CHAPTER 4

THE EFFECT OF WOOD SPECIES AND THERMAL MODIFICATION ON THE SORPTION ISOTHERMS PROPERTIES

4.1 Introduction

This chapter reports upon investigations on the sorption properties of six tropical hardwoods and two thermally modified woods (*A. mangium* and *E. malaccense*). The wood samples were ground to fine particles and examined using the DVS apparatus as explained in Chapter 3. The EMC was determined over a range of RH values in order to produce sorption isotherms. The H-H model was used as an analysis tool for sorption behaviour. The effect of cell wall stiffness upon the sorption hysteresis behaviour is examined.

4.2 Materials and Methods

4.2.1 Material preparation

4.2.1.1 Six tropical hardwoods

The first part of this study examined in more detail whether wood species affected the sorption isotherm properties. Six tropical hardwood species, namely, chengal (*Neobalanocarpus heimii*), kapur (*Dryobalanops* spp.), keruing (*Dipterocarpus* spp.), ramin (*Gonystylus* spp.), acacia (*Acacia mangium*) and *E. malaccense* (*Endospermum malaccense*) (only heartwood) were used in this study. The kiln dried wood samples were obtained from the Forest Research Institute Malaysia (FRIM), Selangor, Malaysia.

4.2.1.2 Thermally modified wood (TMW)

For the purposes of this study, two tropical hardwoods, *A. mangium* and *E. malaccense* (only heartwood) were selected. The kiln dried wood samples were thermally modified using an oil-heating process carried at the FRIM.

The size of the specimens for the modification was 20 x 20 x 175 mm (tangential x radial x longitudinal). The oil curing processes were performed using an ordinary stainless steel tank and palm oil was used as the heating medium as it is organic in nature, readily available and possesses a high boiling point. The palm oil was poured into the tank and heated up to 80 ^{o}C and the temperature was gradually increased to one of three specified temperatures (180, 200, 220 ^{o}C).

The wood samples were submerged in the heated oil by placing them in a metal cage. The wood samples were taken out by batches starting with the treatment at temperature of 180 ^{o}C at intervals of 1, 2 and 3 hours of the exposure time. The samples were then wiped with a clean cloth to remove the excess oil. In this sorption study, only the centre of the wood samples (e.g. clear from the oil) was used, in order to prevent any oil contamination affecting the results.

The modified wood samples were ground to fine particles and passed through a BS410-1:2000 mesh sieve no. 20 (0.841 mm sieve opening) as described previously.

4.2.2 Determination of sorption isotherms and kinetics with DVS

The samples were placed in the DVS for dynamic vapour sorption studies. The methodology has been fully explained in Chapter 2, however the schedule for this study was set with additional RH steps at 0, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 85, 90 and 95% RH and in reverse sequence for the desorption isotherm at a temperature of 25 ^{o}C.

4.2.3 Determination of chemical composition of wood

Chemical analyses were carried out at FRIM on air-dry wood meal, which was passed through a BS 60 mesh sieve (250 microns). The chemical components were determined and the respective methods employed were:

(a)	Holocellulose	Determination of Holocellulose, according to the method of Wise *et al.* (1946)
(b)	Alpha(α) cellulose	TAPPI T 203 om-93 Alpha-, Beta- and Gamma-cellulose in Pulp (TAPPI 1994)
(c)	Lignin	TAPPI T 222 om-88 Acid-insoluble Lignin in Wood and Pulp (TAPPI 1994)
(d)	Ethanol-Toluene solubility	TAPPI T 204 cm-97 Solvent Extractives of Wood and Pulp (TAPPI 2000)

4.1.4 Analysis of sorption isotherms data with the H-H model

Thie H-H model analysis has been discussed in detail in Chapters 1 and 2.

4.3 RESULTS AND DISCUSSION

4.3.1 Sorption behaviour

4.3.1.1 Isotherm plots of tropical hardwoods

All of the tropical hardwood species showed the classic IUPAC Type II isotherms. However, there were differences in the total amount of moisture content present in the samples at higher RH values. The differences in adsorption and desorption behaviour are illustrated in Figure 4.1. There is a little difference in MC in the range between 0 to 60% RH, however, when the RH increases beyond 60%, each of the wood species started to behave differently. These differences are not just random

since the reproducibility study in Section 2.2.4, shows the data is highly reproducible. At the targeted 95% RH, ramin had the highest MC followed by *E. malaccense*, *Dryobalanops* spp., *Dipterocarpus* spp., *A. mangium* and *N. heimii* (*Neobalanocarpus heimii*), with values of 21.6, 20.3, 20.2, 19.5, 19.1 and 18.2%, respectively. *N. heimii* and *A. mangium*, which has a high extractives content, exhibited lower MCs compared with other wood species that had low extractive contents (*Gonystylus* spp., *Dryobalanops* spp., *Dipterocarpus* spp., *E. malaccense*) (Table 4.1). However, the correlation between the MC and the extractives content is weak. Wangaard and Grandos (1967) and Chong and Achmadi (1991) have reported that tropical wood species with high extractive contents exhibit lower MC due to the cell wall bulking effect of extractives. They found the removal of extractives caused an increase in MC at higher relative humidities.

Caron (2010) reported that the extractives can be located in the micropores of the wood cell wall and may be responsible for the differences in dimensional stability. These differences have been explained previously, in Section 3.3.2 which was also attributed as due to the variations in chemical composition and crystallinity of cellulose. Skaar (1972) reported that there is not much difference in sorption behaviour between wood species grown in temperate regions.

Table 4.1 Chemical composition of the tropical hardwoods

Wood species	Holocellu-lose (%)	Alpha(α)-cellulose (%)	Hemicellu-lose (%)	Lignin (%)	Extractives (%)	Sum (%)
N. heimii	a. 65.2	a. 45.2	a. 20.0	a. 27.9	a. 9.1	a. 102.2
	b. 65.3	b. 46.1	b. 19.2	b. 27.4	b. 11.1	b. 103.8
Dryobalanops spp.	a. 64.5	a. 48.2	a. 16.3	a. 36.5	a. 2.2	a. 103.2
	b. 64.8	b. 48.0	b. 16.8	b. 36.7	b. 1.5	b. 103.0
Dipterocarpus spp.	a. 70.0	a. 47.7	a. 22.3	a. 30.1	a. 2.2	a. 102.3
	b. 70.8	b. 46.9	b. 23.9	b. 30.3	b. 1.9	b. 103.0
Gonystylus spp.	a. 73.7	a. 49.9	a. 23.8	a. 21.9	a. 1.6	a. 97.2
	b. 73.2	b. 48.9	b. 24.3	b. 22.3	b. 1.5	b. 97
A. mangium	a. 61.1	a. 34.7	a. 26.4	a. 30.2	a. 11.0	a. 102.3
	b. 61.3	b. 34.1	b. 27.2	b. 30.0	b. 8.1	b. 99.4
E. malaccense	a. 73.0	a. 45.4	a. 27.6	a. 27.9	a. 2.6	a. 103.5
	b. 73.8	b. 46.3	b. 27.5	b. 27.4	b. 2.3	b. 103.5

Note: Two measurements (a, b)

