European Beech Wood Modification Using Gas- and Liquid-phase Acetylation

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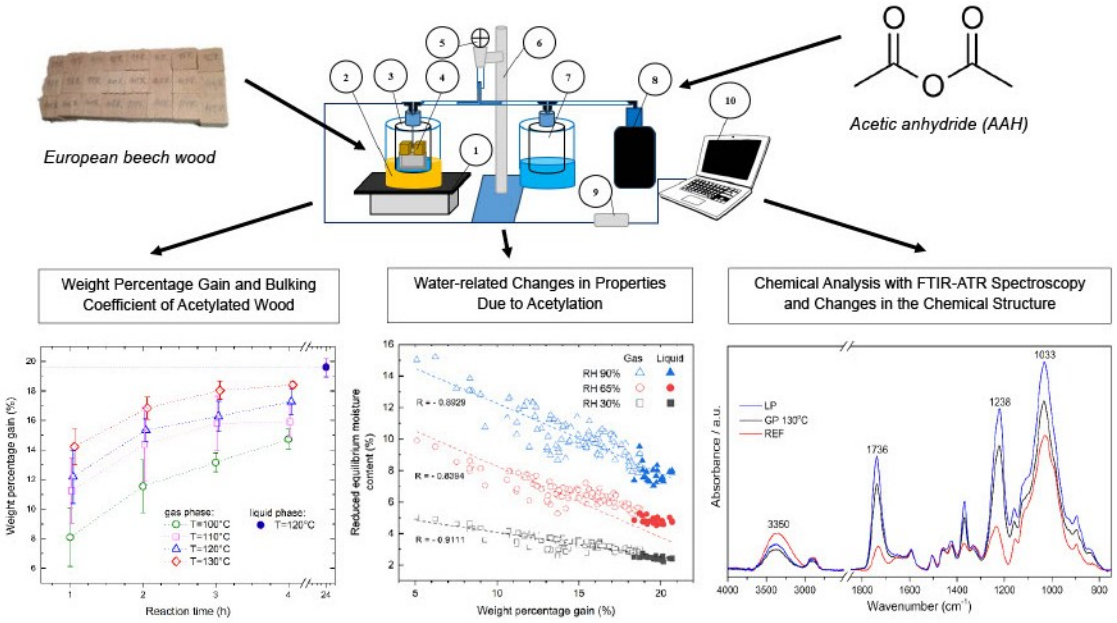
GRAPHICAL ABSTRACT



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Wood treatments involving chemical reactions are increasingly common in the construction industry, with acetylation being one of the most widely applied methods. In this study, European beech wood (*Fagus sylvatica* L.) was modified using acetylation in both traditional liquid phase (LP) and gas phase (GP) under varying temperatures (100 to 130 °C) and reaction times (1 to 4 h). The two methods were compared based on weight percentage gain (WPG), bulking coefficient (BC), water-related properties, and chemical changes confirmed by Fourier transform attenuated total reflectance infrared (FTIR-ATR) spectroscopy. The results showed that LP acetylation achieved the highest WPG (19.6%), while GP acetylation provided comparable results under higher temperatures and extended reaction times. Both methods significantly reduced equilibrium moisture content, water absorption, and volumetric swelling, thereby enhancing dimensional stability compared to reference (REF) samples. FTIR analysis confirmed substitution of hydroxyl groups by acetyl groups in both phases. Despite slightly lower WPG values in some regimes, GP acetylation provided similar improvements in water-related properties with reduced consumption of acetic anhydride (AAH). This indicates its strong potential for industrial applications, although further research is necessary to optimize the process for large-scale European beech wood components.

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Keywords: Anti-swelling efficiency; Bulking coefficient; Reduced equilibrium moisture content; Fagus sylvatica L.; Fourier transform infrared spectroscopy; Water repellence efficiency; Weight percentage gain

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INTRODUCTION

Active chemical modification, in which chemical groups are covalently bound to polymers in the cell walls, is one effective method of enhancing the properties of wood (Popescu *et al*. 2014). Fungal resistance, dimensional stability, and a reduced equilibrium moisture content (EMC) are the properties most often mentioned (Homan and Jorissen 2004). The acetylation of wood is one of the best-known methods of active chemical modification. Jones and Sandberg (2020) describe this process as a reaction in which an electrophilic agent (acetic anhydride, AAH) reacts with available nucleophilic hydroxyl groups (OH) in the wood. This is a single-addition chemical reaction, meaning the reaction of one acetyl group with one OH group without any polymerization (Rowell 1983; Sandberg 2017). By reducing the number of OH groups during acetylation, these primary functional groups are subsequently prevented from interacting with moisture in the wood (Popescu *et al*. 2014). Another important factor is the reduction of available space for water

molecules in the cell walls (Hill *et al*. 2005; Keplinger *et al*. 2015; Thybring *et al*. 2020; Diagistis *et al*. 2021). A further advantage of this method is the non-toxicity of the acetylated material, as the chemical composition primarily consists of carbon, oxygen, and hydrogen (Hill 2006; Mantanis 2017). While Corsican pine (*Pinus radiata*) is commonly used in commercial acetylation applications (Jones and Sandberg 2020), other wood species have also been studied, including beech (Militz 1991a,b), spruce, Scots pine (Larsson and Simonson 1994; Diagaitis *et al*. 2021), and poplar (Bongers and Becters 2003; Gu *et al*. 2015).

The traditional method of acetylation consists of impregnating wood with acetic anhydride (AAH) and subsequently curing it at an elevated temperature (Mantanis 2017; Diagaitis *et al*. 2021). The result of the acetylation reaction itself is influenced by several factors. Hill (2006) divided these factors into four main categories: (1) The characteristics and pre-treatment of the wood samples, such as species and density; (2) the reaction medium, including whether pure AAH or a solution is used, and whether a catalyst is present; (3) reaction variables, such as temperature, reaction time, and ambient pressure; and (4) the post-reaction cleaning procedure, which may involve solvent extraction, vacuum with heating, or water soaking. Although today most acetylation reactions are conducted without catalysts (Larsson-Brelid 2013; Rowell 2016; Mantanis 2017), earlier methods employed compounds such as potassium acetate, urea-ammonium sulphate, and potassium carbonate (Rowell 1983; Hill 2006; Sandberg *et al*. 2017). Despite the effectiveness of this traditional method, one of its main limitations is the requirement for deep penetration of the liquid reagent into the wood. While Hill's classification outlines the factors the influence the reaction once the reagent is already present within the wood, in liquid-phase acetylation the ability to achieve sufficient penetration becomes an essential operational step. Therefore, when attention is focused specifically on the penetration stage, the permeability of the wood species, the method of application, and the properties of the impregnating agent become the most critical determinants (Larsson-Brelid 2002). During the acetylation process, the impregnated wood is heated to temperatures typically ranging from 100 to 180 °C. In contrast, the reaction rate increases significantly at higher temperatures, but the mechanical properties decrease. Also, the degree of substitution may decrease, thus reducing the efficiency of the acetylation reaction (Li *et al.* 2018, Qin *et al.* 2019). The acetylation reaction is exothermic, and higher temperatures increase the reaction rate. However, excessive heat may cause thermal degradation of the wood material with a loss of mechanical strength. Residual chemicals (acetic acid – AA, and unreacted AAH) are removed from the wood after the process (Sandberg *et al*. 2021). Hill (2006) suggests the possibility that AA may cause cell wall swelling and thus promote the reaction rate. AAH alone is not capable of significantly swelling the cell wall. The main difference between these substances is that AAH serves as a primary acetylating agent, while AA functions as both a solvent and a coreagent in the acetylation process (Rout *et al.* 2024).

