

## **CHEMICAL MODIFICATION OF POPLAR WOOD IN GAS- AND LIQUID-PHASE ACETYLATION**

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### **ABSTRACT**

With the pure acetic anhydride as acetylation agent for the poplar wood acetylation modification, the influence of the processing temperature (140-175°C) and the processing time (2-4 h) on the acetylation yield with both gas- and liquid-phase methods was investigated. Experimental results showed that as the temperature and the reaction time increase, the acetylation yield increases gradually. The acetylation yield was above 26 % with the temperature of 175°C for 4 hours with gas-phase method. A modified rate equation was applied to the results of the acetylation of wood. The rate parameters such as the rate constant, ultimate extent of the reaction, and the reagent diffusion factor for the modified equation were calculated.

**KEYWORDS:** Poplar wood acetylation, gas- and liquid-phase method, acetic anhydride, reaction rate.

### **INTRODUCTION**

Due to its utilization as a sustainable and carbon-neutral resource, wood modification has been shown to be very important in improving bio-material performances. Although there are several cost-intensive ways, e.g. pyrolysis (Gu et al. 2013), esterification (Peng et al. 2008; Yan et al. 2008; Xiong et al. 2009; Zhao et al. 2009), hydrogenation (Elliott 2007; Tang et al. 2009), and catalytic reforming (Gayubo et al. 2004a,b; Nilsen et al. 2007), the acetylation is still a promising method to upgrade the ordinary wood substrate. With great dimensional stability (Stamm and

Tarkow 1947), resistance to weathering (Feist et al. 1991) and biodegradation (Ohkoshi et al. 1999), wood acetylation with acetic anhydride has always received the most attention and the acetylated product is even commercialized in European countries. Meanwhile, fundamental studies on the topic continue until now, which will contribute to the progressive application of acetylation. For wood acetylation as chemical modification, the agent of acetic anhydride reacting with molecules of wood on hydroxyl, hydrophobic acetyl replaced the hydrophilic hydroxyl. Acetylated wood have advantages such as uniform density, smooth surface, dimensional stability, strong corrosion resistance, low heat ductility and decreasing the toxicity, etc.

Current research found low acetylation agent efficiency, e.g., about 85 % of anhydride not participating in the reaction (Kazuya and Yuko 2004, Eiichi and Kazuya 2009). Acetylated materials are produced in all cases but different reactions can lead to different performances, and the benefits of the acetylation treatment are strongly dependent on the process conditions and methods. For instance, the by-products generated by the different acetylation methods may bring a variable impact on the material properties. With acetyl chloride as reactant, a strong acid - hydrochloric acid - is released, which catalyzes the hydrolysis of cellulose and leads to important strength losses of the material (Hill 2006). A weaker acid - acetic acid - is liberated when acetylation is performed with acetic anhydride during liquid-phase acetylation, but this compound is generally hard to remove from wood after reaction, imparting an undesirable odor to the wood and causing strength losses or the corrosion of metal fasteners (Larsson 2002; Li et al. 2000). Some researchers found that potassium acetate KAc (Li et al. 2001; Obataya and Minato 2008, 2009a,b) showed catalytic effect for wood acetylation and reaction kinetics were also discussed (Ramsden and Blake 1997; Hill et al. 1998; Minato and Ogura 2003; Minato 2004). Pyridine could also be used as a catalyst in order to address the effect of the anhydride type on the sorption and the biological properties of modified wood (Papadopoulos and Hill 2002, 2003, Papadopoulos et al. 2008a, b). However, little attention has been paid to the difference of gas- and liquid-phase acetylation.

In the present paper, a comparative study on the acetylation of poplar wood by gas- and liquid-phase methods is proposed, and the differences between the two reaction processes were also investigated. Furthermore, the reaction rate of gas-phase is compared to that of the liquid-phase acetylation, for the purpose of indicating the potential of gas-phase acetylation method for extraordinary rapid acetylation of wood.

## MATERIAL AND METHODS

Poplar wood (size 20×20×10 mm), produced in Jiangsu, with 105°C drying for 24 h was applied as substrate in the experiments. A DHG-9146 type electro-thermal constant temperature drying oven and a Nicolet FT-IR infrared spectrometer were used as characterization instruments.

