Advances in Natural Science
Vol. **4**, No. **1**, **2011**, pp.52-57
www.cscanada.net

ISSN 1715-7862 [PRINT]
ISSN 1715-7870 [ONLINE]
www.cscanada.org

XRD Characterization of Phenol Liquefied Chinese Fir Residues

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Abstract: The amount of wood residue is used as a measurement of the extent of wood liquefaction. Characterization of the residue from wood liquefaction provides a new approach to understand some fundamental aspects of the liquefaction reaction. This paper adopts X-ray diffraction to characterize the changes of groups and mechanism of reaction of the residue crystallinity in the liquefaction process of Chinese Fir. The XRD analysis of liquefaction residue showed that amorphous region is firstly damaged so that the crystallinity could be in the trend of increasing in the liquefaction process of Chinese fir in most cases with the time's prolonging. However, cellulose crystalline region begins to be destroyed under the higher liquefied temperature (170℃） or in the case of higher P/W (w/w) ratio (5), leading to the relative decreased trend of crystallinity.
Key words: Chinese Fir; XRD; Liquefaction; Residue

DOI: 10.3968/j.ans.1715787020110401007

INTRODUCTION

Chinese fir is one of the main mimosa tree species in the south of China. At present the scale of planting has been quite big. Fir liquefaction objects can be used to replace phenol in the phenolic resin manufacturing carpentry. [1] To make full use of the rich resources and to maximize the economic value is positive. Studies have shown that, under certain conditions, the phenol or more hydroxyl alcohol can make lumber realize liquefaction. The cellulose, half cellulose and lignin of wood could change into liquid substances with certain biological activity, and become a kind of polymer material. The utilization rate can reach 100%, so wood liquefaction becomes a new field of wood research in recent years. [2-4] Liquefaction, as one of the main ways of biomass use, has been paid more attention by the domestic and foreign scholars.

The crystallinity index is the percentage of crystalline region made of cellulose for the whole, which reflects the degree of cellulose crystallization of the wood, and also reflects the physical and chemical properties of the wood fiber to some extent. As a result, the research of wood crystallinity would be helpful in learning about the property of wood fibrous material from the structure and composition. At present, the

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† Received April 10, 2011; accepted June 17, 2011.

main methods of determination of wood crystallinity include X-ray diffraction method (XRD), Infrared spectroscopy (IR), Nuclear magnetic resonance spectroscopy (NMR) and Dynamic mechanical spectroscopy (DMS). This paper adopts XRD to characterize the variation of the residue crystallinity in the liquefaction process of Chinese Fir.

MATERIALS AND METHODS

Experimental Materials

Chinese Fir (*Cunningham ia lanceolata*) tree wood was purchased from Chengdu Tree Farm of Chinese Academy of Forestry, it was 36 years old and its diameter was 230mm. The wood was sawn on a laboratory table saw after debarked and the saw dust was collected. The particles were reduced in a Wiley mill to fine powder of 20-200 mesh. The wood powder were oven dried at 103±2℃ for more than 12 hours and then cooled to room temperature before used for the liquefied tests. Liquid analytical grade phenol was used as the liquefaction reagent. Sulfuric acid (98% concentration) was purchased from Beijing Chemical Factory as the catalyst of liquefaction. All other chemicals were analytical grade.

Experimental Method

Preparation of Chinese Fir liquefied Residues

Wood flour, phenol (added with different liquor ratio) and catalyst (according to quality percent of the liquefier phenol) were mixed in a container until a uniform mixture was obtained. The mixture was then transferred to the 500ml three-neck flask reactor equipped with a condenser and a stirring system. Open the stirring apparatus (stirring rate of 1058rpm) for liquefying reaction and time the reaction to predetermined liquefied time. The liquefied mixture was diluted with acetone and filtered with Whattman medium flow filter paper. Adopt glass crucible filter (type of G3, aperture of filter board: 16~30μm), filter in the Vacuum Pump (vacuum degree: 0.095MPa), use acetone to flush liquefied content until filtrate is colorless, and then get insoluble residue. The insoluble residues were oven dried at 105℃ over 6 hours and stored in a desiccator.

X-ray Diffraction Analysis of Chinese Fir Liquefaction Residue

The wood liquefaction residues were ground into powder by a mortar before the XRD measurements. XRD measurements were performed on an X-ray Diffractometer (XRD-6000X, Shimadzu Co., Japan). The scanning range was 5 ~ 40deg at a scanning rate of 2deg/min and the stepping was 0.2deg.

The relative crystallinity c (%) was calculated according to the proportion of diffraction peak crystallization area to the total area, by the following formula 1:

$$c(\%) = \frac{I_a - I_b}{I_a} \times 100 \qquad (1)$$

Here, I_a is the total area under the diffraction peak and I_b is the area of amorphous region.

RESULTS AND DISCUSSION

Phenol, ratio of phenol to Chinese Fir (w/w), liquefied temperature, catalyst content and liquefied time are the main factors which influence the phenol liquefaction efficiency of Chinese Fir.