Recovery and recycling of AAH from acetylation processes typically involves the disposal of unreacted reagent using controlled hydrolysis procedures. This step is necessary due to the low efficiency of using the reagent with high volumes of AA. Therefore, the removal of AA from the wood and its conversion back to AAH is required (Frihart *et al*. 2021). Standard processing methods include pouring the reaction contents into ice water (Andjelkovic *et al.* 2006), or using aqueous pyridine solutions (Lin *et al.* 2023), which lead to hydrolysis of excess/unreacted AAH to AA. Thermal dehydration of AA at 700 °C or above is then followed by regeneration of AAH (Ichino *et al.* 1984). More sophisticated recycling approaches focus on maintaining the integrity of the reaction system over

multiple cycles, thereby compensating for liquid loss during reactions and filtration by adding an appropriate amount of fresh AAH. In a recycling strategy, both the catalyst and the reagent can be recovered and still active. The disadvantage of this approach is the increasing concentration of the catalyst in the liquid phase, when AAH is preferentially consumed (Imre *et al.* 2020).

In contrast to the traditional liquid phase (LP) method, several studies favour the use of the acetylation reaction in the gas phase (GP) due to several advantages. The main reason is the generally greater reactivity of chemical agents in the GP, which should shorten the reaction time and consume less reagent than in the LP, thereby reducing treatment costs and increasing product competitiveness (Wang *et al*. 2024). Additionally, GP acetylation is operationally less demanding than LP, typically involving, for example, less energy use, more sparing consumption of chemicals, reduced environmental impacts, and a smaller increase in the weight of the wood. Using acetylation in the vapour phase, a reduction in the consumption of the modifying agent was found with the help of the modification gradient of acetylated wood (Futemma and Obataya 2012; Hasegawa *et al*. 2019). Gu *et al*. (2015) describe the acetylation of poplar wood in the gas phase at higher temperatures (140 to 175 °C) as extremely rapid compared to the liquid phase. However, despite the above advantages, the general use of AAH gas reduces the efficiency of the process due to the induction period – during which the reaction proceeds only slowly until sufficient reagent has diffused into the cell-wall structure (Nishino 1991), and also the low penetration of AAH from the longitudinal directions of the wood (Rowell *et al.* 1986; Sandberg *et al.* 2021). In the gas phase, this limitation cannot be compensated for by the application of external pressure as effectively as in liquid-phase processes, because gaseous AAH compresses without generating the hydraulic driving force needed to overcome the resistance of the wood structure.

Acetylation in the gas phase has also been tested with catalysts such as sodium acetate. Changes in hygroscopicity and dimensional stability are closely related to the weight percent gain (WPG) achieved during the process (Obataya and Minato 2009) regardless of the AAH phase used (gas or liquid). The WPG is an easily determined indicator for quality modification, but the real cause of changes is the replacement of OH groups by acetyl groups, which reduces the affinity of wood for water. However, some studies suggest that the extent of OH substitution is irrelevant and that dimensional stability depends mainly on the bulk effect of the cell wall (Jones and Hill 2007; Papadopoulos 2010; Čermák *et al*. 2022). During chemical modification, the functional groups of AAH remain in the cell wall after drying, leading to an increase in wood volume due to the bulking effect, while by-products such as AA evaporate (Sandberg *et al*. 2017). The presence of covalently bound acetyl groups of the nanopores in the cell wall matrix reduces the EMC of acetylated wood. These groups are no longer available to bond with water molecules (Papadopoulos and Hill 2003; Hill 2006; Popescu *et al*. 2014, Čermák *et al*. 2022). Compared with untreated wood, the swelling and shrinkage values of acetylated wood are 70% to 75% lower (Jones and Hill 2007; Rowell 2014), while the anti-swelling efficiency (ASE) is comparable, with leaching levels reported below 1% (Čermák *et al*. 2022). Hill (2006) states that the nanopores in fully swollen wood are 2 to 4 nm in size, with relatively low molecular weight molecules having a greater chance of diffusing into the cell wall. This treatment provides a material that is resistant to decay and more dimensionally stable with good mechanical strength (Sandberg *et al*. 2021).

In general, woods that are suitable for acetylation are characterized by easy drying, good liquid impregnability and density of up to 700 kg/m^3. Highly unstable wood species

such as European beech require an adaptation of process parameters; otherwise, there is a high risk of distortion and surface cracking (Bollmus *et al.* 2015). This experiment is part of a broader research effort aimed at using gas acetylation to modify real-size beech elements with limited occurrence of undesirable defects created during modification.

According to some studies, the gas phase of anhydride is more effective and faster compared to liquid impregnation. The aim of this work was to find the optimal conditions (time, temperature) for acetylation of European beech that would ensure at least comparable properties (EMC_R, *ASE*, *WRE* etc.) with the liquid phase. Therefore, it is hypothesized that (H1) GP acetylation can deliver comparable water-related improvements to LP when appropriate process conditions are applied; (H2) Higher reaction temperatures and longer treatment times in GP acetylation will increase the degree of modification; and (H3) GP will induce cell-wall chemical changes comparable to LP, detectable by FTIR-ATR spectroscopy.

EXPERIMENTAL

Materials

The acetic anhydride (Penta Chemicals Unlimited, min. 99%, Czech Republic) used in the present study was purchased from P-LAB a.s. European beech sapwood (*Fagus sylvatica* L.) from the University Forest Enterprise Masaryk Forest in Křtiny (Czech Republic) was used for acetylation.

For the LP and REF sets, 48 samples were used, but for individual gaseous acetylation conditions, the set was reduced to 6 due to the number of variants. All samples were examined to ensure they were without defects, cracks or false heartwood. The sample dimensions were 20×20×20 mm (L×R×T). Samples were dried at 103 °C for 24 h before modification to reach zero moisture content.

Methods

Wood acetylation

The liquid phase (LP) acetylation was carried out according to the procedure described by Čermák *et al*. (2022). The beech samples were immersed in liquid AAH and vacuum impregnated (Vacucell, BMT USA, MMM Group, USA) at 20 kPa for 30 min. The impregnated samples were transferred to a closed glass container with AAH at the bottom and placed on a stainless-steel stand without contact with the anhydride. A silicone grid was inserted between the stand and the samples. The glass container was left in the drying oven at 120 °C for 24 h. Samples were dried at 103 °C for 24 h after modification. The *WPG* was calculated for each sample after drying according to Eq. 1.

The gas phase (GP) acetylation was performed in a vacuum distillation apparatus (Fig. 1), with the wood samples separated from the AAH by a grate. The process started with a vacuum phase (20 kPa, 30 min), during which it reached a process temperature of 60 °C, and intensive AAH evaporation occurred and impregnation of wood. Subsequently, the vacuum was changed to atmospheric pressure and the process continued to react at the appropriate temperature (100, 110, 120 or 130 °C) for a certain reaction time (1, 2, 3 or 4 h).

