

Investigation of acetylation degree of mercerized pine wood (*Pinus sylvestris* L.) dried by different methods

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Abstract: *Investigation of acetylation degree of mercerized pine wood (*Pinus sylvestris* L.) dried by different methods.* In this study the acetylation degree of mercerized pine wood was studied (*Pinus sylvestris* L.) depending on the reaction time. Chips used in this mercerization process were air-dry. Then the effect of the drying method on the chip acetylation efficiency was evaluated. The reaction progress was measured by values of the acid number (AN) and of the weight percent gain (WPG). It was found that with increasing esterification time its yield increases. Also the method of removing water from the timber structure has an influence on the degree of esterification. The worst results were obtained for chips dried under vacuum.

Keywords: pine, acetylation, mercerization, drying

INTRODUCTION

In order to improve the properties of wood and eliminate its disadvantages it is subjected to modification. The modification methods can be active or passive (Hill, 2006). Chemical modification of wood is an active method and should be presented as a reaction between the reactive groups from wood and modifying, mainly acetylating, agent. There arise covalent bonds between OH groups and acetylating compound (Rowell, 2005). The most widely used method for the chemical modification of wood, also in technical scale, is acetylation using acetic anhydride (CH₃CO)₂O as a reagent. The reaction rate can be increased by the use of catalysts which can be pyridine, zinc chloride, ammonium sulfate, urea and sodium acetate (Doczekalska, 2010). Wood acetylation reaction can be carried out even without using a catalyst because the mercerization takes to move apart from each carbohydrate chains in the wood. As a result of this there is an easier access of the acetylating agent to hydroxyl groups.

Factors that affect mainly the reaction rate is temperature, time and method of drying wood (Hill, 2006). Generally, the longer reaction time the greater number of functional groups of wood are substituted. Some methods of drying depends on the moisture of the material which affects the acetylating agent access to hydroxyl groups of wood.

The aim of this study was to carry out esterification (acetylation) of crumbled and mercerized with acetic anhydride pine wood (*Pinus sylvestris* L.).

The effect of reaction time on the degree of esterification and the dependence of wood mercerization drying method on the reactivity of wood was estimated. The degree of wood acetylation was measured using the acid number (AN) and the weight percent gain (WPG).

MATERIAL AND METHODS

Scots pine sapwood was used in the study, in the chips fraction of 0.5-1.0 mm. Acetylation was carried out using acetic anhydride. The reaction was carried out under reflux,

which was xylene (pure). Mercerization of wood was carried out in 10% sodium hydroxide for 1 hour at room temperature.

Wood acetylation reaction was carried out on mercerized wood chips in three drying variants:

- 1) air-dried wood chips,
- 2) air-dried wood chips with the water removed by azeotropic cap,
- 3) wood chips dried in a vacuum oven. Wood chips were dried in a vacuum oven at 70°C at a pressure of 0.4 kPa. The drying process was led in 48 h.

In the variant I and II of acetylation reaction respectively, it was collected 2.15g of chips with a moisture content of 7.6% (2 g based on absolutely dry wood) and for variant III – 2 g of chips were dried under vacuum and placed in a round bottom flask of 250 cm³. It was added 9.4 ml (1mol/dm³) of acetic anhydride and 100 cm³ of xylene to the flask, then it was flask with a reflux condenser connected and placed in a dish heating. Reactions were conducted with air-dry chips (variant I) for times the reaction of 2, 4 and 8 h. Reactions using azeotropic cap (variant II) and vacuum-dried chips (variant III) were carried out only at the time of 4h. Wood after modification was extracted with a mixture of chloroform-ethanol (93:7, v/v) for 8 hours. Then it was WPG and acid number (AN) determined by titration (Doczekalska, 2010).

RESULTS AND DISCUSSION

Acid number (AN) of raw pine wood was calculated as 2.1. Such a high value is due to the content of resin acids present in some species of conifers, including pines. A zero value AN of mercerized wood was due to its neutralization with NaOH. The data (Fig. 1, Tab. 1.) shows that with increasing reaction time there is an increase in both values of the acid number and weight percent gain. For a given values of time, the acetylation process efficiency is directly proportional to its duration. The difference between the yield of the modification for 2 and 4 h is small - amounts to 0.7 for DT and 1.8% for WPG. However, for a reaction time of 8h process efficiency increases significantly compared to the response time of 4h - AN change by 4.5 and WPG change by 7.2%. The same observations have been described in the literature (Marcovich et al., 2001, Doczekalska, 2010).

For these data, the particle size of esterification factor and its chemical structure has a significant impact on the degree of wood modification. In the next step, it was examined how the process of wood acetylation runs. Process lasted 4 hours. Wood was dried with three different methods.

