Evolution of Waster Cotton Fiber Hydro-Char Physicochemical Structure during Hydrothermal Carbonation

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Abstract: In order to study the hydrothermal behavior of cotton fiber, the carbonization process and structural evolution of discarded cotton fiber (WCF) under hydrothermal conditions were discussed use microcrystalline cellulose (MCC) and glucose as model compounds. The results showed that high temperature was beneficial to the hydrolysis of discarded cotton fiber, and the yield of the sugar was 4.5% which was lower than that of MCC 6.51%. WFC and MCC are carbonized in 240~260 ℃ and 220~240 ℃ respectively, while the carbonation temperature of glucose is lower than 220 ℃. The quality ratio of C/O in WCF and glucose hydrothermal products is 5.79 and 5.85 respectively; three kinds of hydrothermal carbonization products have similar crystal structure and oxygen-containing functional groups, and the WCF carbonization products contain a lot of irregular particles while the main products of glucose carbonization are 0.5 μm carbon microspheres (CMCC). The results show that glucose is an important intermediate product of WCF hydrolysis carbonation, and there are two main paths of cotton fiber hydrothermal carbonization: some cotton fibers are completely hydrolyzed into glucose and the nucleation is formed, and then the carbon microspheres are grown; for the other part, the glucose ring of the polysaccharide oligosaccharide formed by the incomplete hydrolysis of cotton fiber in the hydrothermal environment of high temperature and pressure breaks, then forms the particulate matters.

Keywords: waste cotton fibers; recycling; carbon microsphere; physicochemical characteristics

1 Introduction

Cotton is one of the most important textile fiber. The global average amount of waste cotton textiles was up to 24 million tons, whereas the comprehensive utilization of it is less than 1% [1], which lead to serious resources waste and environmental pollution. The wearability of cotton fabrics will decrease with the extension of time, so it is difficult for the waste cotton fiber to be used for textile fiber again. In addition, cotton contains the highest percentage of cellulose among various biological materials. Hydrothermal carbonization is a new treatment technology of biological material, using water as reaction solvent to convert biomass materials into a series of high value-added products in subcritical water (temperature 180~350 ℃, pressure 2~20MPa) [2][3]. This technology can be apply in micro/nano carbon materials、pollutants adsorption removal and battery electrode. The technology has no requirement on mechanical properties of fiber and provides a new way for high value reuse of waste cotton.

Now researchers have successfully using hydrothermal method to convert biomass materials such as glucose [4]、sugar [5] and starch [6] into carbon microspheres(CMSs), and proposed LaMer [7] growth model of carbon microspheres. However, compared with oligosaccharide, cotton has more complex chemical structure and composition, making it difficult to degrade into microspheres under hydrothermal conditions. In order to promote carbonization of cotton and prepare CMSs, the first procedure is to figure out the carbonization process and microstructure evolution of waste cotton fiber under hydrothermal conditions. For the purpose of reducing the uncertainty factors of research, modeling cotton fiber is necessary. Microcrystalline cellulose is straight-chain polysaccharides that consist of β-(1-4)-linked glucose repeating unit, whose chemical structure is similar with the cell wall of cotton fiber. As a degradation product of cellulose, microcrystalline cellulose can be regarded as pure when compared with cotton fiber. The polymerization degree is only about 220, which is far below cotton cellulose in the secondary wall whose polymerization degree is 13000-15000. In addition, glucose is the most representative model of compounds among biomass, and the most important intermediate in the process of hydrothermal carbonization [8][9]. Researches on hydrothermal carbonization of glucose can helps to figure out the carbonation process of cotton fiber. Therefore, this paper will study on the carbonation process and mechanism of cotton fiber by means of modeling compounds under hydrothermal conditions.

2 Experimental

2.1 Experiment materials and equipments

Waste cotton fabrics were obtained from Graafland textile Co. Ltd. (Shanxi, China); microcrystalline cellulose, glucose and ethanol (chemicals are pure) were purchased Tianjin science and technology development co., Ltd. (Tianjin, China). The main reactor is autoclave, purchased from Runchang petrochemical equipment co. Ltd. (Dalian China), 1000mL, whose maximum operating temperature and pressure is 42 MPa and 500 ℃ respectively.

