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Synthesis and Optimization Study of Microcrystalline Cellulose (MCC) through Acid Hydrolysis from Confiscated Cigarette

Kaarthiga Manogaran[1] and Akmal Hadi Ma'Radzi[1,2*]

[1]Faculty of Chemical Engineering & Technology, Universiti Malaysia Perlis (UniMAP), 02600 Arau, Perlis, Malaysia

[2]Centre of Excellence for Biomass Utilization (CoEBU), Universiti Malaysia Perlis (UniMAP), 02600 Arau, Perlis, Malaysia

ABSTRACT

Tobacco is a type of plant which is used to make some products such as cigarettes and cigarettes are known to have a lot of harmful effects. There are few factors which causes the Royal Malaysian Custom Department to confiscate cigarettes which are white smuggled cigarette, contraband and false while storing the confiscated cigarettes for long time does not give any benefits. Therefore, cigarette butts which are chosen for this research study come from these confiscated cigarettes to utilize the waste. The tobacco was first undergoing alkaline pretreatment followed by bleaching process. Finally, hydrolysis process was done to synthesize microcrystalline cellulose (MCC). In this research, various acids (hydrochloric acid, sulphuric acid, and nitric acid) were used for the hydrolysis process. It was found that the best acid to synthesize MCC was nitric acid where the highest percentage of MCC yield was 76.83%. Scanning electron microscopy (SEM) shows the surface morphology of MCC which is observed to be like rod-like structure, while X-ray diffraction (XRD) results indicate that the crystalline and crystalline size of MCC was 74.28% and 4.61nm, respectively. FTIR spectra shows a successful removal of lignin structure from raw cigarette butts after hydrolysis process. Besides that, optimization of acid hydrolysis using Design of Expert software (DOE) were conducted where three independent variables were chosen which are hydrolysis time, hydrolysis temperature and acid concentration (nitric acid). Through this study, the highest yield of MCC obtained was 78% and the optimum conditions of parameters are 60 minutes, 60°C and 1.25M of nitric acid. The results of this study can be used to eliminate the hazards of the cigarette butts scattered in the environment and create the added value for the overall process.

Keywords: Cigarette Butts, Acid hydrolysis, Microcrystalline Cellulose, Optimization, Characterization.

1. INTRODUCTION

Tobacco is a species of plant where this plant is mainly grown for the leaves, which will be dried and fermented before being used to make tobacco products. The types of tobacco products are cigarettes, cigars, bidis and many more. Tobacco contains numerous other potentially dangerous chemicals and there is a substance called nicotine that can caused addiction, which eventually becomes difficult for many smokers to quit smoking (Cigarettes and Other Tobacco Products Drug Facts, 2021). However, nicotine prevents people from stopping smoking because nicotine dissolves quickly or is absorbed into the blood. Hence, people and the younger generation began smoking to relieve stress for a short time (Assres, 2018).

*Corresponding author: akmalhadi@unimap.edu.my

Illegal cigarettes are basically described as "the manufacture, importation, purchase, sale, or custody of tobacco products in violation of legislation". It was stated that illegal cigarettes in Malaysia accounted for 62% of worldwide sales in 2019, with just an overall number of 12 billion sticks of illicit cigarettessold in the nation and about RM74.97 million worth illegal cigarettes were confiscated, resulting in tax revenue of RM661.9 million, with 2,104 instances reported (Daim, 2021). Since there's numerous of confiscated tobacco which kept in building of Royal Malaysian Custom Department, it takes up space without giving any benefit. Therefore, the solution to this problem by extracting the cellulose acetate in cigarette filter which made from purified natural cellulose can turn into useful material such as microcrystalline cellulose and others.

The demand for cellulose increasing mainly in renewable material application because cellulose is a biodegradable and renewable polymer that which can be extracted from a variety of sources such as vegetables and fruits. Cellulose is in great demand as cellulose molecule are synthesized and biologically reassembled into microfibrils, and some are made of crystalline and amorphous domains (Junadi *et al.,* 2019). One of the most demanding products made using cellulose in microcrystalline cellulose. Researchers are currently investigating the extraction of high-quality microcrystalline cellulose (MCC) with different properties such as crystalline, surface area, morphology structure, particle size and thermal stability. For this reason, the MCC has a wide range of applications in the food, cosmetics, and medical industries (Junadi *et al.,* 2019). One of the methods to produced microcrystalline cellulose (MCC) are through acid hydrolysis which is cheaper method. Through this hydrolysis method, the MCC can analysis through characterization in terms of yield, morphology, crystallinity and crystallinity size where it is measured using Fourier Transform Infrared-ray (FTIR) Spectroscopy, X-ray Diffraction (XRD), Scanning Electron Microscope (SEM).

