

Dielectric barrier discharge plasma pretreatment on hydrolysis of microcrystalline cellulose

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Abstract

Dielectric barrier discharge (DBD) plasma was used as a pretreatment method for downstream hydrolysis of microcrystalline cellulose (MCC). The degree of polymerization (DP) of MCC decreased after it was pretreated by DBD plasma under a carrier gas of air/argon. The effectiveness of depolymerization was found to be influenced by the crystallinity of MCC when under the pretreatment of DBD plasma. With the addition of tert-butyl alcohol in the treated MCC water suspension solution, depolymerization effectiveness of MCC was inhibited. When MCC was pretreated by DBD plasma for 30 min, the total reducing sugar concentration (TRSC) and liquefaction yield (LY) of pretreated-MCC (PMCC) increased by 82.98% and 34.18% respectively compared with those for raw MCC.

Keywords: Dielectric barrier discharge, plasma, cellulose, pretreatment, depolymerization

(Some figures may appear in colour only in the online journal)

1. Introduction

The world's dependence on fossil energies promotes the production of alternative energy using renewable raw materials [1, 2]. As the richest renewable biopolymer in nature, cellulose attracts much interest for the production of biofuels [3], or platform-chemicals (such as 5-hydroxymethyl-furfural, levulinic acid, etc), via hydrolysis [4–6]. Many techniques for the hydrolysis of cellulose have been reported recently, including mineral acid hydrolysis [7, 8], enzymatic hydrolysis [9], supercritical water-hydrolysis [10], etc. Due to the high crystallinity of cellulose, efficient hydrolysis of cellulose needs tough hydrolysis conditions [11, 12], which may not only cause loss of carbohydrate, but also increases the special requirement of instruments [13, 14]. Therefore, an efficient pretreatment method before hydrolysis under mild conditions was desirable.

In recent years, various pretreatment methods have been reported, such as ball milling, acid/alkaline/organic solvent treatment, steam explosion, and other electrical and biological

methods [15–18]. An effective pretreatment method of cellulose was expected to exhibit high sugar yields and low energy/catalyst consumption under mild conditions during the downstream hydrolysis process. An effective pretreatment method of cellulose still urgently requires exploration.

Plasma technology was attracting more and more attention because of its characteristic advantages [19–21], such as maintaining a steady discharge condition easily under atmospheric pressure, multiple physical effectiveness, generating plentiful radical species, etc. Plasma technology has recently been investigated as a pretreatment method of lignocellulosic materials for the production of biofuels [22–24]. Schultz-jensen *et al* [25] discovered that 78% of glucose was released from the plasma-pretreated cellulose, whereas a 52% ethanol yield was obtained. Kolarova *et al* [26] and Flynn *et al* [27] found that plasma pretreatment resulted in surface ablation and significantly increased the roughness of cellulose. And, radical species was believed to play an important part for the pretreatment effectiveness of cellulose. However, the key role of plasma during pretreatment

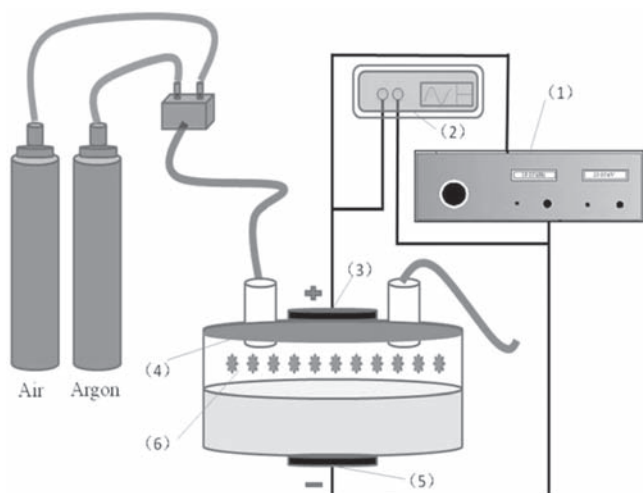


Figure 1. DBD-plasma pretreatment experimental diagram.

process is still unclear and the exact pretreatment mechanism has not been decided.

This work aims to develop an efficient pretreatment method for the cellulose before downstream hydrolysis process. DBD plasma technology was used as a pretreatment method for the microcrystalline cellulose (MCC) in this paper. Effectiveness of DBD plasma pretreatment for hydrolysis of MCC was studied. Pretreatment mechanism was initially discussed.

