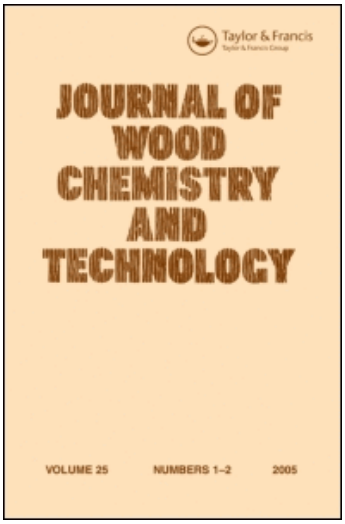


**Journal of Wood Chemistry and Technology**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597282

# Acetylation of Wood with Various Catalysts

Nihat Sami Çetin[a]; Nilgül Özmen[a]; Emre Birinci[a]
[a] Kahramanmaraş Sütçü İmam University, Faculty of Forestry, Kahramanmaraş, Turkey

First published on: 03 May 2011

**To cite this Article** Çetin, Nihat Sami , Özmen, Nilgül and Birinci, Emre(2011) 'Acetylation of Wood with Various Catalysts', Journal of Wood Chemistry and Technology, 31: 2, 142 — 153, First published on: 03 May 2011 (iFirst)
**To link to this Article: DOI:** 10.1080/02773813.2010.503981
**URL:** http://dx.doi.org/10.1080/02773813.2010.503981

*Journal of Wood Chemistry and Technology*, 31: 142–153, 2011

ISSN 0277-3813 print / 1532-2319 online
DOI: 10.1080/02773813.2010.503981



# Acetylation of Wood with Various Catalysts

**Nihat Sami Çetin, Nilgül Özmen, and Emre Birinci**
Kahramanmaraş Sütçü İmam University, Faculty of Forestry,
Kahramanmaraş, Turkey



**Abstract:** The purpose of this study was to compare two different acetylation mechanisms using acetic anhydride (AA) or vinyl acetate (VA) modification with using various catalysts. Acetylation of Scots pine wood flour with acetic anhydride could be significantly improved in the presence of potassium acetate, potassium carbonate, and sodium carbonate at 100°C. Sodium carbonate had low effect on VA acetylation, potassium acetate was found to be more effective, and potassium carbonate was better for vinyl acetate modification of wood flour. The two modification methods and the effect of different catalysts on AA or VA modification were characterized by infrared and NMR spectra and analyzed in detail. The acetylation of Scots pine flour with VA and AA showed almost the same WPG values for catalysts when based on long reaction times.

**Keywords:** Acetic anhydride, vinyl acetate, potassium acetate, potassium carbonate, sodium carbonate

## 1. INTRODUCTION

The chemical modification of wood has been the subject of research for many decades and dates back to 1928.[1] The chemical modification of wood with various reagents, including anhydrides (such as acetic, succinic, maleic, propionic, butyric, hexanoic, crotonic, and methacrylic), isocyanates, formaldehyde, acetaldehyde, epoxides (such as ethylene or propylene oxide, glycidyl methacrylate, allyl glycidyl ether, etc.), has been the subject of research for many decades.[2–9] Most of the modifications have been performed to improve

This paper has been carried out with financial support from the Kahramanmaras Sutcu Imam University-BAP 2010/3-12M. The authors wish to express their thanks to Mr. Alan Lightbody, UK, for his valuable suggestions and critical reading of the manuscript.

Address correspondence to Nihat Sami Çetin, Kahramanmaraş Sütçü İmam University, Faculty of Forestry, Kahramanmaraş 46060, Turkey. E-mail: nihatcetin@ksu.edu.tr

dimensional stability or decay resistance of the material. Among all the chemical modification reactions studied, acetylation with acetic anhydride is the most promising. An acetylation reaction has been the subject of extensive research and commercialization[9] and is currently in process. There are reports of a commercial acetylation plant for solid wood in Japan but few details are available.[8] In the Netherlands, Titan Wood is the first company to produce acetylated wood with acetic anhydride on a commercial scale. It is expected that, in the future, acetylated wood will replace the more toxic preservative treatments in many applications.[10]

Acetic anhydride modification can be performed with or without catalysts and co-solvents. [11] In earlier studies, various catalysts (such as pyridine, 4-dimethylamino pyridine, N-methyl pyrolidine, dimethyl formamide, potassium acetate, sodium acetate, zinc chloride, magnesium per chlorate, magnesium chloride hexahydrate, etc.) were used in acetylation of wood with acetic anhydride in order to increase reaction rate.[11–16] The main drawback of the acetic anhydride process is the formation of acetic acid as a by-product, which causes an unpleasant odor, corrosion of metal, and may reduce the strength of the material.[17]

Maritime pine sapwood has recently been successfully acetylated with a new transesterification reaction using vinyl acetate and a potassium carbonate catalyst.[18] The main advantages of this new technique are that vinyl acetate is cheaper than acetic anhydride and that acetaldehyde is produced as a by-product. Acetaldehyde is a non-acidic, low boiling point (bp $= 21^{\circ}$C) compound that is easily removed from modified wood after reaction.