Fig. 1a illustrates the apparatus used for wood gas-phase acetylation. Acetic anhydride (10 ml) was placed in the bottom of a glass flask (100 cm<sup>3</sup>) equipped with a reflux condenser. To prevent the reagent from rippling and wetting the wood specimens, glass filling and PTFE mesh were added. The wood sample was then placed in glass flasks, and the flask was heated at 140-175°C for 0.5-4 h using an oil bath. After the treatment, the wood sample was removed from the flasks and soaked in cold water to stop the reaction. Fig. 1b illustrates the apparatus used for wood liquid-phase acetylation. Similarly, acetic anhydride (30 ml) was placed in the bottom of a glass flask (100 cm<sup>3</sup>) equipped with a reflux condenser. And the wood sample was directly placed in glass flasks, then the flask was heated at 90-130°C for 2-10 h using an oil bath. After the treatment, the wood sample was removed from the flasks and soaked in cold water to stop the reaction.

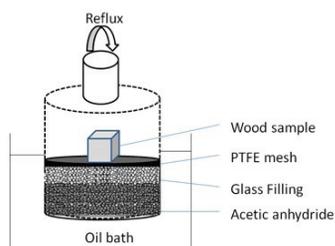


Fig. 1a: Apparatus for gas-phase acetylation.

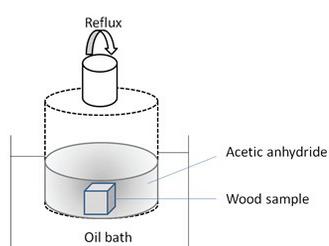
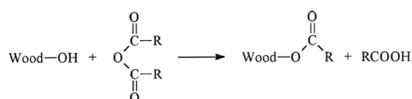


Fig. 1b: Apparatus for liquid-phase acetylation.

The reaction between wood and linear chain anhydrides is a single site reaction as depicted in chemical formula (see below). The extent of reaction was calculated as weight percent gain (WPG) determined by the differences in oven dry weight of the sample before modification ( $W_1$ ) and after modification ( $W_2$ ) according to equation (weight percent gain (WPG) =  $(W_2 - W_1) / W_1 \times 100\%$ ).



Anhydride modification scheme, where  $R = \text{CH}_3$  (acetic anhydride).

## RESULTS AND DISCUSSION

### Acetylation analysis

Fig. 2a showed the effects of the reaction temperature and reaction time on the WPG of treated samples. The WPG increased with the increase of reaction temperature and reaction time. The acetylated wood measured 6.69 % WPG at 1 h and 14.92 % WPG at 2 h when the reaction temperature was 140°C. Then the acetylated wood showed a small weight gain with the increase of temperature and the WPG was 18.79 % at 4 h. At 140°C, the WPGs of the acetylated wood increased quickly with the reaction period from 1 to 2 h.

At 150°C, the WPG was only 0.29 % more than that at 140°C when the reaction time reached 2 h. At 150°C, the acetylated wood was measured 19.73 % WPG at 4 h, which was 0.94 % more than that at 140°C in the same reaction time. Therefore, the improvement of the reaction temperature due to the effect of promoting initial stage of acetylation reaction was obvious.

At 160°C the WPG of the acetylated wood increased quickly than that at 150°C, e.g., the WPG was 18.87 % at 2 h. The acetylated wood showed a small weight gain after reacting for 3 h. The WPG of two periods from 3 to 4 h were 0.05, 0.11 % respectively. It was shown that the reaction time was not the prominent factor for the increase of acetylated rate.

The WPG of the acetylated wood increased obviously when the reaction temperature reached 170°C above. At 170°C, as the reaction time increased from 2 to 4 h, the WPG of acetylated wood increased from 21.82 to 24.07 %. At 175°C, the WPG of acetylated wood increased from 21.92 to 26.09 % at the same conditions. This WPG result apparently exceeded the recent wood acetylation result with the similar reaction time (Antonios and Georgia 2010). Thus it can be seen, with reaction temperature 170°C above, increasing the temperature led to the

WPG increase apparently, which was related to a tendency to the carbonization of the acetylated sample as the temperature increased.