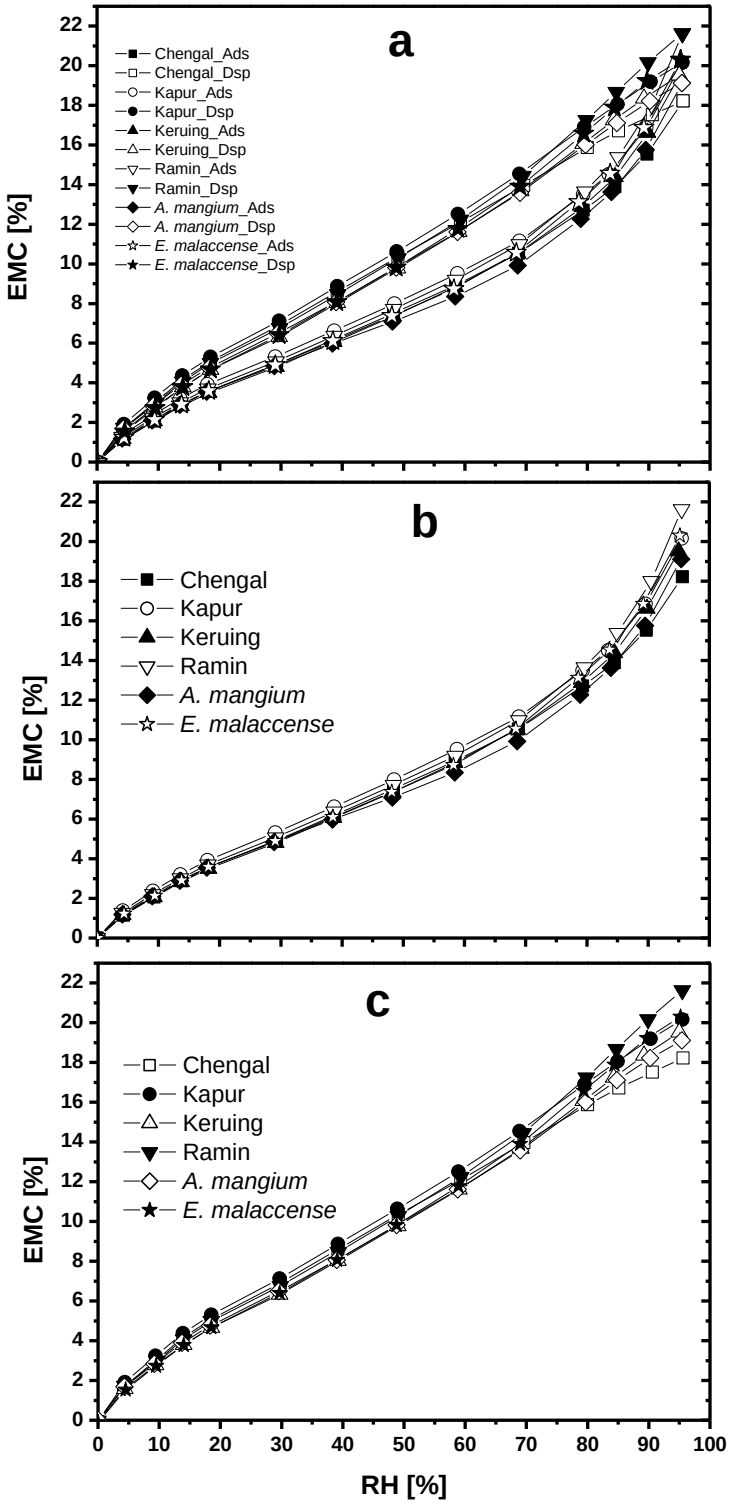

Figure 4.1 Sorption isotherms for six tropical hardwoods: a) isotherms curves, b) adsorption, c) desorption.

4.3.1.2 Running time

In Section 3.3.1, the general sorption behaviour of wood has been explained. Compared with unmodified wood, the thermally modified wood showed significant differences in terms of EMC and the total running time. Generally, oil-heat/thermal modification on both *A. mangium* and *E. malaccense* caused a reduction in the EMC recorded during the sorption process. The EMC decreased as the temperature and time of modification increased. As the treatment temperature increased from 180 ^{o}C (Figure 4.2b, 4.3b) to 220 ^{o}C (Figure 4.2d, 4.3d) the total running time, for a complete cycle of adsorption and desorption isotherms, decreased for *A. mangium* and *E. malaccense* that was exposed to 1, 2 and 3 hour's treatment time.

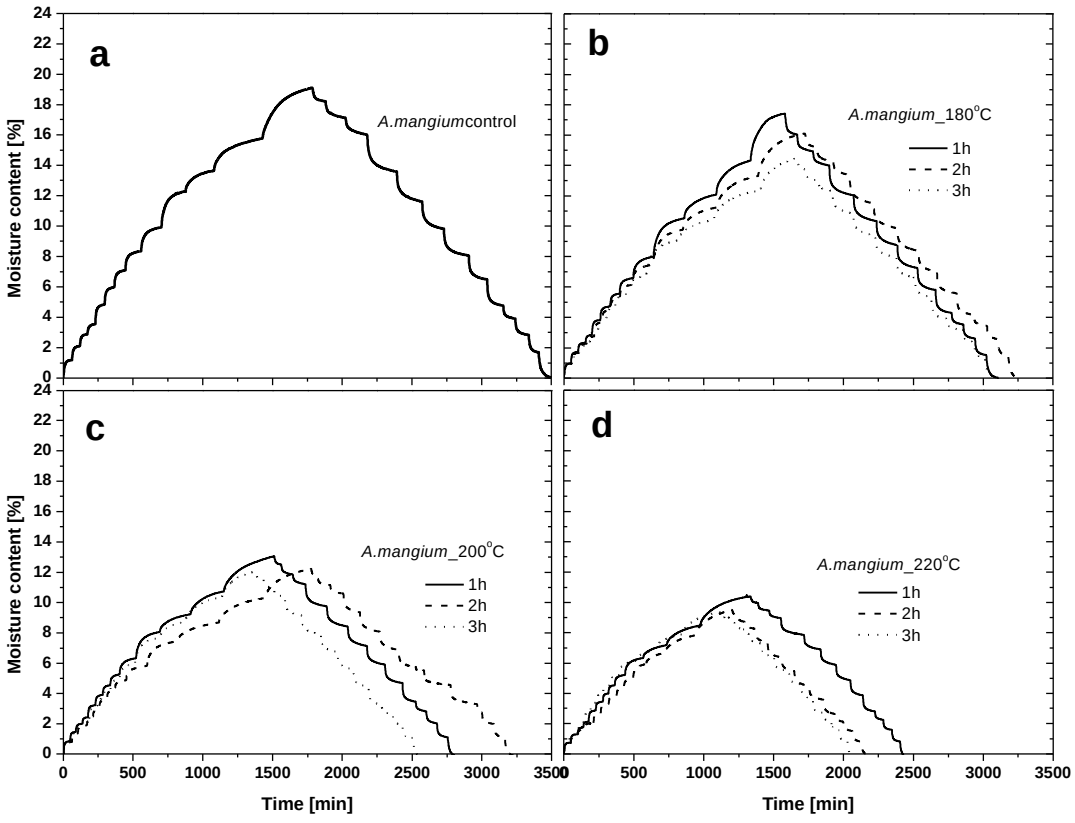

Figure 4.2 Relationship between EMC and sorption time for one sorption cycle with *A. mangium* control (a) thermal modification at 180 ^{o}C for 1, 2, 3 hours (b) thermal modification at 200 ^{o}C for 1, 2, 3 hours (c) and thermal modification at 220 ^{o}C for 1, 2, 3 hours (d).

At 220 °C (Figure 4.2d) and 200 °C (Figure 4.3c) a relationship between the thermal modification time and the total running time was found, where an increase in modification time from 1 to 3 hours produced a decrease in the total running time. However, the total running time is only an approximate guide that can be affected by other external influences as described in Section 3.3.1.

