Sorption of water and ethanol pure vapours and vapour mixtures by four hardwoods

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Sorption of pure vapours and vapour mixtures by four hardwoods. Thermodynamic and kinetic aspects

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Abstract

Water is a universal solvent and swelling agent that is widely used in wood industry in association with organic solvents and salts, whether for the fractionation of biomass and the production of bio-based synthons for the chemical industry, the application of sizing agents and painting for the paper industry, or the incorporation of preservatives to enhance wood durability for the timber industry. The relevance of solvents and technical treatments used for wood-based products requires a proper identification of the specific role of each solvent on wood biopolymers to better understand and predict their influence on wood properties. In particular, wood impregnated with aqueous solutions of organic solvents have shown to give rise to greater swelling than that observed in pure water, described as “hyperswelling”. To understand this phenomenon, the first step is to examine the existing interactions between wood microstructure and the different solvents present in these mixtures. This study is an attempt to bring to light the sorption behaviour of four different hardwoods in water–ethanol vapour mixtures containing increasing molar fractions of ethanol from 0 to 100%. Contrasted sorption behaviour in pure solvents were observed according to wood species having different biochemical composition. This behaviour highlights the different affinities of ethanol and water for the macromolecules present in the wood microstructure. With mixed solvents, peculiar effects were confirmed in sorption behaviour of woods with lower mixed solvent uptake at high partial pressures compared to pure solvents. It is also shown that part of the sorbed ethanol molecules remains chemisorbed in the wood structures at the end of the desorption process.

1. Introduction

Wood is a renewable biomaterial that is used since thousands of years for many purposes such as energy, building material, paper, tools, furniture or packaging. Considering the importance of wood in the current environmental context and the development of bio-economy in many industrial sectors, better characterizing the properties of wood according to species and environmental conditions while considering its specific hierarchical microstructure is of great concern. In particular, the fractionation of biomass by organosolv pulping (Thoresen et al. 2020) and the production of bio-based synthons for the chemical industry in biorefineries (Abu-Omar et al. 2021) involve the use of water in association with salts and/or organic solvents. The interaction of wood with water-dilutable solvents or the action of pure organic solvents on incompletely dried wood are also relevant for surface treatments and incorporation of additives in the timber industry (Chronopoulos et al. 2020). In this regard, the relevance of solvents and technical treatments used for wood-based products requires a proper identification of the specific role of each solvent on the macromolecules present in the wood cell layer and their influence on wood properties. Therefore, the sorption mechanisms of water, organic solvents and their mixtures, their distribution and physico-chemical interactions within wood microstructure needs to be better described and understood.

The extent of wood swelling is very dependent on the nature of sorbed liquids (Gordy 1939). Correlations between the physico-chemical properties of the sorbed liquids and their effect on wood swelling has been

mainly discussed in terms of size and polarity of solvent molecules. Various researchers have documented a negative relationship between the molar mass of solvent molecules and the rate of wood swelling. This correlation can be attributed to the increased challenge faced by larger molecules in diffusing into the intricate structure of wood cell walls (Stamm and Loughborough 1942; Stamm and Tarkow 1950). On the other hand, Nayer and Hossfeld observed a greater and faster uptake of polar liquids into wood cell walls (Nayer and Hossfeld 1949), due to their higher bonding capacity towards wood biopolymers. Mantanis *et al*. studied the effect of a wide variety of pure solvents on the swelling of various wood species (Mantanis et al. 1994a, b, 1995), and confirmed these observations. They found that both higher hydrogen bonding capacity and smaller size of the solvent molecules contribute to the extent of wood swelling. Thus, considering only pure water and organic solvents, the swelling of wood at saturation is well documented (Obataya and Shibutani 2005; Engelund et al. 2013; Bossu et al. 2018).

Nevertheless, in numerous industrial applications, the combination of organic solvents with water is common practice, and water is already inherently present within the microstructure of wood. The phenomena related to the influence of aqueous solutions containing organic solvents on wood are intricate and have resulted in remarkable observations. Indeed, it was observed that an aqueous mixed solvent could induce more swelling than either of the pure solvents (Robertson 1964). Several authors pointed out this synergistic effect of aqueous mixed solvents on wood swelling (Meier et al. 2005; Chang et al. 2009, 2012; Bossu et al. 2018). Meier *et al.* reported that aqueous solutions of ethanol generate “hyperswelling” (Meier et al. 2005), resulting from specific interactions with the biopolymers constituting wood microstructure. More precisely, greater swelling was observed for a 50% volume fraction of ethanol in water. Nishida *et al.* obtained similar results on gels of acetylated lignin (Nishida et al. 2003), showing no swelling in ethanol but eight times the initial volume when swelled in a 50%mol water/ethanol mixture. But despite the numerous works that report this phenomenon, few works hypothesize a mechanism that would explain its origin.

Bossu *et al.* made microscopic observations of cell walls after swelling of poplar wood in water/ethanol mixtures (Bossu et al. 2018), and showed that ethanol generates intercellular decohesion and disbonding of the different wood cell wall layers. This phenomenon is assumed to be at the origin of the hyperswelling of wood in water/ethanol mixtures, as the release of constraints between the wood cell wall layers is likely to promote greater swelling of the cell walls by water. The synergic effect of the solvents on wood cell wall swelling in this case would consist in a structural mechanism rather than a change in the volume of solvent uptake. This hypothesis suggests that the modification of the microstructure enable to reach higher swelling rate for similar quantities of sorbed water.

To check this hypothesis, a step forward would be to study the effect of mixed vapours on the sorption behaviour of a greater diversity of wood species considering their specific microstructure. With this objective, this work focuses on the sorption properties of four hardwoods, with contrasted biochemical composition, exposed to various water/ethanol mixtures.

