CHAPTER FOUR

RESULTS

AND DISCUSSION

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4 Results and Discussion

The test results presented in this chapter consist of three parts, beginning with the factors affecting formaldehyde emission, followed by the comparison of quantifying techniques and analytical methods, and, lastly, the methodologies for the minimisation of formaldehyde.

4.1 The Effect of the Variation of Moisture Content on Formaldehyde Emission

The emission of formaldehyde in relation to the moisture content (MC) is given in Table 4.1.1 and Figures 4.1.1 to 4.1.4. The results show a linear relationship between the emission of formaldehyde and the moisture content in which the higher the moisture content, the higher the emission of formaldehyde. This led to intensified interest to determine the actual increase in formaldehyde emission with the plywood moisture content. Therefore, the moisture content of wood veneers was controlled at 6%, 10%, 14% and 18%, which are classified as the usual operational standards for much of the plywood manufacturing industry.

In general, plywood has a minimum of three layers with a thicker inner core (IC) between the surface veneer (SV) and back veneer (BV), which consist of the same thickness. The moisture content may be present in the inner core, surface veneer or back veneer or all layers, which, therefore, requires further investigation. It was predicted that the moisture content of each layer of plywood has a significant effect on the formaldehyde emission. It is therefore interesting to differentiate the emission characteristics between the inner core and the surface veneers as well as the back veneer.

4.1.1 Results of Formaldehyde Emission with Changes in Moisture Content

Plywood, comprising multiple species, was accumulated for statistical evaluation of the moisture content changes in altering the formaldehyde emission. Across the measured panels, formaldehyde emission decreased with a reduction in the moisture content. The formaldehyde emission decreased in the following order of moisture contents: 18% > 14% > 10% > 6%, for all of the plywood samples tested.

It was evidenced that the highest formaldehyde emission was obtained from the plywood with the greatest moisture content at 18%. The lowest formaldehyde emission was measured at a moisture content of 6% while the emission of a moisture content of 10 % and 14% lie in between (Table 4.1.1). As the moisture content decreased from 18% to 6% (MC 18/6), the formaldehyde emission value of *binuang* plywood measured through the desiccator-chromotropic acid (DC-CA) method declined drastically, by 54%. With the same moisture content changes, the greatest formaldehyde reduction was again observed for other species, ranging from 54% to 67% (Figure 4.1.1). The moisture content decreased from 14% to 6% (MC 14/6) caused a reduction of about 44 %, and 30 % when it was decreased from 10% to 6% (MC 10/6).

The same batch of specimens was evaluated using the desiccator-acetyl acetone (DC-AA) method in the confirmation test. The results, as shown in Figure 4.1.2, indicate that the highest discharge of formaldehyde was again shown by a moisture content of 18%. This was followed by a moisture content of 14% and then a moisture content of 10%, with the lowest being a moisture content of 6%. Again, the greatest formaldehyde reduction of at least 51% was found for MC 18/6.

Table 4.1.1 Formaldehyde emission analysed by the desiccator-chromotropic acid (DC-CA) method

Plywood Species	Formaldehyde emission by DC-CA (µg/mL)			
	MC 6%	**MC 10%**	**MC 14%**	**MC 18%**
Binunag	0.32	0.45	0.54	0.70
Batai	0.20	0.30	0.36	0.49
Kapur	0.12	0.17	0.20	0.30
Keruing	0.17	0.26	0.33	0.46
Laran	0.30	0.41	0.50	0.66
Magas	0.22	0.32	0.38	0.51
Red seraya	0.13	0.20	0.30	0.39
Sedaman	0.19	0.28	0.35	0.48
White seraya	0.24	0.34	0.41	0.59
Yellow seraya	0.29	0.37	0.46	0.63

** MC= moisture content;*
*** MC of surface veneer, back veneer and inner core were fixed at equal percentage*
(e.g. MC 6 % = [6 + 6 + 6], MC 10 % = [10 + 10 + 10], MC 14 % = [14 + 14 + 14] & MC 18 % = [18 + 18 + 18])

Apart from the equal moisture content for each layer of plywood sample, the 3 ply test samples were also prepared with different moisture content, with the first set having 6% moisture content at the surface veneer with increasing moisture content from 6% to 18% in the inner core layer. The second set had 10% moisture content at the surface veneer with increasing moisture content from 6% to 18% in the inner core layer. The same for the third and fourth set having 14% and 18% moisture content at the surface veneers, respectively. Meanwhile, the moisture content for the back veneer was controlled at the same level as the surface veneer, and both was having the same thickness as usual. The moisture content of each layer was written in a combination form of MC [SV + IC + BV], as shown by Table 3.2 in Chapter 3.

Overall, 100% of the tested samples from *batai, kapur, keruing, laran, sedaman, red seraya, white seraya* and *yellow seraya* plywood manufactured with higher moisture content of inner core, emitted more formaldehyde gas whereas both *binuang* and *magas* plywood achieved only 92% using the DC-CA method (Figure 4.1.3). These findings indicate that the influence of moisture content in the inner core was stronger than the surface veneer in determining the formaldehyde emission.

The influences became more significant when the combination of MC [6 + 18 + 6] was compared to MC [18 + 6 + 18] giving the largest difference of formaldehyde emission, ranging from 10% to 25%. This was followed by a mean value of 10% which was found between MC [10 + 18 + 10] and MC [18 + 10 + 18]. The least difference, however, was between MC [10 + 14 + 10] with MC [14 + 10 + 14], which gave a maximum of only 6%. Further comparisons have been illustrated in Figure 4.1.3 & 4.1.4.

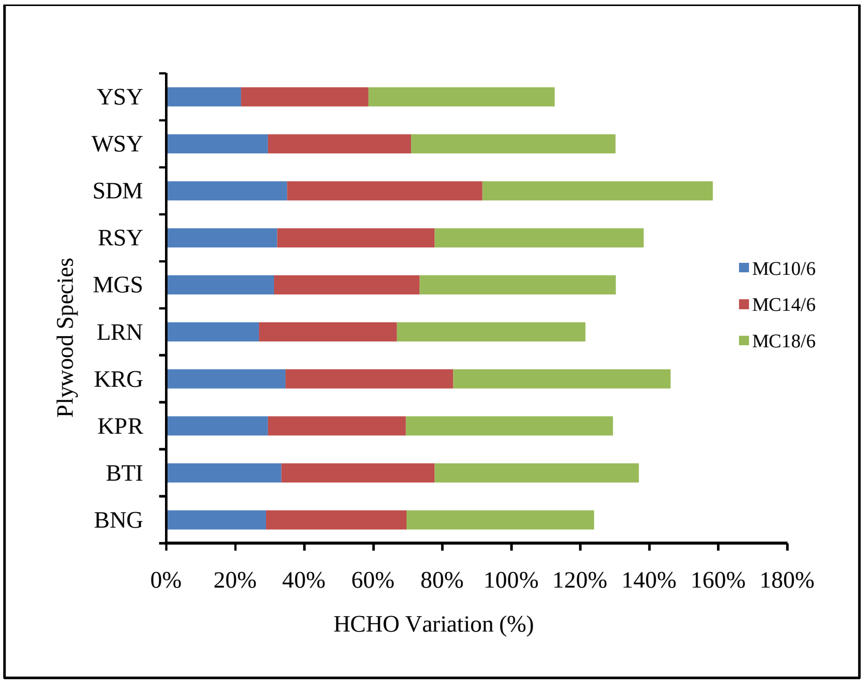


Figure 4.1.1: The largest formaldehyde reduction at MC (18/6) was followed by MC (14/6) and MC (10/6) using the desiccator-chromotropic acid (DC-CA) method.

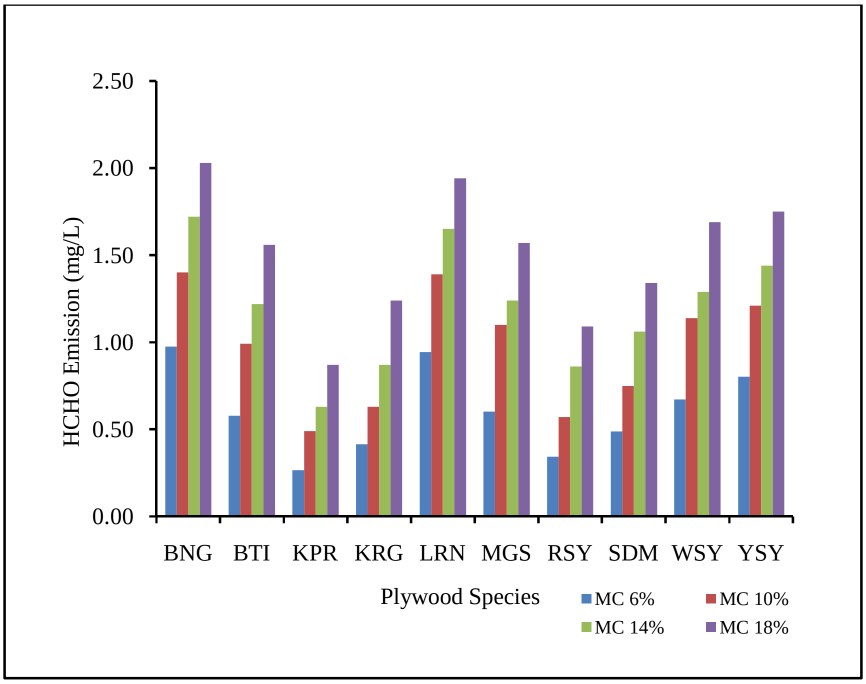


Figure 4.1.2: Formaldehyde emission in accordance with various MC as measured by the desiccator-acetyl acetone (DC-AA) method.

* [BNG= *binuang*, BTI= *batai*, KPR= *kapur*, KRG= *keruing*, LRN= *laran*, MGS= *magas*, RSY= *red seraya*, SDM= *sedaman*, WSY= *white seraya*, YSY= *yellow seraya*]

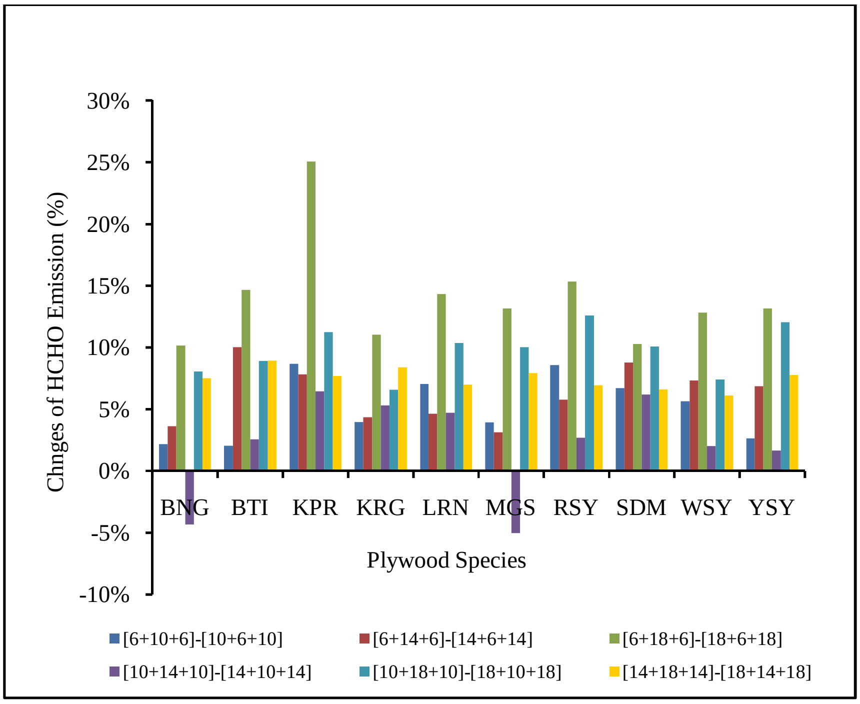


Figure 4.1.3: Comparison of formaldehyde emission relative to different moisture content combinations by desiccator-chromotropic acid (DC-CA) method.

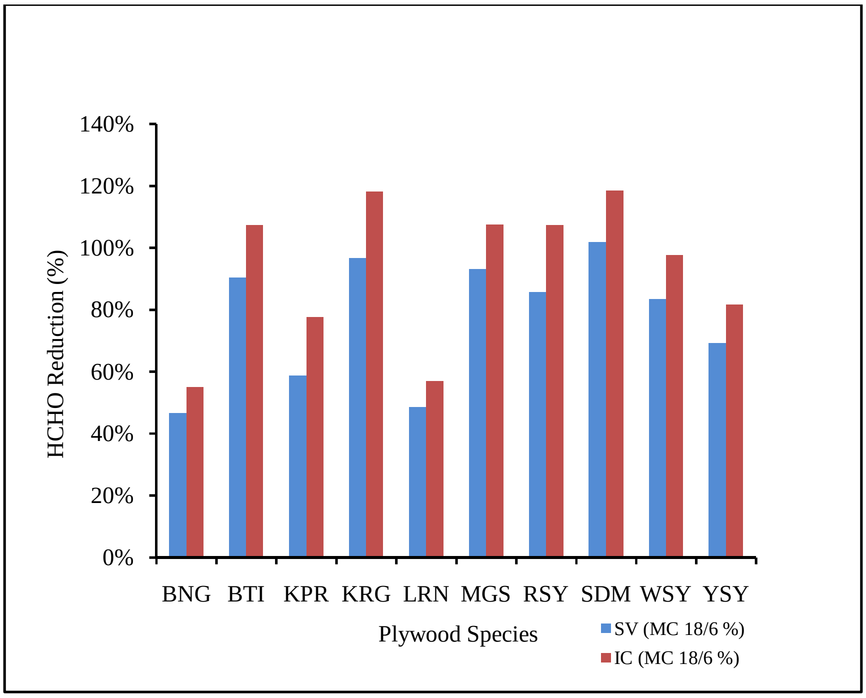


Figure 4.1.4: Comparison of formaldehyde reduction with the decrease of moisture content, MC (18/6) between surface veneer and inner core of plywood using the desiccator-acetyl acetone (DC-AA) method.

* [BNG= *binuang*, BTI= *batai*, KPR= *kapur*, KRG= *keruing*, LRN= *laran*, MGS= *magas*, RSY= *red seraya*, SDM= *sedaman*, WSY= *white seraya*, YSY= *yellow seraya*]

4.1.2 Discussion of Formaldehyde Emission with Changes in Moisture Content

Formaldehyde is basically a hydrophilic molecule with a high tendency to dissolve in water. The potentially greater source of emission comes from the formaldehyde dissolved in the water or moisture of the boards. The decrease in emission appears to be related to a lack of moisture movement out of the panel (Wolcott *et al*., 1996). These findings help to explain the trend of formaldehyde emission in the order MC 6% < MC 10% < MC 14% < MC 18% in the current study. The formaldehyde reduction was enhanced by the decrease in moisture content, and the larger of the decrease, the lesser the pathway for the formaldehyde to be released from the plywood specimens. Therefore, the largest formaldehyde reduction was detected when the moisture content 6% was reduced from a moisture content of 18%. The previous works by Rofael *et al*. (2010) demonstrated a similar formaldehyde decrease of about 60% with a decrease of moisture content from 10% to 4% (MC 10/4) using the perforator and chamber methods.

The chemical breakdown of cured resin through hydrolysis is a potentially greater source of formaldehyde emission (Stuligross & Koutsky, 1985). The hydrolysis of weakly bound formaldehyde from *N*-methylol groups, acetals and hemiacetals, and hydrolysis of methylene ether bridges in more severe cases, also increases the emission of formaldehyde (Aydin *et al*., 2006). In the presence of moisture, urea formaldehyde resin is slightly hydrolysed (Aydin *et al*., 2006). The hydrolysis was enhanced by the elevation in moisture content, which drives formaldehyde emission to higher values (Table 4.1.1 & Figure 4.1.2). As wood readily exchanges moisture with air, the moisture content was evidenced to play an important role in the formaldehyde emission (Figure 4.1.5).

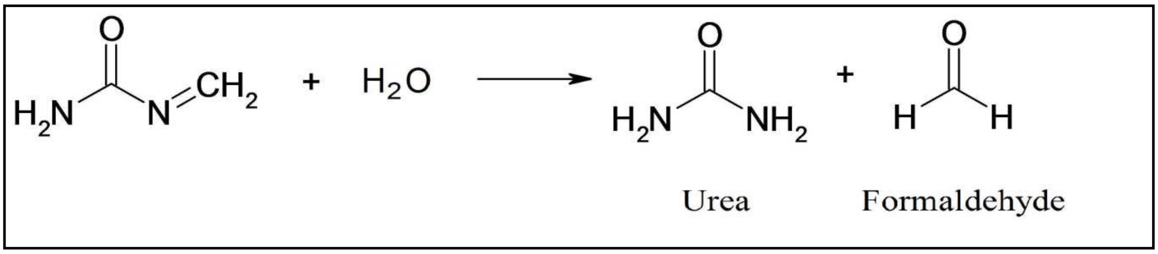


Figure 4.1.5: The presence of water results in the hydrolysis of the C=N bond and release of the formaldehyde.