Effect of Liquefied Time on Crystallinity

With the extension of reaction time, crystallinity will change in the evolution from Chinese Fir wood flour to residue. When reaction temperature was 150℃, the ratio of phenol to Chinese Fir (w/w) was 4/1, catalyst

content was 6%,and liquefied time were 60min,120min,180min respectively, effect of liquefaction time on residue crystallinity can be depicted in Fig.1. 0min in the Figure is the China fir control group.

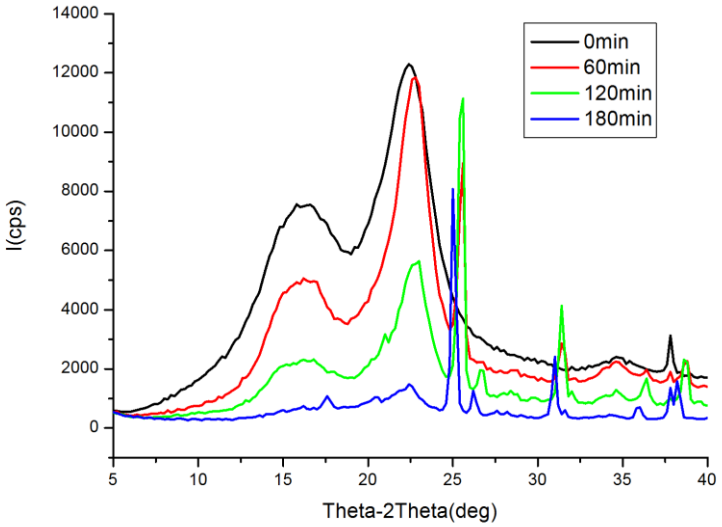

Figure 1
Effect of Liquefied Time on Crystallinity of the Wood Liquefied Residue

It can be seen from Fig.1 that Chinese fir wood flour as the control group gets diffraction peak at 16deg and 22deg, which shows appearing smooth surface, and this is the reflection of cellulose crystalline region. Residue at the time of 60min、120min、180min has weakened differently in the diffraction peak of 16deg and 22deg,which shows that cellulose crystalline regions are damaged to various extents, proving cellulose of the liquefaction residue is liquefied gradually, with the extension of time, reduction of peak becomes more and more significant, which illustrates that the liquefaction degree and efficiency of cellulose become higher and higher.

Meanwhile, it appears new diffraction peak different from China fir wood flour at 25deg, and the peak becomes stronger and stronger with the extension of time, which shows that new crystalline region comes about. The new crystalline region may be the newly polymer generated by liquefaction.

Effect of Liquefied Temperature on Crystallinity

When the P/W ratio is 4/1, catalyst content is 6%,and liquefied time are 30min,60min, 90min,120min,150min,180min respectively, effect of liquefied temperature on crystallinity can be seen in Fig . 2.

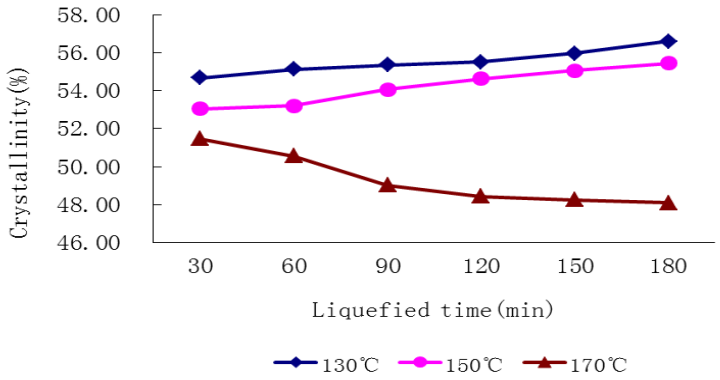

Figure 2
Effect of Temperature on Crystallinity

The crystallinity of liquefied wood residue was increased as the function of time at 130 ℃ and 150 ℃ (as seen in Fig. 2). But it was decreased with the extension of time at 170 ℃.The reason is that at 130℃ and 150℃, lignin and other amorphous region in China fir degraded first along with the proceeding of liquefaction, whereas the crystalline region of the cellulose wasn't damaged, which makes relative crystallinity go up. A similar result was also found by other researchers. But under the higher temperature of 170℃,cellulose of the residue is damaged more and more, which causes crystallinity to decease.

Then in the meantime, the higher the temperature, the smaller the residue crystallinity becomes. The likely cause for this is that higher temperature makes cellulose response more quickly and crystalline region is damaged.

Effect of Catalyst Contents on Crystallinity

When the reaction temperature is 150℃, the quality ratio of phenol and Chinese Fir is 4/1, and liquefied time are 30min,60min,90min,120min,150min,180min respectively, Effect of catalyst content on crystallinity can be seen in Fig 3.