2. EXPERIMENTALS

2.1 Chemicals and Materials

The raw material of this research which is the confiscated cigarettes were supplied by Royal Malaysian Custom Department. The chemical use for pre-treatment of the cigarette butts was sodium hydroxide (99%) (HumbG Chemical) while hydrogen peroxide (96%), H_2O2 (98%) (Bendosen) was used to bleach the cigarette butts. Various acids, which were hydrochloride acid (99%), sulfuric acid (99%), nitric acid (99%) (Fisher Scientific) were used for hydrolysis process of MCC.

2.2 Apparatus and Equipment

The instrumentation that was used for research are Scanning Electron Microscopy or also known as SEM (JEOL, JSM-6010LV, USA), Fourier-Transform Infrared Spectroscopy or also known as FTIR (Perkin Elmer, Spectrum 65, USA) and X-Ray Diffraction or also known as XRD (Bruker AXS, D2 Phaser, Germany). Other instrument was used are analytical balance (BS 224S, Sartorius, Germany). All the instruments were located is Faculty of Chemical Engineering Technology, Universiti Malaysia Perlis (UniMAP).

2.3 Sample preparation

Cigarette butts which were supplied by Royal Malaysian Custom Department were cut into small pieces manually using scissors prior to use to increase the surface area of the sample. Then the butts which were cut was oven dried for 30 minutes at 70°C. This process was carried out to ensure there was no water or moisture content in the cut butts before the next step. Then the dried cigarette butts were undergoing alkaline pre-treatment using a 4% NaOH solution for 2 hours at 80°C.

This process was done using a hot plate under constant stirring (Azum *et al*., 2021). This process was repeated twice, and then the sample was filtered and rinsed using cold distilled water to remove the lignin after each treatment. The purpose of this process is not only to remove lignin but also to swell up cellulose which ease the next process which was the hydrolysis process (Fouad *et al.,* 2020). Next process bleaching process was done by mixing with 3% H_2O_2 for 2 hours at 80℃. The bleaching process was repeated twice where the sample was rinsed with distilled water after each process. The pre-treated and bleached cigarette butts was dried using oven at 60℃.

2.4 Isolation of Microcrystalline Cellulose (Acid Hydrolysis)

6g of pre-treated and bleached sample was hydrolyzed using 1.5M HCl at 80℃ for 2 hours. The liquid to solid ratio for this research was 20:1. This hydrolysis process was done using a hot plate and magnetic stirrer under constant stirring. Once the hydrolysis process was done, the sample was rinsed using distilled water and filtered using filter paper. The sample which was filter was dried for 24 hours at 60℃ (Baruah *et al.,* 2020). The sample obtained was then sieved to obtain MCC. The MCC was weighted, and the yield were calculated based on the dried weight of MCC after hydrolysis process and initial weight of confiscated cigarette butt weight as shown in Equation 1. After drying process, the sample was in a desiccator until next step. The same step is repeated for 1.5M of H_2SO_4, 1.5M of HNO_3.

$$\text{Percentage of MCC yield } \% = \left(\frac{\text{Dried weight of MCC after hydrolysis process}}{\text{Weight of pre} - \text{treated and bleached sample}}\right) \times 100 \quad (1)$$

2.5 Sample and Statistical Technique

2.5.1 Scanning Electron Microscopy (SEM)

The MCC powder was observed under SEM and the powder was dried before the observing process. Around 10mg of MCC powder was coated with platinum and was mounted on a conductive carbon tape pasted aluminum plate with width and length of 1cm x 1cm. The MCC powder on the plate will be vacuum sputter coated with platinum layer using sputter coater (Quorum, Q150R, S, UK). Then the MCC powder sample will be observed under SEM (JEOL, JSM-6010LV, USA) and from the micrographs produce, the surface morphology of MCC was studied for as well cigarette butts and pre-treated and bleached sample.

2.5.2 Fourier -Transform Infrared Spectroscopy (FTIR)

The MCC powder sample was mixed with potassium bromide (KBr). Then the mixture was pelletized, and the pellet was used to analyze using Fourier-Transform Infrared Spectroscopy or also known as FTIR (Perkin Elmer, Spectrum 65, USA) at the wavelength of 4000 cm^{-1} to 500 cm^{-1}.