The comparison was direct and easier when each layer was conditioned to the equal moisture content. However, these ideal conditions were not easily achieved and the thickness of the inner core and surface veneer was different. In addition, the lower moisture content may cause splitting of the surface veneer and back veneer while higher moisture content could causes delaminating of the inner core. Therefore, the moisture content for a variety of combinations that provide good bonding was checked for its formaldehyde emission. The findings showed that the moisture influence of the inner core was stronger than the surface veneer in altering the formaldehyde emission (Figure 4.1.3; 4.1.4). The plywood matrix includes macromolecules, mainly cellulose, which is linked to water by the hydrogen bonds (Casieri *et al*., 2004; Haughton & Murphy, 2003).

The moisture loses easier from the surface veneer than the inner core to the surrounding as water vaporises during the pre-press for cold tacking and during the thermal-bonding step. The vaporisation rate was enhanced by the larger exposure area of the surface veneer and the efficient heat conduction through direct contact of the heated platen to the surface veneer in thermal pressing process. As a result, the initial moisture content of the surface veneer was reduced drastically compared to inner core.

The greater emission of formaldehyde, which was enhanced by the higher moisture content of the inner core, could also result from the larger portion of the inner core than the surface veneer inasmuch as their thickness ratio is 2:1. Hence, the effect of the surface veneer's initial moisture content to the formaldehyde emission is less obvious than the inner core. These findings were confirmed according to the moisture content check using a prone type moisture meter, which is based on measurements of the conductivity between two nails inserted into the plywood (Casieri *et al*., 2004). A higher moisture content of the inner core prevents complete cross linking, thereby weakening the adhesive and causing greater formaldehyde emission, and clearly enhances the rate of free formaldehyde emission from the boards (Myers, 1983).

When H_2O molecules absorb enough heat energy generated by the exothermic reaction of urea formaldehyde based resin with ammonium chloride (hardener), moisture tends to evaporate from both of its outer layer as well as through the edge side of the plywood. Rapid vaporisation occurred when plywood was thermally pressed at 115 ± 5°C, which was also reported by Jiang (2002).

With a longer conditioning time and different mechanism based method (DC-AA), the same response was observed. Again, the influence of moisture content on the panel's formaldehyde emission was much stronger from the inner core region than the surface veneer among the ten types of wood species tested.

4.2 The Effect of the Variation of Wood Species on Formaldehyde Emission

A number of wood species were used to investigate the formaldehyde emission of plywood panels. This includes the commonly used and important commercial value timber, in order to enlarge the data coverage of the investigation. Solid wood smells, and, thus emits volatile organic compounds (VOCs), which include formaldehyde (Jones, 2010). The different odours were noted, together with the different levels of formaldehyde emission from a variety of timber species, as evidenced from the results obtained. Although they were bonded with the same type of urea formaldehyde base glue mix with an equivalent spreads volume, and produced by using veneers conditioned to a constant moisture content (MC 6%), which underwent the same manufacturing procedures in accordance with standard operation parameters, the formaldehyde emission varies among the different plywood species. Generally, it was expected that only the free formaldehyde from uncured urea formaldehyde and hydrolysis of glue bond-line contributed to the emission. Due to the increasing concern in respect of the natural wood character, a thorough investigation of the effects of wood species on formaldehyde emission was undertaken.

The properties of wood species were no more sidetracked from giving significant influence to the formaldehyde emission. This was declared by the California Code of Regulations, Sections 93120-93120.12 that bonded with Composite Wood Products Airborne Toxic Control Measure, by California Air Resource Board (CARB). Instead of formaldehyde emitted from the urea formaldehyde moiety of traditional composite wood panels, the wood derived formaldehyde emission is a more significant part of the total formaldehyde emissions (Bikerland *et al.*, 2010). Therefore, the dependency of wood physical properties, such as colour, pH and porosity (Table 4.2.1), on formaldehyde emission is discussed in details.

Some part of the further investigation used a veneer without glue bonding as test specimens to quantify their effects on the total emission. The attribution of solid wood in formaldehyde emission was expected within 3% to 5%. Nevertheless, the influence of wood borne formaldehyde was evidenced. This further indicates that there could be a reaction between urea formaldehyde glue mix and the active components in woody material giving rise to different levels of formaldehyde emissions.

Table 4.2.1: Physical description of various wood species

Species	**Domain Colour**	**pH** [a]	**Porosity** [b] **(%)**
Binuang	Yellowish	Acidic (mild)	High
Batai	Reddish	Acidic (mild)	High
Kapur	Reddish	Acidic	Low
Keruing	Reddish	Acidic	Low
Laran	Yellowish	Acidic (mild)	High
Magas	Yellowish	Acidic	High
Red seraya	Reddish	Acidic	Low
Sedaman	Reddish	Acidic	High
White seraya	Reddish	Acidic (mild)	Low
Yellow seraya	Yellowish	Acidic (mild)	Low

[a] pH≤ 5.5 (acidic) and pH≥ 5.8 (mild acidic)
[b] Porosity 56 % to 68 % (low) and porosity 72% to 78% (high)

4.2.1 Results of Formaldehyde Emission with Changes in Woody Colour

Table 4.2.2 shows the domain colour of a variety of wood samples. They were divided into two main groups. The greatest emission was found for *binuang,* measured using the small chamber-chromotropic acid (SC-CA) method, followed by *laran* and *yellow seraya* plywood (Table 4.2.3). The yellowish species remained as the top three in both chromatographic analyses using the liquid-liquid extraction (LLE) and solid phase micro-extraction (SPME) methods. However, the formaldehyde emission values obtained were different due to the different testing parameters, which will be further discussed in section 4.3. In contrast, *kapur* board gave the lowest emission magnitude, followed by the two other reddish species of *red seraya* and *keruing* plywood. Their formaldehyde emission value, measured by the SC-CA method, was at least 55% lower than the *yellow seraya*. A similar observation was also obtained by LLE (60% lower) and SPME (67% lower) analyses. Overall, the emission of formaldehyde from the yellowish species is always higher than those of the reddish wood except for the *magas* plywood.

By using visual inspection, the two main groups were further classified into subgroups based on the light to darker colour (Table 4.2.2) due to the different emission behaviours within the same domain colour. The differences between *yellow seraya*, *laran* and *binuang* with *magas* (yellowish species with the lowest formaldehyde emission) were changed from 25% to 32%. For the reddish wood species, the difference in formaldehyde emission from kapur plywood ranged from 13% to 61% (Table 4.2.3). Similar changes were also obtained by the LLE and SPME methods (Table 4.2.4 to 4.2.6).

As shown in Table 4.2.7, solid wood without glue adhesion released their different amount of natural borne formaldehyde. Again, the yellowish solid wood emits greater formaldehyde of about two fold to that of the reddish species.

Table 4.2.2: Colour descriptions of different varieties of wood species

Species	**Domain Colour** (Intensity)	**Colour Description** (From light to darker colour)
Binunag	Yellowish (Y1)	Light yellow with a greenish tinge
Laran	Yellowish (Y2)	Light yellow
Yellow seraya	Yellowish (Y3)	Yellow brownish
Magas	Yellowish (Y4)	Yellow greyish
White seraya	Reddish (R1)	Light pink with reddish tint
Batai	Reddish (R2)	Pink
Sedaman	Reddish (R3)	Pink with a reddish tint
Keruing	Reddish (R4)	Light brown
Red seraya	Reddish (R5)	Dark Red
Kapur	Reddish (R6)	Dark brown with yellowish nut-brown streaks

* Colour intensity is checked by visual inspection. The number increases when the colour becomes darker

Table 4.2.3: Formaldehyde emission with woody colour by the small chamber-chromotropic acid (SC-CA) method

Plywood	**Colour Intensity**	**SC-CA (µg/mL)**
Binunag	Yellowish (Y1)	0.22
Laran	Yellowish (Y2)	0.21
Yellow seraya	Yellowish (Y3)	0.20
Magas	Yellowish (Y4)	0.15
White seraya	Reddish (R1)	0.18
Batai	Reddish (R2)	0.12
Sedaman	Reddish (R3)	0.11
Keruing	Reddish (R4)	0.09
Red seraya	Reddish (R5)	0.08
Kapur	Reddish (R6)	0.07

** Colour intensity arranged from light to dark colour, Y1 to Y4 and R1 to R6*

Table 4.2.4: Formaldehyde emission with woody colour by the liquid-liquid extraction analysed by GC/FID (LLE-FID) method

Plywood	**Colour Intensity**	**LLE-FID (mg/L)**
Binunag	Yellowish (Y1)	1.84
Laran	Yellowish (Y2)	1.21
Yellow seraya	Yellowish (Y3)	0.96
Magas	Yellowish (Y4)	0.69
White seraya	Reddish (R1)	0.72
Batai	Reddish (R2)	0.59
Sedaman	Reddish (R3)	0.42
Keruing	Reddish (R4)	0.32
Red seraya	Reddish (R5)	0.24
Kapur	Reddish (R6)	0.10

Table 4.2.5: Formaldehyde emission with woody colour by the solid phase micro-extraction sampling from absorbing solution (SPME-A) method

Plywood	**Colour Intensity**	**SPME-A (mg/L)**
Binunag	Yellowish (Y1)	1.46
Laran	Yellowish (Y2)	1.20
Yellow seraya	Yellowish (Y3)	1.11
Magas	Yellowish (Y4)	0.76
White seraya	Reddish (R1)	0.86
Batai	Reddish (R2)	0.70
Sedaman	Reddish (R3)	0.54
Keruing	Reddish (R4)	0.44
Red seraya	Reddish (R5)	0.37
Kapur	Reddish (R6)	0.30

** Colour intensity arranged from light to dark colour, Y1 to Y4 and R1 to R6*

Table 4.2.6: Formaldehyde emission with woody colour by the solid phase micro-extraction air sampling directly from wood specimen (SPME-W) method

Plywood	**Colour Intensity**	**SPME-W (mg/L)**
Binunag	Yellowish (Y1)	1.65
Laran	Yellowish (Y2)	1.20
Yellow seraya	Yellowish (Y3)	1.18
Magas	Yellowish (Y4)	0.91
White seraya	Reddish (R1)	0.99
Batai	Reddish (R2)	0.83
Sedaman	Reddish (R3)	0.59
Keruing	Reddish (R4)	0.48
Red seraya	Reddish (R5)	0.43
Kapur	Reddish (R6)	0.35

Table 4.2.7: Formaldehyde emission of solid wood (SW) and plywood (PW) in accordance with the colour of wood species

Species	**Colour Intensity**	**Formaldehyde Emission by DC-AA (mg/L)**		**Percentage of (SW/PW) (%)**
		SW	**PW**	
Binunag	Yellowish (Y1)	0.03	0.97	3.1
Laran	Yellowish (Y2)	0.03	0.94	3.2
Yellow seraya	Yellowish (Y3)	0.03	0.80	3.8
Magas	Yellowish (Y4)	0.02	0.60	3.3
White seraya	Reddish (R1)	0.02	0.67	3.0
Batai	Reddish (R2)	0.02	0.58	3.4
Sedaman	Reddish (R3)	0.02	0.49	4.1
Keruing	Reddish (R4)	0.02	0.41	4.9
Red seraya	Reddish (R5)	0.01	0.34	2.9
Kapur	Reddish (R6)	0.01	0.27	3.7

* Colour intensity arranged from light to dark colour, Y1 to Y4 and R1 to R6;
** SW= solid wood and PW= plywood

4.2.2 Results of Formaldehyde Emission with Changes in Woody pH

The pH of wood species was determined by grinding the solid wood samples to pass through a 50 mesh screen (0.279 mm) and then 1 g of the resulting wood flour was immersed in 20 mL of distilled water for 20 minutes of extraction time. This was done after the veneers were conditioned to a moisture content of 6% to eliminate the influence of moisture to pH, which affects the formaldehyde emission.

To evaluate the woody pH in greater detail, the samples were divided into 2 sub-groups, i.e. pH ≤ 5.5 (acidic) and pH ≥ 5.8 (mild acidic). In the first group, pH 4.7 and 4.9 were the two most acidity values, which belong to *kapur* and *red seraya*, respectively. They showed the lowest formaldehyde emission, below 0.4 mg/L by the SPME-A analysis. The amounts of emission become higher as the pH increased in value for the majority of plywood samples except magas. When the pH 4.7 was approaching pH 5.3, the increase in formaldehyde emission ranged from 47% to 80% (Table 4.2.8). It then increased continuously from 1.11 mg/L at pH 6.1 up to 1.46 mg/L at pH 6.2.

The largest difference was recorded between *kapur* and *binuang* plywood, which was also categorised as the most acidic and the weakest. Although some species had a very close pH, the formaldehyde off gassed was different, such as *keruing* with *sedaman* and *laran* with *binuang*, as stated in the Table 4.2.8; 4.2.9 and Figure 4.2.1; 4.2.2. The decreasing trend of formaldehyde emission using the DC-AA, DC-CA, SC-CA and LLE methods were also found to parallel the reduction in woody pH.

Table 4.2.8: Formaldehyde emission with woody pH in descending trend by the solid phase micro-extraction sampling from absorbing solution (SPME-A) method

Plywood	**pH**	**SPME-A (mg/L)**
Binuang	6.24	1.46
Laran	6.19	1.20
Yellow seraya	6.08	1.11
White seraya	5.89	0.86
Batai	5.76	0.70
Magas	5.52	0.76
Sedaman	5.34	0.54
Keruing	5.32	0.44
Red seraya	4.93	0.37
Kapur	4.73	0.30

Table 4.2.9: Formaldehyde emission with woody pH in descending trend by the solid phase micro-extraction air sampling directly from wood specimen (SPME-W) method

Plywood	**pH**	**SPME-W (mg/L)**
Binung	6.24	1.65
Laran	6.19	1.48
Yellow seraya	6.08	1.18
White seraya	5.89	0.99
Batai	5.76	0.83
Magas	5.52	0.91
Sedaman	5.34	0.59
Keruing	5.32	0.48
Red seraya	4.93	0.43
Kapur	4.73	0.35

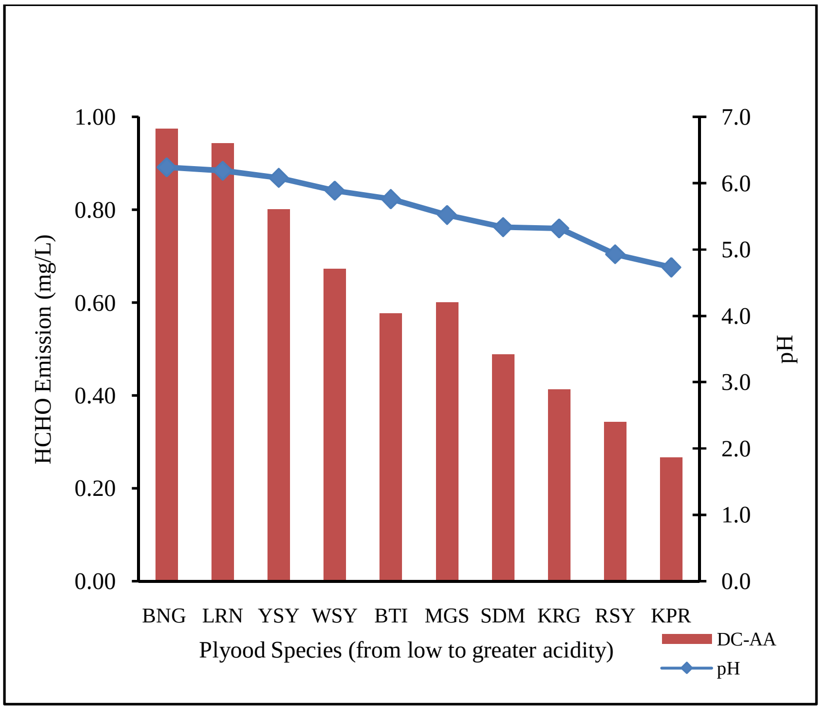


Figure 4.2.1: Formaldehyde emission of a variety of wood species with respect to woody pH in descending trend by the desiccator-acetyl acetone (DC-AA) method.

