Carbohydrate Polymers 79 (2010) 164–169

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

The dependence of pyrolysis behavior on the crystal state of cellulose

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ARTICLE INFO

Article history:
Received 12 June 2009
Received in revised form 18 July 2009
Accepted 20 July 2009
Available online 24 July 2009

Keywords:
Cellulose
Crystal form
Pyrolysis
Ionic liquid
Regeneration

ABSTRACT

Cellulose was dissolved in the ionic liquid 1-butyl-3-methylimidazolium chloride, and then regenerated from the solution by using different methods. Thermogravimetric analysis (TG)-Differential Scanning Calorimetry (DSC), X-ray diffraction (XRD), and Scanning Electron Microscopy (SEM) were used to characterize the structure of the original and regenerated cellulose. Cellulose II or amorphous cellulose was obtained by pouring cellulose solution into de-ioned water or pouring de-ioned water into cellulose solution, respectively. The pyrolysis behavior of original and regenerated cellulose was tested in a fixed bed reactor. The pyrolysis of cellulose I gave high content of furfural and 1,4;3,6-dianhydro-alpha-D-glucopyranose in the liquid products, and cellulose II and amorphous cellulose gave high content of furfural and 5-(hydroxymethyl)-2-furancarboxyaldehyde, with 5-(hydroxymethyl)-2-furancarboxyaldehyde the highest for cellulose II and furfural the highest for amorphous cellulose. And the treatment of the cellulose samples favored the removal of oxygen in the form of CO_2 in the pyrolysis.

1. Introduction

The efficient utilization of biomass as a source of clean energy and chemicals has attracted much research attentions in recent years amid to fossil fuel energy crisis as well as clean energy drive (Aho et al., 2008). Since cellulose is the most abundant, inexpensive, and bio-renewable material in the world, the conversion of cellulose into synthetic fuels and useful chemicals has attracted increasing attentions (Baratieri, Baggio, Fiori, & Grigiante, 2008). However, due to the formation of hydrogen-bond in polydisperse linear glucose polymer chains, cellulose is insoluble in most conventional solvents and makes the thermal conversion of cellulose more difficult.

Pretreatments of cellulose have been investigated in many recent studies, acid and base pretreatment are the generally used method (Yang & Wyman, 2008). Pretreatments could sometimes make the material easier be handled in the subsequent processing steps. Recently, imidazolium ionic liquids (ILs), which were famous for many attractive properties, such as chemical and thermal stability, non-flammability and immeasurably low vapor pressure, had been found having strong abilities of destroying the chain structure of cellulose (Remsing, Swatloski, Rogers, & Moyna, 2006). It is found that biomass can be converted to useful chemicals by biological or thermo-chemical processes like gasification or pyrolytic liquefaction (Engelen, Zhang, Draelants, & Baron, 2003). Pyrolysis is an effective approach to obtain versatile chemicals from biomass. ILs pretreatment offers a potential approach to change the structures and properties of cellulose to facilitate the pyrolysis of cellulose into value-added products more efficiently.

Cellulose can be precipitated from ILs solution with the addition of water (Swatloski, Spear, Holbrey, & Rogers, 2002). The properties of regenerated cellulose were studied by many researchers (Kilpeläinen et al., 2007; Kuo & Lee, 2009; Laus et al., 2005; Zhai, Chen, & Ma, 2007). Two kinds of crystal form of the regenerated cellulose were reported, that is cellulose II and amorphous cellulose.

At present, most researches about the cellulose regenerated from ionic liquids focus on its properties, to our knowledge, there is no report on the pyrolysis of the regenerated cellulose from ILs.

In present work, 1-butyl-3-methylimidazolium chloride (BmimCl) is used as solvent for cellulose dissolution, and the influence of different precipitation conditions on the structure and physico-chemical properties of regenerated cellulose is investigated, furthermore the pyrolysis behaviors of the three kinds of cellulose are discussed.

2. Experimental

2.1. Materials

The reagent 1-methylimidazole was purchased from Linhai Kaile Chemical Plants (Zhejiang, China), and was distilled before use. 1-Chlorobutane was purchased from Kelong Chemical Reagent Plants (Sichuan, China), and used as received. The cellulose sample used in this study was microcrystalline cellulose (MCC), AR.