2. Materials and Methods

2.1 Materials

Four types of hardwood were used in this study, namely Poplar, Oak, Chestnut and Walnut. Specimens were collected from branches of four different wood species collected in March 2019 in two distinct French agroforestry systems : *(i)* trees from hedgerows (Saint-Etienne-en-Coglès, Brittany) - pedunculate oak (48° 21' 5.62" N; 1° 12' 16.654" W) and common chestnut (48° 21' 5.62" N; 1° 12' 16.654" W); *(ii)* trees from an intraparcellar cropping system (Terres de Roumassouze, Vénézobres, Occitania) - hybrid walnut *Juglans x Intermedia* (44° 7' 37.934" N; 4° 5' 0.067" E) and poplar *cultivar Beaupré* (44° 7' 37.934" N; 4° 5' 0.067" E). The specimens were conditioned as follows by BioWooEB - CIRAD (Montpellier, France): 300 x 14 x 2.6 mm long heartwood sticks were cut from branch sections, in the longitudinal direction, considering the width of the sticks in the T direction and thickness in the R direction and then stored for a year in climatic chambers at 20°C ± 2°C and 65% ± 5% relative humidity. Later, specimens were stored at room temperature and 45% ± 5% relative humidity before sorption measurements. Biochemical compositions of the different hardwoods were determined at LERMAB (Nancy, France) and are given in Table 1 (note that α-Cellulose contents are lower in wood branches at the expense of hemicelluloses). Oak and walnut wood are both characterize by high content of extractives. Oak wood extractives have been widely characterized for wine and spirits aging in wooden barrels. Ellagitannins (polyphenols, hydrolysable tannins) represent 10% of the dry weight in oak heartwood. They are responsible for the high durability of wood. Walnut heartwood extractives have also mainly composed of ellagitannins. (Fukuda et al. 2003; Yalcin et al. 2018) Deionised water and pure ethanol (Sigma-Aldrich) used for sorption experiments were outgassed before use. The binary mixtures of ethanol and water were prepared with 1:2 and 2:1 ratios, *i.e.* mass fractions of 33.3% and 66.6% ethanol in the aqueous mixture, respectively. These mass fractions are displayed as 33% and 66% in the legends of the figures for the sake of clarity.

Table 1
Biochemical composition of the four hardwoods used in this study

Species	Extractives* (%)	Klason Lignin (%)	Holocellulose (%)	α-Cellulose (%)	Hemicelluloses (%)
Poplar	4.09	22.82	68.73	20.9	47.83
Chesnut	7.75	17.36	64.48	16.87	47.61
Oak	10.29	16.29	63.85	18.46	45.39
Walnut	11.49	20.67	63.67	21.5	42.17

* sum of extractives after successive extraction using dichloromethane, acetone, toluene/ethanol (1V/2V) mixture and water. These extractives have not been identified in this study, however, according to the literature, the obtained extractives are mostly tannins, terpenes in the case of Oak, whereas they are made of flavonoids, lignans and sterols in the case Walnut (Peng et al. 1991; Balaban and Uçar 2001; Heim et

al. 2021). In the case of Poplar and Chestnut, which have lower extractive contents, sterols and terpenoids are the most present (Szadkowska et al. 2021).

2.2 Methods

Isothermal sorption analyses were performed using a Dynamic Vapour Sorption (DVS) Resolution apparatus (Surface Measurements Systems, London, UK). This apparatus allows determining accurate sorption isotherms at different temperatures and using a pre-set range of partial pressures. The device contains two measurement pans *i.e.*, reference and sample holders, suspended from the arms of a Cahn ultra-sensitive magnetic compensation microbalance, which is capable of measuring sample mass change as low as 0.1 µg. The two measurement pans were connected to the microbalance by hanging wires sitting in a linked double chamber, which is located in a thermostatically controlled cabinet. A constant flow of dry nitrogen gas (100 mL/min), into which is mixed another nitrogen stream containing the vapor, passes through the chambers, thus maintaining a constant partial pressure of vapour. A typical run starts in isothermal conditions from 0% partial pressure and then increases to 80% with successive steps of 20%, before decreasing back to 0% in the reverse order. Successive steps of partial pressures of vapour in nitrogen were set for determining the whole sorption isotherm. The typical duration of sorption cycle was 6 days. The equilibrium criterion was decided based on the slope of the curve mass versus time. This parameter, namely dm/dt, was set as 0.004% which resulted in a ~ 23 hours of time required for each partial pressure in case of ethanol and aqueous mixtures, whereas only ~ 5 hours were required in case of pure water. Interestingly, the desorption processes were faster in case of ethanol and aqueous mixtures for each partial pressure, *i.e.* only 10 hours were required whereas there was no significative change in the case of pure water compared to sorption times. All the experiments were conducted at 25°C. The saturation pressures of the mixed solvents have been calculated considering that ethanol/water mixtures are an ideal system on all the molar fractions investigated. In this case, the total pressure of the mixture can be calculated according to the Dalton law:

$$\mathrm{x}_{\mathrm{ethanol}}=\frac{\mathrm{p}_{\mathrm{ethanol}}}{\mathrm{p}_{\mathrm{ethanol}}+\mathrm{p}_{\mathrm{water}}}$$

1

According to the Raoult law, $\mathrm{p}_{\mathrm{ethanol}}=\mathrm{x}_{\mathrm{ethanol}}\ \mathrm{p}_{\mathrm{ethanol}}^{*}$, in which $\mathrm{p}_{\mathrm{ethanol}}^{*}$ refers to the vapour pressure of pure ethanol whereas $\mathrm{p}_{\mathrm{ethanol}}$ refers to the vapour pressure of ethanol in the water/ethanol mixture. In a symmetric fashion, the same equation can be written for water.

Assuming that ethanol and water vapours are perfect gases, the vapour pressure of mixtures can therefore be estimated as:

$$\mathrm{p}_{\mathrm{mix}}=\mathrm{p}_{\mathrm{ethanol}}+\mathrm{p}_{\mathrm{water}}$$

2

At saturation, the saturation pressure of the mixture can therefore be written:

$$p_{mix}^{sat} = p_{ethanol}^{sat} + p_{water}^{sat}$$

3

where $p_{ethanol}^{sat}$ is the saturation pressure of ethanol in the water/ethanol mixture and p_{water}^{sat} is the saturation pressure of water in the same mixture. It can be concluded that:

$$p_{mix}^{sat} = p_{ethanol}^{*,sat} + x_{water}(p_{water}^{*,sat} - p_{ethanol}^{*,sat})$$

4

The relative pressure of the mixture can therefore be written as:

$$\frac{p_{mix}}{p_{mix}^{sat}} = \frac{x_{ethanol}\, p_{ethanol}^{*} + x_{water}\, p_{water}^{*}}{p_{ethanol}^{*,sat} + x_{water}\,(p_{water}^{*,sat} - p_{ethanol}^{*,sat})}$$

5

The saturation pressures of the pure sorbates were measured at 25°C in our sorption apparatus. They were found to be 3200 Pa and 7866 Pa for water and ethanol respectively.