2.5.3 X-Ray Diffraction (XRD)

The MCC sample which was dried using oven was placed into the well of sample holder and pressed well. Then the pressed MCC sample was analyzed with analyzed with Cu Kα radiation (λ =1.5406) at room temperature from 10 to 30^o using XRD (Bruker AXS, D2 Phaser, Germany). The crystallinity index, *Crl* was determined using Equation 2.

$$Crl\ (\%) = \frac{(I_{200} - I_{am})}{I_{200}} x\ 100 \qquad (2)$$

where I_{200} is intensity of 200 lattice diffraction at $2\theta\theta$ = 22.5° while I_{am} is intensity different at $2\theta\theta$ = 18.9° (Baruah *et al.,* 2020). Crystallinity size was calculated using Scherrer equation which shown below (Equation 3) (Bokuniaeva & Vorokh, 2019):

$$L = \frac{k\lambda}{\beta\ cos\ \Theta} \qquad (3)$$

where L is size of crystalline size (nm), k is known to be Scherrer constant (0.84), λ is known to be X-ray wavelength (0.15418nm) and β known as full width half maximum of lattice plane reflection in radian.

2.6 Isolation of Microcrystalline Cellulose (Acid Hydrolysis)

There were three parameters used for optimization study for the best hydrolysis condition. The parameters involved for this research were acid concentration, hydrolysis time and hydrolysis temperature. Then the data interpretation for MCC yield production was carried out using Design of Expert (DOE) software where it is used to analyze the independent variable' effects. A collection of mathematical and statistical techniques called Response Surface Methodology (RSM) was used to study the hydrolysis parameter on MCC yield. The range of the ratio of acid concentration (0.5M-2M), hydrolysis time (60min-150min), and hydrolysis temperature (60°C-90°C) are obtained from literature review. The range of acid concentration that was used was 0.5M to 1.5M. The second parameter was hydrolysis time which ranged from 60min to 150min. The last parameter used for this research was hydrolysis temperature which ranged from 60°C to 90°C.

3. RESULTS AND DISCUSSION

3.1 Percentage of MCC yield by different acid hydrolysis

The percentage of MCC yield which was obtained after acid hydrolysis using various acids was tabulated in Table 1. In this research, solid-to-liquid ratio (1:20), hydrolysis time (2 hours), hydrolysis temperature (80°C) and molarity of acid (1.5M), the amount of pre-treated and bleached sample (6g) is kept constant. The acids used for the acid hydrolysis process are 1.5M of hydrochloric acid (HCl), 1.5M of nitric acid (HNO_3) and 1.5M of sulphuric acid (H_2SO_4).

Table 1. Percentage of MCC yield obtain after various acid hydrolysis process

Various Acid (1.5M)	Percentage of MCC yield (%)
HCl	76.16
HNO_3	76.83
H_2SO_4	69.33

Based on Table 1, the highest yield of MCC was obtained from 1.5M of nitric acid (HNO_3) shows the data of highest percentage of MCC followed by 1.5M of hydrochloride acid (HCl) and 1.5M of sulphuric acid (H_2SO_4). A possible reason why MCC yield for H_2SO_4 and HCl is high because both acids are stronger acid compared to nitric acid due to their polarity. The polarity of HCl is more polar than nitric acid. H_2SO_4 has more stable conjugate based compared to HNO_3. The polarity and stable conjugated cause the acid to fully dissociate in water and produced hydronium ions which degrade the amorphous region more compared to HNO_3. According to Nur Hanani *et al.* (2017), nitric acid has the highest percentage of yield where it synthesized around 83. 5%. The possibility nitric acid shows high percentage of MCC yield is due to the capability of nitric acid to hydrolyze more of cellulose's amorphous area, contributing to an increase in percentage of MCC yield. Mineral acids in nitric acid contain hydrogen ions can penetrate and eliminate excess of amorphous areas in cellulose, increasing MCC yield percentage. Moreover, nitric acid can react fast with cellulose at a particular time (Kharismi *et al*., 2018). Besides that, sample preparation, geographical conditions, climate, and analysis method also can cause differences in percentage of MCC yield (Fouad *et al*., 2020).

3.2 Characterization of Microcrystalline Cellulose (MCC)

In this research, three types of characterization are analysis for the raw cigarette butts or also known as untreated raw material (RCB), pre-treated and bleached cigarette butts (PBCB) and microcrystalline cellulose (MCC). One of the analyses studied was the morphological structure of these samples through Scanning electron microscopy (SEM). All three samples have a rod-like structure. The function and crystallinity structure of these samples was studied through Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Each characterization of these samples is explained in detail.

3.4.1 Scanning Electron Microscopy (SEM)

SEM microscopy of raw cigarette butts (RCB), pre-treated, bleached cigarette butts (PBCB) and microcrystalline cellulose (MCC) is studied, and it is presented through Figure 1. The MCC sample is synthesized using 1.5M of nitric acid. Figure 1 shows the surface morphology of raw cigarette butts which seemed to be long continuous rod-structures where the raw cigarette butts (RCB) consist of 95% of microscopic-sized fibrous cellulose acetate and 5% of remaining composition are plasticizer which used to bear the cellulose acetate fibers (Benavente *et al*., 2019). Besides that, heavy metals such iron, manganese and more were also contained in cigarette butts (Benavente *et al.,* 2019).