2.2 Experiment process

Deionized water (600 mL) was added into a beaker containing 12 g of dextrose, microcrystalline cellulose, and the faded scrap of cotton fabric after washing debris. The mixture was stirred for at 400 r/min for 30 min at room temperature until it dissolved or dispersed in water. Then, the mixture poured into the autoclave whose reactor fill is 60%. The mixture was left to react at the 200~280 °C for a certain time and then cooled to room temperature. The resulting solids were washed, filtrated off and dried under a vacuum at 120 °C for 4 h.

2.3 Materials characterization

Field-emission scanning electron microscopy (FESEM; JSM-6700F, JEOL, Tokyo, Japan) was used to examine the morphologies of the different samples. The chemical structures of the samples were examined by X-ray photoelectron spectroscopy (XPS) measurements recorded on a PHI5700 spectrometer (Physical Electronics, Chanhassen, MN, USA) using an Al Kr radiation (hv = 1486.6 eV). Fourier transformation infrared (FT-IR) spectra were recorded using a Tensor 27 spectrometer (Bruker) in the infrared domain between 4000 cm^{-1}1and 500 cm^{-1} at a resolution of 4 cm^{-1}. The content of C and H elements in samples were performed on the Vario Micro cube element Analyzer produced by Germany ELEMENTAR; The samples surface chemical structure was measured by VG Multilab 2000 X-Ray Photoelectron spectrometer; The liquid phase of product was examined by HPLC (PerkinElmer, USA); Refraction Differential Detector (RID) measurements recorded on SH1011 spectrum analysis column.

3 Results and discussion

3.1 Analysis of three materials' decomposition in subcritical water

Analysis of HPLC shows that the main product of cotton and microcrystalline cellulose is glucose under hydrosis condition. Figure 1(a) are the yields of glucose hydrolyzed from cotton fiber under different temperatures. It shows that high temperature is benefit to the hydrolysis of cotton. An important phenomenon was observed that the yield of glucose reached maximum to about 4.5% at 240 ℃ after 2.5 h while its original level does not exceed 0.05% does not exceed 0.05%, and then decreased continuously to a much lower and turn to zero at 260 ℃, 1.5 h. While the temperature is 280 ℃, no glucose can be detected in liquid products. Figure 1b is the yields of glucose hydrolyzed from microcrystalline cellulose under different temperatures. The highest yield is observed to 7.87% under 220 ℃, 1.5 h while 4.6% can be obtained at 200 ℃, 2.5 h. When the temperature increased to 260 ℃, there is no glucose can be detected in the product.

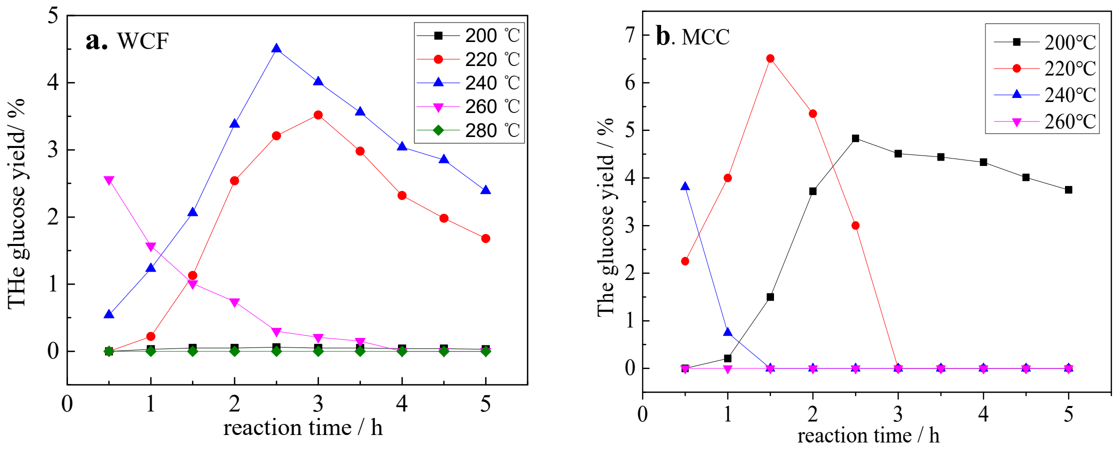

Fig.1 Glucose yield curve of WCF and MCC hydrolysis

Fig.1 The glucose yield curves of waste cotton fiber and microcrystalline cellulose hydrolysis