3. Results and Discussion

3.1. Pure vapours

The sorption of water and ethanol on the four wood species can be discussed, first considering pure solvent vapour sorption. In case of pure water, the sorption isotherms obtained have identical general shape as can be seen in Fig. 1.

The adsorption branches are rather linear, indicative of a rather mild wood/water affinity, in the Henry's law sense. A slight inflexion was however observed at p/p° = 0.25, indicating a possible transition between adsorption and absorption regimes. Indeed, adsorption requires interaction sites and usually these sites interact first with sorbates. Once these sites are completed, other sorption processes can take place, such as absorption, or adsorption with less interactive sites. As above-mentioned, common features can be observed with the four woods used in this study. It can be deduced that the differences in terms of composition of lignin and extractives do not modify the water sorption isotherms. The desorption branches are also rather linear, even though a thin parallel hysteresis is observed. Therefore, it can be concluded that water sorption process can be considered as almost reversible for all studied hardwoods. This general behaviour is consistent with the studies reviewed in the past by Shi and Avramidis. (Shi and Avramidis 2017) In other words, the preferential interaction of water with the hydrophilic fraction of the cell wall layer is little disturbed by the presence of extractives compounds. The structure of the ellagitannins extractives present in oak and walnut wood present several hydroxyl

functions. (Puech et al. 1999; Jourdes et al. 2003; García-Estévez et al. 2017) The extraneous substances present in the cell wall in these two wood species may thus participate to water sorption. The shape of the observed hysteresis loops is typical of an activated sorption process, which requires more energy for the adsorption process, compared to the desorption process. This is compatible with a swelling mechanism in which the sorbate would be absorbed inside the bulk of the wood specimen. In terms of water uptake, it can be noted that for all the four woods studied in this work, the uptake is ~ 130 mg g^{-1} at p/p° = 0.8, regardless of the type of wood studied. Based on the slopes of the sorption isotherms, it can be assumed or anticipated that more water would adsorb at higher partial pressures, where capillary (or vessel) condensation effects would become significant.

In the case of pure ethanol (Fig. 2), the sorption isotherms are different to those observed with water. They not superimposed to one another as it was the case for pure water sorption, indicating that ethanol interacts with the wood specimens through sorption sites, which are of different nature and concentration between the different hardwoods.

The sorption isotherms of Oak and Walnut exhibit similar shapes. The adsorption branches of both woods are almost linear indicating a non-specific interaction between wood and ethanol. However, the desorption branches are not parallel at all to the adsorption branches, as shown by the large hysteresis loop observed. Additionally, back to p/p_0 = 0, a quantitative irreversibility can be measured (between 1.5 and 2.5 wt%). This large hysteresis loop can be explained by assuming that upon adsorption, ethanol reacts with, or modifies, the wood cells. After modification or reaction, ethanol is likely difficult to be removed from the wood samples. We postulate that ethanol could react, through chemisorption, with the extraneous substances like ellagitannins present in the cell wall of these two species, which might modify its interaction with ethanol by reducing the number of accessible adsorption sites. Similar observations have already been reported for red wine tannins, where ethanol was proved to reduce the chemical interactions with salivary proteins. (Serafini et al. 1997) In the case of Chestnut and Poplar woods, the affinity of ethanol is enhanced compared to Oak and Walnut, as the slopes of the adsorption branches at low relative pressure are higher. The sorption branches are not linear which indicates that the interaction sites are heterogeneous. Similar conclusions as Oak and Walnut can be drawn with respect to the hysteresis and irreversibility at p/p° = 0. Additionally, it is interesting to note that the irreversibility after desorption is higher for Walnut and Oak, compared to Chestnut and Poplar, while their affinity for ethanol is lower.

For explaining these observations, the composition of these specimens has to be considered (Table 1). The main difference between these two pairs of specimens is their extractive contents. Indeed, it can be noted that Poplar and Chestnut have lower extractive contents (4.1% and 7.7% respectively) compared to Oak and Walnut (10.3% and 11.5% respectively). Water seems to be adsorbed, regardless of this parameter, whereas it seems to strongly affect ethanol sorption. It can be deduced that higher contents of extractives prevent ethanol interactions with the hydrophilic macromolecules of the cell wall layer (amorphous cellulose and hemicellulose) whereas this does not affect water sorption. Additionally, a confirmation of this particular interaction for ethanol can be seen on the sorption isotherms shown in

Fig. 2. An inflexion of the adsorption branches (at p/p° = 0.2) indicates the transition between sorption processes. This could be due to the extractive components which are less present in Chestnut and Poplar specimens.

A high affinity is usually the indication of a strong interaction leading to some irreversibility after the completion of the sorption isotherm. However, this is true only if one sorption process is present. In fact, if different sorption phenomena occur upon increasing pressure, the correlation is not always true. In other words, ethanol can be first adsorbed with a rather low affinity and as the pressure increases, ethanol can react with the extractives. As more extractives are present in Walnut and Oak, their sorption isotherm would present both lower affinity and higher irreversibility, compared to Chestnut and Poplar.

These findings are different to those obtained by Bossu *et al*. (Bossu et al. 2018) Indeed, in the case of Poplar veneers, these authors noted that there was almost no adsorption at low relative pressures (around 0.1 wt% up to p/p° = 0.3), while at p/p° = 0.8% the ethanol uptake was very close to the data obtained in this study. This discrepancy could originate from the equilibration times used in that study, which could have been underestimated. (Bossu et al. 2018)

This affinity can be also quantified by the Henry's constants which have been derived for each system (Table 2).

These Henry's constants values are the confirmation that water has a very similar interaction for the four specimens as the values are very close to one another. On the other hand, Chestnut and Poplar have a higher affinity towards ethanol compared to Walnut and Oak, as previously inferred from the adsorption branches at low relative pressure. Interestingly, when comparing water and ethanol affinities, Chestnut and Poplar have higher affinities for ethanol compared to those for water. This is the opposite for Walnut and Oak.