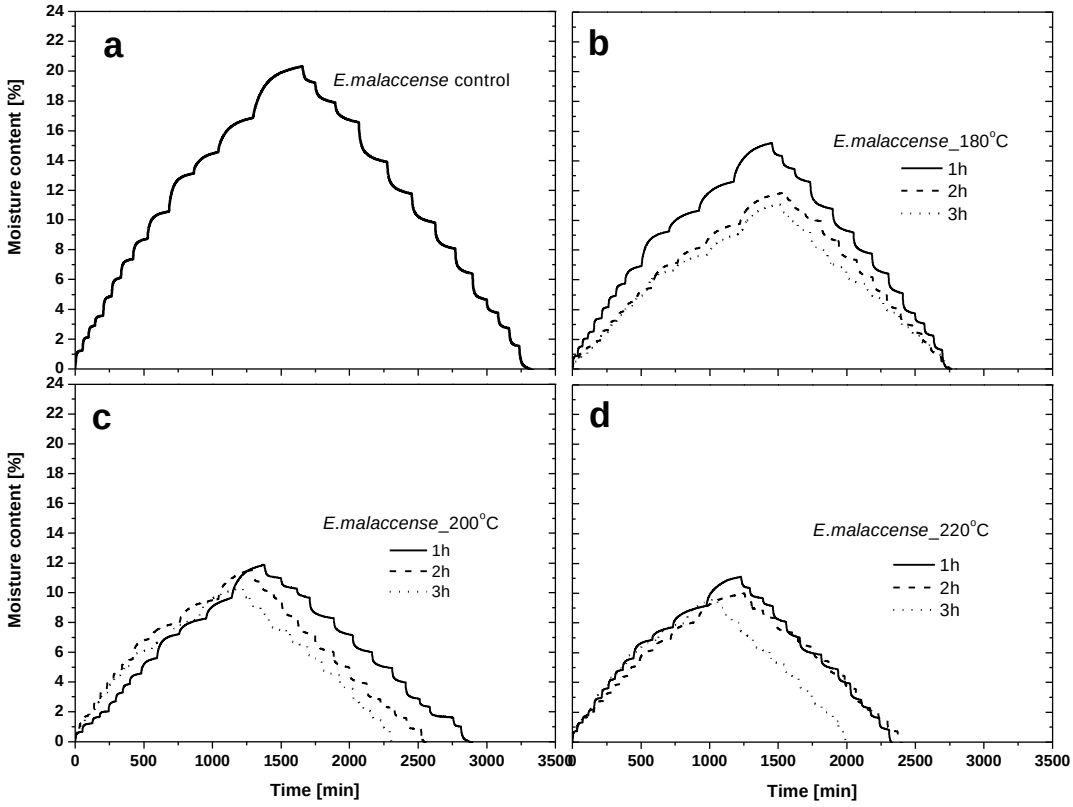

Figure 4.3 Relationship between EMC and sorption time for one sorption cycle with *E. malaccense* control (a), thermal modification at 180 °C for 1, 2, 3 hours (b), thermal modification at 200 °C for 1, 2, 3 hours (c) and thermal modification at 220 °C for 1, 2, 3 hours (d).

4.3.1.3 Comparison of sorption isotherms of thermally modified Wood (TMW)

In addition to investigating the effect of wood species upon sorption behaviour, another study was conducted upon the influence of thermal modification. The reduction

in EMC over the whole hygroscopic range due to thermal modification is well known and can be attributed to a number of effects, (a) There is a substantial loss of hemicelluloses, resulting in a reduction of overall OH groups and some conversion to reactive compounds such as furfural may occur leading to potential cross-linking reactions, (b) Lignin can become more cross-linked, resulting in a restraining effect upon cell wall expansion, (c) There may be an increase in cellulose crystalline content resulting in a reduction of accessible OH groups (Hill 2006), (d) the cell wall is much stiffer and less able to deform to accept sorbed water. However, thermal modification may lead to some micro-cracks or void formation in the cell wall which could potentially offset the EMC reduction to some extent because of an increase in capillary condensation.

Generally, the results showed that thermal modification caused a reduction in EMC for both *A. mangium* and *E. malaccense* and this decreased in relation to the temperature and time of the treatment (Figure 4.4). The moisture adsorption isotherms showed the characteristic sigmoid IUPAC Type II, curves with sorption hysteresis, as is seen in Figures 4.4(a, b, c, d, e and f). In this study, the decreases in EMC values for treatments at 180, 200 and 220 ^{o}C and for 1, 2 and 3 hours showed different behaviour between *A. mangium* and *E. malaccense* (Table 4.2). The reduction of EMC of the TMW hardwoods may be due to the variation of chemical composition (Table 4.3 and 4.4). The maximum percentage decreases at the target 95% RH were at the modification temperature of 220 ^{o}C and time of 3 hours (*A. mangium* with 51% and *E. malaccense* with 52.7%).

Substantial differences in behaviour were found with TMW of the two hardwoods at a modification temperature of 180 ^{o}C (Table 4.2 and Figure 4.4). It was noted that *E. malaccense* was more affected by thermal modification than *A. mangium*

with respect to water sorption. In *A. mangium* TMW, Table 4.3 shows an increase of relative cellulose content and a decrease of hemicelluloses, however the relative lignin content is relatively stable after the thermal modification. Comparatively, in *E. malaccense* TMW, Table 4.4 there was a large increase in relative lignin content, a slight reduction in hemicelluloses (except at a modification temperature of 180 ^{o}C and time of 3 hours) and a slight increase of relative cellulose content. The changes in chemical composition between *A. mangium* TMW and *E. malacccense* after thermal modification may explain the differences in sorption properties. However, modification at temperatures of 200 and 220 ^{o}C for 1, 2 and 3 hours, did not show any significant differences in EMC (Figure 4.4) and chemical composition (Table 4.3 and 4.4) between the two hardwoods.

Table 4.2 The percentage decreases of EMC at the target 95% RH at various temperatures and times of *A. mangium* and *E. Malaccense* thermal modification

Thermal modification		The decreases of EMC at the target 95% RH	
Temperature (^{o}C)	Time (hour)	*A. mangium* (%)	*E. malaccense* (%)
180	1	8.9	25.1
	2	15.8	41.4
	3	24.3	45.4
200	1	31.7	41.5
	2	36.1	43.2
	3	37.0	49.2
220	1	45.7	45.3
	2	50.3	50.8
	3	51.0	52.7

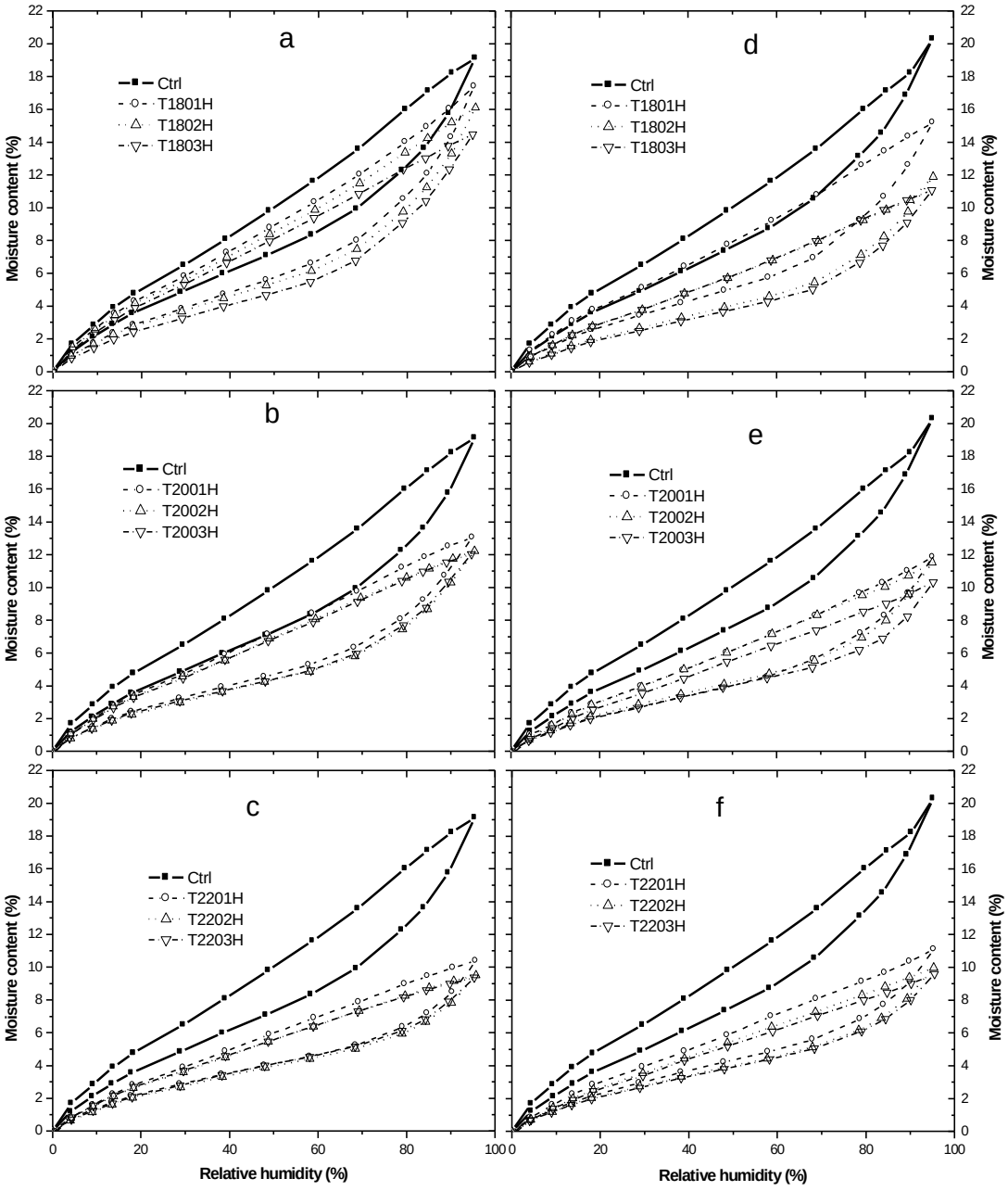

Figure 4.4 Experimental isotherms for, *A. mangium* (a, b and c) and *E. malaccense* (d, e and f) at different treatment times (1H-1 hour, 2H-2 hours, 3H-3 hours) and temperatures (180, 200 and 220 ^{o}C).