In subcritical water, the diffusion coefficients and dynamic viscosity of the water are increased with the increasing of Ion-product constant. It provides a contrary circumstance for hydrothermal hydrolysis and conversion of cellulose. The water not only as a reaction medium but as a reactant to accelerate the decomposition of cellulose, and the main product is glucose [10]. In General, the trends of cotton and cellulose hydrolysis to glucose are similar, whereas the glucose easily decomposition in subcritical water, which reduced the yield as a whole. The research results show the speed of glucose decomposition rate is fast than cellulose hydrolysis rate [11]. Both of cotton and microcrystalline cellulose, the degradation pathways are cellulose-glucose-Glucose. It's worth noting that when the temperature is too high, some insoluble matters that formed by cellulose will package the glucose, hindering the hydrolysis of cellulose to oligosaccharides. In terms of the structure of cotton fiber, the encapsulation effect is more apparently. The reason is that cotton wrapped with a layer of wax, pectin and proteins. Wax is a hydrophobic barrier layer made up of lipids that covered in cotton fiber surface, maintenancing cleaning and water proofing of cellulose surface. Wax, pectin and protein have relatively stable structure which reduced the contact area of cotton cellulose and water and decreased the hydrolysis rate of glucose under low temperatures [12][13].

To further analyze the stability of glucose under hydrothermal conditions, the paper using the same testing method to study the residual rate of glucose in hydrothermal conditions. Results show that glucose under hydrothermal conditions is very unstable and the decomposition rates increased rapidly with the increasing of temperature. As shown in Figure 2, hydrolysis of glucose is 29.7% at 180 °C for 1 h while only 49.9% remained under 200 °C 1 h. With the extension of reaction time, glucose decomposed and the residual rate decreases; When the temperature is above 240 °C, glucose can be decomposed completely in 1 h and the residual rate close to 0%.

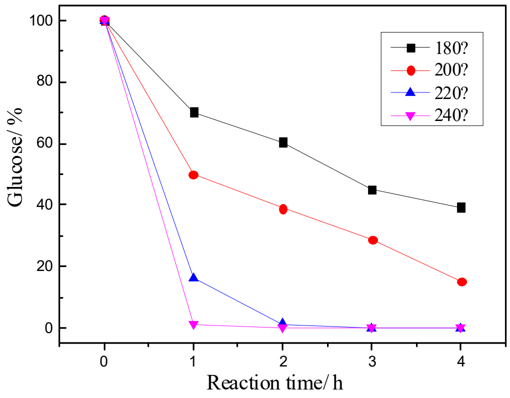

Fig.2 The residual curve of glucose hydrothermal decomposition

3.2 Elemental analysis of hydrothermal carbonation products

Fig 3 is element analysis of solid products, namely waste cotton fiber, microcrystalline cellulose and glucose under different temperature conditions (8 h). The figure shows that the carbon content of products rises as the water temperature increases. The carbon content of waste cotton fiber and microcrystalline cellulose hydrothermal carbonation products have a step type process which caused by the rapidly carbonization after the temperature is reached. The carbonization temperature of microcrystalline cellulose is 220°C~240 °C while the carbonization temperature of waste cotton fiber is 240~260 °C, which illustrates the carbonization temperature of cellulose is lower than waste cotton fiber. The C content of cotton fiber carbonized products is 75.46% when the reaction temperature is 280 °C. However, hydrothermal carbonation products of glucose have higher carbon content at the same temperature. At 240 °C, C content of cotton fiber carbonized products is 78.52%. The C content of glucose also have a step type process between160~220 °C. This is because when the water temperature is below 180 °C, hydrothermal products contain a lot of intermolecular dehydration of glucose polymers. When the temperature exceeds 200 °C, the degree of hydrolysis of glucose molecules significantly increased and the products are mainly formed by the polymerization of small molecules, causing the extent of carbonation increases apparently. The C content of products has a reducing trend at 260 °C. This is because high temperature causes decomposition of products. In addition, the C content of three materials' products are far lower than ordinary activated carbon (about 90%) [14][15] while the O content are more, which shows that there is an abundance of oxygen groups in the surface of the hydrothermal carbonation products.

