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Catalytic pyrolysis of cellulose in ionic liquid [bmim]OTf

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ABSTRACT

This study discussed the catalytic cracking process of cellulose in ionic liquid 1-butyl-3-methylimidazolium trifluoromethanesulfonate ([bmim]OTF) under 180 °C, 240 °C and 340 °C, found that [bmim]OTF is an effective catalyst which can effectively reduce the pyrolysis temperature(nearly 200 °C) of the cellulose. FRIR, XRD and SEM were used to analyze the structure characterization of fiber before and after the cracking; GC–MS was used for liquid phase products analysis; GC was used to analyze gas phase products. The results showed that the cellulose pyrolysis in [bmim]OTf mainly generated CO_2, CO and H_2, also generated 2-furfuryl alcohol, 2,5-dimethyl-1,5-diallyl-3-alcohol, 1,4-butyrolactone, 5-methyl furfural, 4-hydroxy butyric acid, vinyl propionate, 1-acetoxyl group-2-butanone, furan formate tetrahydrofuran methyl ester liquid product, and thus simulated the evolution mechanism of cellulose pyrolysis products based on the basic model of cellulose monomer.

1. Introduction

With the globally non-renewable energy depletion, the environmental pollution and ecological destruction caused by fossil fuels exploitation, it is necessary to find alternative energy sources and to develop high efficiency and energy saving technology (Bulushev & Ross, 2011). As a kind of renewable, high capacity and low pollution carbon resource, biomass might gradually replace part of fossil fuels which could significantly ease the energy crisis and environmental pollution. At present, one of the hot spots in the research of biomass development and utilization is to produce liquid fuel oil using biomass pyrolysis technology, then obtain liquid fuel oil through further separation and purification or use for other industrial raw materials (Bridgwater, 2012; Czernik & Bridgwater, 2004). However, the composition of biomass pyrolysis products is complex (Zhu, Zhu, Xiao, & Yi, 2012) and the process of pyrolysis and evolution mechanism of products are yet to be studied. Since Cellulose is the most abundant substance in biomass (Huang, Kuan, Chiueh, & Lo, 2011), taking cellulose as model compound to explore its pyrolysis law is helpful for the understanding of the process and mechanism of biomass pyrolysis.

As a new type of green solvent, ionic liquids exhibit very good physicochemical properties (Egashira, Asai, Yoshimoto, & Morita, 2011; Hallett & Welton, 2011; Liu, Cheng, Zhang, Wang, & Yu, 2008) including high thermal and chemical stability, negligible vapour pressure, nonflammability, high conductivity and widely tuneable properties by the appropriate selection of the cation or anion in their structure. It has great potential in the study of cellulose dissolution and pyrolysis. In 2002 Swatloski (Swatloski, Spear, Holbrey. & Rogers, 2002) firstly reported ionic liquids such as chloride 1-butyl-3-methyl imidazole on cellulose dissolution, since then researchers conducted a series of experiments. Kosan, Michels, and Meister (2008) found [bmim]Cl, [emim]Cl, [bmim]Ac and [emim]Ac plasma liquid can greatly dissolve cellulose. Moreover anion for acetic acid ions liquid are better than chlorine ions on cellulose dissolution; Zhao et al., (2012) found cellulose which was not pretreated can dissolve quickly in the phosphate types of ionic liquid, and the cellulose fibers would change. The study of the mechanism of cellulose dissolved in ionic liquid (André, Marsh, Shusheng, & Staiger, 2009; Cao et al., (2009) found that ionic liquid weakened the hydrogen bonding between cellulose intermolecular and intramolecular, which leaded to a disconnection of molecular chain thus promoted its dissolution. Therefore, using ionic liquids as reaction media is benefit for the depolymerization cracking of cellulose. Olivier-Bourbigou, Magna, and Morvan (2010) who used ionic liquids as reaction media catalyzed, dissolved and destroyed the cellulose glycosidic bond. Xiao, Bing, Wang, Fang, and Zhang (2014) added the $AlCl_3$ into the mixed ionic liquid of DMSO-[bmim]Cl, which produced 54.9% HMF of cellulose pyrolysis. Jun, Liu, Liu, Sun, and

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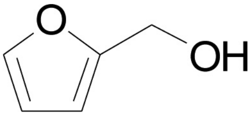
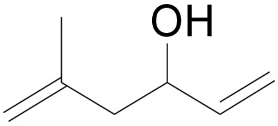
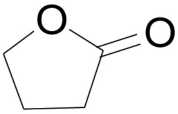
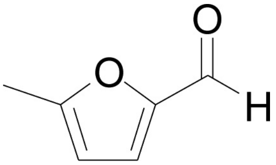
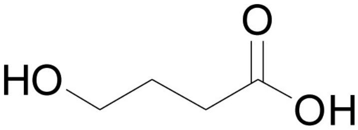
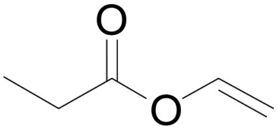
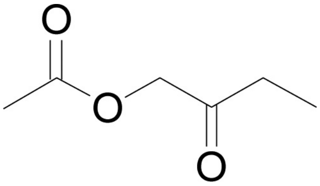
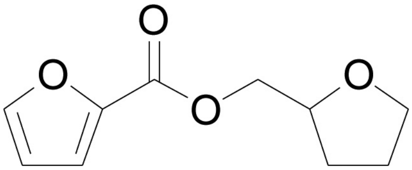
Table 1
The distribution of main liquid products of cellulose pyrolysis under different temperature.