Table 4.3 Chemical composition of *A. mangium* TMW after the removal of the extractives content

Wood species	Treatment temperature (^{o}C)	Treatment time (h)	Holocellu-lose (%)	Alpha(α)-cellulose (%)	Hemicellu-lose (%)	Lignin (%)
A. mangium	Control	Control	a. 66.9	a. 38.0	a. 28.9	a. 33.1
			b. 67.1	b. 37.3	b. 29.8	b. 32.9
	180	1	a. 68.8	a. 42.9	a. 25.9	a. 32.0
			b. 71.6	b. 45.1	b. 26.4	b. 32.6
		2	a. 68.7	a. 50.9	a. 17.8	a. 32.0
			b. 66.4	b. 48.2	b. 18.1	b. 32.6
		3	a. 69.9	a. 54.4	a. 15.6	a. 30.1
			b. 69.8	b. 54.1	b. 15.7	b. 30.2
	200	1	a. 63.2	a. 46.1	a. 17.1	a. 33.3
			b. 63.9	b. 47.0	b. 16.9	b. 33.4
		2	a. 63.1	a. 48.7	a. 14.5	a. 36.9
			b. 63.4	b. 48.2	b. 15.3	b. 36.6
		3	a. 66.8	a. 48.8	a. 18.0	a. 33.2
			b. 66.1	b. 43.7	b. 22.4	b. 33.9
	220	1	a. 61.6	a. 43.1	a. 18.4	a. 38.4
			b. 63.9	b. 46.9	b. 17.1	b. 36.1
		2	a. 67.4	a. 48.6	a. 18.9	a. 32.6
			b. 68.6	b. 47.7	b. 20.9	b. 31.4
		3	a. 64.8	a. 41.5	a. 23.3	a. 35.2
			b. 65.9	b. 47.5	b. 18.4	b. 34.1

Note: Two measurements (a, b)

Table 4.4 Chemical composition of *E. malaccense* TMW after the removal of the extractives content

Wood species	Treatment temperature (°C)	Treatment time (h)	Holocellu-lose (%)	Alpha(α)-cellulose (%)	Hemicellu-lose (%)	Lignin (%)
E. malaccense	Control	Control	a. 72.3	a. 45.0	a. 27.4	a. 27.7
			b. 72.9	b. 45.8	b. 27.2	b. 27.1
	180	1	a. 67.8	a. 40.0	a. 23.2	a. 26.6
			b. 64.2	b. 36.7	b. 25.2	b. 33.0
		2	a. 62.8	a. 30.0	a. 26.9	a. 30.6
			b. 62.9	b. 30.7	b. 26.7	b. 30.8
		3	a. 58.8	a. 47.2	a. 11.6	a. 41.2
			b. 58.4	b. 49.4	b. 9.0	b. 41.6
	200	1	a. 61.9	a. 32.9	a. 29.0	a. 38.1
			b. 61.7	b. 31.8	b. 29.9	b. 38.3
		2	a. 65.6	a. 43.2	a. 22.4	a. 34.4
			b. 66.7	b. 44.0	b. 22.6	b. 33.3
		3	a. 64.1	a. 41.2	a. 22.9	a. 35.3
			b. 64.2	b. 45.6	b. 18.6	b. 38.9
	220	1	a. 64.2	a. 45.4	a. 18.8	a. 35.8
			b. 64.2	b. 43.1	b. 21.1	b. 35.8
		2	a. 62.9	a. 39.8	a. 23.2	a. 37.1
			b. 64.2	b. 42.3	b. 21.9	b. 35.8
		3	a. 59.5	a. 38.8	a. 20.6	a. 40.5
			b. 55.6	b. 37.6	b. 18.0	b. 44.4

Note: Two measurements (a, b)

Table 4.5 Fitted and physical constants calculated from the H-H model in adsorption

Wood species	A	B	C	R^2	K_1	K_2	W
N. heimii	3.43	0.11	0.001	0.99	5.54	0.70	282.6
Dryobalanops spp.	2.69	0.12	0.001	0.99	7.22	0.73	292.5
Dipterocarpus spp.	3.33	0.12	0.001	0.99	5.87	0.75	310.4
Gonystylus spp.	2.90	0.13	0.0012	0.98	6.74	0.77	312.8
A. mangium	2.93	0.14	0.0012	0.99	7.39	0.76	335.9
E. malaccense	3.17	0.13	0.0012	0.99	6.23	0.77	317.5

4.3.2 Hailwood-Horrobin fitting to the experimental data

4.3.2.1 Unmodified tropical hardwood species

The six tropical hardwoods and thermally modified wood were analysed using the H-H model. A full description of the H-H theory was given in Chapter 2 (Section 2.5). In Table 4.5 is shown the values of A, B, C, R^2, K_1, K_2 and W of the woods studied. The R^2 (coefficient of determination) values range from 0.988 to 0.995, indicating a good fit to the experimental results.

R^2 is a statistical measure of the proportion of variation that can be explained by the regression line. The physical constants K_1, K_2, W obtained were found to be in good agreement with those previously reported by Spalt (1958) and Wangaard and Grandos (1967) on different wood species. *N. heimii* has a lower value of K_1 compared with other wood species. A low K_1 implies a decrease in the activity of hydrated wood with

respect to both the activities of dry wood and dissolved water (Skaar 1988). This indicates that there are less adsorption sites for water which may be due to the bulking by the high extractives content of *N. heimii*. However, the H-H model is incapable of distinguishing bulking from site removal.

The constant K_2 value is comparable for all wood species. K_2 shows the activity of dissolved water in the wood cell wall per unit relative vapour pressure. Okoh and Skaar (1980) reported that the K_2 value must be unity if it has the same activity as liquid water. The K_2 values vary approximately between 0.70 and 0.77, indicating that the dissolved water shows a lower activity that liquid water (Papadopoulos and Hill 2003). This indicates that the freedom of motion of water in the cell wall micropores is lower than that in liquid water. In this H-H fitting, W, or the molecular weight per sorption site, for different species showed differences, with *A. mangium* having the highest value at 335.9 and the lowest for *N. heimii* at 282.6. Although the model provides excellent fits to the data, the physical interpretation of the fitting parameters is still debated, as indeed is the case for all sorption models.

The results from the H-H fits to the data for the six hardwood species are presented in Figure 4.5. The sigmoidal adsorption isotherm curve of the total water content was deconvoluted into hydration water or monolayer (Mh) water and dissolution water or polylayer (Ms) water components. The fits are generally satisfactory although in general, the total MC above 90% RH is slightly overestimated. *E. malaccense* (Figure 4.5f) however shows a very good fit between the total water (H-H model) and experimental data of MC. The plots indicate that there is little difference in the monolayer water between species. Where differences are found, this occurs with

the polylayer water content. However, the interpretation is of course dependent upon which model is adopted.

