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ESTIMATION OF FORMALDEHYDE EMISSION FROM COMPOSITE WOOD PRODUCTS

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By

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Author's Declaration

I hereby declare that I am the sole author of this thesis with a help of literature listed in references. This is a true copy of the thesis titled "*Estimation of formaldehyde emission from composite wood products*", including any required final revisions, as accepted by the examiners. I understand that my thesis may be made electronically available to the public.

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Dedication

I dedicate this dissertation to the memory of my Father, who taught me that dreams could become truth once I really believe in that.
I dedicate this work to my Mother, who taught me how to be patient to persevere and always encouraging me to be a better person.
I dedicate this work to my Wife: for her continuous support and for those times when she knew that I will be away from her.
Without their wisdom, guidance, supports, and knowledge I would never been who I am. Thanks for all the love you give me each day of my life. That has given me the strength to continue my search for success and happiness.
I will love you forever.

Biography

Mohamed Zidan Mohamed Salem

Mohamed Z.M. Salem *was born in Alexandria, Egypt on June 30, 1977. He was raised in Alexandria city, until 1995. Four years later, he graduated with a Bachelor of Science degree from the Forestry and Wood Technology Department, Faculty of Agriculture (El–Shatby), Alexandria University in 1999 and working as assistant. Upon graduating, Mohamed enrolled in Alexandria University where he pursued his Master of Science in Wood Technology and obtained it on 2004.*

In the summer of 2007, Mohamed was awarded a full scholarship from the Czech Republic, Ministry of Education, Youth and Sport to obtain his PhD degree; he enthusiastically accepted such an opportunity to do so. He attended the Faculty of Forestry and Wood Sciences at the Czech University of Life Sciences Prague on October of 2008 with the hope of obtaining a PhD degree.

ABSTRACT

Formaldehyde is mainly used to produce synthetic resins and adhesives by reaction with phenols, urea, and melamine. Urea–formaldehyde (UF) resin is a major commercial adhesive, especially within the forest products industry. Composite wood products (CWPs) bonded with formaldehyde–based resins can be toxic due to the formaldehyde emission (FE). Formaldehyde has been a major concern in the forest products industry in recent years, and its emission is an important factor in evaluating the environmental and health effects of CWPs. In terms of being a health hazard, formaldehyde was found to be a primary irritant of the respiratory airways and a skin sensitizer in some individuals. Some suggestion has been made that formaldehyde can also be carcinogenic. This suggestion should be treated with caution as it derives from preliminary experiments on rats and mice exposed to very high formaldehyde levels.

In this study, different types of particleboard (PB) with uncoated (P2), laminated (PL) and veneered (PV), uncoated medium density fiberboard (MDF) and laminated MDF (MDFL), high density fiberboard (MDF) and plywood (PLW) used in interiors (PLY) and for construction (PLYs) are widely used in products such as subflooring, door cores, cabinets, paneling, and furniture. These types were obtained from commercial wood manufacturing plants in the Czech Republic. In addition, different types of flooring panels were also measured for their FE. All specimens were conditioned to equilibrium at a controlled–room temperature and relative humidity (RH). The majority of these wood products are bonded with formaldehyde–based resin adhesive. Emissions of formaldehyde potentially can arise from any of the materials that compose a panel.

A number of CWPs (primarily PB, MDF, HDF and PLW) of different thicknesses (2.5, 3.2, 8, 12, 15, 16, 18, 19, 21, 22, 24 and 25 mm) were measured for their FE. All the samples were delivered to the laboratories of Wood processing, Faculty of Forestry and Wood Sciences Prague and Timber Research and Development Institute (VVÚD) in Prague, Czech Republic. The FE of CWPs were evaluated by one or more than one of the most frequently used European test methods: the European chamber (EN 717–1), the gas analysis method (EN 717–2) and the perforator method (EN 120) and with the American small–scale chamber (ASTM D 6007–02).

This work has shown a comparison between the different methods by determining the correlation coefficient (r) among different parameters. The coefficient of determination (R^2) by extracting equations was applied for regression analysis. The main findings of the study was clearly showed that the methods produced proportional results, and the variation between the methods could be explained by differences in test conditions such as loading factor, temperature, RH, duration of test and air exchange rate. Another important factor is the variation was in treatment of the sample; for example, sealing of the edges, sealing of the back, and conditioning before measurement. Most of the boards measured in this study were in the class emission E1and The FE values of PLW samples were lower than those of the PB and MDF samples.

The significant effects of manufacturing variables (board type and thickness) as well as the effect of different types of formaldehyde–based resins [UF, melamine urea formaldehyde (MUF) and phenol formaldehyde (PF)] on the FE were investigated. Laminating and decreasing the board thickness had a highly significant effect ($P < 0.01$) on decreasing the formaldehyde parameters. When the E1 type adhesives were employed, a wide variation in the quantity of formaldehyde was observed among the three product types.

The high amount of FE measured by gas analysis method was observed from PV/UF followed by P2/UF. In the middles values it was found that the uncoated MDF/MUF emitted formaldehyde with values equal PL/UF, in contrast the laminated MDF/MUF had an amount less than the values from particleboards, whereas the PLW values from PLYs/PF had the lowest amount of FE. In addition, this results in comparable with the chamber values for the same board type.

Different standard methods are used to determine the formaldehyde release from PB; some of them are defined as European, Japanese and American standards. The formaldehyde release from PB (uncoated and laminated of 16–19 mm thickness) were measured with EN 717–2 and EN 120 methods. The EN 717–1, Japanese desiccator method (JIS A 1460) and American large chamber (ASTM E1333–96) values were measured by the conversion factor. The two types of PB studies showed differences in their formaldehyde parameters. It was concluded that the amount of formaldehyde released from the most of the manufactured boards resulted in the emission class El. The PBs E1–emission class had approximately the same value according to the test methods and similar behavior was observed in the relationship between the EN 120 values and EN 717–1, JIS A 1460, the proposed California Air Resource Board (CARB) Phase 1 and 2.

The inter–laboratory comparison of FE from PB used for non–structural and interior application as furniture materials was performed by the American small test chamber (ASTM D 6007–02) in two laboratories. The outliers resulted from two laboratories showed that there were a different between the FE from two laboratories (laboratory 1 had a high number of numerically distant from the rest of the data than laboratory 2), also the coefficient of variation ranged between 24.23–26.18% and 5.36–8.79%, for laboratories 1 and 2 respectively. The comparison of these results showed that laboratory 2 gives better accuracy than laboratory 1.

The conclusions to be drawn from this thesis may contribute to a correct application of the methods used to determine the FE from CWPs and further develop the formaldehyde regulations.

Keywords: *Formaldehyde emission, Formaldehyde content, EN 717–1, EN 717–2, EN 120, ASTM D 6007–02, Composite wood products*

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List of Abbreviations

AAA	Acetoacetanilide
Acac	Acetylacetone
ACH	Air Changes per Hour
ANOVA	Analysis of Variance
ANSI	American National Standards Institute
AS/NZS	Australian and New Zealand Standard
ASTM	American Society for Testing and Materials
ATCM	Airborne Toxic Control Measure
AWPA	Australian Wood Panels Association Incorporated
BAA	Berkeley Analytical Associates
BACT	Best Available Control Technology
CARB	California Air Resources Board
CHD	1,3–cyclohexanedione
CNSL	Cashew nut shell liquid
CPL	Continuous Press Laminates
CRD	Completely Randomized Design
CSP	Closing Settlement Price
CTMP	Chemo–Thermomechanical Technique
CWPs	Composite Wood Products
DDL	3,5–diacetyl–1,4–dihydrolutidine
DMC	Dynamic MicroChamber
DME	Dimethoxyethanal
DNPH	2,4–dinitrophenylhydrazine
E1	European emission class 1
E2	European emission class 2
EF	Emission Factor
EN	European standards
EPA	European Particleboard Association
EPA	Environmental Protection Agency
EPI	Emulsion Polymer Isocyanate
F–star	Limitation of formaldehyde emission categories according to JIS
FC	Formaldehyde Content
FE	Formaldehyde Emission
FLEC	Field Laboratory Emission Cell
FSEM	Formaldehyde Surface Emission Monitor
GC	Gas Chromatography
GC/MS	Gas chromatographic/mass spectrometric
GLM	General Linear Model
HDF	High Density Fiberboard
HPLC	High Pressure Liquid Chromatography
HUD	Department of Housing and Urban Development
HWPW	Hardwood Plywood
HWPW–CC	Hardwood Plywood Composite Core
HWPW–VC	Hardwood Plywood Veneer Core
IARC	International Agency for Research on Cancer
ISO	International Organization for Standardization
JAS	Japanese Agricultural Standard
JIS	Japanese Industry Standards
LOD	Limit of Detection
LPM	Low–Pressure Melamine
LS Means	Least Square Means
MC %	Moisture Content
MDF	Medium Density Fiberboard
MDI	Methylene diphenyl diisocyanate
MF	Melamine–Formaldehyde
MUF	Melamine–Urea–Formaldehyde
NAF	No–Added Formaldehyde
OSB	Oriented Strand Board
Phase 1	The CARB new standards, Phase 1
Phase 2	The CARB new standards, Phase 2
PB	Particleboard
PET	Polyethylene Terephthalate
PFS	Passive Flux Sampler
PF	Phenol–Formaldehyde
pMDI	Polymeric Methylene Diphenyl Diisocyanate
PLW	Plywood
PVAc	PolyVinyl Acetate
SBS	Sick Building Syndrome
SER	Specific Emission Rate
SG	Specific Gravity
SHS	Sick House Syndrome
SWPW	Softwood Plywood
TAC	Toxic Air Contaminant
TMP	Thermomechanical Process
TN	Tris (hydroxyl) Nitromethan
TOL	Target–Operating Limits
TVOC	Total Volatile Organic Compounds
TPC	Third Party Certifier
UF	Urea–Formaldehyde
UMF	Urea Melamine–Formaldehyde
ULEF	Ultra–Low–Emitting Formaldehyde
VOCs	Volatile Organic Compounds
WKI	Wilhelm–Klauditz–Institut, Holzforschung= Fraunhofer–Institut for wood research
WHO	World Health Organization

1. INTRODUCTION

Since the energy crisis in the early 1970s, there has been a decided trend towards tightly constructed buildings that conserve energy and reduce costs. The downside of these well–intended efforts has been a lowering of air exchange rates, such that many chemical contaminants are trapped indoors where people spend most of their lives. These contaminants may include volatile organic compounds (VOCs), such as formaldehyde, that have been suggested by some to be among the factors responsible for this air quality deterioration.

Composite wood products (CWPs) are often targeted for strict emission regulations or prohibited altogether despite the fact that industry has reduced formaldehyde emission (FE) of raw panels by more than 80% over the past twenty years to minimize indoor air contaminants. Moreover, most consumer products made with composite panels are not used in a raw form, but instead have some type of surface finish over the substrate that generally acts as a barrier to off–gassing, thereby reducing emissions.

The World Health Organization (WHO) has reclassified formaldehyde from category 3 (effect not yet to be classified) of carcenogenous materials to category 1 (proven as human carcenogenous). Therefore, a new regulation is to be expected regarding the reduction of limit and guideline values for FE from wood–based materials used in home construction, including products made with urea–formaldehyde (UF) resins [particleboard (PB), hardwood plywood (HWPW), medium density fiberboard (MDF) and paneling)] and those made with phenol–formaldehyde (PF) resin [(softwood plywood (SWPW), oriented strand board (OSB)] (Kelly *et al.,* 1999).

The toxicity of wood–based panels bonded with formaldehyde–based resins due to the FE and the associated possible health hazard, could act as an obstacle to their acceptance by the public, given the prevailing climate of environmental awareness and concern. As a result, the European and Northern American governments have already or are about to impose regulations limiting the FE from building materials and from the materials used for the manufacture of furniture and fitments (Kavvouras *et al.,* 1998).

Many consumer products containing formaldehyde–based resins release formaldehyde vapor, leading to consumer dissatisfaction and health–related complaints. These emissions have resulted in various symptoms, the most common of which is irritation of the eyes and the upper respiratory tract. Formaldehyde has also been found to produce nasal carcinomas in mice and rats after exposure to 14.1 and 5.6 ppm of formaldehyde, respectively, over a long period. These findings have led to an intensified interest in the indoor environment. Consumer products, specifically construction materials, are a major source of formaldehyde in the indoor environment (Pickrell *et al.,* 1986).

UF is one of the main glues used in wood industries so far. It contains free formaldehyde and its amount is directly proportional to its bonding strength. UF resin with a small amount of free formaldehyde can be produced by a low F/U molar ratio, but if the molar ratio were excessively lowered, bonding strength and the other properties of resin would deteriorate. The products bonded with UF resin still cause free FEs, which pollute the environment and harm people's health (Levendis, 1992). Consequently, lowering the amount of free formaldehyde in UF resins and enhancing bonding strength have become the focus of study for many scientists.

The major disadvantage associated with UF adhesives as compared with other thermosetting wood adhesives, such as PF and polymeric diisocyanates, is the FE and the lack of resistance to moist conditions, especially in combination with heat. These conditions lead to a reversal of the bond–forming reactions and the release of formaldehyde. For this reason, UF resins are usually used for the manufacture of products intended for interior use only.

These days, melamine–formaldehyde (MF) and melamine–urea–formaldehyde (MUF) resins are mainly used as thermosetting wood adhesives for wood panels. Both resins give excellent adhesive performance, good moisture resistance and tend to produce lower FE than UF resins.

However, adhesives are the integral component of these products, which conventionally contain UF, UMF, MF or PF. FE from these materials, can last for years with little decay. Now, manufacturers are able to modify the production processes and use alternative adhesives to reduce FE (US EPA, 1996). Currently, regulation standards in many countries exist regarding the maximum amount of free formaldehyde allowed within a unit weight of the CWPs. Here, the amount of formaldehyde is tested based upon the condition used in European test methods. Many European standards are based upon the formaldehyde content (FC) in milligrams. Products classified as E1 grade are generally considered as acceptable for indoor applications.

Occupational exposure to formaldehyde by inhalation is mainly from three types of sources: thermal or chemical decomposition of formaldehyde–based resins, FE from aqueous solutions (for example, embalming fluids), and the production of formaldehyde resulting from the combustion of a variety of organic compounds (for example, exhaust gases).

In 1992, the California Air Resources Board (CARB) identified formaldehyde as a toxic air contaminant (TAC) based primarily on the determination that it was a human carcinogen with no known safe level of exposure (CARB, 1992). Exposure to formaldehyde has both non–cancer and cancer health effects. The non–cancer health effects of formaldehyde are eye, nose, and/or throat irritation. The International Agency for Research on Cancer (IARC, 2004) conducted an evaluation of formaldehyde and concluded that there is sufficient evidence that formaldehyde causes nasopharyngeal cancer in humans (*i.e.*, in the region of the throat behind the nose). At concentrations above 0.1 ppm in air, formaldehyde can irritate the eyes and mucous membranes, resulting in watery eyes. Formaldehyde inhaled at this concentration may cause headaches, a burning sensation in the throat, and difficulty breathing, as well as triggering or aggravating asthma symptoms.

The CARB adopted a new regulation in April 2007 to reduce the FEs from CWPs, including PB, MDF and HWPW [Airborne Toxic Control Measure (ATCM), CARB, 2007]. The modified version of this regulation was finally approved in April 2008. This regulation proposed the reduction of FE standards in two phases; Phase 1 limits (effective from January 2009) are roughly equivalent to the European E1 emission class that is the Japanese *F*** class. Phase 2 limits (effective from January 2010 and January 2011) are comparable to the Japanese *F**** limits, the so–called E0 levels in Europe. This new regulation established the most stringent FE limits on wood products in the United States and required that wood panels and products manufactured from wood panels be certified by a "third party" laboratory (Third Party Certifier, TPC) approved by the CARB. There are special provisions for manufacturers using NAF (No–Added Formaldehyde) & ULEF (Ultra–Low–Emitting Formaldehyde) resins (*i.e.*, reduced testing frequency, exemption from third party certification).

To measure the levels of FE, many different methods have been used. In Europe, the perforator method has long been used. For this method, special apparatus is needed. The European particleboard association (EPA) originally developed this test procedure in the late 1970s and called it the perforator method, which is a simple method that was established in 1984 as European standard EN 120. In North America, Australia and Asia, however, the desiccator method was adopted. The desiccator test was developed in the middle of the 1970s in Japan and standardized in the United States in 1983.

The estimation of the formaldehyde level is performed spectrophotometrically in all of the existing methods, including in the Fraunhofer–Institute for Wood Research WKI (Wilhelm–Klauditz–Institut, Holzforschung), perforator and desiccator methods. The FE is an important factor in the evaluation of the environmental and health effects of CWPs. There are many methods used to determine the FE for example, perforator method (EN 120, 1992), chamber method (EN 717–1, 2004), gas analysis method (EN 717–2, 1994), flask method (EN 717–3, 1996), desiccator methods (JIS A 1460, 2001) and small chamber method (JIS A 1901, 2003), American large chamber ASTM E 1333–96 (2002b) and small chamber ASTM D 6007–02 (2002a).

2. OBJECTIVES

The main objectives of the present investigation are summarized in the following points.

1. Collecting of different types of particleboard (PB) with uncoated (P2), laminated (PL) and veneered (PV), uncoated medium density fiberboard (MDF) and laminated MDF (MDFL), high density fiberboard (HDF) and plywood (PLW) used in interiors (PLY) and for construction (PLYs) from the commercial plants in the Czech Republic in order to determine the amount of free formaldehyde emitted using three quite different European standard test methods namely: chamber test (EN 717–1), gas analysis (EN 717–2) and perforator (EN 120) methods. Moreover, the formaldehyde emission (FE) was determined according to CARB method as described in the American small–scale chamber (ASTM D 6007–02). In addition, measuring the FE from different types of flooring panels.
2. Comparison the relationships between the different methods of analysis by determination the correlation coefficient.
3. Evaluation of some industrial factors affects FE from CWPs.

These objectives were achieved by the following points:

1. Determination of formaldehyde concentrations release from different wood–based panels using different standard test methods and study the effect of board coating and board thickness on the formaldehyde release as well as the effect of different types of formaldehyde–based resins.
2. Determination of the relationships between different methods and estimation the relationships between some of formaldehyde values determined in the present work and the international standard limitation using the conversion factor equations, which have been developed by the literatures.
3. Evaluation of inter–laboratory comparison of formaldehyde release from particleboards using ASTM D 6007–02.

3. REVIEW OF LITERATURE

The production worldwide of particleboard (*i.e.,* PB), medium density fiberboard (*i.e.,* MDF), hardwood plywood (*i.e.,* HWPW), high–density fiberboard (*i.e.,* HDF), oriented strand board (*i.e.,* OSB) and other composite panels have increased dramatically over the past several years. Few issues in the forest products industry rival the debate and concern over the formaldehyde emission (*i.e.,* FE) of from products bonded with formaldehyde–based resins adhesive resin. Therefore, the increasing use of formaldehyde–emitting panel products in the more tightly constructed homes led to numerous complaints.

3.1 Measuring of formaldehyde emission with Different Test Methods

Table 1 show the different test methods used for determination the FE from CWPs used in different countries. In a global market it is of vital importance to be able to compare products with FE classes like E1 in Europe with *F**** and *F***** in Japan (JIS A 1460; JAS 233, 2001). It is also important that inter–laboratory tests are performed to make it meaningful to compare the results and possible to evaluate the variation that can be expected in the results obtained by different laboratories.

Table 1: The different test methods for measuring the formaldehyde released from composite wood products

Test method	Standard, standard draft or name
Chamber	EN 717–1, ASTM E 1333, ASTM D 6007, JIS A 1901, JIS A 1911, ISO 1246–1, ISO 12460–2
Gas analysis	EN 717–2, ISO 12460–3
Flask method	EN 717–3, AWPA method
Desiccator	ASTM D 5582, JIS A 1460, JAS 235, JAS, 233, AS/NZS 4266. 16, ISO 12460–4
Perforator	EN 120, ISO 12460–5
Other	FLEC, DMC

FLEC: Field Laboratory Emission Cell.
DMC: Dynamic Microchamber.

Determination of FE according to reference methods as the European chamber method (EN 717–1) requires, for example, chamber facilities and measurements until steady–state condition. There is, however, also a need for simpler and less time–consuming standard test methods for production control and similar tasks.

As some of the commonly used simple methods are performed at increased temperature (as EN 717–2 and EN 717–3) or includes extraction with solvents (EN 120), it cannot be expected that these methods always result in evaluations in compliance with results obtained by the chamber reference method (Risholm–Sundman *et al.,* 2007).

Some main characteristics of the methods are given as follow and Yu and Crump (1999) discuss them in an article. In 2000 WKI became the first European test institute which was recognized to do formaldehyde tests according to JIS A 1460 standards as official test organization.

3.1.1 Regulations and Testing

From the article review that has been written by Yu and Crump (1999) there have been reductions in the level of FEs from panel products over the last 15 years. New European standards for PB and MDF control the free formaldehyde content of panel products using an extractable formaldehyde test. Some countries including Germany, Denmark, Sweden and Austria also have regulations, which refer to emission limits when materials are tested in a large–scale chamber. The German Prohibited Chemicals Ordinance (1994) prohibits the use of wood–based panel products that generate an equilibrium formaldehyde concentration above 0.1 ppm in air when tested in an environmental chamber. The German Institute of Building Technology incorporates this limit of 0.1 ppm in a guideline (ETB–Richtlinie, 1981) that allows only the E1 and E1b emission classes of CWPs (coated or uncoated) to be used in buildings.

In Denmark, Sweden, Finland and USA similar regulations based on formaldehyde concentration measured using environmental chambers are also in place. In other countries such as Holland, Switzerland and in the UK, the extractable formaldehyde content (*i.e.*, FC) of the board is used for the control of FE from the panel products. In addition to regulatory standards for controlling the FE from CWPs produced by the manufacturer, various types of product labeling schemes are being developed. For example in Denmark and in Germany, labeling schemes have been introduced which take account of the possible health effects caused by the amount of emission from the product.

Emission databases being produced in both Europe and in America, including the European Data Base on Indoor Air Pollution Sources in Buildings and the Source Ranking Database produced by the US Environmental Protection Agency (EPA), are expected to increase consumer demand for low emitting products in the future. These developments will also lead to an increased requirement for the testing of products to determine the FE rate as part of product development and quality control procedures.

In support of the EC Construction Products Directive Essential Requirement Hygiene, Health and Environment: Safety in Use, the technical committee CEN TC112 has developed a European standard EN 717–1 for measuring FE based on chamber test methods. The standard prescribes three types of chambers: 0.225 m^3, 1 m^3 and room–sized chambers (12–52 m^3) for the measurement of the steady–state formaldehyde concentration produced by wood–based products. The developments of the standard, the definition of the steady–state formaldehyde concentration and the use of smaller chambers (0.225 and 1 m^3) have been reviewed elsewhere. In order to undertake the tests described in EN 717–1, specialized environmental chamber test facilities are required and measurements of formaldehyde release are taken twice daily for up to 28 days. The test is therefore expensive to undertake on a routine basis. Other test methods that determine the extractable FC of wood–based materials are applied and some are European standard methods. These take less time to provide a test result, but the relationship between the extractable FC of the board and formaldehyde release under normal conditions of product use is complex. There is therefore a need for simpler tests that determine emission rates that can be directly compared with the results of the environmental chamber test.

In North America, a small chamber method from the ASTM D 6007–02 (ASTM, 2002a) is being adopted by some of the CWPs manufacturers for testing of FE from their panel products. Correlation between the small chamber and the large chamber ASTM E 1333–96 (ASTM, 2002b) methods has been established. The ASTM D 6007–02 requires the board sample to be kept in the chamber (0.02–1 m^3) until a steady–state concentration is attained. In some production plants, the use of the small–scale chamber has replaced the traditional desiccator test (ASTM D 5582–00, 2006).

3.1.1.1 Europe's Formaldehyde Regulations

Most European nations have passed laws that regulate formaldehyde, now known as the E1 emissions class. Standards such as EN 312, EN 622–5 and EN 300 all require that the 0.1 $mg/m^3.h$ level be met. Testing for this mainly uses the EN 120 and EN 717–1. In 2004, the EN 13986 (2002) established emission classes E1 and E2 for use in construction (the E1 level is most common). These standards basically require testing to be done on formaldehyde containing wood products used in construction (Table 2). In 2006, these same methods and the associated limits became effective for panel production.