liquid products	structural formula	180 °C	240 °C	340 °C
2-furfuryl alcohol		√		√
5-methyl-1,5-hexadiene-3-ol		√		
gamma-Butyrolactone		√		
5-methyl furfural		√	√	
4-hydroxybutanoic acid			√	√
Propionic acid vinyl ester			√	
1-acetoxy-2-butanone			√	
Furan formate tetrahydrofuran methyl ester			√	

Tao (2010) produced biomass pyrolysis oil by using microwave to pyrolysis of straw and sawdust in the ionic liquid. Liu, Zhang, and Zhao (2013) studied microwave-assisted direct conversion of cellulose into HMF in ionic liquids catalyzed by $ZrCl_4$. Under optimal conditions, a high HMF yield up to 51.4% was obtained from cellulose in 3.5 min under microwave irradiation at 400 W. Yan, Zhang, Xin, Bing, and Lin (2014)developed a new method for the hydrolysis of cellulose into reducing sugar in ionic liquids catalyzed by a core–shell $Fe_3O_4@SiO_2–SO_3H$ acid catalyst, which was prepared by the immobilization of sulfonic acid groups on the surface of silica-encapsulated Fe_3O_4 nanoparticles. The $Fe_3O_4@SiO_2–SO_3H$ showed a good activity with reducing sugar yield of 73.2% under the moderate conditions of 130 °C after 8 h reaction.

Although there are many researches on ionic liquid dissolving or cellulose cracking, most of them were limited in the researches about the effect of cellulose dissolution and cracking. Since the researches on the process and product evolution of ionic liquid catalytic cracking of cellulose is rare, this study researched the catalytic cracking products under different temperature using ionic liquid [bmim]OTf as reaction medium, then explore the evolution mechanism of cellulose pyrolysis products.

2. Experiment

2.1. Chemicals and samples

Microcrystalline cellulose powder (particle size of 50 μm, Aladdin reagent). *N*-Methyl imidazole(a purity of 99% or more, Aladdin reagent). Three fluorinated methyl sulfonic acid potassium(a purity of 99% or more, Aladdin reagent). 1-Chlorobutane (AR, Aladdin reagent). Methylene chloride(AR, Tianjin wind ship chemical technology co., LTD).

2.2. The synthesis of ionic liquid [bmim]OTf

[bmim]OTf adopts two-step synthesis and the specific operation process are as follows:

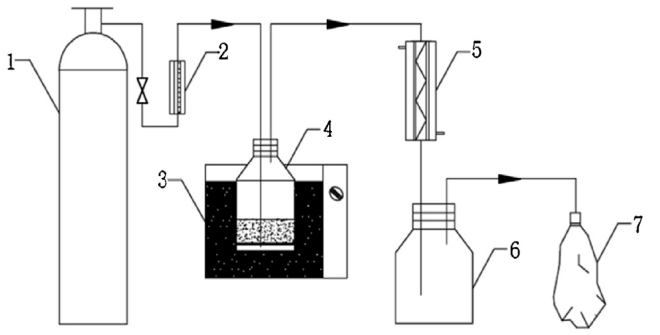


Fig. 1. Experimental flow chart. (1) Nitrogen bottle; (2) mass flow meter; (3) heating device; (4) reactor; (5) condenser tube; (6) liquid bottle; (7) aluminum foil sample.

(1) The synthesis of [bmim]Cl: Molar ratio of *N*-methyl imidazole to chlorobutane 1:1 were mixed in a dry 250 ml flask with condensing facility, then heated with stirring for 48 h under 70 °C. After reaction, reactants were washed for three times using ethyl acetate, and then streamed to remove ethyl acetate at 80 °C. Finally, the pale yellow viscous liquid [bmim]Cl was obtained.

(2) The synthesis of [bmim]OTf: Molar ratio of potassium trifluoromethanesulfonate to [bmim]Cl 1:1 were mixed, using dichloromethane as solvent, reflux condensation for 48 h under 60 °C. After removing the dichloromethane by reduced pressure distillation at 40 °C, the milky viscous liquid [bmim]OTf is obtained finally.

2.3. *The pyrolysis of microcrystalline cellulose in [bmim]OTf*

Flow chart of the experiment is shown in Fig. 1. Nitrogen was used as carrier gas. Gas produced from the reactor was purged with nitrogen into aluminum foil bag. Nitrogen flow was controlled at 5 ml/min by mass flow controller. Used a glass sand at the bottom of the reactor to ensure nitrogen take away gas phase products. 1.000 g microcrystalline cellulose and 10,000 g [bmim]OTf were added into reactor. Nitrogen was kept aerating until the reactor contained no more air but only nitrogen. The reactor is connected to the aluminum foil bags, and then using magnetic stirring for 2 h under the condition of 180 °C, 240 °C and 340 °C, respectively. When pyrolysis reaction finished, close the heating device and aerate moderate amount of nitrogen. The gas phase products are collected under the nitrogen purging aluminum foil sample bag while volatile liquid products are collected in a liquid bottle after the condensation. Deionized water and dichloromethane were added while the reactor was cooled to room temperature, and then the cracking solid products were collected and dried by suction filtration. Liquid products was added into the separatory funnel, after stratification, the lower liquid was evaporated to remove the methylene chloride in order to obtain difficult volatile liquid products.