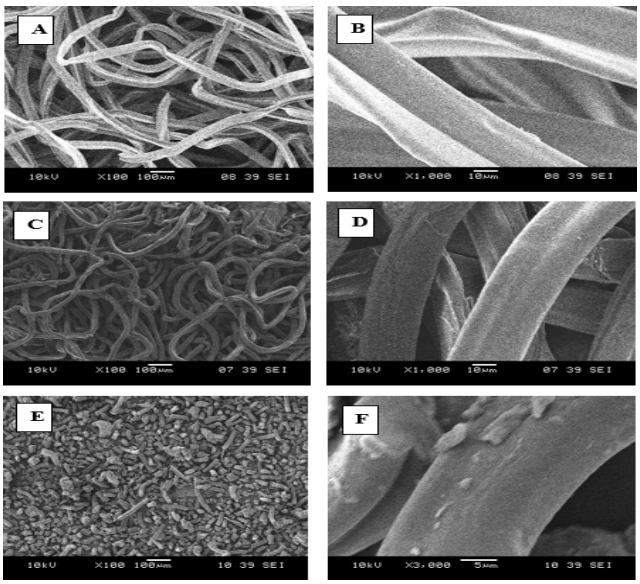

Figure 1. SEM microscopy of RCB (A & B), PBCB (C&D) and MCC (D&F) at different magnifications

Based on Figure 1 (C) and (D), the surface morphology of pre-treated and bleached cigarette butts (PBCB) seemed to be long, continuous, more ruptured and irrigated-like rod-structure, indicating that the sample is swollen during pre-treatment and bleaching process (Fouad *et al.,* 2020). Moreover, in Figure 1 (C), the smoother PBCB indicated the removal of lignin which might indicate the presence of lignin in FTIR analysis. Figure 1 shows the surface morphology of MCC like small size rod structure cellulose. The structure of MCC is smaller version of cellulose compared to RCB and PBCB. According to Fouad *et al*., (2020), this result might be due to depolymerization process where the hydronium ions from nitric acid, HNO_3 which used for hydrolysis to penetrate the internal cellulose and degrade the weak amorphous regions in the cellulose.

3.2.2 Crystallinity Analysis

Figure 2 shows diffraction pattern were obtained by using scan range between angle 10° to 30° of 2-Theta and 0.2 seconds per step. The crystallinity index (*CrI*) and the average of crystallinity size of the direction 200 lattice plane was calculated using Scherer Equation (2). Figure 2 shows three samples which are raw cigarette butts or also known as raw material (RCB), pre-treated and bleached cigarette butts (PBCB) and microcrystalline cellulose (MCC).

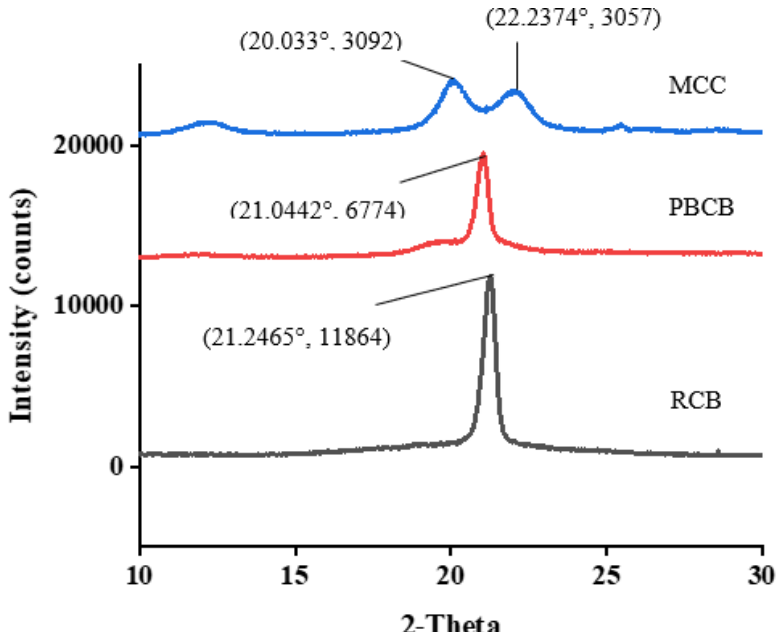

Figure 2. X-ray diffraction patterns (XRD) of RCB, PBCB and MCC

Figure 2 illustrates the XRD pattern for all three sample and all the sample showed prominent peaks around 20.033°, 21.0442°, 21.2465° and 22.2374° which lie corresponded to the respectively (200) crystallographic plane. Table 2 shows the crystallinity (%) and crystallite size of RCB, PBCB and MCC from confiscated cigarettes.