2. Materials and methods

2.1. Material

MMC (Analytical Reagent, AR), 3, 5-dinitrosalicylic acid (AR) and anhydrous sodium sulfite (AR) were purchased from Shanghai Sinopharm Chemical Reagent Co., Ltd, China. Sulfuric acid (95%) (AR) was obtained from Shanghai suyuan Chemical Reagent Co. Ltd, China. Glucose and potassium sodium tartrate (AR) were purchased from Guangdong Guanghua Scientist Co. Ltd, China. Acetonitrile (AR) and tert-butyl alcohol were obtained from Xilong chemical engineering Co. Ltd, China. MCC with different crystallinity was prepared. MCC-1's crystallinity is 82.8%; MCC-2's crystallinity was 57.4%, which was prepared using MCC-1 as raw material by milling.

2.2. Experimental procedure

Figure 1 shows experimental diagram of MCC's DBD plasma pretreatment process. DBD reactor was a hollow cylindrical shape with 40 mm height and 80 mm diameter. The gap between electrodes was 15 mm. High frequency-high voltage alternating current power was used here. Oscilloscope was used to monitor voltage waveform, two circular copper plates were used as electrodes. Plasma was generated in the gap of reactor, which was between the high voltage electrode and the ground electrode. Raw MCC was prepared as suspension and the suspension was placed in the gap of reactor, and was

pretreated by plasma there. Then the pretreated samples were filtered, dried and collected as PMCC. All hydrolysis reactions for PMCC were carried in hydrothermal reactors.

Discharge voltage was adjusted at 22.0 ± 0.5 kV and discharge frequency was adjusted at 15.0 ± 0.5 kHz when air was used as carrier gas of DBD process. And discharge voltage was 19.0 ± 0.5 kV and discharge frequency was 15.0 ± 0.5 kHz when argon was used. PMCC was hydrolyzed under the conditions optimized (sulfuric acid concentration is 10% w/w, hydrolysis temperature is 180°C , solid-liquid ratio is 1:15 and hydrolysis time is 80 min).

2.3. Preparation of pretreated-MCC (PMCC) samples

0.5 g MCC was added into 25 ml deionized water, and then it was stirred at 2000 rpm for 10 min to prepare MCC water suspension solution. The suspension solution was then pretreated by DBD plasma immediately. Then the pretreated suspension solution was filtered and washed three times with deionized water; the filter residue was dried at 50°C for 24 h.

2.4. Analytical methodology

2.4.1. (3,5-dinitrosalicylic acid) DNS determination method.

DNS determination method was used to detect total reducing sugar concentration (TRSC) in hydrolysis solution. 3,5-dinitrosalicylic acid solution reacted with reducing sugars and then 3-amino-5-nitro salicylic acid would be generated in alkali solution. The concentration of reducing sugars in hydrolysis solution was quantitatively detected using colorimeter at 532 nm.

2.4.2. Liquefaction yield (LY) of MCC/PMCC calculation.

Liquefaction yield (LY) of MCC/PMCC was calculated using the following equation:

$$LY = \frac{\text{raw cellulose(g)} - \text{residue(g)}}{\text{raw cellulose(g)}} \times 100\%. \quad (1)$$

LY of MCC/PMCC was calculated after MCC or PMCC sample was hydrolyzed under optimal hydrolysis conditions.

2.4.3. Determination of degree of polymerization (DP)

2.4.3.1. Sample preparing. MCC/PMCC solutions were prepared according FZ/T 50010. 3-2011 [28]. Certain MCC/PMCC was dissolved in copper ammonia solution. The copper ammonia solution was prepared as: copper sulphate (75 g) was dissolved into 500 ml deionized water. Then ammonia water was added into the copper sulphate solution until sediment ($\text{Cu}(\text{OH})_2$) completely formed. The sediment ($\text{Cu}(\text{OH})_2$) was separated and washed until no sulfate radical could be detected. Then, the sediment was dissolved in 600 ml ammonia water. In addition, 200 ml deionized water, 5.6 g sodium hydroxide and 1.6 g sucrose

were added into the solution. The copper ammonia solution was kept in brown bottle to avoid light.