3.1.1.2 Japan's Formaldehyde Regulations

In 2002, the Japanese Industry Standards (JIS) Committee amended the Japanese Building Standard Code in response to public health concerns over poor indoor air quality, what many call Sick Building Syndrome (SBS). Under the revised standard, all new habitable building construction in Japan requires that there be technical standards in place to regulate the air quality. One of the restrictions placed on building materials is the allowable level of formaldehyde emissions.

As of July 2003, testing and certification requirements have been established for products that contain formaldehyde, namely composite wood building materials. The new standard also makes ventilation systems mandatory in all habitable buildings. A few of the building materials include PLW, wood flooring, structural panels, laminated veneer lumber, adhesives, paints and many others. Because it is very difficult, if not impossible, to eliminate formaldehyde from a building completely, the standard employs a tiered rating system based on the amount of FE a building material gives off. These are from one star to four–star ratings, with the four–stars rating representing the lowest amount of FE (Table 2).

In contrast to building material standards in Europe and Japan, the proposed Phase 1 and Phase 2 standards for HWPW, PB, and MDF, with effective dates in the 2009 to 2012 timeframe, are product–specific.

Based on the use of published equations correlating the results of a selected FE/content tests (Risholm–Sundman *et al.*, 2007) and results from a study to compare the metrics used in the U.S. and Europe (Groah *et al.*, 1991), the relative stringency of the proposed standards has been estimated and shown in Table 3.

Table 2: Current formaldehyde emission standards for wood–based panels in Europe, Australia, the U.S.A. and Japan.

Country	Standard	Test method	Board class	Limit value
Europe	EN 13986	EN 717–1 EN 120	E1–PB, MDF, OSB	≤ 0.1 ppm ≤ 8 mg/100 g o.d. board
		EN 717–1 EN 717–2	E1–PLW	≤ 0.1 ppm ≤ 3.5 mg/(h.m^2)
		EN 717–1 EN 120	E2–PB, MDF, OSB	> 0.1 ppm > 8 ≤ 30 mg/100 g o.d. board
		EN 717–1 EN 717–2	E2–PLW	> 0.1 ppm > 3.5 ≤ 8.0 mg/(h.m^2)
Australia & New Zealand	AS/NZS 1859–1 & 2	AS/NZS 4266.16 (Desiccator)	E0–PB, MDF E1–PB E1–MDF E2–PB, MDF	≤ 0.5 mg/L ≤ 1.5 mg/L ≤ 1.0 mg/L ≤ 4.5 mg/L
USA	ANSI A 208.1 & 2	ASTM E1333 (large chamber)	PB MDF	≤ 0.18 or 0.09 ppm ≤ 0.21 or 0.11 ppm
Japan	JIS A 5908 & 5905	JIS A 1460 (Desiccator)	*F*** *F****/“E0” *F*****/“SE0”	≤ 1.5 mg/L ≤ 0.5 mg/L ≤ 0.3 mg/L

Table 3: Proposed Airborne Toxic Control Measure (ATCM) for composite wood products.

Standard	Product(s)	Test Method	Numerical Value	≈ E1333 (ppm)
CARB–Phase1	HWPW	E1333	0.08 ppm	0.08
„„	PB	E1333	0.18 ppm	0.18
„„	MDF	E1333	0.21 ppm	0.21
CARB–Phase2	HWPW	E1333	0.05 ppm	0.05
„„	PB	E1333	0.09 ppm	0.09
„„	MDF	E1333	0.11 ppm	0.11
E1	HWPW	EN 717–1	0.12 mg/m^3	0.14
„„	PB	EN 717–1	0.12 mg/m^3	0.14
„„	PB,MDF	EN 120	8 mg/100 g o.d. board	0.10
F***	All	JIS A1460	0.5 mg/L	0.07
F****	All	JIS A1460	0.3 mg/L	0.04

The F–star standards apply to all wood products specified in the CARB standards. The “≈ E1333” values were calculated using data in ASTM E 1333–96 (ASTM, 2002a), Battelle 1996 and Risholm–Sundman *et al.*, (2007).

From the Table 3, the equivalent U.S. large chamber test value ASTM E 1333–96 (ASTM, 2002b) for the European E1, Japanese *F**** and *F***** standards applicable to CWPs subject to the proposed ATCM.

Although the CARB regulation is only valid in California many CWP plants around the world have already been certified to satisfy the CARB requirements and the number of application for certification is continuously rising. In February 2009, the American National Standards Institute (ANSI) has approved revised national voluntary standards for ANSI A208.1–2009 for PB and ANSI A208.2–2009 for MDF for Interior Applications (Tables 4 and 5).

Table 4: The CARB new standards, Phase 1 and Phase 2 formaldehyde emission Standards for HWPW, PB, and MDF, (CARB 2008)[a].

Effective Date	Phase 1 (P1) and Phase 2 (P2) Emission Standards (ppm)				
	HWPW–VC	**HWPW–CC**	**PB**	**MDF**	**Thin MDF**
01.01.2009	P1: 0.08	–	P1: 0.18	P1: 0.21	P1: 0.21
01.07.2009	–	P1: 0.08	–	–	–
01.01.2010	P2: 0.05	–	–	–	–
01.01.2011	–	–	P2: 0.09	P2: 0.11	–
01.01.2012	–	–	–	–	P2: 0.13
01.07.2012	–	P2: 0.05	–	–	–

([a]) Based on the primary test method [ASTM E 1333–96 (ASTM 2002b)] in ppm. HWPW–VC = veneer core; HWPW–CC= composite core.

Table 5: Industry average concentration and emission factor (EF) results for PB and HWPW combined, and MDF in 2002 and concentration and emission factor limits required by Phase 1 (Jan 2009) and Phase 2 (Jan 2011–Jul 2012) of the ATCM. Also shown are Phase 1 and 2 target–operating limits (TOL) arbitrarily set at two–thirds of the ATCM limits.

Parameter	Units	PB&HWPW			MDF		
		2002	**Phase 1**	**Phase 2**	**2002**	**Phase 1**	**Phase 2**
Concentration	Ppm	0.18	0.18	0.09	0.25	0.21	0.11
Concentration	$\mu g/m^3$	221	221	110	307	258	135
EF	$\mu g/m^2h$	259	259	129	585	492	257
TOL EF	$\mu g/m^2h$	Na	173	86	Na	328	172

Na = Not applicable

There are many methods used by literatures to measure the FE from CWPs as sorted above. However, there are an unconventional methods used as a new ways to measure the FE from CWPs.

Myers (1983a) tested a number of commercial panel products, primarily PB and HWPW, for their FE behavior using desiccator, perforator, and dynamic chamber methods. The results were analyzed in terms of the source of formaldehyde observed in the tests (free vs. hydrolytically produced) and the potential utility of the tests as product standards for boards in mobile homes. A greater than tenfold range of FE was observed, well above and below levels that would be acceptable for proposed mobile home air levels. It was demonstrated that observed maxima in dynamic concentration–time curves were due to depletion of initial board free formaldehyde (as measured by perforator) and emission of hydrolytically produced formaldehyde at a lower rate. The 2–hour desiccator test measures less than 0.5% of the board's initial free formaldehyde content and therefore does not necessarily reflect resin hydrolytic stability. Approximate linear correlations were observed between desiccator or perforator values and dynamic chamber concentrations. However, large deviations occurred from the linear regressions. It was concluded that without large safety factors and/or much more testing to clarify those deviations neither the desiccator nor the perforator test could provide reliable product standards for board emission.

A critical literature review has been carried out by Myers (1984a) on the influence of ventilation rate (N, hr^{-1}) and board loading (L, m^2/m^3) on steady state formaldehyde concentrations (C_s, ppm) resulting from PB and PW emissions. Large differences exist among boards in the extent to which their formaldehyde concentrations change with N or L in laboratory chambers. Much of the concentration versus N and L data obtained from controlled chamber experiments can be described by a two–parameter equation involving the ratio N/L as the independent variable. Although this equation has a theoretical basis, it should be regarded as semi–empirical because of deviations beyond $N/L \approx 8$ m/hr. and because a true steady state cannot be maintained indefinitely. Concentration versus N/L data for dwellings under controlled conditions are meager; more testing is needed before effects here can be quantified or chamber results reliably extrapolated to dwellings.

A survey of FE rates from US manufactured PB, HWPW paneling, and MDF products has been performed using a Formaldehyde Surface Emission Monitor (FSEM) by Matthews *et al.*, (1986). The results indicate approximately two orders of magnitude variation in CH_2O emission rates between weakly emitting paneling and strongly emitting fiberboard products. The measured CH_2O emission rates for PB, HWPW paneling, and MDF products averaged 0.30, 0.17 and 1.5 mg/m^2.h respectively. The FSEM has also been used to determine the CH_2O emission rate of carpet–covered PB underlayment in two unfurnished research homes. Measurements were conducted at 16 different temperature and RH conditions ranging from 17–29 °C and 41%–88% RH to field–test the response of the FSEM to varying CH_2O emission strength resulting from the variable environmental conditions. Substituting the FSEM CH_2O emission rate data into a simple steady–state, CH_2O concentration model (that does not account for variation in temperature and RH conditions) gave good agreement between FSEM–modeled and measured CH_2O concentrations.

Large chamber test procedures, ASTM E 1333–96 (ASTM, 2002b) have been established and are routinely used by Liles *et al.*, (1996) to monitor CWPs performance relative to federal FEs standards established by the US Department of Housing and Urban Development (HUD). Georgia–Pacific Resins, Inc. tested product samples in an automated, 44–L aluminum DMC, suitable for FEs measurements.

The ASTM E 1333 large chamber test method is the primary method for determining FE potential from UF bonded wood panel products. The precision of the large chamber air sampling and chromotropic acid analytical procedure (NIOSH Method 3500) was examined by comparing the differences between formaldehyde concentrations from simultaneous air samples taken at two sampling ports in chambers operated by two laboratories (Groah *et al.,* 1998). Based on this approach, a precision of the analytical procedure was indicated at least as low as 0.003 ppm in the 0.020 to 0.300 ppm range of air concentrations, a range defining most low–formaldehyde–emitting wood panel products. Differences between two air exchange rate measuring techniques were compared: totalizing gas meter and carbon monoxide tracer gas. Good agreement among the two air exchange rate measuring techniques was demonstrated.

The FE from wood–based building materials is usually determined in large chambers at a defined temperature, humidity and ventilation rate. A simpler method, the FLEC, is described by Risholm–Sundman (1999) for determination of the FE and it is compared with the traditional chamber method. The formaldehyde from FLEC is collected on a silicagel cartridge impregnated with 2,4–dinitrophenylhydrazine (DNPH) and analyzed with HPLC. The FLEC is easier to operate, requires a smaller sample, fewer analyses and is also more flexible than the chamber method. The emissions from different parts of a sample can be measured. Another advantage is that the equipment can be used to determine the VOCs emission at the same time. The FLEC method gives a good correlation to the chamber method for different building products. It also gives a good recovery. An average recovery of 98% was achieved, when two different FLEC–cells were tested with known formaldehyde sources with emissions of 0.06–0.7 mg/m^2.h.

In order to evaluate more simple laboratory methods for determining the FE from three–layer parquet floor by Risholm–Sundman and Wallin (1999), the two closed container methods (flask, EN 717–3 and JAS according to JIS A 5908, 1994) and two emission cell methods (FLEC and desiccator lid) have been compared with the 1 m^3 chamber method. The best correlation with the chamber method is achieved with the emission cells. The emission rates from different parts of a parquet sample (the front, the back and the edges) give different results. The FE from the back surface can be 20 times higher than from the front, so it is very important to do the test on the normally exposed surface. In addition, the conditioning time affects the emission rate and should be maintained in a standardized way, so that results can be compared. The correlation between the chamber and the FLEC and desiccator lid methods is good.

In response to concerns about the possible adverse health effects caused by FE from wood–based products, the wood panel products industry has developed and produced lower emission materials over the past 15 years. There is a need for a reliable and inexpensive method in the industry to measure FE from some products that can be used on a routine basis and can provide data comparable to the environmental chamber test prescribed in EN 717–1. Yu *et al.,* (1999) developed a 2.4–litre microchamber test in the UK, at the Building Research Establishment, as a bench–top method for measuring the FE from wood–based materials. Microchamber tests of newly manufactured boards that were preconditioned for 28 days showed good correlation with the steady–state values obtained from the 1 m^3 chamber tests determined in accordance with the EN 717–1 standard. The airflow rate, the ratio of air change to material loading in the chamber and the amount of exposed edges were shown to affect the measurement of emission rates.

Indoor air quality problems resulting from the emission of VOCs have become an issue of increasing concern. Emissions from building and furnishing materials, which are frequently constructed from PB and MDF, are a potentially important contributor of indoor VOCs. In the research of Baumann *et al.*, 2000, VOC emissions from PB and MDF were measured in small (53–L) stainless steel chambers for 4 days. Samples were collected from 53 of the 61 U.S. mills that produce PB and MDF. Each mill identified the predominant tree species used to manufacture the panels. Laboratory tests were conducted at room temperature and RH 45%. Gas chromatographic/mass spectrometric (GC/MS) analysis was used to identify and quantify VOC compounds. The predominant compounds identified in the emissions from PB and MDF samples were terpenes and aldehydes, although small straight–chain alcohols and ketones were also found. This study describes the aldehyde emission data, excluding formaldehyde. The tests showed differences in VOC composition and emission factors by product and tree type. On average, aldehyde emissions from southern pine MDF samples considerably exceeded the aldehyde emissions from southern pine PB. Emissions from all other MDF samples, however, were lower than those from PB samples in the same species group. With the exception of formaldehyde, aldehydes are not added to the adhesives used to bond wood, and they have not previously been reported as extractable compounds in wood.

A test method for measuring formaldehyde from UF resins at high temperature was developed by Tohmura *et al.*, 2000 and used to assess the influence of the reaction pH on the FE and heat stability of the cured resins. Additionally, solid–state ^{13}C CP/MAS nuclear magnetic resonance (NMR) techniques were used to investigate the structure of cured UF resins before and after high temperature heating. FEs during the cure were related to the UF resins' methylol group content. The heat stability of cured UF resins synthesized under strongly acidic conditions was much higher than that of the other resins, which were prepared in weakly acidic and alkaline media. Solid–state ^{13}C CP/MAS NMR spectra showed that FE from cured UF resins after heating is mainly ascribable to decreased methylol groups and dimethylene ether linkages. Significantly, it was revealed that uron structures characteristically found in the cured UF resin synthesized under strongly acidic medium indicated high heat stability.

JIS A 5908 measured the FEs from MDF bonded with UF, MF and the co–polycondensation resin of UMF and MF as the typical standard methods by Kim and Kim (2005a). While the UF resin showed a desiccator value of 7.05 ppm and a perforator value of 12.1 mg/100 g oven dry panel (o.d.), the MF resin exhibited a desiccator value of 0.6 ppm and a perforator value of 2.88

mg/100 g o.d. board. According to the JIS and the European standard, the FE level of the MDF panels made with UF resin in this study was E2 grade. The FE level was dramatically reduced by the addition of MF resin. This is because the addition of formaldehyde to melamine occurs more easily and completely than its addition to urea, even though the condensation reaction of melamine with formaldehyde is similar to that between urea and formaldehyde. These two methods, the desiccator method and the perforator method, produced proportionally equivalent results. GC, a more sensitive and advanced method, was also used. The samples used for GC were gathered during the experiment involving the perforator method. The FE levels obtained from GC were similar to those obtained from the perforator method. The FCs measured by GC were directly proportional to the perforator values.

The combustion of PB and glued veneer was studied by Risholm–Sundman and Vestin 2005, in order to evaluate if there are any negative effects on the environment from incineration of waste with adhesive. The PB was made with UF resin and the veneers were glued with different types of adhesives, UF, polyvinyl acetate (PVAc), emulsion polymer isocyanate (EPI), MUF and phenol resorcinol formaldehyde. The combustion tests were carried out in a fluidized sand bed reactor with a good oxygen supply at temperatures between 500 °C and 1000 °C for PB and at 750 °C and 850 °C for glued veneer. The emissions were compared with the emissions from combustion of pure wood and pellets made from wood. The results show that the emissions from both PB and glued veneer are similar to the emissions from pure wood. It can be seen that the FE varied during the test, the results were between 0.2 mg/m^3 and 5.9 mg/m^3 for PB and between 0.1 mg/m^3 and 3.9 mg/m^3 for wood pellets. Most likely these variations are due to fluctuations in the burning conditions. Two different analytical methods were used for the analyses, the acetylacetone and the chromotropic acid methods, and both gave similar results. The FE from all types of glued veneer was < 0.2 mg/m^3.

According to desiccator and perforator standards, Kim *et al.,* (2006a) found that, the FE level of flooring was ≤ E1 grade. The FE of MDF and PB was 3.48 mg/L PB and 5.38 mg/L by the desiccator method, and 8.57 and 10.21 mg/100 g o.d. PB by the perforator method, respectively. A 20 L small chamber was developed in Japan with performance in compliance with ASTM, ECA reports, and ENV 13419–1. To determine FE, the peak areas of each wood–based composite were calculated from aldehyde chromatograms obtained using the 20 L small chamber method.

According to the article gives a comparison between commonly used European test methods: EN 717–1, EN 717–2, EN 717–3 and EN 120, and Japanese test methods: [desiccator methods (JIS A 1460) and (JAS MAFF 233)] and small chamber method (JIS A 1901), for determination of FE from solid wood, PB, PLW and MDF. Risholm–Sundman *et al.,* (2007) founded that;

factors like edge sealing, conditioning of the sample before the test and test temperature have a large effect on the final emission result. The Japanese limit for *F***** of 0.3 mg/L (in desiccator) for PBs was found to be equivalent to 0.04 mg/m^3 in the European chamber test and 2.8 mg/100 g o.d. board in the perforator test. The variations in inter–laboratory tests are much larger than in intra–laboratory tests; the coefficient of variation is 16% and 6% for the chamber method, 25% and 3.5% for the gas analysis method and 15% and 5.2% for the desiccator method.

A new passive flux sampler (PFS) was developed by Shinohara *et al.*, (2007) to measure emission rates of formaldehyde and to determine emission sources in indoor environments. The sampler consisted of a glass Petri dish containing a DNPH–impregnated sheet. Formaldehyde emitted from a source material diffused through the inside of the PFS and was adsorbed onto the DNPH sheet. The FE rates could be determined from the quantities adsorbed. The lower determination limits were 9.2 and 2.3 μg/m^2.h for 2–and 8–h sampling periods. The recovery rate and the precision of the PFS were 82.9% and 8.26%, respectively. The emission rates measured by PFS were in good agreement with the emission rates measured by the chamber method (R^2 = 0.96). This shows that it is possible to take measurements of the FE rates from sources in a room and to compare them. In addition, the sampler can be used to elucidate the emission characteristics of a source by carrying out emission measurements with different air–layer thicknesses inside the PFS and at different temperatures. The dependency of the emission rate on the thickness of the air layer inside the PFS indicated whether the internal mass transfer inside the source material or the diffusion in the gas–phase boundary layer controlled the FE rate from a material. In addition, as a pilot study, the FE rates were measured, and the largest emission source of formaldehyde could be identified from among several suspected materials in a model house by using the PFS.

Measurements of FE from wooden boards, insulation and paints were performed by Kolarik *et al.,* (2009) as a part of a project aiming to identify major sources of formaldehyde among construction and finishing products in Danish residential buildings. The methodology of measuring followed EN 717–1. The concentrations differed widely between tested materials. The initial concentration ranged from below 0.01 mg/m^3 to 0.115 mg/m^3 and it dropped below 0.01 mg/m^3 for 7 out of 12 the investigated materials at the end of the measuring period, while for the remaining 5 materials it did not change noticeably. All measured concentrations were below Danish requirements, however performed calculations of formaldehyde concentration in a room finished with investigated materials suggest that indoor concentrations above 0.1 mg/m^3 recommended by WHO are well–founded, and concentrations as high as 0.5 mg/m^3 can be expected.

Also Shinohara *et al.,* (2009) used the PFSs to measure emission rates of carbonyl compounds and VOCs from many of the building materials and furnishings present in a room in a reinforced concrete building in Tokyo, Japan. The emission flux of formaldehyde from a desk was high (125 μg/m^2.h), whereas fluxes from a door and flooring were low (21.5 and 16.5 μg/m^2.h, respectively). The indoor and outdoor concentrations of formaldehyde were 61.5 and 8.64 μg/m^3, respectively.

The FEs from the PLW made using formaldehyde–free cornstarch–tannin adhesives were determined according to the European Standard (ISO/CD 12460–4, 2007) using a glass desiccator by Moubarik *et al.,* 2009. The 24–h desiccator method uses a common glass desiccator with a volume of 10 L. It was found that cornstarch–tannin panels which did not contain formaldehyde and with an emission equal to that of heated. The FE results were, however, considerably lower than those observed for the commercial PF resin (2.62 mg/m^2.h). Emission value from cornstarch–tannin was 0.2 mg/m^2.h due to the formaldehyde generated just by heating of the wood, and is not due to the resin and by wood only control was 0.17 mg/m^2.h.

Park *et al.,* 2010 attempted to establish empirical correlations between three test methods (*i.e.,* 24–hour desiccator, 1 m^3 chamber, and perforator) for PLW, PB, and MDF, particularly emphasizing on correlations between the 24–hour desiccators and the 1 m^3 chamber method. The desiccator method found statistically high correlations with other two methods, resulting in regression coefficient values ranging from 0.96 to 0.88 for PLW, PB, and MDF samples. In particular, the desiccator method had an empirically high correlation with the 1 m^3 chamber method that had been adopted as the reference method of comparing regionally different test methods of measuring the FE of wood–based composite panels by the ISO/TC89.

Roffael *et al.,* (2010) reported that, in Europe, the perforator method is the mostly used laboratory method of the wood–based panel industry. Usually, the measured perforator value depends on the moisture content (MC%) of the boards. According to DIBt–100, the measured perforator values are corrected to common MC of 6.5% using an established equation proposed by Jann and Deppe (1990). The correction factor of Jann and Deppe (1990) is based on the assumption that particle– and fiberboards change their perforator values to the same extent regardless whether increasing or decreasing the MC in the range of $3 \leq H \leq 9\%$. Application of this correction factor to particle– and fiberboards of higher MC than 6.5% can lead to biased corrected results in favor of low emission. The corrected values can also lead to paradoxical relation between the perforator values and emission in the low–emission region.

Six European laboratories used chamber method (EN ISO 16000–9) for the determination of VOC and FEs from a wood based panel (PB), was reported by Yrieix *et al.,* 2010. Formaldehyde results showed standard deviation of only 17.4% for a mean concentration of 57.6 μgm^{-3} after 28 testing days. In general, results are similar to recent inter–laboratory comparison studies even if wood based panels can be considered as heterogeneous materials.

3.2 Factors Affecting Formaldehyde Emission

The FE from CWPs can be influenced by exogenous and endogenous factors. The exogenous factors include temperature, humidity, air movement over the panel surface, air change rate and the local formaldehyde concentration within the space where the material is placed. The endogenous factors include the wood species, moisture content of the wood flakes, the type and the chemical composition of the adhesive binder used, the additives (*i.e.,* catalysts and formaldehyde scavengers) added, the arrangement of the multi–layer board, the surface treatment, the density of the board and the manufacturing conditions, (*i.e.,* temperature and duration of the hot pressing process).

The chemical constitution of the binding resin has an important effect upon the FE from the wood–based panel. For a particular type of resin, the molar ratio of urea to formaldehyde is an important variable. It has been shown that within a certain range of molar ratios there is an almost linear relationship between the molar ratio, the FE (measured by the WKI flask method) and the extractable FC determined by the EN 120. A decrease in the FC of the resin leads to a decrease in the FE rate of the finished product. FE was demonstrated by Sundin (1985) to level off at a U:F molar ratio of about 0.95. The cross–linking of the resin during manufacture of board products is achieved by a combination of heat and hardener.