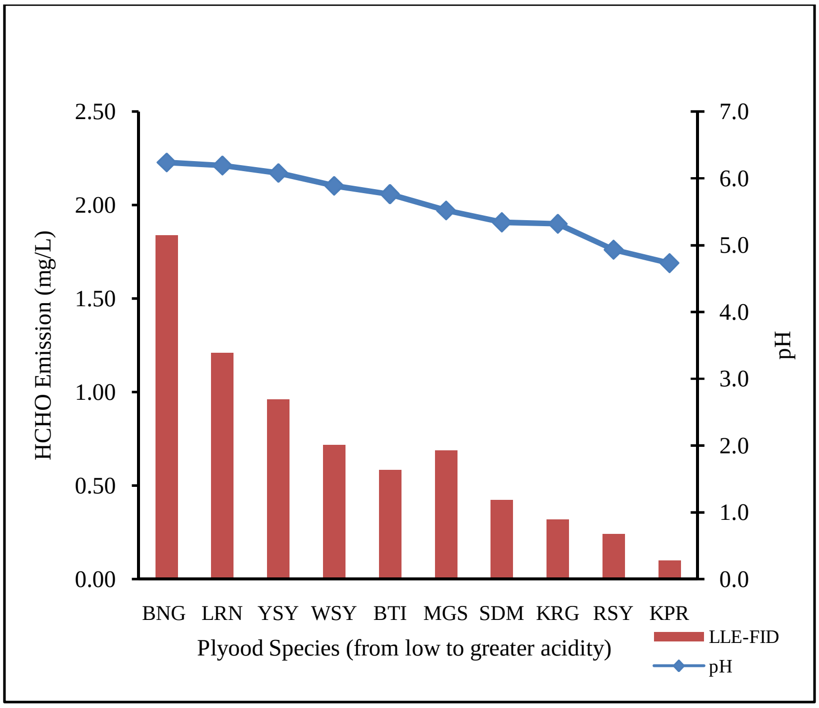


Figure 4.2.2: Formaldehyde emission of a variety of wood species with respect to woody pH in descending trend by the liquid-liquid extraction analysed by GC/FID (LLE-FID) method.

* [BNG= *binuang*, BTI= *batai*, KPR= *kapur*, KRG= *keruing*, LRN= *laran*, MGS= *magas*, RSY= *red seraya*, SDM= *sedaman*, WSY= *white seraya*, YSY= *yellow seraya*]

4.2.3 Results of Formaldehyde Emission with Changes in Woody Porosity

The objective of this study was to generate a relationship between wood porosity with formaldehyde emission for tropical hardwoods. According to Usta (2003), the porosity is calculated from the cell wall materials based on the oven dry mass and volume, in terms of density ratio to the ideal specific gravity value, as given by,

$$P = 1 - \frac{D}{1.53} \tag{1}$$

where,

P = porosity

D = density, g/cm^3

1.53 = ideal specific gravity value for a lignified cellulosic cell wall, g/cm^3

To investigate the porosity effect on the formaldehyde emission, the plywood samples were divided into low porosity (56% to 67%) and high porosity (72% to 78%), as seen in Table 4.2.1. The formaldehyde emission with respect to the mean porosity is given in detail in Table 4.2.10. The highest emission was again shown by *binuang*, which showed the highest porosity percentage (PP) of about 78%, followed by *laran*, *magas*, *sedaman*, *red seraya* and *kapur*. The decrease in formaldehyde emission paralleled the reduction trend of corresponding wood porosity.

In addition, the difference between the largest and the smallest porosity gave a divergence of 83% in formaldehyde emission by LLE analysis. However, it was not the largest difference found in current research. In fact, although *keruing* had the lowest porosity its formaldehyde emission was higher than both *red seraya* and *kapur*, which both had a greater porosity.

Graphically, the influence of porosity on *keruing*, *white seraya* and *yellow seraya* were found to be insignificant. Within the low porous group, the volatile formaldehyde obtained from LLE-FID analysis ranged from 0.10 mg/L to approximately 0.72 mg/L, in an incongruent trend. Generally, there is a weak relationship between the formaldehyde emissions and the woody porosity for the low porous group (Figure 4.2.3). The high porosity group, however, showed a positive relationship with the formaldehyde emission, as expressed either in the same LLE-FID method or by different test methods (Figure 4.2.4). Although the porosity of white seraya and red seraya were very similar (with a difference of less than 1%), their formaldehyde emission tendency were found to be different, resulting in a subsequent difference of 67%.

Table 4.2.10: Formaldehyde emission with woody porosity in descending trend by the liquid-liquid extraction analysed by GC/FID (LLE- FID) method

Plywood Species	**Porosity (%)**	**LLE-FID (mg/L)**
Binuang	77.8%	1.84
Laran	75.6%	1.21
Magas	74.6%	0.69
Batai	73.7%	0.59
Sedaman	72.7%	0.42
White seraya	67.1%	0.72
Red seraya	66.5%	0.24
Yellow seraya	63.9%	0.96
Kapur	59.4%	0.10
Keruing	55.8%	0.32

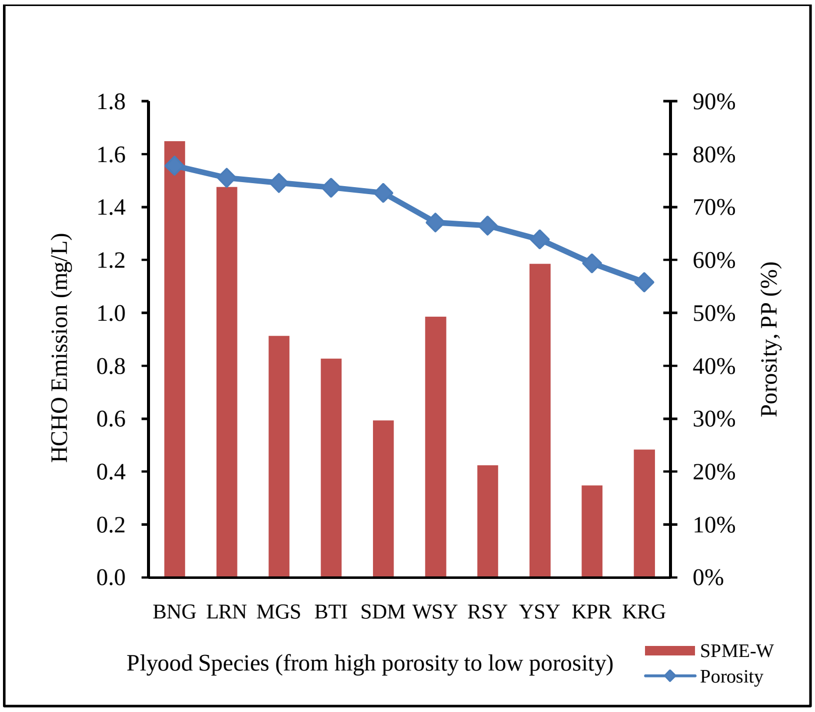


Figure 4.2.3: Formaldehyde emission with different woody porosity in decreasing trend by the solid phase micro-extraction air sampling directly from wood specimen (SPME-W) method

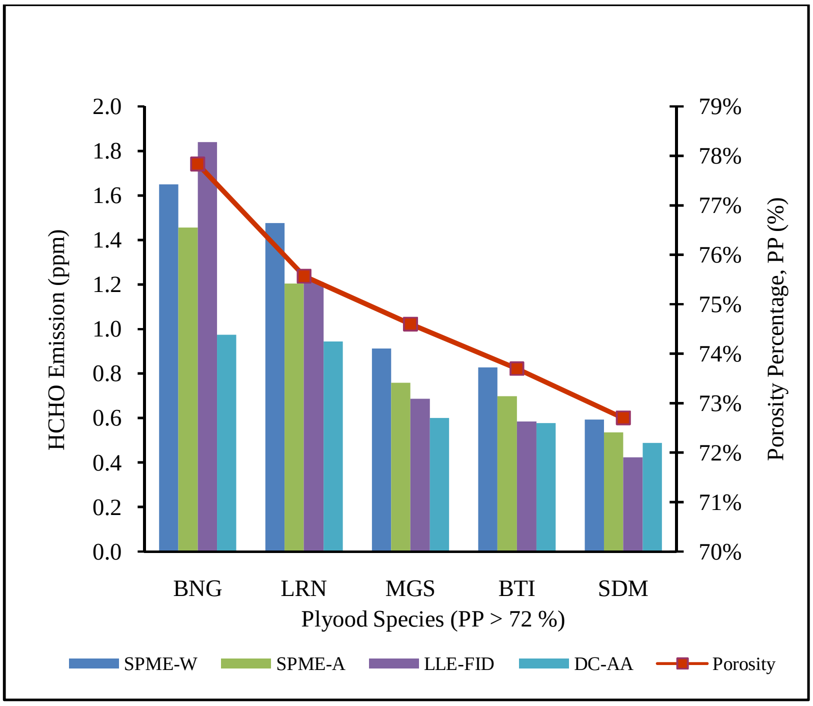


Figure 4.2.4: Formaldehyde emission of high porosity plywood (PP > 72%) in decreasing trend using different test methods.

* [BNG= *binuang*, BTI= *batai*, KPR= *kapur*, KRG= *keruing*, LRN= *laran*, MGS= *magas*, RSY= *red seraya*, SDM= *sedaman*, WSY= *white seraya*, YSY= *yellow seraya*]

4.2.4 Discussion of Formaldehyde Emission with Changes in Woody Colour

The differences in formaldehyde emission according to woody colour could be due to the higher formaldehyde content in yellowish solid wood than the reddish species. The yellowish veneers with higher native formaldehyde contents when bonded to form plywood tend to emit a greater amount of formaldehyde (Figures 4.2.5 & 4.2.6). The origin of colour in natural wood has been reported to be related to chromophores among the extractives as well as the chromophoric groups in the lignin (Burtin *et al*. 1998; Falkehag *et al*., 1966; Haughton & Murphy, 2003). Formaldehyde can be formed from these extractives and lignin together with cellulose and hemicelluloses (Schafer & Roffael, 2000), which are likely to change among different wood species. Therefore, the variation of wood species and the accompanying differences in woody colour have a distinctive effect on the emission of formaldehyde. In addition, different woody colours have different VOCs, and their natural borne formaldehyde also varies among the species within the same domain colour groups. As a result, both the dark brown solid wood and plywood test samples gave the lowest formaldehyde emission followed by the reddish and pinkish in the current study. Besides that, larger amount of formaldehyde were detected from the brighter yellowish species than the greyish yellow species.

The wood species and their colour have become important factors for immediate formaldehyde visual inspection, which can be used to predict and compare the formaldehyde emission of plywood qualitatively. A similar descending trend in emission was observed from light yellowish wood to the dark colour of the reddish species in the continuous trial (DC-AA, DC-CA & SC-CA) and again in the confirmation tests (LLE-FID, SPME-A & SPME-W), thereby increasing the reliability of the finding that individual tropical hardwood species of different woody colours emit formaldehyde at different levels.

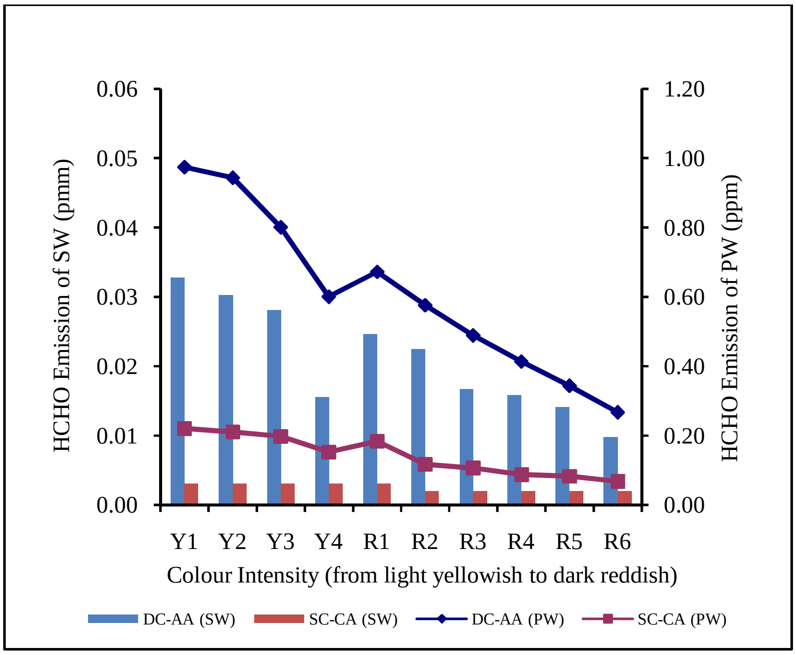


Figure 4.2.5: Formaldehyde emission in decreasing trend shown by solid wood (SW) and plywood (PW) with different colours as performed using the desiccator-acetyl acetone (DC-AA) and small chamber-chromotropic acid (SC-CA) methods.

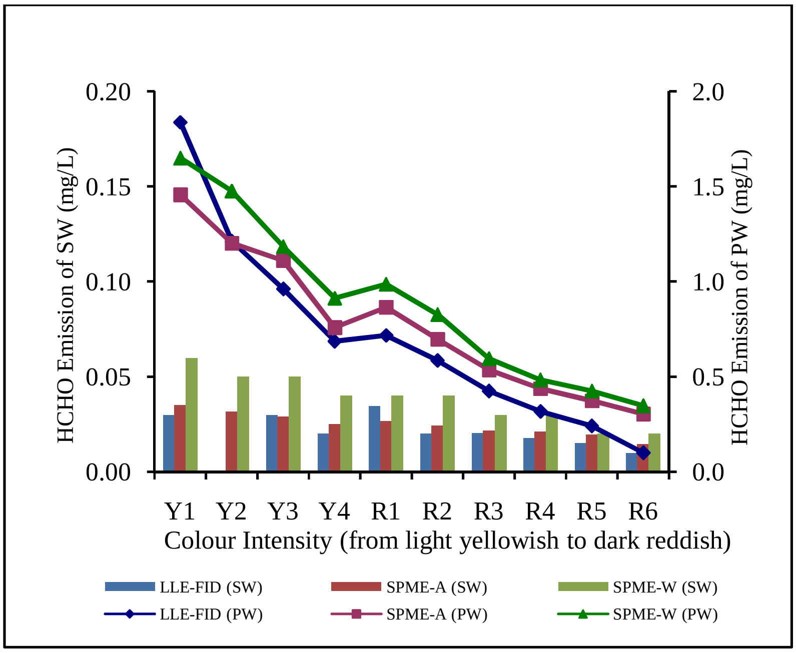


Figure 4.2.6: Formaldehyde emission in decreasing trend shown by solid wood (SW) and plywood (PW) with different colour as performed using the solid phase micro-extraction (SPME-A & SPME-W) and liquid-liquid extraction analysed by GC/FID (LLE-FID) methods.

*[Y1=light yellow with a greenish tinge, Y2=light yellow, Y3=yellow brownish, Y4=yellow greyish, R1=light pink with reddish tint, R2=pink, R3=pink with a reddish tint, R4=dark brown with yellowish nut-brown streaks, R5=dark red, R6=light brown]

4.2.5 Discussion of Formaldehyde Emission with Changes in Woody pH

The changes in formaldehyde emission were quantified with the relationship with pH for different wood species. Overall, the wood exhibited pH in the acidic level (Wengert, 1998). The more acidic the wood species, the less formaldehyde emitted (Table 4.2.8 to 4.2.9). Panels manufactured from *kapur* with the most acidic pH gave the lowest formaldehyde emission. Similarly, a low level of formaldehyde emission was noted for other specimens with pH < 5.5, including *red seraya*, *keruing* and *sedaman*. This is in agreement with the fact that pressed boards release acetyl groups and later turns into acetic acid, which functions as formaldehyde scavenger.

In contrast, the more basic wood substrates retard the adhesive cure rate (Wengert, 1998), which tends to deteriorate the bond integrity of the plywood and enhances its formaldehyde emission, especially in the presence of water. These tests revealed that the emission of formaldehyde decreases as the pH turns more acidic. *Magas*, with a lower pH, however, emits more formaldehyde, which is different from the other wood species. This could be caused by other factors, especially the woody colour effects. It is reasonable to think that the dependency of formaldehyde emission on wood species is not solely reliant on the pH value.

A similar pattern of results illustrating that the decreasing trend of formaldehyde emission was paralleled to the reduction in woody pH was obtained using different test methods. These observations help to increase the reliability of the finding that the pH effect of individual tropical hardwood species on the formaldehyde emission was significant.

Generally, the pH values are always linked to the mechanical properties of wood panels by other researchers (Wengert, 1998). The correlation between the formaldehyde emission values of plywood with the respective pH is rarely found. In the current study, the best linear regression with R^2 = 0.8863 was obtained by plotting the amounts of volatile formaldehyde by the SPME-A methods versus the woody pH. This was followed by the SPME-W method with R^2 = 0.8799 and SC-CA method with R^2 = 0.8789 (Figure 4.2.7 to 4.2.9). The findings again demonstrate that the pH effect can be a predictor of formaldehyde emission.