2.4.3.2. Degree of polymerization (DP) calculation. Degree of polymerization (DP) of MCC/PMCC was calculated using the following equation [28]:

$$DP^{0.905} = 0.75\eta. \quad (2)$$

Here, η is intrinsic viscosity, which can be known based on relative viscosity η_0 according FZ/T 50010. 3-2011 [28]. And, η_0 can be calculated using the following equation [28]:

$$\eta_0 = h_n * t. \quad (3)$$

Here, η_0 is relative viscosity; h_n is viscometer constant, which is 0.863 in this paper; t is outflow time of the sample.

2.4.4. X-ray diffraction (XRD) analysis. X-ray diffraction (XRD) of MCC and PMCC samples were recorded with BRUKER (D2 PHASER) radiation ($\lambda = 0.1541$ nm) using a PANalytical Xpert Pro instrument at 25 °C with a silicium mono-crystal sample holder at step size of 0.017°. The intensity (Miller indices) as a function of 2θ was measured while the angle range was 5–40°. Crystallinity index (CI) was measured by the Segal method [29] using the height of I_{200} (characterizes both crystalline and amorphous material, $2\theta = 22.7^\circ$) and I_{am} (the minimum between the peaks at (200) and (110) represents only amorphous material $\sim 10^\circ$) as described below:

$$CI = \frac{I_{200} - I_{am}}{I_{200}} \times 100\%. \quad (4)$$

2.4.5. Fourier transforms infrared spectroscopy (FTIR) analysis. The group-variation of PMCC with DBD plasma pretreatment time was examined by FTIR. FTIR spectrum (4000–500 cm^{-1}) of sample was recorded by a Bruker Vertex 80 V FTIR vacuum spectrometer (Ettlingen, Germany) with a resolution of 2 cm^{-1} and 32 scans per sample. 2 mg of raw MCC or PMCC along with 200 mg of spectroscopic grade KBr was pressed to produce clear pellets. The background spectrum of KBr was subtracted from that of sample.

3. Results and discussion

3.1. Setup and optimization of dilute acid hydrolysis of MCC

A hydrolysis process of MCC in dilute acid solution was established and optimized. Firstly, different diluted acid solutions (H_2SO_4 , H_3PO_4 , and HNO_3) were evaluated. The effect of different acid solution (the concentration of hydrogen ion in the acid solutions was kept in constant) on the hydrolysis efficiency of MCC was investigated under moderate hydrolysis temperature of 160 °C. Experimental result showed that the highest hydrolysis efficiency of MCC was obtained in sulfuric acid solution with concentration 6% (w/w). Liquefaction yield (LY) of 48% was achieved when MCC was hydrolyzed under conditions: 100 min, 160 °C, 6%

Table 1. Result of orthogonal experiment ($L_9(3^4)$).

Entry	A (%)	B (min)	C (°C)	D (w/w)	TRSC (g/L)
E1	2	80	140	1:10	4.92
E2	2	100	160	1:15	5.86
E3	2	120	180	1:20	8.08
E4	4	80	160	1:20	4.52
E5	4	100	180	1:10	15.68
E6	4	120	140	1:15	4.72
E7	10	80	180	1:15	22.38
E8	10	100	140	1:20	6.92
E9	10	120	160	1:10	8.95

sulfuric acid solution. LY of MCC reached maximum value of 34% in those other dilute acid solutions under the same hydrolysis conditions as above.

Hydrolysis process of MCC in dilute sulfuric acid solution was further optimized in terms of the total reducing sugar concentration (TRSC) using an orthogonal experiment with respect to sulfuric acid concentration (A, w/w), hydrolysis time (B, min), hydrolysis temperature (C, °C) and solid-liquid ratio (D, w/w). DNS determination method was used to detect total reducing sugar concentration (TRSC) in hydrolysis solution. An orthogonal experiment of $L_9(3^4)$ was established in this part and the experimental results were shown in table 1. The highest TRSC of 22.38 g l^{-1} with a LY value of 68.6% was achieved in E7 in hydrolysis solution of MCC, indicating that the optimal conditions for MCC hydrolysis were obtained by sulfuric acid concentration of 10% (w/w), hydrolysis temperature of 180 °C, solid-liquid ratio of 1:15 and hydrolysis time of 80 min. The variation of TRSC in hydrolysis solution with hydrolysis time was also intensively studied. TRSC of MCC in hydrolysis solution was determined with hydrolysis time of 80 min, 100 min, 120 min, 140 min, 160 min and 180 min under the optimal hydrolysis conditions (sulfuric acid concentration 10%(w/w); hydrolysis temperature 180 °C; solid-liquid ratio 1:15), in which the results were shown in figure 2(a). TRSC in hydrolysis solution firstly increased, then decreased with increasing pretreatment time, and the highest TRSC of 34.68 g l^{-1} was achieved with a pretreatment time of 140 min, suggesting that the reducing sugar released in hydrolysis solution was further polymerized when the hydrolysis time further increased from 140 min to 180 min. The variation of LY of MCC with hydrolysis time was also determined and the result was shown in figure 2(b). LY of MCC also firstly increased then decreased when MCC was hydrolyzed over 140 min, which was due to the polymerization reaction of the reducing sugar released in solution. The polymerization reactions occurred intensively when MCC was hydrolyzed beyond 140 min, which leads to the formation of new insoluble fractions.