Acids present in most wood can act as hardener but amounts are not sufficient to attain the required cross–linking of the UF resin. Catalysts such as ammonium chloride and/or ammonium sulphate are used, which will undergo hydrolysis in aqueous solution to produce acids to accelerate the condensation reaction. There is a small amount of free formaldehyde in the liquid resin (generally less than 0.1%) which is used during the cross–linking of the resin. The free formaldehyde is present in various forms in the manufactured board. It can react with moisture present in the wood fiber to form methylene glycol, polymethylene glycol and polyoxymethylene hemiacetal etc.; it can also undergo labile binding to the wood fiber or to the polymer resin. This free formaldehyde will in time migrate and be released into the atmosphere, especially under high temperature and when exposed in a well–ventilated environment. The FE of the CWPs is not limited to the emission of the free FC of the board. The FE can also come from the thermolysis of wood lignin and polysaccharides in the wood fiber, which will further contribute towards the FE from the manufactured board.

The hydrolysis of the partially cured and cured resin will continuously produce formaldehyde that will be emitted. The hydrolysis is acid–base catalyzed and is influenced by temperature, the moisture content and the pH in the board. Depending on the species, the wood particles can liberate acids under certain temperature and moisture conditions. These can cause a shift towards a lower pH, which may cause hydrolysis of the N–methylol group and to a lesser extent, the methylene ether linkages in the UF resin. The majority of the formaldehyde first emitted from a new wood–based board comes from the free formaldehyde present in the material. The emission typically declines exponentially until a steady–state level is reached (Yu and Crump, 1999).

3.2.1 Effect of Mole Ratio on Formaldehyde Emission

Mayer (1979) and Myers (1983b) reported that, the FC of the UF resins used by the PB industry has been sharply decreasing over the years. While the UF resins used at the beginning of the industrial production of PB had mole ratios of U:F being 1.8:1 or more, today the mole ratio is 1.1:1 and is still decreasing.

A critical review was made of the literature concerned by Myers (1984b) with how the F:U ratio affects FE from PB and PLW bonded with UF adhesives, and how this ratio affects certain other adhesive and board properties. It is difficult to quantify the dependence of various properties on mole ratio or determine lower limits of mole ratio for a particular property because of the range in resin, board, and testing parameters used in the cited studies. However, the available data do at least suggest the following limitations on F:U in conventional UF PB systems for maintenance of acceptable properties: 1) F:U < 1.2 or even < 1.1 to meet the German El emission standard, 2) F:U < 1.3 or possibly < 1.2 to meet the tentative NPA emission standard for U.S. mobile homes, 3) F:U ≥ 1.2 for bending strength and modulus of rupture, 4) F:U ≥ 1.1 or possibly ≥ 1.2 for internal bond, 5) F:U ≥ 1.2 or possibly ≥ 1.3 for 24–hour thickness swell. These conflicting limitations strongly indicate that problems exist in depending solely on mole ratio reductions to produce low emission UF PB with acceptable physical properties.

The test of FE from MDF manufactured in a commercial pilot plant using seven different UF resins with molar ratios between 1.85 and 1.05 were evaluated by Meyer *et al.,* (1985). Formaldehyde release measured with the 2 h. U.S. desiccator test ranged from 8.6 mg/L to 0.3 mg/L after 6 weeks. European perforator standard values ranged from 80 to 9 mg/100 g o.d. board. Low molar ratio resin produced MDF with FE rates that were sufficiently low to meet the requirement of the German wood product class E1 and the 0.1 ppm requirement of ASHRAE 62 (1981) or similar standards for minimum acceptable indoor air quality at reasonable product loading ratios.

The effect of melamine content MUF resins on the FE and resin structure was investigated by Tohmura *et al.,* (2001) using six MUF resins synthesized with different F/(M+U) and M/U molar ratios. The FE from the PW decreased as the F/(M+U) molar ratio decreased and the M/U molar ratio increased. In addition, the bond performance was enhanced as the M/U molar ratio increased in the MUF resins with a fixed F/(M+U) molar ratio. Quantitative solution ^{13}C NMR spectra of MUF resins revealed that the MUF resins with high melamine content consisted of more highly branched cross–linkage structure and free melamine compared to the resins with low melamine contents. Furthermore, solid–state ^{13}C CP–MAS NMR spectra of cured MUF resins proved that more methylol groups, dimethylene ether, and branched methylene structures were present in the MUF resins with a higher F/(M+U) molar ratio, leading to increased bond strength and FE.

Que *et al.,* (2007) obtained that, there were good relationships between the methods studied for determining the FE from PB (the desiccators, JIS A 5908 and the EN 120, compared with the 1 m^3 chamber method SS 270236) with correlation coefficients of > 0.9. The value of FE decreased linearly with the mole ratio of F/U down to 1.05 where the effect smoothed out. The heat treatment lowered the perforator value with resins that had mole ratios ≥ 1.15, at the two lowest mole ratios 0.97 and 1.01; there was a tendency for the heat treatment to increase the perforator value. Also after the boards were stored for 6 months at 23 °C and 50% RH, the perforator values were unchanged or negligibly changed with the lower mole ratios and there was a more pronounced change with a higher mole ratio of 1.27.

3.2.2 Effect of Wood Species, Panel Density, Press Temperature, Press Time, Moisture Content and Resin Content on Formaldehyde Emission

Increasing of shelling ratio from 32% to 45% caused significantly higher FC in PB. Fine particles can be compressed easily during the hot pressing. For this reason, higher shelling ratio causes more compact and tighter structures. Formaldehyde is released at higher amounts and easily from PBs produced at lower shelling ratio during hot pressing and storage.

As a result of more amount of formaldehyde release, these boards consist of lower formaldehyde during the test (Boehme and Roffael, 1990). In addition, UF adhesive was used at the level of 11% of the oven dry weight of particles in the face layers during manufacturing. Related to this, increasing of face layer particle usage ratio caused more amount of adhesive applying. Increase of adhesive amount related to the increase of shelling ratio cause more formaldehyde release during the tests (Marutzky, 1994).

PBs at 0.60 g/cm^3 SG had lower FC than that of panels at 0.70 g/cm^3, significantly. Boards at higher specific gravities have tighter and more compact structure. This gives higher formaldehyde values for these boards in perforator test due to low formaldehyde release during the hot pressing. In addition, adhesive usage amount is related to the particle amount. Increase of SG causes more adhesive usage amount for PB production. Based on statistical analysis, raw material type affected the FC of the PB. Increasing of pine particles amount on the board caused higher FE values.

When beech particles are used for PB manufacturing, it is reasonable to suppose that the bigger the vessel surface, the higher the formaldehyde release from the respective boards during hot pressing and one week since their manufacture up to the beginning of the test. For this reason, boards consisting higher amount of beech particles had lower FC (Martinez and Belanche, 2000). The second reason explaining the effect of wood species on the FE of PB is acetyl groups in the wood. During the hot pressing, acetyl groups release from the wood and acetic acid is formed. This acid is a formaldehyde scavenger. Beech wood consists of more acetic acid than pine. A similar effect of wood species on the FE was also reported in previous studies (Çolakoğlu, 1993).

To study the factors affect PLW–FE and FC, such as raw materials, manufacturing processes, stacking conditions, etc. In order to show the influence of veneer wood species on FE and FC, several groups of PLW panels have been manufactured by Martínez and Belanche (2000) in the laboratory using commercial UF resins. Four veneer wood species have been studied: *Ceiba pentandra*, *Fagus silvatica*, *Pycnathus angolensis* and *Aucoumea klaineana*. FE and FC from the PW have been determined according to EN 717–2 and EN 120 respectively. There are two main reasons explaining the differences between the FE and FC the panels showed. The first one being that the formaldehyde present in the adhesive interacts in a distinct way with each wood species and the second one that FE and FC values are affected by the anatomy of the respective wood species.

Jiang *et al.*, (2002) studied the effects of adhesive type and press variables (press temperature, press time, mat resin content, mat moisture content, and board density) and their interaction on VOC emissions arising from hot–pressing mixed–hardwood PB. Three adhesive types: UF, PF, and polymeric methylene diphenyl diisocyanate resin (pMDI). The results revealed that FE from UF was the most abundant components of the VOC emissions. The most significant press variables controlling VOC emissions were press time, mat resin content, press temperature, and interactions among these three variables. In general, FEs arising from hardwood PB hot–pressing was significantly lower than those from softwood PB. However, FEs from UF–bonded hardwood PB was significantly higher than from the softwood UF–bonded PB.

In the production of PBs, two different press temperatures, press times, pressures and three different adhesive use ratios were used by Nemli (2002). The best manufacturing variables were determined for the PB produced from E1 type adhesive. The effects of these manufacturing variables on FE, bending strength, internal bonding strength and thickness swelling were investigated. According to the results, when the E1 type adhesive was employed, the use of 11%

and 9% adhesive use ratios for the outer and middle layers, respectively, 200 °C press temperature, 150 s press time and 32.5 kg/cm^2 pressure were found to be enough. It was suggested that at 180 °C, the PBs required 150 s press time and 35 kg/cm^2 pressure. It was found that in the production of E1 type PB, the use of low emission adhesive was not enough, and all of the production parameters should be taken into account together. In addition, it was concluded that the amount of FE of manufactured PBs should be low. Equally, the PBs should meet the required physical and mechanical properties as stated in the relevant standards.

Three types of adhesives UF, PF and pMDI were used to bond PB during the investigation of the effect of hot–pressing variables on VOC emissions related to Wang *et al.,* (2003). The variables examined included press temperature, press time, mat moisture content, resin content, and panel density. FEs was significantly affected by press temperature and press time for panels pressed with all adhesives. For panels pressed with both UF and PF resins, mat moisture content significantly affected FE, but mat resin content and panel density did not have a significant effect on FEs.

Aydin *et al.,* (2006) reported that, the FE values of poplar and spruce PLW panels decreased with increasing veneer moisture content for UF and modified UF by M+UF. The FE content of panels decreased with melamine addition into the UF glue mixture.

As the best manufacturing parameters determined for E1 grade PB manufacturing from UF adhesive, Nemli and Öztürk (2006) studied the effects of specific gravity (SG), shelling ratio, wood species, and pressure on the FC of PB. Increasing of SG, shelling ratio, and pressure increased the FC. PB made from particles consisting higher amount of beech particles had lower FC than that of panel from particles consisting higher amount of pine particles.

To determine the changes in FEs of eucalyptus PBs produced from logs stored under different conditions, Çolak *et al.,* (2009) found that, the FE values of the PBs produced from the logs stored under water or indoor conditions and pressed at 150 °C were found to be 1.21 and 1.34 mg/100 g o.d. board, respectively. These values were clearly lower than those of the panels produced from steamed log parts (1.88 mg/100 g o.d. board) and the log parts stored in outdoor conditions (1.92 mg/100 g o.d. board). The FE values of the PBs pressed at 190 °C were found to be 0.72 mg/100 g o.d. board for group I (indoor condition for 2 months), 0.98 mg/100 g o.d. board for group II (outdoor condition for 4 months), 0.79 mg/100g o.d. board for group III (under water for 3 months) and 0.82 mg/100 g o.d. board for group IV (steaming). There were similar interactions among the FE values of the panels pressed at 190 °C and those of the panels pressed at 150 °C. However, the differences among the emission values of the panels pressed at 190 °C were lower. This may be due to the degradation and splitting of the acetyl groups at this temperature.

3.2.3 Effect of Temperature on Formaldehyde Emission

Roffael, 1993 reported that press temperature during PB production effected the emission of formaldehyde from the presses. Roffael theorized that thermolysis of wood led to formaldehyde formation from lignin and polysaccharides. However, this work was concerned with emission from the press section of a PB plant where formaldehyde was also present in the glues and did not report results for wood alone and therefore the result may not relate to solid wood samples. Roffael has also carried out some fundamental work examining the formation of formaldehyde from various wood components when they are heated (Roffael, 2002). He found that the wood contains a number of molecules, which under heating break down to produce formaldehyde. It was also found that these emissions increased with temperature from 40 °C to 150 °C. Roffael also measured emission from pulp and particles of pine and spruce as they were heated for three hours at temperatures or 40 °C, 100 °C and 150 °C. He found that emission increased substantially from 40 °C to 150 °C. Interestingly, he also found that some wood extractives act as formaldehyde scavengers.

The effect of temperatures of 23, 29 and 50 °C on FE and VOCs emission from laminate flooring type A (with PB as substrate) and type B (with HDF) was examined by Wiglusz *et al.,* (2002). At 23 and 29 °C, the measurements did not show any emissions of formaldehyde and very low emissions of VOCs. At a temperature of 50 °C, type A showed a high initial FE and VOCs, which decreased with time. The emission from type B was much lower. In conclusion, some laminate flooring may affect the chemical contamination of indoor air with the use of floor heating.

Kim and Kim (2005b) studied the effect of various temperatures room, 37 and 50 °C, on FE from floor materials, such as laminate and PLW–floorings, and furniture materials, such as MDF and PB veneered with decorative paper foil, by desiccator method. The initial FE of the laminate flooring and PLW–flooring was 1.44 and 0.63 mg/L, and for MDF and PB it was 4.73 and 4.95 mg/L, respectively. Floor materials were under E1 grade while furniture materials were under E2 grade in terms of FE. Because of the under heating system, the flooring materials were exposed to 37 and 50 °C, while the furniture materials mostly existed at room temperature. At 37 and 50 °C, the FE level of the flooring materials was already under 0.3 ppm (*F***** level by JIS A 1460 2001 application possibility without area limit) after 10 days and the emission had decreased further (0.03–0.10 mg/L) after 28 days. These levels are not injurious to the human body and will not cause sick house syndrome (SHS).

3.2.4 Effect of Edge Sealing on Formaldehyde Emission

To measure the formaldehyde surface emissions from PB and MDF with JIS A 1460 method, the edge of each sample was sealed with either parafilm, polyethylene wax or aluminum foil. To determine the effect of thickness, emissions from PB and MDF of 9, 12, 15, 18 and 20 mm thicknesses were measured by Kim *et al.*, (2006b). The difference between sealing methods was relatively small but the difference from unsealed was large, confirming the need for a test procedure incorporating edge sealing. The reduction rate of FE from PB and MDF was 50–80% for flooring materials and about 30% for furniture materials. The greater core porosity in PB than in MDF may have caused the large reduction of FE from the edge sealed samples. The amount of formaldehyde emitted from the edge was significantly higher in PB than in MDF. These results need to be considered when using the desiccator test to measure FE from flooring and furniture materials.

3.2.5 Effect of Adding Some chemical component to the Resin or Wood on Formaldehyde Emission

The effects of PLW on formaldehyde and volatile acetic acid emissions treated with borax and boric acid were investigated by Çolak and Çolakoğlu, 2004. The treated PLW samples were manufactured by using two different methods; each veneer was first impregnated by a dipping method before the first group of PLW was manufactured. The second group of PLW panels was produced by adding preservatives (borax, boric acid) into the glue mixture. Two types of UF and PF resins were used as adhesives. The emissions of formaldehyde of the PLW were measured by using desiccator method (JIS A 5908). The amount of acetic acid in distilled water taken from the desiccator was determined by using HPLC. The results revealed that boron compounds affected the emission values of panels differently. Borax showed decreasing effect on the FE, whereas boric acid showed increasing effect.

It was reported that by Nemli *et al.,* (2004) that, the impregnation of wood particles with 5% mimosa bark extract and brushing of it to board surfaces and edges significantly decreased the FE ($P < 0.001$). This may be due to polyphenolic extractives in the bark. Increasing board density from 0.60 to 0.70 g/cm^3 decreased the FE ($P < 0.01$). This is because of low porosity and difficult diffusion on the high board density. Longer press time caused an improvement in the FE of the PB ($P < 0.001$) as it would be expected. In addition, Nemli and Çolakoğlu (2005a) found that, the FE of PBs containing 50% mimosa bark particles decreased from 1.48 to 0.66 mg/100 g o.d. board. They reported that decrease in FE values in might be due to the high amounts of polyphenolic extractives in bark, especially tannin.

FEs from wood PBs bonded with pine and wattle tannin–based adhesives, using hardeners paraformaldehyde, hexamethylenetetramine and TN (tris(hydroxyl)nitromethan), were measured by the perforator method by Kim and Kim (2004). All PBs made using the wattle tannin systems with the three different hardeners were satisfied grade E1, while in the case of pine tannin only the use of the hexamine hardener led to grade E1 being satisfied. This tendency was attributed to the curing mechanism of the hardener, the reactivity of the tannin molecule toward formaldehyde and the fast reactivity toward formaldehyde of pine tannin, due to the inclusion of phloroglucinolic A–rings within its molecular structure. Hexamine was effective at reducing FE in tannin–based adhesives when used as the hardener. Being a more sensitive and advanced method, it was also used. The samples used for GC were gathered during the perforator method. The FE levels obtained from GC were similar to those obtained from the perforator method.

PB prepared by adding 12% total resin solids of adhesives composed of commercial pine tannin extract with paraformaldehyde, or glyoxal or pMDI respectively. The FE results found by Ballerini *et al.*, (2005) were, however, considerably lower than those observed for the tannin–formaldehyde system. Emission values from 95% Tannin + 5% paraformaldehyde, 88% Tannin + 12% glyoxal, 85% Tannin + 12% glyoxal + 3% triacetin and 70% Tannin + 21% pMDI + 9% glyoxal were 4.7, 0.6, 0.6 and 0.6 mg/100 g o.d. boards and the 0.6 mg/100 g o.d. board due to the formaldehyde generated just by the heating of wood, and are not due to the resin, as can be seen by the constant value regardless of changes in the proportion glyoxal that used as a hardener.

Kim and Kim (2005c) carried out an experiment to investigate the effect of adding PVAc, for reducing the FE level, on the adhesion properties of MF resin for fancy veneer and PLW in engineered flooring. To determine the level of FE, they used the desiccator method. The FE level decreased with increased additions of PVAc.

FEs from wood–based panels bonded with pine and wattle tannin–based adhesives, UF, MF, and co–polycondensed resin of MUF were measured by Eom *et al.*, (2005) using JIS A 1460 and EN 120. In FE, all particleboards made using the wattle tannin–based adhesive with three different hardeners, paraformaldehyde, hexamethylenetetramine, and tris(hydroxyl)nitromethan (TN), satisfied the requirements of grade E1. Only those made using the pine tannin–based adhesive with the hexamine as hardener met the grade E1 requirements. Hexamine was effective in reducing FE in tannin–based adhesives when used as the hardener. While the UF resin showed a desiccators value of 7.1 mg/L and a perforator value of 12.1 mg/100 g o.d. board, the MF resin exhibited a desiccator value of 0.6 mg/L and a perforator value of 2.9 mg/l00 g o.d board. According to the JIS and the EN, the FE level of the MDF panels made with UF resin in this study came under grade E2. The FE level was dramatically reduced by the addition of MF resin.

The desiccator and perforator methods produced proportionally equivalent results. GC, a more sensitive and advanced method, was also used. The samples for GC were gathered during the experiment involving the perforator method. The FCs measured by GC were directly proportional to the perforator values.

The FE values measured using the flask method (EN 717–3) of PLW panels produced with UF resin (U/F mol ratio: 1/1.74) was used as adhesive glue mixture containing borax were lower than those of control panels. The highest decrease (23%) was seen in PLW panels produced with adhesive containing borax of 10% by solid weight. However, when the quantity of borax added to the adhesive solution was increased from 5% to 10%, the FE did not decrease in the same rate (Çolakoğlu and Demirkir, 2006).

Also Eom *et al.,* (2006) investigated the effect of adding additive as tannin, rice husk and charcoal, for reducing the FE level, on the adhesion properties of UF resin for PB. They have controlled the hot–pressing time, temperature and pressure to determine the bonding strength and FE. Blends of various UF resin/additives (tannin, rice husk and charcoal) compositions were prepared. To determine and compare the effect of additives (tannin, rice husk and charcoal) content, 0, 5, 10 and 15%, by weight of UF resin, were used. NH_4Cl as hardener added. To determine the level of FE, we used the desiccator, perforator and 20 L–small chamber method. The FE level decreased with increased additions of additive (except rice husk). In addition, increased hot–pressing time decreased FE level. At a charcoal replacement ratio of only 15%, the FE level is under *F***** grade (emit < 0.3 mg/L). Furthermore, rice husk was poor in FE than tannin and charcoal.

Jin–shu *et al.,* (2006) found that, the components in waste tea leaves could react with formaldehyde to serve as a raw material in the production of low FE boards. In his study, waste tea leaves and UF adhesive were employed in the preparation of waste tea leaves PB (WTLB). An orthogonal experimental method was applied to investigate the effects of process parameters on FE of WTLB. The results indicated that, waste tea leaves had the ability to abate FE from boards.

Kim *et al.,* (2006c) investigated the effect of bio–scavengers on the FE of MF resins for engineered flooring. Four varieties of bio–scavengers, tannin powder, wheat flour, rice husk flour, and charcoal, were added to MF resin at 5 wt.–%. MF–charcoal was most effective in reducing FE because of its porous nature. Although the hydroxyl groups of the bio–scavengers were effective in reducing FE.

Lin *et al.,* (2006) reported that, when nano–SiO_2, using KH–550 silane as a coupling agent, was added to UF resin by discontinuous ultrasonic vibration, below 1.5%, the amount of free formaldehyde decreased. The performance indices of PLW, PB and MDF, hot–pressed by nano–

SiO_2 (1%)/UF resin (F/U molar ratio = 1.2), exceeded the requirements of the National Standard. Their free FE reached E1 grade.

Wang *et al.,* (2006) reported that, the FE from UF (molar ratio 1:3) and UF:MDI = 6:1 in the presence of NH_4Cl were 36.77 and 7.88 mg/100 g o.d. board, respectively, so the Commercial UF could be used to manufacture a UF–MDI adhesive PB, leading to low formaldehyde emissions that meet E1 grade requirements.

To reduce surface FE from PB made with a UF resin of this kind, manufacturers may include one or more additives to the resin such as catalysts (sodium chloride, sodium sulfate, ammonium sulfate), scavengers (low mole ratio urea solution), and/or wax emulsions (for moisture retention). The other UF resin was a methanol–UF resin that was used to produce approximately 48% of the reported volume of production. As for the straight polymer UF resin, surface FE may be reduced by use of the same additives mentioned above, as well as magnesium chloride–hexahydrate. The remaining 1% of reported production was manufactured with a blended PF–UF resin (CARB, 2007).

Volcanic pozzolan was added as a scavenger at the level of 1, 3, 5, and 10 wt.% of UF resin for PB manufacture for the purpose to reduce the FE by Kim *et al.,* (2007). Formaldehyde was determined by desiccator method. With increasing pozzolan content, the FE was decreased. Because pozzolan has a rough and irregular surface with porous form, it can be used as a scavenger for PBs at a content up to 10 wt.% without any detrimental effect on the physical and mechanical properties.

Uchiyama *et al.,* (2007) studied the effects of natural compounds (Urea, catechin and vanillin) on reducing FE from PLW. The micro–emission cell, with an internal volume of 35 ml, the maximum exposed test surface area of 177 cm^2 and an air purge flow rate of 50 ml/min, was used to measure specific emission rate (SER). In the case of no reducer treatment, FE from PLW was fast and SERs were 4.4 $mg/m^2.h$ at 30 °C and 15 $mg/m^2.h$ at 60 °C. When this PLW was treated with the natural compounds, the SERs of formaldehyde were decreased at all temperatures. In the case of urea treatment, the SERs of formaldehyde decreased to 0.30 $mg/m^2.h$ at 30 °C and 0.65 $mg/m^2.h$ at 60 °C. When the urea treatment was applied to the inside of kitchen cabinet (made from PLW), the concentration of formaldehyde was reduced substantially from 1600 to 130 $\mu g/m^3$. The reducing effect of formaldehyde continued during the observation period (6 months), with a mean concentration of 100 $\mu g/m^3$. Reducers in the PLW would react with released formaldehyde. Application of natural compounds such as urea, catechin and vanillin could provide a simple and effective approach for suppressing FE from PLW.

Despres *et al.*, (2008) prepared amino–resin precursors by the addition of a new, colorless, nonvolatile and nontoxic aldehyde, dimethoxyethanal (DME), to melamine or urea to give resins for boards that were able to harden, however they were underperforming because of the lower reactivity of DME in relation to formaldehyde. Melamine and urea reacts with one and two (melamine up to three) molecules of DME to form M–DME and U–DME (called DU), but the subsequent cross–linking reaction to form bridges does not occur unless the reaction is catalyzed during resin preparation by the addition of glyoxylic acid. Such bridges between two melamine molecules form only up to the formation of dimers and no more.