An alternative description of these sorption isotherms can be gained by using the GAB approach, which is classically used for biomass-based materials (Anderson 1946). This model was first developed for extending the sorption isotherm modelling of the BET approach (Brunauer et al. 1938) by considering the adsorption interaction level not only of surface monolayers but also between interacting multilayers. It has been recently rationalized in the case of water sorption by wood specimens (Bertolin et al. 2020). The GAB theory is formally similar to other modifications of the BET model (Dent 1977) but also to models based on different approaches (Hailwood and Horrobin 1946; Okoh and Skaar 1980).

Table 2
Sorbate – specimen Henry's constants derived at low relative pressure at 25°C.

	Henry's constant / $mg.g^{-1}$	
Specimen	Water	Ethanol
Chesnut	192	255
Walnut	196	124
Oak	186	129
Poplar	205	229

As an example, in (Hailwood and Horrobin 1946), researchers proposed a model to explain the water absorption behavior of polymer gels. In their study, the authors specifically defined the strongest sorption interaction as the absorption of hydration water molecules that directly interact with the polymer. Concomitantly, a weaker sorption interaction was attributed to "solved" water, which contributes to the gel swelling. One can observe that the formal similarity between the BET and GAB models suggests that, solely relying on uptake isotherms, it becomes challenging to differentiate between surface adsorption and bulk absorption phenomena. (Prothon and Ahrné 2004). Interestingly, the GAB approach was also proved to be successful for modelling the sorption of vapours penetrating inside low specific surface area materials, particularly in food science. Indeed, a distinction between "bound" and "free" sorbate instead of monolayer and multilayer adsorption was further introduced by Quirijns *et al*. (Quirijns et al. 2005). Even if this distinction is still an issue, it is strongly supported by the observation that on wood samples, typical GAB monolayer sorption values are more than one hundred times larger than monolayer adsorption values measured using non-penetrating nitrogen derived using the BET model (Clair et al. 2008; Bratasz et al. 2012; Bossu et al. 2018). According to the GAB model:

$$\frac{W}{W_m}=\frac{K_{GAB}\times C_{GAB}}{(1\text{-}K_{GAB}\times p/p^o)(1\text{-}K_{GAB}\times p/p^o+K_{GAB}\times C_{GAB}\times p/p^o)}\times\frac{p}{p^o}$$

6

where W is the weight uptake at p/p°, W_m is the monolayer capacity, here expressed as $mg.g^{-1}$. This weight uptake corresponds to "bound" sorbate species. C_{GAB} is an energetic constant related to the ratio between the Gibbs free energies of bound and free sorbate, whereas K_{GAB} is defined as the ratio between the Gibbs free energy of the liquid in the bulk and that of the free sorbate. It can be noted that C_{GAB} and k_{GAB} are reminiscent of the C_{BET} parameter in which multilayer interaction has been ignored. Indeed, C_{GAB} can be defined as :

$$C_{GAB}=C_o\exp(\frac{H_o\text{-}H_n}{RT})$$

7

where H_o and H_n correspond to the molar sorption enthalpy of the mono and multilayers, respectively. K_{GAB} is defined according to the following equation :

$$k_{GAB}=k_o\exp\left(\frac{H_n-H_L}{RT}\right)$$

8

where k_o represents the entropic factor and H_L the molar enthalpy of adsorption of the bulk liquid. The comparison of the C_{GAB} values is sensible, whereas absolute values are difficult to discuss, as are the C_{BET} values in the BET model.

The values of the GAB constants for the four specimens in presence of water and ethanol vapours are reported in Tables 3 and 4. In the case of water sorption, Chestnut shows a higher sorption capacity, and also a higher specific surface area. Additionally, this specimen shows a lower monolayer interaction as its C_{GAB} parameter is lower compared to those obtained with the other specimens. On the other hand, the other three specimens exhibit very similar interaction parameters, again indicative of similar wood/water interactions. We already reminded the fact that the K_{GAB} parameter is essentially of entropic nature. Its low value (< 1) regardless of the nature of the specimen, suggests here that water molecules sorbed during the multilayer building process, once monolayer capacity completed, are clearly more structured than they are in the liquid water phase. The C_{GAB} values are very similar, which confirms that the water/specimen interaction does not depend on the nature of the wood.

Table 3
GAB parameters for water sorption on the four specimens. The specific surface area were determined, taking the cross-sectional area of water as 0.105 nm^2. (Trens et al. 1996; Rouquerol et al. 2013)

	C_{GAB}	K_{GAB}	W_m / $mg.g^{-1}$	r^2	S_{GAB} / $m^2.g^{-1}$
Chestnut	6.46	0.79	58	0.9999	206
Walnut	8.32	0.85	51	0.9999	179
Oak	7.18	0.84	52	0.9999	182
Poplar	7.32	0.84	53	0.9999	187

Table 4
GAB parameters for ethanol sorption on the four specimens. The specific surface area were determined, taking the cross-sectional area of ethanol as 0.145 nm^2. (Tang et al. 2019)

	C_{GAB}	K_{GAB}	$W_m / mg.g^{-1}$	r^2	$S_{GAB} / m^2.g^{-1}$
Chestnut	10.74	0.53	81	0.9999	153
Walnut	2.02	0.44	140	0.9983	-
Oak	2.52	0.37	143	0.9998	-
Poplar	11.47	0.57	67	0.9998	127

Compared to water sorption, several comments can be put forward, considering ethanol sorption in the light of the GAB model. Concerning the derivation of the specific surface area, the model failed when applied to Walnut and Oak. Indeed, in these cases, the calculated monolayer uptake is obtained at relative pressure above 1, which is the indication that this model cannot be used in a correct fashion. In the case of Chestnut and Poplar, the specific surface areas could be derived. They are lower than those derived using water as sorbate. A reason for this discrepancy can be found in the cross-sectional area taken for ethanol which is less common than that used for water and therefore less robust. It can be also argued that ethanol is a larger molecule, compared to water, which makes it more difficult to accommodate all the surface of the specimens. The GAB parameters obtained for Chestnut and Poplar are also of interest. They are consistent with the conclusions drawn from calculated Henry's constant. Indeed, the C_{GAB} parameters are higher compared to those obtained from water sorption, which is the indication that ethanol has a higher affinity for these specimens. This affinity could be related to the interaction with the macromolecules of the walls which are more accessible when less extractives are present. As discussed above, the irreversibility would be related to the presence of extractives, which is more visible in the case of Oak and Chestnut. Additionally, the K_{GAB} are lower, which shows that, for all the specimens, the ethanol adsorbed in the multilayer building process is less structured than in the case of water.