3.2. Pretreatment of MCC by DBD plasma

The MCC water suspension solution was prepared and then pretreated by DBD plasma immediately for 10 min, 20 min, 30 min, 40 min and 50 min, respectively under carrier gas of

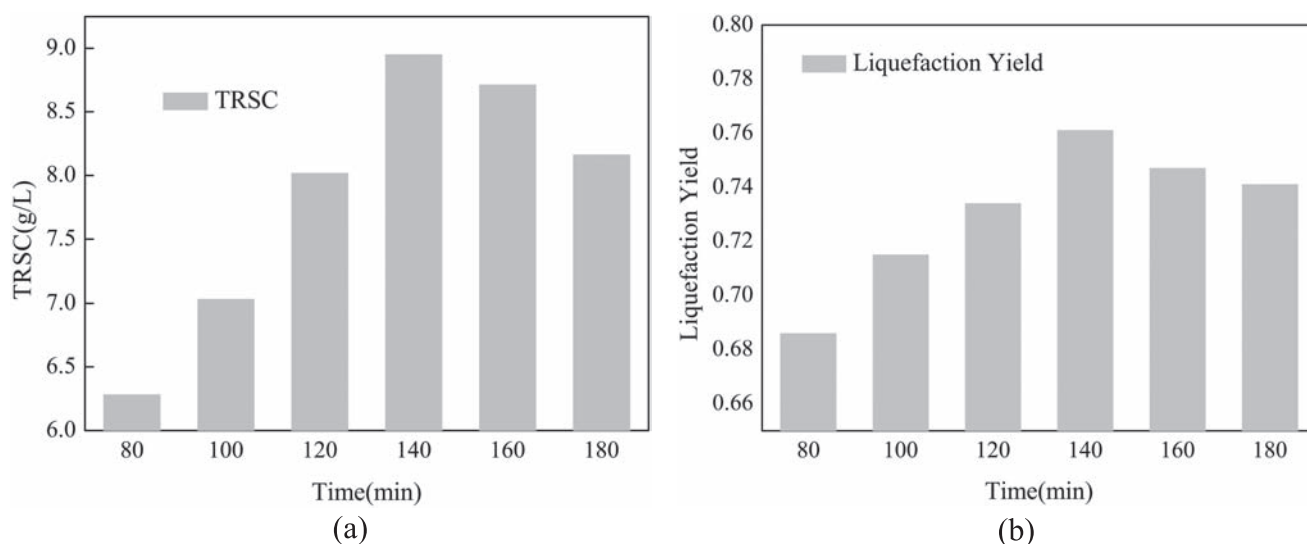


Figure 2. (a) Variation of the TRSC with pretreatment time. (b) Variation of liquefaction yield with pretreatment time.

Table 2. Variation of degree of polymerization with pretreatment time.

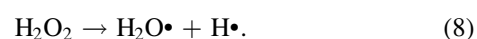
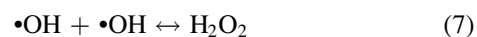
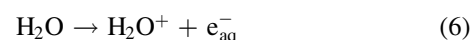
DBD time (min)	Degree of polymerization (DP)	
	MCC-1	MCC-2
0	215	215
10	209	201
20	188	166
30	131	101
40	112	87
50	105	78

air, alternation waveform of voltage of 22.0 ± 0.5 kV and frequency of 15.0 ± 0.5 kHz. Besides, MCC with different crystallinity (MCC-1, 82.8%; MCC-2, 57.4%) was used to analyze the effectiveness of crystallinity on MCC pretreatment. Degree of polymerization (DP) of raw MCC or pretreated-MCC (PMCC) was determined and calculated by equation (2) according to FZ/T 50010 [28], and the result was shown in table 2. DP of MCC-1 and MCC-2 decreased with increasing DBD plasma pretreatment time. In addition, DP of MCC-2 with low crystallinity decreased more sharply than that of MCC-1 with high crystallinity, as can be evidenced by the fact that DP of MCC-1 and MCC-2 dropped from 215 to 105 and 78 respectively when it was pretreated by DBD plasma for 50 min. It could result from the reason that DBD plasma pretreatment exhibited stronger performance of depolymerization on amorphous domain of MCC than crystalline region [30].