In this study, classical acetylation of wood with acetic anhydride was compared with the acetylation method using vinyl acetate. In addition, the effect of various catalysts (potassium acetate, potassium carbonate, and sodium carbonate) on both acetylation methods of the modification of wood was determined.

As far as the authors are aware, there have been no reports of potassium carbonate and sodium carbonate being used in the acetylation of wood using acetic anhydride, and no reports of potassium acetate and sodium carbonate being used for the acetylation of wood using vinyl acetate. The reactions were performed on Scots pine (*Pinus slyvestris*) sapwood flour with dimethyl formamide as a solvent. Modified samples were characterized by weight percent gain (WPG) calculations, FTIR, and $^{13}$C CP-MAS NMR spectroscopy.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals

Acetic anhydride (AA), vinyl acetate (VA), dimethyl formamide (DMF), potassium acetate ($CH_3COOK$), potassium carbonate ($K_2CO_3$), sodium carbonate

($Na_2CO_3$), and pyridine were obtained from Merck. All chemicals were used as supplied without further purification.

## 2.2. Preparation of Wood Flour

For wood modification, Scots pine (*Pinus* slyvestris) sapwood was ground using a hammer mill and sieved to a size of 40 meshes. Before reaction, the samples were subjected to Soxhlet extraction with deionized water for 6 h, and then with a mixture of toluene:acetone:ethanol (4/1/1, vol./vol.) for 6 h. This was done to remove extractive materials from wood. After that, samples were oven-dried at 105°C, then allowed to cool in a desiccator containing phosphorous pentoxide, to cool to ambient temperature, before determination of weight.



## 2.3. Acetylation of Wood Flour

Extractive-free Scots pine sapwood flour was transferred to a round bottom flask containing DMF solution with acetic anhydride (AA) or vinyl acetate. All reactions were performed at 100°C. Initial vinyl acetate transesterification reaction conditions were derived from an earlier publication.[18]

Reaction was carried out with and without the inclusion of three catalysts, viz. potassium acetate, potassium carbonate, sodium carbonate. Various AA or VA concentrations (0, 14, 28, 42, 56, 70 mmol AA or VA/g dry wood), reaction times (30, 60, 120, 180, 360, 720 and 1440 min), various catalyst types and amounts (0.51, 1.02, 1.53, 2.04 mmol $CH_3COOK$, 0.36, 0.72, 1.1, 1.45 mmol $K_2CO_3$, 0.47, 0.94, 1.42, 1.89 mmol $Na_2CO_3$/g dry wood) were studied. For each reaction 1g wood flour was used and each set of conditions was repeated three times. At the end of the reaction, all modified samples were Soxhlet extracted with deionized water for 6 hours, then with toluene:acetone:ethanol mixture (4/1/1, vol./vol.) for 6 hours. This was done to remove excess unreacted chemicals and by-products. The Soxhlet thimble and contents were oven-dried overnight at 105°C, transferred to a desiccator containing phosphorus pentoxide until cool, then weight gain levels were calculated.

The weight percentage gain (WPG) was calculated according to the following equations, respectively.

$$WPG(\%) = \frac{W_2 - W_1}{W_1} \times 100$$

$W_1$ = Before treatment sample weight

$W_2$ = After treatment sample weight

## 2.4. Infrared Spectroscopy

Infrared absorption spectra of acetylated and unmodified wood flour were obtained with the KBr (potassium bromide) technique, using a Shimatzu 8400s FT-IR spectrometer, at a resolution of 4 $cm^{-1}$ (40 scans). In each case, 1% w/w of oven dry wood flour was dispersed in a matrix of KBr and pressed to form pellets.

## 2.5. $^{13}C$ and NMR CP-MAS Analysis

Solid state $^{13}C$ CP-MAS (Cross Polarisation-Magic Angle Spinning) NMR spectra of Scots pine wood flour were performed at room temperature on a Bruker DPX-400 NMR spectrometer (Bruker), using MAS rates of 4 and 8 kHz, a frequency of 100.61 MHz for $^{13}C$ NMR.