In order to show the superiority of gas-phase method, we carried on liquid-phase acetylation experiments for comparison. The experimental results (Fig. 2b) showed that the WPG reached the maximum value at 8 h in liquid phase and the acetylated wood showed a small decrease trend when continual increasing the temperature.

At 110°C, the WPG was 8.3 % at 2 h in liquid phase, which was 0.3 % less than that at 170°C for 0.5 h in gas phase. At 120°C, the WPG was 17.91 % at 8 h, which had a certain increase in small degree as compared with that at 110°C. At 120°C, as the reaction time increased from 4 to 8 h, the WPG of acetylated wood increased from 12.36 to 17.91 %.

When the reaction temperature reached 130°C, the increase of WPG was obvious as the reaction time increased. The WPG was 22.63 % at 8 h. Under the conditions of 130°C, the excretion of massive acetic acid as the by-products of acetylation promoted the increase of WPG in some degree. In addition, we also found that the WPG increased was apparent with the reaction time range of 4-8 h during liquid-phase acetylation.

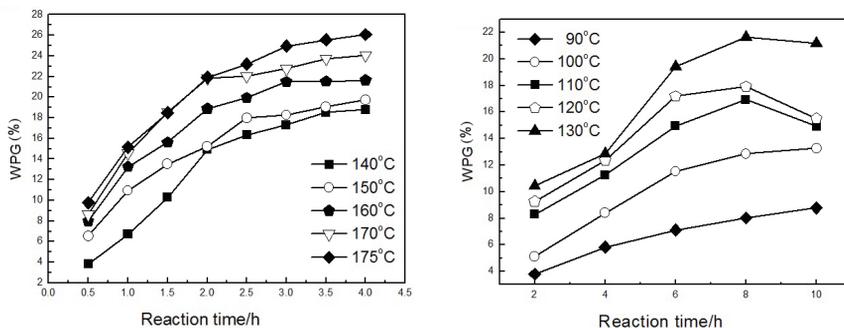


Fig. 2a: Weight percent gain of gas-phase acetylation.

Fig. 2b: Weight percent gain of liquid-phase acetylation.

To characterize the reaction profile of gas- and liquid-phase acetylation methods, we applied the modified rate Eq. 1 (Minato 2004):

$$\text{WPG} = a \times (1 - e^{-kt})^{1/n} \quad (1)$$

where:  $t$  - the reaction time,  
 $a$  - the ultimate WPG (%);  
 $k$  - the rate constant ( $\text{h}^{-1}$ );  
 $n$  - factor that reflects the hindrance to the diffusion of the reagent at the reaction site.

Tab. 1 summarizes the reaction parameters. The high  $k$  value in the gas-phase acetylation indicated an accelerated reaction compared with liquid-phase acetylation. For both acetylation methods, the reaction rate constant also increased with the increase of reaction temperature. In addition, the high  $n$  value in the gas-phase acetylation suggested a diffusion-controlled reaction in which the supply of reagent is at a reduced rate compared with the rate of reaction within the wood cell wall. Furthermore, the gas-phase acetylation reaction effect was obviously greater than that of the KAc catalyzed or pyridine catalyzed acetylation results.

Tab. 1: Estimated acetylation reaction parameters.

| Reaction system                 | Temperature (°C) | A (%) | K (h <sup>-1</sup> ) | n     | Coefficient R <sup>2</sup> |
|---------------------------------|------------------|-------|----------------------|-------|----------------------------|
| Gas-phase acetylation           | 140              | 20.08 | 1.06                 | 1.82  | 0.962                      |
|                                 | 150              | 20.80 | 1.26                 | 1.93  | 0.990                      |
|                                 | 160              | 22.73 | 1.68                 | 1.98  | 0.991                      |
|                                 | 170              | 24.79 | 2.53                 | 3.51  | 0.989                      |
|                                 | 175              | 27.02 | 5.94                 | 7.24  | 0.994                      |
| Liquid-phase acetylation        | 90               | 10.51 | 0.0801               | 0.335 | 0.991                      |
|                                 | 100              | 15.64 | 0.0999               | 0.488 | 0.976                      |
|                                 | 110              | 19.44 | 0.240                | 0.985 | 0.943                      |
|                                 | 120              | 20.39 | 0.285                | 1.05  | 0.952                      |
|                                 | 130              | 27.05 | 0.385                | 1.94  | 0.941                      |
| KAc catalyzed <sup>a</sup>      | 120              | 30    | 0.735                | 9.61  | 0.991                      |
| Pyridine catalyzed <sup>a</sup> | 120              | 30    | 0.442                | 5.34  | 0.973                      |

a: data from reference results (Obataya and Minato 2008).