3.2. Mixed vapours

In the liquid phase, mixed solvents are known to induce specific behaviours towards wood swelling compared to pure solvents. It can be assumed that the sorption properties of wood samples do result from synergistic effects. Water/ethanol vapour mixtures were therefore tested and for these experiments, two different compositions were chosen (33.3% and 66.6% molar mass ratio of water). A comparison of the mixed vapours sorbed on the four wood samples is shown in Fig. 4.

The sorption isotherms shapes were observed to be similar, regardless of the water/ethanol ratio and wood sample, indicating that the solvent mixtures average the interactions ruling governing the sorption process. Compared to pure systems, this observation is reminiscent of the case of pure water with which very similar sorption isotherms were obtained for all tested species (see Fig. 1). However, in the case of mixed vapours, for both ethanol concentrations, the sorption isotherms exhibit wide hysteresis loops

which have only been found in the case of pure ethanol sorption isotherms. Additionally, differences can also be distinguished at p/p° = 0 on the desorption branches where the data are more scattered for 66.6% ethanol.

These observations could be interpreted as intermediate situations between pure water and pure ethanol sorption isotherms. Indeed, the large hysteresis loops can be related to ethanol whereas the similarity of the shape of the adsorption branches is more reminiscent of pure water sorption. To obtain more insight on these results, the sorption isotherms were gathered for each wood specimen and solvent mixture in Fig. 5.

For all the woods tested, it can be observed that the mass uptake at high p/p^o is lower for mixtures compared to pure solvents. This observation tends to indicate that the phenomenon of wood hyper-swelling in mixed solvents is not resulting from a higher quantity of sorbed solvent but rather related to the enhancement of wood cell wall swelling ability after they have been modified by ethanol molecules. Such hypothesis is consistent with Bossu *et al*, who already observed this synergistic effect, in case of poplar veneers in water/ethanol mixed solvents (Bossu et al. 2018).

Interestingly, except in the case of chestnut, the maximum mass uptakes of the mixtures are very close to that obtained using pure ethanol. It can be concluded that for these three wood species, ethanol rules the maximal sorption capacity of the cell wall layer at high relative pressure when water/ethanol mixtures are being used. Furthermore, in the case of Chestnut, despite a higher ethanol sorption, the ethanol/water mixtures do not adsorb more than in the other wood specimens. These effects strongly suggest a synergistic mechanism through which ethanol co-adsorption limits the accessibility of water to hydrophilic sites. It is also interesting to observe that the sorbate retention at the end of desorption process, also observed in the presence of ethanol, is independent on the ethanol concentration in the vapour. This suggests that the presence of water does not affect the accessibility of the sorption sites responsible for strong interactions with ethanol.

The evolution of the sorption isotherm shape can also be discussed, even though the saturation pressure of both pure sorbates is different. This is the reason why the Raoult's law was used to determine a saturation pressure for the mixture. It can be observed that, for all the specimens, the adsorption branches of the sorption isotherms obtained in case of vapour mixtures are very close to that of water up to a relative pressure of $p/p^o = 0.5$. This is the indication that the mixture adsorption is ruled by the water species in the mixture on the most active surface sites, which always interact at low relative pressure. As the Henry's constant is related to a specific surface site/sorbate interaction, it cannot be derived for mixtures. However, it can be concluded that in water/ethanol mixtures, water drives the sorption process on the most active sites, that is up to relative pressure p/p_0 of 0.5. At higher relative pressure on the adsorption branches and also on the desorption branches, the shape of the sorption isotherms is similar to that of the pure ethanol sorption isotherms, suggesting that the ethanol is responsible for the hysteresis loop obtained in case of mixed solvents. Indeed, the amount of ethanol in the mixture seems to

have a direct impact on the size of the hysteresis loop. In other words, the size of hysteresis loop increases with increasing molar mass fraction of ethanol.

The maximum mass uptakes can be better seen in Fig. 6 (A) for each specimen and water/ethanol mixture. The results presented are at the thermodynamic equilibrium. As mentioned in the experimental section, the equilibrium criterion was taken as the slope of the mass variation versus time. However, it is clear that diffusion plays an important role in sorption processes involving complex structures such as woods. We therefore also focused on the equilibration times recorded for each sorption isotherm, which provide information on the kinetics of adsorption and desorption. The results are presented in Fig. 6 (B-D).

When looking at the full sorption cycle times, clear differences can be observed (Fig. 6, (B)). The sorption cycle time in case of pure water is the shortest, regardless of the wood concerned (around 40 hours). When ethanol is adsorbed, pure or in water/ethanol mixtures, the sorption duration is much longer, around 120 hours reaching up to 185 hours in the case of Walnut when pure ethanol is adsorbed. The results are consistent with the lower values obtained for constant K_{GAB} in the GAB model obtained in the case of ethanol, despite the fact that the GAB model failed in the case of Walnut and Oak. Indeed, as ethanol sorbed during the multilayer mechanism is less structured than in the case of water, it can be deduced that it takes much longer time to reach equilibrium.

When studying adsorption and desorption kinetics of water, these two processes require similar durations, which is consistent with the reversibility of the sorption processes already discussed. In case of mixtures and pure ethanol, adsorption processes were two to four times longer than desorption processes. However, in the case of pure ethanol sorption by Walnut, adsorption and desorption time were quite similar, making this sorption process the longest observed in this study, which may be related to the highest extractives content (11.5%) found in Walnut. The kinetic differences observed between water and ethanol mixtures sorption can be rationalized by keeping in mind that in the latter cases, significant irreversibility could be measured. In other words, if the desorption of ethanol and ethanol mixtures is faster that the corresponding sorption processes, it is because a part of the sorbed ethanol molecules remains chemisorbed in the wood structures, whereas the loosely bound and absorbed molecules are easily desorbed.