When air was used as carrier gas in DBD plasma pretreatment process, nitrogen oxides were generated by activation of air in discharge space, which was suggested to play an important role for depolymerization effectiveness of MCC [30]. In order to further investigate on the pretreatment mechanism, argon was used as carrier gas in DBD process for pretreatment of MCC (with an alternation waveform of voltage at 19.5 ± 0.5 kV and frequency at 15 ± 0.5 kHz). DP

of MCC-1 (CI = 82.8%) and MCC-2 decreased from 215 to 107 and 80 respectively when it was pretreated for 50 min under argon atmosphere, illustrating that depolymerization effectiveness of MCC still existed when argon was used.

The depolymerization mechanism of MCC in DBD plasma pretreatment can be summarized in equations (5)–(8). Lots of radical species (hydroxyl radical, hydrogen peroxide, hydrated electron, etc) are generated in treated MCC water suspension solution via activation of water in DBD process [31, 32]:



It was conventionally considered that MCC was presumably depolymerized via these radical species. In order to verify this hypothesis, tert-butyl alcohol (4%, w/w) was added into the MCC water suspension solution as scavenger of radical species, and DP of pretreated MCC in MCC water suspension solution with tert-butyl alcohol was determined. DP of MCC-1 (CI = 82.8%) and MCC-2 (CI = 57.4%) decreased from 215 to 175 and 135 respectively when it was pretreated for 50 min, indicating that depolymerization effectiveness of MCC was inhibited with addition of tert-butyl alcohol, which supported the hypothesis above. It could be concluded that radical species, such as hydroxyl radical, hydrogen peroxide, etc, which were generated from activation of water in DBD process, played an important role for depolymerization effectiveness of MCC. It was suggested that with the attacking of the radical species, the intramolecular and intermolecular O–H bonds in MCC molecules were destroyed. And β -1,4-glycosidic bonds between two anhydroglucose would also be cleaved by the constant attacking of the radical species, which resulted at the depolymerization of MCC.