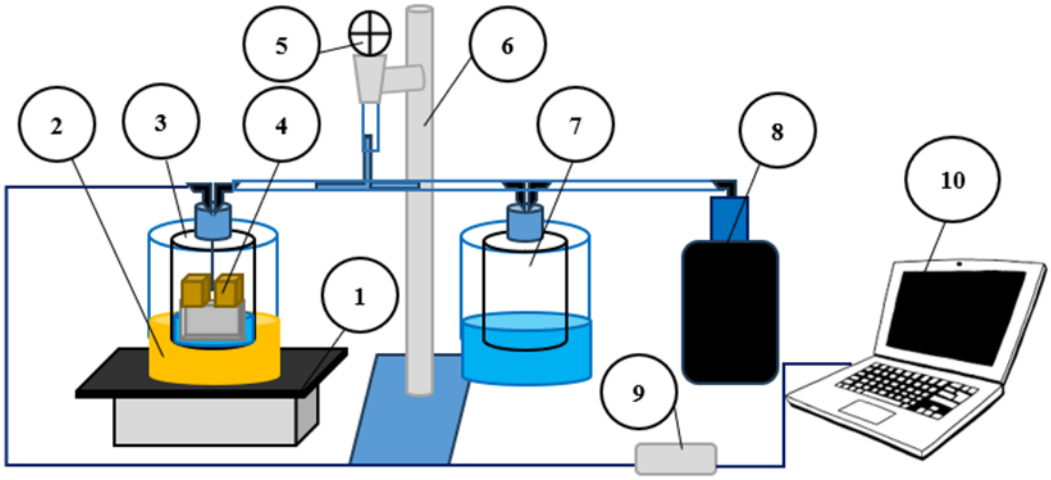

Fig. 1. Vacuum distillation apparatus (1: heating plate, 2: sand bath, 3: heated bottle, 4: wood samples, 5: vacuum gauge, 6: stand, 7: cooled bottle, 8: vacuum pump, 9: thermocouple, and 10: computer)

The samples were gradually removed from the heated flask and transferred to a drying oven where they were left for 1.0 h at 120 °C. Subsequently, samples were weighed, and their dimensions were measured after cooling. Measurement was repeated after one week of being stored in an air-conditioned room (to check the stabilisation of the *WPG* value), when the samples were dried again at 103±2°C for 24 h. *WPG* and the bulking coefficient (*BC*) were calculated according to Eq. 1 and 2, where m_0 is the weight of sample before modification and m_{m0} is the weight of the modified wood sample (it was always the same sample). V_0 is the volume of the sample before modification and V_{m0} is the volume of the modified wood sample:

$$WPG = \frac{(m_{m0} - m_0)}{m_0} \times 100\ (\%) \quad (1) \qquad BC = \frac{(V_{m0} - V_0)}{V_0} \times 100\ (\%) \quad (2)$$

Water-related properties

The samples (six for each group) were stored in an air-conditioned chamber (Memmert CTC/TTC 256, Germany) at 20 °C and the appropriate relative humidity (*RH*) – 30%, 65%, or 90%. After 14 days, they were all taken out, weighed, and their dimensions measured. The measurements were repeated after two days to control the equilibrium state. The reduced equilibrium moisture content (EMC_R) for individual states was calculated according to Eq. 3, where m_{m0} is the oven-dry weight of the modified wood sample, m_m is the weight of the modified wood sample in equilibrium with the atmosphere at the given relative humidity, and m_0 is the oven-dry weight of the specimen before modification (these were separate groups of LP, GP, and REF samples). The reduced moisture exclusion efficiency (MEE_R) was calculated using Eq. 4. The values used for the calculation represented the EMC_R of the unmodified control samples (EMC_{Ru}) and the modified test samples (EMC_{Rm}).

The samples (six for each group) were immersed in demineralised water and soaked for a certain time (2, 4, 6, 10, 24, 48, 72, 384, 720 or 2,160 h). After each period, the samples were removed from the water, lightly dried with a paper towel, weighed and measured. The demineralised water was initially changed after each measurement, later every 14 days. Finally, the samples were dried (103 °C for 24 h) and weighed at 0%

moisture content. The water repellence efficiency (*WRE*) was calculated using Eq. 5 from the moisture content values of unmodified samples (MC_u) and modified samples (MC_m) after the soaking test.

The anti-swelling efficiency (*ASE*) was calculated according to Eq. 6, where S_u represents the volumetric swelling of unmodified wood and S_m the volumetric swelling of modified wood.

$$EMC_R = \frac{(m_m - m_{m0})}{m_0} \times 100\ [\%] \quad (3)$$

$$MEE_R = \frac{(EMC_{Ru} - EMC_{Rm})}{EMC_{Ru}} \times 100\ [\%] \quad (4)$$

$$WRE = \frac{(MC_u - MC_m)}{MC_u} \times 100\ [\%] \quad (5)$$

$$ASE = \frac{(S_u - S_m)}{S_u} \times 100\ [\%] \quad (6)$$

Chemical analysis of wood

Acetylated samples from both GP/LP stages were ground from their original dimensions into wood dust using an MM 400 oscillating mill (Retsch, Germany). FTIR analysis of wood dust was performed using a Vertex 70 infrared spectrometer (Bruker, Germany) in attenuated total reflectance (ATR) mode with a Platinum-ATR module equipped with a diamond crystal. Spectra were collected in the range of 4.500 to 400 cm^{-1} with a spectral resolution of 2 cm^{-1}. Two samples from each group (acetylated GP/LP and reference) were analysed, with three measurements taken per sample.

The resulting data were analysed using Omnic software (Thermo Scientific, USA). After baseline correction, the areas of the selected peaks were determined, and these peak area values were subsequently normalised to the area of the peak at 1.504 cm^{-1} corresponding to the -C=C δ vibration of the lignin aromatic ring.

Data evaluation

Data were statistically analysed using Statistica 14 (TIBCO Software Inc, USA); the Kruskal-Wallis test (due to low number of samples and unequally sized data sets) was used to compare the effect of time for each reaction temperature (100 to 130 °C) at the significance level of $P \leq 0.05$ (marked with letters in the Results and Discussion section). All results from the GP modification groups were compared with those from the LP acetylation (to verify whether the GP acetylation under specific condition is comparable to the LP, marked with number in the Results and Discussion section one). Individual dependencies were displayed in the form of graphs created in OriginPro (version 9.0), where a linear correlation analysis was also performed and the correlation coefficient showed in individual graphs.

RESULTS AND DISCUSSION

Weight Percentage Gain and Bulking Coefficient of Acetylated Wood

In the acetylation of beech wood by the GP method, different reaction temperatures and times were used to determine a process that would compete with LP acetylation. The mean values of the parameters describing the result of the acetylation process (WPG and bulking coefficient (BC)) are given in Table 1 and Fig. 1. The LP acetylation resulted in WPG percentage values of 19.6%, is comparable to the results of other reported studies (Bollmus *et al*. 2015; Gu *et al*. 2015; Čermák *et al*. 2022). For example, Gu *et al*. (2015)

report similar WPG of 20.4% already after only 8 h of reaction time in LP acetylation. However, in order to achieve the maximum value of LP acetylation and to adhere to the methodological procedure of the previous experiment (Čermák *et al*. 2022), a relatively long reaction time of 24 h was used in the present study. The LP modification resulted in higher *WPG* than all GP groups based on the average value; however, the differences between GP acetylation at higher temperatures for the longest reaction times (>110 °C, 3–4 h) and LP acetylation were not statistically significant. It is clear from the mean values, that GP acetylation led to a higher *WPG* value with increasing temperature and longer reaction time, but no significant differences were found between individual reaction times within the same temperature (Table 1). It should be noted that all statistical analysis were affected by the lower number of samples and higher variability of values, especially for lower reaction times (Fig. 2). From the perspective of increasing durability only when using the highest temperature (130 °C), the required *WPG* was achieved, which is capable of ensuring sufficient resistance to degradation by wood-decay fungi and should be at least in the range of 17 to 20 % (Rowell *et al.* 2009).