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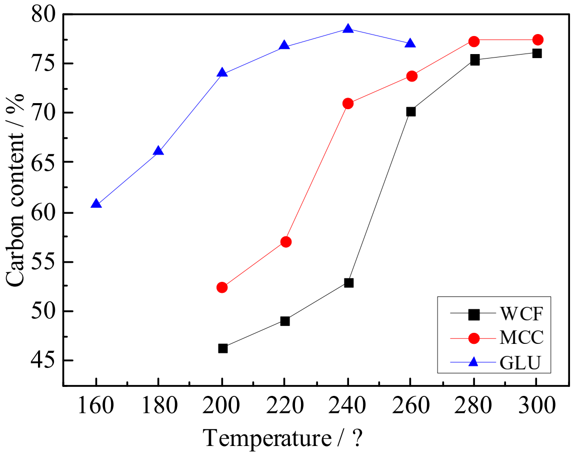
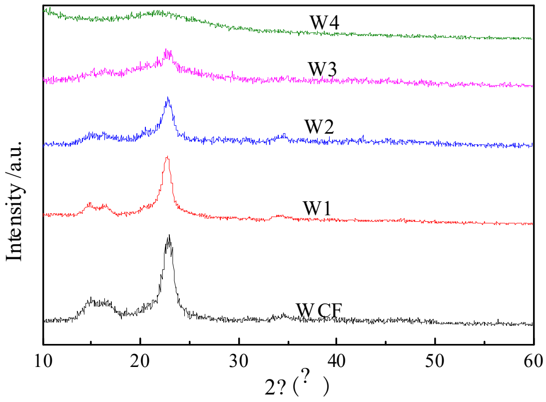


Fig.3 The elemental analysis of carbonized products of three substances in different temperature

3.3 The crystal structure analysis of hydrothermal carbonization products



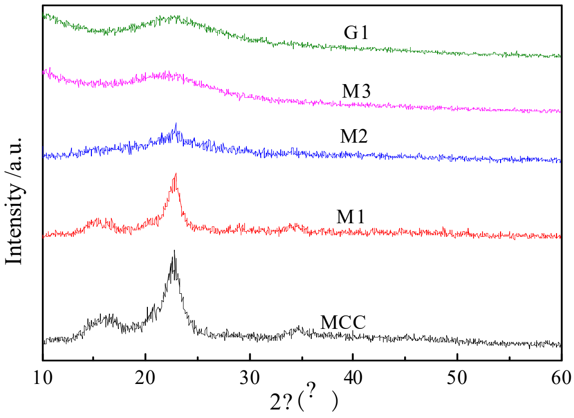


Fig.4 The XRD patterns of hydrothermal products in insulation 8 h

W1: WCF 200 ℃; W2: WCF 220 ℃; W3: WCF 240 ℃; W4: WCF 260 ℃;

M1: MCC 200 ℃; M2: MCC 220 ℃; M3: MCC 240 ℃; G1: Glucose 200 ℃;

Fig. 4 is the XRD spectra of products of cotton fiber, microcrystalline cellulose and glucose. The chart shows that cellulose and cotton fiber have the same crystal structure. With the increase of temperature, both of carbonized products show the transformation trends of crystalline into amorphous. The characteristic peaks of cellulose I can't be found at 220 ℃ and 240 ℃, which illustrates that the gradually increased water temperature can lead to the destroy of crystal structure of cotton fiber and cellulose. Comparing with microcrystalline cellulose, cotton fiber completely carbonized occurs at high temperature, and both of the carbonized products have a similar crystal structure, which exist a large crystal surface at $2\theta=22.7°$ (crystal surface index is 002). This surface is the diffraction peak of aromatic carbon layer structure, which illustrates that there is a highly disordered structure in the products and the degree of graphitization is very low. The reasons for the high carbonization temperature of cotton fiber are that the strong hydrogen bonds and stable glycosidic linkage make the cotton cellulose-macromolecule very stable [16]. When the water temperature is below 250 ℃, cellulose hydrolysis occurs mainly in the surface, thus generating the cellobiose and glucose.