### FTIR analysis

The absorption peaks of related groups in acetylation are: -OH absorption peak at 3400 cm<sup>-1</sup>, saturated esters carbonyl absorption peak at 1742 cm<sup>-1</sup>, -CH of acetate, absorption peak at 1384 cm<sup>-1</sup>, C-O of acetyl absorption peak at 1248 cm<sup>-1</sup>. The absorption peaks of acetylated wood related groups were strengthened obviously as shown in Fig. 3a. And integration of FTIR data of several related absorption peaks resulted was also shown in Fig. 3b.

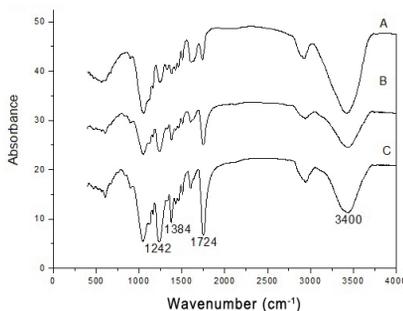


Fig. 3a: Comprehensive comparison of different treatment acetylation samples.

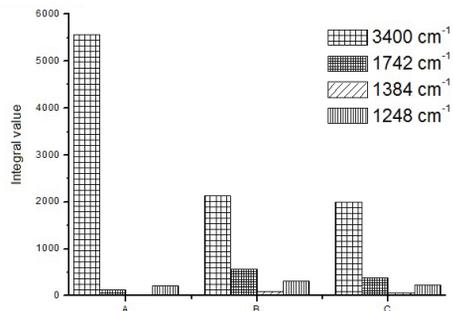


Fig. 3b: Integral value of related groups absorption peaks.

Note: A) the substrate sample; B) the acetylated wood with liquid-phase acetylation at 130°C for 8 h; C) the acetylated wood with gas-phase acetylation at 175°C for 4 h.

The hydroxyl absorption peak at 3400 cm<sup>-1</sup> had largely reduced after acetylation as shown in Fig. 3b, the amount of reduced hydroxyl was above 60 %. Because of some water content in the wood, the amount of reduced hydroxyl can't reach zero. As compared with the substrate sample, we can see the acetylation significantly occur from several of acetyl characteristic peaks, especially the absorption peak of saturated esters carbonyl at 1742 cm<sup>-1</sup> increased obviously,

average amounting up to 300 times or so, e.g., the maximum group can reach 373.76 times. Meanwhile, the average amount of the absorption peak of -CH in the acetate at 1384  $\text{cm}^{-1}$  increased up to 158 times and the average amount of the absorption peaks of acetyl C-O at 1248  $\text{cm}^{-1}$  up to about 50 times.

## CONCLUSIONS

Gas- and liquid-phase acetylation was conducted on poplar wood with different reaction time and temperature. As the extension of the temperature and reaction time, the acetylation yield increased gradually. For gas-phase acetylation, the acetylation yield was above 26 % with the temperature of 175°C for 4 hours. The acetylation rate is 2.27 %/h in liquid-phase acetylation and the acetylation ratio of gas-phase is 7.21 %/h, which was 3.18 times of the former method. The weight gain, WPG (%), attained at reaction time  $t$  (h), for various temperatures of different acetylation methods were analyzed by applying a modified rate equation  $WPG = a \times (1 - e^{-kt})^{1/n}$ , where  $a$  is the ultimate weight gain (%),  $k$  is the rate constant ( $\text{h}^{-1}$ ), and  $n$  is a measure of the hindrance against the diffusion of reagent. The above acetylation rate parameters results indicated the potential of gas-phase acetylation method for extraordinary rapid acetylation of wood. Therefore, the gas-phase method is a high yield of acetylation method with the advantage of pure acetic anhydride as reagent, no adding other solvents and short reaction period.

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