4. Conclusion

This study was conducted to interrogate the sorption behaviour of four hardwood species in pure water and ethanol vapours and their mixtures in different proportions. Dynamic Vapour Sorption was employed to assess if the modification of wood swelling properties could be explained by contrasting sorption behaviour of the different hardwoods as the result of wood/vapour and wood biopolymers interactions. The four hardwood species showed synergistic effects in mixed vapours, as the amount of mixed vapours uptake at high partial pressures was found to be lower than for pure vapours. It was also shown that part of the sorbed ethanol molecules remains chemisorbed in the wood structures at the end of the

desorption process. These results are related to different behaviour of wood species towards sorption / desorption process in relation with their specific microstructure and biochemical composition, higher contents of extractives being responsible for interactions with ethanol. More specifically, it is shown that ethanol has a higher affinity compared to water which could be related to the interaction with the macromolecules of the cells walls. The extractives clearly play a prominent role in these vapours sorption processes in the sense that their presence induces higher irreversibility, as shown for Oak and Walnut. This irreversibility observed at the end of the desorption is not correlated by the Henry's constants as these parameters do not refer to the same processes. Additionally, it has been shown that the ethanol adsorbed as multilayers, which is reminiscent of an absorption process, is less structured than in the case of water. In terms of kinetics, Walnut exhibited the longest time of full desorption of ethanol which can be related to its higher extractives contents leading to a higher ethanol irreversibility.

Investigations on the impact of the selective interactions of pure vapours or vapour mixtures towards wood microstructures during static and dynamic mechanical measurements are in progress.

Declarations

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Author contributions

F.D.R found the financial support from the EU. P.T., F.D.R and N.L.M. designed the experimental protocols. P.Y. did the experiments. P.Y. and P.T.wrote the first draft. J.B. , N.L.M. and S. C. updated the references section. P.T. and F.D.R. assessed the sorption isotherms. F.D.R. added the GAB approach to the results section. All authors reviewed the manuscript. P.T. submitted the manuscript to the Journal?

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Data availability

The raw data to reproduce the results are available from the corresponding author upon reasonable request.

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Figures

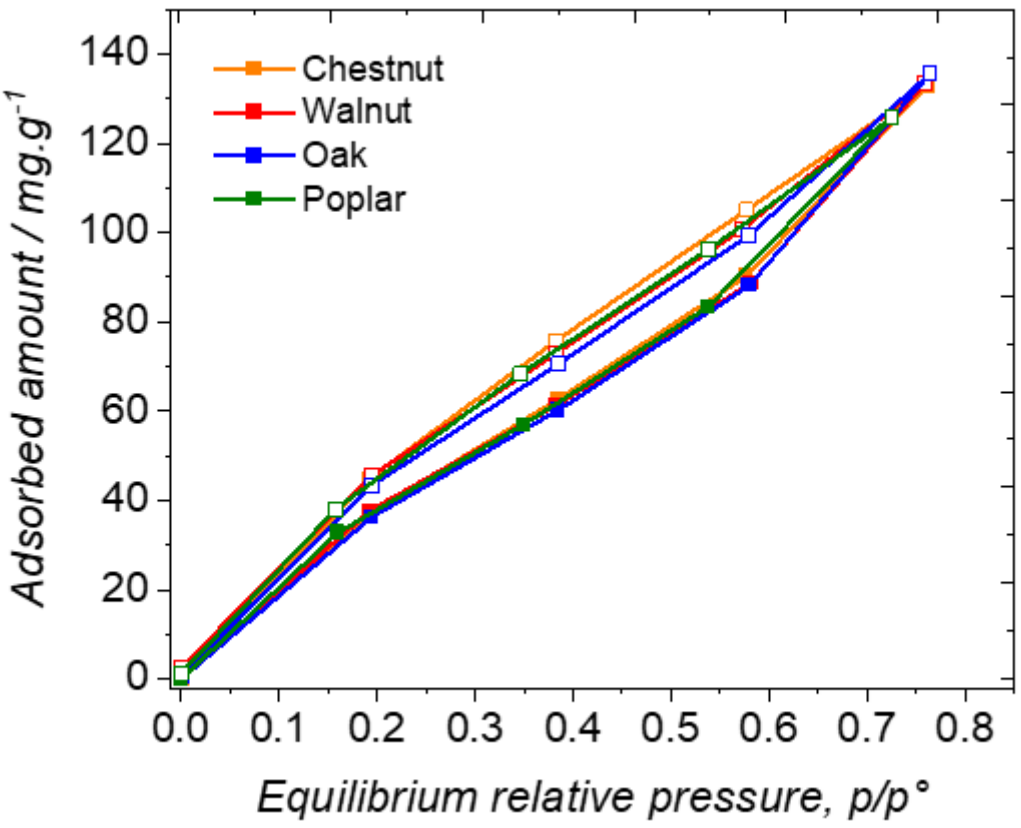

Figure 1

Sorption isotherms of pure water vapour by the four hardwoods at 25°C.