## 3. RESULTS AND DISCUSSION

Scots pine sapwood flour was esterified with either acetic anhydride (AA) or vinyl acetate (VA) and the reaction mechanisms are shown in Figure 1. In order to compare the classical acetic anhydride modification with the new VA technique, the same reaction protocols were applied to both methods. The reaction with VA was performed with various amounts of VA in DMF at 100°C for 3 hours with 1.1 mmol $K_2CO_3$/g dry wood as catalyst. There was no weight gain without solvent (DMF) or without catalyst ($K_2CO_3$) when VA was used. AA modification conditions were exactly similar with VA modification but no catalyst was used with AA.

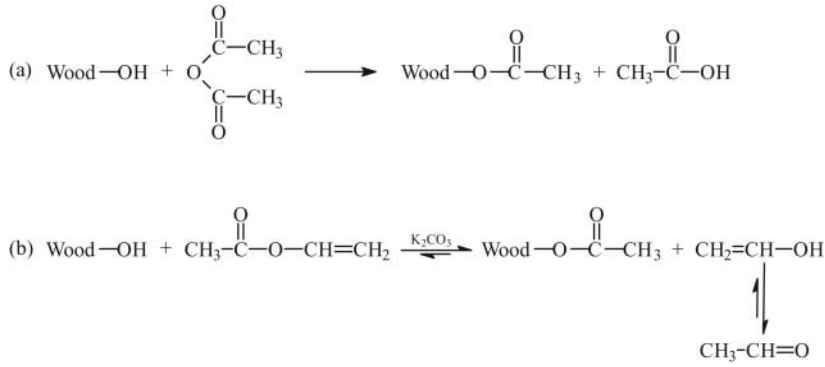


***Figure 1.*** (a) Acetylation of wood by classical acetic anhydride method. (b) Acetylation of wood by transesterification reaction (vinyl acetate).

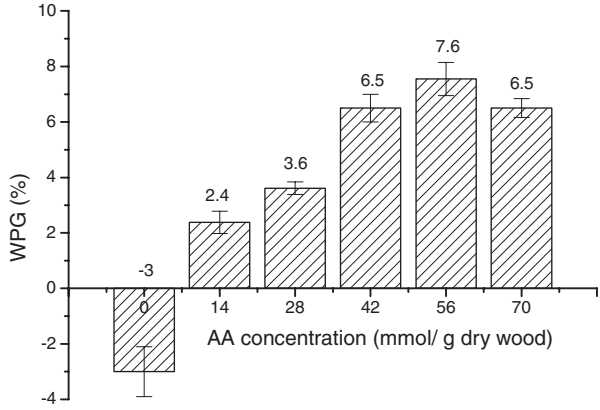


***Figure 2.*** Effect of AA concentration (mmol AA/g dry wood) on WPG values (reaction time 3 h, reaction temperature 100°C, without catalyst).

Figures 2 and 3 show the relationship between concentration of acetic anhydride or vinyl acetate and WPG values of acetylated wood. As can be seen from the figures, increasing the reagent concentration caused an increase in WPG values. For both reagents, 56 mmol AA or VA/g of dry wood gave maximum WPG values 7.6 and 15.1, respectively.

Modified samples were characterized by FTIR spectroscopy (Figure 4). No spectral difference was noted between the two acetylation methods. Acetylated samples ($W_{AA}$ and $W_{VA}$) were easily identified in the FTIR spectra; the emergence of a carbonyl stretching vibration at 1745 $cm^{-1}$ ($\nu_{C=O}$) in the spectra confirmed the formation of ester bonds after reactions with AA-c and

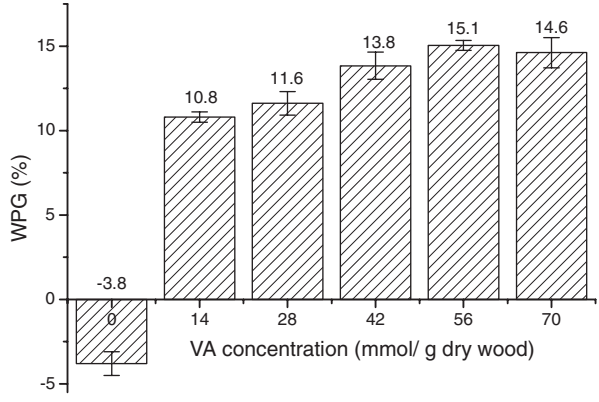


***Figure 3.*** Effect of VA concentration (mmol VA/g dry wood) on WPG values (reaction time 3 h, reaction temperature 100°C, with 1,1 mmol $K_2CO_3$/g dry wood catalyst).