Table 1. Mean Value and Coefficient of Variation of WPG and BC from the GP- and LP-Acetylation Processes

	T (°C)	*t* (h)	WPG (%)	BC - V (%)
Gas Phase	100	1	8.1 (24.5)^{1a}	11.5 (15.3)^{1a}
		2	11.6 (15.4)^{1a}	13.9 (10.6)^{1a}
		3	13.2 (4.8)^{1a}	15.1 (9.1)^{1a}
		4	14.7 (4.6)^{1a}	15.4 (6.5)^{1a}
	110	1	11.2 (19.8)^{1a}	12.5 (15.1)^{1a}
		2	14.4 (17.5)^{1a}	15.1 (12)^{2a}
		3	15.8 (11.7)^{2a}	17.3 (18.7)^{2a}
		4	15.9 (6.9)^{2a}	18.2 (7.3)^{2a}
	120	1	12.2 (9.6)^{1a}	13.4 (14.1)^{1a}
		2	15.3 (5.0)^{1a}	16.6 (10.1)^{2a}
		3	16.3 (6.3)^{2a}	18.0 (5.4)^{2a}
		4	17.3 (5.0)^{2a}	18.8 (8.3)^{2a}
	130	1	14.2 (8.6)^{1a}	14.9 (3.3)^{1a}
		2	16.8 (4.5)^{2a}	17.1 (4.9)^{2a}
		3	18.0 (3.4)^{2a}	18.5 (5.4)^{2a}
		4	18.4 (1.2)^{2a}	18.9 (5.0)^{2a}
Liquid Phase	120	24	19.6 (3.2)^{2}	19.6 (6.1)^{2}

Statistically significant differences ($P < 0.05$) are indicated when comparing individual GP with LP acetylation (number) and different reaction times within individual temperatures (letters).

The WPG results for GP-acetylation (100 to 130 °C) in the present study gave lower values than Gu *et al*. (2015) and Wang *et al*. (2024) due to their use of higher reaction temperatures (140 to 220 °C). However, higher temperatures (170 to 200 °C) can lead to thermal degradation of wood, which causes a decrease in strength and flexibility in bending with increasing temperature and longer reaction time (Sandberg *et al*. 2021). Another disadvantage of using a high temperature (220 °C) is the course of the deacetylation and dehydration reactions (Wang *et al*. 2024). The difference in WPG between GP and LP acetylation can be explained by the diffusion behaviour and distribution of AAH within the wood structure. In LP acetylation, liquid AAH penetrates deeply and uniformly into the cell lumina and walls, allowing extensive substitution of hydroxyl groups with acetyl

groups (Rowell *et al*. 1990). In GP acetylation, the AAH vapour diffuses through the porous structure of the wood, where it may adsorb onto cell wall surfaces or condense within lumina. The extent and depth of reaction depend on vapour concentration, temperature, and exposure time. Under mild conditions, penetration tends to be slower and less uniform, which limits the overall *WPG* – especially in the early stages of the reaction. The lower *WPG* values following GP acetylation were influenced by the loss of unreacted AAH during the process. In LP acetylation, higher WPG values were facilitated by the initial impregnation, which ensured better reactant distribution. To prevent premature formation of excessive acetic acid, it is essential to impregnate thick solid wood with AAH under cold conditions (Rowell 1986; Sandberg *et al*. 2021).

A dependence similar to that of *WPG* was obtained from the *BC* results as well. Higher mean values of *BC* were obtained with increasing temperature and reaction time. Also for this parameter, no statistically significant effect of reaction time within individual temperature was found. The highest *BC* value was achieved at 130 °C and 4 h, which was the closest one to the *BC* value for LP acetylation. Unlike *WPG*, *BC* obtained by LP acetylation were statistically comparable to GP acetylation at a temperature of 110 and 120 °C even with reaction time of 2 h (Table 1). Čermák *et al.* (2022) found a *WPG* value of 24.9% and a *BC* of 18.4% for beech wood. Despite achieving significantly higher *WPG*, *BC* remained almost the same. For this reason, it can be concluded that even with a higher *WPG* value, *BC* does not change and therefore the statistical difference between LP and GP stages at higher temperatures and longer reaction times was insignificant. This dependence is influenced, in addition to the reaction parameters, by the type of wood used – *BC* values for acetylated pine (*WPG* 23%) and acetylated poplar (*WPG* 18.7%) were 11.8% and 6.8%, respectively (Dong *et al*. 2016).

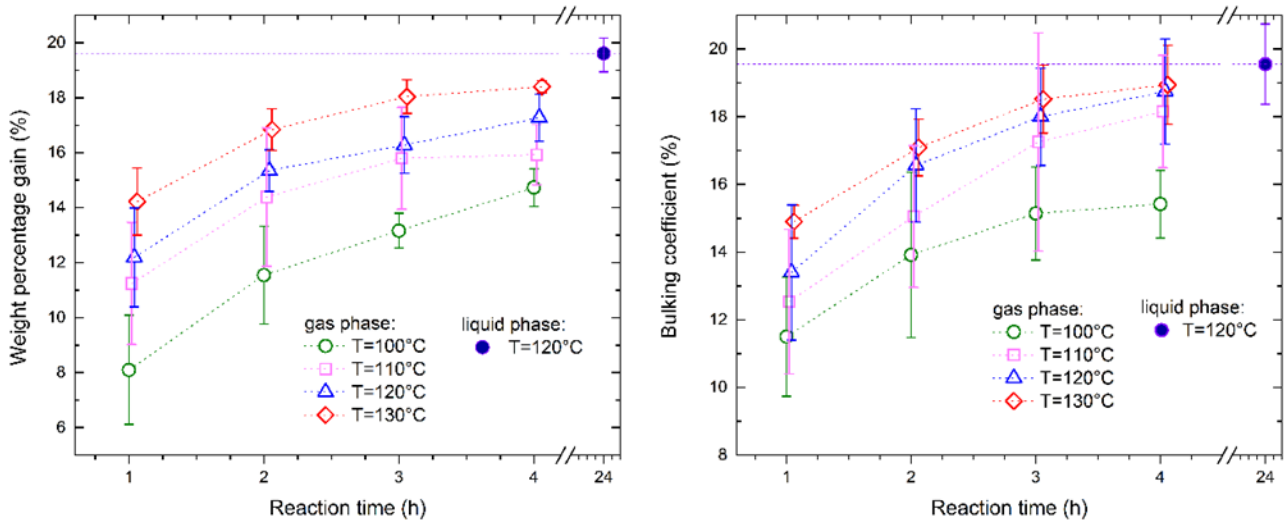

Fig. 2. Scatter plots showing WPG (left) and BC (right) values obtained at different acetylation temperatures and reaction times

In Fig. 3, a strong correlation (R = 0.88) between *WPG* and *BC* values can be seen. Bulking coefficient describes the volume changes due to modification which are caused by the volume occupied by the reagent in the cell wall.