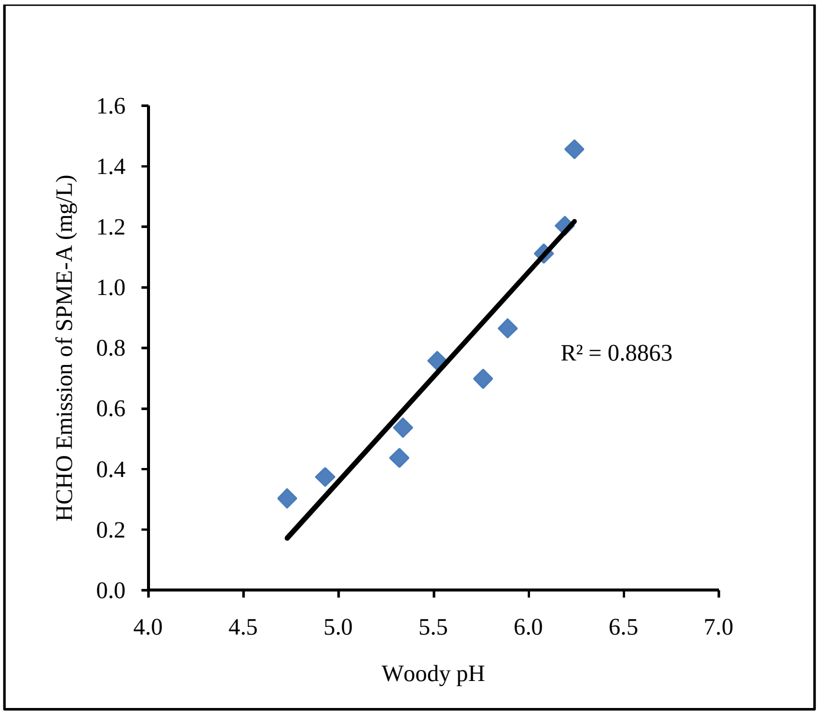


Figure 4.2.7: Linear correlation of formaldehyde emission with woody pH by the solid phase micro-extraction sampling from absorbing solution (SPME-A) method.

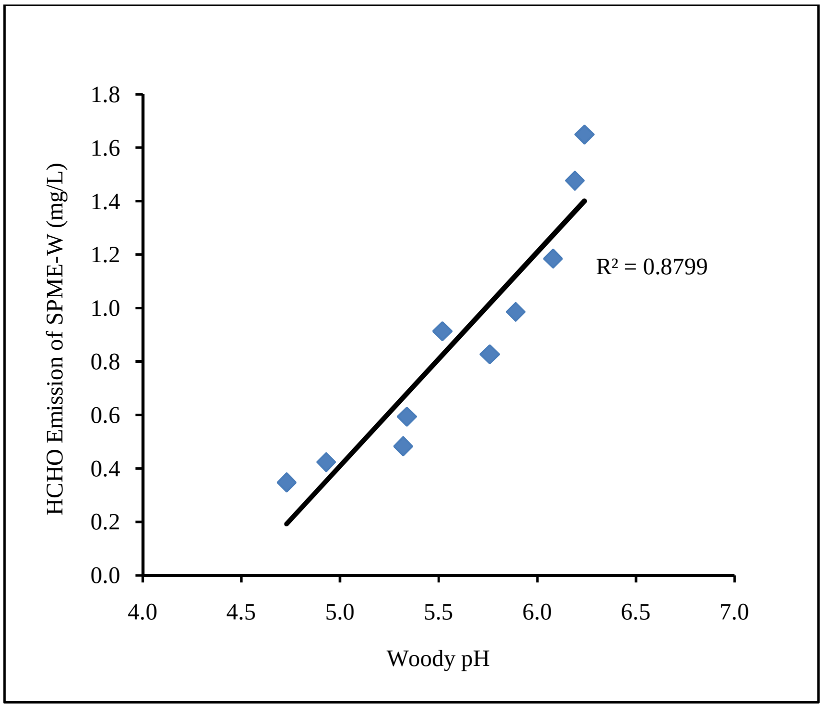


Figure 4.2.8: Linear correlation of formaldehyde emission with woody pH by the solid phase micro-extraction air sampling directly from wood specimen (SPME-W) method.

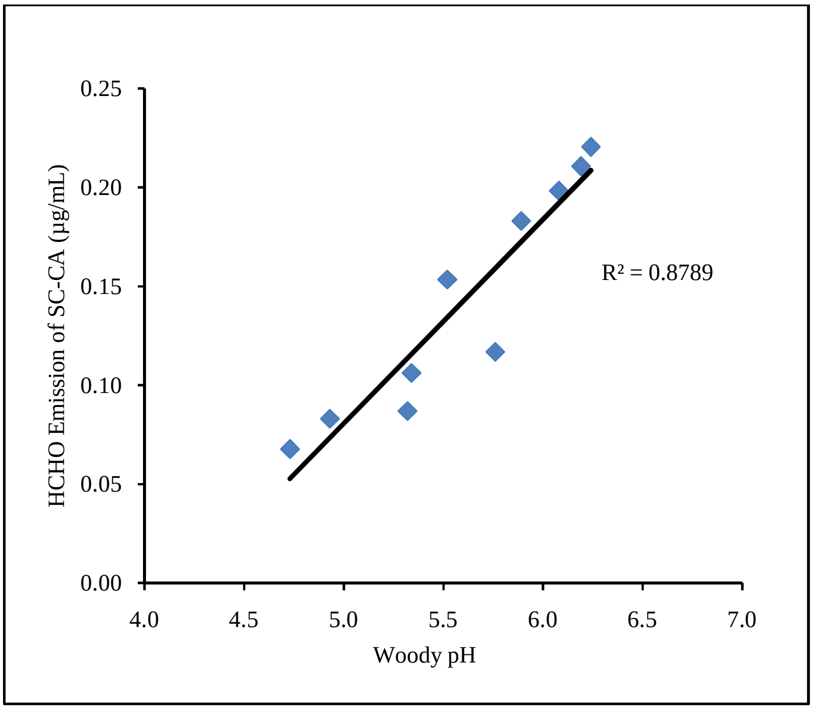


Figure 4.2.9: Linear correlation of formaldehyde emission with woody pH by the small chamber-chromotropic acid (SC-CA) method.

4.2.6 Discussion of Formaldehyde Emission with Change in Woody Porosity

Within the morphological features, a usually overlooked aspect that should be considered to have an effect on the formaldehyde emission is the woody porosity. In comparison with other construction materials such as concrete, metal and stones, wood has lower density. In fact, both wood and plywood are anatomically porous materials (Casieri *et al*., 2004; Haughton & Murphy, 2003). They contain air pockets in cell lumens and show different anatomical characteristics, such as the ratio of early-wood to late-wood and heartwood to sapwood, minerals and extractable substances. For some species, minerals and extractable substances may also affect their density (FPL, 2010). Therefore, the three-dimensional porous network varies among the wood species.

Preliminary experimental results provide evidence that higher porosity (PP > 72%) enhances the emission of formaldehyde through the ready void volume, such as in the case of *binuang*, *laran*, *magas*, *batai* and *sedaman* plywood. The best linear regression was obtained by plotting the volatile formaldehyde collected by the LLE-FID method (y) versus the percentage of porosity/ voids (x), as expressed in a linear curve. For a number of species that limited to high porous wood, the increase in formaldehyde emission was proportional with the growth of porosity giving a correlation coefficient, $R^2 = 0.9629$ at a given moisture content. This was followed by the SPME-A method with $R^2 = 0.939$ and SPME-W method with $R^2 = 0.9051$, respectively (Figure 4.2.10 to 4.2.12).

The formaldehyde present in the adhesives interacts in a distinct way with each wood species and in forming compounds with the cellulose of wood. As the reaction is reversible, the compounds formed will then represent stores of formaldehyde inside the wood. Therefore, the anatomy of the respective wood species will influence the formaldehyde content and emission as well. In addition, the species with greater porosity consists of bigger vessels surface which exposed at the plywood edge. It has been reported that the bigger the vessels surface, the more the formaldehyde is expected to be released from the respective boards (Martinez & Belanche, 2000).

Therefore, the less porous woods with higher density should act as a barrier to the emission of formaldehyde fume. However, the relationship between low porosity wood to formaldehyde emission was not obvious. The relationship did not follow the developed regression equations of formaldehyde emission as predicted in accordance with porosities. Overall, the results obtained do not completely support the previous findings. This could be caused by the influence of other factors, such as the woody colour and pH, as discussed earlier.

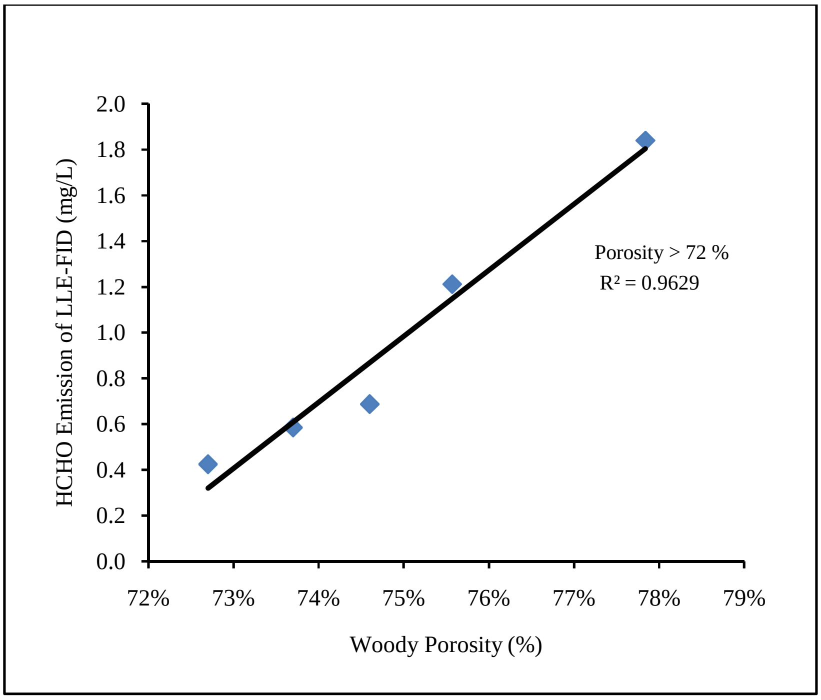


Figure 4.2.10: The relationship of formaldehyde emissions with woody porosity by the liquid-liquid extraction analysed by GC/FID (LLE-FID) method.

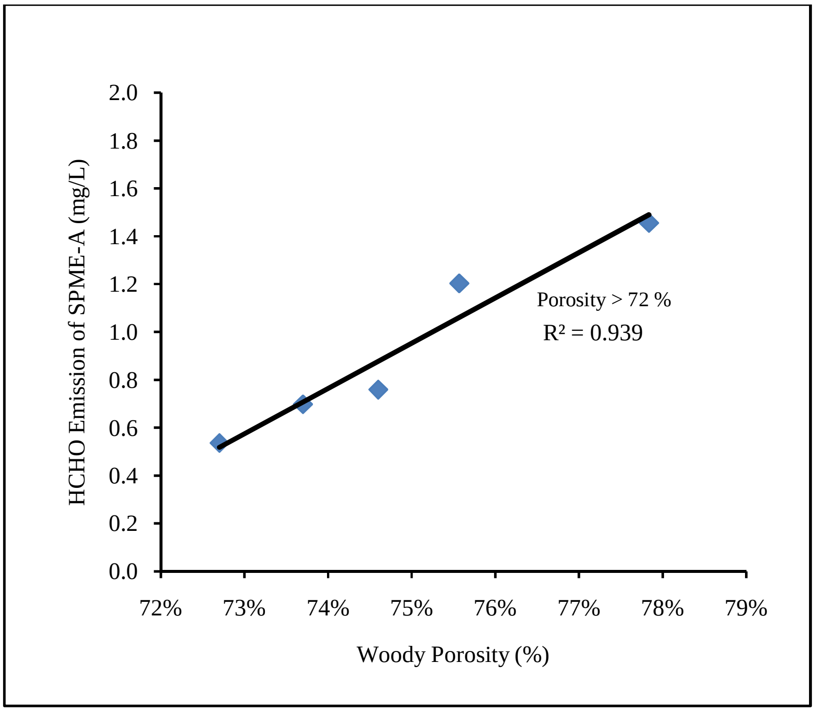


Figure 4.2.11: The relationship of formaldehyde emissions with woody porosity by the solid phase micro-extraction sampling from absorbing solution (SPME-A) method.

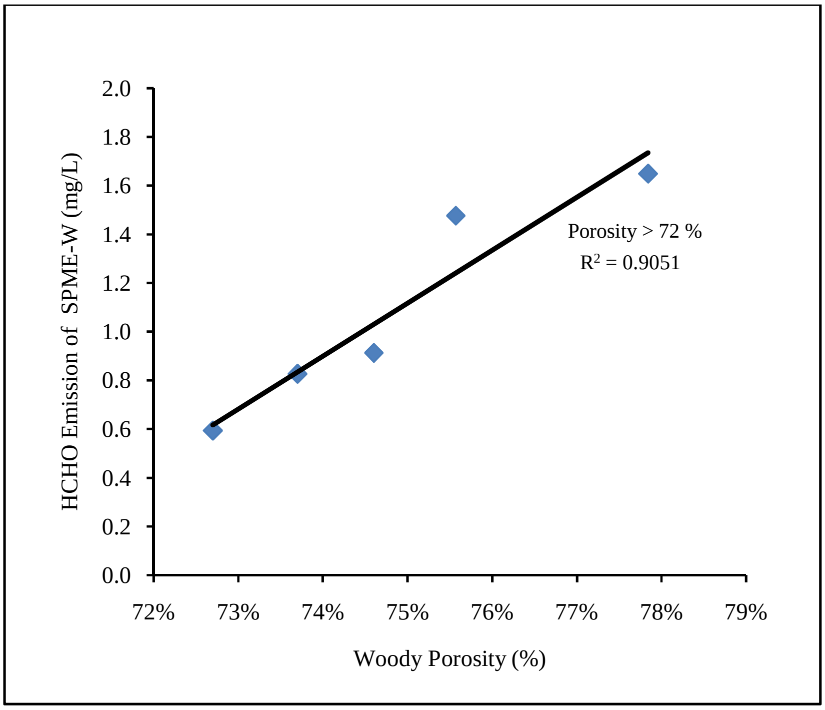


Figure 4.2.12: The relationship of formaldehyde emissions with woody porosity by the solid phase micro-extraction air sampling directly from wood specimen (SPME-W) method.

Again, it was evidenced that the formaldehyde emission of plywood panel was not solely dependent on one factor. The influence of moisture content was significant whereas the timber wood species in terms of pH, colour and porosity play an important role in altering the emission rate and also the amount of formaldehyde liberated. These findings demonstrate that a combination of factors should be used as a predictor of plywood formaldehyde emission.

4.3 Relationship of Evaluation Methodology to Formaldehyde Emission

The formaldehyde emission of plywood is assessed by the analysis using the conventional as well as the newly improved test methods for comparison and correlation studies. In the earlier part of this study, the standard testing method of DC-AA, DC-CA and SC-CA were used for determining the effect of moisture content and wood properties on the formaldehyde emission. However, the more advance SPME and LLE were used together in the latter part and also for the formaldehyde minimisation studies.

For methodology comparison study, the DC-AA and SC-CA, two representative spectrophotometric methods were compared with chromatographic LLE using a combination of different detectors that form LLE-FID and LLE-ECD methods (Table 4.3.1). In addition, the SPME-A and SPME-W methods were included for comparison. All of the comparison results are presented and discussed in details. The DC-CA method is excluded from comparison as it only measured the most easily liberated portion of the free formaldehyde (Myers, 1983).

Table 4.3.1: Analytical methodologies with their correspondence standards

Item	Method	Analytical technique	Standard
1	DC-AA	Spectrophotometry	JAS 233
2	DC-CA	Spectrophotometry	ASTM 5582
3	SC-CA	Spectrophotometry	ASTM D6007
4	LLE-FID	Chromatography	EPA Method 556
5	LLE-ECD	Chromatography	EPA Method 556
6	SPME-A	Chromatography	Nil
7	SPME-W	Chromatography	Nil

* Ref. JAS 233, ASTM 5582, ASTM D6007, EPA Method 556;

** DC-AA=desiccator-acetyl acetone, DC-CA= desiccator-chromotropic aicd, SC-CA= small chamber-chromotropic acid, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD= liquid-liquid extraction analysed by GC/ECD, SPME-A= solid phase micro- extraction sampling by absorbing solution, SPME-W= solid phase micro-extraction air sampling directly from wood specimen

4.3.1 Comparison of SPME and Standard Methods for Initial Formaldehyde Emission

The formaldehyde values of the same board analysed by spectrophotometric and chromatographic methods were found to be different. Even within the same spectrophotometric techniques, the formaldehyde sampled by DC-AA (0.27 mg/L to 0.97 mg/L) and SC-CA (0.07 µg/mL to 0.22 µg/mL) were also different. A similar observation was found for the LLE-FID, SPME-A and SPME-W methods in the chromatographic analyses, as shown in Table 4.3.2.