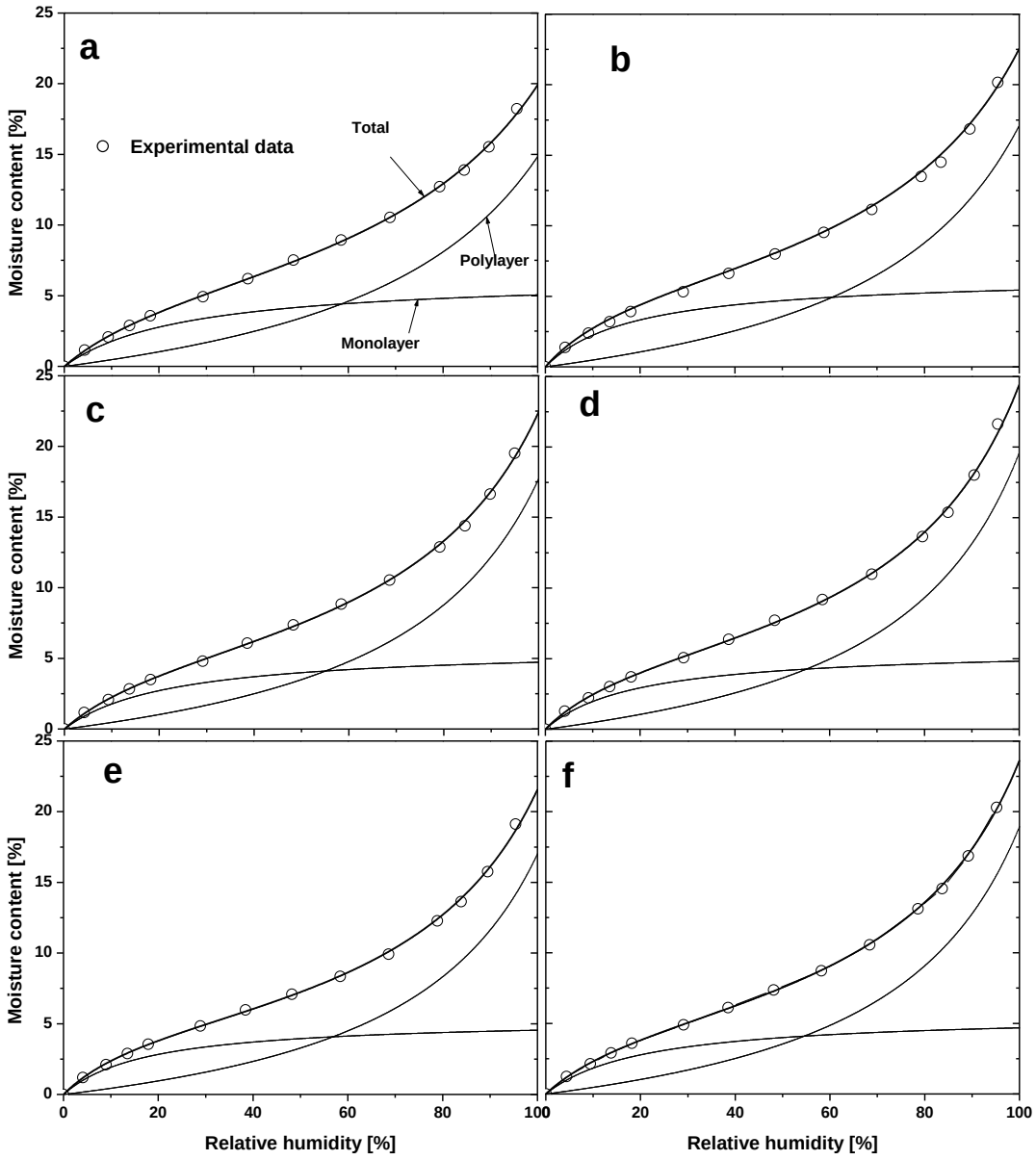

Figure 4.5 H-H model fits the experimental data on six hardwoods: (a) *Neobalanocarpus heimii*, (b) *Dryobalanops* spp., (c) *Dipterocarpus* spp., (d) *Gonystylus* spp., (e) *A. mangium* & (f) *E. malaccense.*

A reduction in polylayer water indicates a reduced ability of the cell wall to swell to accommodate sorbed water; or a bulking of the cell wall by extractives. Values for Mh, Ms and total water (Mh + Ms, giving a crude estimate of fibre saturation point (FSP) or projected FSP (p-FSP) at 100% RH) are given in Table 4.6. With a value of 19.9%, *N. heimii* had the lowest p-FSP compared with the six hardwoods, *A. mangium* (21.6%), *Dipterocarpus spp*. (22.4%), *Dryobalanops spp.* (22.6%), *E. malaccense* (23.6%), and *Gonystylus spp*. (24.4%) respectively. The use of the term p-FSP is to distinguish this parameter from FSP values obtained by other methods, as explained in Chapter 2 (Section 2.6). The lower values for *N. heimii* and *A. mangium* may be due to the bulking effects of extractives as discussed previously.

Table 4.6 Values for monolayer (Mh) and polylayer (Ms) water derived from H-H fits projected to 100% RH

Wood species	Mh (%)	Ms (%)	Mh + Ms (%)
N. heimii	5.06	14.86	19.92
Dryobalanops spp.	5.45	17.11	22.56
Dipterocarpus spp.	4.73	17.69	22.42
Gonystylus spp.	4.83	19.60	24.43
A. mangium	4.55	17.02	21.57
E. malaccense	4.69	18.94	23.63

4.3.2.2 Hailwood-Horrobin (H-H) fitting for thermally modified wood (TMW)

As with the study on different wood species, the fitted curve using the H-H model coincided well with the experimental data of thermally modified wood (Figure 4.6). For clarity, only data for two wood species at 180 ^{o}C and for 1, 2 and 3 h is shown. Similar results were obtained for other temperatures. The values for p-FSP obtained from the H-H fits to the data are presented in Figure 4.7. The p-FSP of the untreated wood in this study was 21.6% (*A. mangium*) and 23.6% (*E. malaccense*).

Thermal modification decreased the p-FSP of *A. mangium* and *E. malaccense*, as was predicted. Treatment at temperatures of 180 ^{o}C, 200 ^{o}C, and 220 ^{o}C progressively decreased the p-FSP values, i.e. in general, the higher the modification temperature, the lower the p-FSP value. However, the reduction of monolayer water of the oleo-thermal modified woods seems to have been little affected by the modification temperature, whereas the change in polylayer water was temperature dependent (Figure 4.8).

After thermal modification, the maximum percentage decrease in projected FSP for *A. mangium* and *E. malaccense* were 54.6% and 56.8% for heating at 220 ^{o}C for 3 h (Figure 4.7c). These data for the FSP obtained using the isotherm projection method shows that *E. malaccense* is more affected by thermal modification at the two lower temperatures. However, at the higher modification temperature, *A. mangium* shows a slightly lower projected FSP.

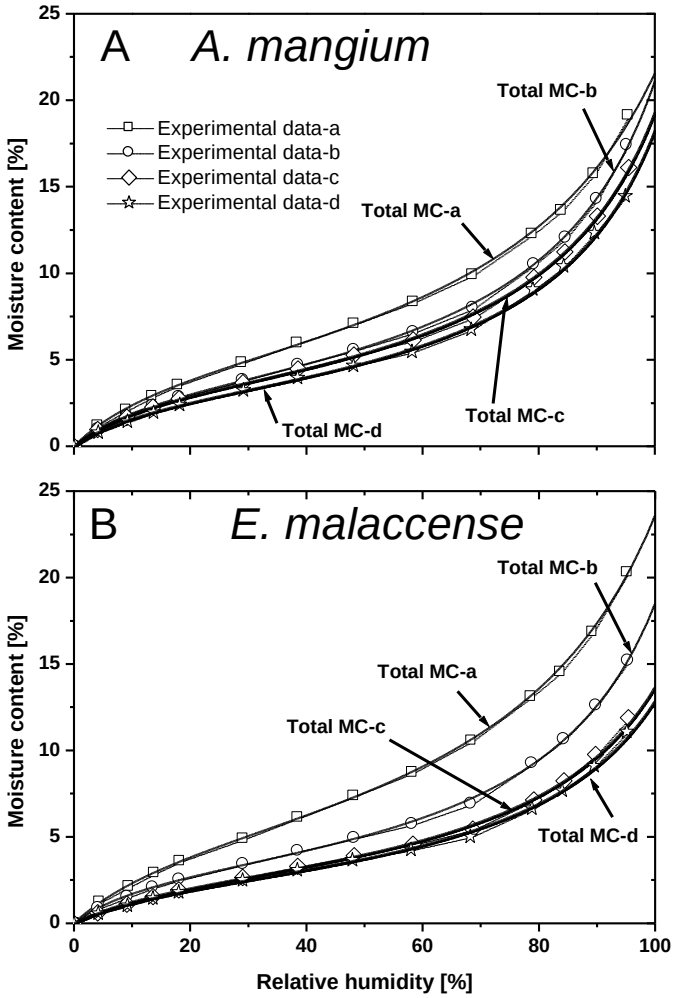

Figure 4.6 The sum of monolayer and polylayer water (H-H model) adsorption isotherm through the RH run compared to experimental MC for the two wood species *A. mangium* (A) and *E. malaccense* (B) with unmodified (a) or thermal modification at different times of 1 h (b), 2 h (c), 3h (d) at 180 ^{o}C.