Table 2. Crystallinity (%) and crystallite size of RCB, PBCB and MCC

Samples	Crystallinity(%)	Crystallite size(nm)
Raw cigarette butts (RCB)	40.31	3.08
Pre-treated and bleached cigarette butts (PBCB)	55.31	3.17
Microcrystalline cellulose (MCC)	74.28	4.61

Based on Table 2, the value of crystallinity of the raw cigarettes butts (RCB), pre-treated and bleached cigarette butts (PBCB), microcrystalline cellulose (MCC) were 40.31%, 55.31% and 74.28%, respectively and it's clearly seen that MCC has the highest crystallinity compared to other two samples. According to Baruah *et al.,* (2020), the MCC has the highest percentage of crystallinity due to the penetration of hydronium ions from nitric acid into the amorphous phase of cellulose where acid hydrolysis fragmentation happened, resulting in crystalline structure. With increasing crystalline index, cellulose fiber toughness and tensile strength improved, improving the mechanical characteristics of MCC, and attempting to make the materials of selection for composite synthesis (Baruah *et al.,* 2020) the crystallinity index of microcrystalline cellulose always located between 55% - 80% according to Holilah *et al.,* (2020). From Table 2, the crystal size for the raw cigarette butts (RCB), pre-treated and bleached cigarette butts (PBCB), microcrystalline cellulose (MCC) are 3.08, 3.17, and 4.61 nm, respectively. MCC size has larger crystallite size compared to other samples due to their co-crystallization and the lateral coalescence of microfibrils which increase the crystal size (Hua *et al.,* 2020).

3.2.3 Molecular Structure Determination

Figure 3 shows the FTIR spectra of three sample which are raw cigarette butts or also known as raw material (RCB), pre-treated and bleached cigarette butts (PBCB) and microcrystalline cellulose (MCC). Based on Figure 3, it is clearly seen that most of the spectra were similar which indicates similarity in the chemical composition in each sample.

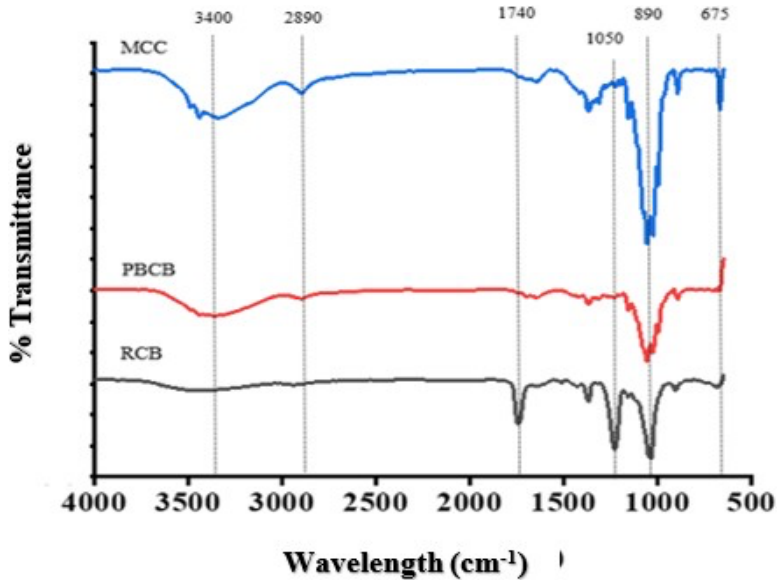

Figure 3. FTIR spectra of RCB, PBCP and MCC

From Figure 3, RCB, PBCB and MCC showed almost similar peak which is 3439.6cm^{-1}, 3355.08cm^{-1} and 3443.01cm^{-1}, respectively where this peak indicates O-H stretching which range between 3500cm^{-1} to 3300cm^{-1} (Fong *et al.,* 2018). RCB shows a peak at 1743.90cm^{-1} which indicates C=O stretching of the methyl ester and carboxyl groups in pectin, uronic ester group in hemicellulose. Besides that, it also can indicate ester linkage of carboxylic group of the ferulic or p-coumaric acids or lignin or hemicellulose. Through this, hemicellulose or lignin is present in raw cigarette butts (Fong *et al.,* 2018). MCC (1654.0cm^{-1}) and PBCB (1648.0cm^{-1}) shows another almost similar peak which is H-O-H stretching due to absorb of water in cellulose (Fong *et al.,* 2018). This peak can also can occurs due to drying process, where even if there's a little moisture still present after drying. 1368.39cm^{-1} (RCB), 1371.0cm^{-1} (PBCB) and 1364.49cm^{-1} (MCC) are almost similar peaks which illustrate C-H bending, waging and vibration aromatic ring of cellulose. RCB shows a strong peak at wavelength of 1230cm^{-1} where it indicates C-O stretching in C-O-C aryl alkyl ether lignin. This