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doi:10.1016/j.carbpol.2009.07.038

2.2. Synthesis of BmimCl ionic liquid

The room temperature ionic liquid BmimCl was synthesized according to literature (Gutowski et al., 2003). 1-Methylimidazole and 1-chlorobutane at a molar ratio of 1:1.3 were added to a round-bottom flask fitted with a reflux condenser, and the reaction was carried out for 72 h at 75 °C with magnetic stirring. The product, a colorless liquid, was cooled to room temperature and washed with ether (25 ml × 3 times). Then the excessive ether was removed out by vacuum rotating.

2.3. Dissolution of cellulose

A mixture of microcrystalline cellulose (1.20 g) in BmimCl (20 g) was heated with mechanical stirring at 120 °C under atmospheric pressure for 3 h until a clear solution was formed.

2.4. Preparation of regenerated cellulose

Two regeneration methods were used for the preparation of regenerated celluloses, that is, the ILs was poured to de-ioned water at 45 °C with stirring, or threefold de-ioned water was poured to ILs mixture with stirring. The precipitants were washed with de-ioned water until no Cl^- was detected to obtain the regenerated samples, which were then dried at 100 °C to invariable weight before use. Regenerated samples prepared through the above processes were coded as RC-1 and RC-2, respectively.

2.5. Characterization of original and regenerated cellulose samples

2.5.1. X-ray diffraction method

XRD measurements were performed on a Philips X'Pert pro MPDX system. The diffracted intensity of Cu Ka radiation ($k = 0.1540$ nm; 40 kV and 25 mA) was measured over the 2θ range from 2° to 40°.

2.5.2. Thermal analysis

Thermogravimetric analysis (TG)-Differential Scanning Calorimetry (DSC) was performed with a SDT Q600 instrument in nitrogen flow with a rate of 100 mL min^{-1}. Al crucibles were used. The samples (~5 mg) were heated from 30 to 500 °C at the rate of 10 °C min^{-1}.

2.5.3. SEM analysis

SEM characterization was performed by using a FEI/PHILIPS Inspect F microscope, at an acceleration voltage of 10 kV and 10.4 mm working distance. Samples were coated with gold using a vacuum sputter-coater to improve the conductivity of the samples and thus the quality of the SEM images.

2.5.4. Degree of polymerization (DP)

The degree of polymerization of samples was determined by the viscosity method (see GB 5888–1986) at 25 ± 0.5 °C using an Ubbelohde capillary viscometer and cupriethylenediamine hydroxide (Cuen.) as the solvent.

2.6. Pyrolysis of MCC and regenerated cellulose

The pyrolysis of the samples was performed in a fixed bed reactor used in our previous work (Qi et al., 2006). Samples were heated from room temperature to 400 °C, and then kept for 1 h. The temperature ramp was 5 °C min^{-1} controlled with Temperature Control Specialists (SKW-1000). The volatile products were swept out by nitrogen at a flow rate of 28 mL min^{-1} and analyzed by packed column gas chromatography. The pyrolysis oil was collected in an ice trap and analyzed by gas chromatography-mass spectrometry (Agilent 5973N GC/MS: column: Innowax; inlet temp.: 250 °C; detector temp.: 250 °C; He Flow: 0.8 mL min^{-1}; mode: split). The pyrolysis of each sample was repeated for at least 3 times, and the error in the yields of liquid, gas and solid was within 0.5%. The GC analysis was also repeated for 3 times, and the error was within 0.3%.

3. Results and discussion

3.1. X-ray analysis

Cellulose is found in a number of variations, generally named cellulose I, II, III, IV (Isogai, Usuda, Kato, Uryu, & Atalla, 1989). Cellulose I is the crystal form of native cellulose (e.g., in paper). Cellulose II is generally formed in regenerated cellulose, e.g., rayon, or mercerized cellulose. The various types of cellulose have well-defined XRD patterns due to the crystalline nature of the cellulose molecules (Mansikkamäki, Lahtinen, & Rissanen, 2007; Takahashi & Matsunaga, 1991).