3.4 The morphologies and structure analysis of hydrothermal carbonization products

Fig. 5 shows SEM images of carbonized products of cotton fiber, microcrystalline cellulose and glucose (8 h). In terms of cotton fiber, fibrous structure can still be observed in products when the reaction temperature is below 240 ℃. If the temperature continues to rise, fibrous structure will disappear, showing irregular granular particles with adhesion phenomena. At 280 ℃, there are some spherical products appearing, but the overall morphology of the products does not change. There are significant differences in hydrochars morphologies of microcrystalline cellulose and cotton fiber. Not only a quantitative of products in micro-crystalline form of the microcrystalline cellulose appeared at 200 ℃, but also already some spherical products appeared. Furthermore, as the water temperature increases, the spherical degree increases gradually. Most of the products' morphologies are spherical with uniform distribution (average 1.8μm) at 260 ℃. In terms of glucose, the morphology of products is mainly spherical with some adhesion phenomena at 180 ℃. What's more, with the increasing of the temperature, carbon microspheres appeared consistently, and the quality are better than microcrystalline cellulose's products. Carbon microspheres have uniform size with good dispersibility at 240 ℃ (average 0.5μm). Combining XRD analysis of cotton and cellulose hydrolysis carbonized products, we can see that glucose is an important intermediate product among the process of cotton fiber transform to carbonaceous microspheres. Only some of the cotton fiber molecular can hydrolyzed to glucose while microcrystalline cellulose hydrolysis rate is much higher under hydrothermal conditions. Based on this, we can speculate that cotton fiber do not react according to the trend 'cellulose → glucose → glucosede composition products', but cellulose-macromolecules of cotton fiber break irregularly and generate polysaccharides with certain molecular weight. These polysaccharides occurs dehydration reaction, making the products become irregular granular.

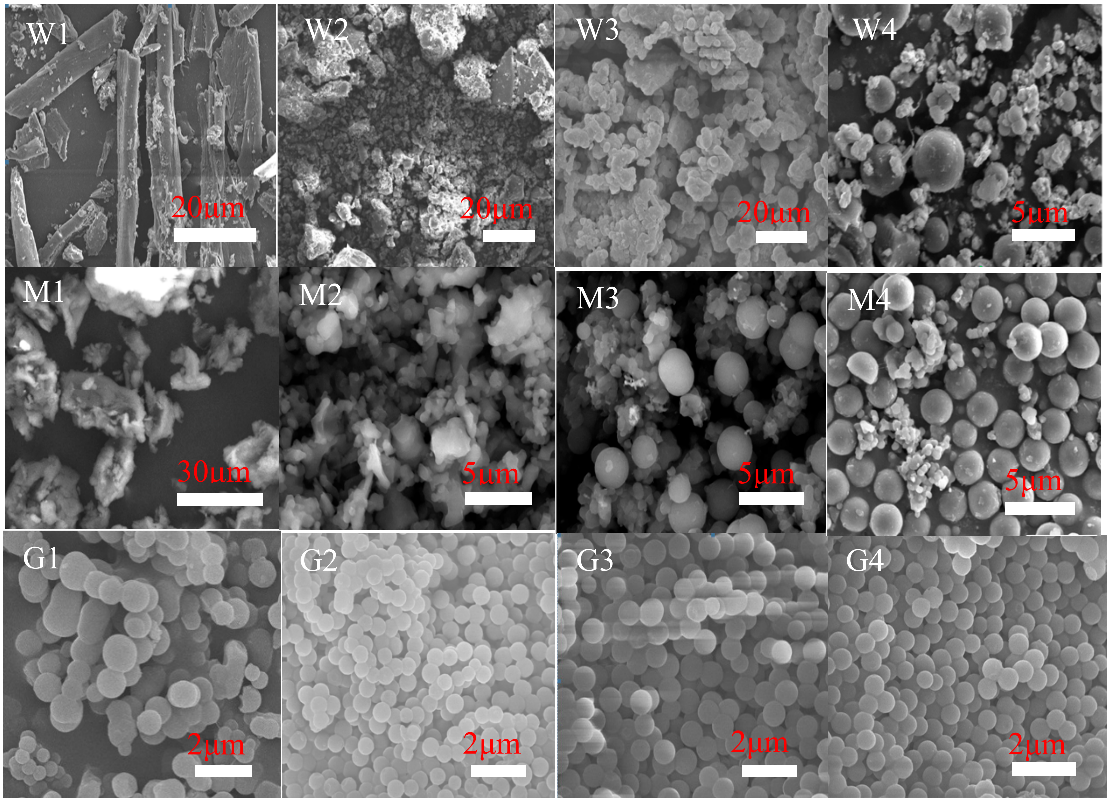


Fig.5 The SEM images of cotton fibers, microcrystalline cellulose and glucose carbonized products

W1: WFC 220 °C; W2: WFC 240 °C; W3: WFC 260 °C; W4: WFC 280 °C;