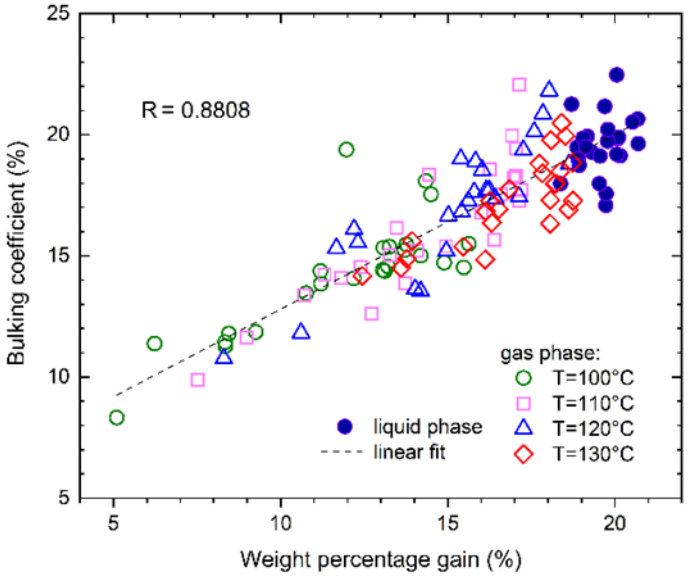

Fig. 3. The dependence of bulking coefficient on the weight percentage gain due to acetylations in gas phase (empty rhombus, triangle, square and circle) and liquid phase (full circle)

Unlike wood swelling related to water absorption, these changes are permanent. Tarkow *et al*. (1955) show that the bulking effect is generally equal to the volume of the acetyl groups, at least until there is 20% acetyl content. Thybring (2013) describes the volume effect of acetylation as being apparent when fully saturated with water. The volume of acetylated wood under this condition is more or less similar to that of unmodified wood, the only difference being the greater amount of moisture in the latter.

Water-related Changes in Properties Due to Acetylation

The acetylation of beech wood (by both methods) led to a reduction in moisture absorption compared to the reference samples, which is shown in the change in the parameters EMC_R and MEE_R in Table 2. The EMC_R values of unmodified beech wood were 5.4% (RH 30%), 10.3% (RH 65%), and 16.1% (RH 90%), while the LP acetylated wood reached almost half the values compared to the REF of beech samples – 2.5% (RH 30%), 4.8% (RH 65%), and 7.8% (RH 90%). In all cases (RH 30%), where a reaction time of 4 hours was used, statistically significant differences were found between the EMC_R of the reference samples and the GP acetylation. At higher temperatures (120 and 130 °C), even shorter time was sufficient. On the contrary, at RH 90%, statistically significant differences were found only for the longest time at 120 °C and all reaction times at 130 °C (Table 2). On the other hand, the EMC_R reduction caused by GP acetylation was in most cases statistically comparable to LP acetylation, except for shorter reaction times (1 to 2 h), where it varied depending on the temperature and relative humidity used. Popescu *et al*. (2014) describe the dependence of EMC_R values on WPG as an approximately linear correlation. The present results also confirm that there was a strong inverse correlation between EMC_R and WPG, which was confirmed for all three levels of relative humidity to which the samples were exposed (R = -0.91 at 30%; R = -0.84 at 65%; R = -0.89 at 90%, Fig. 5).

There was an observable trend where the mean EMC_R value of GP acetylated samples decreased with increasing temperature and reaction time at all three RH values (30%, 65%, and 90%). However, the effect of reaction time at the same temperature was

not statistically significant. For longer reaction times and at higher temperatures, more hydrophilic hydroxyl groups were replaced by hydrophobic acetylated groups (Fig. 8). Despite the higher acetylation process temperatures (>145 °C) used, Wang *et al*. (2024), showed that increasing reaction time led to decrease in the *EMC* value, similarly to the results obtained in the present experiment. This dependence was influenced by the availability of hydroxyl groups, which decreases with the increasing amount of modification, thus limiting the available space inside the cell walls (Hill *et al*. 2005; Popescu *et al*. 2014; Beck *et al*. 2017; Thybring and Fredriksson 2021).

Table 2. Mean Value and Coefficient of Variation of EMC_R and MEE_R at Different RH Values (30%, 65% and 90%) from GP and LP Acetylation and Ref Samples

			***RH* = 30%**		***RH* = 65%**		***RH* = 90%**	
	***T* (°C)**	***t* (h)**	**EMC_R (%)**	**MEE_R (%)**	**EMC_R (%)**	**MEE_R (%)**	**EMC_R (%)**	**MEE_R (%)**
Gas Phase	100	1	4.3 (14.7)^{1a}	20.8 (55.9)^{1a}	8.3 (14.2)^{1a}	19.7 (57.9)^{1a}	12.9 (14.7)^{1a}	19.8 (59.3)^{1a}
		2	3.6 (18.0)^{2a}	33.8 (35.1)^{1a}	7.0 (14.7)^{1a}	32.3 (30.7)^{1a}	10.9 (16.6)^{2a}	32.2 (34.9)^{1a}
		3	3.3 (12.1)^{2a}	38.6 (19.2)^{1a}	6.6 (9.2)^{2a}	35.7 (16.5)^{1a}	10.4 (10.5)^{2a}	35.5 (19.0)^{1a}
		4	3.1 (12.4)^{2a*}	42.2 (16.8)^{2a}	6.2 (10.4)^{2a*}	39.7 (15.6)^{2a}	10.1 (11.0)^{2a}	37.4 (18.3)^{2a}
	110	1	4.1 (8.3)^{1a}	24.9 (24.9)^{1a}	7.7 (7.5)^{1a}	25.4 (22.0)^{1a}	12.2 (5.7)^{1a}	24.0 (17.7)^{1a}
		2	3.6 (10.8)^{1a}	33.6 (21.3)^{1a}	7.0 (9.4)^{1a}	31.7 (20.2)^{1a}	10.9 (9.2)^{1a}	32.0 (18.8)^{1a}
		3	3.2 (7.2)^{2a}	40.4 (10.5)^{2a}	6.3 (4.4)^{2a}	38.3 (7.1)^{2a}	10.3 (4.4)^{2a}	35.8 (7.5)^{1a}
		4	3.1 (5.3)^{2a*}	42.1 (7.1)^{2a}	6.2 (4.6)^{2a*}	39.7 (7.0)^{2a}	9.8 (6.8)^{2a}	38.9 (10.2)^{2a}
	120	1	3.8 (6.4)^{1a}	29.2 (15.5)^{1a}	7.4 (5.6)^{1a}	28.3 (14.1)^{1a}	11.9 (6.1)^{1a}	26.2 (17.0)^{1a}
		2	3.5 (4.0)^{1a}	36.2 (12.4)^{1a}	6.5 (3.9)^{2a}	37.9 (9.7)^{1a}	10.1 (3.9)^{2a}	37.2 (6.2)^{1a}
		3	3.2 (12.3)^{2a*}	41.9 (6.6)^{2a}	6.5 (7.3)^{2a}	41.3 (8.1)^{2a}	9.9 (4.1)^{2a}	38.3 (4.9)^{2a}
		4	3.0 (17.0)^{2a*}	42.7 (9.3)^{2a}	6.3 (6.0)^{2a}	42.3 (8.7)^{2a}	9.7 (8.0)^{2a*}	39.8 (11.7)^{2a}
	130	1	3.6 (5.6)^{1a}	34.3 (9.8)^{1a}	6.6 (4.1)^{2a}	36.2 (6.7)^{1a}	9.7 (5.8)^{2a*}	40.0 (8.1)^{2a}
		2	3.2 (3.2)^{2a}	40.8 (4.1)^{2a}	5.9 (3.3)^{2a*}	42.7 (4.1)^{2a}	9.0 (2.8)^{2a*}	43.9 (2.8)^{2a}
		3	3.0 (4.0)^{2a*}	44.2 (4.1)^{2a}	5.7 (2.4)^{2a*}	44.9 (2.8)^{2a}	8.6 (5.5)^{2a*}	46.7 (6.0)^{2a}
		4	2.8 (3.4)^{2a*}	47.5 (1.4)^{2a}	5.4 (3.4)^{2a*}	47.6 (3.4)^{2a}	8.3 (5.7)^{2a*}	48.7 (5.2)^{2a}
Liquid Phase	120	24	2.5 (4.7)^{2*}	54.3 (3.5)^{2}	4.8 (4.3)^{2*}	53.1 (3.4)^{2}	7.8 (6.7)^{2*}	51.7 (5.4)^{2}
Reference	–	–	5.4 (2.4)^{1*}	–	10.3 (2.4)^{1*}	–	16.1 (3.7)^{1*}	–