Fig. 1 shows the X-ray diffraction patterns of microcrystalline cellulose and RC-1, RC-2 from ILs solution. The crystalline parameters are listed in Table 1. The original cellulose displays a crystal structure of cellulose I with typical diffraction peaks for the plane (0 0 2) at $2\theta = 22.6$, (1 0 1) at $2\theta = 14.8°$ and (10$\bar{1}$) at $2\theta = 16.3°$ (Wong, Kasapis, & Tan, 2009). After dissolution and subsequent precipitation with precipitation reagent, the structure of the regenerated cellulose exhibits remarkably changes. The different sequences of introducing de-ioned water lead to different crystal forms of regenerated cellulose. RC-1 has the crystal form of cellulose II according to the three characteristic X-ray diffraction peaks at 11.7° for (101), 20.3° for (10$\bar{1}$) and 21.7° for the (0 0 2) plane, but RC-2 displays only a broad diffused diffraction peak around 2θ of 22.5° indicating an amorphous structure (Kuo & Lee, 2009). The crystalline degree of cellulose after regeneration, determined by Jade software, decreased from 62.9% for MCC to 46.2% for RC-1, and 13.0% for RC-2, as shown in Table 1.

These results indicate that the structure of cellulose is destroyed and the crystal form transformation mainly occurs during dissolution and precipitation process. RC-1 and RC-2 are obtained by the same precipitation reagent (de-ioned water), but different sequence of pouring water is applied. The difference in structure between RC-1 and RC-2 indicates that the sequence of pouring water in the precipitation process of cellulose is a key factor on the crystal form of regenerated cellulose. Zhai et al. (2007) obtained cellulose II by the preparation of regenerated cellulose film from BmimCl solution using a glass plate and then washing with

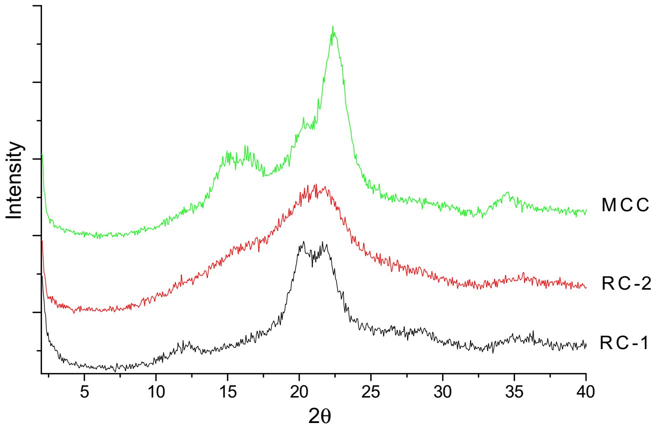

Fig. 1. X-ray diffraction patterns of microcrystalline cellulose and regenerated RC-1, RC-2.

Table 1
Crystalline parameters and DP of microcrystalline cellulose and regenerated RC-1, RC-2.

Samples	Crystallinity (%)	Major diffraction peak			DP
MCC	62.9	14.8°(1 0 1)	16.3°(10$\bar{1}$)	22.6°(002)	329
RC-1	46.2	11.7°(1 0 1)	20.3°(10$\bar{1}$)	21.7°(002)	317
RC-2	13.0	22.5°			299

The figures in parentheses indicate planes.

de-ioned water. Kilpeläinen et al. (2007) reported the preparation of amorphous cellulose under rapid mechanical stirring from BmimCl solution. The above data in our experiment indicate that the crystal form of cellulose as well as the crystalline degree is controllable by varying precipitation process. Cellulose II or amorphous cellulose can be obtained by simply pouring cellulose solution into precipitation reagent or pouring precipitation reagent into cellulose solution, respectively.

3.2. DSC-TG measurements

DSC-TG curves of the original cellulose, RC-1 and RC-2 are illustrated in Fig. 2. Table 2 shows the onset, endset temperatures and weight loss values determined from TG curves for MCC, RC-1 and RC-2, and the corresponding endothermic peak and the enthalpy from DSC curves. From the thermogravimetric curves, it can be observed that the weight loss (%) of the original cellulose (94.5%) is higher than that of the regenerated cellulose samples (80.3–80.5%) over the range of 30–500 °C. For the two regenerated samples, the onset temperatures of pyrolysis as well as the endset temperatures have similar value, and they are all lower than those for the original sample.