M1: MCC 200 °C; M2: MCC 220 °C; M3: MCC 240 °C; M3: MCC 260 °C;

G1: Glucose 180 °C; G1: Glucose 200 °C; G1: Glucose 220 °C; G1: Glucose 240 °C

3.5 Chemical characteristics of hydrothermal carbonization products

In order to further investigate the process of hydrothermal carbonization of cotton fiber, the chemical structure of the products and glucose are analyzed. Figure 6 is IR spectra of three kinds of carbonized products and glucose. As shown in the figure, three substances contain the same functional groups, which is similar to glucose [17]. In this chart, the bands at 3441cm^{-1} and 1023cm^{-1}assigned to –OH stretching vibration absorptions, the bands at 2923cm^{-1} attributed to C-H stretching vibration absorptions and the bands at 1299 cm^{-1}、1208 cm^{-1} assigned to C-O-C stretching vibration absorptions [18]. It should be noted that there have been some new characteristic peaks for these three substances. There are characteristic vibration peaks of benzene ring at 1509cm^{-1} and vibration absorption peak of C=C at 1614cm^{-1}. However, these characteristic peaks of glucose are strongest while it is the weakest for hydrothermal products of cotton fiber [19]. As to cotton fiber hydrothermal carbonization products, vibration absorption peaks of -C=O and symmetric stretching vibration absorption peaks of –COOH are stronger than the corresponding parts of glucose and microcrystalline cellulose at 2850 cm^{-1} and 1398 cm^{-1}. Infrared spectroscopy shows that cotton fiber, microcrystalline cellulose and glucose react for dehydration carbonization and aromatization in the process of hydrothermal degradation. SEM image analysis shows that three substances' carbonization paths and chemical reactions have overlap part in hydrothermal environment. That is some macromolecules of cotton fiber and microcrystalline cellulose hydrolyze into glucose monomers, and then the glucose dehydration and fragmentation reactions leading to the formation of hydrothermal carbonization products [20]. Besides, infrared spectra indicate that aromatization process should occur after the glucose decomposition. Therefore, the characteristic peaks of benzene ring in hydrothermal products of glucose are stronger and the degree of carbonation is higher. However, inter- and intra- molecular dehydration of cotton fiber in carbonization process is stronger, which results in higher content of -C=O and –COOR.

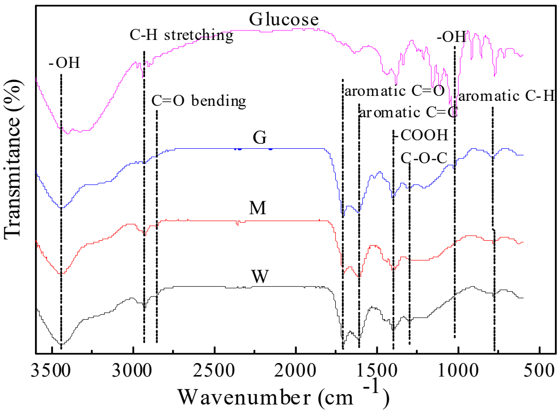


Fig.6 FT-IR patterns of glucose and carbonized products of three substances

G: Carbonized product of Glucose (240 °C); M: Carbonized product of MCC (260 °C);

W: Carbonized product of WCF (280 °C)

The oxygen-containing functional groups in hydrothermal products surface of cotton fiber and glucose were investigated by X-ray photoelectron spectroscopy. As shown in Figure 7, both of the products have the same kind of multi-peaks. In figure 7 (a, b), it contains four signals attributed, respectively, to the aliphatic/aromatic carbon group (R-C6H5) (284.5eV), Phenol, ethanol, and ether groups (-C-O) (285.2eV), carbonyl groups (-C=O) at (287.3eV) and carboxylic groups, esters and lactones (–COOH) (289.2eV). In addition, in figure 7b and 7d, three multi-peaks in XPS spectrum of O1s are respectively at 531.7eV、532.5eV and 533.5eV, which are the typical structure of carbonyl group (-C=O), hydroxyl group (C-OH) and ester group (C-O-C). Calculating the areas of multi-peaks of C1sandO1s, we can conclude that the C/O mass ratios in the surface of hydrochars are 5.79 and 5.85 [21], which indicates that the carbonation degree of glucose is higher than cotton fiber. The peak area of R-C6H5 in carbonized products of glucose is larger while the peak area of-C=O and –COOH is bigger in cotton fiber hydrothermal carbonization products, indicating that carbonation process of cotton fiber and glucose are different. In the hydrolysis stage, with complex chemical structure, cotton fiber cannot hydrolyze completely, but molecular chain will break. Large molecules occur inter- and intra- molecular dehydration reaction under hydrothermal conditions, making oxygen-containing functional groups become more in the products which reduced carbonization degree. Glucose under-go fragmentation and carbonize into microspheres by intermolecular dehydration and aromatic condensation. This analysis can also verify the above speculation of SEM image analysis.