The use of glyoxylic acid during the reaction has allowed the formation of different oligomers formed by both aldol condensation and condensation of melamine and glyoxylic acid with two molecules of melamine to form dimers. These were observed by ^{13}C NMR and MALDI–TOF (matrix–assisted laser desorption/ionization mass spectroscopy). However, the addition of 20% pMDI was necessary to satisfy the relevant mechanical strength standards of panels prepared with these resins. pMDI contributed to cross–linking of M–DME and DU by its reaction to form urethane bridges according to reactions already described. FE was down to what would be expected obtained by just heating the wood chips in absence of adhesives. The panels emission was sufficiently low to even satisfy the most severe relevant *F***** JIS A 5908. These adhesives are colorless as MUF and UF resins.

For the purpose to investigate the characteristics on reduction of formaldehyde and TVOC emission from MDF as furniture materials with added volcanic pozzolan. Pozzolan was added as a scavenger to UF resin for MDF manufacture. Formaldehyde was determined by desiccator and 20 L small chamber methods as Korean standards method. Kim (2009a) founded that, with increasing pozzolan, FE was decreased. Because pozzolan has a rough and irregular surface with porous form, it can be used as a scavenger for MDFs by capturing and absorbing formaldehyde, thereby reducing the FE of the MDF during the manufacturing process. These results were confirmed by the reduced FEs of the MDF with increasing pozzolan content.

At the same manner, Kim (2009b) mad another objective to develop environment–friendly adhesives for face fancy veneer bonding of engineered flooring using the natural tannin form bark in the wood. The natural wattle tannin adhesive and tannin/PVAc hybrid adhesives were used to replace UF resin in the formaldehyde–based resin system in order to reduce FE from the adhesives used between PLWs and fancy veneers. The standard FE test (desiccator method) and FLEC were used. By desiccator method and FLEC, the FE level of each adhesive showed the similar tendency. All adhesives satisfied the E1 grade (below 1.5 mg/L) and E0 grade (below 0.5 mg/L) with UV coating.

Sensogut *et al.,* (2009) have studied the effects of borax pentahydrate edited to UF on the bonding characteristics and free FC. Additions of borax pentahydrate into the adhesive mixture statistically reduced the free FC.

Buyuksari *et al.,* (2010) investigated that, the addition of cone particle improved greatly reduced their FEs. Decrease in the FE of the panels containing the cone particles was attributed to high amount of phenolic extractives of the stone pinecones. The condensed tannin, due to its phenolic nature, can react with formaldehyde in the adhesive, even at normal temperatures. This results in lower FE from the panels containing the cone particles.

Amino resin precursors prepared by Despres *et al.,* (2010) by the addition of a new, colorless, non–volatile and non–toxic aldehyde, dimethoxyethanal (DME), to urea gave resins for boards that while able to harden were underperforming due to the lower reactivity of DME in relation to formaldehyde. Urea reacts with one and even two molecules of DME to form UDME and $U(DME)_2$ (called DU). In conclusion, the reaction of 20% pMDI with DU, a urea–DME resin precursor containing no formaldehyde, and where the aldehyde used is non–toxic and nonvolatile, allows the preparation of PBs of excellent properties and this at acceptably fast board pressing times. The panels prepared have very weak FE, only the proportion emitted in heating the wood chips and no formaldehyde emitted from the adhesive as no formaldehyde was used.

The effect of adding the powder of waste PET (polyethylene terephthalate) bottles and borax pentahydrate in equal amounts to the UF adhesive on the free FC was studied by Ozalp (2010). Experiments were conducted on three layered PLW of beech (*Fagus orientalis*) and poplar (*Populus x eureamericana*), which were produced using UF adhesive to which powdered PET bottle and borax pentahydrate were added in certain amounts. The free FC was measured according to EN 717–2. The obtained results were then compared. It can be seen that the addition of powdered PET bottle and borax pentahydrate to the adhesive mixture used on the PLW significantly reduced the free FC.

Cashew nut shell liquid (CNSL)–formaldehyde (CF) resin and CF/PVAc resin were applied for the maple face of the veneer bonding on PLW by Kim (2010) to discuss the reduction of FE from engineered flooring. The CF resin was used to replace UF resin in the formaldehyde–based resin system in order to reduce FE from the adhesives used between the PLWs and fancy veneers. For the CF/PVAc resins, 5, 10, 20 or 30% of PVAc was added to the CF resin. The CF/PVAc resins showed better bonding than the commercial natural tannin adhesive with a higher level of wood penetration. The standard FE test and a VOC analyzer were used to determine the formaldehyde and VOC emissions, respectively, from the engineered floorings.

The CF resin and CF/PVAc resin systems with UV coating satisfied the E1 and E0 grades of the Korean Standard.

3.2.6 Effect of Manufacturing Processes on Formaldehyde Emission

Groah *et al.,* (1984) and Grigoriou (1987) reported that, the FE decreased due to lamination of wood–based composite panel's surface with decorative vinyl film and melamine impregnated paper. Myers (1986a) wrote a paper review of the literature dealing with the many post–manufacture board treatments used to reduce FE from UF bonded boards. Such treatments have almost solely used one or more of five chemical or physical principles: 1) formaldehyde reaction with NH_3, 2) formaldehyde reaction with oxygenated sulfur compounds, 3) formaldehyde reaction with organic–NH functionality, 4) pH adjustment, and 5) physical barrier. He has categorized the available reports according to four primary board treatment methods that use the five principles in different ways. The four primary treatment methods are 1. Application of scavengers as solids or aqueous solutions. Ammonium bicarbonate and carbonate have been used as solid powders, while the solutions involved a variety of ammonium salts, ammonium and alkali metal salts with sulfur–containing anions, and urea and other compounds having –NH functionality; 2. Exposure to scavengers as gases. NH, is the primary reactant here, with minor effort using SO_2; 3. Application of coatings.

A variety of polymeric formulations have been examined as physical barriers, often supplemented by incorporating a scavenger such as urea; 4. Lamination with barrier materials. Barrier materials have included polymer films, metal films, and impregnated papers, the last also incorporating scavengers. Firm, detailed conclusions or recommendations about the effectiveness of these methods are difficult to make due to 1) lack of information, 2) the wide variety of materials and processes employed, and 3) the importance and variety of economic and processing considerations required in selecting among options for a manufacturing process. Clearly, however, each of the four treatment methods can achieve major reductions in initial FE; most reported improvements are by at least a factor of 2 and many exceed a factor of 10. Often, scavengers can supplement the barrier properties of coatings or laminates. There is a strong need for additional aging studies to verify the long–term reliability of these treatments. At present he suggest that impregnation of boards with aqueous solutions (method 1) is likely to be the most reliable because it should permit the use of a large scavenger excess and also allow neutralization of board acidity to reduce resin hydrolysis.

The effects of waiting time of alder (*Alnus glutinosa*) veneers before drying, on some properties of PLW including the FE, were investigated by Çolakoğlu *et al.,* (2002). There were no significant differences among the FE values of PLW as shown. It has been stated in the literature that the FE of PLW is related to acetyl groups in wood (Çolakoğlu *et al.,* 1998). Therefore, IR spectra of all test groups were obtained to determine the effects of waiting time of veneers before the drying process on acetyl groups. Then, the absorption bands of carboxyl group (≈ 740/cm) were compared. Similar spectra were obtained for each test group.

In addition, Nemli and Çolakoğlu (2005b) found that, the CPL (continuous press laminates) coated PB had lower FE value than those of melamine–impregnated paper and wood veneer coated panels. This may be due to more tight structure of the CPL.

Roffael *et al.,* (2007) reported that, the cold water extracts from pulps produced by the chemo–thermomechanical technique (CTMP process) contain higher amounts of formate and acetate ions compared to cold water extracts from pulps produced by the thermomechanical process (TMP process). The FE from CTMP is lower than that from TMP due to Cannizzaro reaction catalyzed by alkali. Moreover, binderless fiberboards from CTMP are significantly lower in the formaldehyde release compared to binderless boards from TMP. The use of MUF–resin increases the FE of the boards from TMP and CTMP. In addition, Roffael 2008 found that FE from binderless fiberboards by flask method after 24 h were 58.1 and 10.5 mg/100 g o.d. fibers with TMP and CTMP respectively.

Kim (2009c) assessed the reproducibility of testing FE behavior from wood flooring composites bonded by UF resin at various manufacturing steps for surface finishing materials. The surface adhesion step of laminate flooring for this research was divided into two steps; HDF only and HDF with LPMs (low–pressure melamine). In the case of engineered flooring, the manufacturing steps were divided into three steps; PLW only, fancy veneer bonded on PLW and UV coated on fancy veneer with PLW. FE decreased at the process of final surface finishing materials; LPMs were applied on the surface of HDF for laminate flooring. Although emissions increased when fancy veneer was bonded onto PLW in the case of engineered flooring, emission was dramatically reduced up to similar level with PLW only when final surface finishing; UV–curable coating was applied on fancy veneer. This study suggests that FE from floorings can be controlled at manufacturing steps for surface finishing.

Likewise Kim *et al.,* (2010) examined the FE behavior of MDF overlaid with three types of uncoated lignocellulosic surface materials (oak decorative veneer, LPM impregnated paper and high pressure melamine impregnated paper) and four types of coated surface materials (coated paper, two types of finishing foils, and PVC) using the FLEC method and a 20 L small chamber method. The uncoated lignocellulosic surface materials exhibited lower FE levels. Coated surface materials in the 20 L small chamber test reduced the FE. In the FLEC test, both the uncoated lignocellulosic surface materials and coated surface materials showed lower FE from MDF.

3.3 Determination of Formaldehyde

In the article of Li *et al.,* (2007) it was found that there were various methods for the determination of formaldehyde have been proposed. Of these, spectrophotometric methods have been widely used for the determination of formaldehyde. Most of these methods are based on the reaction of formaldehyde with organic reagents and/or inorganic reagents, such as Schiff's reagents, pararosaniline, *p*–phenylenediamine, Chromotropic acid, J acid, phenyl J acid, *p*–aminoazobenzene, brilliant cresyl blue–bromate, and malachite green–sulfite. However, some of the spectrophotometric methods are not sensitive enough and can be subject to numerous interferences from coexisting substances. HPLC with DNPH as a derivatization agent is the most frequently used method. Recently, HPLC system coupled with a diode array detector for formaldehyde determination after derivatization with ethyl 3–oxobutanoate. The limit of detection (LOD) was 0.024 μg/ml. HPLC procedures, however, require long analysis time, and are sometimes less sensitive.

There are many fluorescence methods used for the determination of formaldehyde. Among them, the fluorometric methods based on the Hantzsch reaction, which involve the cyclization of amine, aldehyde and β–diketone to form a dihydropyridine derivative, have been widely used for the detection of formaldehyde in aqueous solutions. Nash (1953) introduced a colorimetric method into analytical chemistry for HCHO; it was based on the Hantzsch reaction of formaldehyde with acetylacetone (*acac*) or 2,4–pentanedione in the presence of ammonia to form a yellow product of 3,5–diactyl–1,4–dihydrolutidine (DDL).

Later, it was found that, without any other changes, highly sensitive measurements could be made by fluorometry instead of spectrophotometry. Fluorescence detection allows the measurement of formaldehyde at the μg/l level. This reagent system results in less quantitative product for the determination of all of the aliphatic aldehydes except formaldehyde because of the mild reaction for analysis. The method however, is time–consuming and needs high temperature. In 1968, there were new reagents for the fluorometric detection of formaldehyde: 5,5–dimethyl–1,3–cyclohexanedione (dimedone) and 1,3–cyclohexanedione (CHD). Both of them offer excellent sensitivity at the detection of HCHO. However, their reactions require high temperature, and furthermore, CHD can suffer positive interference from H_2O_2.

A novel reagent, acetoacetanilide (AAA), was introduced by Li *et al.,* (2007) to the determination of formaldehyde based on Hantzsch reaction. A simple and highly sensitive fluorometric method was achieved by using AAA. The main advantages in the use of this reagent are: the reaction is carried out at room temperature without any heating system, the cyclization product based on Hantzsch reaction is soluble in water, and the product can be detected by spectrophotometry and fluorometry. The maximum absorption wavelength of the product occurs at 368 nm, and the maximum excitation and emission wavelengths are found at 370 and 470 nm, respectively. Several important experimental variables of the procedures were examined; particularly, the reaction temperature, reaction time, concentrations of reagents, and pH of the reagent solution were optimized for improving the detecting sensitivity. The calibration graph was linear in the range of 1×10^{-7}–1×10^{-6} M or much higher concentrations. The limit of detection (LOD), based on three times of the standard deviation of the reagent blank, was 2.0×10^{-8} M. The proposed method was applied to the determination of formaldehyde in environmental water samples. Many foreign species commonly existing in water samples did not interfere with the determination of formaldehyde in the proposed method.

Different analytical techniques for the quantification of formaldehyde are critically compared by Salthammer and Mentese (2008). It was found that the *acac* and DNPH method are in very good agreement for formaldehyde.

A significant improvement in the PTR–MS instrument sensitivity to formaldehyde was obtained by drying the air sample to a dew point of –30 °C using a cold trap to condense and freeze water vapor (Jobson and McCoskey, 2010). At warmer trap temperatures, there was significant uptake of formaldehyde and other water soluble organics, suggesting the presence of a quasiliquid layer on the ice surface. By removing water vapor to a low constant dew point, the PTR–MS can be operated at low *E/N* ratios, significantly increasing normalized sensitivities for all organics and removing their humidity dependence due to reactions with $H^+(H2O)_2$. At an *E/N* ratio of 80 Td, the formaldehyde normalized sensitivity was 25 Hz/ppbv per MHz H_3O^+ with an estimated detection limit of 78 pptv. Field testing demonstrated good agreement between HCHO measurements made at ambient humidity and corrected for water vapor effects compared to dehumidified sampling at –30 °C. Field testing also revealed that at an *E/N* ratio of 100 Td or lower there was a significant ion signal at *m/z* = 49, likely CH_3OOH. Sampling drying and operation at low *E/N* ratios enables sensitive measurements of HCHO and potentially CH_3OOH, both important tropospheric photoproducts.

3.4 Present–day Resin Technologies

In this Best Available Control Technology (BACT) assessment of present–day resin technologies, an evaluation of currently used and laboratory tested resins, and production processes that may be used to achieve the maximum feasible FE reductions from HWPW, PB, and MDF was conducted. Resin technologies can be applied to all three regulated products (HWPW, PB, and MDF), although adjustments in resins may be necessary to accommodate the different manufacturing processes. In addition, the assessment also considers the results of the CARB (2003) Survey, patent searches, a literature review, and consultations with resin suppliers, panel manufacturers, and academia. In this analysis, resin systems were evaluated in consideration of the need to meet selected structural properties.

3.4.1 Urea–formaldehyde Resins

Presently, UF resins are the most widely used adhesives in the manufacture of HWPW, PB, and MDF, which produces boards with the highest HCHO surface emissions (*i.e.,* ASTM E1333 values). The basic chemical reaction in UF resins involves bond formation between amine and hydroxyl groups on the resin components. New technologies seek to find alternative components that are able to form irreversible bonds with HCHO to reduce the amount of free HCHO that remains in the final product. To produce HWPW, PB, and MDF with a UF resin that would achieve lower FEs, manufacturers may choose to use resins with lower F:U mole ratios (*i.e.,* less than 1.0), add different amounts or mixtures of scavengers and hardeners, and/or apply decreased press times and temperatures (Wolcott *et al.,* 1996). Limited studies indicate the potential to meet the *F***** standards, but it is not clear as to how low an ASTM E1333 value can be achieved using a UF resin, as efforts made to date to lower surface FE from HWPW, PB, and MDF are not well documented in the open literature.

3.4.2 Melamine–urea–formaldehyde Resins

The most widely used approach for decreasing surface FEs from boards made with a UF resin is to lower the F:U mole ratio of the base resin. Presently, mole ratios are reported to range from 1.05 to 1.2, depending on the specific formulation of the resin (Baumann, 1997). However, when the F:U mole ratio is lowered below 1.0 (*i.e.,* more moles of urea than HCHO), adjustments must be made to the resin to moderate unwanted changes in the physical and structural properties of the board. The addition of melamine during resin synthesis is often used to improve the durability and stability of a board, and its addition can also decrease surface FEs by acting as cross–linking agent.

Relative to lowering FEs, Dunky (1995) developed a MUF resin using a very low mole ratio UF resin (F:U = 0.75 to 0.90) and adding 15 to 23% melamine by weight to achieve very low HCHO concentrations. With respect to HCHO content, the panels exhibited DIN EN 120 values less than 2.0 mg/100 g o.d. board (approximate ATSM E1333 value of 0.025 ppm). Akzo Nobel (2005 and 2006) is currently conducting laboratory trials on a MUF resin made with a low mole ratio UF resin (F:U = 1.05 to 1.15), melamine, and a catcher compound. The catcher is specifically formulated to decrease FEs from PB produced with the MUF resin. PB, ranging in thickness from 16 to 28 mm, has been produced at a press temperature of 185 °C and a 10.8 s/mm press time. While the resin system is still in laboratory trials, it has shown good success in terms of producing PB with low JIS A1460 values (less than 0.3 mg/L ≈ ASTM E1333 value of 0.04 ppm) and improving durability when applied at a 10% by weight resin dosage. This resin system has the potential to be used to make PB with very low FEs.

3.4.3 Melamine–formaldehyde Resins

Melamine–formaldehyde resins are excellent exterior wood adhesives because of their water resistance. Kim and Kim (2005a) conducted a range of FE tests (*i.e.*, EN 120 and JIS A 1460) on 8 mm MDF made from Korean pine (4% MC) and bonded with a MF resin. The resin had a F:M mole ratio of 1.75. Before the MDF was pressed, three–parts (to resin) of 25% ammonium chloride (hardener) and 13 parts of 44% wax solution (for waterproofing) were added to the base MF resin. The MDF made with the MF resin displayed a JIS A1460 value of 0.6 ppm and a DIN EN 120 value of 2.88 mg/100 g o.d. board, which complies with the Japanese *F****** and nearly the *F******* standard.

Pizzi *et al.,* (1996) examined the strength and FE properties of PB made under laboratory conditions with either a 0.5 or 1.1 mole ratio MF resin containing ammonium chloride (*i.e.,* 15–parts by weight of a 20% solution). Hexamine (*i.e.,* 38–parts by weight of a 40% solution) was added to the 0.5 mole ratio MF resin to determine if hexamine addition could compensate for the resin's lower melamine content. Observed differences in dry internal bond strength and DIN EN 120 results are shown in Table 6 for PB made with the two MF resins.

These results confirm that the addition of hexamine to a low mole ratio MF resin allows for the production of PB with similar internal bond strengths as PB made with higher mole ratio MF resins. In addition, the DIN EN 120 value of the PB made with the hexamine–hardened MF resin was approximately 50% lower than the value of the higher mole ratio MF resin without hexamine.

Overall, it appears that adding hexamine as a hardener to MF resins may be an effective way to lower FEs and maintain internal bond strength in PB. Further research is needed to identify the optimal amount of hexamine to add to MF resins for the manufacture of PB with acceptable internal bond strengths and low FEs. The findings from these studies demonstrate the potential for using MF resins to produce PB or MDF with low FE properties.

Table 6: Comparison of strength and formaldehyde emission properties of particleboard made with two melamine formaldehyde resins[a].

Resin or Particleboard Parameter	Resin	
	MF Alone	MF+Hexamine
MF Mole Ratio (Parts by Weight)	1.10 (174)	0.50 (154)
Dry Internal Bond Pressure (MPa)	0.77	0.65
DIN EN 120 (mg HCHO/100g o.d. board)	6.90	3.50

(a) Source: Pizzi *et al.*, 1996. DIN EN 120 refers to the European perforator test. The press time for PB made with either resin was 4–minutes.

3.4.4 Phenol–formaldehyde Resins

PF resins are commonly used in PB for exterior applications that must be durable under wet and/or humid conditions. They typically exhibit low FE rates (Battelle, 1996), and selected commercially available products would likely comply with the proposed Phase 2 standards that would take effect in 2011 to 2012.

Industry representatives have expressed concern over the longer press times and higher press temperatures required for producing products with PF versus UF resins, as these changes result in higher energy consumption and decreased productivity. However, recent studies have shown that adding compounds such as esters, lactones, or organic carbonates to PF resins can reduce cure times (Conner *et al.,* 2002; Lorenz and Conner, 2000; Pizzi *et al.,* 1997).

3.4.5 Methylene Diisocyanate (MDI) Resins

Since the 1970's, MDI has been increasingly used in the manufacture of MDF (Eckelman, 1997). As a non–polar, low viscosity liquid that wets the wood surface and penetrates deep into the wood structure, MDI resins penetrate further than PF resins, thus creating one of the most durable adhesive networks. While more expensive than any other resin discussed in this section, there are no FEs associated with its use, enabling PB and MDF made with this adhesive to meet the proposed Phase 2 standards that would take effect in 2011 to 2012.

A number of other properties that make MDI a desirable adhesive for composite wood products include: 1) Fast polymerization rate (making it suitable for use as core resin) and ability to form bonds with wood with a high moisture content, including green wood (Connor 2001 and Frihart, 2005); 2) Low volatility–less resin is used to manufacture products with comparable structural properties (Marra, 1992); and 3) Lower energy–related production costs due to the use of lower press temperatures, faster press cycles, and shorter drying times (Connor, 2001).

At the industrial–scale, research on isocyanates is presently focused on their use as a copolymerization agent in existing resins, which have led to the creation of hybrid resin systems (*i.e.,* UF–MDI, PF–MDI, PUF–MDI, PMUF–MDI, and PUFTMDI) that outperform traditional wood resins (Lei *et al.,* 2006).

3.4.6 Methylene Diisocyanate (MDI) Hybrid Resins

3.4.6.1 Urea–Formaldehyde–MDI (UF–MDI) Resins

CWPs made with UF resins are only used for interior applications because they have very low water resistance properties. However, researchers working with MDI hybrids have recently created an exterior–grade UF–MDI hybrid resin for use in a range of applications (Mansouri *et al.,* 2006).

By using a UF–MDI resin made by adding MDI (10 to 15% by weight) to a UF resin, the water resistance of PLW was substantially upgraded. Wieland *et al.,* (2006) found that adding ammonium sulfate (approximately 2% by weight) could further accelerate PLW curing times. In PW, the strength of the bond lines made with a UF/MDI hybrid resin are much improved relative to those made with a UF resin due to the greater number of urethane crosslinks that form between isocyanate and UF methylol groups.

Mansouri *et al.,* (2006) examined the changes to structural properties in PLW made with UF–MDI hybrid resins ranging from 5 to 15% MDI by weight. The test material was a three–layer beech veneer PLW bonded with a base UF resin (F:U mole ratio = 1.6 to 1.8) that was modified by the addition of ammonium sulfate (2% solution), wheat flour (30% by weight), and MDI. The results show that as the amount of MDI is increased, the boiling water performance of the PLW improved (*i.e.,* after 11–minutes the tensile strength of the control was four– to five–times lower than the PLW made with any of the UF–MDI hybrid resins).

While the selected measures of tensile strength were all improved by the addition of MDI to the UF resin, the extent of improvement is much greater when 10 to 15% MDI is added vs. only 5%. To produce PLW with exterior–grade properties using a UF resin, greater amounts of MDI would need to be added to achieve the required level of water resistance. Nevertheless, the tensile strength and water resistance properties of PLW made with a UF resin can be considerably improved by the addition of 10 to 15% MDI by weight.

3.4.6.2 Phenol–formaldehyde–MDI (PF–MDI) Resins

Phenol–formaldehyde and MDI resins have been used to manufacture PLW and OSB for exterior applications outside the U.S. because of their excellent water resistance. Presently, PF resins dominate the market for exterior and marine–grade PLW (Pizzi *et al.,* 1995); however, PF resins are less effective when used to bind wood veneers with high moisture contents. This limitation may be overcome by adding MDI to a PF resin (as in a PF–MDI hybrid), as it raises the moisture tolerance of the resin, promotes resin curing, and enables a stronger bond–line to develop between the PLW veneers.

When used alone, full curing of a MDI resin requires veneer moisture contents to be above 10% and curing time is not affected until the veneer moisture content is greater than 18% (Zheng, 2002). Compared to PF resins, MDI resins have a faster cure rate at lower press temperature and better resin network stability at lower adhesive spread levels (Conner, 2001), and are currently used in industrial applications to upgrade the performance of traditional wood resins (Lei *et al.,* 2006).