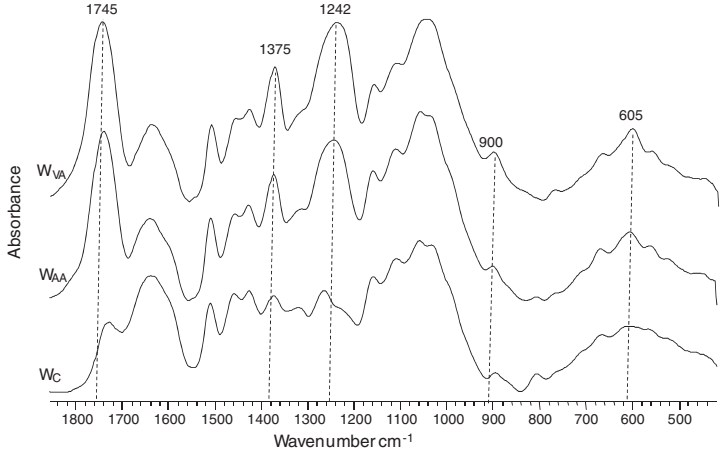


***Figure 4.*** The 1900 to 450 $cm^{-1}$ region of the infrared spectra for acetic anhydride modified ($W_{AA} = 7{,}6\%$ WPG), vinyl acetate modified ($W_{VA} = 16\%$ WPG), and unmodified ($W_C$) Scots pine wood flour.



VA. In addition, the intensity of the band at 1242 $cm^{-1}$ also increased and was associated with the C-O stretching vibration ($\nu_{C\text{-}O}$) of the acetyl moieties. The in-plane bending ($\delta_{C\text{-}H}$) and out-of-plane bending ($\gamma_{C\text{-}H}$) vibrations of the methyl groups introduced are also observed at 1375 and 900 $cm^{-1}$, respectively.[19] The intensity of the band at 605 $cm^{-1}$ also increased and was associated with some vibrations of the grafted methyl groups.[20]

The effect of catalysts (potassium acetate, potassium carbonate, sodium carbonate) and catalyst amounts on WPG values of AA or VA modification was now studied. A series of reactions were performed (AA or VA concentration was chosen as 56 mmol AA or VA/g dry wood, since the best WPG values were obtained with this concentration value; see Figures 2 and 3) and results are presented in Figure 5. When a very low amount of catalyst (0.36 mmol/g dry wood) was added to the reaction environment, it had a significant effect on WPG values of AA or VA modification.

As can be seen from Figure 5a, the WPG of the catalyzed acetylation was much greater than that of the uncatalyzed reaction for AA. Maximum WPG values 22%, 21%, 18% WPG were obtained with 1.02 mmol $CH_3COOK$, 0.72 mmol $K_2CO_3$, 0.94 mmol $Na_2CO_3$/g dry wood amount, respectively. The amounts of each of the catalysts studied were sufficient to maximize AA modification. In a previous study,[15,16,21,22] 20% WPG value was obtained with $CH_3COOK$ catalyzed (at 10% catalyst loading) acetylation at 120°C.

Without catalyst, the AA modified samples showed very low WPG value (7% WPG) compared to catalyzed reactions. But all the catalysts studied had a significant effect on WPG values for AA modification. It was found that

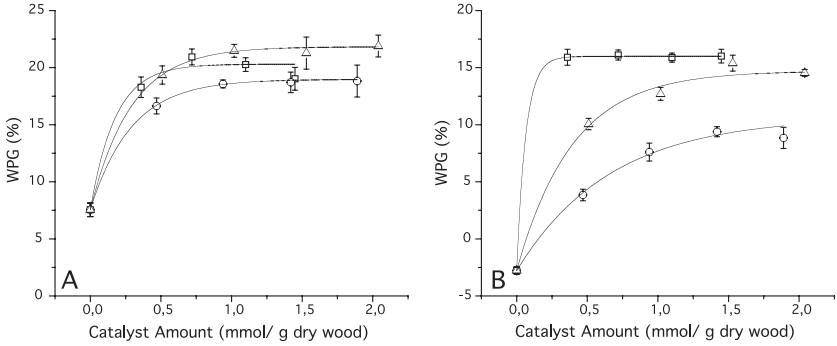


***Figure 5.*** Effect of catalyst type and amount on WPG values of AA (A) or VA modification (B). (Square: $K_2CO_3$, circle: $Na_2CO_3$, triangle: $CH_3COOK$, reaction time 3 h, reaction temperature 100°C, acetic anhydride or vinyl acetate amount 56 mmol AA or VA/g dry wood).



increasing the catalyst amount to 0.5 mmol/g dry wood increased the WPG values significantly (7 to ∼18%) using AA modification. Higher catalyst concentrations did not increase the WPG values significantly.