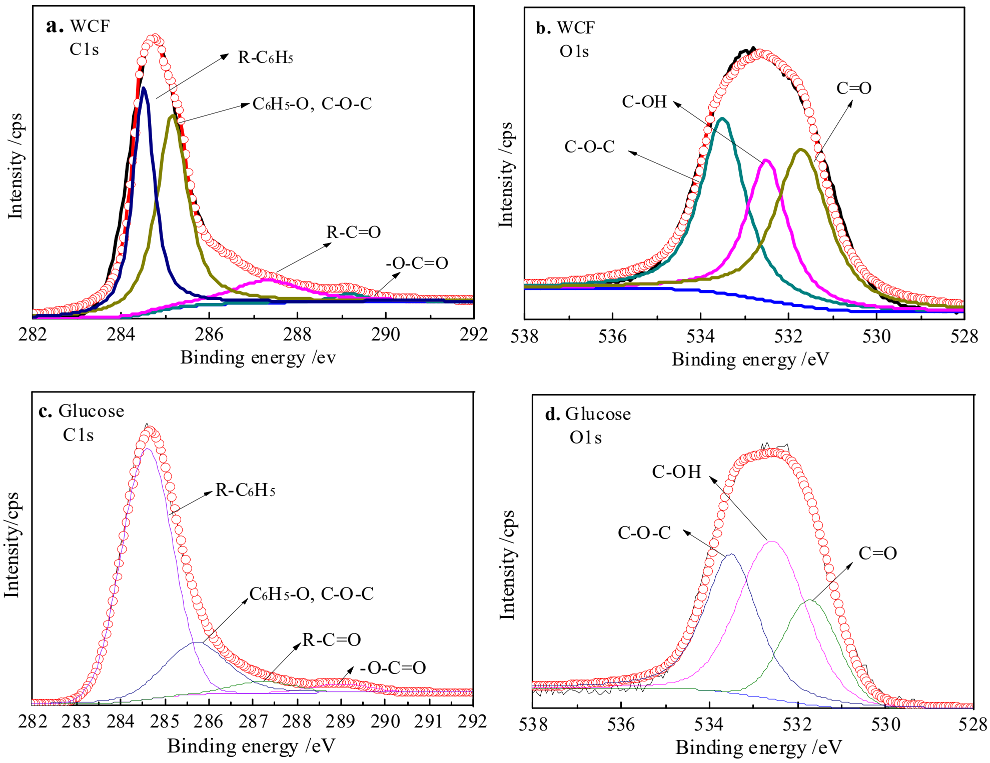
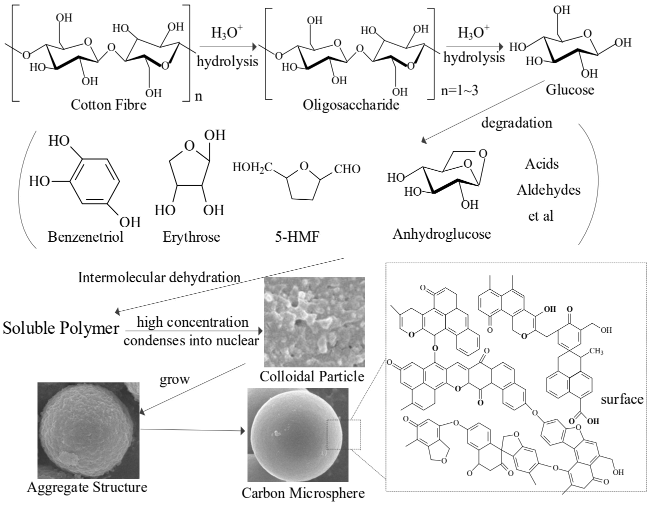