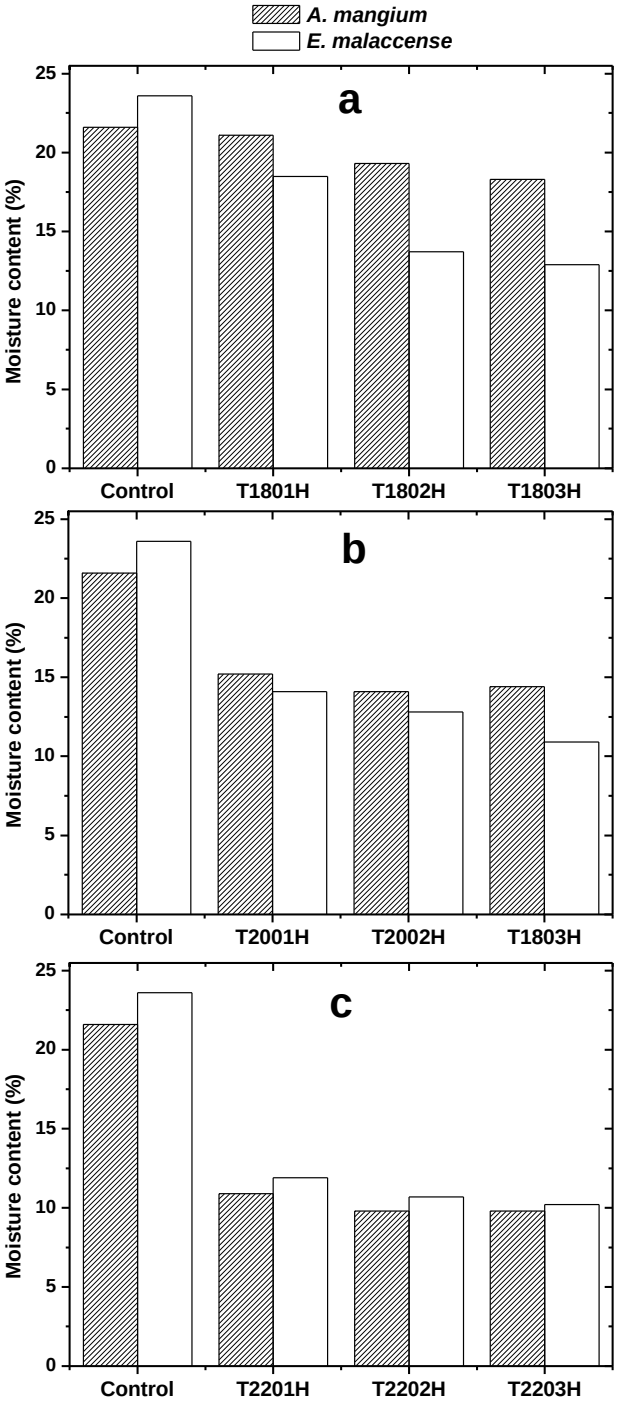

Figure 4.7 Values for p-FSP water derived from H-H fits projected to 100% RH for *A. mangium* and *E. malaccense* at different thermal modification temperatures (a-T180 ^{o}C, b -T200 ^{o}C and c-T220 ^{o}C) and treatment times (1H-1 hour, 2H-2 hours and 3H-3hours).

Figures 4.8 (a, b, c, d, e and f) shows the sorption isotherms deconvoluted into monolayer (Mh) and polylayer (Ms) components according to the H-H model. The difference between the behaviour of *A. mangium* (a) and *E. malaccense* (d) at the lowest thermal modification temperature (180 ^{o}C), was due to the slight reduction in Mh and Ms water for *A. mangium* compared to the much larger reduction in both for *E. malaccense*. For 180 ^{o}C and 3h, Ms was reduced by 9.4% (*A. mangium*) and 43.9% (*E. malaccense*) with respect to the control. For modification at 220 ^{o}C, the Ms was reduced by more than 58.2% (*A. mangium*) and 59.2% (*E. malaccense*).

With *E. malaccense* at all the modification times and temperatures, except 180 ^{o}C at 1h; the reduction in water sorption was much greater for Ms compared to Mh. However, the overall decrease in Mh is nonetheless of the order of 50%, which may be a result of the reduction in accessible OH groups. The reduction in Ms presumably reflects the decreased capacity of expansion of the cell wall due to increased matrix stiffness and increased lignin cross-linking.

With *A. mangium* there is initially a much greater reduction in Mh water at the lowest modification temperature. The reduction in Ms becomes more dominant as the temperature of modification increases. Thus after an initial reduction in Mh, this parameter is relatively insensitive to the effect of prolonged heating. This behaviour is very interesting and may possibly provide an insight into cell wall changes occurring as a result of thermal modification.

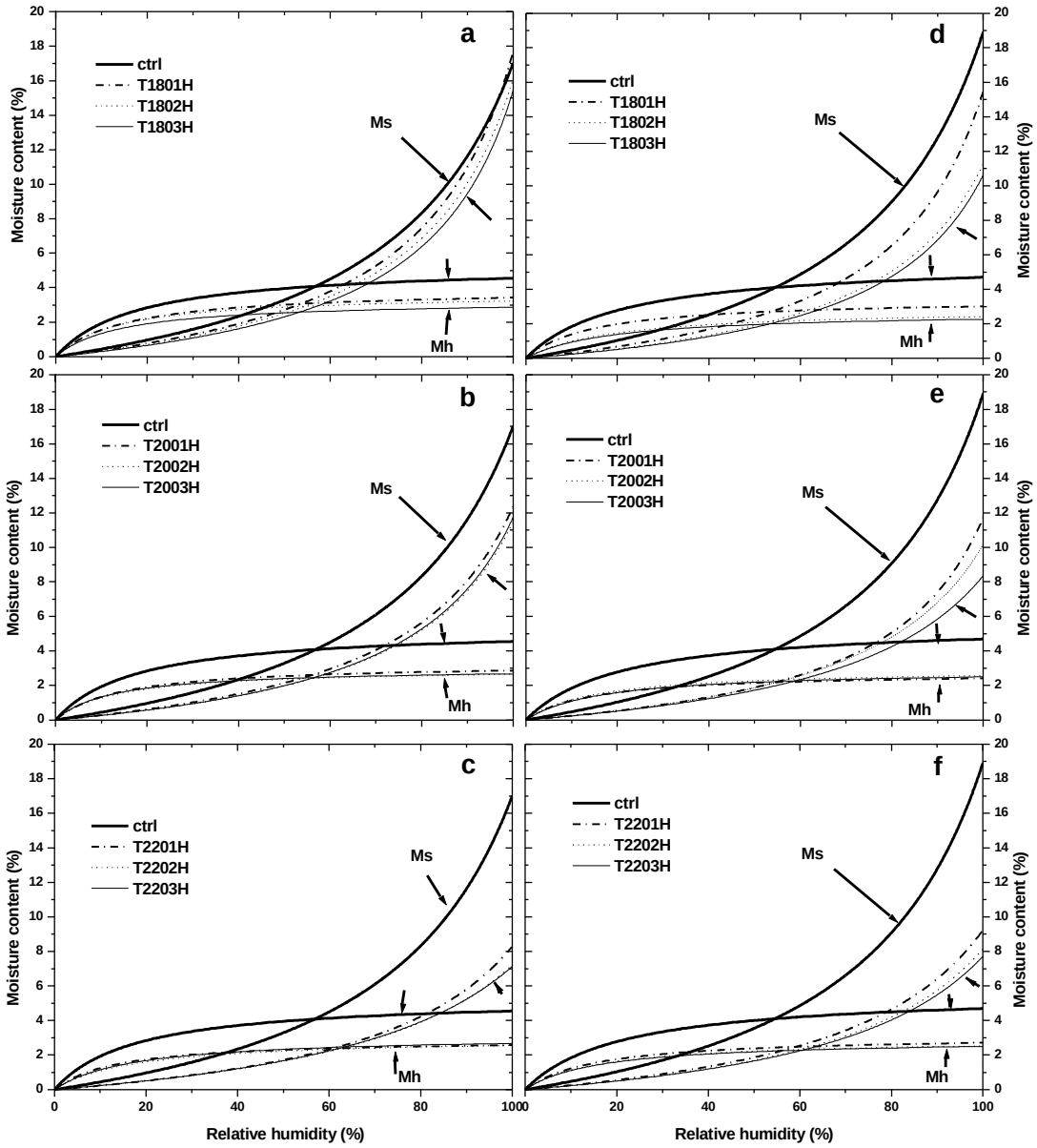

Figure 4.8 Monolayer (Mh) water and polylayer (Ms) water using the H-H model for *A. mangium* (a, b and c) and *E. malaccense* (d, e and f) at different treatment times (1H-1 hour, 2H-2 hours and 3H-3hours) and temperatures (180 ^{o}C, 200 ^{o}C and 220 ^{o}C).