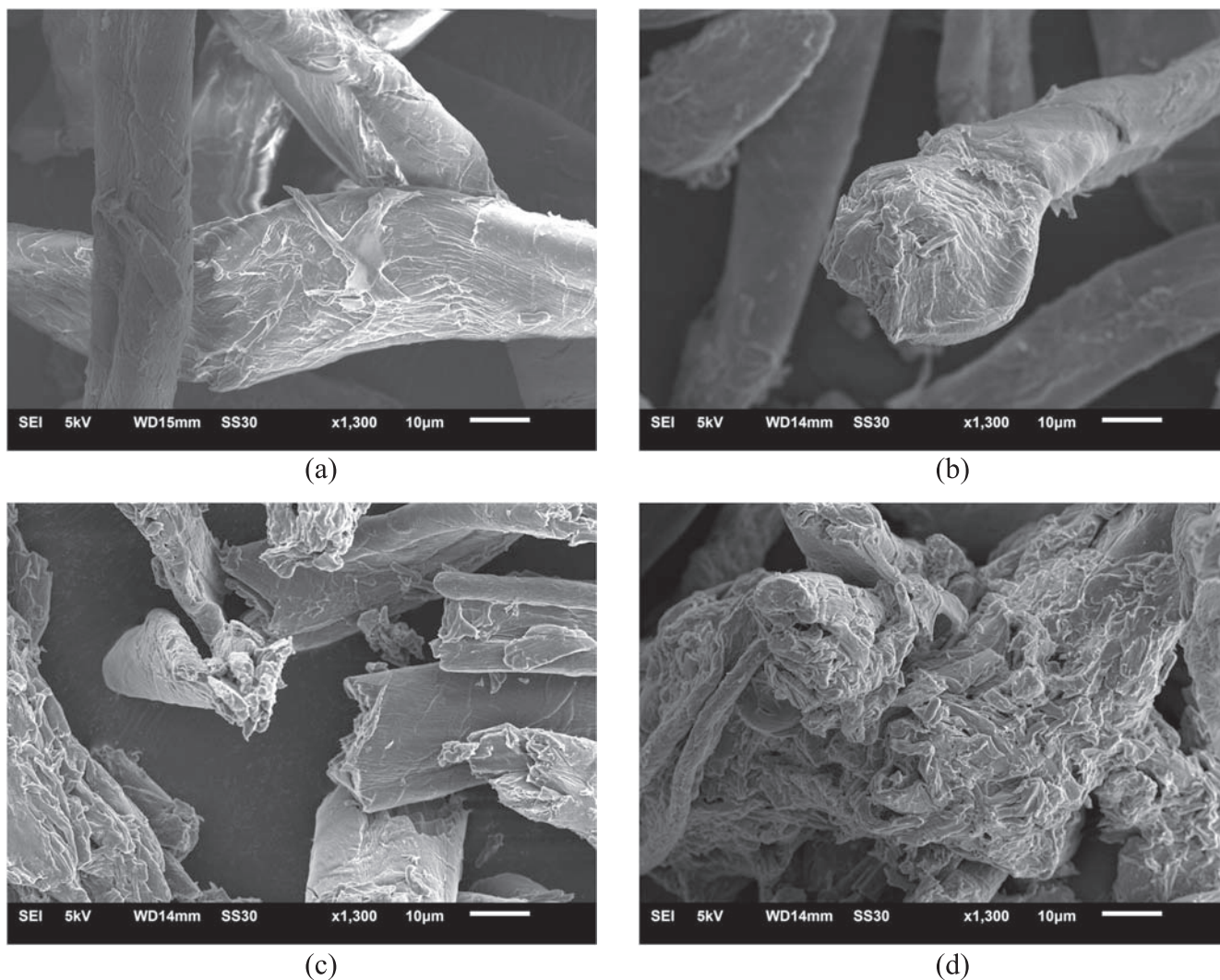


Figure 3. SEM images of MCC and PMCC for 10 min, 30 min and 50 min ((a), (b), (c) and (d) are for raw MCC, 10 min PMCC, 30 min PMCC and 50 min PMCC, respectively)

3.3. Characterization of PMCC samples

Physical appearance variation of PMCC with DBD plasma pretreatment time was characterized by SEM. Figure 3 showed that Raw MCC exhibited a long strip and smooth surface, while 30 min PMCC exhibited short strip with some cut sections. The MCC fibrils' length was shortened by 30 min PMCC when comparing with raw MCC, even though it was difficult to measure. In addition, porous loose structure could be discovered from 50 min PMCC proving that the performance of DBD plasma pretreatment on physical appearance of PMCC.

Figure 4 showed the peak absorption of 3345 cm^{-1} (A_{3345}) decreased with increasing DBD plasma pretreatment time, indicating that the intramolecular and intermolecular O-H bonds of MCC were partly broken during DBD plasma pretreatment process. Peak of 2900 cm^{-1} (A_{2900}) is attributed to the stretching vibration of C-H bonds in MCC molecules [33]. K value ($K = A_{3345}/A_{2900}$ (A_{3345} : absorbance of peak 3345 cm^{-1} ; A_{2900} : absorbance of peak 2900 cm^{-1})) [34] of MCC decreased, confirming that the number of O-H bonds in

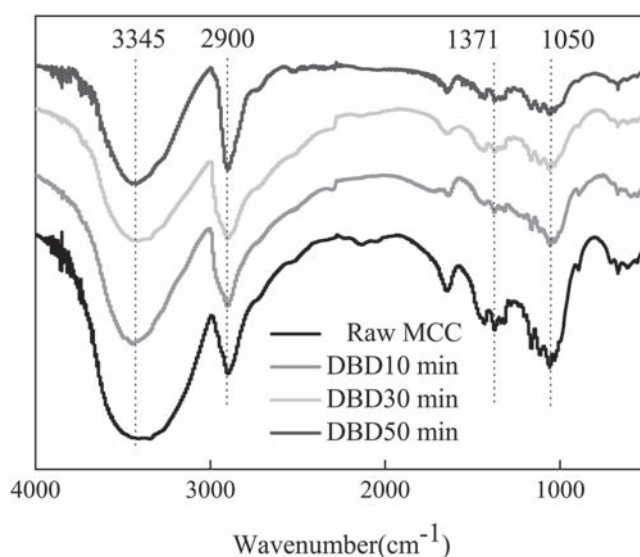


Figure 4. FTIR determination results of MCC and PMCC for 10 min, 30 min and 50 min.