2.4. *Product analysis methods*

FTIR(Fourier transform infrared spectrum, brooke in German, tensor27), XRD (X-ray diffraction, Dandong diffraction instrument factory, TD2500 type) and SEM (electronic scanning electron microscopy, the German Zeiss EVO 10) were used to analyze the solid products.

GC–MS (gas chromatography–mass spectrometry instrument, GCMSD5975, Agilent) was used to analyze the liquid products. A chromatographic column HP-INNOWax (30 m, diameter of 0.25 mm) was chosen: thickness of 0.25 lm, flow rate of 1 ml/min, diversion ratio: 20:1. Initial temperature of chromatographic column is 40 °C, then was increased to 220 °C as a rate of 5 °C/min, then was kept for 5 min. The interface temperature of GC–MS is 280 °C with the source of EI (70 ev), EM voltage 1106 V, solvent delay 3 min.

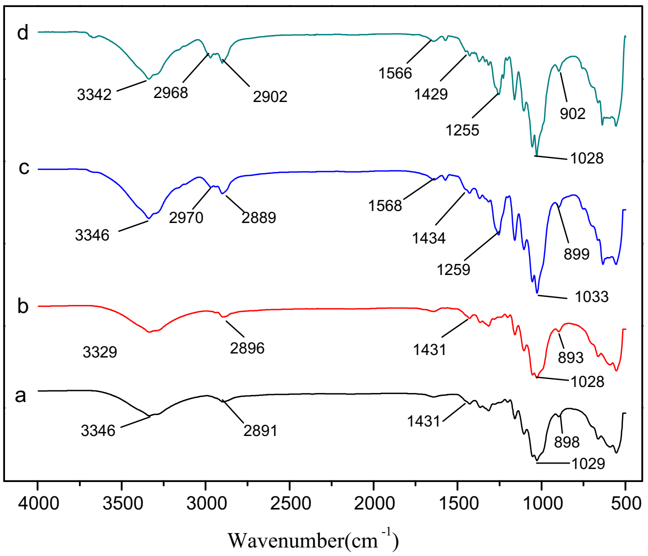


Fig. 2. Infrared spectra of cellulose. (a) Cellulose raw materials; (b) pyrolized cellulose under 180 °C; (c) pyrolized cellulose under 240 °C; (d) pyrolized cellulose under 340 °C.

GC(Gas chromatograph, GC9790) was used to analyze the gas phase: Chromatographic column: GDX-104; Column temperature: 40 °C; Bridge: 100 mA; Detector: TCD thermal conductivity detector; Injection port: 100 °C; The carrier gas: nitrogen; Column pressure before I: 0.28 MPa, Column pressure before II pressure: 0.20 MPa, the total pressure: 0.3 MPa; Sample quantity: 1 ml.

3. Results and discussion

3.1. *The analysis of solid phase products of cellulose pyrolysis*

3.1.1. *FTIR analysis*

Fourier transform infrared spectrum was used for the analysis of cellulose raw materials and cellulose cracked under 180 °C, 240 °C, 340 °C in ionic liquid [bmim]OTf. The results are shown in Fig. 2. The infrared absorption peak position of cellulose cracked under 180 °C is same as the raw materials, however, cellulose cracked under 240 °C and 340 °C produced a new infrared absorption peak.

The intramolecular hydroxyl OH stretching vibration appears at the 3500–3300 cm^{-1}. There is a CH stretching vibration peak near 2900 cm^{-1}, and the bending vibration of cellulose CH_2 is 1431 cm^{-1}, the 1000–1100 cm^{-1} is a sugar COH stretching peak, and the 898 cm^{-1} is a β-(1,4)-glycosidic bond vibration peak. Compared with the cellulose raw materials, a new infrared adsorption peak of the cellulose cracked under 240 °C and 340 °C appeared at 2968 cm^{-1}, 1566 cm^{-1} and 1259 cm^{-1}. And the 2968 cm^{-1} is attributed to the symmetric stretching of CH_2, which means cellulose structure has changed and molecular chain ruptured and generated Substance of olefin structure. 1566 cm^{-1} is corresponding with carboxyl group(–COOH) antisymmetric expansion which means that carboxylic acid was generated during the cracking process; absorption peak at 1259 cm^{-1} is the cyclic anhydride COC antisymmetric expansion which shows that the annular carboxylic acid was generated.

3.1.2. *XRD analysis*

The X-ray diffraction diagram of cellulose cracked in the ionic liquid [bmim]OTf under 180 °C, 240 °C, 340 °C and cellulose raw

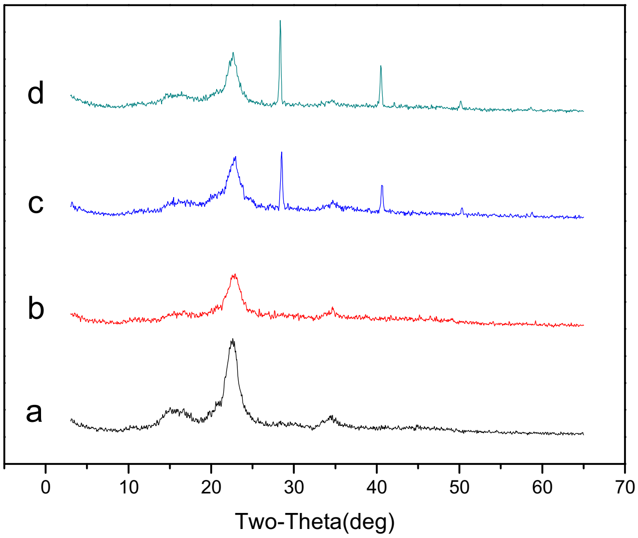


Fig. 3. X-ray diffraction pattern of the cellulose. (a) Cellulose raw materials(CRM); (b) pyrolized cellulose under 180 °C; (c) pyrolized cellulose under 240 °C; (d) pyrolized cellulose under 340 °C.