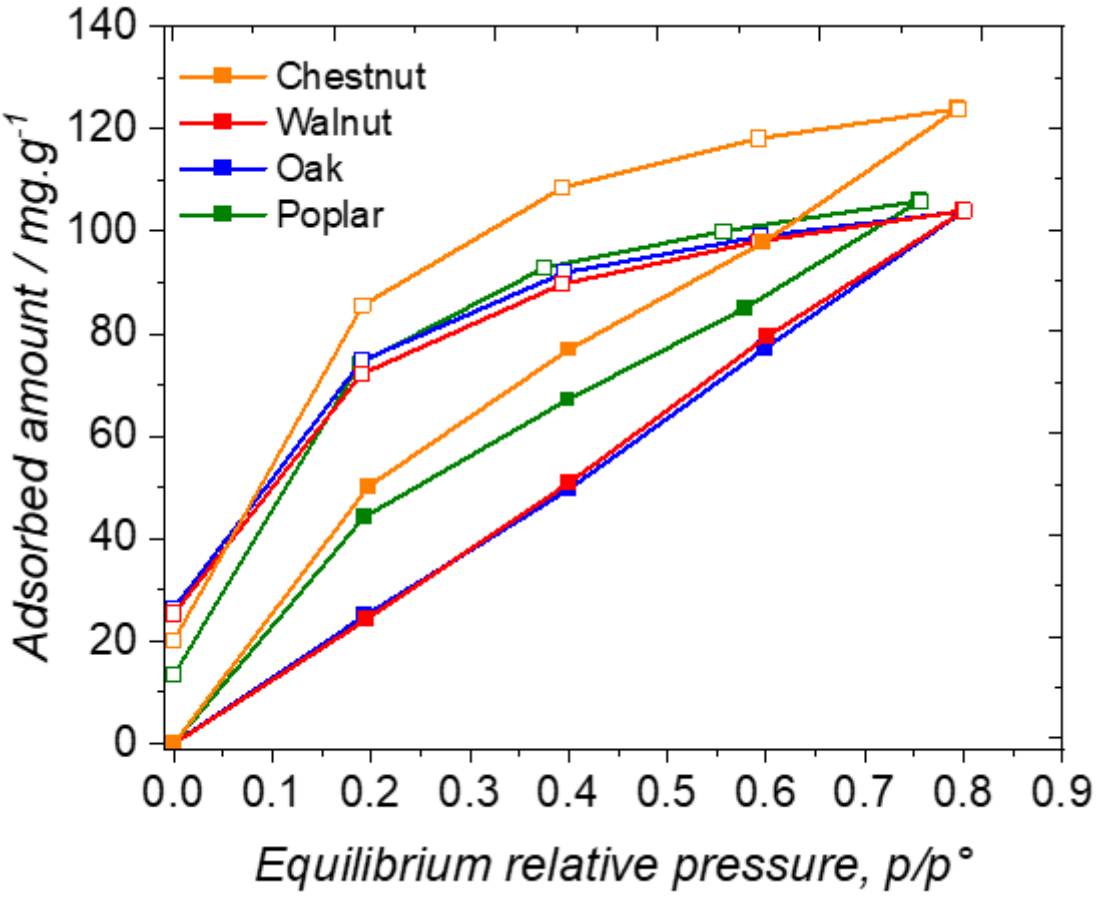

Figure 2

Sorption isotherms of the four hardwoods in pure ethanol vapour at 25°C.

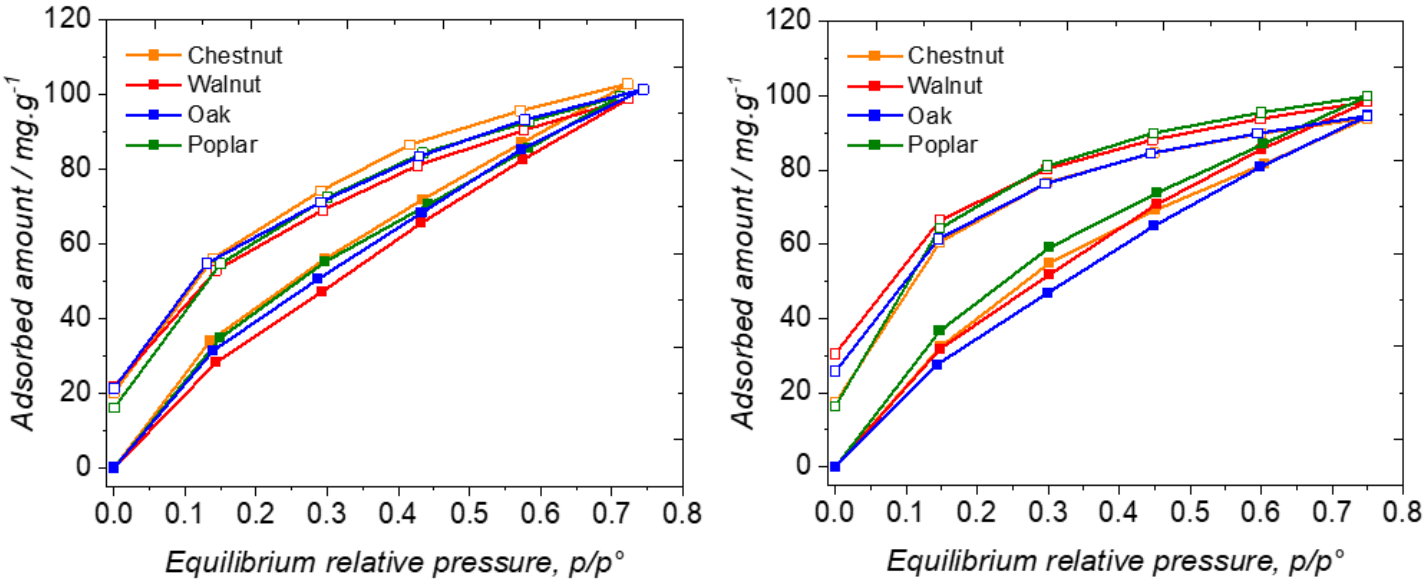

Figure 3

Figure 4. Sorption isotherms of the four hardwoods using water / ethanol mixtures. (left) 66.6% water, (right) 33.3% water.