shows that there is a presence of lignin in RBC (Fong *et al.,* 2018). At peaks of 1158 cm^{-1} (MCC) shows a peak which indicates C-O-C stretching of the β-1, 4-glycosidic ring which located between the D- glycose units of cellulose (Fong *et al.,* 2018). Finally, PBCB and MCC shows almost similar peak which is 895.58cm^{-1} and 895.22cm^{-1}, respectively where this peak indicates glyosidic C-H deformation with ring vibration contribution and O-H bending where it happens in β-glyosidic linkage between anhydroglucose units in cellulose.

3.3 Optimization of Acid Hydrolysis

The optimization studies in different conditions were studied by 17 runs which is suggested by DOE and the response of yield of MCC (%) which shown in Table 3.

Table 3. The parameter and yield for optimization of MCC

Run	Factor1: Hydrolysis time	Factor 2: Temperature	Factor 3:Acid concentration	Response 1: yield
1	150	75	0.5	76.6
2	150	60	1.25	74
3	105	60	2.0	70
4	150	75	2.0	68
5	60	75	0.5	72.75
6	150	90	1.25	71.25
7	105	75	1.25	76.6
8	60	60	1.25	78
9	60	90	1.25	77.6
10	105	75	1.25	76.6
11	105	75	1.25	76.6
12	60	75	2.0	73.25
13	105	75	1.25	76.6
14	105	90	2.0	65
15	105	75	1.25	76.6
16	105	60	0.5	71
17	105	90	0.5	72.6

From the optimization studies, the highest yield of MCC obtained from these studies was 78% where this data can be obtained from run 8, in the condition of 60 minutes, 60 ℃ and 1.25M while the lowest yield of MCC obtained from these studies was 65% from run 14, in condition of 105 minutes, 90℃ and 2M.

3.4 Analysis of Variance (ANOVA)

Analysis of Variance or also known to be (ANOVA) is a type of statistical method which used study type of statistical relationship between the mean of independent variable. Besides that, ANOVA is also used to determine the signification and fitness of the model. In this research, ANOVA is used to measure the type of statistical relationship between hydrolysis time, hydrolysis temperature and acid concentration and the signification and fitness of this optimization of MCC process. Data from ANOVA for response surface quadratic model for the optimization of MCC model is shown in Table 4.

For this study, the model F-value of 16.38 indicates that the model is significantly affecting the yield of MCC and only 0.07% chance that an F-value this large could occur due to noise. Acid concentration has a great impact on the optimization response as acid concentration has the F-value of 34.86 with only 0.17% chance that the F-value is large occur due to noise compared to hydrolysis time and hydrolysis temperature with the F-value of 17.26 and 5.36 respectively. p-values indicates the signification of each variable p-values less than 0.0500 indicate model terms are significant.

Table 4. ANOVA for response surface quadratic model of optimization of MCC

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	211.67	9	23.52	16.38	0.0007
A-time	17.26	1	17.26	12.02	0.0105
B-temperature	5.36	1	5.36	3.73	0.0946
C-Acid Concentration	34.86	1	34.86	24.28	0.0017
AB	1.38	1	1.38	0.9614	0.3595
AC	20.70	1	20.70	14.42	0.0067
BC	10.89	1	10.89	7.58	0.0283
A^2	2.74	1	2.74	1.91	0.2099
B^2	20.26	1	20.26	14.11	0.0071
C^2	95.25	1	95.25	66.33	< 0.0001
Residual	10.05	7	1.44		
Lack of Fit	10.05	3	3.35		
Pure Error	0.0000	4	0.0000		
Cor Total	221.73	16			

Based on Table 4, two linear term which is A (hydrolysis time) and C (acid concentration) is significant while B (hydrolysis temperature) indicates not signification with p-value of 0.0948. Based on the two factors, AC (hydrolysis time and acid concentration) and BC (hydrolysis temperature and acid concentration) are signification while in the second -order term B^2 (hydrolysis temperature) and C^2 (acid concentration) are significant model terms. ANOVA is used to verify the statistical significance of the mean square variation square ratio and mean square residual error. R^2 is used to measure of the quantity of variation around the model's mean while adeq Precision is used measures the signal to noise ratio Based on Table 5 which shows the statistical data of ANOVA, the R^2 data we obtained are 0.9547. The R^2 in this study is good as the closer the R^2 value to 1, the better the data fits to the model. The adeq precision ration obtain is 12.8594 which indicates an adequate signal as adeq precision ratio greater than 4 is desirable. Therefore, this model can used to navigate the design space. The coefficient variation (C.V.) obtains for this research is 1.63% while the standard deviation obtain is 1.20. Both of this parameter value is low indicate the reproducibility of the model.