materials was shown in Fig. 3. From the figure, the main peak and second peak of both cellulose raw materials and cellulose cracked appeared at 22.0° and 18.0° respectively, which represented diffraction intensity of the crystalline and amorphous regions (Segal, Creely, Martin, & Conrad, 1959). Compared to the cellulose raw materials, the cellulose cracked under 180 °C did not show a new diffraction peaks, while the cellulose cracked under 240 °C and 340 °C showed new diffraction peaks at $2\theta = 28.5°$ and 40.6°, which means the crystalline surface of cellulose was damaged leading to a change of crystal structure. The reason might be the rearrangement of crystalline and amorphous regions of the cellulose after cleavage.

Crystallinity of cellulose mainly affects the mechanical properties of cellulose and fiber quality. In general, with the increasing of crystallinity, the breaking strength, stiffness and stability of cellulose will increase while moisture absorption, adsorption, accessibility and reactivity will reduce (Lin, Guo, Fang, & Wang, 2013). The crystallinity of cellulose was calculated by peak intensity method and the calculation formula is as follows:

$$\mathrm{CrI} = \frac{I_{002} - I_{am}}{I_{002}} \times 100\%$$

In the formula: I_{002} is crystal plane diffraction intensity that is diffraction intensity at $2\theta = 22°$; I_{am} is diffraction intensity in the amorphous region of $2\theta = 18°$.

Calculation results: 79.6%(CRM); 69.4%(180 °C); 59.5%(240 °C); 62.4%(340 °C). The crystallinity is significantly lower after cracking cellulose which shows that cellulose chain was broken and crystalline region was destroyed. The crystallinity of cellulose pyrolysis under 340 °C is larger than 240 °C that probably because the amorphous region of cellulose is damaged which resulted in increased proportion of crystalline region thus to make the crystallinity become large.

3.1.3. SEM analysis

The observation of cellulose raw materials and cellulose cracked in the ionic liquid [bmim]OTf under 180 °C, 240 °C, 340 °C through the scanning electron microscope (SEM) is shown in Fig. 4. The figure shows that the surface of cellulose raw materials is smooth with a tight structure. The surface of cellulose cracked under 180 °C becomes rough with more folds and more obvious holes while under 240 °C the surface presents disordering with the breaking of cellulose which then fall off into pieces. Under 340 °C, the surface holes got bigger and the gully was more obvious. These phenomena show that the structure of the cellulose in ionic liquid at low temperature has changed obviously and [bmim]OTf has obvious catalytic effect which reduces the cellulose pyrolysis temperature. On the other hand, the structure of cellulose was destroyed more seriously with the increase of temperature.

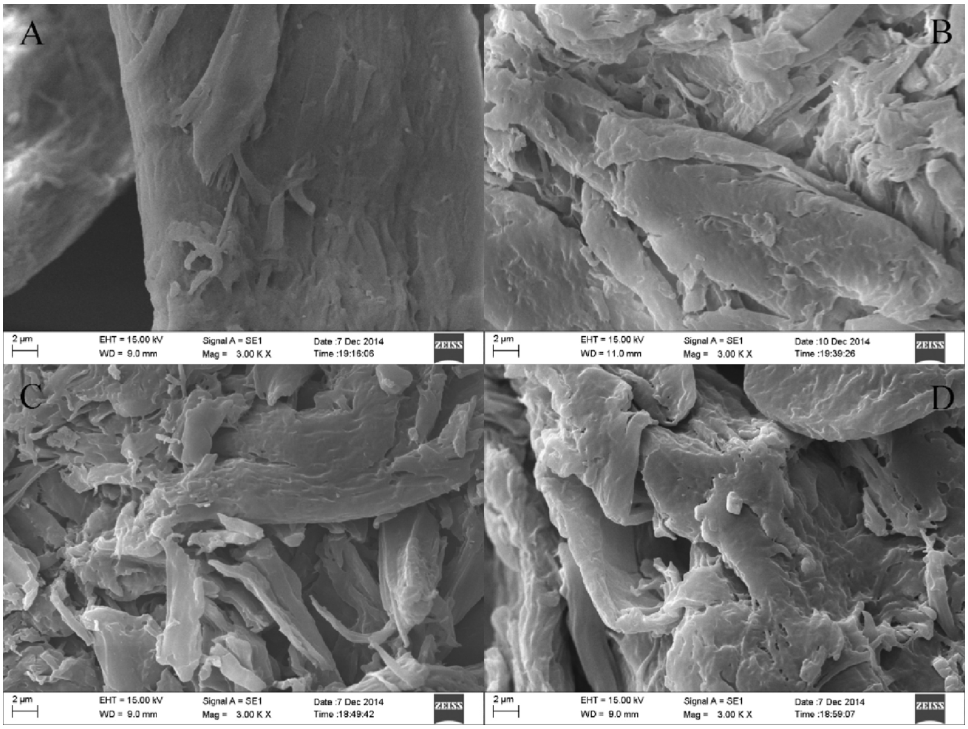


Fig. 4. The SEM of cellulose. (A) Cellulose raw materials; (B) pyrolized cellulose under 180 °C; (C) pyrolized cellulose under 240 °C; (D) pyrolized cellulose under 340 °C.