In addition, great differences are found among the pyrolysis behaviors of the samples in the DSC thermogram. For the untreated cellulose, the major endothermic peak appears at 352 °C and the enthalpy of decomposition is 365.4 J/g. It is demonstrated that the position of the endothermic peak of the treated cellulose is lower than the untreated cellulose. Both TG and DSC curves show that there are extremum at 352 °C for the MCC, and about 339 °C for regenerated cellulose samples, respectively. Although the RC-1 and RC-2 show a similar endothermic peak, the enthalpy of decomposition are different, about 100.4 J/g for RC-1 and 86.3 J/g for RC-2, all of which are much smaller than that for untreated sample.

The data above indicate that the difference in enthalpy, onset, endset, degradation temperature might be originated from the variation in structure. Because of the changed structure and decreased crystalline degree, lower energy is needed when treated samples are employed for pyrolysis, namely the regenerated cellulose is easy for decomposition than the original cellulose. RC-1 and RC-2 have a lower onset degradation temperature and lower degradation energy. Among the samples, the enthalpy of decomposition of RC-2 is the lowest because of its amorphous structure and lowest crystallinity. It illustrates that the thermal properties of cellulose change a lot during the dissolution, and different precipitation affects the thermal stability of the regenerated cellulose.

3.3. SEM results

The morphology of microcrystalline cellulose and regenerated cellulose are investigated by analyzing the sample films, and the results are shown in Fig. 3. Compared to the original cellulose, the structure of regenerated cellulose changes markedly. The original cellulose is unfixed scrappy material. After dissolution and regeneration, the structure of cellulose is destroyed. It can be seen that RC-2 displays uniformity, indicating a dense texture, and is more smooth and glassy than RC-1 which has a rough surface and porous structure. These above may be the reason for the regenerated cellulose samples having lower decompounding temperature than that of original samples (see DSC-TG section).