Table 5. Statistical data of ANOVA

Parameter	Value	Parameter	Value
Std. Dev.	1.20	R^2	0.9547
Mean	73.71	Adjusted R^2	0.8964
C.V. %	1.63	Predicted R^2	0.2746
		Adeq Precision	12.8594

3.4.1 Reaction between Hydrolysis Time and Hydrolysis Temperature

Figure 4 shows the 2D contour plot and 3D graph which indicates the relationship between hydrolysis time and hydrolysis temperature on MCC yield in percentage (%). The oval darker region in the contour plot between the hydrolysis time and hydrolysis temperature the maximum MCC yield percentage. Based on the prediction, the plot and graph show that 76.6% is the optimum percentage of yield of MCC of and the optimum condition for the optimum MCC yield are 105 minutes (hydrolysis time) and 75°C (hydrolysis temperature) which located in the midpoint (red

dot) where the midpoint in the contour plot indicates the prediction done by Design of Expert (DOE). Based on Figure 4, it is clearly seen that the hydrolysis time and hydrolysis temperature increase towards the midpoint which indicates the increase of MCC yield. The lighter region surrounding the midpoint indicates the percentage of MCC yield drop.

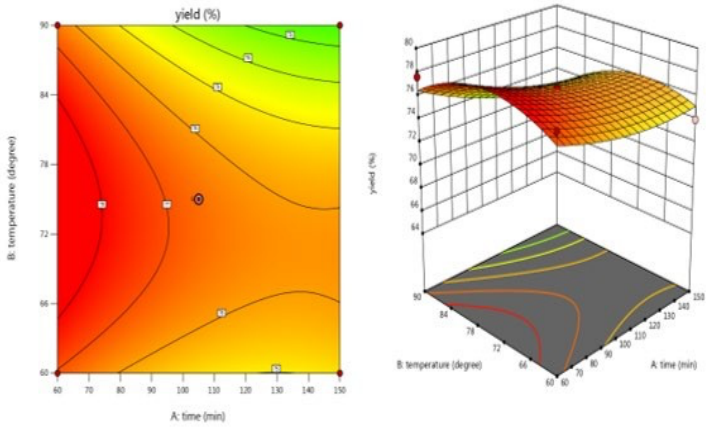

Figure 4. 2D and 3D graph for hydrolysis time and hydrolysis temperature

Based on the 3D graph in Figure 4, the shape of saddle indicates that the hydrolysis temperature has effect on percentage of yield of MCC compared to hydrolysis time. Based on the 3D graph, the yield of MCC eventually decrease when the temperature and time increase than the predicted parameter value as it can cause more amorphous area of cellulose to be hydrolyze or less amorphous area is hydrolyzed is the temperature and time is lower compared to the predicated parameter value.

3.4.2 Reaction between Hydrolysis Time and Acid Concentration

Figure 5 shows the 2D contour plot and 3D graph which indicates the relationship between hydrolysis time and acid concentration on MCC yield in percentage (%). The oval darker region in the contour plot between the hydrolysis time and acid concentration the maximum MCC yield percentage. Based on the prediction, the plot and graph show that 76.6% is the optimum percentage of yield of MCC of and the optimum condition for the optimum MCC yield are 105 minutes (hydrolysis time), and 1.25M (acid concentration) which located in the midpoint (red dot) where the midpoint in the contour plot indicates the prediction done by Design of Expert (DOE). Based on Figure 5, it is clearly seen that the hydrolysis time and acid concentration increase towards the midpoint which indicates the increase of MCC yield. The lighter region surrounding the midpoint indicates the percentage of MCC yield drop.