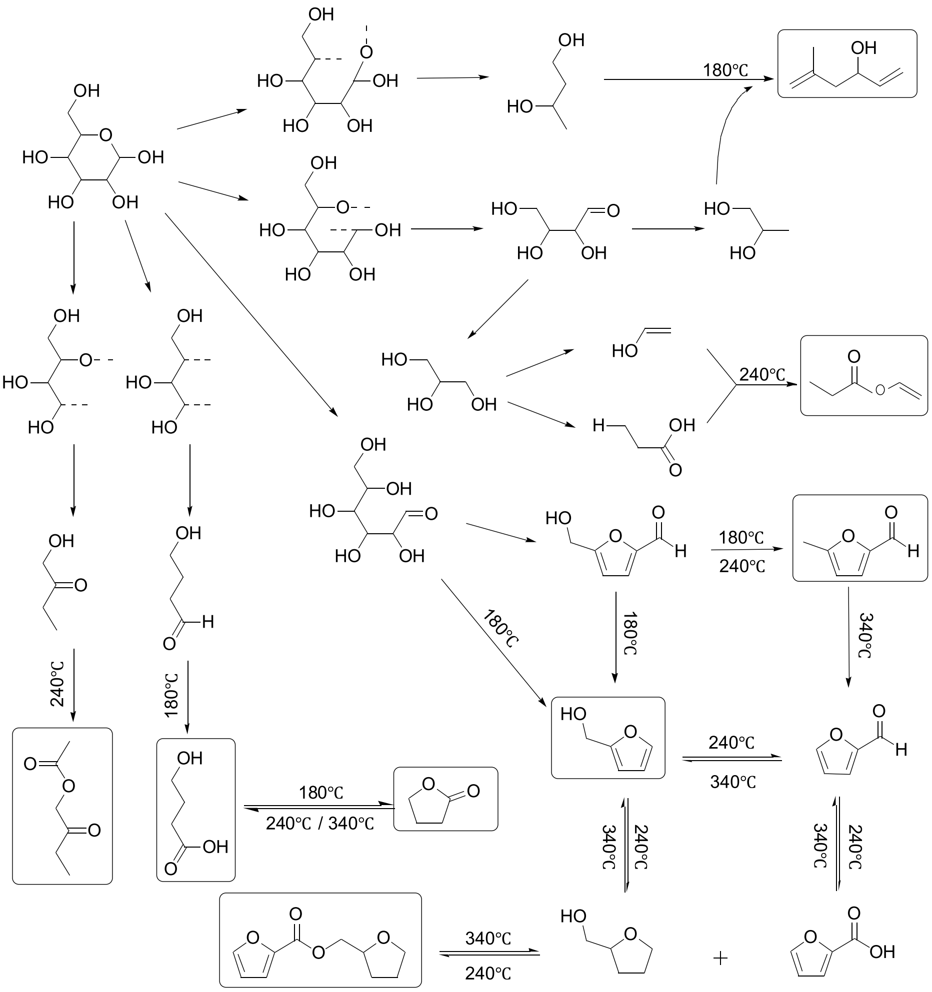


Fig. 5. Evolution process of cellulose pyrolysis products.

3.2. *The analysis of the liquid phase products of cellulose pyrolysis*

GC–MS was used to analyze liquid products of cellulose pyrolysis. The distribution of main liquid products of cellulose pyrolysis under different temperature is shown in Table 1.

The majority products of cellulose molecular cracking under 180 °C are 2-furfuryl alcohol, 5-methyl-1,5-hexadiene-3-ol, gamma-Butyrolactone, 5-methyl furfural; The majority products of cellulose molecular cracking under 240 °C are 5-methyl furfural, 4-hydroxybutanoic acid, Propionic acid vinyl ester, 1-acetoxyl-2-butanone, furan formate tetrahydrofuran methyl ester. The majority products of cellulose molecular cracking under 340 °C are 2-furfuryl alcohol, 4-hydroxybutanoic acid. From the basic model of cellulose monomer, the evolution process of the cellulose pyrolysis products can be inferred as shown in Fig. 5.

In generally, during the reaction of cellulose pyrolysis, the hydrolysis reaction happens first and generates glucose monomers and other small molecule compounds (Shen and Gu, 2009). Due to the acidic ionic liquids are used in the experiments which pays a strong role in catalytic pyrolysis of cellulose, cellulose can be cracked under low temperature to generate a large number of small molecule compounds mainly produced by the pyrolysis of glucose monomers.

The evolution process of 1-acetoxy-2-butanone is shown in Fig. 6(1). Glucose monomers were fractured and formed four-carbon fragment and two-carbon fragment. And two-carbon fragment eventually translate into carbon monoxide while four-carbon fragment translate into 1-hydroxy-2-butanone which finally form 1-acetoxy-2-butanone through dehydration with acetic acid.

The evolution process of 2-furfuryl alcohol, 5-methyl furfural and furan formate tetrahydrofuran methyl ester are shown in Fig. 6(2). Glucose monomers dehydrated repeatedly several times after the ring opening and formed 5-HMF and 2-furfuryl alcohol (Liao, Luo, Wang, & Yu, 2003; Wang, Liao, Tan, Luo, & Cen, 2003). The side chain of 5-HMF was fractured and generated 5-methyl furfural and furfural then 2-furfuryl alcohol and furfural generated furan formic acid and tetrahydrofuran methanol by means of oxidation reduction reaction. They ultimately generates furan formate tetrahydrofuran methyl ester through esterification reactions.