Statistically significant differences ($P < 0.05$) are indicated when comparing individual GP with LP acetylation (number), different reaction times within individual temperatures (letters) and comparison with REF (asterisk).

The highest MEE_R values were achieved, in agreement with EMC_R results, by LP acetylation – between 52 and 54%, depending on RH (Table 2). Čermák *et al*. (2022) in their experiment obtained an *MEE* value for acetylated beech samples of 56.5% at 95% RH, which is almost similar to the one obtained in the present work for LP acetylation. The most effective combination of conditions for GP (130 °C/4 h) achieved about 10% lower MEE_R value than LP acetylation, yet no statistically significant differences were found between them. While no significant effect of reaction time on this parameter was found at individual temperatures, in the case of comparison with LP, only times of 3 and 4 hours of GP acetylation achieved similar results, regardless of temperature (Table 2). Only at the highest RH (90%) were all reaction times statistically comparable to LP, although here too a trend of increasing mean *MEE* value with increasing reaction time was clearly visible.

The mean values of the investigated characteristics (MC_{max}, *WRE*, S_m, and *ASE*) of modified wood are given in Table 3. The maximum moisture content (MC_{max}) of unmodified beech wood was 107%, while modification with liquid AAH reduced it to 67%.

Table 3. Mean Values and Coefficient of Variations of MC_{max}, *WRE*, S_m and *ASE* from GP and LP Acetylation and Ref Samples

	T (°C)	*t* (h)	MC_{max} (%)	WRE (%)	S_m (%)	ASE (%)
Gas Phase	100	1	92.5 (6.5)	13.6 (41.6)[1a]	12.2 (12.5)	47.4 (13.8)[1a]
		2	83.3 (8.9)	22.2 (31.2)[2a]	10.6 (16.0)	55.9 (11.1)[1a]
		3	81.3 (5.2)	24.0 (16.5)[2a]	8.6 (22.0)	63.1 (12.9)[2a]
		4	73.7 (8.1)	31.1 (22.7)[2a]	8.5 (14.2)	63.6 (8.1)[2a]
	110	1	81.2 (6.9)	24.1 (21.8)[2a]	8.8 (26.5)	63.5 (12.7)[1a]
		2	83.3 (4.1)	22.2 (14.5)[2a]	7.2 (15.2)	68.5 (7.0)[2a]
		3	79.4 (7.2)	25.8 (20.6)[2a]	7.2 (9.6)	69.1 (4.3)[2a]
		4	78.7 (8.2)	26.4 (22.9)[2a]	6.6 (4.7)	71.6 (1.9)[2a]
	120	1	77.7 (12.7)	27.4 (33.8)[2a]	9.2 (8.1)	60.4 (5.3)[1a]
		2	73.9 (8.8)	30.9 (19.7)[2a]	7.3 (11.5)	68.7 (5.2)[2a]
		3	72.8 (10.4)	32.0 (22.1)[2a]	6.3 (15.8)	72.8 (5.9)[2a]
		4	71.4 (11.3)	33.3 (22.7)[2a]	5.6 (9.3)	76.0 (2.9)[2a]
	130	1	69.9 (6.9)	34.7 (13.0)[2a]	7.8 (15.8)	66.6 (7.9)[1a]
		2	68.5 (9.2)	36.0 (16.4)[2a]	5.5 (18.1)	65.9 (13.6)[2a]
		3	66.6 (9.5)	37.7 (15.7)[2a]	5.6 (20.1)	75.9 (6.4)[2a]
		4	64.5 (9.8)	39.8 (14.8)[2a]	4.9 (12.2)	78.9 (2.6)[2a]
Liquid Phase	120	24	66.9 (5.6)	37.5 (9.4)[2]	4.5 (10.4)	80.5 (2.5)[2]
Reference	–	–	107 (3.6)	–	23.3 (4.0)	–

Statistically significant differences ($P < 0.05$) are indicated when comparing individual GP with LP acetylation (number) and different reaction times within individual temperatures (letters).

The GP modification was less effective in most cases, except when a temperature of 130 ºC was used for a longer time, in which case the modified samples showed values comparable to or even lower than those achieved by LP acetylation. In general, it can be said that, for GP acetylation, the MC_{max} value decreased with increasing temperature and reaction time, indicating an improvement in *WRE* under these conditions. However, the

effect of reaction time on this characteristic at a single temperature generally were not been shown to be statistically significant. Due to the higher variability of individual data sets, statistically significant differences between LP and GP acetylation were also not demonstrated, except for the mildest conditions of 110 ºC /1 h. (Table 3). In GP acetylation, with increasing temperature, shorter times were sufficient to achieve values comparable to LP acetylation, while at 130 ºC the modification time was no longer essential for this comparison. The reduction in MC_{max} of acetylated wood was partly due to a lower *EMC*, where the cell wall can absorb less bound water (Hill *et al*. 2005). However, this does not explain the overall difference, where there was a decrease of more than 30% after acetylation. In high-density woods such as beech, the cell wall in fibre tissue may swell into the lumen during modification (Sander *et al*. 2003), reducing the porosity and therefore the available space for free water, which represents a further decrease in the total water content of the wood in addition to the reduction in the bound water content. LP acetylation achieved the best results due to the highest *WPG*. It is clear from Fig. 6 that these characteristics were significantly influenced by the achieved *WPG* (R = 0.62), where MC_{max} decreases with increasing *WPG* and thus *WRE* increases. This relationship is again based on the known changes induced by acetylation: a decrease in the amount of bound water (*EMC*) and a greater swelling of the cell wall (*BC*) with increasing *WPG*.