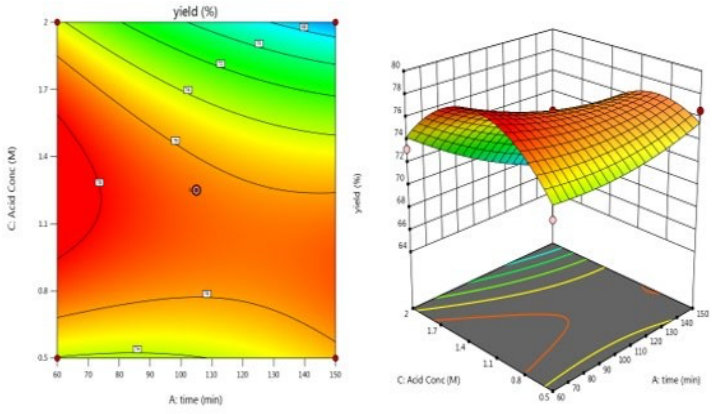

Figure 5. 3D graph for hydrolysis time and acid concentration

Based on the 3D graph, The yield of MCC eventually decrease when the acid concentration and time increase than the predicted parameter value as it can cause more amorphous area of cellulose to be hydrolyze or less amorphous area is hydrolyzed is the acid concentration and time is lower compared to the predicated parameter value. Based on the 3D graph in Figure 5, the shape of saddle indicates that the acid concentration has effect on percentage of yield of MCC compared to hydrolysis time however the graph indicates this combine effect is less effective for MCC yield compared to the combine variable of hydrolysis time and hydrolysis temperature as it shows a bit of green and blue region. According to Fong *et al*., (2018), the green and blue region indicates combine variable is less effective compared to other combine variable in the research.

3.4.3 Reaction between Hydrolysis Temperature and Acid Concentration

Figure 6 shows the 2D contour plot and 3D graph which indicates the relationship between hydrolysis temperature and acid concentration on MCC yield in percentage (%). The oval darker region in the contour plot between the hydrolysis time and hydrolysis temperature the maximum MCC yield percentage. Based on the prediction, the plot and graph show that 76.6% is the optimum percentage of yield of MCC of and the optimum condition for the optimum MCC yield are 75°C (hydrolysis temperature) and 1.25M (acid concentration) which located in the midpoint (red dot) where the midpoint in the contour plot indicates the prediction done by Design of Expert (DOE). Based on Figure 6, it is clearly seen that the hydrolysis temperature and acid concentration increase towards the midpoint which indicates the increase of MCC yield. The lighter region surrounding the midpoint indicates the percentage of MCC yield drop.

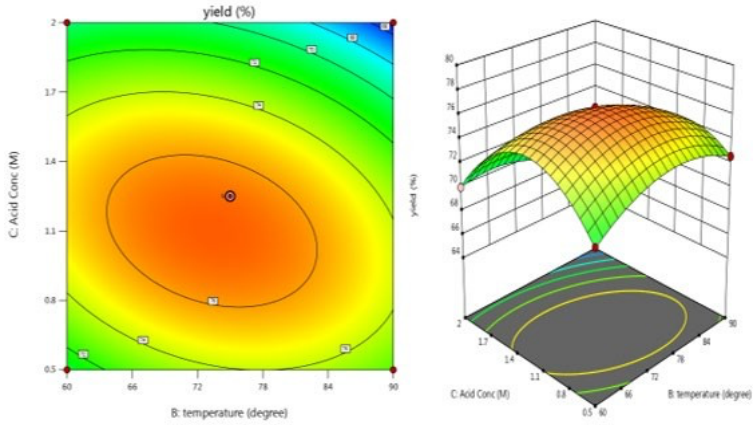

Figure 6. Graph for hydrolysis temperature and acid concentration

Based on the 3D graph, the yield of MCC eventually decrease when the temperature and acid concentration increase than the predicted parameter value as it can cause more amorphous area of cellulose to be hydrolyze or less amorphous area is hydrolysed, and the temperature and acid concentration is lower compared to the predicated parameter value. Based on the 3D graph in Figure 6, shows that the combine effect of acid concentration and hydrolysis temperature less effective compared to another combine effect parameter as this combine variable shows more blur and green region compared to other combine variable. According to Fong *et al.,* (2018), the green and blue region indicates combine variable is less effective compared to other combine variable in the research.

4. CONCLUSION

The synthesis of microcrystalline cellulose through various acids using hydrolysis processes succeeded with nitric acid showing a higher percentage of microcrystalline cellulose yield of 76.83% compared to hydrochloric acid and sulphuric acid, 76.16% and 69.33%, respectively. Through SEM, microcrystalline cellulose is successfully synthesized through cigarette butts by degrading the amorphous region and causing the microcrystalline cellulose structure to be a shorter rod structure. Through crystallinity analysis, the crystallinity and crystallinity size for three samples which were RCB, PBCB and microcrystalline cellulose were 40.31% (3.08nm), 55.31% (3.17nm) and 74.28% (4.61nm), respectively. From FTIR, it shown that the raw cigarette butts contain some fractions of lignin, and it is successfully removed after pre-treatment and bleaching process where the lignin peak is absent in pre-treated and bleached sample, and microcrystalline cellulose sample. The optimum condition for the extraction was achieved in Run 8 where the percentage of yield obtained is 78%. The optimum parameters to achieve were at 60 min, 60°C and 1.25 molarity of nitric acid.

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