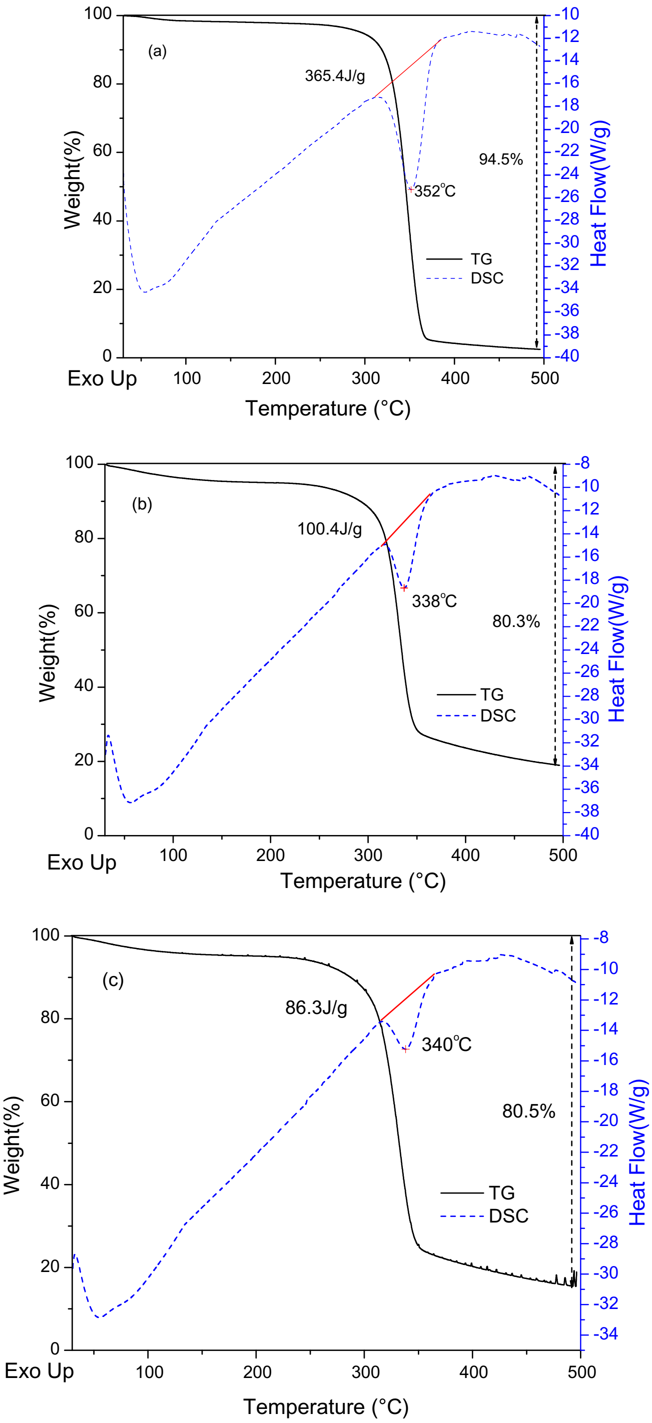

Fig. 2. TG-DSC of microcrystalline cellulose (a) and regenerated RC-1 (b), RC-2 (c).

3.4. Degree of polymerization (DP)

The DP values of both the starting cellulose and the regenerated cellulose are determined by capillary viscometry in

Table 2
Onset, endset temperature, and weight loss, in the thermal analysis processes of MCC, RC-1 and RC-2 samples obtained from the TG curves, and the endothermic peak temperature and the enthalpy from DSC curves.

Samples	Onset (°C)	Endothermic peak (°C)	Endset (°C)	Enthalpy (J/g)	Weight loss (%)
MCC	329	352	361	365.4	94.5
RC-1	315	338	345	100.4	80.3
RC-2	312	340	348	86.3	80.5

Table 3
Yield of products from the pyrolysis of samples at 400 °C for 1 h.

Samples	Liquid yields (%)	Solid residues (%)	Gas + losses (%)
MCC	46.5	26.6	26.9
RC-1	49.3	27.0	23.7
RC-2	49.0	25.8	25.2

cupriethylenediamine hydroxide. Table 1 shows the DP value of the original cellulose and the regenerated cellulose. The degree of polymerization of the cellulose sample is found to be 329. The treatment of the cellulose in BmimCl at 120 °C for 3 h results in a slight degradation of the cellulose macromolecules. A similar observation was reported by Liu, Sun, Zhang, Ren, and Geng (2006). But the degradation value in their report is higher than that in our experiment. The authors reported that the DP of regenerated cellulose decreased from 1309.6 to 750.5 in BmimCl. This may be explained by the presence of lignin and other components, as well as regeneration method, sugarcane bagasse cellulose, isolated from ground bagasse was employed in their research.

3.5. Pyrolysis results

Table 3 shows the yield of products from the pyrolysis of samples at 400 °C for 1 h with temperature ramp of 5 °C min^{-1}. After dissolution and precipitation, both RC-1 and RC-2 have an increase in yield of liquid products, while the amount of solid residues does not vary significantly, and a slight decrease in the gaseous products is observed. The results of GC analysis show that the gaseous products from the pyrolysis of MCC consist largely of CO_2, CH_4 and CO with lower concentrations of H_2, C_2H_4, and C_2H_6, which is distinctly different from that of regenerated cellulose (shown in Table 4). For the latter, the content of CO has obviously decreased. Compared with the slight increase in CH_4 content, there is significant increase in CO_2 content in gaseous products of the regenerated cellulose and the increase is in line with the decrease of crystalline degree. The decreased crystallinity of cellulose material is found to favour the removal of oxygen in the form of CO_2 under pyrolysis, which might enhance the stability and quality of the bio-oil produced

Table 4
Compositions of the components of the gas from the pyrolysis of samples at 400 °C for 1 h (vol.%).