The trends of formaldehyde emission, as measured by both SPME-A and SPME-W on different wood species paralleled the values from those of the LLE-FID and of the spectrophotometric methods. In general, the SPME-A and SPME-W readings are higher than the others. The largest difference was found between the SPME-A and SC-CA method giving a mean divergence of 85% with standard deviation (SD) of only 0.8%.

Table 4.3.2: Formaldehyde emission for various plywood species in ascending pattern as evaluated by different methods

Plywood species	**Formaldehyde Emission (ppm), n=30**				
	Spectrophotometric		**Chromatographic**		
	DC-AA	**SC-CA**	**LLE-FID**	**SPME-A**	**SPME-W**
Kapur	0.27	0.07	0.10	0.30	0.35
Red seraya	0.34	0.08	0.24	0.37	0.43
Keruing	0.41	0.09	0.32	0.44	0.48
Sedaman	0.49	0.11	0.42	0.54	0.59
Batai	0.58	0.12	0.59	0.70	0.83
Magas	0.60	0.15	0.69	0.76	0.91
White seraya	0.67	0.18	0.72	0.86	0.99
Yellow seraya	0.80	0.20	0.96	1.11	1.18
Laran	0.94	0.21	1.21	1.20	1.48
Binuang	0.97	0.22	1.84	1.46	1.65

* DC-AA=desiccator-acetyl acetone, SC-CA= small chamber-chromotropic acid, LLE-FID=liquid-liquid extraction analysed by GC/FID, SPME-A= solid phase micro-extraction sampling by absorbing solution, SPME-W=solid phase micro-extraction air sampling directly from wood specimen.

Initially, the obvious difference found between the SPME-A and SC-CA method is most likely attributed to the edge sealing effects. Unlike the SPME-A, the SC-CA collects formaldehyde liberated from the specimen’s surface excluding its edges, which were well sealed with paraffin wax. Previous work showed that the emission from the edges is much higher than from the three-layer parquet floor surface (Risholm-Sundman & Wallin, 1999). The differences could also have been caused by different loading values (14.02 m^2/m^3 for SPME-A and 0.95 m^2/m^3 for SC-CA, see Table 3.3a; 3.3b) and the total exposed area of the sample in which the ratio for the SPME-A is 1.4 more than the SC-CA method.

Higher loading configurations together with the open edge specimens resulted in greater emission, and, consequently, gave a greater concentration value in the SPME methods. These results respond in parallel to the observation of other researchers (Kim *et al*., 2006a; Kim *et al*., 2006b) who found that the formaldehyde value of particleboard and medium density fibreboard decreased when the edges were sealed. In addition, the longer emission interval, approximately 10 times that of the SC-CA method has increased the volatile formaldehyde trapped in the absorbing solution, and, consequently, gave greater concentration value using the SPME-A method.

Since the DC-AA and LLE-FID methods share the same specimens of the SPME-A, their differences were found to be much lower. The same absorbing solution, however, results in a higher formaldehyde emission value using SPME-A than DC-AA. This could be explained by the use of the correct fibre and excellent derivatising agent for formaldehyde extraction, together with the low average coefficient of variation obtained (below 0.08). The polydimethylsiloxane-divinylbenzene (PDMS-DVB) fibre and *O*-(2,3,4,5,6 pentafluorobenzyl) hydroxylamine hydrochloride (PFBHA) have been reported to give maximum response in previous studies (Martos & Pawliszyn, 1998; Saison *et al*., 2009; Deng *et al*., 2004). In addition, the PFBHA of 17 mg/mL concentration was in flavoured in the derivatise reactions (Deng *et al*., 2004; Lee & Tsai, 2008). It was found to completely react with the aldehyde within a few seconds, forming GC compatible oxime (Li *et al*., 2005), see Figure 4.3.1. These advantages prove that SPME is highly sensitive for formaldehyde analysis.

Formaldehyde collected in the absorbing solution in desiccators reacted with the acetyl acetone reagent (DC-AA) and those from the small chamber were tested by using chromotropic acid (SC-CA), see Figure 4.3.2; 4.3.3. The developed yellowish dihydrolutidine (DDL) and purple chromogen, however, were very sensitive and decomposed easily when exposed to light. The use of chromatographic analyses via SPME in the current studies could prevent the risk of colour degradation.

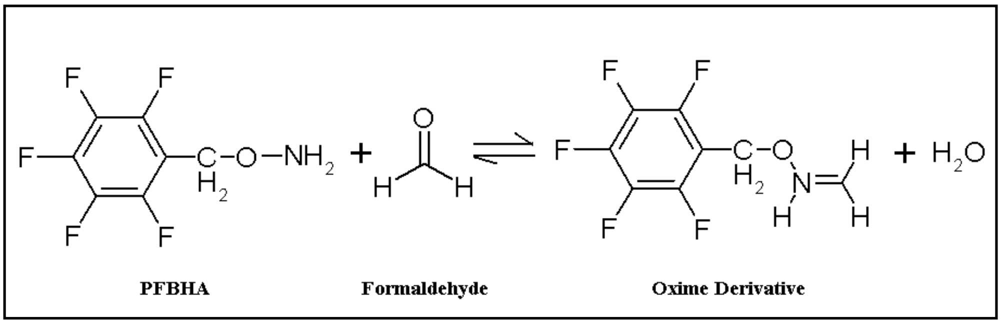


Figure 4.3.1: The reaction of PFBHA with formaldehyde forms GC compatible formaldehyde-oxime.

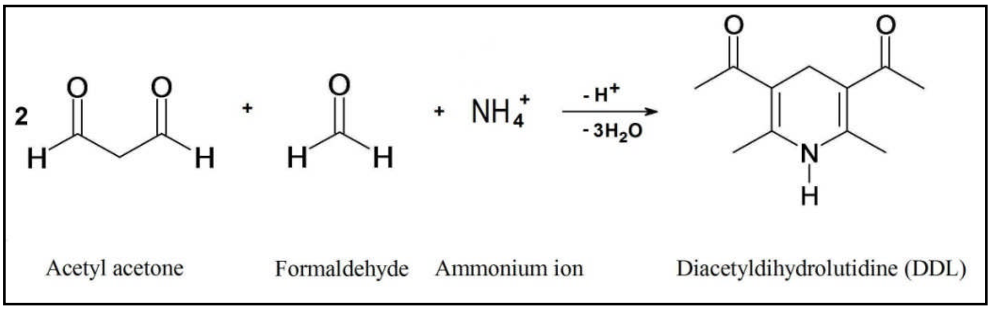


Figure 4.3.2: The reaction of acetyl acetone with formaldehyde forms yellowish dihydrolutidine (DDL).

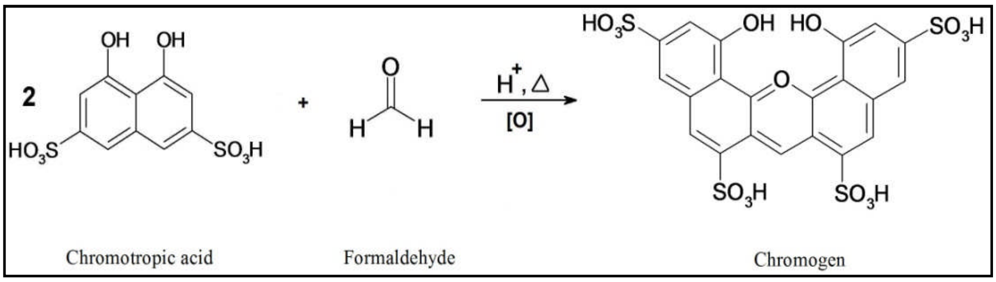


Figure 4.3.3: The reaction of chromotropic acid with formaldehyde forms purple chromogen.

Compared to SPME-A, approximately 81% of the sample using the LLE-FID method showed a lower magnitude of formaldehyde. This could result from incomplete extraction and the loss of analyte. According to EPA Method 556, the formaldehyde in absorbing solution has to be extracted into hexane because the capillary column is intolerant of water phases. However, some residue of the formaldehyde remains and is not extracted due to the greater chemical attraction of the formaldehyde to water than any other organic solvent (US Department of Health and Human Services, 1999). This was evidenced by the detection of formaldehyde-oxime corresponding peak (RT 12 min) in the second extraction. In addition, acid washing several times and sample transferring could stimulate the loss of the compound of interest.

4.3.2 Comparison of SPME and Standard Methods for Ultra-low Formaldehyde Emission

In general, formaldehyde will be reduced after plywood panels undergo the pre or post manufacture treatments. Different methods have been used to qualify and quantify the minimisation of formaldehyde emissions. In this case, the LLE-ECD and SPME-W methods aim to provide a better resolution and improve sensitivity in the ultra-low levels of formaldehyde evaluation. The details of efficacy of treatments will be described in the next section.

The ECD was known to be an efficient detector for solvent extraction under EPA Method 556. The SPME-W method is a modification of the SPME-A in which no absorbing solution is used. Both the SPME methods shared the same operation parameters during GC/MS analysis and gave a similar response with regards to the magnitude of formaldehyde emission (Figure 4.3.4). When the veneer thickness of *red seraya* plywood panels increased from 0.6 mm to 1.8 mm, the formaldehyde emissions measured by the

LLE-ECD method was always lower than both the SPME-A and SPME-W analyses. The results of using FID and ECD as detector in LLE gave a very similar value. Their difference was within 50% if compared with SPME-A and 61% if compared with the SPME-W method. The difference of SPME-A and SPME-W with DC-AA is much smaller, in the range of 33% to 47%.

The formaldehyde emission values obtained for the SPME-W method are always higher than those obtained from the SPME-A although the sampling fibre, derivatising and extracting parameters remain unchanged. The difference between the SPME-W method and the SPME-A method is below 12%, as shown by the majority of the post manufacture treated plywood species, which include the *batai*, *binuang*, *kapur*, *magas*, *red seraya* and *white seraya* plywood. Meanwhile, the other species - *keruing*, *sedaman* and *yellow seraya* plywood - gave differences in the range of 21% to 31% (Figure 4.3.5). Again, a similar result in terms of pattern and response to plywood species are shown by both the LLE-FID and LLE-ECD methods. The DC-AA method, however, demonstrated an equivalent emission value for the majority of the plywood samples. In comparison, the SPME methods gave significant differences for the various plywood species in the study (Figure 4.3.5).

After both the pre and post treatments, very low formaldehyde emission were expected, and, therefore, ECD was used as a detector for the LLE analysis while air sampling directly from plywood specimens was used for the SPME-W method. The direct extraction from plywood specimens could eliminate the risk of lost analyte, and, therefore a higher reading by the SPME-W method was obtained compared to the other methods. The higher diffusion of the formaldehyde in air than in water best explains this finding (Cancho *et al*., 2001).

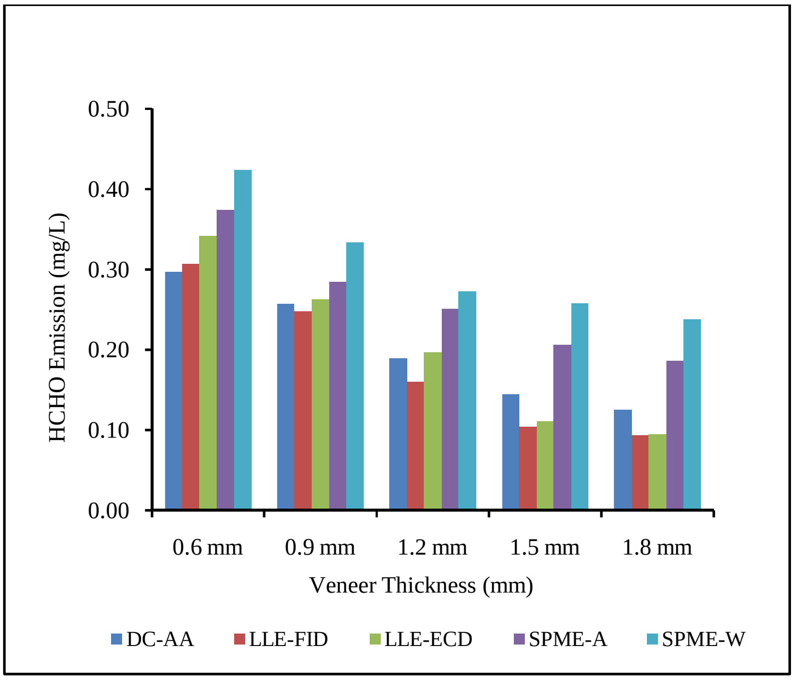


Figure 4.3.4: Formaldehyde emissions in descending trend with respect to different veneer thickness of pre-treatment

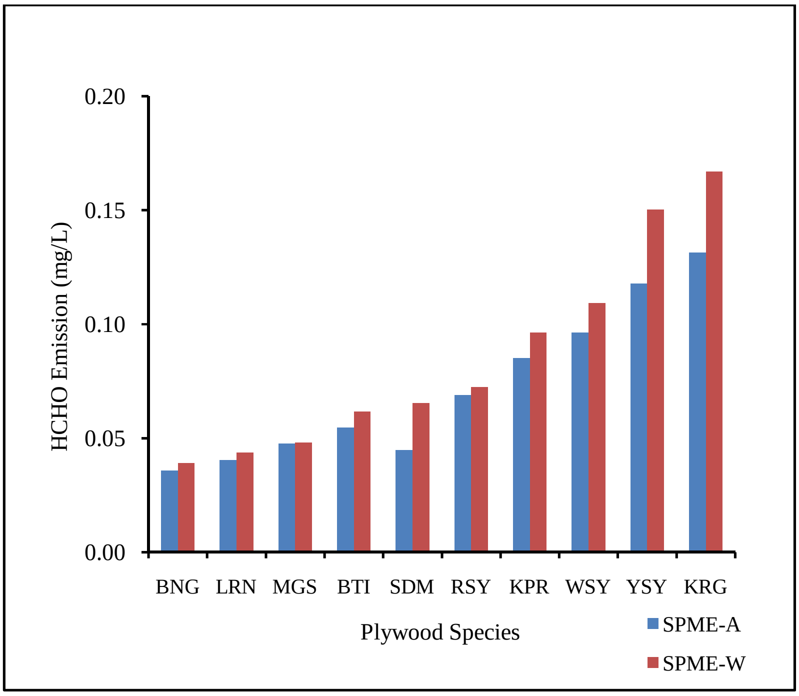


Figure 4.3.5: Formaldehyde emissions after scavenging post treatment between the SPME-A and SPME-W in ascending trend with respect to a variety of plywood species.

* DC-AA=desiccator-acetyl acetone, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD=liquid-liquid extraction analysed by GC/ECD SPME-A= solid phase micro-extraction sampling by absorbing solution, SPME-W=solid phase micro-extraction air sampling directly from wood specimen;

** [BNG= *binuang*, BTI= *batai*, KPR= *kapur*, KRG= *keruing*, LRN= *laran*, MGS= *magas*, RSY= *red seraya*, SDM= *sedaman*, WSY=*white seraya*, YSY= *yellow seraya*]

When compared with the SPME-A method, the specimens with different veneer thickness gave lower formaldehyde emission by LLE-ECD analysis although both used the same absorbing solution. The tendency of volatile formaldehyde to stay in aqueous solution enhances the obvious differences. The similar emission value by the LLE-FID and LLE-ECD methods demonstrates the sensitivity of both detectors for volatile formaldehyde evaluations. Based on the results obtained, no significant difference was found for the formaldehyde emission between plywood with veneer thickness of 1.5 mm and 1.8 mm by the LLE-ECD method although it was originally developed for evaluating lower values of formaldehyde emission (Figure 4.3.4). Therefore, the SPME-A and SPME-W are recommended. The efficiency and suitability of the SPME methods for the determination of low levels of formaldehyde emissions are studied.

The formaldehyde emission by SPME-A and SPMW-W showed a consistent rate of increase in parallel with the decrease in veneer thickness. Both produced good correlations with the DC-AA and LLE methods in the veneer thickness test. Thus indicating that they are potential alternatives for the determination of formaldehyde and able to give better performance or at least eliminate the shortcomings demonstrated by the standard methods. Apart from conventional methods, the differences among ultra-low formaldehyde emissions after chemical treatments are identifiable using the SPME methods. This overcomes the limitation problem discovered with the DC-CA method. Contrary to the California air resource board-Phase I establishment, the use of chromotropic acid in the DC-CA method was not recommended for the Phase II (0.05 ppm) compliance products. It was not designed for evaluating the very low emissions of hardwood plywood as originally developed (ARB, 2010).