3.4.6.3 Phenol–urea–formaldehyde–MDI (PUF–MDI) Resins

Phenol–urea–formaldehyde (PUF) resins have been used for exterior applications since the early 1990's (Pizzi, 1994). To reduce resin cost, increasing amounts of urea have been added, which affects a number of structural properties in PB, especially water resistance (Osman *et al.,* 2005). To counterbalance the effects of urea, MDI can be added to improve the performance of the board and to accelerate the curing process.

Osman *et al.,* 2005 examined the properties of 16 mm PB made with four PUF resins, to evaluate the changes resulting from additions of MDI and urea. The control PUF resin had a solids content of 59% and contained approximately 40% U by weight. The test resins were PUF + 10% MDI, PUF + 10% MDI + 15% U, and PUF + 10% MDI + 20% urea.

With respect to resin viscosity, addition of MDI alone had no effect relative to the PUF control, but urea additions resulted in sizable reductions. While only minor changes were observed in PB density (*i.e.,* 1 to 2% higher than the PUF control), the addition of 10% MDI to the PUF resin dramatically increased the wet internal bond strength of PB compared to the PUF control, except with addition of 20% U. With further research, it is conceivable that a cost–competitive PUF–MDI hybrid resin may be developed to allow manufacturers to produce PB with the desired structural properties and low HCHO surface emissions.

3.4.6.4 Phenol–melamine–Urea–Formaldehyde–MDI (PMUF–MDI) Resins

PMUF resin is used to manufacture exterior–grade composite wood panels. The resin is made by co–reaction of a PMUF resin with 5 to 10% phenol (Cremonini *et al.,* 1996). Lei *et al.,* (2006) evaluated the effects of adding small increments of MDI to a PMUF resin on PB performance. The base PMUF resin had P:M:U:F mole ratio of 0.11 phenol, 0.33 melamine, 1.18 urea, and 2.15 formaldehyde, plus ammonium sulfate (3% by weight). Small additions of MDI did not appear to affect PB dry internal bond strength, as the value for PB made with 100% MDI was only 14% higher than for the PB made with 100% PMUF resin.

Far greater changes were observed in wet internal bond strength where additions of 5 or 10% MDI raised values by more than two fold (*i.e.,* 0.21 to 0.23 vs. 0.09 MPa). When the amount of MDI was 25% or more, wet internal bond strength was increased by four or five fold relative to the PMUF control. Densities of the PB ranged from 653 to 727 kg/m^3 in measurements made before or after the wet internal bond test.

While lower densities were measured in PB made with 85% or more MDI before the wet internal bond test, the reductions were not consistently observed after the wet internal bond test. At lower MDI additions (*i.e.,* 10 to 25%), PB density appeared to be consistently higher relative to PB made with the PMUF resin without added MDI. In conclusion, as for the other MDI hybrid resins discussed previously (*i.e.,* UF–MDI, PF–MDI, PUF–MDI) adding small amounts of MDI to a PMUF resin was also found to dramatically increase the performance of PB. For PMUF resins, the largest improvement was observed for wet internal bond strength, where additions of 5 to 10% MDI are likely to result in only a small increase in resin cost.

3.5 Formaldehyde Emission from Boards

As discussed above from the literatures, the FE from CWPs can be influenced by exogenous and endogenous factors. The exogenous factors include temperature, humidity, air movement over the panel surface, air change rate and the local formaldehyde concentration within the space where the material is placed.

The endogenous factors include the wood species, moisture content of the wood flakes, the type and the chemical composition of the adhesive binder used, the additives (*i.e.,* catalysts and formaldehyde scavengers) added, the arrangement of the multi–layer board, the surface treatment, the density of the board and the manufacturing conditions, (*i.e.,* temperature and duration of the hot pressing process). The chemical constitution of the binding resin has an important effect upon the formaldehyde release from the wood–based panel. For a particular, type of resin the molar ratio of F:U is an important variable. It has been shown that within a certain range of molar ratios there is an almost linear relationship between the molar ratio, the formaldehyde release (measured by the WKI flask method) and the extractable FC determined by the perforator test.

A decrease in the FC of the resin leads to a decrease in the FE rate of the finished product. Formaldehyde release was demonstrated to level off at a F:U molar ratio of about 0.95. The cross–linking of the resin during manufacture of board products is achieved by a combination of heat and hardener. Acids present in most wood can act as hardener but amounts are not sufficient to attain the required cross–linking of the urea formaldehyde resin. Catalysts such as ammonium chloride and/or ammonium sulphate are used, which will undergo hydrolysis in aqueous solution to produce acids to accelerate the condensation reaction. There is a small amount of free formaldehyde in the liquid resin (generally less than 0.1%) which is used during the cross–linking of the resin.

The free formaldehyde is present in various forms in the manufactured board. It can react with moisture present in the wood fiber to form methylene glycol, polymethylene glycol and polyoxymethylene hemiacetal etc.; it can also undergo labile binding to the wood fiber or to the polymer resin. This ’free formaldehyde’ will in time migrate and be released into the atmosphere, especially under high temperature and when exposed in a well–ventilated environment.

The FE of the CWPs is not limited to the emission of the free FC of the board. The release of formaldehyde can also come from the thermolysis of wood lignin and polysaccharides in the wood fiber, which will further contribute towards the FE from the manufactured board. The hydrolysis of the partially cured and cured resin will continuously produce formaldehyde that will be emitted. The hydrolysis is acid–base catalyzed and is influenced by temperature, the moisture content and the pH in the board.

Depending on the species, the wood particles can liberate acids under certain temperature and moisture conditions. These can cause a shift towards a lower pH, which may cause hydrolysis of the N–methylol group and to a lesser extent, the methylene ether linkages in the urea formaldehyde resin. The majority of the formaldehyde first emitted from a new wood–based board comes from the free formaldehyde present in the material. The emission typically declines exponentially until a steady–state level is reached. Initially the emission is dominated by the free formaldehyde present in the newly formed board and as the material ages, the bonded formaldehyde that is most susceptible to hydrolysis will make an increasing contribution to the emission.

3.6 Mechanism of The Aldehydes and Ketones from Wood

Mechanisms that may form aldehydes and ketones in extractives and wood products include thermal, enzymatic, and microbial degradation. Research conducted on the oxidative degradation of plant material has yielded some information about how certain types of aldehydes and ketones are formed. However, these mechanisms do not account for the variety of aldehydes and ketones observed in the wood product emissions and in some cases, the mechanisms occur under conditions that are distinctly different from wood products manufacturing conditions.

The presence of formaldehyde in emissions from wood that does not contain adhesive resin has been explained by thermal degradation of polysaccharides in the wood (Schäfer and Roffael, 1996), but this does not explain findings that show FEs from wood that had never been heated (Meyer and Boehme, 1997). In the work of Faix *et al.,* (1990 and 1991), pyrolysis of milled wood lignin at 450 °C yielded benzaldehyde and pyrolysis of spruce and pine wood at 450 °C generated formaldehyde, acetaldehyde, 2–propenal, butanal and butanone (methylethyl ketone MEK), which were attributed to the breakdown of the polysaccharide fraction of the wood. Conditions of pyrolysis are extreme and not oxidative, and during manufacture of wood products, only wood particles for PB are likely to be exposed to such extreme conditions and then only for a very brief time.

Enzymatic pathways for the oxidation of fatty acids to form hexanal and nonanal have been described for non–woody plants (Hamilton–Kemp and Andersen, 1986; Hatanaka *et al.*, 1976), but no such pathway has been described for other aldehydes. In short, although pathways exist for some of the aldehydes and ketones that are observed in wood product emissions, there are no mechanisms for other aldehydes (for example, pentanal, heptanal and octanal). With the exception of hexanal and nonanal, there is no explanation of how the aldehydes and ketones could be formed at room temperature or under the relatively mild conditions that are encountered in wood products manufacturing.

4. MATERIALS AND METHODS

Formaldehyde is considered a dangerous substance and its presence in the indoor environment is limited in many countries. As wood–based panels are possible sources of formaldehyde emission (*i.e.,* FE), during recent years a lot of work has been done to define analytical test methods in order to determine and limit the potential FE or formaldehyde content (*i.e.,* FC) of these materials. As national regulations were established in some countries limiting the formaldehyde release of wood–based panels, exports of boards, semi–manufactured, or finished products (furniture, etc.) are dependent on the ability to demonstrate conformity with the different national's rules. The standard method for measuring the FE from wood based panels is to use a test chamber. Three different sizes, ≥ 12 m^3, 1 m^3 and 0.225 m^3, are proposed in the new European standard (EN 717–1) for FE determination.

Products covered under the California air board resources (*i.e.,* CARB) certification scheme are hardwood plywood (*i.e.,* HWPW), medium density fiberboard (*i.e.,* MDF) and particleboard (*i.e.,* PB) manufactured in accordance with recognized national or international standards and which have FEs which meet the requirements of CARB and the applicable CARB limits like ASTM E1333–96 (ASTM, 2002b) and ASTM D 6007–02 (ASTM, 2002a) for MDF, PB and plywood (*i.e.,* PLW) and AS/NZS 4266.16 (2001) for MDF and PB.

As measuring the FE in a chamber takes time and requires specialized and expensive equipment, simpler laboratory methods which can be used for in homogeneous products to give results with good correlation to the chamber methods are needed, other methods like the perforator method (EN 120), gas analysis (EN 717–2) and flask method (EN 717–3) have been used.

4.1 Collection and Preparation of the Test Specimens

For wood–based composites, were chose MDF, PLW, HDF and PB with different edge thicknesses and different types as furniture material and construction purposes (uncoated and laminated boards). Currently, these are extensively used in new apartment interiors and in the remodeling market in the Czech Republic and other countries.

Samples in desired dimension shown in Table 7 with different thickness laminated or without lamination from large panels of different types of PB, MDF, high–density fiberboard (*i.e.,* HDF) and PLW, which bonded with formaldehyde–based resin adhesive, were collected from commercial plants in the Czech Republic wood producer's, were measured according to EN 717–2 and EN 120 by the cooperation with the laboratory of Timber Research and Development Institute, (VVÚD–Prague).

The largest samples were analyzed after one week open conditioning at 20 °C, 65% RH according to EN 717–1 which situated at the laboratory of Wood Processing Department (Faculty of Forestry and Wood Sciences, Czech University of Life Sciences) and the smaller samples were analyzed according to EN 717–1 small chamber at VVÚD. In addition, the FE was determined from some types of wood products according to CARB method, ASTM D 6007–02 (ASTM, 2002b) at VVÚD.

Table 7: The different types and thicknesses of composite wood products used to measure the formaldehyde release by gas analysis and perforator methods.

Board type	**PB**						**MDF**		**HDF**	**PLW**		
	P2			**PL**		**PV**	**MDF**	**MDFL**		**PLY**		**PLYs**
Thickness (mm)	12–18	8–10	19	8–22	19	8–24	3.2–18	2.5–19	3.2	8	15–25	15–21
N° of Samples	23	17	4	15	4	20	14	6	6	3	13	15

P2: boards for interior fitments (including furniture) for use in dry conditions (EN 312–2, 2003), PL: laminated particleboard, PV: Veneered Particleboard, MDF: general purpose boards for use in dry conditions, MDFL: laminated MDF, PLY: non–structural and interior applications plywood, PLYs: structural plywood. HDF: Uncoated high density fiberboard.

For the determination of the reproducibility within one lab, at least 3 specimens of each type from each product were used to measure the FE. Samples, cut to size and packed in plastic, were analyzed in different laboratories in the Czech Republic.

The emission of formaldehyde from P2 with 12 and 16 mm samples were analyzed by ASTM D 6007–02. The emission from PLW with 8 mm was measured by EN 717–1 large chamber.

4.1.1 Determination of Formaldehyde Emission from Different Types of Wood Flooring

Different types of wood flooring like laminated flooring, multilayer wood flooring, flooring panel PVC/HDF and Floor panel PVC were measured for their FE using EN 717–1 small–scale chamber.

4.2 Determination of Formaldehyde Emission with European Standard Test Methods

In wood industry, formaldehyde is one of the main ingredients for making amino and phenol formaldehyde resin and at the same time, it is the main suspect. It is very difficult to consume the last traces of formaldehyde during resin manufacturing and this un–reacted free formaldehyde gas comes out to the environment causing air pollution. Secondary after curing also, from amino resins, formaldehyde gas emits through bond hydrolysis.

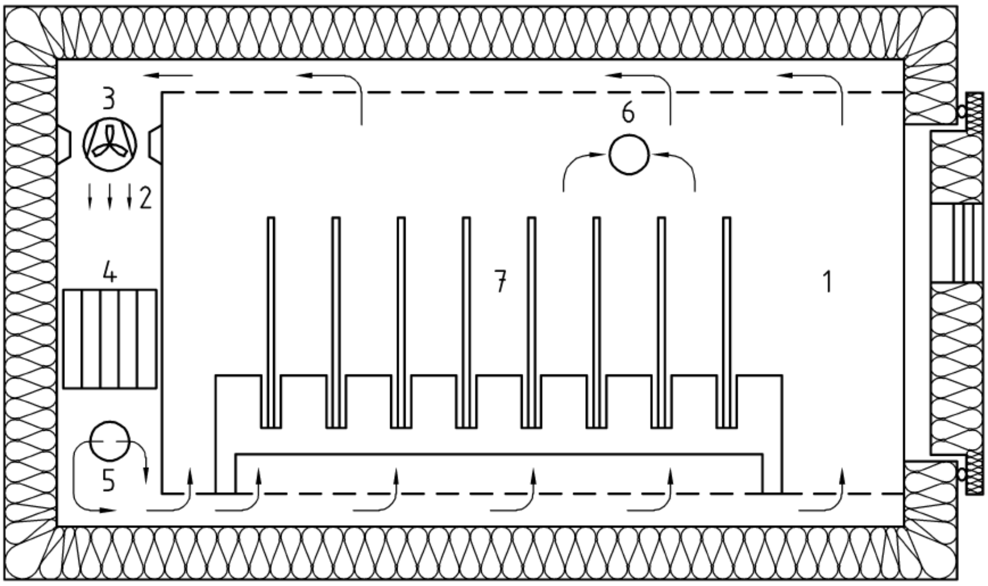
One can smell formaldehyde gas coming out of the panels used in indoor constructions like cabinets, wardrobes etc. Emissions occur during manufacturing of panels and subsequent uses of wood panel causing health hazard. Some of the main characteristics of the methods are given and they are also discussed in articles by Yu and Crump (1999) and Salem *et al.*, (2009).

4.2.1 Chamber Test Method (EN 717–1)

Test pieces of known surface area, are placed vertically and approximately in the center of the chambers with size 12 m^3 and 0.225 m^3, parallel to direction of the air flow, with their faces separated by a minimum distance of 200 mm for the large chamber (Figures 1A and 1B). The temperature, relative humidity, air velocity and exchange rate are controlled at defined values.

Formaldehyde emitted from the test pieces mixes with the air in the chamber. The air in the chamber is sampled periodically and the first air sampling was made after 3 h loading the chamber and starting the test procedure. The formaldehyde concentration is determined by drawing air from the chamber through gas washing bottles (impinger flasks) containing water, which absorbs the formaldehyde.

The concentration of formaldehyde in the chamber atmosphere is calculated from the concentration in the water in the gas washing bottles and the volume of the sampled air. It is expressed in mg/m^3 or ppm. Sampling is periodically continued until the formaldehyde concentration in the chamber has reached a steady–state. The conditions by European chamber method are showed on Table 8 (a and b).



1 Test chamber
2 Air inlet
3 Ventilation fan
4 Equipment, controlling temperature
5 Steam injection, controlling relative humidity
6 Air outlet
7 Test pieces

Figure 1A: The construction scheme for a large test chamber with parallel air flow.

Figure 1B: Example of loading the large test chamber with beech HWPW samples.

Table 8a: Determination of the formaldehyde emission with the European large chamber method.

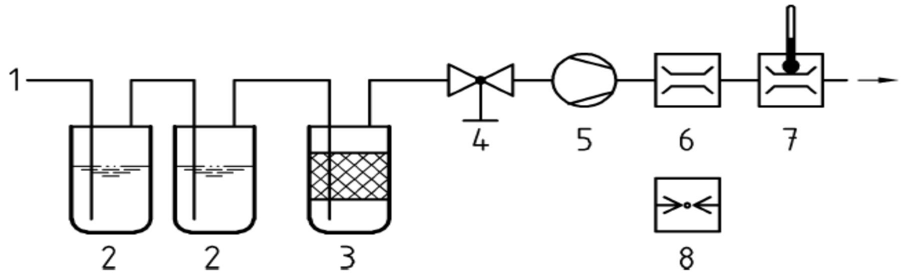
Method	**EN 717–1 (May 2004) – For wood–based panels**
Chamber material	Stainless Steel large chamber (Weiss Technik 12SD/15IU)
Chamber volume	12 m^3
Loading factor	1 m^2/m^3 for wood–based panels
Sample area	One board per 4 m^3
Test piece	1 m x 2 m x board thickness
Conditioning	One week open conditioning at 20 °C, 65% RH
Test duration	2–4 weeks
Temperature	23 ± 0.5 °C
Humidity	45 ± 3%
Air exchanges	1.0 ± 0.05/h
Air velocity	0.1–0.3 m/s
Results	Steady state emission in mg/m^3 rounded to the next 0.01 mg/m^3. Steady state is reached when the decline of the formaldehyde concentration is ≤ 5% over a testing time of 4 days
Determination limit	0.01 mg/m^3 (E1 class ≤ 0.1 ppm).

Table 8b: Determination of the formaldehyde emission with the European small chamber method.

Method	**EN 717–1 (May 2004) – For wood–based panels**
Chamber material	Stainless Steel small chamber.
Chamber volume	0.225 m^3
Loading factor	1 m^2/m^3 for wood–based panels and flooring
Sample area	Two pieces with a total area of 0.225 m^2 for panels and flooring
Edge sealing	The edges are partly sealed (1.5 m open edge/m²) for wood–based panels. All edges are sealed for flooring and only the front (2 pieces back to back) side is open. The cut ends are sealed for timber structures
Conditioning	No
Test duration	2–4 weeks
Temperature	23 ± 0.5 °C
Humidity	45 ± 3%
Air exchanges	1.0 ± 0.05/h
Air velocity	0.1–0.3 m/s
Results	Steady state emission value (mg/m^3) and test duration (hours)
Determination limit	0.01 mg/m^3 (E1 class ≤ 0.1 ppm)

4.2.1.1 Air Sampling and Analysis

At least 25 ml of water were added to each of the two gas washing bottles and connect them to the apparatus (Figure 2). The air from the chamber was sampled periodically by passing a minimum of 120 l, at a rate of approximately 2 l/min, through the gas washing bottles.



1	Sampling tube	5	Gas sampling pump
2	Gas washing bottles	6	Gas flow meter
3	Silica absorber	7	Gas meter with thermometer
4	Gas flow valve	8	Air pressure meter

Figure 2: The sampling system for the determination of formaldehyde concentration in air from the chamber.

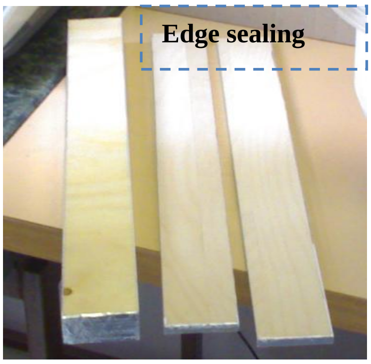
4.2.2 Gas Analysis Method (EN 717–2)

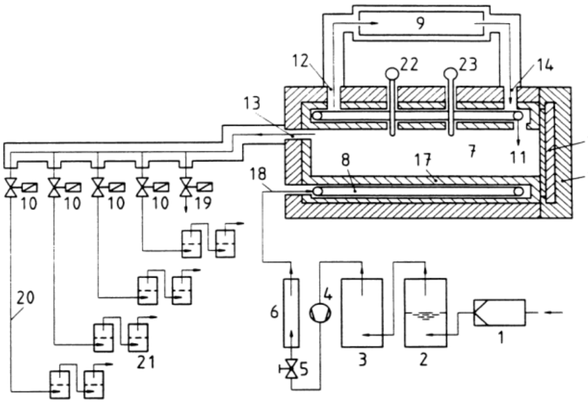
A test piece of known surface area with edge sealed is placed in a closed chamber (Figure 3) in which the temperature, RH, airflow and pressure are controlled to defined values. Formaldehyde released from the test piece mixes with the air in the chamber. This air is continually drawn from the chamber and passes through gas wash bottles, containing water, which absorbs the released formaldehyde. At the end of the test, the formaldehyde concentration is determined photometrically.

The formaldehyde release is calculated from this concentration, the sampling time and the exposed area of the test piece and is expressed in mg/m^2.h. The conditions used by the gas analysis method are showed on Table 9.

Table 9: Determination of formaldehyde emission by the gas analysis method.

Method	EN 717–2 (1994) – For wood–based panels
Chamber material	Glass
Chamber volume	4 L
Loading factor	0.4 x 0.05 m
Edge sealing	Yes
Test duration	4 hours
Temperature	(60 ± 0.5) °C
Humidity	≤ 3 %
Ventilation (air flow)	(60 ± 3) l/h
Results	Average emission during 4 hours from two samples expressed in mg HCHO/(m^2.h)
Emission Class	E1 ≤ 3.5 mg HCHO/(m^2.h)





1	Air filter	13	Outlet of test air
2	wash bottle	14	Heating medium (inlet)
3	Desiccator	15	Insulation
4	Air pump	16	Test chamber door
5	Needle valve	17	Double casing
6	Equipment for measurement of air flow	18	Inlet of air (heating coil)
7	Test chamber	19	Magnetic valve for purging
8	Heating coil	20	Connection tube
9	Thermostat	21	Pairs of wash bottles
10	Magnetic valves	22	Pressure monitor
11	Inlet of air (test chamber)	23	Temperature monitor
12	Heating medium (outlet)		

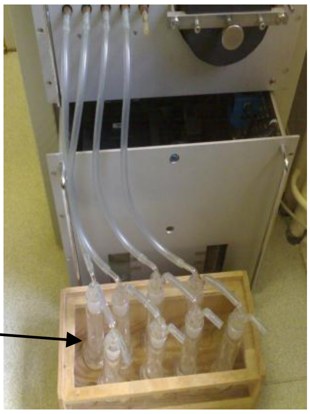


Figure 3: Scheme of gas analysis apparatus.

4.2.3 Perforator Method (EN 120)

The perforator method, describes determination of FC in wood based panels by extraction in a perforator. About 110 g of test pieces are weighted to an accuracy of 0.1 g and put into round bottom flask (Figure 4). 600 ml of pure toluene ($C_6H_5CH_3$) are added. Subsequently, the round bottom flask is connected to the perforator. About 1000 ml of distilled water is poured into the perforator attachment, leaving a space of 20 mm to 30 mm between the surface of the water and the siphon outlet. The condenser and the gas absorption equipment are then connected. The absorption bulb of the gas absorption equipment is filled with about 100 ml of distilled water and connected to the apparatus. When the apparatus has been assembled, the cooling water and heating are turned on.

The extraction is carried on for two hours, starting at the moment that the first bubbles pass through the filter insert. After these two hours, the heating is switched off and the gas absorption bulb is removed. The water contained in the perforator is, after cooling to room temperature, transferred into the volumetric flask by means of the stop cock.

The perforator is rinsed twice, each time with 200 ml of distilled water. The rinsing water is poured into the volumetric flask and the toluene discarded. The water contained in the absorption bulb of the gas absorption equipment is poured into the flask. The volume of the water contained in the flask is then made up to 2000 ml with distilled water. The extractions are carried out in duplicate. The FC of this aqueous solution is determined photometrically by acetylacetone (*acac*) method and expressed in weight mg/100 g o.d. board.

The conditions by the perforator method are showed on Table 10. The moisture content H (in mass % m/m) of the wood based panel is given by the following formula (EN 322, 1993):

$$H = \frac{m_1 - m_0}{m_0} \times 100$$

Where:

- m_1: is the mass of the test pieces before drying, in gm.
- m_0: is the mass of the test pieces after drying, in gm.

The EN 120 values for PBs and MDF with different moisture contents were corrected to boards conditioned to a moisture content H of 6.5%.