The evolution process of gamma-Butyrolactone and 4-hydroxybutanoic acid are shown in Fig. 6(3). Glucose monomers was fractured and generated four-carbon fragment and tow-carbon fragment. The four-carbon fragment eventually transformed into 4-hydroxybutyraldehyde and then the 4-hydroxybutanoic acid was generated by the oxidation reaction. In fact, 4-hydroxybutanoic acid will be dehydrated to form a cyclic structure of gamma-Butyrolactone. Both can be transformed into each other under different temperatures.

The evolution process of Propionic acid vinyl ester is shown in Fig. 7(1). Glucose monomers firstly generate glycerol by fracture. Glycerol forms ethenol and propionic acid by dehydration reaction(Iii, Pithawalla, Naworal, & Thomas, 2007; Nimlos,

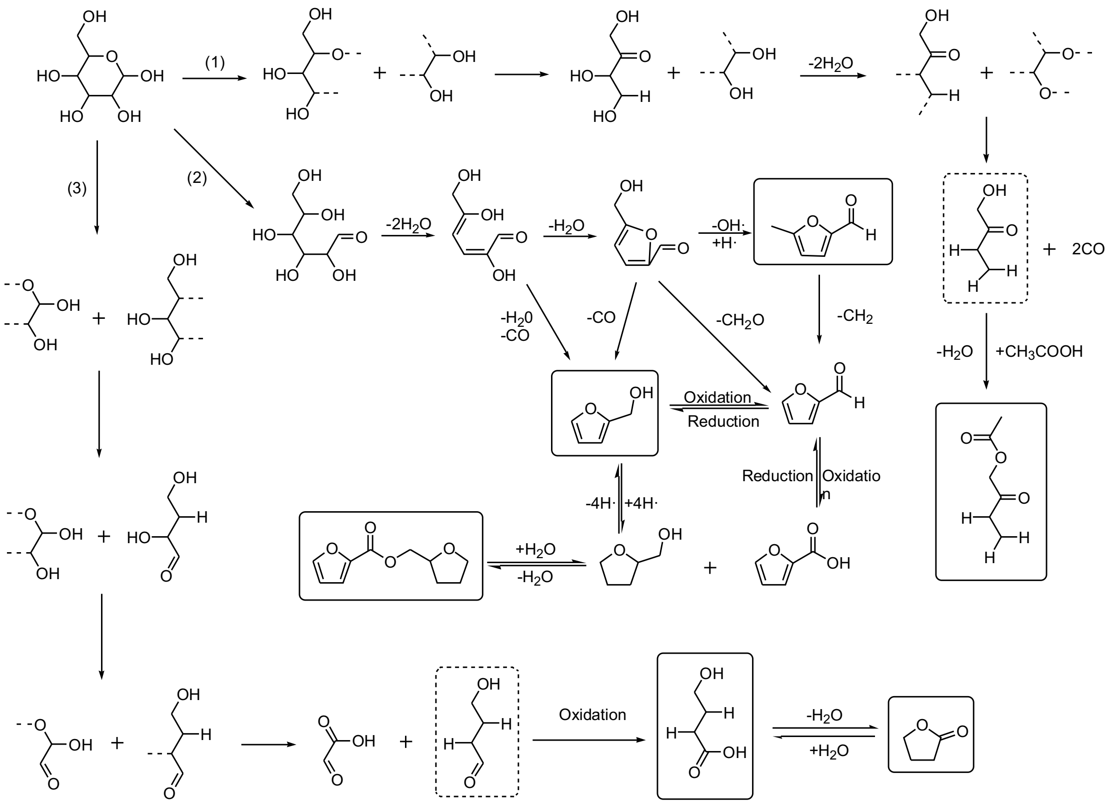


Fig. 6. The evolution of 1-acetoxyl group-2-butanone, 2-furfuryl alcohol, 5-methyl furfural, furan formate tetrahydrofuran methyl ester, 1,4-butyl lactone and 4-hydroxy butyric acid.