In addition, the DC-AA, also known as the standard quality control method, showed almost equivalent readings for the different species of plywood after scavenging treatment (Figure 4.3.6). The sensitivity of DC-AA decreased for the panels emitting ultra-low volatile formaldehyde, particularly below 0.1 mg/L. Hence, SPME was a better alternative for the evaluation of low levels of formaldehyde. Meantime, it also gave appropriate results for both the original and initial emission. Again, the SPME methods were highlighted and its convenience of application for plywood formaldehyde determination was evidenced.

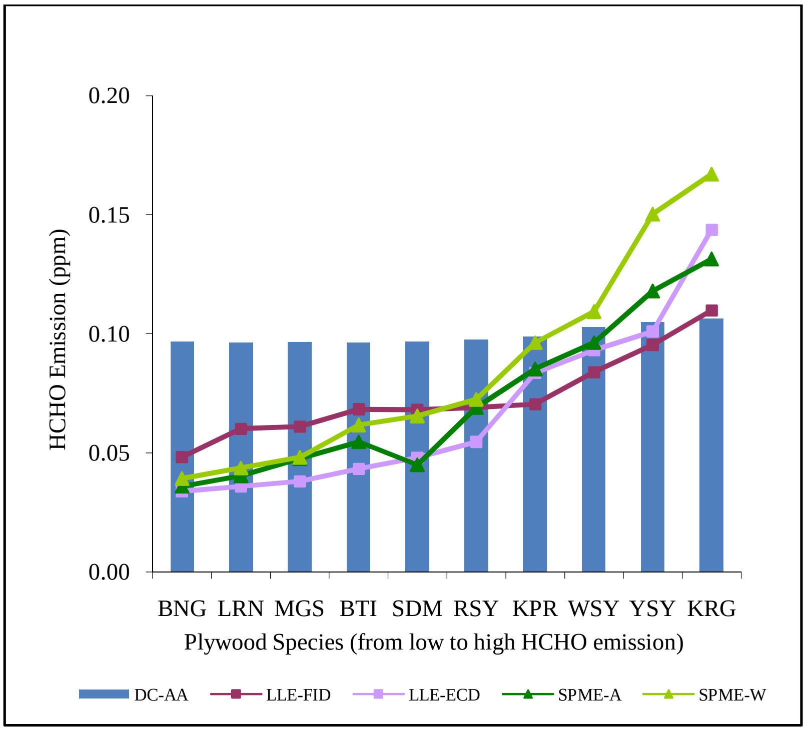


Figure 4.3.6: Similar minimisation trends as performed by different methods.

* DC-AA=desiccator-acetyl acetone,LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD=liquid-liquid extraction analysed by GC/ECD, SPME-A= solid phase micro-extraction sampling by absorbing solution, SPME-W=solid phase micro-extraction air sampling directly from wood specimen

4.3.3 Validation of Methods

The validation of different test methods was carried out by establishing the following criteria, linearity, precision, recovery and detection limits. The linearity of the selected methods is assessed as the correlation coefficients, R^2. This was evaluated graphically through the plot of absorbance value or the peak area as a function of analyte concentration. The satisfying R^2 value of 0.9982 for SPME exhibited better linearity in comparison with the SC-CA ($R^2 = 0.9911$) and LLE-ECD ($R^2 = 0.9927$), while there was also little difference from DC-AA ($R^2 = 0.9994$) and LLE-FID ($R^2 = 0.9973$) (Table 4.3.3). The SPME method enabled a wide range of extraction. It quantified the very low emission of the volatile formaldehyde compounds and thus overcame the less sensitive spectrophotometry analysis for very low concentrations (below 0.1 ppm); the shortcoming of both the desiccator and small chamber methods.

Table 4.3.3: Correlation coefficient (R^2) values of the different methods utilised

Method	**Correlation coefficient, R^2**
DC-AA	0.9994
SC-CA	0.9911
LLE-FID	0.9973
LLE-ECD	0.9927
SPME-A & SPME-W	0.9982

* DC-AA=desiccator-acetyl acetone, SC-CA= small chamber-chromotropic acid, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD= liquid-liquid extraction analysed by GC/ECD, SPME-A= solid phase micro-extraction sampling by absorbing solution, SPME-W= solid phase micro-extraction air sampling directly from wood specimen

Method precision was evaluated in terms of repeatability or relative standard deviation (RSD) by using a blank sample spiked with a standard formaldehyde solution of 1 ppm. Compared to the LLE-ECD (RSD 2.7%), SC-CA (RSD 4.3%) and LLE-FID (RSD 5.0%) methods, both the SPME (RSD 1.8%) and DC-AA (RSD 1.4%) methods showed better repeatability. The SPME has proven to be a reliable alternative with high consistency and validity for the determination of volatile formaldehyde. The results indicated that all RSD values were well under 5% (Figure 4.3.7), which means that acceptable repeatability was guaranteed for the utilised methods.

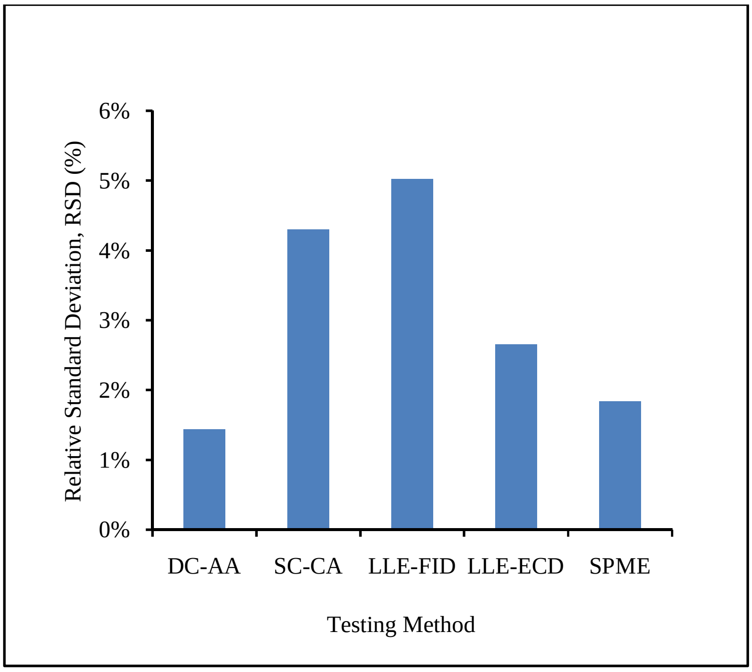


Figure 4.3.7: Relative standard deviation comparison of different testing methods.

Additional works were carried out to further compare the repeatability of SPME-A and SPME-W. The SPME-W data, which was subjected to original and also post scavenging treated plywood species, showed the best repeatability (RSD below 5.6%), thereby demonstrating its high consistency and validity (Table 4.3.4; 4.3.5). This was followed by the LLE-ECD method (RSD below 5.9%) and the DC-AA method (RSD below 6.4%). Although it did not perform as well as SPME-W, the SPME-A gave satisfactory repeatability (RSD below 6.5%). It was slightly better than the SC-CA (RSD below 8.3 %) and LLE-FID (RSD below 9.3%). The SPMEs have proved to be a reliable alternative in the determination of volatile formaldehyde like the other official methods.

Table 4.3.4: Repeatability of different methods with respect to original panel

Plywood species	**Repeatability, RSD (%, n = 30)**				
	DC-AA	**SC-CA**	**LLE-FID**	**SPME-A**	**SPME-W**
Kapur	6.4	5.9	6.6	1.3	1.2
Red seraya	6.0	3.3	6.1	1.2	4.4
Keruing	1.8	4.2	4.9	3.1	1.5
Sedaman	4.5	8.3	1.9	5.9	4.4
Batai	1.7	2.5	7.2	1.5	2.9
Magas	3.3	2.0	5.0	3.0	2.5
White seraya	2.3	5.7	5.3	1.3	5.0
Yellow seraya	1.1	1.6	5.6	2.3	1.2
Laran	1.3	2.4	9.3	3.8	4.0
Binuang	1.7	3.4	4.6	6.5	3.0

Table 4.3.5: Repeatability of different methods with respect to post treated panel

Plywood species	**Repeatability, RSD (%, n = 30)**				
	DC-AA	**LLE-FID**	**LLE-ECD**	**SPME-A**	**SPME-W**
Kapur	2.4	2.0	2.4	2.6	1.8
Red seraya	2.7	6.2	4.9	0.5	2.9
Keruing	5.5	3.2	5.9	1.8	3.2
Sedaman	3.7	6.1	0.9	1.7	4.1
Batai	1.0	7.1	1.4	4.2	4.3
Magas	3.3	3.8	1.8	2.7	0.6
White seraya	4.2	6.1	2.3	1.8	5.0
Yellow seraya	4.4	4.4	4.5	4.2	5.6
Laran	1.9	4.5	2.4	1.9	3.8
Binuang	2.7	4.5	3.7	4.3	0.8

* DC-AA=desiccator-acetyl acetone, SC-CA= small chamber-chromotropic acid, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD= liquid-liquid extraction analysed by GC/ECD, SPME-A= solid phase micro-extraction sampling by absorbing solution, SPME-W= solid phase micro-extraction air sampling directly from wood specimen

A formaldehyde standard solution at 1 ppm was used for current accuracy study and the response of different test methods was recorded. The accuracy was evaluated by comparing the formaldehyde concentration calculated in accordance with the absorbance value (DC-AA and SC-CA methods) and the peak area (SPME and LLE methods) with the concentration obtained through titration. The formaldehyde value subjected to various test methods and gave satisfying recovery (REC) in the range of 92% to 103% (Figure 4.3.8). The majority appeared to be very good except for the SC-CA method (REC 80%). The SPME method gave the best recovery (REC 102%). In between, there were LLE-FID (REC 92%), DC-AA (REC 97%) and LLE-ECD (REC 103%) methods with their respective recovery. The recovery obtained has polished the performance of the SPME method and further improved its feasibility for quantitative analysis of formaldehyde in plywood. Consequently, the recovery performance of the different methods chosen is acceptable.

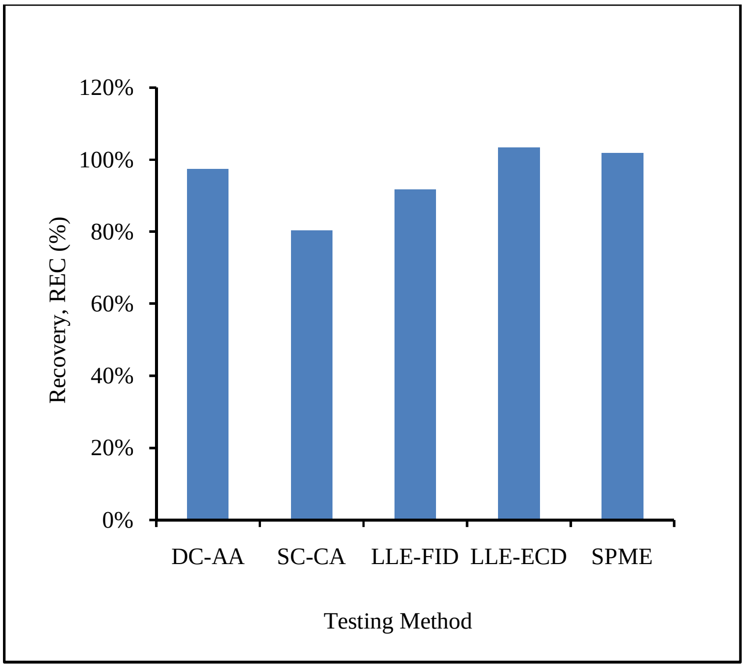


Figure 4.3.8: Recovery comparison of different testing methods.

* DC-AA=desiccator-acetyl acetone, SC-CA= small chamber-chromotropic acid, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD= liquid-liquid extraction analysed by GC/ECD, SPME= solid phase micro-extraction

The limit of detection (LOD) was defined as the analyte concentration giving an absorbance or peak area equal to the blank, plus three standard deviations (SD). The limit of quantification (LOQ) was calculated from the sum of the analyte concentration giving an absorbance or peak area equal to the blank and 10 standard deviations (SD). In addition to the SPME method, the LOD of 0.01 mg/L and LOQ of 0.02 mg/L were obtained (Table 4.3.6), thus enlarging the coverage of the SPME for trace levels of formaldehyde determination, which can be used as targets for treated plywood and also for future research efforts. These achievements confirm that SPME is highly sensitive for analysis of formaldehyde. Again, the SPME method gave satisfying results with high consistency and validity for ultra-low levels of formaldehyde determinations.

Table 4.3.6: The comparison of the LOD and LOQ between different methods

Limits	DC-AA	SC-CA	LLE-FID	LLE-ECD	SPME
LOD (X+3SD)	0.03	0.05	0.02	0.02	0.01
LOQ (X+10SD)	0.05	0.06	0.03	0.03	0.02

* DC-AA=desiccator-acetyl acetone, SC-CA= small chamber-chromotropic acid, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD= liquid-liquid extraction analysed by GC/ECD, SPME= solid phase micro-extraction;
** X= mean of blank, SD= standard deviation

4.3.4 Correlation of SPME-A with standard methods

Correlation was carried out to evaluate the various methods used to measure the formaldehyde emission. It was also used to simultaneously harmonise the variations that occurred for different test methods. A linear regression analysis was done for the SPME-A method with corresponding DC-AA values, which produced a very good correlation coefficient, $R^2 = 0.9767$ (Figure 4.3.10). This was the best coefficient obtained although the SPME technique was clearly different from the DC-AA method in terms of the method of derivatisation, headspace sampling and chromatographic analysis system.

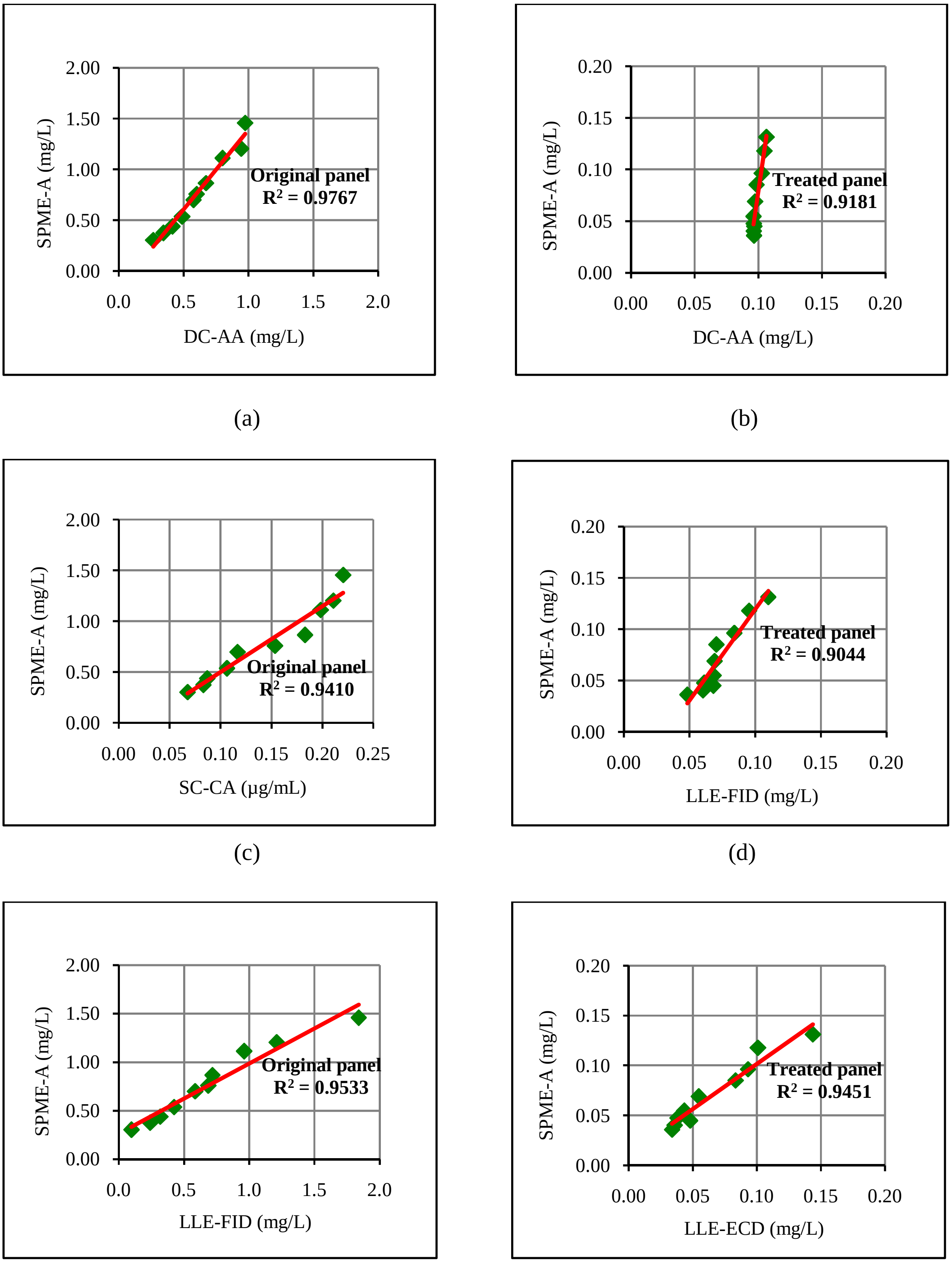
As evaluated by the Student's t-test, all correlations achieved a confidence level of 95%, which indicates that the test results obtained were comparable (Yung & Lo, 2013; 2012) and that SPME-A is an alternative technique with great potential for the quantitative analysis of formaldehyde in plywood. The good correlation is probably due to the fact that both methods share the same source of absorbing solution, the distilled water matrix. This was proven to be an excellent formaldehyde absorber as performed in both the desiccator-spectrophotometric and SPME-chromatographic results; see Table 4.3.2. Furthermore, the diffusion of analytes into a smaller headspace was an advantage, as, according to Yung & Lo (2012); Cancho *et al*. (2001), the SPME-formaldehyde loading rate is enhanced. In addition, the extraction efficiency has been strongly improved through the effect of agitations (Bao *et al*., 1998).