Component (vol.%)	MCC	RC-1	RC-2
H_2	4.7	4.0	3.9
CO	19.3	4.2	4.4
CH_4	21.8	29.0	25.3
CO_2	52.1	59.1	62.4
C_2H_4	0.7	2.0	1.5
C_2H_6	1.5	1.8	2.4

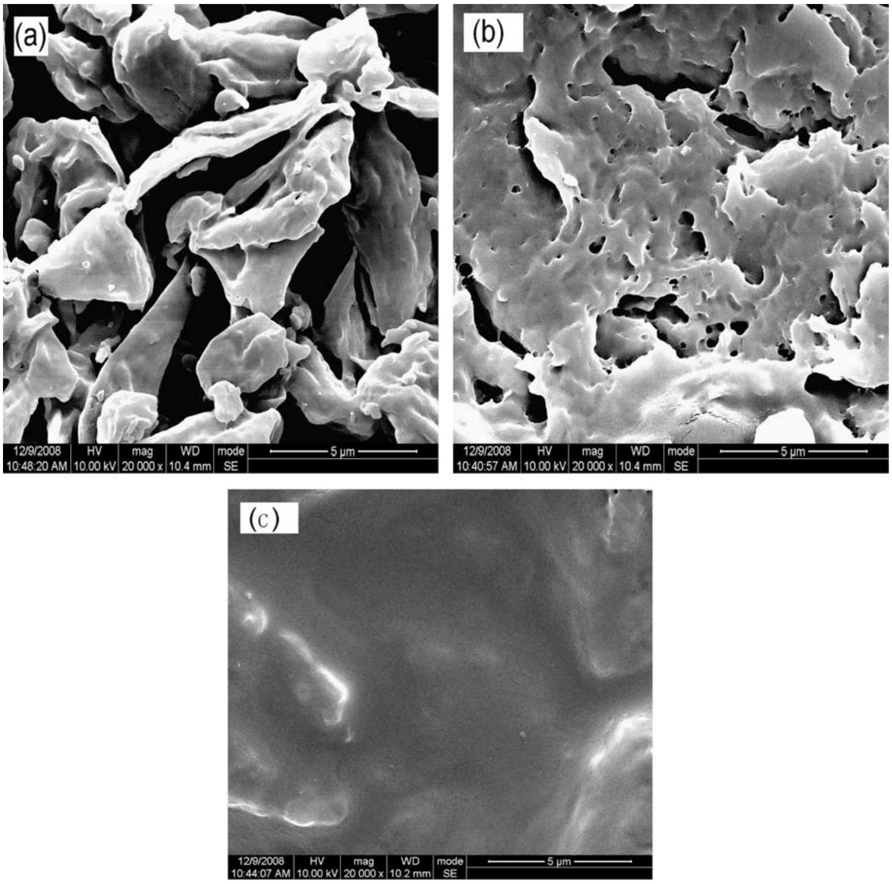

Fig. 3. SEM morphology of microcrystalline cellulose (a) and regenerated RC-1 (b), RC-2 (c).

(Antonakou, Lappas, Nilsen, Bouzga, & Stöcker, 2006; Luik, Johannes, Palu, Luik, & Kruusement, 2007).

The compositions of the main components of the pyrolytic liquid obtained from MCC and regenerated cellulose determined by GC/MS are given in Table 5. The pyrolysis oil of these samples contains mainly carboxylic, carbonylic, furan compounds, such as acetic acid, furfural, propanoic acid, 1-hydroxy-2-propanone, 1-(2-furanyl)-ethanone, 5-methyl-2-furancarboxyaldehyde, 3-methyl-1,2-cyclopentanedione, and levoglucosecone, 1,4;3,6-dianhydro-alpha-D-glucopyranose,5-(hydroxymethyl)-2-furancarboxyaldehyde. And, the total content of furfural, acetic acid, 1,4;3,6-dianhydro-alpha-D-glucopyranose and 5-(hydroxymethyl)-2-furancarboxyaldehyde is 47.8–55.6% in the pyrolytic liquids of samples at 400 °C. The pyrolysis of different samples gives similar kinds of liquid products, but the composition of liquid product varies from one sample to another. The content of furfural is observed to be the highest in pyrolytic liquids of MCC and RC-2, and the second one is 1,4;3,6-dianhydro-alpha-D-glucopyranose for MCC, 5-(hydroxymethyl)-2-furancarboxyaldehyde for RC-2, but the content of 5-(hydroxymethyl)-2-furancarboxyaldehyde increases in that of RC-1 and become the highest one at the expense of furfural. It is clear that the content of 5-(hydroxymethyl)-2- furancarboxyaldehyde is lower than that of 1,4;3,6-dianhydro-alpha-D-glucopyranose in the pyrolytic liquids of MCC, but the content of the former is higher than that of the latter in the pyrolytic liquids of RC-1 and RC-2. These results illustrate that the pyrolysis of regenerated cellulose (RC-1) prepared from ILs solution poured into de-ioned water is favourable to 5-(hydroxymethyl)-2-furancarbox-yaldehyde formation, a versatile intermediate in chemical industry (Zhang, Holladay, Brown, & Zhang, 2007). However, the pyrolytic liquids of MCC and RC-2 have a distinct high content of furfural. It indicates that the changes of pyrolysis liquid yield and liquid composition are mainly resulted from the different crystal structure after dissolution and regeneration process, for the DP of cellulose is proved to have no obvious change after dissolution and regeneration.