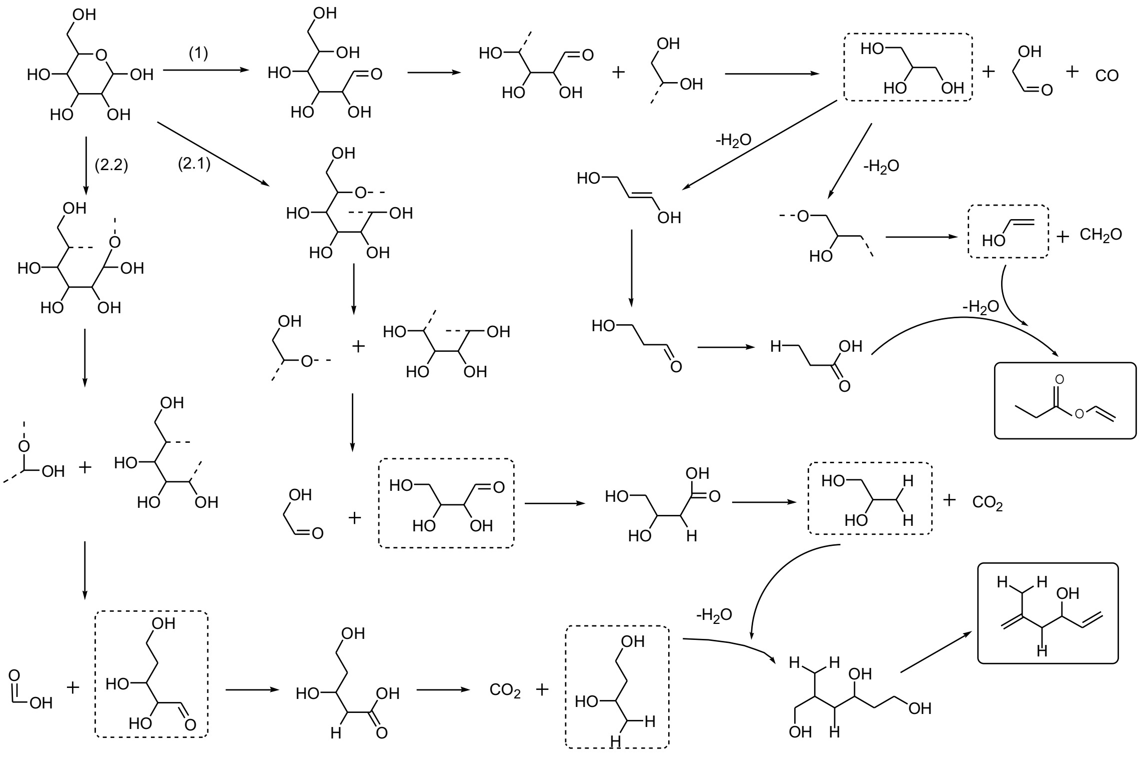


Fig. 7. The evolution of vinyl propionate and 5-methyl-1,5-diallyl-3-alcohol.

Blanksby, Ellison, & Evans, 2003) and then generate vinyl propionate through esterification reaction.

The evolution process of 5-methyl-1,5-hexadiene-3-ol is shown in Fig. 7(2.1) and (2.2). Glucose monomers generate 1,2-Propanediol and 1,3-butyleneglycol by different fracture mechanisms thus eventually form 5-methyl-1,5-hexadiene-3-ol through intermolecular and intramolecular dehydration.

3.3. *Cellulose pyrolysis gas phase products analysis*

Due to the small amount of experimental materials and gas production, especially under high temperature it is difficult to collect gaseous products to make accurate analysis, the gas phase products generated by catalytic cracking of cellulose in [bmim]OTf under 140 °C, 160 °C, 180 °C and 200 °C were analyzed qualitatively.

Through the analysis of gas chromatography, CO and CO_2 were produced at 140 °C which means ionic liquid [bmim]OTf will make cellulose cracking take place in a relatively low temperature. Generally considering that the generation of CO is produced by dehydroxylation of compounds with hydroxyl groups while CO_2 is generated by decarboxylated of compounds with carboxy groups. Moreover, the generation of CO_2 is also associated with cellulose internal dehydrated.

It generates H_2 at 180 °C in addition to CO_2 and CO but the content is less. H_2 was generated by cleavage and deformation of C=C and CH key groups. The content of H_2 and CO increased at 200 °C which shows that high temperature favors the formation of H_2 and CO.

4. Conclusions

This study discussed the catalytic cracking process of cellulose in ionic liquid [bmim]OTf under 180 °C, 240 °C and 340 °C, we found that [bmim]OTf is an effective catalyst which can effectively reduce the pyrolysis temperature of cellulose. Under the situation without ionic liquid, cellulose only dehydrated at the low temperature while started cracking at 315 °C (Liu, Jiang, & Huang, 2009). Which means [bmim]OTf shortened nearly 200 °C temperature range for cellulose pyrolysis.

The results showed that it produced a new infrared absorption peak under 240 °C and 340 °C after pyrolysis of cellulose by FTIR analysis which explained the process of pyrolysis of cellulose chain rifted and produced olefin and carboxyl structure; The XRD analysis showed that cellulose crystal structure had changed and the crystallinity had significantly decreased; the SEM analysis found that the surface holes of cellulose became bigger as the pyrolysis temperature increased, the gully was more obvious and the damage of structure was more serious. GC analysis showed that CO_2, CO and less H_2 were generated during the process and high temperature was helpful for the generation of H_2 and CO. The analysis of liquid phase products of cellulose pyrolysis by GC–MS showed that the major products of cellulose molecular cracking under 180 °C, 240 °C and 340 °C are 2-furfuryl alcohol, 2,5-dimethyl-1,5-diallyl-3-alcohol, 1,4-butyrolactone, 5-methyl furfural, 4-hydroxy butyric acid, propionic acid vinyl ester, 1-acetoxyl group-2-butanone, tetrahydrofuran methanol ester. At last the evolution mechanism of cellulose pyrolysis products was simulated based on the model of glucose monomer.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2016.04.052.

References

André, P., Marsh, K. N., Shusheng, P., & Staiger, M. P. (2009). Ionic liquids and their interaction with cellulose. *Chemical Reviews*, *109*(12), 6712–6728.

Bridgwater, A. V. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass & Bioenergy*, *38*(2), 68–94.

Bulushev, D. A., & Ross, J. R. H. (2011). Catalysis for conversion of biomass to fuels via pyrolysis and gasification: a review. *Catalysis Today*, *171*(1), 1–13.