4.3.3 Sorption hysteresis

4.3.3.1 Absolute hysteresis (AH) and hysteresis ratio (HR) of six tropical hardwood species

All the wood species showed differences in AH values. The AH increased between 5-80% RH and rapidly decreased in the range of 80-90% RH apart from with *N. heimii* and *Dryobalanops* spp. where it decreased at 70% and 85% RH, respectively (Figure 4.9). *N. heimii* displayed the highest AH value between 0 and 50% RH but *A. mangium* had the largest AH between 60 and 90% RH. As noted, both *N. heimii* and *A. mangium* were higher in extractives content compared to the other wood species (Table 4.1). The reason for this change could be related to matrix stiffness being increased by the presence of a high extractives content in the cell wall micropores according to the theory of extractives functioning as bulking agents in the cell wall. This reduces the cell wall MC and thereby indirectly reduces plasticisation of the matrix. This may indicate that a stiffer matrix is impeding the response of the cell wall macromolecules to the entry or exit of water molecules in wood cell wall. Such behaviour is consistent with the model for sorption hysteresis being related to the dynamic response of the cell wall matrix in response of the cell wall matrix in response to the ingress or egress of water molecules (Section 2.9). This is only a tentative hypothesis at the moment and requires further study.

In Figure 4.10 is shown the hysteresis ratio (HR) or normalised values for the wood species. For most of the wood species studied, their HR remained constant in the range of 5-60% RH and then rapidly decreased in the range of 60-90% RH. However, *N. heimii* and *A. mangium* behaved differently. *N. heimii* displayed the highest HR in the range of 0-50% RH which then decreased until 90% RH. *A. mangium* remained

constant in the RH range of 5-40% and then started to increase until it exceeded that of *N. heimii* in the RH range of 60-90%. The values of AH and HR seem to agree with each other in behaviour.

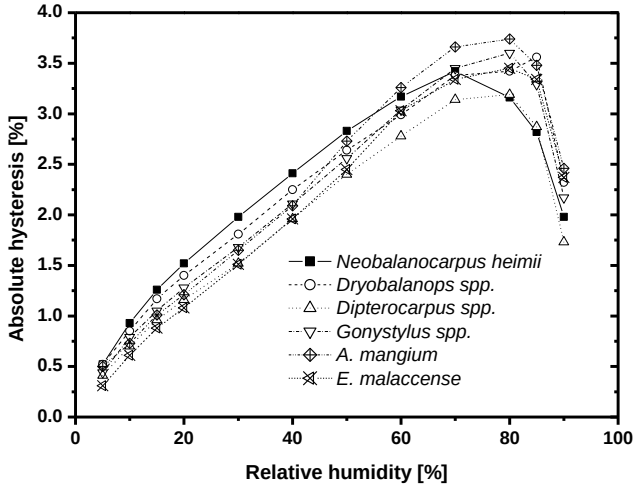

Figure 4.9 Absolute hysteresis between adsorption and desorption curves of *Neobalanocarpus heimii*, *Dryobalanops* spp., *Dipterocarpus* spp., *Gonystylus* spp., *A. mangium* and *E. malaccense* at different values of RH.

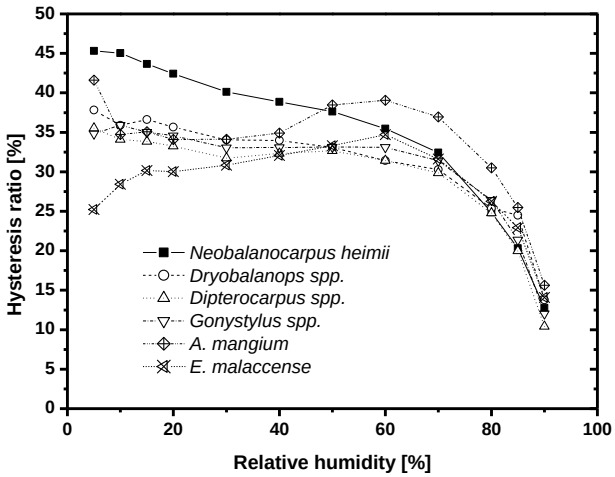

Figure 4.10 Hysteresis ratio of *Neobalanocarpus heimii*, *Dryobalanops* spp., *Dipterocarpus* spp., *Gonystylus* spp., *A. mangium* and *E. malaccense* at different values of RH.

4.3.3.2 Absolute hysteresis and hysteresis ratio of thermally modified wood (TMW)

When wood is subjected to thermal modification, there is a loss of amorphous polysaccharides, increased cross-linking in the cell wall with the lignin, possibly enhanced by furfural formation. Hence, the cell wall matrix is stiffer than before and there is a reduction in total OH content. According to the model for hysteresis presented earlier in the thesis, a stiffer cell wall matrix would be expected to exhibit larger hysteresis. However, because of the OH content reduction, thermal modification also reduces the sorptive capacity of the wood so that an increase in hysteresis can potentially be offset by the lower EMC.

The different hardwood species and modification parameters (temperature and time) both affected the AH (Figure 4.11) and the HR (Figure 4.12). The AH of TMW is lower that the control except in Figure 4.11a (*A. mangium*) and in one case with Figure 4.11d (*E. malaccense*). At 220 ^{o}C (Figure 4.11c, f) TMW for both hardwood species show a reduction in AH values with increase of modification time (1, 2, 3 h). However, the HR is clearly higher with TMW compared with controls for both hardwood species (Figure 4.12). This takes into account the fact that the total sorption is lower. In general, thermal modification resulted in an increase of HR, even though the AH was decreased. Hence, the magnitude of hysteresis is also dependent on the sorption capacity of the wood cell wall. However, as treatment temperature and time increase, the effect of reduction of total sorption capacity dominates with a related reduction in HR. Only at the higher modification temperatures and over the lower end of the RH range was the HR lower than the control sample due to reduced effect of lower EMC (Figure 4.12c, f).