The evaluation of formaldehyde emission by the SPME-A and SC-CA methods on the same plywood panels was compared. The SPME-A value ranged from 0.30 ppm to 1.46 ppm while the SC-CA value ranged from 0.07 ppm to 0.22 ppm. The experimental facilities among these two methods are totally different. The initial difference is most likely attributed to the edge sealing effects in the SC-CA, as discussed earlier. Furthermore, there is no specific treatment for the SPME-A specimens, but air was let to circulate freely across all the SC-CA specimen surfaces for 7 days of seasoning time before the emission test, and, therefore, encouraging lower but steady-state measurement.

Overall, each of the facilities in SPME-A and SC-CA creates a different pathway from the earlier stage of sample preparation to the sampling process, and, finally, the analysis techniques for formaldehyde. The linear regression of formaldehyde generated by SPME-A and SC-CA was presented by an empirical correlation with a correlation coefficient of only 0.941 which was also the lowest among correlation of SPME-A with other methods.

The empirical correlation between SPME-A with LLE-FID, produced a linear regression with a satisfying correlation coefficient of 0.9533 (Figure 4.3.9). This was slightly lower than that obtained by the SPME-A and DC-AA, although the same absorbing solution was shared by these methods. Incomplete solvent extraction could be the root cause as the LLE is not for the evaluation of high formaldehyde concentration as initially designed by the EPA.

The drastic drop in the formaldehyde value measured by the SPME-A after the post treatments best correlated with the LLE-ECD, giving a coefficient of 0.9451. Again, linear regression was obtained with the correlation coefficient of only 0.9044 between SPME-A and LLE-FID. Nevertheless, it is acceptable and only slightly lower than the correlation between SPME-A and DC-AA that giving coefficient of 0.9181 (Figure 4.3.9). Although the LLE is known for the evaluation of trace amounts of formaldehyde better correlation is expected for the post treated panels. As demonstrated, the optimised SPME-A method forms a better correlation with the ordinary methods for the original untreated plywood than the post treated panels. The preference of formaldehyde to stay in water phases has affected the extraction and deteriorates the final concentration obtained.



(a) (b)

(c) (d)

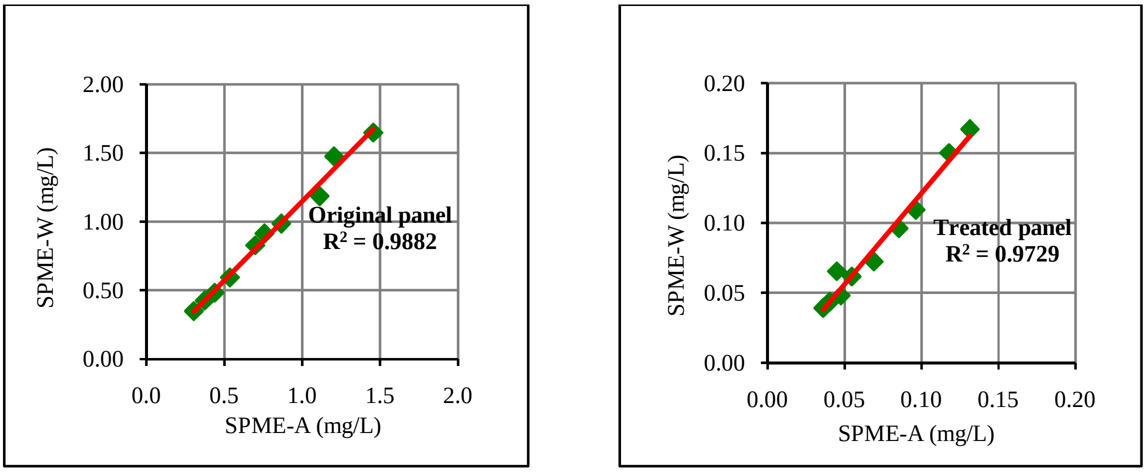
(e) (f)

Figure 4.3.9 (a)-(f): Relationship of formaldehyde emission of solid phase micro-extraction sampling from absorbing solution (SPME-A) with standard methods for original untreated and post treated panels.

4.3.5 Correlation of SPME-W with standard methods

The SPME-W was developed to improve sampling efficiency and save test specimens as well as to overcome the non-zero blank problem. It is only different from the SPME-A in the initial part of formaldehyde sampling. Without using a water based absorber as a medium to collect formaldehyde off gassed from wood composite, the plywood itself is sized into smaller dimension and fed into a vial for headspace extraction. SPME-W gave the higher magnitude most of the time for the results of the air sampling directly from plywood specimens.

Both of the SPME-A and SPME-W methods are well correlated and give the best correlation coefficient for the original untreated plywood ($R^2 = 0.9882$) as well as the post treated panels ($R^2 = 0.9729$), see Figure 4.3.10. They adopted the same testing set up, equivalent detector and similar extraction parameters.



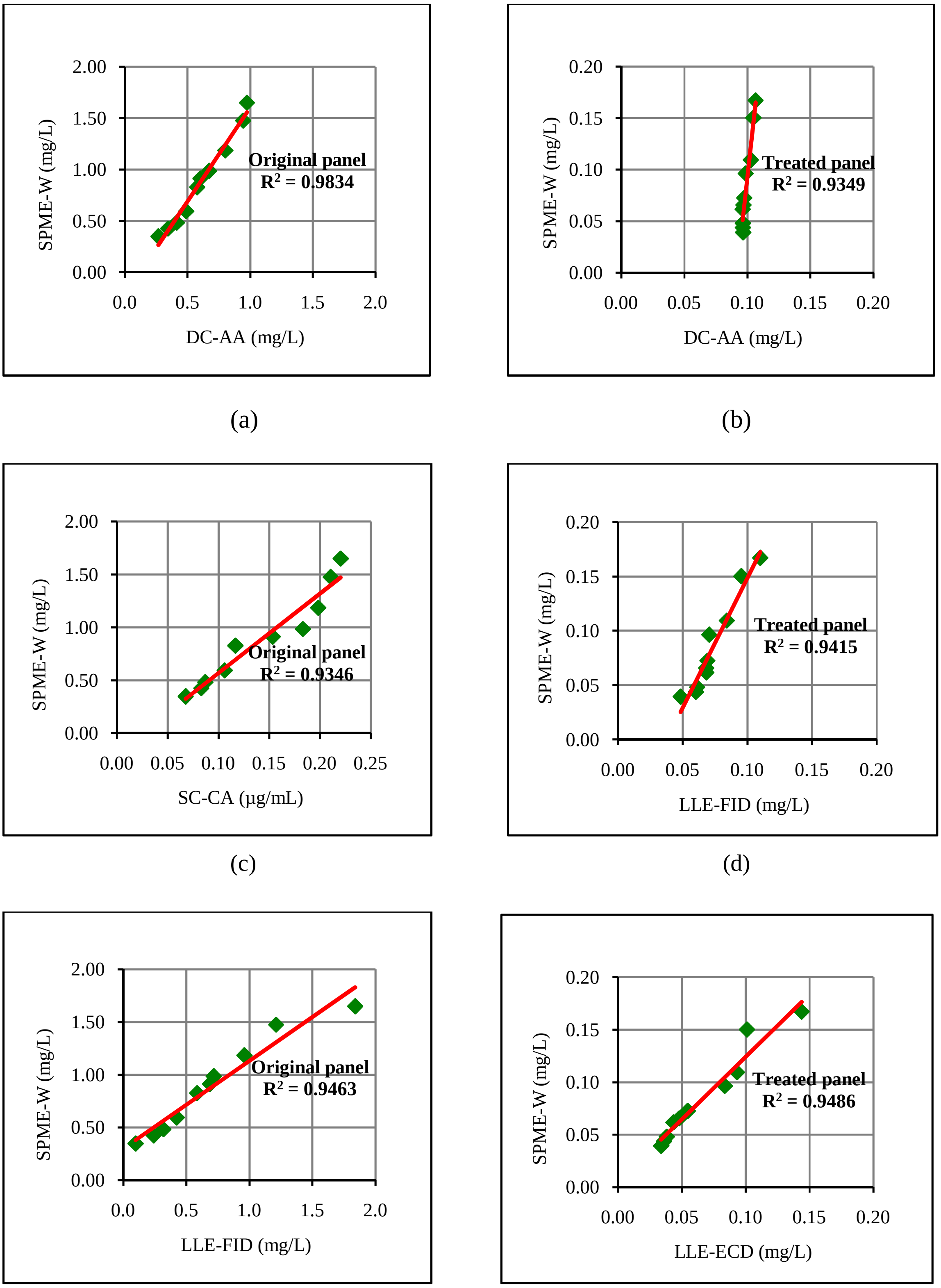
(a) (b)

Figure 4.3.10 (a)-(b): Relationship of formaldehyde emission of solid phase micro-extraction sampling from absorbing solution (SPME-A) and air sampling directly from wood specimen (SPME-W) for original untreated and post treated panels.

The direct extraction by SPME-W helped to shorten the testing period while improving the method’s efficiency, and, in addition, eliminating the contamination problem as formaldehyde occurs in the air either naturally or from other phenomenon, which easily dissolves into the aqueous based absorbent. Basically, the water dissolved formaldehyde is a measurement of the high probability emission in a controlled temperature and humidity. Measuring the formaldehyde directly from the wood composite provided readings more similar to the real emission from wood based products and panelling as well as furniture in normal life. According to quoted studies, the emission of formaldehyde from urea formaldehyde based composite does not terminate within its serviceable life term.

Instead of that, the SPME-W is evidenced to give an appropriate emission value in a shorter sampling and monitoring time when compared to the standard methods. It correlated well with SC-CA (R^2 = 0.9346), LLE-FID (R^2 = 0.9463) and DC-AA (R^2 = 0.9834) methods for the untreated samples (Figure 4.3.11).

After chemical treatment, the SPME-W best correlated with the LLE-ECD (R^2 = 0.9486), followed by correlation with LLE-FID (R^2 = 0.9415) with the lowest being DC-AA (R^2 = 0.9349). Apart from as previously quoted, the correlations performed by LLE-FID and LLE-ECD to SPME-W are much better for the post treated samples. Both detectors evidenced equal sensitivity to trace amounts of formaldehyde analysis. Technically, SPME-W is applicable for formaldehyde determination like the other standard methods.



(a) (b)

(c) (d)

(e) (f)

Figure 4.3.11 (a)-(f): Relationship of formaldehyde emission of solid phase micro-extraction air sampling directly from plywood specimen (SPME-W) with standard methods for original untreated and post treated panels.

Overall, both SPME-A and SPME-W showed good correlation with the standard test methods by giving a correlation coefficient above 0.9. In details, the correlation of SPME-A with the standard methods is much better in original untreated plywood evaluation than the post treated panels. The SPME-W method, however, correlated well with the standard methods for both high and ultra-low formaldehyde emissions. An obvious difference was noticed, especially in their relationship with the DC-AA method (Figure 4.3.9; 4.3.11).

The SPME-W uses neither organic solvent nor aqueous based solvent, which could eliminate the risk of formaldehyde degradation that usually happens during the diffusion of volatile formaldehyde into the aqueous base absorbing solution or during the solvent extraction. Whereas the aqueous base absorbing solution has to be analysed immediately after sampling, the SPME-W allows for a longer storage interval. The plywood specimen could be stored in a sealed vial that is conditioned to 20°C or an even lower temperature before the chromatographic analysis. Furthermore, the risk of contamination could be minimised by using solid specimens in the SPME-W method.

4.4 Formaldehyde Minimisation Solutions

The research concerning the minimisation of formaldehyde emission from plywood panels that can adversely affect indoor air quality is focused upon in the final part. From the literature survey, there were sufficient data to support the findings of a manifold decrease of formaldehyde by lowering the formaldehyde/urea (F/U) molar ratio. The reduction of molar ratio, however, induces thickness swell (F/U < 1.3) and internal bond (F/U < 1.2) problems (Ebewele *et al*., 1994). Presumably, although health risk issue and greater cost burden could be covered, there are still conspicuous problems with the substitution by using alternate fossil fuel based binders. The emission of formaldehyde could not be removed totally although no added formaldehyde resin was used because wood itself contains native formaldehyde.

For better indoor air quality, there are many concerns about the formaldehyde reduction methods as the urea formaldehyde follows a continuous reaction throughout its service life/ lifetime and the urea formaldehyde composite out gassing formaldehyde in the environment for long periods after manufacture and installation (ARB, 2012). By remaining the use of urea formaldehyde, we increase the veneer thickness at the surface parts with the aim of reducing the formaldehyde emission. In addition, post treatment onto plywood with scavenger solutions is undertaken to facilitate the minimisation.

4.4.1 Results of Formaldehyde Minimisation with Veneer Thickness Control

Overall, only 20% of the plywood samples reached the JAS- F4 star level using the DC-AA method, and 30% passed the CARB-PI but all out of CARB-PII limitations. These standards are essential requirements for wood products to be entitled as ‘low formaldehyde emission’ panel. Therefore, the plywood panels have to be treated to upgrade their formaldehyde class by considering the effect of the veneer thickness as the natural barrier to the formaldehyde.

The formaldehyde emission values of plywood with a surface veneer of 0.6 mm were found to be the highest. The emission value declined with the increase of veneer thickness (VT) in the trend of VT 0.6 mm followed by VT 0.9 mm, VT 1.2 mm, VT 1.5 mm with the lowest being VT 1.8 mm. In fact, the thicker the veneer, the lower the emission of formaldehyde. The initial readings using SPME-W vary from a high of 0.42 mg/L to a low of 0.24 mg/L with an increase in veneer thickness from 0.6 mm to 1.8 mm (Table 4.4.1).

As VT 0.6 mm increased 1.5 fold to 0.9 mm, a minimum increase of veneer thickness has recorded the least drop of formaldehyde emission, 21% using the SPME-W method. This was followed by a satisfactory formaldehyde minimisation of 36% and 38% when veneer thickness was increased 2 to 2.5 fold of 0.6 mm, respectively. The 43% drop was the greatest formaldehyde minimisation in respect of the largest increase of veneer thickness, from 0.6 mm to 1.8 mm. Generally, the formaldehyde emission was minimised with the linear increase in veneer thickness of 1.5, 2, and 2.5 to 3 fold (Figure 4.4.1).

A similar formaldehyde reduction was recorded by other methods with the largest reduction (3 fold) being recorded. The formaldehyde minimisation was about 49% using SPME-A and 57% using the DC-AA methods. Up to 71% minimisation of the formaldehyde emission was achieved using LLE-FID and LLE-ECD (Figure 4.4.1). Overall, the formaldehyde minimisation was inversely proportional to the increase in veneer thickness for plywood panels as performed.