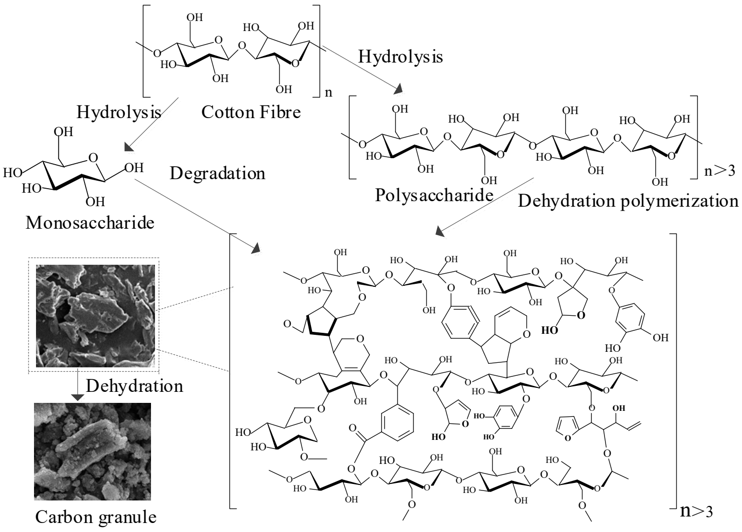
Fig.7 The XPS spectra of carbonized products of WCF (280 °C) and Glucose (240 °C)

3.6 The formation and mechanism of hydrothermal carbonization products from cotton fiber

Through previous research [22][23] and experimental analysis, we can see that there are two paths in cotton fiber's carbonation (Fig.8). First, the hydronium ions generated by water attack glycosidic linkage of cotton cellulose macromolecule, making the hydrolysis of cotton. But due to the stability of cotton fiber structure and limited hydronium ions, only some cotton can give rise to monosaccharides, other parts of the chain form oligomers [24][25]. Monosaccharides and oligomers reacted along different paths: (i) Glucose splitting into four-carbon sugar, phloroglucinol, furan, organic acids, aldehydes and so on [26][27]. These substances formed soluble polymer by intermolecular dehydration and aromatization. Some hydroxyl groups of monomer molecules occur dehydration to form C=O, while other molecules form C=C through the enoltautomeric or intramolecular dehydration. Subsequently, aromatic clusters may be produced by the condensation reaction of the aromatized molecules. When the concentration of aromatic clusters in the aqueous solution reaches the critical supersaturation point, a burst nucleation takes place. The nuclear so formed grow outwards by diffusion towards the surface of the chemical species present in the solution. (ii) Oligomers formed by cotton hydrolysis cannot further hydrolysis. The ring of glucose breaks under high temperature and pressure hydrothermal environment which under-go intra-/inter- molecular dehydration and fragmentation reactions, leading to the increase of carbon content. The main products are organic matters which are insoluble in water. After the reaction, the morphologies of hydrothermal carbonization products are irregular and bonding of particles.



(a) WCF carbonization path (i)



(b) WCF carbonization path (ii)

Fig.8 The mechanism diagram of WCF hydrothermal carbonization paths

4. Conclusions

The carbonation process and structural characteristics of cotton under hydrothermal conditions was discussed use the waste cotton as the object and microcrystalline cellulose and glucose as the model compounds. Main conclusions can be conclued as following: cotton fiber can be carbonized into carbonaceous microspheres under hydrothermal treatment and the C content of the carbonation process and structural characteristics of cotton under hydrothermal conditions can up to 75.46%. The products of cotton fiber, cellulose and glucose have similar crystal structures and oxygen-containing functional groups. The carbonization reaction conditions of microcrystalline cellulose and glucose obviously lower than cotton fiber. Also, the products structure and performance are better than that of cotton fiber products. Glucose is an important intermediate as cotton fiber hydrolyzed into microspheres, which cracks easily under the condition of hydrothermal. Only part of cotton fiber can hydrolysis to glucose, leading to two different kinds of dehydrate carbonization paths. The main morphology of the carbonation process and structural characteristics of cotton under hydrothermal conditions is irregular particles. As the results of this study, lowering the pH value of reaction system may contribute to carbonize the cotton fiber into carbonaceous microspheres under hydrothermal conditions.

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Author Contributions: Shi Sheng and Hou Wensheng conceived and designed the experiments; Zhang Suying performed the experiments; Zhang Meiling and Yan Zhifeng analyzed the data and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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