In the case of PBs (EN 312, 2003) with different moisture contents (in the range of $3\% \leq H \leq 10\%$), the EN 120 test value is multiplied by a factor F which is calculated from the equation:

$F = -0.133H + 1.86$

In the case of MDF (EN 622–1, 2003) with different moisture contents, the EN 120 test value is multiplied by a factor F that is calculated from the following equations:

- For MDF panels with moisture contents in the range of $4\% \leq H \leq 9\%$: $F = -0.133H + 1.86$
- For MDF panels with moisture contents $H < 4\%$ and $H > 9\%$: $F = 0.636 + 3.12e^{(-0.346\,H)}$

Table 10: Determination of formaldehyde content by the perforator method.

Method	**EN 120 (1992) – For wood–based panels**
Loading factor	25 mm x 25 mm, 110 g
Sealing	No
Conditioning	The test pieces are conditioned to a constant mass at a temperature of (23 ± 1) °C and RH (45 ± 5)%
Test duration	2.5 hours
Temperature	Toluene extraction at 110 °C
Air exchanges	No
Results	Average emission expressed in mg HCHO/100 g o.d. board
Emission Class	E1 ≤ 8 mg HCHO/100 g o.d. board

Today perforator method is the most common laboratory method to worldwide, especially in manufacturing and quality control of welded wood products. The test is very sensitive to the moisture content in the material and in the toluene during the extraction of the free formaldehyde (Marutzky, 1989). Storage conditions and the species of wood (Romeis, 1989) can also affect the perforator value. The test is only suitable for uncoated PB and MDF and cannot be used to characterize emission or ageing of the material (Flentge and Meyer, 1990).

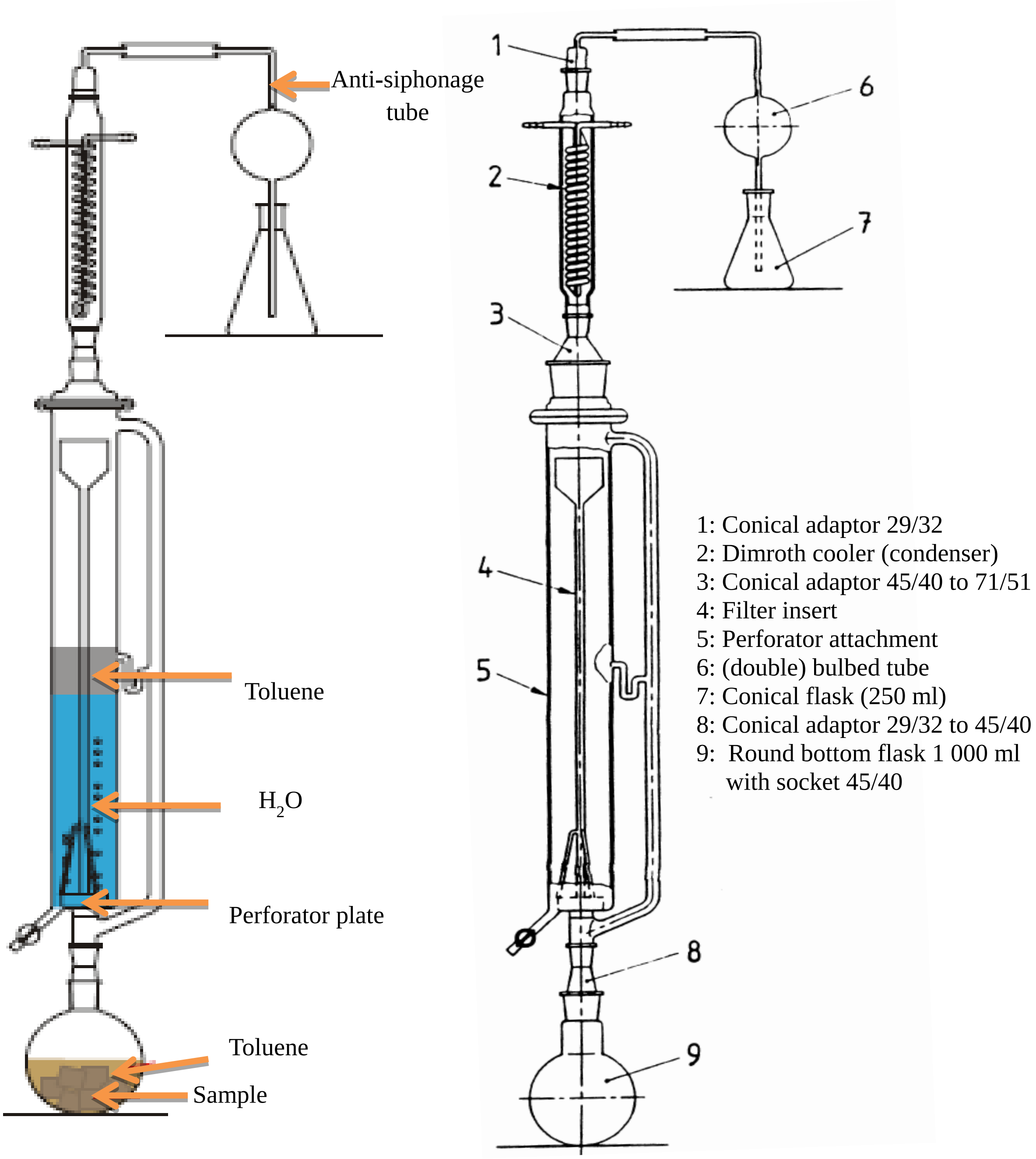


Figure 4: Extraction apparatus used for perforator method.

4.3 Determination of Formaldehyde Content of the Aqueous Solutions

The determination is based on the Hantzsch reaction (Nash, 1953) in which aqueous formaldehyde reacts with ammonium ions from ammonium acetate and acetylacetone (*i.e., acac*) shows in Figure 5 to yield 3,5–diacetyl–1,4–dihydrolutidine (*i.e.,* DDL). The reaction is highly specific to formaldehyde. Formaldehyde concentration was determined by reading the color of the DDL at 412 nm using a spectrophotometer.

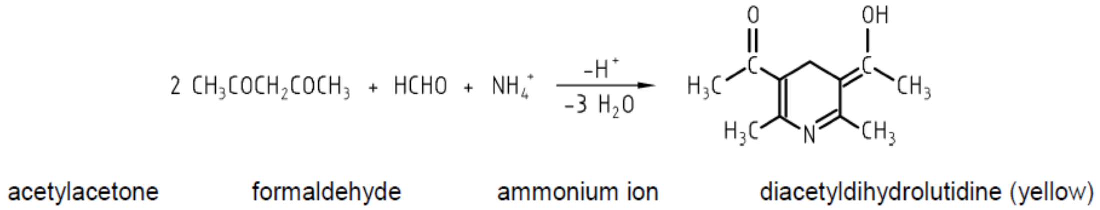


Figure 5: Reaction scheme of the acetylacetone method.

4.3.1 Reagents

- 4 ml *acac* are added to a 1 000 ml volumetric flask and made up to the mark with water.
- 200 g ammonium acetate are dissolved in water in a 1 000 ml volumetric flask and made up to the mark.

4.3.2 Procedure

According to EN 717–1, EN 717–2 and EN 120, 10 ml are taken from the aqueous solution is then added, using a precision burette, to 10 ml *acac* solution and 10 ml ammonium acetate solution in a 50 ml flask. The flask is Stoppard, shaken and warmed for 15 min in a water bath at 40 °C. The solution is cooled to room temperature protected against the influence of light for about 1 h.

The absorbance of this solution is determined at a wavelength of 412 nm against distilled water using a spectrophotometer (E spectrometer Unicam Helios) with a cell of 50 mm path–length for the EN 717–1 and EN 717–2 and 10 mm for EN 120. A blank value is determined in parallel, using a solution made up of 10 ml water, 10 ml *acac* solution and 10 ml ammonium acetate solution and is taken into consideration when calculating the FC of the sample solution.

4.4 Calibration Curve

The calibration curve is produced from a standard formaldehyde solution, the concentration of which has been determined by iodometric titration. The calibration was checked at least once a week.

4.4.1 Formaldehyde Standard Solution Reagents

4.4.1.1 Reagents

- Standard iodine solution $c(I_2)$ = 0.05 mol/1;
- Standard sodium thiosulfate solution $c(Na_2S_2O_3)$ 0.1 mol/1;
- Standard sodium hydroxide solution *c*(NaOH) = 1 mol/1;
- Standard sulfuric acid solution *c*(H2SO4) = 1 mol/1;
- Starch solution 1% *m/m*.

The solutions were standardized before use. About (1 g for EN 717–1 and EN 717–2 and 2.5 g for EN 120) formaldehyde solution (concentration 35% to 40%) is diluted in a 1 000 ml volumetric flask with distilled water and made up to the mark. The exact formaldehyde concentration of this solution is determined as follows: 20 ml of the formaldehyde standard solution is mixed with 25 ml iodine solution and 10 ml sodium hydroxide solution. After 15 min standing, protected from light, 15 ml of sulfuric acid solution is added.

The surplus iodine is back–titrated with the thiosulfate solution. At the end of the titration, some drops of starch solution are added as an indicator. A blank test with 20 ml distilled water is carried out in parallel. The FC is calculated as follows:

$c(HCHO) = (V\mathrm{o} - V) \times 15 \times c(Na_2S_2O_3) \times 1\,000/20$

Where:

- ***c*** (HCHO) is the formaldehyde concentration, in milligrams per liter;
- ***c*** $(Na_2S_2O_3)$ is the thiousulfate concentration in mols per liter;
- ***V*** is the volume of thiosulfate titration solution, in millimeters;
- ***Vo*** is the volume of thiosulfate titration solution for the blank, in milliliters.

4.4.2 Formaldehyde Calibration Solution

From the concentration value determined above we calculated the volume of the formaldehyde solution which contained about (3 mg for EN 717–1 and EN 717–2 and 15 mg for EN 120) formaldehyde and transferred this volume, using a microburette, to a 1000 ml volumetric flask and made up to the mark with water. 1 ml of this calibration solution contains about 3 μg formaldehyde for EN 717–1 and EN 717–2 and 15 μg formaldehyde for EN 120.

4.4.2.1 Determination of the Standard Curve

The 0 ml, 5 ml, 10 ml, 20 ml, 50 ml and 100 ml of formaldehyde calibration solution were pipetted into a 100 ml volumetric flask and made up to the mark with water. 10 ml of each dilution are analyzed photometrically by the same procedure as described in 4.2.4.2.

The absorbance values are plotted against the formaldehyde concentrations. The slope *f* of the graph is either determined graphically, or calculated.

Figure 6 shows an example value of the slope *f* (0.0024 mg/ml) measured for EN 717–1 from the standard formaldehyde curve and Figure 7 shows another example value of the slope *f* (0.0121 mg/ml) measured for EN 120 and EN 717–2.

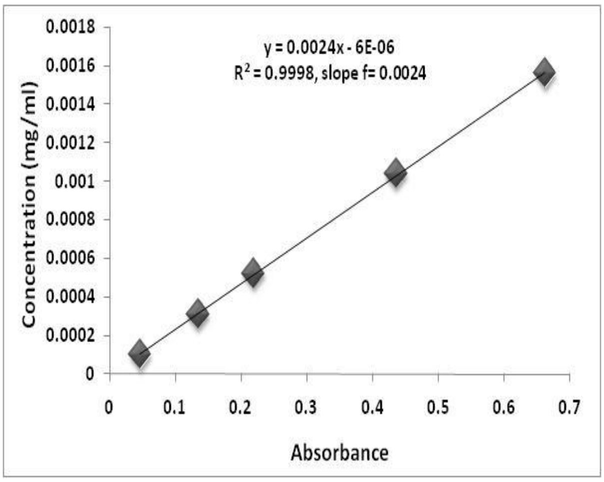


Figure 6: Example of calibration curve for formaldehyde determined by acetylacetone method (path length 50 mm).

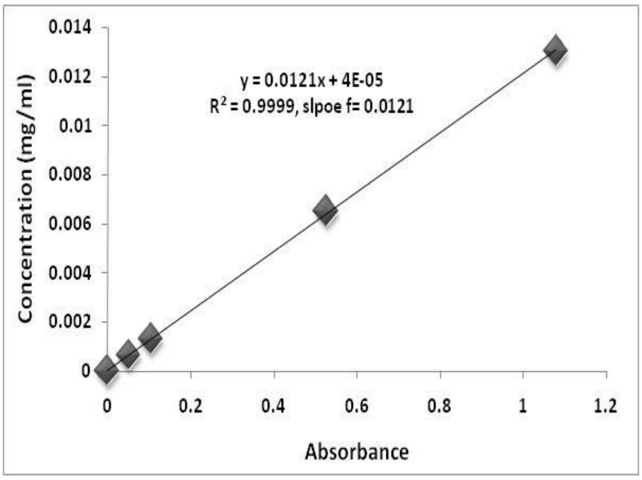


Figure 7: Example of calibration curve for formaldehyde determined by acetylacetone method (path length 10 mm).

4.5 Calculation of the Amount of Absorbed Formaldehyde

4.5.1 Chamber Value

The amount of formaldehyde absorbed in the water of the gas washing bottles is calculated by the following equation:

$$G = \left(A_s - A_b\right) \times f \times V_{sol}$$

Where:

- ***G*** is the amount of formaldehyde in each of the trapping solutions, in mg;
- ***As*** is the absorbance of the solution from the gas washing bottle;
- ***Ab*** is the absorbance of the blank value;
- ***f*** is the slope of the calibration curve for the standard formaldehyde solution, in mg/ml;
- ***Vsol*** is the volume of the trapping solution, in ml.

The values of *G* from both trapping solutions are added to give the total amount of formaldehyde *G*tot.

4.5.1.1 Calculation of Formaldehyde Emission

The FE from the wood–based panels being tested is expressed as the concentration in the air of the test chamber and is calculated by the following equation:

$$c = G_{tot} / V_{air}$$

- ➢ ***c*** is the formaldehyde concentration, in mg/m^3;
- ➢ $\boldsymbol{G_{tot}}$ is the total amount of formaldehyde trapped, in mg;
- ➢ $\boldsymbol{V_{air}}$ is the volume of the air sample, in m^3.

The volume of the sampled air was corrected to a standard temperature of 23 °C and a standard air pressure of 1 013 hPa.

4.5.2 Gas Analysis Value

From each 1 h, sampling period the gas analysis value *Gi* is determined and calculated by the following equation:

$$Gi = \frac{(A_S - A_B) \times f \times v}{F} [mg / m^2 h]$$

Where:

- ➢ ***Gi*** is the formaldehyde content of the solution from each hourly sample in mg divided by the area of the exposed, unsealed surface;
- ➢ ***i*** is the first, second, third or fourth hour;
- ➢ $\boldsymbol{A_S}$ is the absorbance of the solution from the wash bottles;
- ➢ $\boldsymbol{A_B}$ is the absorbance of distilled water;
- ➢ ***f*** is the slope of the calibration curve for standard formaldehyde solution, in mg/ml;
- ➢ ***F*** is the combined area of the emitting (unsealed) surfaces, in m^2;
- ➢ ***V*** is the volume of the volumetric flask, in ml.

4.5.2.1 Calculation of Results

As a rule the formaldehyde concentration of the liquid absorbent, taken during the first hour is lower than the content of the second hour, as the temperature of the test piece over the first hour does not reach 60 °C immediately. In this case, the gas analysis value is calculated from the sum of the contents for hours 2 to 4 and is related to the surface area (*F*) of the test piece. If the maximum of formaldehyde concentration is reached during the first hour, the sum of all four hourly–samples is used for the calculation.

Consequently, the average gas analysis value *G*m of a test piece is calculated according to the appropriate equation:

$$G_m = \frac{G_2 + G_3 + G_4}{3} \quad \text{or} \quad G_m = \frac{G_1 + G_2 + G_3 + G_4}{4}$$

Where:

- ***Gm*** is the average gas analysis value of test piece, in mg HCHO/m^2.h.

The gas analysis value of the board is calculated from the *G*m values of the test pieces.

4.5.3 Perforator Value

The FC, known as the "Perforator value" is expressed in mg formaldehyde/100g o.d. board, and is calculated by the following formula:

Perforator value= $\frac{(A_S - A_B)\times f \times (100 + H)\times V}{m_H}$ mg/100 g o.d. board.

Where:

- A_S is the absorbance of the analyzed extraction solution
- A_B is the absorbance of an analysis with distilled or demineralized water
- f is the slope of the standard curve (in mg/ml)
- H is the moisture content of the wood–based panel in percent
- m_H is the mass of the test pieces, in grams
- V is the volume of the volumetric flask (2000 ml)

The perforator value of a wood–based panel is considered to be the mean value of the results of the two or three extraction. Results expressed to one decimal place.

4.6 Determination of the Formaldehyde Concentration in Air from CWPs Using a Small Scale Chamber (ASTM D 6007–02)

4.6.1 Principles

This test method measures the formaldehyde concentrations in air from wood products under defined test conditions of temperature and RH. Results obtained from this small–scale chamber test method are intended to be comparable to results obtained testing larger product samples by the large chamber test method for wood products, Test Method ASTM E 1333. The results may be correlated to values obtained from the Method ASTM E 1333. The quantity of formaldehyde in an air sample from the small chamber is determined by a modification of NIOSH 3500 chromotropic acid test procedure.

4.6.2 Sample Material Handling and Specimen Conditioning

Formaldehyde concentration levels obtained by this small–scale method may differ from expected in full–scale indoor environments. Variations in product loading, temperature, relative humidity, and air exchange will affect formaldehyde emission rates and thus likely indoor air formaldehyde concentrations. This test method requires the use of a chamber of 0.02 to 1 m^3 in volume to evaluate the formaldehyde concentration in air using the following controlled conditions: conditioning of specimens prior to testing, exposed surface area of the specimens in the test chamber, test chamber temperature and relative humidity, the *Q/A* ratio, and air circulation within the chamber. The definitions of terms specific to this standard were shown in Table 11 used in standard face and back configuration and combination testing.

The *Q/A* ratios shown in Table 12 are used for testing wood panel products containing formaldehyde. Each small chamber will have a unique value for the make–up air flow (*Q*) dependent on the sample surface area used, and the type of product tested.

Table 11: Operating parameters specified for Berkeley Analytical Associates (BAA) small–scale chambers as specified by ASTM Method D 6007–2. Values are show for each of two product categories: PB and HWPW combined, and MDF.

Parameter	Units	PB & HWPW	MDF
Chamber volume (V)	m^3	0.067	0.067
ACH (N)	h^{-1}	1.0	1.0
Inlet air flow (Q)	m^3/h	0.067	0.067
Loading (L)	m^2/m^3	0.85	0.52
Q/A or N/L	m/h	1.173	1.905
Emitting area (A)	m^2	0.057	0.035
X & Y Dimension	M	0.169	0.132

V—volume of closed system—the interior volume of the test chamber, m^3.
N—air change rate, (N is equal to *Q/V*)—the ratio of conditioned and filtered air that enters or is replaced in the small chamber in one hour divided by the interior volume of the small chamber, air changes per hour (ACH).
L—loading ratio,(*L* is equal to *A/V*) —the total exposed surface area, excluding panel edges, of the product being tested divided by the test chamber’s interior volume, m^2/m^3.
Q—make–up air flow — the quantity of conditioned and filtered air fed into the chamber per unit time, m^3/h.
N/L —ratio— (*N/L* is equivalent to *Q/A*) the ratio of air flow through the chamber to sample surface area, m/h, as follows: $N/L = \frac{Q/V}{A/V} = (Q/V)\times(V/A) = Q/A$

Table 12: Determining the Q/A ratios, ±2%.

ASTM E1333 Loading Ratio (m^2/m^3)	**ASTM D 6007–02 N/L or Q/A**	**Product Type**
0.95	0.526	HWPW wall paneling
0.43	1.173	PB flooring panels, industrial PB, industrial HWPW
0.26	1.905	MDF
0.13	3.846	PB door core

4.6.3 Conditioning

Condition test specimens with a minimum distance of 0.15 m between each specimen was done with controlling the temperature and RH. The formaldehyde concentration in the air within 0.3 m of where panels are conditioned was not more than 0.1 ppm during the conditioning period.

4.6.4 Procedure

4.6.4.1 Test Procedure for Materials

The chamber was purged by running empty or with the use of filters designed to reduce the formaldehyde background concentration in air, or both. The formaldehyde background concentration in air of the empty operating chamber was not exceeding 0.02 ppm. The chamber surfaces were cleaned with water when the formaldehyde background concentrations approached 0.02 ppm. The specimens were located in the chamber so that the conditioned air stream circulated over all panel surfaces. The chamber was operated at 25 ± 1 °C and 50 ± 4% RH. The temperature, RH, and barometric pressure were recorded during the testing period. The chamber test was conducted at a given *Q/A* ratio. The specimens were remained in the operating chamber until a steady state formaldehyde concentration is reached. The time was estimated using the following equation:

$$t = \frac{-1n(1 - Ct/Cs)V}{Q + KA}$$ Where:

- ***t*** time to any percent of Cs less than 100% (such as 99.9999999999, and so forth),
- ***C*t** concentration at time, *t*,
- ***C*s** steady state formaldehyde concentration,
- ***A*** product surface area, m^2,
- ***V*** chamber volume, m^3,
- ***K*** mass transfer coefficient, m/h, and
- **−1*n*** negative natural log.

4.6.4.2 Air Sampling

The air sampling lines was purged for 1 min. At the sampling station, the air was bubbled through a single impinge containing 20 ml of a 1% sodium bisulfite ($NaHSO_3$) solution. A filter trap was placed between the impinger and the flowmeter. The calibrated flowmeter was set to maintain an average airflow of 1 ± 0.05 L/min for 30 min with time measured accurately to within 5 s. Specimens in chamber until they achieve steady state emission (estimate) or until back to back tests show no difference, considering accuracy of analytical method. Following air sampling, analyze the collection solution. Tables 13 and 14 showed the proposed conditions used for determination the FE from wood composite products. Figure 8 shows the scheme of the apparatus used by American small chamber method.

Table 13: Determination of formaldehyde emission according to the American small chamber method.

Method	**ASTM D 6007 – 02**
Chamber material	Stainless Steel
Chamber volume	0.225 and 1 m^3
Loading ratio	See table 14
Edge sealing	all edges normally sealed
Conditioning	1 week
Test duration	To steady state
Temperature	25 °C
Humidity	50%
Air exchanges	0.5/h
Result in	mg/m^3 or ppm
Determination limit	0.01 mg/m^3

Table 14: Loading ratio for different types of composite wood products according to ASTM D 6007–02.

Product	(m^2/m^3)
HWPW wall paneling	0.95
PB flooring materials	0.43
Industrial PB, Industrial HWPW, MDF	0.26

Figure 8: American small–scale chamber (1 m^3) used for determining formaldehyde concentration in air from wood products.

4.6.4.3 Analysis of Air Samples

4 ml of the $NaHSO_3$ solution was pipeted from the impinger into each of three 16 by 150–mm screwcap test tubes for triplicate analysis of each impinger sample. In parallel 4 ml of 1%, $NaHSO_3$ was pipeted into a 16 × 150–mm screwcap test tube to act as a reagent blank. A 0.1 ml of 1% chromotropic acid reagent was added to each test tube and shacked well after addition.

A 6.0 ml concentrated sulfuric acid (H_2SO_4) was pipeted slowly and carefully into each test tube and allowed to flow down the side of test tube. The color develops was let until turned to purple. The absorbance readings were analyzed in UV/vis spectrophotometer at wave length 580 nm.

4.6.4.3.1 Chromotropic Acid Method

In the presence of concentrated sulfuric acid, chromotropic acid (1,8–dihydroxynaphthalene–3,6–disulfonic acid) reacts with formaldehyde to give a red–violet hydroxydiphenylmethane derivative (see Figure 9). In the second step of the reaction, a violet quinoid oxidation product is formed with atmospheric oxygen. The concentrated sulfuric acid is a catalyst for dehydration and oxidation. The absorption maximum at 580 nm is used for UV/vis detection. The reaction is specific for formaldehyde when the pH value is < 1.0.

Nevertheless, the method has been standardized in the USA by National Institute for Occupational Safety and Health (NIOSH) and is used for the determination of formaldehyde in large–scale chambers, in small–scale chambers, and in the desiccator method.