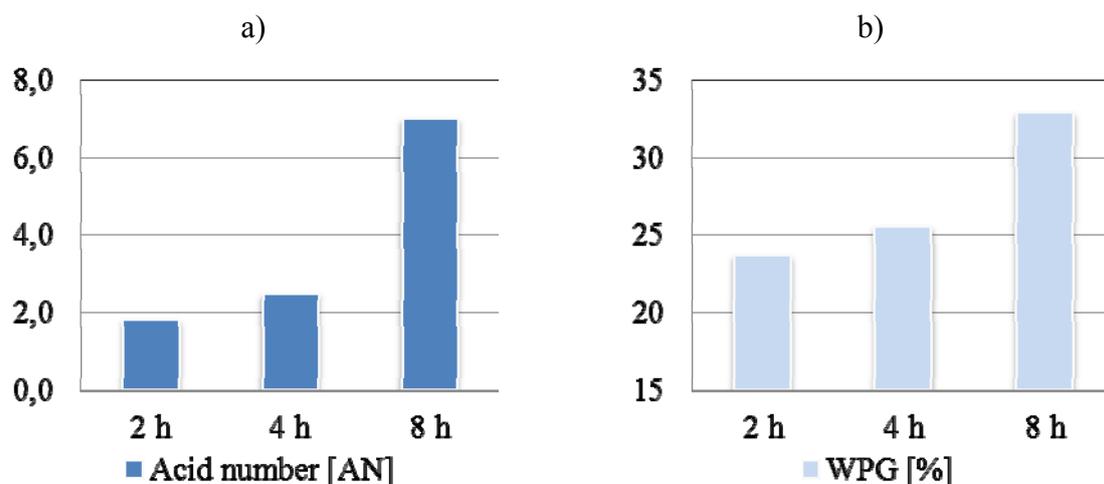


Fig.1. Air-dried wood chips AN a) and WPG b) dependence on the reaction time

Tab. 1. Calculations results of acid number (AN) and rate of weight gain for chips dried by different methods

	4h - air-dried wood chips	4h – vacuum dried wood chips	4h – wood chips, water removed by azeotropic cap
Acid number [AN]	2,5	2,7	5,0
WPG [%]	25,5	17,0	21,3

The moisture content of the wood has a positive effect on the efficiency of the process. Water causes swelling of the cell wall, which facilitates penetration into the interior anhydride. In the case where the wood is completely dry cell wall is not available for reagent (Hill, 2006).

It was made an attempt to verify this assertion, checking how a method of drying pine chips, (aggressive method of removing water from the wood structure) affects the degree of modification. The presented data show that the moisture content of the wood has a pronounced effect on the performance of acetylation reaction measured by coefficients AN and WPG. The worst results are obtained in the case of the vacuum drying of wood chips.

This may result from the fact that during the most intense drying method pores are getting narrowed and closed (in papermaking, the term actinic is used) through which the reagent, in this case acetic anhydride, has limited access to the interior of the wood. In the case of vacuum drying method application wood obtained a zero humidity, which is the lowest WPG amounting to 17%.

The highest value of WPG was obtained for air-dried wood that was characterized by the highest initial moisture content. In this case, the way of removing water proceeded in the mildest conditions, which could affect the behavior of the porous structure of wood chips.

CONCLUSION

The obtained results allow to draw the following conclusions:

1. The obtained values of AN and WPG indicate that with increasing running time of the esterification there is an increasing number of substitution of the hydroxyl groups of pine wood tested, the reaction efficiency is increased.

2. A method of removing water from the wood structure has an impact on the degree of esterification. Water causes swelling of the cell wall, which facilitates the penetration of acetic anhydride to the inside. Increasing the intensity of the process of removing water from the timber causes the deterioration of its acetylation. The worst conditions of modification were obtained for chips in which the water was removed by vacuum and at elevated temperatures.

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Streszczenie: *Badanie stopnia acetylacji merceryzowanego drewna sosny (Pinus sylvestris L.) suszonego różnymi metodami. W pracy badano stopień acetylacji merceryzowanego drewna sosny (Pinus sylvestris L.), w zależności od czasu acetylacji. Wióry po procesie merceryzacji sezonowano do osiągnięcia wilgotności powietrzno suchej. Następnie zbadano wpływ metody suszenia wiórów na wydajność procesu acetylacji. Postęp reakcji mierzony był wartościami liczby kwasowej (AN) i wskaźnika procentowej zmiany masy (WPG). Stwierdzono, że wraz z wydłużeniem czasu prowadzenia estryfikacji zwiększa się wydajność reakcji oraz że sposób usuwania wody ze struktury drewna ma wpływ na jego stopień estryfikacji. Najniższy stopień acetylacji (Najgorsze wyniki acetylacji) drewna merceryzowanego uzyskano dla drewna suszonego metodą próżniową, najwyższy natomiast dla drewna suszonego na powietrzu.*

Słowa kluczowe: sosna, acetylacja, merceryzacja, suszenie

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