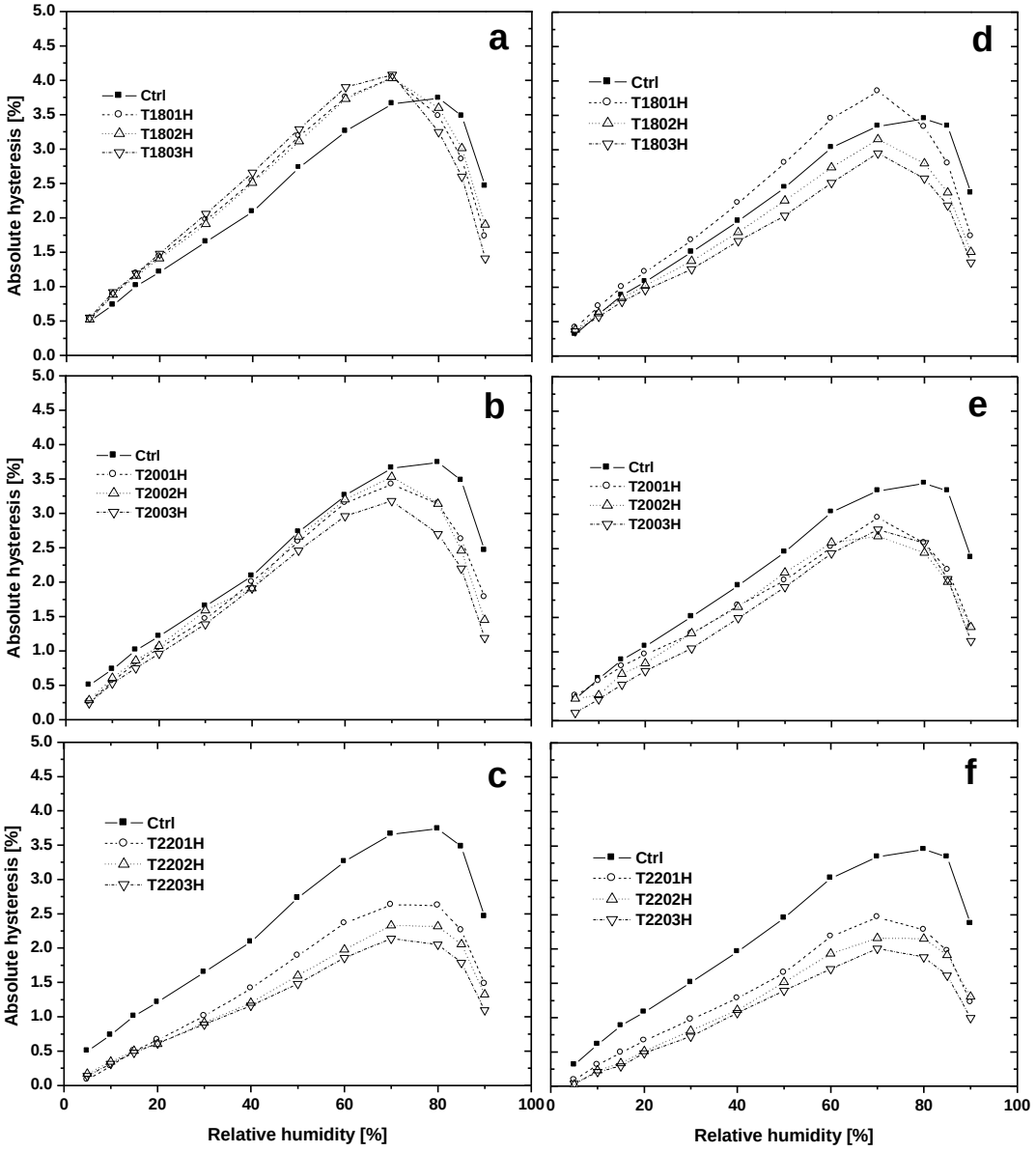

Figure 4.11 Absolute hysteresis between adsorption and desorption curves (obtained by subtraction of EMCs) of *A. mangium* and *E. malaccense* (modified and unmodified) at various RH. For the following wood are *A. mangium* (a, b and c) and *E. malaccense* (d, e and f) at different treatment times (1H-1 hour, 2H-2 hours, 3H-3hours) and temperatures (180, 200 and 220 ^{o}C).

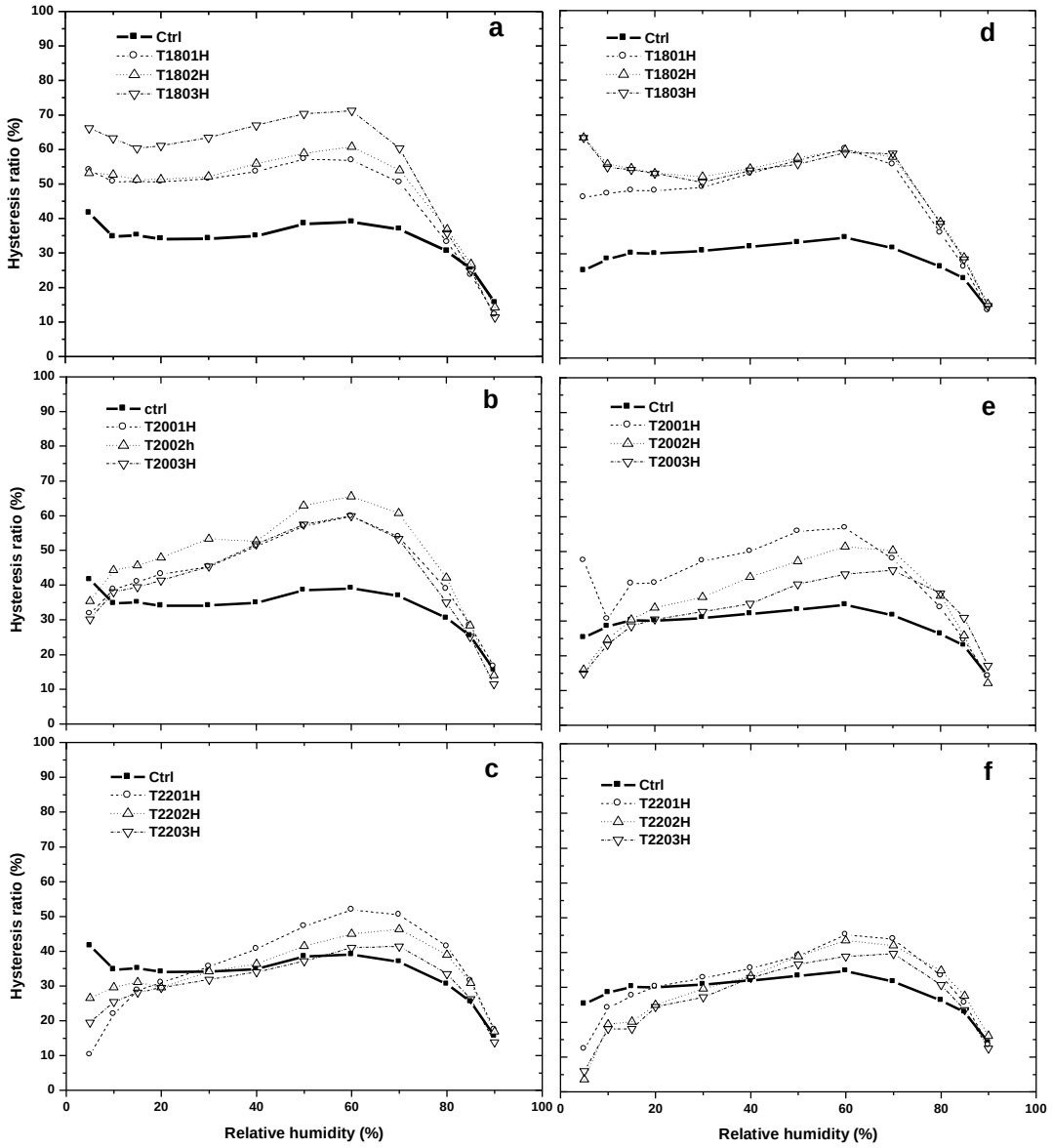

Figure 4.12 Hysteresis ratio of *A. mangium* and *E. malaccense* (modified and unmodified) at various RH. For the following wood are *A. mangium* (a, b and c) and *E. malaccense* (d, e and f) at different treatment times (1H-1 hour, 2H-2 hours, 3H-3hours) and temperatures (180, 200 and 220 ^{o}C).

4.4 Conclusions

The sorption behaviour of fine particles of wood taken from six hardwood species and thermally modified wood has been investigated. This study showed that there were differences in the adsorption/desorption behaviour among the unmodified tropical hardwoods and with the thermally modified wood. Wood species with high extractives content showed reduced EMC. Thermally modified wood showed a reduced EMC at each RH in sorption isotherms. This may be due to chemical variation (i.e. loss of hemicelluloses) due to the thermal modification. Temperature of modification was found to have greater influence on EMC than modification time. The adsorption isotherms were analysed using the H-H model, with excellent fits to the experimental data of the hardwood species and thermally modified wood. The projected fibre saturation point (p-FSP), monolayer and polylayer water were reduced at a range of RH values for thermally modified wood. In the hardwood species, the high extractives content of the wood affected the value of p-FSP, monolayer and polylayer water. Increased stiffness of the cell wall of thermally modified wood appears to be associated with a higher hysteresis ratio. This can be seen with the loss of hemicelluloses and increasing of cellulose content which resulting less OH content. It is known that the lignin becomes more cross-linked due to modification resulting in restraint of cell wall expansion. However, when absolute hysteresis is determined the reduced overall EMC masks this effect. This relationship between water vapour sorption and cell wall matrix stiffness may provide further insights into sorption hysteresis.