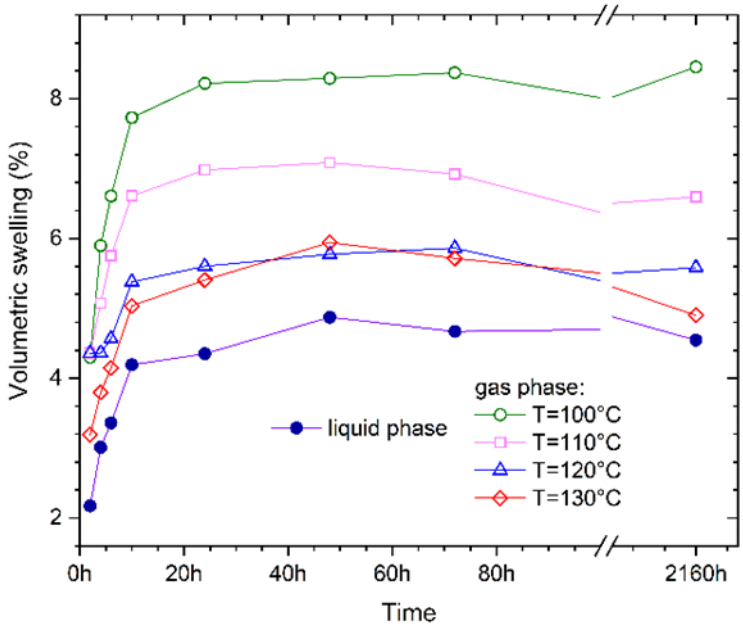

Fig. 4. The S_m values during 2,160 h of water soaking according to the process temperature acetylated in the gas (GP) and liquid (LP) phases

Similar trends were found for volumetric swelling and *ASE*: S_m decreased with increasing temperature and time of GP acetylation, with the lowest swelling value being reached at a temperature of 130 ºC and 4 h, which was close to the value achieved during LP acetylation. The volumetric swelling of acetylated wood (LP) was a fifth that of unmodified wood, which reached 23.3% (Table 3). It is clear from Fig. 4 that both acetylated and untreated samples needed approximately the same time (10 h) to reach maximum volumetric swelling and subsequently the value did not change significantly over the next three months. The *ASE* of acetylated wood (LP) reached a value of 80.5%,

which is comparable to the 75.6% reported by Rowell and Dickerson (2014) for beech wood with a *WPG* of 17.5%. The *ASE* of LP-acetylated wood differed significantly from the values achieved using GP only if the shortest reaction time, usually 1 hour, was used at a given temperature (Table 3). Also, no statistical differences were found for this parameter when using different reaction times at the same temperature. Identical results were also found for S_m, from which the *ASE* parameter is calculated. In Fig. 5 a strong dependence (R = 0.87) can be observed between the *ASE* and *WPG* parameters, which was also shown by Thybring (2013) for different wood species based on the compilation of experimental data from the literature. Generally, the excellent dimensional stability of acetylated wood is attributed to the "bulking effect", in which the cell wall is previously swollen by bulky acetyl groups while its maximum water swelling remains unchanged (Obataya and Gril 2005). Due to the strong relationship between BC and WPG (Fig. 3), the WPG level affects how much of the total wood swelling can still be caused by bound water. Therefore, the primary effect of acetylation on dimensional changes appears to relate to the smaller changes in moisture content in acetylated wood than untreated wood under similar climatic conditions (Zelinka *et al*. 2022).

Likewise, when soaking the samples, the swelling values of the beech wood samples were reduced during the acetylation process in both phases (GP and LP). Like the *EMC* values, the *ASE* values were dependent on the *WPG* value, with its higher value giving better *ASE* results. In most cases, a greater improvement was achieved with LP-acetylation than with GP-acetylation. The higher temperature of the process also contributed to its improvement in the context of a more detailed comparison of GP acetylation. The correlation between *WPG* and *ASE* and *MEE* values was relatively good, with these values increasing with increasing degree of acetylation (Thybring 2013; Zelinka 2022). In the case of thickness swelling, acetylation treatment resulted in a 61% reduction in swelling in *Populus alba* L., and 53% in the species *Fagus sylvatica* L. (Ajdinaj *et al*. 2013; Baufleur *et al*. 2022).

When comparing the dependence of EMC_R and *ASE* (Fig. 5) on the WPG value, it was reported that both investigated parameters improve with increasing WPG independently of the phase type (GP or LP).

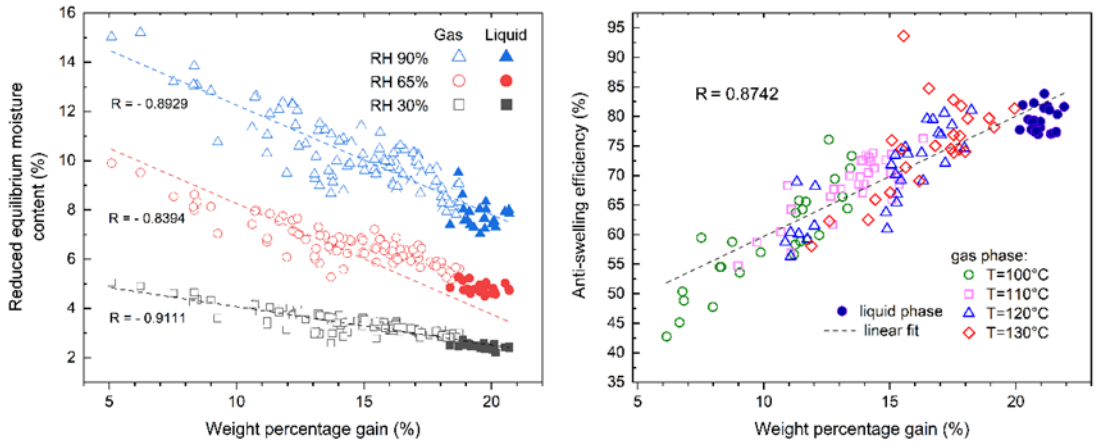

Fig. 5. The dependence of EMC_R on WPG at different relative humidities for acetylated GP (empty circle, rhombus, square) and LP (full circle, rhombus, square) samples – left. The dependence of ASE on the WPG for acetylated GP (empty rhombus, triangle, square and circle) and LP (full circle) samples – right.

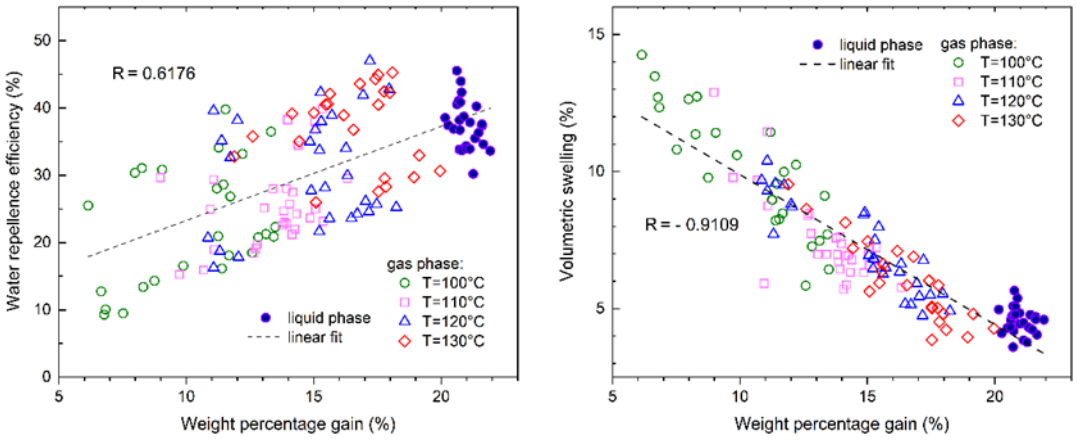

Fig. 6. The dependence of WRE (left) and Sm (right) on WPG for acetylated GP (empty rhombus, triangle, square and circle), LP (full circle) and Ref (full square) samples

When obtaining an 18% WPG value or higher in the GP phase, EMC_R and *ASE* results are comparable to LP acetylated samples. The dimensional stability of wood increases with increasing acetyl content and ASE results are therefore comparable to other experimental results (Militz 1991; Thygesen *et al*. 2010; Rowell 2014).