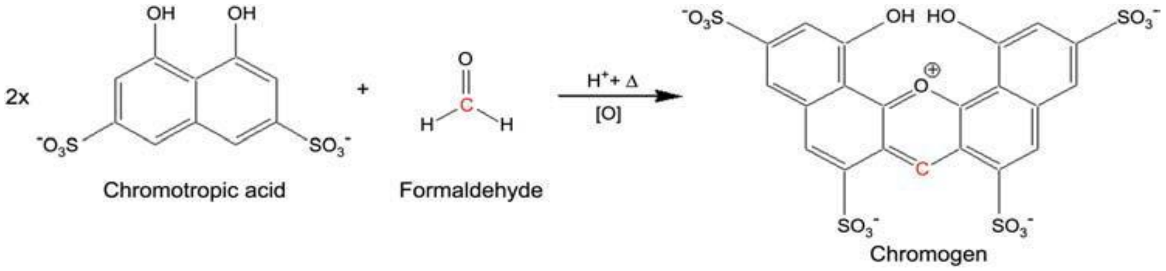


Figure 9: Reaction of chromotropic acid (1,8–dihydroxynaphthalene–3,6–disulfonic acid) with formaldehyde to form the active chromogen.

4.6.4.4 Calculation

Convert the volume of air sampled to the volume of air at standard conditions as follows:

$$Vs = \frac{V \times P \times 298}{101 \times (T + 273)}$$

Where:

- ***Vs*** volume of air at standard conditions (101 kPa and 298 K), L,
- ***V*** volume of air sampled, L,
- ***P*** barometric pressure, kPa, and
- ***T*** temperature of sample air, °C.

The total micrograms of formaldehyde collected were calculated in each impinger sample as follows:

$$Ct = Ca \times Fa$$

Where:

- ***Ct*** total formaldehyde in the sample, μg,
- ***Ca*** total quantity of formaldehyde in the sample aliquots taken from the impinger as determined from the calibration curve, μg, and
- ***Fa*** aliquot factor = sampling solution volume (mL)/aliquot used (mL)

The concentration of formaldehyde in air in the small chamber was calculated as follows:

$$Cs = \frac{Ct \times 24.47}{Vs \times 30.03}$$

Where:

- ***Cs*** parts of formaldehyde per million parts air, ppm,
- ***30.03*** molecular weight of formaldehyde, and
- ***24.47*** μL of formaldehyde gas in 1 μmol at 101 kPa and 298 K.

4.7 Converting Between Methods

PBs panels that were classified as uncoated (P2) and laminated (PL) with 16, 18 and 19 mm of thicknesses (Table 15) and fiberboard panels showed in Table 7 with 2.5, 18 and 19 mm (MDF laminated) and 3.2, 16 and 18 mm (MDF without lamination), were supplied from different plants in the Czech Republic. These samples were used to calculate and estimate the formaldehyde values extracted from the conversion factors equations.

The test samples from each type of panel were cut into 500 mm × 500 mm samples at the mill and then delivered to the laboratory. The delivered samples were wrapped with polyethylene film prior to further cutting into test specimens of size 25 mm × 25 mm (≈ 110 g) in order to measure the FC by EN 120. The samples wrapped in the film were kept in a humidity–controlled room at 20 °C and 65% relative humidity for one week.

Table 15: Number of specimens used for perforator and gas analysis tests according to the thickness of particleboards.

Board type	**P2**			**PL**		
Thickness (mm)	16	18	19	16	18	19
Number of samples	5	5	3	3	5	3

P2: boards for interior fitments (including furniture) for use in dry conditions.
PL: laminated particleboard.

4.7.1 Formaldehyde Release

FC of PBs and fiberboards were determined according to perforator methods as EN 120 standard. The perforator method is still a widespread method for production control.

Actually, the EN 717–1 and ASTM E 1333–96 are the reference methods for the evaluation of the FE. In these methods, samples were placed in a constant humidity chamber with controlling the temperature and air was continuously replaced. The test was completed once constant emission reached and this might take several weeks. The emission classes from PB and MDF panels measured by EN 717–1, ASTM E1333–96 and JIS A 1460 were shown in Table 2. The FE from PB and MDF were calculated according to the CARB (2007) new standards, the Phase 1 emission, 2009 was 0.18 ppm and Phase 2, 2011 was 0.09 ppm. For MDF, the Phase 1 was 0.21 ppm and Phase 2 was 0.11 ppm. A comparison of the test conditions and formaldehyde standards for PBs and in Europe vs. those in the U.S. that were shown in Table 16 (Analyscentrum, 2006; Groah *et al.,* 1991; Risholm–Sundman *et al.,* 2007).

Table 16: Test specifications in the European EN 717–1 and U.S. E1333 chamber–based tests for measuring the formaldehyde emission from particleboards.

Test Parameter	EN 717–1	ASTM E1333
Loading rate (m^2/m^3)	1.00	0.43
Min. chamber size (m^3)	0.225	22
Temperature (°C)	23 ± 1	25 ± 1
Relative humidity (RH %)	45 ± 5	50 ± 4
Air exchange rate (hr^{-1})	1 ± 0.1	0.5 ± 0.05
Edge sealing	Partial	None
Conditioning	None	One week ± 3 h
Test duration	2–4 weeks	16–20 h
HCHO emission limit	0.12 mg/m^3 (E1)	< 0.3 ppm

4.7.2 Conversion Factor Equations

In attempting to reconcile the relationship between measures of PB and MDF panel FC between Europe and Japan methods, Risholm–Sundman *et al.,* (2007) developed linear equations correlating the values of EN 717–1 and EN 120 tests to the JIS A1460 test. The equations developed and listed in Table 17 were used to develop the relationships between the EN 717–1 and EN 120 tests, for subsequent comparison with ASTM E 1333 test.

Table 17: Equations for comparing the formaldehyde test values measured by European, Japanese, and U.S. protocols.

For converting:	Equation
EN 120 → EN 717–1	0.012*[EN 120] + 0.005 = EN 717–1 (mg/m^3)
EN 120 → JIS A1460	0.0825*[EN 120] + 0.0816 = JIS A1460 (mg/L)
EN 717–1 → ASTM E1333	[EN 717–1]*0.98 = ASTM E1333 (ppm)
EN 717–1 → JIS A1460	6.8561*[EN 717–1] + 0.0463 = JIS A1460 (mg/L)

Note: The EN 717–1 standard is in mg m^{-3}. While a 20% adjustment could account for differences in edge sealing, etc., the units must then be converted to ppm by dividing the EN 717–1 concentration by 1.23 mg m^{-3} ppm^{-1}. Thus, the adjustment factor used above is 0.98 (= 1.2/1.23) (Groah *et al.,* 1991).

4.8 Study the Effect of Different Types of Formaldehyde–Based Resins on the Formaldehyde Release

Wood–based panels used in this case were PB, MDF and PLW, with thickness 12 (T12), 16 (T16) and 18 (T18) mm, were supplied from commercial plants in the Czech Republic. Samples of PBs with 500 mm × 500 mm were cut at the mill from three full–sized boards formatted with 2840 × 1830, 2750 × 1830 and 2810 × 1810 mm from each of T12, T16 and T18 for uncoated (P2), laminated (PL) and veneered (PV) PBs, respectively.

In addition, the uncoated MDF samples were cut from 2750 × 1840 mm boards for each T12, T16 and T18. The laminated MDF samples were taken from the boards with dimension 2750 × 1840 mm for T16 and T18 and from 2440 × 1220 mm for T12; these boards were laminated with high–pressure laminate.

The uncoated PLW samples used in interior application (PLY) were cut from each of three panels with dimension 250 × 125 cm of T12, T16, and T18. These panels were produced from beech veneers. Samples of PLW with T12 and T18 used in construction applications (PLYs) were cut from panels with 125 × 250 cm and produced from birch veneer and with T16, panels were produced from poplar veneer. The numbers of different types of PB, MDF and PLW samples for gas analysis and chamber tests were determined according to board thickness (Table 18).

All the samples were delivered to the laboratory of Timber Research and Development Institute (VVÚD) in Prague, Czech Republic. The delivered samples were wrapped with polyethylene film prior to further cutting into test specimens in order to measure the formaldehyde release with EN 717–1 and EN 717–2.

The uncoated PLW samples are conditioned for 4 weeks at 20 °C and 65% RH before measuring the formaldehyde release by EN 717–2 according to German Federal Health Office (BGA, 1977). Particleboards and MDF samples were analyzed directly after opening the polyethylene film and sealing the edges (Risholm–Sundman *et al.*, 2007). In parallel, two test pieces from each of thickness with a total surface area 0.225 m^2 were cut from 500 mm × 500 mm samples for formaldehyde measurement by EN 717–1.

The samples measured by European small chamber (EN 717–1) were not conditioned before the test.

The different types of PB and MDF are produced for many different purposes, especially for the production of furniture and internal equipment of interiors. MDF is produced from wood fiber (especially spruce), bonded together by MUF resin.

The three types of PB panels used in this study were bonded with a high quality wholesome UF resin. The veneered PBs are created by the European oak decorative veneer, which is pressed onto the board in both sides. PLY panels were bonded with MUF resin adhesive and PLYs panels were bonded with PF resin.

In order to achieve these aims, the formaldehyde values of different wood–based panels measured by gas analysis method were analyzed separately for each of PBs, MDF and PLW using the general linear model (GLM) procedure for a completely randomized design with;

1. Three PB types (P2, PL and PV) × 3 board thicknesses (T12, T16 and T18),
2. Two MDF type (uncoated and laminated MDF) × 3 board thicknesses (T12, T16 and T18) and
3. Two PB types (PLY and PLYs) × 3 board thicknesses (T12, T16 and T18). A two–factor analysis of variance (ANOVA) with different repetitions was utilized to assess which factors significantly influenced the FE (Steel and Torrie, 1989). Duncan's multiple–range test (1954)

was used to determine differences between the means ($\alpha = 0.05$). Formaldehyde values are reported as least square of means (LS Means) with 95% confidence intervals (95% CI).

For the comparisons between the formaldehyde values from PB, MDF and PLW panels bonded with different types of resins (MDF and PLY with MUF, PB with UF and PLYs with PF), the presented all values measured by EN 717–2 method were analyzed with the same statistical analysis as described above.

For more interpretation, linear correlations were applied to the gas analysis versus European small chamber values using the CORR option.

Table 18: Number of specimens used for gas analysis and chamber tests.

Wood product		**PB**			**MDF**		**PLW**	
Board type		P2	PL	PV	Uncoated MDF	Laminated MDF	PLY	PLYs
Thickness (mm)		12–18	12–18	12–18	12–18	12–18	12–18	12–18
Number of samples	**EN 717–2**	36	22	24	28	26	20	22
	EN 717–1	6	6	6	6	6	6	6

4.9 Inter–laboratory Comparison of Formaldehyde Release from Particleboards Using ASTM D 6007–02

The inter–laboratory comparison of the emission of formaldehyde from freshly produced PBs with 16 mm thick–E1, used for non–structural and interior application as furniture materials supplied from a commercial PB plant in the Czech Republic was performed by the American small–scale test chamber (ASTM D 6007–02) in two laboratories.

FE was measured from freshly produced PBs with 16 mm thick–E1 (May, 2010) bonded with MUF adhesive resin (Table 19). The boards were classified into two groups; the first group from 1–5 was PL and the second group from 6–10 was P2. The boards were manufactured in three layers with Norway spruce (*Picea abies* L.) particles (17.5% of fine particles for each face and back layer with 65% of coarse particles for the core layer).

The laminated boards were coated with melamine–impregnated decorative paper on both sides with grammage 80 g/m^2. The temperature, pressure and specific press time used to manufacture the boards were 195 °C, 3.43 MPa and 14 s/mm, respectively. For the melamine–impregnated papers, alpha cellulose decorative papers were impregnated with MUF adhesives (62% solid content). The press conditions for coating the melamine–impregnated decorative papers to the particleboard surfaces were 180 °C press temperature, 2.6 MPa pressure and 25 s press time.

The randomly selected panels (10 panels for each group) with nominal dimensions 2000 mm × 1100 mm × 16 mm, which computed the full number of samples, were wrapped with polyethylene film. The delivered panels were cut into test samples in order to measure the FE by ASTM D 6007–02. Nine samples, representing randomly distributed portions of an entire panel, were tested in three groups of three (Figure 10), resulting in three test results, which were averaged to represent one data point for the panel. The samples were edge–sealed with aluminum tape and conditioned at 23 °C ± 0.5 °C and 50% ± 5% relative humidity (RH) for 10 days before analysis.

Table 19: Properties and composition of melamine–urea–formaldehyde adhesive resin

Parameter	MUF[a]
Resin content (%)[b]	Face: 11, Core: 7
Solid resin content (%)	62
Melamine content (wt % to MUF resin)	4 (in powder form)
Viscosity (mPa.s at 20 °C)	150–600
pH at 20 °C	9.0–11
Density	1150–1250 kg/m³
wax (%)[c]	0.5
Hardener % (NH_4NO_3)[c]	3 (57% urea as solid content)
F/(M + U) molar ratio	1.1 (1.1:1)
Free formaldehyde	< 0.2%

[a] Letter M represents melamine, letter U represents urea and letter F represents formaldehyde.
[b] percent based on oven dry weight of wood particles.
[c] Percent based on solid content of MUF.

The experiment was performed in a 1 and 0.225 m^3 small–scale chamber system in laboratory 1 (Lab. 1) and 2 (Lab. 2), respectively. The dimensions of the test samples in the chambers were: 3 pieces of 220 mm × 220 mm and 3 pieces of 200 mm × 80 mm for Lab. 1 and Lab. 2, respectively. The differences between the two chambers and their experimental conditions were presented in Table 20.

The statistical analyses of the results was carried out employing a basic statistical procedure, which included the calculation of means, medians, minimum and maximum values, quartiles, standard deviations (SD), standard error of mean (SEM), variance and relative coefficient of variations (CV%). The test for data normality was done employing the normal Quantile plot. Also identification of outliers, defined as the values exceeding 1.5 times the interval between quartiles, *i.e.*, the interval between the 75% value and the 25% value were done. Moreover, the one– and two–way analysis of variance was done to investigate the significant effect of the laboratory and sample on the formaldehyde emitted from particleboards. All analyses were done using SAS software.

Where:

$\bar{X} = \sum_{1}^{n} x / n$ Mean (where n= test results per cell)

$S = \sqrt{\sum_{1}^{n} (x - \bar{x})^2 / (n-1)}$ Cell standard deviation

$CV\% = \frac{S}{\bar{X}} \times 100$ Coefficient of Variance

$SEM = \frac{S}{\sqrt{n}}$ Standard error of the cell means

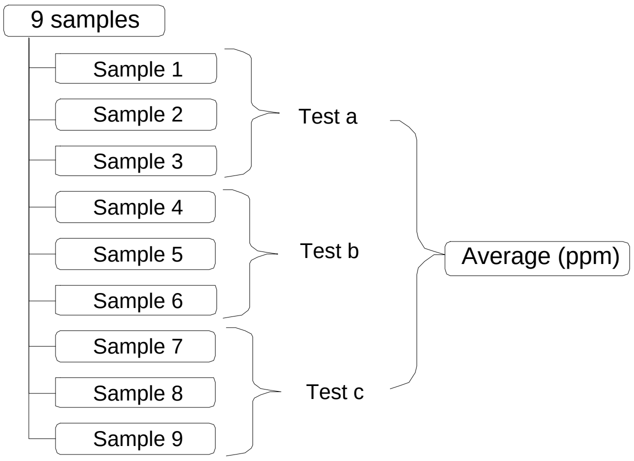


Figure 10: Schematic sampling and formaldehyde emission measurements from particleboard by small–scale chamber.

Table 20: Differences between ASTM D 6007–02 chambers and their experimental conditions.

Laboratory	Chambers				Conditions			
	V (m^3)	Wall material	*L* (m^2/m^3)	Fan speed (m/s)	Temp. (°C)	RH (%)	*N* (h^{-1})	*Q/A* (m/h)
1	1	Aluminum	0.43	(2–5)	24 ± 3	50 ± 5	2	4.651
2	0.225	Aluminum	0.43	(2–5)	25 ±1	50 ± 4	0.5016	1.167

For legend, see Table 11.

4.10 Statistical Design and Analysis

Data of FE were analyzed separately for each test method and type of wood product used in this study to measure FE. On the other hand, data analyses were performed with an SAS”8 software package (SAS, 2001) and STATISTICA”8 using the variables affected the FE from CWPs.

The significance of different variables was determined using the general linear model with the option PROC GLM procedure in the SAS software package, for a completely randomized design (CRD) with:

3 types of PBs (P2, PL and PV) × 3 thicknesses, 2 types of PLW (PLY and PLYs) × 3 thicknesses and 2 types of MDF (uncoated with 2.5, 18 and 19 mm thick and laminated with 3.2, 16 and 18 mm thick), in a factorial arrangement with different repetitions (Steel and Torrie, 1989). Means were tested for their significance using a least square means test (LS Means) with the statistical model:

$Y = \mu + A_i + B_j + A_i{}^{*}B_j + E_{ij}$, corresponding to a factorial design of two factors with i and j levels for each factor. Differences among means with $P < 0.05$, determined using a LS Means, were accepted as representing statistically significant differences and followed by Tukey–Kramer multiple comparisons (Kramer, 1956 and 1957).

The different between the means of board types and thicknesses were calculated using Duncan’s multiple–range test (Duncan, 1955).

Correlation among different methods was done by determination of Pearson's correlation coefficient (r) using the CORR option of SAS and the coefficient of determination (R^2) by extracting equations was applied for regression analysis. In addition, the multiple regressions used the ‘PROC STEPWISE’ procedure of SAS were done for more explanations.

5. RESULTS AND DISCUSSION

Various reconstituted wood panel products such as particleboard (*i.e.,* PB), plywood (*i.e.,* PLW), high density fiberboard (*i.e.,* HDF) and medium density fiberboard (*i.e.,* MDF), have become increasingly popular, and are being used for manufacturing furniture, cabinets, or various building products. These products are mainly bonded with formaldehyde–based resin adhesives such as urea formaldehyde (*i.e.,* UF), melamine urea formaldehyde (*i.e.,* MUF), phenol formaldehyde (*i.e.,* PF), etc. In particular, UF resin possesses some advantages such as fast curing, good performance in the panel, water solubility and lower price. In spite of these advantages, two main disadvantages of using UF resin were formaldehyde emission (*i.e.,* FE) from the panels and lower resistance to water. The FE of wood–based panel products has been received great attention from public as well as the wood industries since formaldehyde has been known as a toxic air contaminant.

FE was one of the most important aspects of UF resin in the last few decades. Amino resins such as UF resin, MUF resin, etc. are mainly responsible for the FE resulting from wood–based composite panels bonded with them. A few excellent reviews on this matter have been published (Meyer and Hermanns, 1985; Myers, 1984). The susceptibility of UF resins to hydrolysis explains the FE of UF resins (Dunky, 1998). The lack of water resistance of UF resin adhesives also limits the use of wood–based composite panels bonded with the UF resin adhesives to non–structural and interior applications.

5.1 Particleboard Panels

5.1.1 Gas Analysis and Perforator Values of Formaldehyde Release from Particleboards

The gas analysis and perforator values that were obtained for the three type boards examined from PB are shown in Table 21. Each value is the mean value from the tested boards. The gas analysis values ranged from 0.24–1.68, from 0.23–1.38 and 0.98–3.06 mg/m^2.h for P2, PL and PV, respectively. In comparison, the perforator values were ranged from 3.83–7.53 and from 4.19 to 8.3 mg/100 g o.d. board for P2 and PL, respectively. Most of the values met the E1 requirements.

The formaldehyde content (*i.e.,* FC) for 22 mm PL was 8.3 mg/100 g o.d. board by the perforator method and these were slightly over the E1 (≤ 8 mg/100 g o.d. board) grade. The sample used for this study emitted a lot of free formaldehyde as measured by EN 120.

Figure 11 shows the values of FC from different thicknesses of PB in comparable with the values of standard methods. Most of the values measured by EN 120 were under the standard limitation except from P2 19 mm, this sample was emitted a lot of free formaldehyde (9.93

mg/100 g o.d. board). In addition, the samples PL with 19 and 22 mm were slightly were over the E1–emission grade (8.08 and 8.3 mg/100 g o.d. board, respectively). On the other hand, all the values measured by EN 717–2 were under the E1–emission class (E1 ≤ 3.5 mg/m^2.h).

Table 21: Values of formaldehyde concentration from particleboard of different types and thicknesses.

Board type	**Thickness (mm)**									
	8	**10**	**12**	**13**	**15**	**16**	**18**	**19**	**22**	**24**
P2	0.46(a)	0.24	0.30	0.65	0.35	0.43	0.63	1.68	–	–
	–	–	(3.83)(b)	–	(4.55)	(5.21)	(7.53)	(9.93)	–	–
PL	0.23	0.28	–	–	–	0.33	0.50	0.84	1.38	–
	(4.19)	(5.23)	–	–	–	(5.75)	(7.41)	(8.08)	(8.30)	–
PV	0.96	–	0.98	–	–	–	1.19	2.52	–	3.06

(a): calculated gas analysis value (mg/m^2.h).
(b): values in brackets are the corrected perforator value (mg/100g o.d. board) at a moisture content of 6.5% (EN 312, 2003).
(–): data not available.

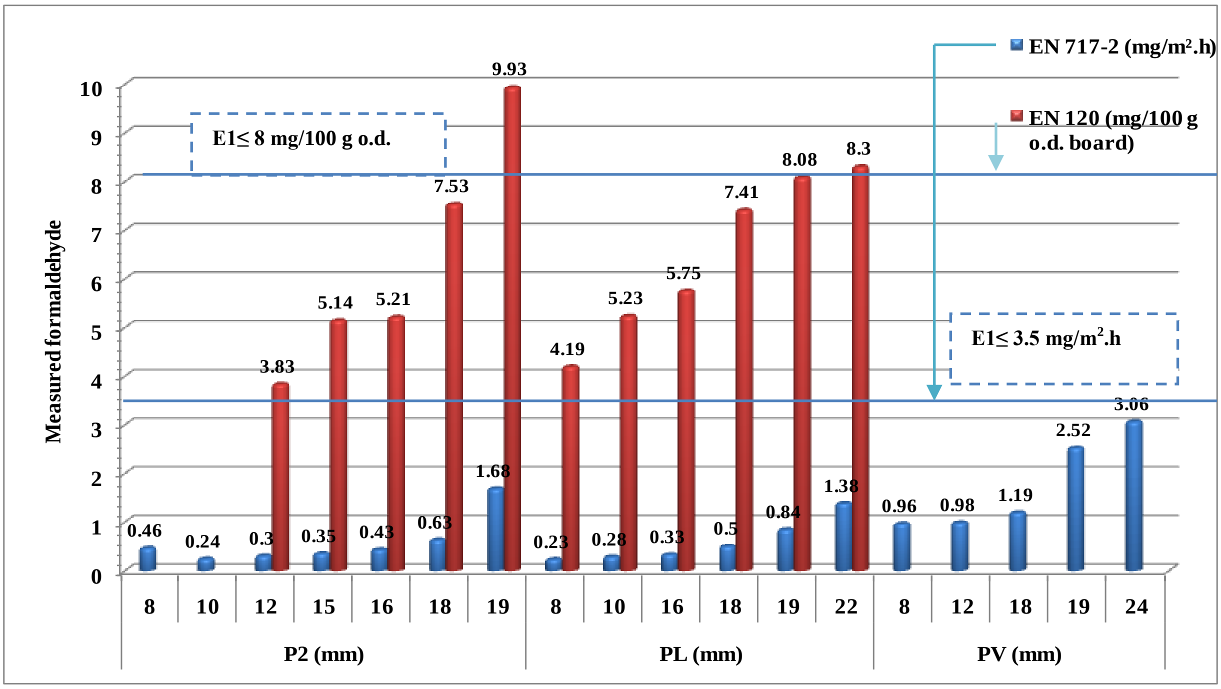
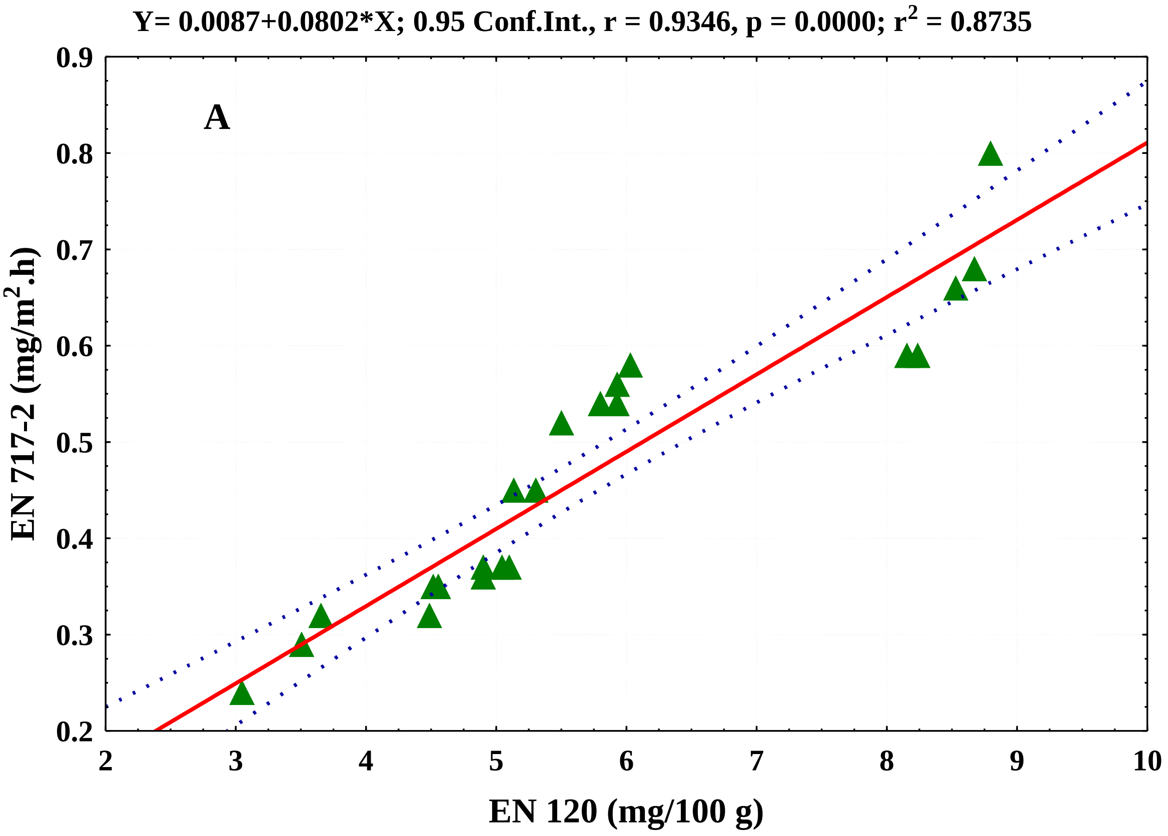


Figure 11: Values of formaldehyde release of particleboards measured by EN 120 and EN 717–2 in comparable with the standard limitation.