Figure 5b shows the effect of catalyst type and amount on the WPG values in the VA modification process. No weight gain was obtained for VA reactions without catalyst (Figure 5b and 7b). The catalyzed VA modified wood showed much higher values of WPG at the same reaction conditions. Of the catalysts studied, $K_2CO_3$ is an excellent catalyst for VA modification; maximum WPG values (16%) were obtained with a very small amount of $K_2CO_3$ (0.35 mmol/g dry wood). The WPG levelled off after 0.36 mmol $K_2CO_3$/g dry wood, and it did not exceed 16% with higher catalyst concentrations using 3 hours reaction times.

At lower catalyst concentrations, $CH_3COOK$ was less effective than $K_2CO_3$. A WPG of 15% was obtained with VA modification, only when the concentration of $CH_3COOK$ was raised to 1.53 mmol catalyst/g dry wood (Figure 5b). $Na_2CO_3$ was not as effective as the other two catalysts and showed the lowest catalytic effect among the studied catalysts (maximum 9% WPG value was obtained at 1.42 mmol $Na_2CO_3$/g dry wood catalyst amount).

Figures 6 and 7 show the FTIR spectrum of acetic anhydride or vinyl acetate modified Scots pine sapwood with various catalysts. An obvious increase in the intensities of the C=O absorption band at 1749 $cm^{-1}$ and CO absorption band at 1260 $cm^{-1}$ were observed, indicating that wood successfully acetylated with both reagents with all studied catalysts.

The FTIR observation was confirmed by the $^{13}C$ NMR spectrum of the samples. The $^{13}C$ NMR spectra of unmodified Scots pine are shown in Figure 8 (W). As can be seen in Figure 8, the dominant pattern of the $^{13}C$ NMR spectra is that of the carbohydrates, namely $C_1$ (107 ppm), $C_4$ crystalline (91 ppm), $C_4$

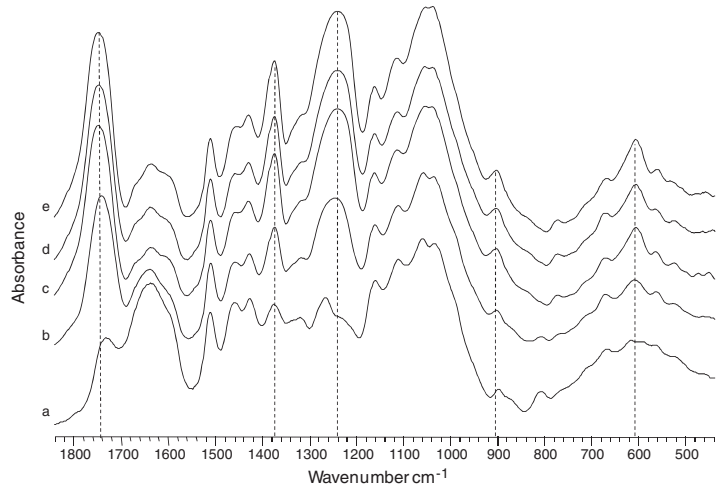


***Figure 6.*** FTIR absorbance spectra of Scots pine sapwood (a). FTIR absorbance spectra of acetic anhydride modified Scots pine sapwood without catalyst (b), with catalysts, $K_2CO_3$ (c), $Na_2CO_3$ (d), $CH_3COOK$ (e).