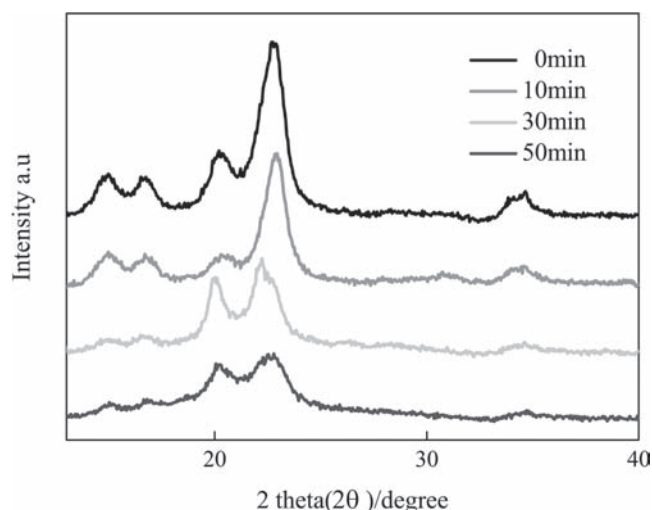


Figure 5. X-ray diffraction pattern of the pretreated MCC (0 min, 10 min, 30 min and 50 min).

Table 3. CI of MCC-1 pretreated by DBD plasma for 0 min, 10 min, 30 min and 50 min.

DBD time (min)	CI (%)
0	82.8
10	82.4
30	73.6
50	58.9

Table 4. Liquefaction yield (LY) and total reductive sugar concentration (TRSC) in hydrolysis solution of PMCC.

DBD time (min)	Liquefaction Yield (%)	TRSC/(g/L)
0	68.60	22.38
10	76.57	29.68
20	87.89	35.73
30	92.05	40.95
40	92.89	41.18
50	93.98	41.75

MCC molecules decreased after pretreatment by DBD plasma. The decreasing of intramolecular and intermolecular O–H bonds in MCC molecules would result in a decreasing of crystallinity-index (CI) of MCC.

Figure 5 showed the XRD characterization. CI of MCC-1 was calculated using equation (4) and the result was listed in table 3, CI of MCC-1 dropped from 82.8% to 82.4%, 73.6% and 58.9% when it was pretreated by DBD plasma for 10 min, 30 min and 50 min, respectively. This result also proved that the intramolecular and intermolecular O–H bonds in MCC molecules were destroyed in DBD plasma pretreatment process.

3.4. Hydrolysis of PMCC

The calculation result of LY of PMCC and TRSC in hydrolysis solution was listed in table 4. Both LY of PMCC and

TRSC in hydrolysis solution increased when DBD plasma pretreatment time increased from 0 min to 50 min. Both LY of PMCC and TRSC shown slower increasing rate in the pretreatment time range of 30–50 min when comparing with the situation in the first 30 min pretreatment time LY of PMCC for 30 min and TRSC in hydrolysis solution for 30 min. PMCC increased by 34.18% and 82.98% respectively when comparing to that for raw MCC, which was probably due to the decreasing rate of DP of PMCC, as mentioned in table 2.

4. Conclusion

Degree of polymerization (DP) of MCC decreased when MCC was pretreated by DBD plasma. DP of MCC decreased almost at the same level after it was pretreated by DBD plasma when air or argon was used as carrier gas, showing that carrier gas would not significantly affect the depolymerization of MCC. When MCC was pretreated by DBD plasma for 30 min, total reducing sugar concentration (TRSC) in hydrolysis solution increased by 82.98% compared to that for raw MCC. Depolymerization effectiveness of MCC was inhibited with addition of tert-butyl alcohol, showing that radical species generated from activation of water in DBD process, played an important role for depolymerization effectiveness of MCC. With the attacking of the radical species, the intramolecular and intermolecular O–H bonds in MCC molecules were destroyed. And β -1,4-glycosidic bonds between two anhydroglucose would also be cleaved by the constant attacking of the radical species, which resulted at the depolymerization of MCC.

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