Based on above analysis, it can be found that the pyrolysis of cellulose I give significant amount of CO in gas phase, while in the liquid, nearly no carbonylic compounds was observed. Compared with cellulose I, the pyrolysis of cellulose II and amorphous cellulose give not only more amounts of CO_2 and CH_4, but also more carbonylic compounds. Furfural and 5-(hydroxymethyl)-2-furancarboxyaldehyde are the major composition in the pyrolytic liquid of cellulose II and amorphous cellulose. The content of 5-(hydroxymethyl)-2-furancarboxyaldehyde is the highest from the pyrolysis of cellulose II, and the content of furfural is the highest from the pyrolysis of amorphous cellulose. Further mechanism studies are needed for the relationship of pyrolysis and crystalline state.

Table 5
Compositions of the main components of the liquid from the pyrolysis of samples at 400 °C for 1 h (%).[a]

Component (%)[a]	MCC	RC-1	RC-2
1-Hydroxy-2-propanone	2.6	4.3	8.1
Furfural	22.0	11.9	22.6
Acetic acid	6.8	8.6	9.8
1-(2-Furanyl)-ethanone	2.3	1.3	1.8
2-Methyl-3-pentanone	–	1.7	2.8
1-(Acetyloxy)-2-butanone	–	1.7	2.4
Propanoic acid	2.1	1.5	2.5
5-Methyl-2-furancarboxaldehyde	6.0	3.4	5.6
2-Furanmethanol	–	2.6	2.4
1,2-Cyclopentanedione	1.6	–	–
3-Methyl-1,2-cyclopentanedione	4.3	2.9	2.9
Cis-1,2-cyclobutanedicanedicarboxylic acid	2.5	–	–
Butanal	–	1.9	2.0
Levoglucosecone	7.5	3.1	2.0
Dihydro-4-hydroxy-2(H)-furanone	–	2.0	–
Heptanal	–	3.1	4.1
1,4;3,6-Dianhydro-alpha-D-glucopyranose	12.9	9.1	8.5
5-(Hydroxymethyl)-2-furancarboxyaldehyde	6.1	19.0	14.7

[a] The amount (%) of the products was evaluated through the peak area; no response factors were introduced.

4. Conclusion

Ionic liquids, 1-butyl-3-methylimidazolium chloride, as an excellent cellulose solvent have strong ability to dissolve cellulose, and could be reused. The structure and physico-chemical properties of cellulose change a lot after dissolution. The regenerated cellulose samples obtained from different precipitation procedures have different thermal properties and morphology. Cellulose II is obtained by pouring ionic liquids solution into precipitation reagent (de-ioned water). And amorphous cellulose is prepared by pouring de-ioned water into ionic liquids solution.

Cellulose II and amorphous cellulose are found to favour the removal of oxygen in the form of CO_2 under pyrolysis, which might enhance the stability and quality of the bio-oil produced. High value-added 5-(hydroxymethyl)-2-furancarboxy-aldehyde can be produced by pyrolysis of cellulose II.

Acknowledgements

This work is financially supported by the National Basic Research Program of China (973 program, No. 2007CB210203) and the Special Research Fund for the Doctoral Program of Higher Education of China (No. 20050610013). The characterization of bio-oils from Analytical and Testing Center of Sichuan University are greatly appreciated. The supervision of academician Qingshi Zhu is highly acknowledged.

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