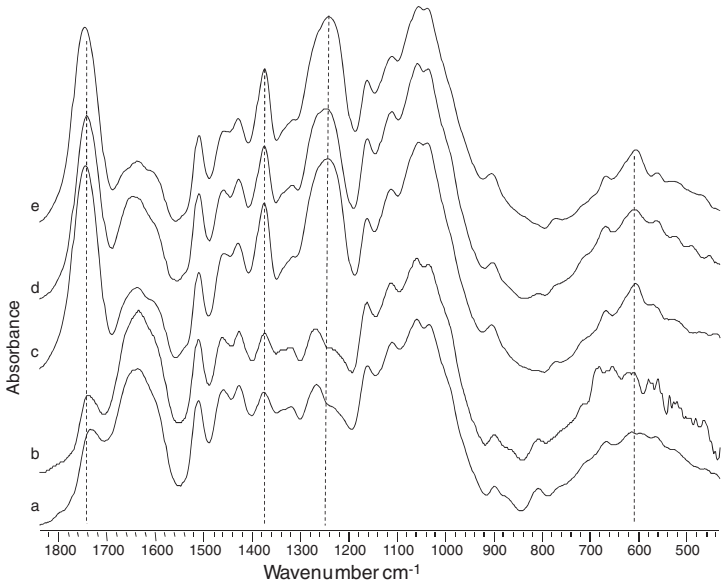


***Figure 7.*** FTIR absorbance spectra of Scots pine sapwood (a). FTIR absorbance spectra of vinyl acetate modified Scots pine sapwood without catalyst (b), with catalysts, $K_2CO_3$ (c), $Na_2CO_3$ (d), $CH_3COOK$ (e).

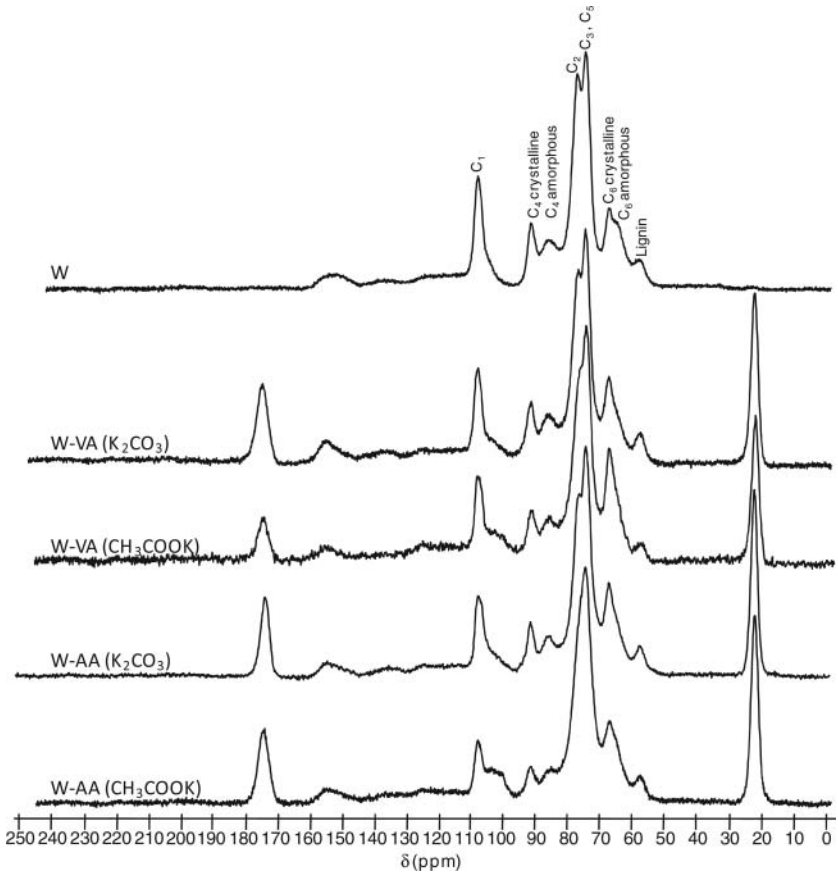


***Figure 8.*** $^{13}C$ CP-MAS NMR spectra of unmodified wood (W), wood acetylated with acetic anhydride (W-AA ($K_2CO_3$) = 24% WPG, W-AA ($CH_3COOK$) = 21% WPG), and vinyl acetate (W-VA ($K_2CO_3$) = 21% WPG, W-VA ($CH_3COOK$) = 17% WPG).

amorphous (86 ppm), $C_2$ (77 ppm), $C_3/C_5$ (75 ppm), $C_6$ crystalline (68 ppm), $C_6$ amorphous (65 ppm).[23,24] The signal at 59 ppm indicates the lignin methoxy groups. The aromatic groups of the lignin appear at 150 ppm as a wide band.