Chemical Analysis with FTIR-ATR Spectroscopy and Changes in the Chemical Structure

The analysis by FTIR-ATR spectroscopy revealed the chemical changes in wood composition after acetylation in both phases (GP and LP). Figure 7 depicts the collected spectra of the GP samples treated at different temperatures (Fig. 7a) and with different types of treatment (Fig. 7b).

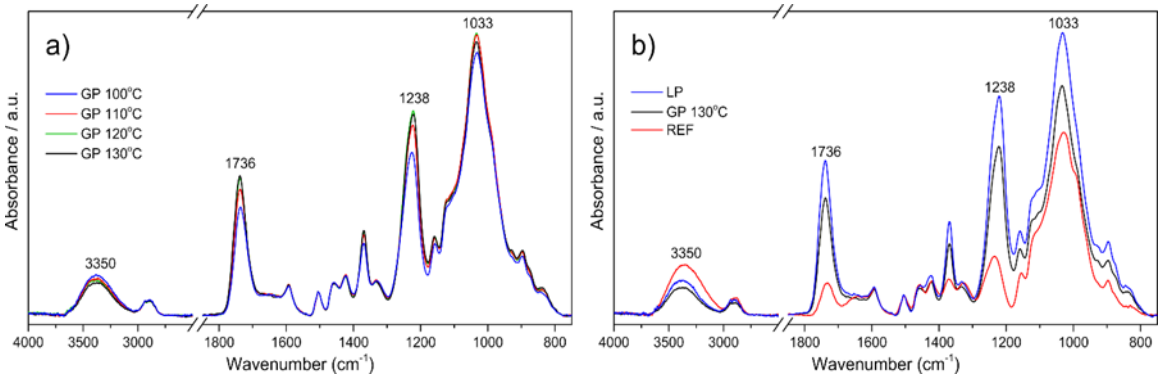

Fig. 7. FTIR-ATR spectra of the investigated samples showing the effect of GP acetylation temperature (a) and the type of acetylation used (b)

The numerical results of the normalised peak areas are shown in Fig. 8. The analysis focused on the peaks at 3350, 1736, 1238 and 1033 cm^{-1}, corresponding to the vibration peaks of (O–H), (C=O), (C–O) and (C–O–C), respectively.

For GP samples treated at different temperatures, a decrease in hydroxyl groups was observed with increasing acetylation temperature, reaching a minimum at 130 °C. The vibration peaks of C=O, C–O and C–O–C reached their highest values at 130, 120, and

110 °C, respectively. This trend, in which acetyl groups replace hydroxyl groups in the cell wall, is confirmed in several other studies (Mohebi 2008; Cetin and Ozmen 2011; Gu *et al*. 2015; Su *et al*. 2019; Wang *et al*. 2024a).

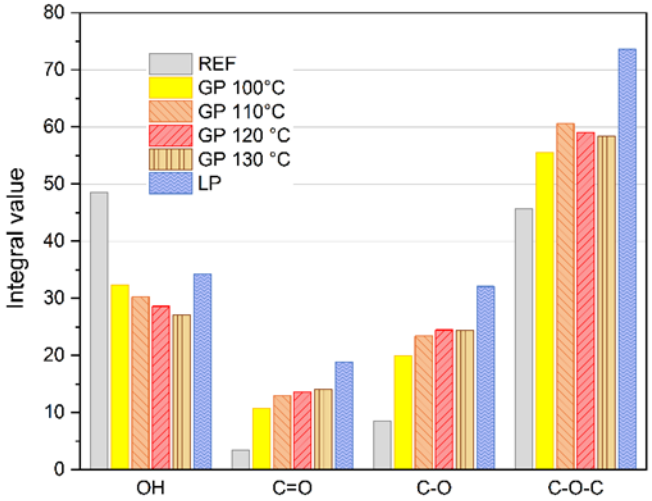

Fig. 8. Bar graph comparing areas of the FTIR vibration bands of selected chemical bonds of acetylated and reference samples

Fodor *et al*. (2018) indicates that acetylation occurs through hemicellulose fractions, where the absorption of C=O and C–O groups is greater in hornbeam wood, while cellulose may undergo only minor changes due to the acetylation reaction – mainly structural in nature. In the case of structural changes in lignin, the color of the wood changes according to the level of phenols.

Both LP and GP samples exhibited a significant decrease in hydroxyl groups compared to the reference sample. The reduction in hydroxyl groups was more pronounced in GP samples. The LP samples showed a significant increase in the other investigated bonds, indicating a higher degree of acetylation. These findings agree with the results of water-related properties (EMC_R and *ASE*), which were better in the case of LP acetylation.

Although FTIR analysis showed a greater reduction in the intensity of hydroxyl groups in GP-acetylated samples, the water-related properties (EMC_R and *ASE*) were more improved in LP-acetylated wood. However, when comparing GP (130 °C) and LP values, no statistically significant differences were obtained in most cases between all the values examined. The exception was usually the shortest reaction time of 1 hour. Nevertheless, GP (130 °C) samples can be considered competitive with LP. This phenomenon can be explained by the lower values of the absorbance peaks for OH groups, which were assessed from FTIR analysis. Mohebby (2008) describes the reduction of functional OH groups in wood cell wall polymers that react with ambient water – a reduction in water absorption due to the bound acetylation groups. Most researchers cite cell wall enlargement and loss of hydrophilic OH groups as important factors, which reduces moisture uptake and subsequently increases the wood's resistance to swelling and decay (Hill and Jones 1996; Hill 2006; Sandberg *et al*. 2021).

CONCLUSIONS

1. Although the liquid phase acetylation achieved slightly better results in almost all measured water-related properties, similar changes in these properties could be achieved by using the gas phase acetylation of beech wood at higher temperature (130 °C). However, it is more appropriate to use a reaction time of 4 hours and a temperature of 120 or 130 °C to ensure a sufficient degree of modification within the wood variability. Lower temperatures and reaction times are not able to ensure sufficient reaction rate leading to significant degree of substitution of OH groups with acetyl ones. Increasing reaction time and temperature in gas phase acetylation led to an increase in weight percentage gain and bulking coefficient, while at the same time there was a decrease in equilibrium moisture content, volumetric swelling, and maximal moisture content of beech wood. Even in gas phase acetylation, the weight percentage gain (WPG) values significantly correlated with water-related properties.
2. Acetylation in the gas phase was able to achieve similar results as liquid acetylation even at sufficiently low temperatures that avoid possible thermal degradation of wood. Due to the lower consumption of acetic anhydride (AAH) during the process, gas phase (GP) acetylation could also find application in industrial modification; however, it is necessary to determine its possibilities in the modification of real-sized wooden elements. For this purpose, it is necessary to design a new GP acetylation device and determine the optimal conditions (temperature, reaction time, pressure) for uniform treatment of European beech.
3. Based on the results of Fourier transform infrared with attenuated total reflectance (FTIR-ATR) chemical analyses, a decrease in OH groups that reacted with AAH in both phases was observed because of acetylation – observed as increases in C=O/C–O/C–O–C band intensities. However, to exploit the potential of gas-phase chemical reactions for wood modification, further research is needed to explore its effects on other wood species and additional wood properties, including durability, mechanical performance, and aesthetic characteristics.

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