Cao, Y., Wu, J., Zhang, J., Li, H., Zhang, Y., & He, J. (2009). Room temperature ionic liquids (RTILs): a new and versatile platform for cellulose processing and derivatization. *Chemical Engineering Journal*, *147*(1), 13–21.

Czernik, S., & Bridgwater, A. V. (2004). Overview of applications of biomass fast pyrolysis oil. *Energy & Fuels*, *18*(2), 590–598.

Egashira, M., Asai, T., Yoshimoto, N., & Morita, M. (2011). Ionic conductivity of ternary electrolyte containing sodium salt and ionic liquid. *Electrochimica Acta*, *58*(5), 95–98.

Hallett, J. P., & Welton, T. (2011). Room-temperature ionic liquids: solvents for synthesis and catalysis. 2. *Chemical Reviews*, *111*(5), 3508–3576.

Huang, Y. F., Kuan, W. H., Chiueh, P. T., & Lo, S. L. (2011). Pyrolysis of biomass by thermal analysis–mass spectrometry (TA–MS). *Bioresource Technology*, *102*(3), 3527–3534.

Iii, J. B. P., Pithawalla, Y. B., Naworal, J. D., & Thomas, C. E. (2007). Carbohydrate pyrolysis mechanisms from isotopic labeling: part 1: the pyrolysis of glycerin: discovery of competing fragmentation mechanisms affording acetaldehyde and formaldehyde and the implications for carbohydrate pyrolysis. *Journal of Analytical & Applied Pyrolysis*, *80*(2), 297–311.

Jun, D. U., Liu, P., Liu, Z. H., Sun, D. G., & Tao, C. Y. (2010). Fast pyrolysis of biomass for bio-oil with ionic liquid and microwave irradiation. *Journal of Fuel Chemistry & Technology*, *38*(5), 554–559.

Kosan, B., Michels, C., & Meister, F. (2008). Dissolution and forming of cellulose with ionic liquids. *Cellulose*, *15*(1), 59–66.

Liao, Y. F., Luo, Z. Y., Wang, S. R., Yu, C. J., & Cen, K. F. (2003). Mechanism of rapid pyrolysis of cellulose I. Experimental research. *Journal of Fuel Chemistry and Technology*, *31*(2), 133–138.

Lin, T., Guo, W., Fang, L., & Wang, Z. (2013). Crystallinity of stalk cotton cellulose by three methods. *Journal of Northeast Forestry University*,

Liu, W., Cheng, L., Zhang, Y., Wang, H., & Yu, M. (2008). The physical properties of aqueous solution of room-temperature ionic liquids based on imidazolium: database and evaluation. *Journal of Molecular Liquids*, *140*(1), 68–72.

Liu, J. L., Jiang, J. C., & Huang, H. T. (2009). Study of thermal transformations of cellulose under curie-point pyrolysis-GC–MS conditions. *Chemistry & Industry of Forest Products*, *29*(5), 47–53.

Liu, B., Zhang, Z., & Zhao, Z. K. (2013). Microwave-assisted catalytic conversion of cellulose into 5-hydroxymethylfurfural in ionic liquids. *Chemical Engineering Journal*, *215–216*(3), 517–521.

Nimlos, M. R., Blanksby, S. J., Ellison, G. B., & Evans, R. J. (2003). Enhancement of 1,2-dehydration of alcohols by alkali cations and protons: a model for dehydration of carbohydrates. *Journal of Analytical & Applied Pyrolysis*, *66*(1), 3–27.

Olivier-Bourbigou, H., Magna, L., & Morvan, D. (2010). Ionic liquids and catalysis: recent progress from knowledge to applications. *Applied Catalysis A General*, *373*(1), 1–56.

Segal, L., Creely, J. J., Martin, A. E., & Conrad, C. M. (1959). An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Textile Research Journal*, *29*(10), 786–794.

Shen, D. K., & Gu, S. (2009). The mechanism for thermal decomposition of cellulose and its main products. *Bioresource Technology*, *100*(24), 6496–6504.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of cellose with ionic liquids. *Journal of the American Chemical Society*, *124*(18), 4974–4975.

Wang, S. R., Liao, Y. F., Tan, H., Luo, Z. Y., & Cen, K. F. (2003). Mechanism of cellulose rapid pyrolysis II. Mechanism analysis. *Journal of Fuel Chemistry & Technology*, *31*(4), 317–321.

Xiao, S., Bing, L., Wang, Y., Fang, Z., & Zhang, Z. (2014). Efficient conversion of cellulose into biofuel precursor 5-hydroxymethylfurfural in dimethyl sulfoxide–ionic liquid mixtures. *Bioresource Technology*, *151*(1), 361–366.

Yan, X., Zhang, Z., Xin, W., Bing, L., & Lin, J. (2014). Hydrolysis of cellulose in ionic liquids catalyzed by a magnetically-recoverable solid acid catalyst. *Chemical Engineering Journal*, *235*(1), 349–355.

Zhao, D., Li, H., Zhang, J., Fu, L., Liu, M., Fu, J., et al. (2012). Dissolution of cellulose in phosphate-based ionic liquids. *Carbohydrate Polymers*, *87*(2), 1490–1494.

Zhu, G., Zhu, X., Xiao, Z., & Yi, F. (2012). Study of cellulose pyrolysis using an in situ visualization technique and thermogravimetric analyzer. *Journal of Analytical & Applied Pyrolysis*, *94*, 126–130.