After acetylation of Scots pine wood with acetic anhydride or vinyl acetate, the methyl band of the acetyl group at 21 ppm and the carboxylic group at 171 ppm show the acetyl groups on the wood components. There was no difference between the VA or AA modified wood spectra with different catalysts. The disappearance (W-AA ($CH_3COOK$) and W-VA ($CH_3COOK$)) or considerable decrease (W-AA ($K_2CO_3$) and W-VA ($K_2CO_3$) in the intensity of the $C_2$ band indicates that acetylation at $C_2$ may have occurred. The disappearance of the

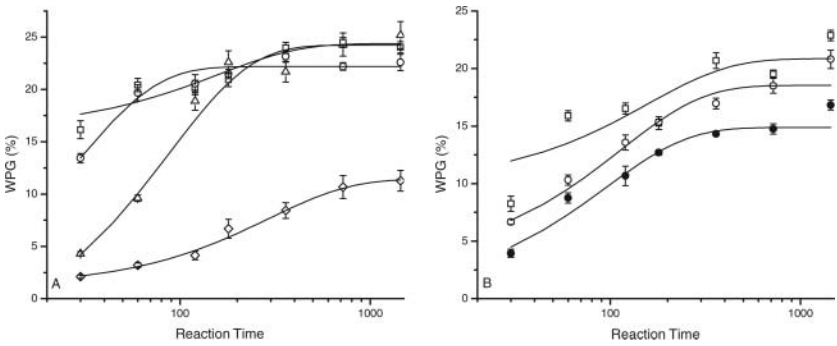


***Figure 9.*** The plots of WPG against the reaction time of AA (A) or VA (B) modification. (Diamond: uncatalyzed, triangle: pyridine, square: $K_2CO_3$, circle: $CH_3COOK$, circle fill: $CH_3COOK$ (low concentration), reaction temperature 100°C, acetic anhydride, or vinyl acetate amount 56 mmol AA or VA/g dry wood).



$C_6$ band (65 ppm at unmodified wood) proves that acetylation also takes place at the amorphous region of $C_6$.

In order to determine the effect of reaction time on AA or VA modification, a series of reactions were carried out. Figures 9a and 9b show the WPG due to the acetylation of wood with AA or VA at 100°C plotted against up to 24 hours reaction time, respectively. For these reactions, $CH_3COOK$ and $K_2CO_3$ were chosen as catalysts, since the best results were obtained with these catalysts with both AA and VA reagent. For AA modification, reactions were also performed without a catalyst and with a pyridine catalyst. In earlier studies,[13,25,26] pyridine was the most widely used catalyst in the acetylation of wood with AA. In order to compare catalytic effects of the catalyst chosen in this study with pyridine, a series of acetylation reactions was performed in the presence of pyridine and results are shown in Figure 9a.

Figure 9a shows that pyridine was also a good catalytic effect in AA modification if adequate reaction time is given. When the acetylation reaction is performed in the presence of $CH_3COOK$ and $K_2CO_3$, the reactions were completed within the first hour and gave around 20% WPG value, whereas when pyridine was used as a catalyst a similar WPG value was obtained after 3 hours reaction time. Indeed, for AA modification, the reaction was extraordinary accelerated in the presence of $K_2CO_3$ catalyst. The WPG reached 16% within 30 minutes in the $K_2CO_3$ compared to 13% with the $CH_3COOK$ catalyzed system. In the uncatalyzed system or pyridine catalyzed system WPG values were 2% and 4%, respectively.

As can be seen from Figure 9a, the WPG value did not exceed 25% with $K_2CO_3$ (23% with $CH_3COOK$) catalyzed acetylation with AA, even after 24 h reaction time. In VA modification (Figure 9b), a maximum of 23% and

21% WPG values were obtained using $K_2CO_3$ and $CH_3COOK$ catalyzed transesterification reactions, respectively.

## 4. CONCLUSIONS

The catalyzed acetylation of Scots pine with acetic anhydride (AA) or vinyl acetate (VA) using potassium carbonate, potassium acetate, and sodium carbonate as catalysts was investigated in this study. The acetylation of wood has been confirmed by WPG calculations, FTIR spectroscopy, and $^{13}C$ CP-MAS NMR analysis. Potassium acetate catalyst gave the best WPG values for both AA and VA modification among the studied catalysts, under the conditions used. In a comparison between AA and VA modification results, the AA modification gave higher WPG values than VA modification at the same reaction conditions.