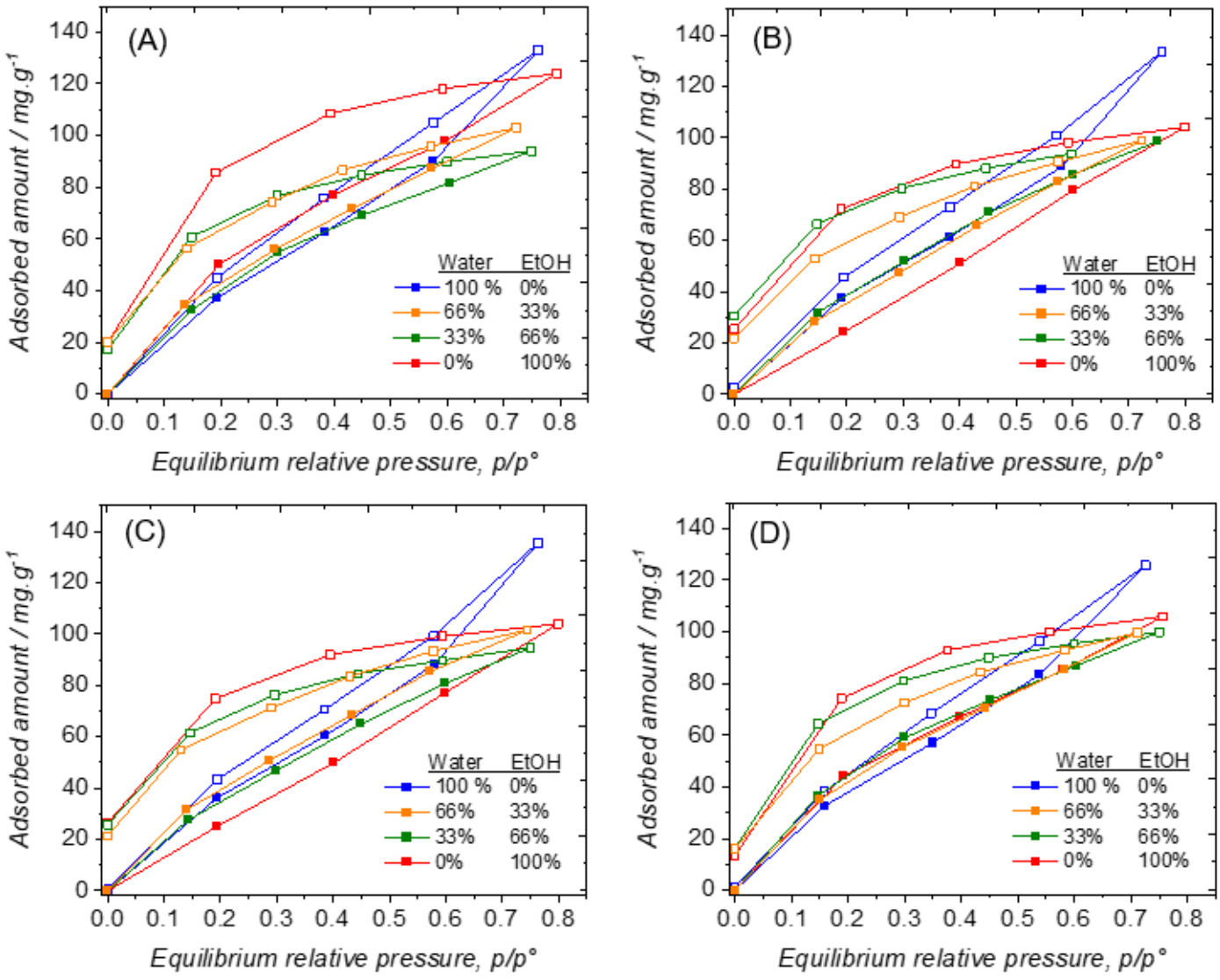

Figure 4

Figure 5. Sorption isotherms of solvents mixtures by (A) Chestnut (B) Walnut, (C) Oak and (D) Poplar. All these sorption isotherms have been determined at 25°C.

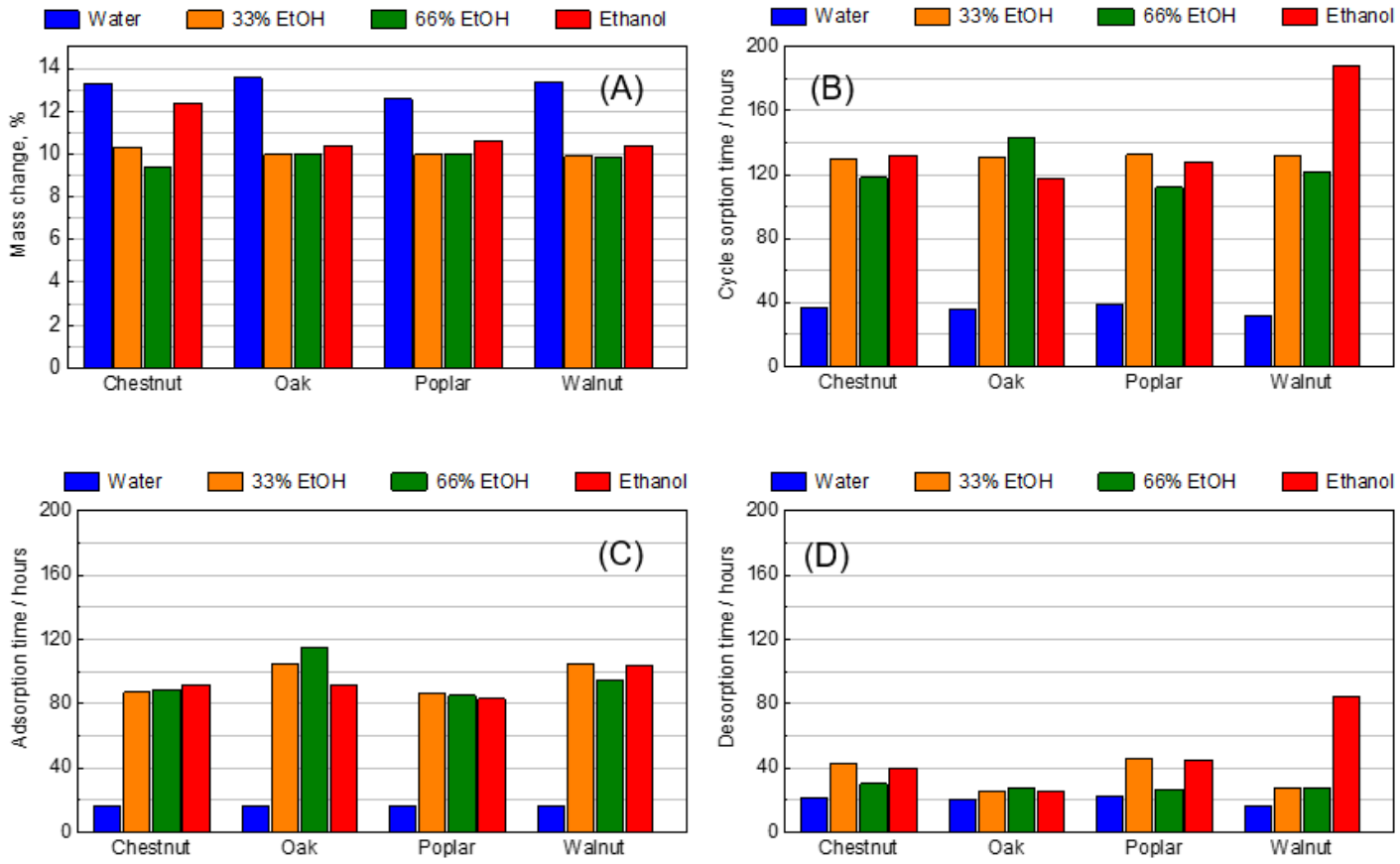

Figure 5

Figure 6. (A) Maximum mass change of each wood with increasing molar mass fraction (%) of ethanol; (B) Sorption cycle time; (C) Full adsorption time and (D) Full desorption time.