of depolymerization, dehydration, and decomposition stage of β-1,4-glycosidic bonds [28]. After a temperature of
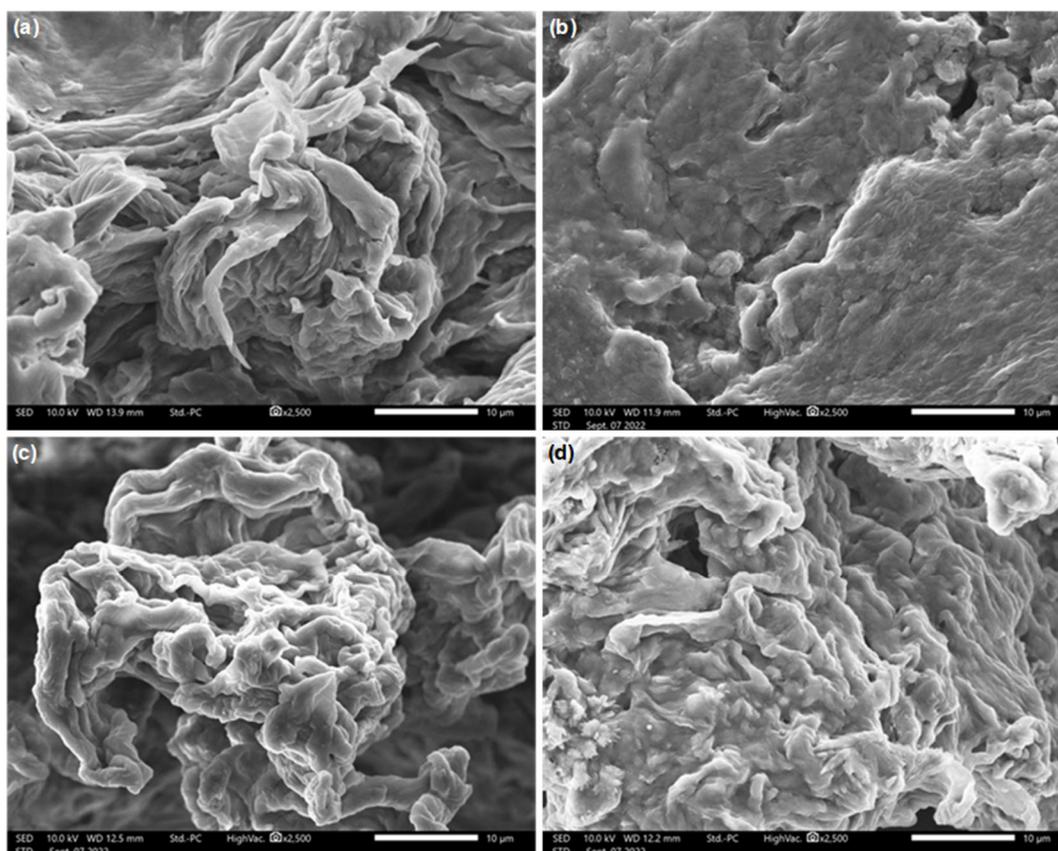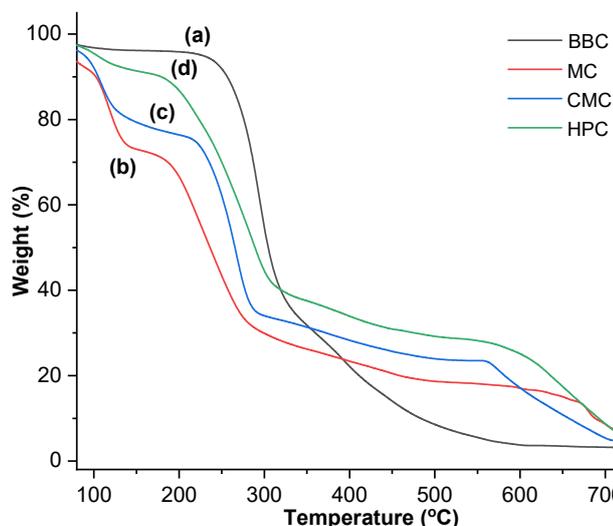

Fig 5. SEM morphologies of (a) BBC, (b) MC, (c) CMC, and (d) HPC

Fig 6. TGA analysis on (a) BBC, (b) MC, (c) CMC, and (d) HPC

450 °C, there was carbonization of compounds from biomacromolecules and condensation of the aromatic rings in lignin [34]. The application of cellulose as a food additive has thermal stability ranging from 200–500 °C [10]. Thus, the thermal stability of cellulose from BB can be applied as an effective food additive.

The first thermal degradation of MC occurred at 101 °C with a weight loss of 9.6% due to the evaporation of water (Fig. 6(b)) [7]. A significant weight loss of 44% occurred at 140–300 °C because of cellulose decomposition. A further thermal decomposition occurred at 300–465 °C with weight loss up to 10% due to the depolymerization of MC into H_2O, CO, and CH_4 [37]. MC shows the temperature at which it decomposes is very high at 325 °C.

As shown in Fig. 6(c), the first thermal degradation of CMC with weight loss of 6.8% at above 100 °C was due to the release of moisture from the CMC by breaking the hydrogen bond [10]. The thermal decomposition temperature further increased from about 220 to 300 °C, indicating a degradation of the carboxylated groups (COO^-) to CO_2 [20]. The weight loss was about 40.5%, probably due to the depolymerization of CMC by forming H_2O, CO_2, and CO. The last weight loss, 10.9% at 300–560 °C present the degradation of CMC product due to the formation of a complex-like structure involving metallic cation, carboxylate anions, and water [20].

The first thermal degradation of HPC with weight loss of 4.8% at above 100 °C, which was due to the release of moisture from the HPC (Fig. 6(d)) [31]. Thermal degradation from 202 to 310 °C with a mass loss of 45% indicates cellulose degradation. The last weight loss 14.3% at 311–578 °C presents the degradation of HPC product due to the loss of H_2O, CO, CO_2, CH_4, and alcohol. Furthermore, thermal degradation at a temperature of 580 °C is the carbonization of non-cellulose compounds.

Thermal degradation of cellulose ethers (MC, CMC, and HPC) is less than that of BBC. During the alkalization stage, NaOH destroys and swells cellulose crystallinity to create cellulose alkali ions before the etherification agent reacts with cellulose alkali ions [20]. As a result, the substitution of ether groups on the cellulose chain reduces the degradation temperature.

■ CONCLUSION

Cellulose has been isolated from BB as white and odorless powder. Cellulose ethers from BBC, such as MC, CMC and HPC, have been synthesized by ultrasonication. Parameters that influence the reaction were analyzed using multivariate statistical modeling RSM. All synthesized cellulose ethers were obtained as white and odorless powders. DS of MC, CMC, and HPC meets the DS value of food additive standards. MC was synthesized optimally with a yield of 96.52% using a composition of cellulose (0.4 g), 50% (w/v) NaOH (10 mL), and dichloromethane (6 mL). CMC was synthesized optimally with a yield of 98.26% using a composition of cellulose (0.4 g), 30% (w/v) NaOH (2 mL), and monochloroacetic acid (1 g). HPC was synthesized optimally with a yield of 97.51% using a composition of cellulose (0.4 g), 10% (w/v) NaOH (2 mL), and propylene oxide (1.5 mL).

■ AUTHOR CONTRIBUTIONS

Safira Zidna Salama conducted methodology-data analysis, conceptualization, investigation and writing

original draft. Venty Suryanti and Maulidan Firdaus performed supervision, conceptualization, review-editing original draft. All authors agreed to the final version of this manuscript.

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