## REFERENCES

1. Rowell, R.M.; Tilmann, A.M.; Simonson, R. A simplified procedure for the acetylation of hardwood and softwood flakes for flakeboard production. J. Wood Chem. Techn. **1986**, *6*(3), 427–448.
2. Stamm, A.J.; Tarkow, H. Dimensional stabilisation of wood. J. Phys. Col. Chem. **1947**, *51*, 493–505.
3. Kumar, S. Chemical modification of wood. Wood Fiber Sci. **1994**, *26*(2), 270–280.
4. Hon, D.N.S. Chemical Modification of Lignocellulosic Materials. In *Wood and Cellulosic Chemistry*; Hon, D.N.S., Ed.; Marcel Dekker, Inc.: New York, 1996, 97–127.
5. Rowell, R.M. Chemical modification of wood. Forest Prod. Abst. **1983**, *6*(12), 363–382.
6. Rowell, R.M. Chemical Modification of Wood. In *Wood and Cellulosic Chemistry*; Hon, D.N.S., Ed.; Marcel Dekker, Inc.; New York, 1996, 703–756.
7. Rowell, R.M. Chemical modification of wood: A short review. Wood Matrl. Sci. Eng. **2006**, *1*, 29–33.
8. Rowell, R.M. Acetylation. Forest Prod. J. **2006**, *56*(9), 4–12.
9. Hill, C.A.S. *Wood Modification: Chemical, Thermal and Other Processes*; John Wiley & Sons: Chichester, UK, 2006.
10. Kattenbroek, B. How to Introduce Acetylated Wood from the First Commercial Production into Europe, *Proceedings of the Second European Conference on Wood Modification*, Göttingen: University of Göttingen, 2005, 398–403.
11. Li, J.Z.; Furuno, T.; Zhou, W.R.; Ren, Q.; Han, X.Z.; Zhao, J.P. Properties of acetylated wood prepared at low temperature in the presence of catalyst. J. Wood Chem. Techn. **2009**, *29*, 241–250.
12. Baird, B.R. Dimensional stabilisation of wood by vapour phase chemical treatment. Wood and Fiber. **1969**, *1*(1), 54–63.
13. Çetin, N.S. *Surface Activation of Lignocellulosic by Chemical Modification*. Ph.D. Thesis, University of Wales, Bangor, UK, 1999.

14. Hill, C.A.S.; Çetin, N.S.; Ozmen, N. Potential catalysts for the acetylation of wood. Holzforschung. **2000**, *54*, 269–272.
15. Obataya, E.; Minato, K. Potassium acetate-catalyzed acetylation of wood at low temperatures I: Simplified method using a mixed reagent. J. Wood Sci. **2009**, *55*, 18–22.
16. Obataya, E.; Minato, K. Potassium acetate-catalyzed acetylation of wood at low temperatures II: Vapour phase acetylation at room temperature. J. Wood Sci. **2009**, *55*, 23–26.
17. Li, J.Z.; Furuno, T.; Katoh, S. Chemical modification of wood by anhydrides without solvents or catalysts. J. Wood Sci. **2000**, *46*, 215–221.
18. Jebrane, M.; Sebe, G. A novel simple route to wood acetylation by transesterification with vinyl acetate. Holzforschung. **2007**, *61*(2), 143–147.
19. Ozmen, N.; Çetin, N.S.; Tingaut, P.; Sebe, G. A new route for functionalisation of wood through transesterification reactions. Euro. Polym. J. **2006**, *42*, 1617–1624.
20. Ozmen, N.; Çetin, N.S.; Tingaut, P.; Sebe, G. Transesterification reaction between acetylated wood and trialkoxysilane coupling agents. J. Appl. Polym. Sci. **2007**, *105*, 570–575.
21. Obataya, E.; Minato, K. Potassium acetate-catalyzed acetylation of wood: Extraordinarily rapid acetylation at 120°C. Wood Sci. Techn. **2009**, *42*, 567–577.
22. Obataya, E.; Minato, K. Potassium acetate-catalyzed acetylation of wood: Reaction rates at low temperatures. Wood Sci. Techn. **2009**, *43*, 405–413.
23. Boonstra, M.G.; Pizzi, A.; Tekely, P.; Pendlebury, J. Chemical modification of Norway spruce and Scots pine. A $^{13}C$ NMR CP-MAS study of the reactivity and reactions of polymeric wood components with acetic anhydride. Holzforschung. **1996**, *50*(3), 215–220.
24. Çetin, N.S.; Ozmen, N.; Tingaut, P.; Sebe, G. New transesterification reaction between acetylated wood and tetrametoxysilane: A feasibility study. Euro. Polym. J. **2005**, *41*, 2704–2710.
25. Hill, C.A.S.; Jones, D. The dimensional stabilisation of Corsican pine sapwood by reaction with carboxylic acid anhydrides. The effect of chain length. Holzforschung. **1996**, *50*, 457–462.
26. Hill, C.A.S.; Jones, D. Dimensional changes in Corsican pine sapwood due to chemical modification with linear chain anhydrides. Holzforschung. **1999**, *53*, 267–271.