Table 4.4.1: Minimisation of formaldehyde emission as affected by veneer thickness

Methods	**Formaldehyde emission vary with veneer thickness (mg/L)**				
	VT 0.6 mm	**VT 0.9 mm**	**VT 1.2 mm**	**VT 1.5 mm**	**VT 1.8 mm**
DC-AA	0.30	0.26	0.19	0.14	0.13
LLE-FID	0.31	0.25	0.16	0.10	0.09
LLE-ECD	0.34	0.26	0.20	0.11	0.10
SPME-A	0.37	0.29	0.25	0.21	0.19
SPME-W	0.42	0.33	0.27	0.26	0.24

* *Red seraya* species with moisture content 6% were selected base to its low native formaldehyde contains, even colour distribution and tolerance to low moisture content against strength defects;

** DC-AA=desiccator-acetyl acetone, SC-CA= small chamber-chromotropic acid, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD= liquid-liquid extraction analysed by GC/ECD, SPME-A= solid phase micro-extraction sampling from absorbing solution, SPME-W= solid phase micro-extraction air sampling directly from wood specimen

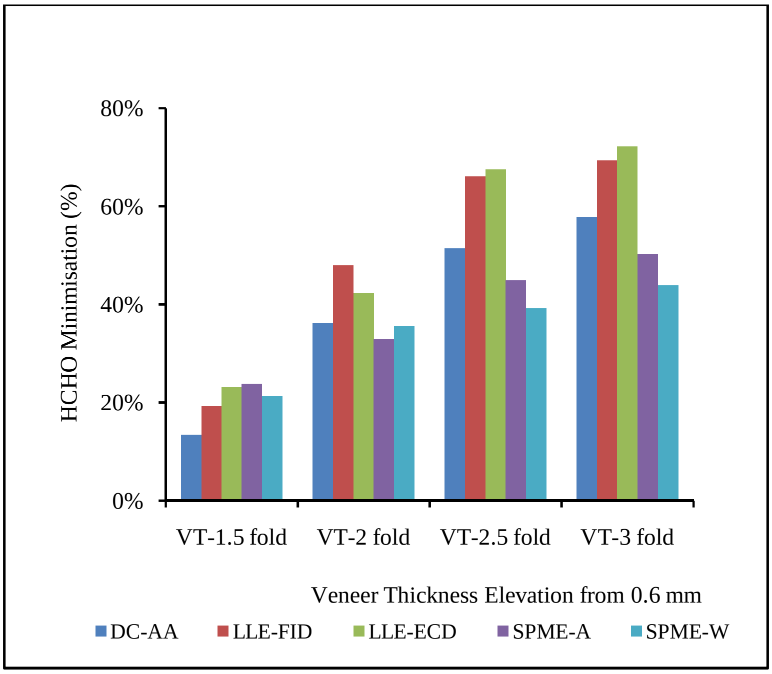


Figure 4.4.1: Formaldehyde minimisation with the increase of veneer thickness in 1.5, 2, 2.5 and 3 fold respectively.

* DC-AA=desiccator-acetyl acetone, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD= liquid-liquid extraction analysed by GC/ECD, SPME-A= solid phase micro-extraction sampling from absorbing solution, SPME-W= solid phase micro-extraction air sampling directly from wood specimen

4.4.2 Results of Formaldehyde Minimisation with Scavenging Treatment

To confirm the formaldehyde emission in response to the scavenging treatment, again ten timber species plywood were tested. The urea based scavenger aqueous solution, FS 25%, with a nearly neutral pH, was coated on both side of the plywood in 5 ± 1 g/ft^2. It was then dried at 60°C prior to sanding and sizing into smaller test samples. The effect of FS 25% is presented in Table 4.4.2. In comparison with the original untreated sample (Table 4.3.2), the emission of treated plywood was very much lower than the initial readings.

Table 4.4.3 has summarises the formaldehyde minimisation with scavenger treatment as measured by different methods. The overall average initial emission level of the ten wood species test is 0.6 mg/L and 80% of the DC-AA value could not meet JAS requirement of 0.3 mg/L. After being treated with FS 25%, the formaldehyde emissions measured from the same panels reduced to a minimum of 63% in minimal whereas the maximum reduction reached as high as 90%. In addition, all of them only emitted 0.11 mg/L and below of formaldehyde, which is considered as a trace amount approaching the native values by the DC-AA method. The treated specimens were also evaluated using the LLE-FID, LLE-ECD, SPME-A and SPME-W methods for verification. Again, a drastic minimisation was obtained for the SPME-A and SPME-W test, recording an average reduction of 87% (Figure 4.4.2). The same was also found for the LLE-FID test with a reduction of about 80%.

Table 4.4.2: Minimisation of formaldehyde emission after scavenging treatment

Plywood Species	**Formaldehyde Emission After Scavenging (mg/L)**				
	DC-AA	**LLE-FID**	**LLE-ECD**	**SPME-A**	**SPME-W**
Binuang	0.10	0.05	0.03	0.04	0.04
Batai	0.10	0.07	0.04	0.05	0.06
Kapur	0.10	0.07	0.08	0.09	0.10
Keruing	0.11	0.11	0.14	0.13	0.17
Laran	0.10	0.06	0.04	0.04	0.04
Magas	0.10	0.06	0.04	0.05	0.05
Red seraya	0.10	0.07	0.05	0.07	0.07
Sedaman	0.10	0.07	0.05	0.05	0.07
White seraya	0.10	0.08	0.09	0.10	0.11
Yellow seraya	0.11	0.10	0.10	0.12	0.15

* DC-AA=desiccator-acetyl acetone, SC-CA= small chamber-chromotropic acid, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD= liquid-liquid extraction analysed by GC/ECD, SPME-A= solid phase micro-extraction sampling by absorbing solution, SPME-W= solid phase micro-extraction air sampling directly from wood specimen

We further recognised that although the samples underwent the same post treatments, their deformation behaviours are different. The higher the initial emission level, the greater the rate of decay, such as happened to the *binuang* and *laran* species from the yellowish group and *batai* and *sedaman* from the reddish group. This is evidenced through the 90% and above reduction using the SPME-A and SPME-W methods, as illustrated by the data used to generate the formaldehyde emission decay curves (Figure 4.4.2).

Table 4.4.3: Summary of formaldehyde minimisation after scavenging treatment

Methodology	**Formaldehyde Deformation (%)**	
	Mean	**Range**
DC-AA	80%	63% - 90%
LLE-FID	80%	30% - 97%
SPME-A	87%	70% - 97%
SPME-W	87%	65% - 98%

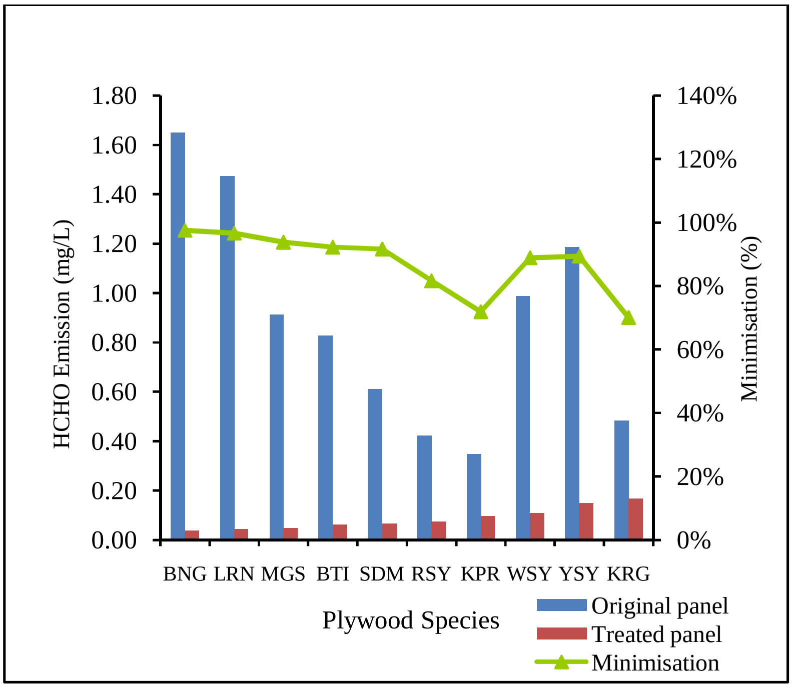


Figure 4.4.2: Effectiveness of FS 25% to minimise formaldehyde emission.

* DC-AA=desiccator-acetyl acetone, LLE-FID=liquid-liquid extraction analysed by GC/FID, LLE-ECD= liquid-liquid extraction analysed by GC/ECD, SPME-A=solid phase micro-extraction sampling by absorbing solution, SPME-W= solid phase micro-extraction air sampling directly from wood specimen;

** [BNG= *binuang*, BTI= *batai*, KPR= *kapur*, KRG= *keruing*, LRN= *laran*, MGS= *magas*, RSY= *red seraya*, SDM= *sedaman*, WSY= *white seraya*, YSY= *yellow seraya*]

4.4.3 Discussion of Veneer Thickness Control

With respect to the effect brought by veneer thickness, the wood species and its moisture content are fixed as constant variables to eliminate their influence on the emission of formaldehyde. *Red seraya* (*Shorea spp.*) was used, the sapwood peels of which peels out in different thickness ranging from 0.6 mm to 1.8 mm, which were conditioned to moisture content of 6% and then glued up in three layers to form plywood test panels. The *Shorea* was selected as it has been classified as an ecologically and commercially important canopy tree species in the forests of Southeast Asia (Tsumura *et al.*, 2010). A moisture content of 6% was selected as it was found to have less effect in facilitating the emission of formaldehyde through the results obtained in part 4.1 of the current study.

The influence of veneer thickness has been highlighted by altering the formaldehyde emissions as a short term solution. Assuming the formaldehyde molecules released from the glue line between the centre core and the surface veneer are mainly diffusion driven, then, their movement could be retarded by a thicker surface veneer as the distance of emission path has been elongated indirectly or possibly blocked, and, therefore, a substantial reduction in the formaldehyde emission can be achieved. This explains the observation as to why the formaldehyde emission of veneer thickness of 0.9 mm was always lower than for the veneer thickness of 0.6 mm.

The retardation of formaldehyde off gassing rate and volume also became more significant when the veneer thickness increased to 1.2 mm then 1.5 mm and 1.8 mm. The greatest effective minimisation of formaldehyde emission was reported for the largest increase in veneer thickness, as plotted by the test site in Figure 4.4.1. For the same graph, the minimisation reached its peak at the veneer thickness 1.5 mm (VT 2.5 fold), which indicates that a veneer thickness of 1.5 mm is sufficient to block most of the formaldehyde emitted from the test samples manufactured with inner cores of equivalent thickness. Indirectly, this could provide a general explanation for the smallest difference found between the veneer thicknesses of 1.5 mm and 1.8 mm (VT 2.5 fold and VT 3 fold). The use of an equivalent thickness for each layer in the plywood helps minimise the formaldehyde emission. The surface veneer acts as a natural barrier of plywood with respect to the VOCs emission, especially the formaldehyde, as evidenced.

4.4.4 Discussion of Scavenging Treatment

The low passing rate (20%) is in accordance with the JAS standard indicated that the majority of the test sample was emitting a great amount of formaldehyde and the plywood panel were disqualified for most of the general applications that complied to JAS and also CARB regulations, considered human and environment hazardous. A lower molar ratio will give wood panels of less formaldehyde emission, albeit of poor structural properties and weaker bond strength (Pizzi, 1989). To overcome this problem, the initial F/U molar ratio was reduced to as low as 1.2, and urea formaldehyde resin scavenging additives, such as ammonium chloride and melamine (Figure 4.4.3), were dosed into the glue mixture.

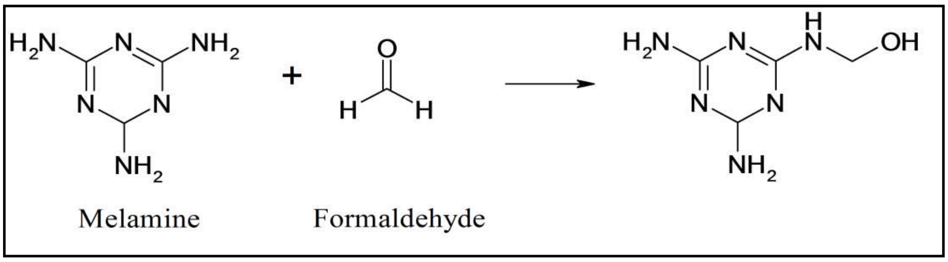


Figure 4.4.3: Reaction of melamine with formaldehyde.

Although beneficial methods have been taken, the F4 star (0.3 mg/L) formaldehyde emission was not promising without the help of the scavenger coating. Including the urea and melamine in the glue mixture as pre-treatment method reduced the availability of the formaldehyde reactive ingredient during glue setting, while post treatment by FS 25% could effectively minimise the formaldehyde off gassing from urea formaldehydes bonded plywood immediately after being hot pressed, as well as retaining its longer term availability for scavenging formaldehyde. The reactions of urea and sodium hydrogen sulphite in FS 25% with formaldehyde are as shown in Figure 4.4.4; 4.4.5.

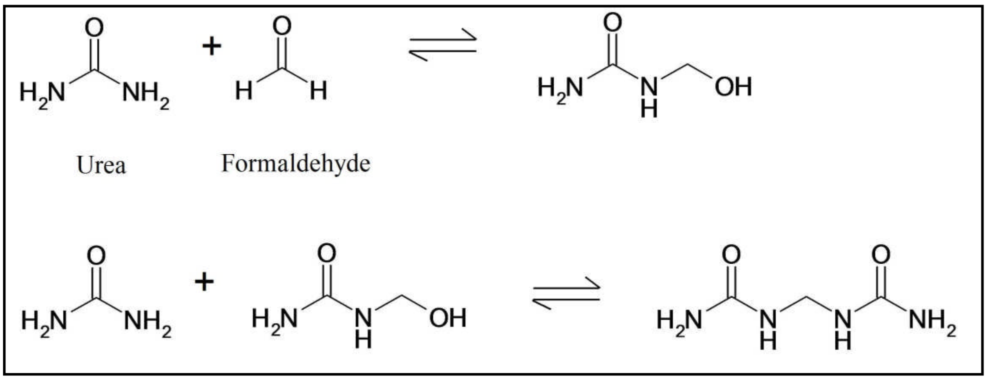


Figure 4.4.4: Reaction of urea with formaldehyde.

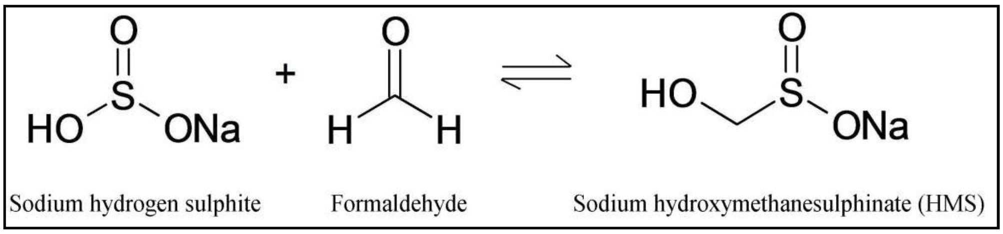


Figure 4.4.5: Reaction of sodium hydrogen sulphite with formaldehyde.

Actually, surface treatment with a lacquer is not a new alternative and, in most cases, would lower the emission (Risholm-Sundman *et al.*, 1998). The formaldehyde scavenger solution of FS 25% used in the current study was found to be effective in minimising the formaldehyde emission, as a long term solution. A large fraction of the reduction, which gave a mean value of 82% to 87%, has been demonstrated (Table 4.4.3). This could be result from the decrease in the initial amount of free formaldehyde present in the freshly pressed panels through the scavenging treatment. In addition, it also helps to capture the non-reacted formaldehyde that is present in the board formed by hydrolysis of the amino-plastic bond in combination with the temperature and relative humidity factors (Pizzi *et al*., 1994). The scavenger solution coating was applied with the board being heating at 60°C in order to minimise the formaldehyde emission arising from the hydrolysis processes.

It turns out to be a necessity to minimise the formaldehyde emission of the urea formaldehyde bonded composite through FS 25% post treatment due to the formaldehyde scavenging ability of the free amines (Birkeland *et al*., 2010; Ayrilmis & Winandy, 2009; Uchiyama *et al*., 2004). One characteristic of wood panel formaldehyde emission of particular interest is the tendency to decrease (decay) with the passing of time (Zinn *et al*., 1990). Also, it should be considered that the FS 25% consists of a higher concentration if compared to previous research publications. Thus, the reduction is higher than numerous literature studies.

The FS 25% treatment helped minimise the formaldehyde but a divergence was found among the different plywood species. In reducing the formaldehyde using boron compounds, Colak & Colakoglu (2004) discovered that each wood species has a different emission potential from each other due to the different chemical content. In the current task, the drastic reduction for FS 25% treated *binuang* and *laran* boards could be explained by their unique emission behaviour, taking into account the porosity and capillary structure of such particular wood species. The porosity of *binuang* is the highest followed by *laran*, and, hence, causes their emission to top the others in earlier evaluation. The formaldehyde molecule found its way out of wood network more easily because of the high porosity. Therefore, formaldehyde liberation is promoted by greater porosity during the scavenging process.

As a result, treated *binuang* soon emits only trace amounts of formaldehyde, as collected by the DC-AA, LLE-FID, LLE-ECD, SPME-A and SPME-W methods. The decay of the treated panel emission level is strongly related to the porosity of a particular plywood species. Thus, the large portion of decrease also found for *sedaman* and *batai* among the other reddish plywood resulted from the greater permeability of the original wood species. The higher the porosity percentage the greater is the decay. This situation has more influence on the formaldehyde emission of panels that underwent post treatment by FS 25% than those without treatment. The average deformation of (83 ± 13) % is considered suitable for describing the effectiveness of FS 25% to minimise the formaldehyde emission of most plywood species.