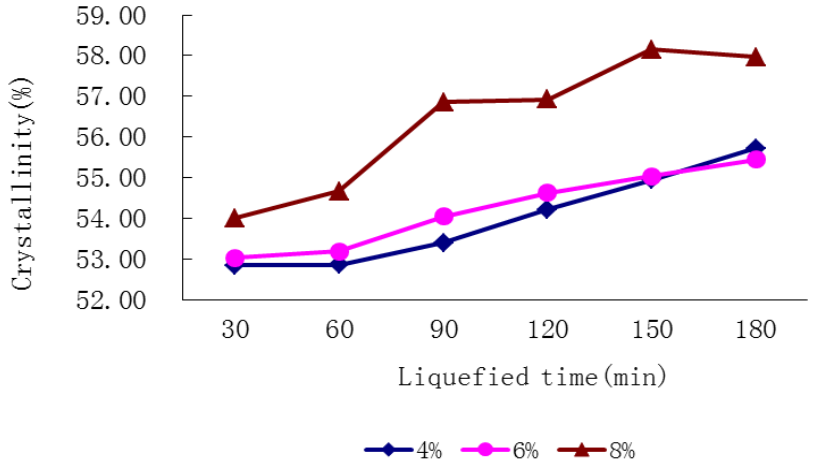

Figure 3
Effect of Catalyst Content on Crystallinity

It can be showed that under the different level of each catalyst, residue crystallinity is increasing with the extension of reaction time, and the explanation of this is that lignin of amorphous region reacts, which makes relative crystallinity increase, meanwhile, the more the catalyst content, the higher crystallinity becomes, and it may be that when the level is higher, lignin of amorphous region reacts, but the reaction of cellulose crystalline region is not obvious, which leads to the increase of relative crystallinity.

Effect of P/W Ratio (w/w) on Crystallinity

Quality ratio of phenol to Chinese Fir is an important index for measuring phenol dosage and also an important factor to influence liquefying efficiency of Chinese Fir. When the reaction temperature is 150℃, catalyst content is 6%, and liquefied time are 30min,60min,90min,120min,150min,180min respectively, Effect of P/W ratio on crystallinity can be seen in Fig 4.

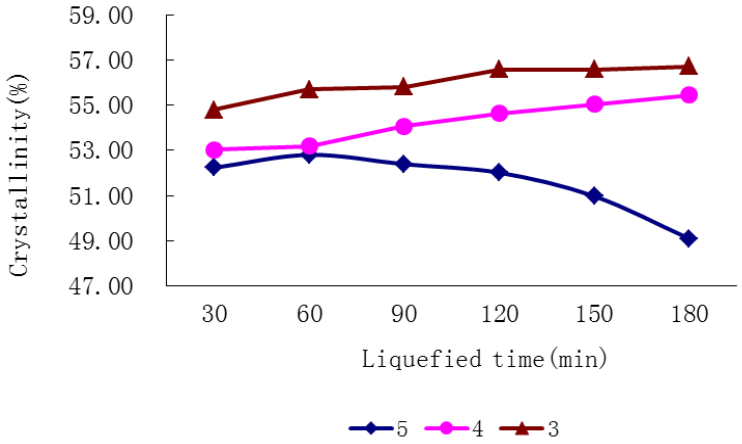

Figure 4
Effect of P/W ratio (w/w) on Crystallinity

It can be seen from Fig. 4 that when P/W ratio is 3, variation trend of residue crystalinity is going up with the extension of reaction time. When P/W ratio is 4, residue crystalinity also rises with the increase of time. But when the ratio is 5, the trend of crystalinity is different from the first two, which declines with the variation of time. The likely reason for this is that when P/W ratio is 3 and 4, lignin of amorphous region reacts first with the proceeding of liquefaction, and the content gets low, while the damage of cellulose crystalline region is not obvious, which makes relative crystalinity rise, but when the ratio is 5, more and more cellulose of the residue is damaged, which leading to the decrease of crystalinity.

It also can be seen that at the same time, the higher the ratio, the smaller the residue crystalinity becomes. The reason for this may be the higher P/W ratio can help cellulose react more quickly, which damage crystalline region, so that crystalinity gets smaller.

CONCLUSIONS

XRD analysis of liquefaction residue indicates that morphous region is damaged prior to crystalline region in the process of liquefaction of Chinese Fir, so that crystalinity increases with the extension of time. But in the situation of high liquefied temperature or high ratio, cellulose crystalline region begins to be damaged, which causes the decrease trend for the relative crystalinity.

In the meantime, when the level of liquefied temperature and ratio go up, crystalinity gets the trend of decrease. It also explains that higher temperature and P/W ratio can help cellulose get reaction, and damage the crystalline region, leading to the decrease of crystalinity. Instead, crystalinity goes up with the increase of catalyst content, which shows that the increase of catalyst content is helpless for cellulose reaction, and catalyst just plays a major role in the reaction of amorphous region materials.

During the liquefaction of Chinese Fir, amorphous region always gets reaction first, but crystalline region can just react well under the higher temperature and P/W ratio, showing as the decrease of crystalinity, meanwhile, new crystalline compounds generated in the reaction process could influence the calculation of crystalinity. In addition the XRD result of the liquefied wood residue also gives a piece of supporting evidence for an explanation to the result in the previous study.

ACKNOWLEDGEMENTS

This work was financially supported by the construction project of Beijing municipal education commission and wood carbon fiber chemistry reaction, the subtle structure and its regulation technology research (201004057).

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