5.1.2 Relationship between Gas Analysis and Perforator Values of Formaldehyde from Particleboards

Figure 12 (A–B) shows a correlation between the gas analysis and the perforator methods for PB panels. Although some measurements were outside the 95% confidence interval of the linear regression, a positive good correlation with R^2 values of 0.87 and 0.88 was found between the gas analysis concentrations and the corresponding average perforator values from the P2 with 12–18 mm (Figure 12A) and P2 with 18 mm (Figure 12B).



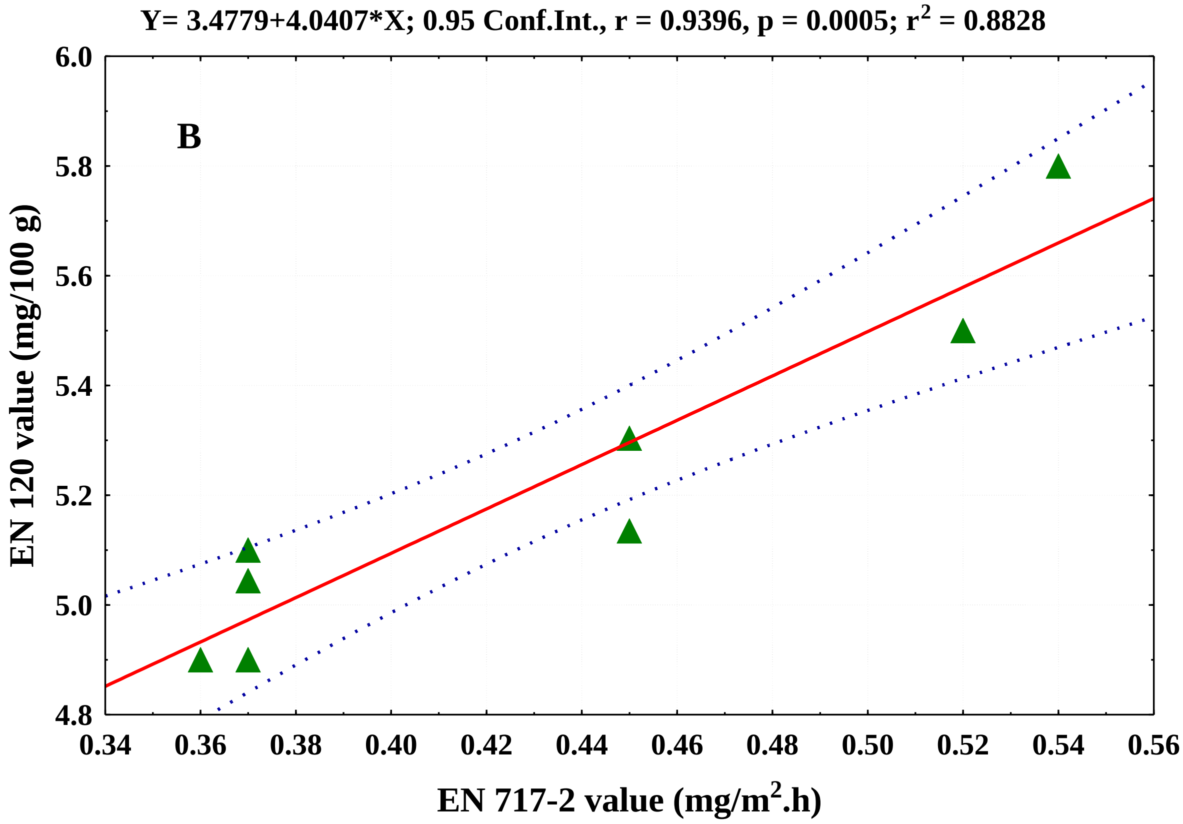


Figure 12: Correlation between EN 717–2 and EN 120 for particleboards P2, thickness 12–18 mm (A) and thickness 18 mm (B).

An empirical polynomial correlation between gas analysis and the perforator values for PL panels with 8–19 mm is presented in Figure 13. The observed correlation showed that, a good relationship between both methods with a positive R^2 0.97. Nearly no measurements were outside the 95% confidence interval of the polynomial regression.

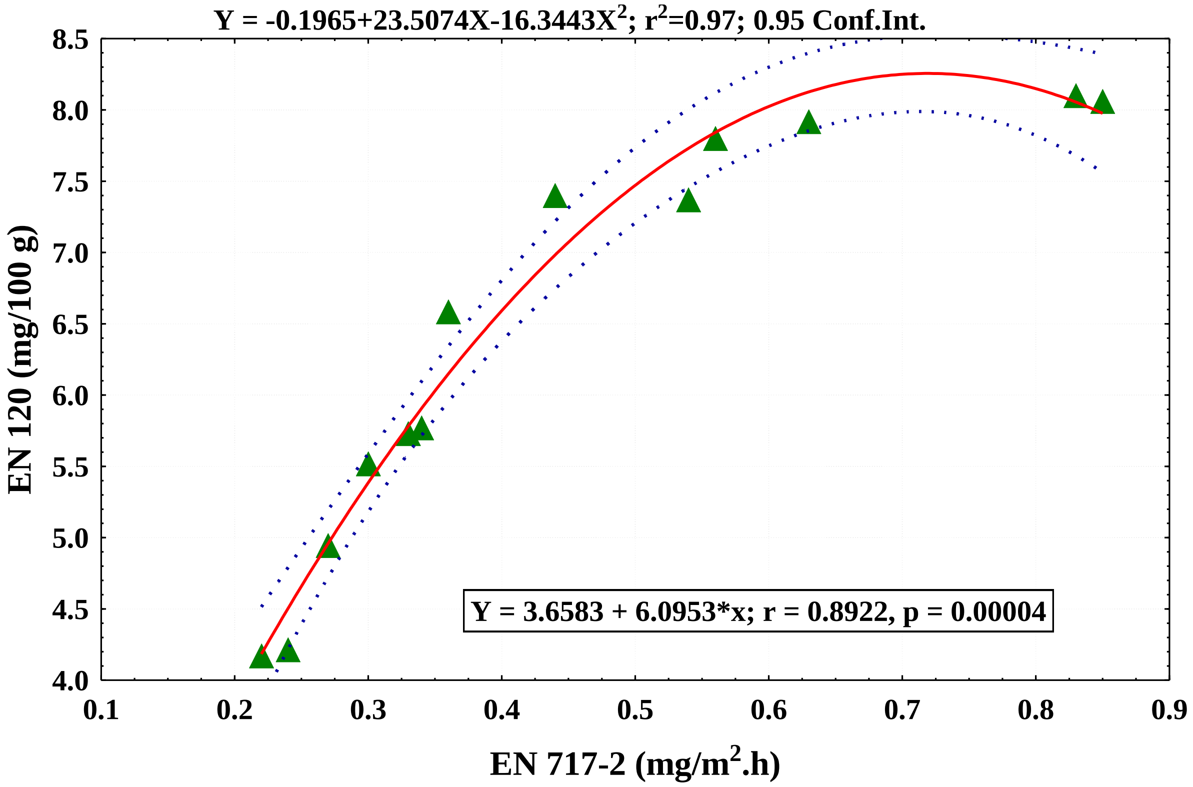


Figure 13: Correlation between EN 717–2 and EN 120 for particleboards PL, thickness 8–19 mm.

The FE values of PBs measured by the perforator method were about ten times in average greater than those from the gas analysis method. In other words, about 1 mg/100 g o.d. board level of the perforator measurement corresponded to about 0.1 $mg/m^2.h$ level of the gas analysis method, which gave a linear correlation. These differences could be attributed to an inherent difference between the two test methods. In other words, the perforator method measures the total extractable content of formaldehyde present in the 100 g o.d. board of the sample, while the gas analysis method measure the amount of formaldehyde emitted out of the sample panel surfaces with edge sealed. In spite of these differences between two methods, a strong positive correlation was found for PB panels as described above.

5.1.3 The Effect of Board Type and Thickness on Formaldehyde Emission from Particleboards

The GLM results related to the influences of PB type (P2, PL, and PV), thickness T1 (16 mm), T2 (18 mm) and T3 (19 mm) and the interaction between them on the FE values, determined by the gas analysis method, showed a highly significant effect. The analysis of variance (ANOVA) resulted in Table 22 showed that there are highly significant effects of board type and thickness ($P < 0.001$) and the interaction between them ($P < 0.001$) on the FE measured by EN 717–2. Furthermore, from Table 22 the FC was affected significantly only by the thickness ($P < 0.001$) as measured by EN 120 and there were no significant effect of board type (P2 and PL) ($P = 0.22$) or the interaction between the board type and thickness on the FC ($P = 0.09$).

Table 22: The ANOVA for the formaldehyde release of particleboards measured by EN 717–2 and EN 120 as affected by board type, thickness and the interaction between them.

Test	*S.O.V.*	*SS*	*DF*	*MS*	*F*	*Sig. Level*
EN 717–2	PB type	6.716217	2	3.35811	151.005	***
	Thickness	9.396459	2	4.69823	211.267	***
	PB type*Thickness	1.386278	4	0.34657	15.5840	***
	Error	0.934013	42	0.02224		
EN 120	PB type	1.080	1	1.08	1.5780	ns
	Thickness	46.52	2	23.26	33.994	***
	PB type*Thickness	3.622	2	1.811	2.6460	ns
	Error	14.369	21	0.684		

(*S.O.V.*) Source of variance. (***) very highly significant ($P < 0.001$), (ns) not significant ($P > 0.05$).
(EN 717–2) R^2= 0.95, *CV* (Coefficient of Variance) = 17.41% (EN 120) R^2= 0.78, *CV* = 11.97%.

It was statistically proven that the application of surface coatings helps significantly decrease the FE of the panels. Covering the PB surfaces helps to bring about low porosity and reduces the formaldehyde released from the surface of the panels. From Table 23 it was noticed that, by Duncan's multiple range test the FE was high affected by PVT3 (2.52 mg/m^2.h) followed by P2T3 (1.68 mg/m^2.h) and the FC was highly affect by P2T3 (9.93 mg/100 g o.d. board) followed by PLT3 (8.08 mg/100 g o.d. board).

It was found that from the studied boards, the veneered boards (1.55 mg/m^2.h) and the boards with T3 (1.68 mg/m^2.h) were emitted high amount of formaldehyde as a mean effect from the studied boards but under the E1–emission class. The FC from boards P2T3 and PLT3 were over the E1–emission class.

As a general, the amount of FE was found to be lower in the produced PBs. Formaldehyde is the chemical compound of UF adhesive. It is used to provide strong and durable bonds. For these reasons, decreasing the adhesive use ratio by decrease the thickness caused a significant reduction in FEs, as well as physical and mechanical properties. Similar results were reported by Nemli and Çolakoğlu (2005 a,b), and Myers (1984b).

From the previous results, it was concluded that the types and thickness from the studied PBs showed significant against the FE measured by EN 717–2. In the production of PBs, the best manufacturing variables should be determined for the PB produced from E1 type adhesive. The effects of these manufacturing variables on FE, bending strength, internal bonding strength and thickness swelling should be taken in considerations.

According to our results and the results from Nemli (2002), when the E1 type adhesive was employed, the use of 11% and 9% adhesive use ratios for the outer and middle layers, respectively, 200 °C press temperature, 150 s press time and 32.5 kg/cm^2 pressure were found to be enough. It was suggested that at 180 °C, the PBs required 150 s press time and 35 kg/cm^2 pressure. It was found that in the production of E1 type PB, the use of low emission adhesive was not enough, and all of the production parameters should be taken into account together. In addition, it was concluded that the amount of FE of manufactured PBs should be low. Equally, the PBs should meet the required physical and mechanical properties as stated in the relevant standards.

Table 23: Values of formaldehyde concentrations for different types and thicknesses of particleboard (8–19 mm) measured by EN 717–2 and EN 120.

Board type	**Thickness (mm)**			**Board mean**
	T1	**T2**	**T3**	
P2	0.460± 0.25^{e} (5.21± 0.31)^{c}	0.625± 0.08^{e} (7.53±1.31)^{b}	1.680± 0.02^{b} (9.93± 0.64)^{a}	0.92± 0.47^{B} (6.76± 1.83)^{A}
PV	0.960± 0.02^{d}	1.190± 0.02^{c}	2.520± 0.02^{a}	1.55± 0.72^{A}
PL	0.230± 0.01^{f} (5.75± 0.03)^{c}	0.506± 0.10^{e} (7.41± 0.52)^{b}	0.840± 0.03^{d} (8.08± 0.03)^{b}	0.52± 0.26^{C} (7.19± 0.94)^{A}
Thickness mean	0.55± 0.30^{C} (5.31± 0.35)^{C}	0.77± 0.28^{B} (7.48± 1.05)^{B}	1.68± 0.72^{A} (9.00± 1.13)^{A}	

Note: Different letters represent statistical differences between the averages of the values (Mean±SD).
Means with the same letter are not significantly different ($P < 0.05$) in accordance with Duncan's multiple range test. EN 120 values in parentheses.

Table 24 showed the significant effect of the interaction between board types and thicknesses on the FE measured by EN 717–2 using Tukey–Kramer multiple comparisons. It was found that most of boards had a highly significant effect on the FE.

Table 24: Comparisons between LS Means for the significant affect the particleboards on the formaldehyde emission measured by EN 717–2.

Board type	**P2T2**	**P2T3**	**P2T1**	**PLT2**	**PLT3**	**PLT1**	**PVT2**	**PVT3**
P2T3	***							
P2T1	ns	***						
PLT2	ns	***	ns					
PLT3	ns	***	***	*				
PLT1	**	***	ns	ns	***			
PVT2	***	***	***	***	*	***		
PVT3	***	***	***	***	***	***	***	
PVT1	*	***	***	***	ns	***	ns	***

(***) $P < 0.001$, (**), $P < 0.01$, (*) $P < 0.05$, (^{ns}) not significant ($P > 0.05$).
Adjustment for Tukey–Kramer Multiple Comparisons.

Although the effect of the interaction between the board type (P2 and PL) and the board thickness (T1, T2 and T3) was not significant on the FC measured by EN 120, there were some boards had a highly significant effect (*P* < 0.001). As shown in Table 25 the boards P2T1, P2T3, PLT2 and PLT3 had a highly significant effect on the FC.

Table 25: Comparisons between LS Means for the significant affect the particleboards on the formaldehyde content measured by EN 120.

Board type	P2T1	P2T2	P2T3	PLT1	PLT2
P2T2	***				
P2T3	***	**			
PLT1	ns	ns	***		
PLT2	***	ns	**	ns	
PLT3	***	ns	ns	ns	ns

For legend, see Table 24.

Figure 14 shows that the Board type (Figure 14A) and thickness (Figure 14B) had a highly significant effect (*P* < 0.001) on the FE measured by EN 717–2, according to LS Means. Clearly, the laminated boards emitted formaldehyde less than the uncoated boards, and an increase in thickness resulted in more emission of formaldehyde.

Moreover, the interaction between the board type and thickness had a highly significant effect on the emission of formaldehyde (Figure 14C). As a general rule, an increase in the thickness of uncoated boards leads to an increase in FE. The veneered boards emitted a high amount of formaldehyde more than the uncoated and laminated boards; it can be explained by using a high amount of UF adhesive to bond the veneer over the PBs.

The increase of covering the boards and the reduction of the thickness caused a significant improvement in FE. Therefore, the amount of FE was found to be lower in the produced PBs. On the other hand it was found that the FC measured by EN 120 from different types of PB was highly affected significantly only by increasing the board thickness (Figure 14E) and wasn’t affected significantly by board type (Figure 14D) or by the interaction between the board type and thickness (Figure 14F). On other meaning there was no significant difference between formaldehyde levels measured in the two types of PB within thicknesses (*P* = 0.09).

5.1.4 Chamber value

The chamber method was applied to measure the emission of formaldehyde from different types of PBs (P2, PL and PV) with thicknesses 12, 16 and 18 mm. The values ranged from 0.048 (PLT12) to 0.123 mg/m^3 (PVT18). All values shown in Table 26 measured below E1–emission class (E1 ≤ 0.124 mg/m^3).

Table 26: Values of formaldehyde emission of wood product (12–18 mm) measured by chamber method.

Wood product	Board type	Thickness (mm)		
		T12	T18	T18
PB	P2	0.074[a]	0.076	0.083
	PV	0.082	0.087	0.123
	PL	0.048	0.049	0.079

([a]) Values in mg/m^3 air

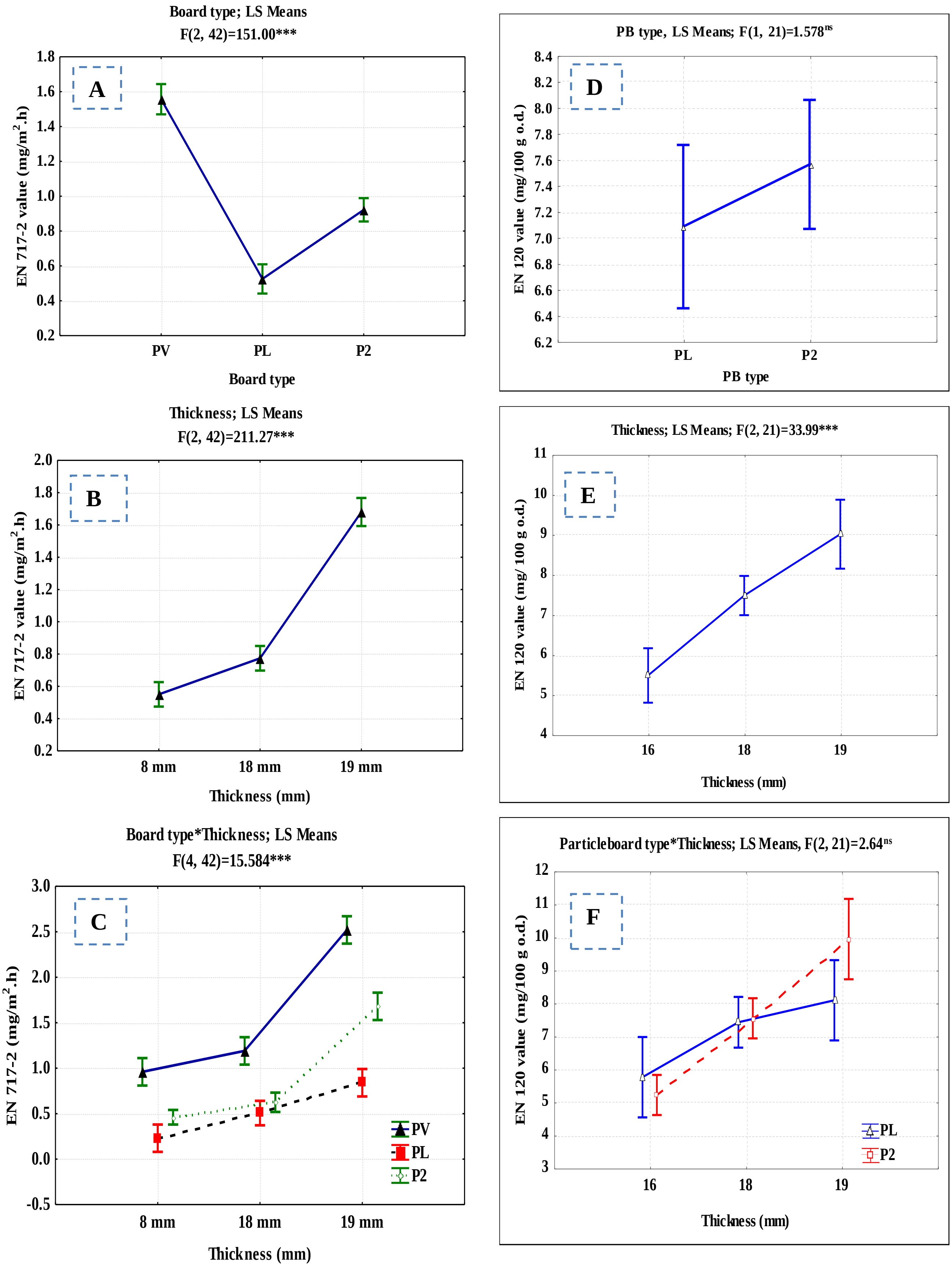


Figure 14: The effect of particleboard types (A,D), thicknesses (B,E) and the interaction between them (C,F) on the formaldehyde release measured by EN 717–2 and EN 120.

5.2 Fiberboard Panels

5.2.1 Gas Analysis and Perforator Values of Formaldehyde Release from Fiberboards

The gas analysis and perforator values shown in Table 27 were 0.38–0.71 mg/m^2.h and 5.03–7.36 mg/100 g o.d. board for the uncoated MDF and 0.3–0.61 mg/m^2.h and 4.25–6.83 mg/100 g o.d. board for the MDFL, respectively. According to both standards, the FE level for MDF and MDFL was at the E1–class emission. The perforator value for HDF with 3.2 mm was 0.95 mg/100 g o.d. board.

Figure 15 shows the values of FC from different thicknesses of two types of MDF in comparable with the values of EN 717–1 and EN 120 standard methods. All of the values measured by the two methods were under the standard limitations.

In spite of the FE values from the same boards being slightly different because of the difference in measuring methods, these two methods produced proportionally equivalent results from PB and MDF boards.

Table 27: Values of formaldehyde content from two types of medium density fiberboard of different types and thicknesses.

Board Type	**Thickness (mm)**				
	2.5	**3.2**	**16**	**18**	**19**
MDF	– –	0.38[a] (5.03)[b]	0.47 (6.38)	0.71 (7.36)	– –
MDFL	0.31 (4.68)	– –	– –	0.61 (6.83)	0.30 (4.25)

([a]) Calculated gas analysis value (mg/m^2.h).
([b]) Values in brackets are the corrected perforator value (mg/100 g o.d. board) at a moisture content of 6.5% (EN 312, 2003).
(–) Data not available.

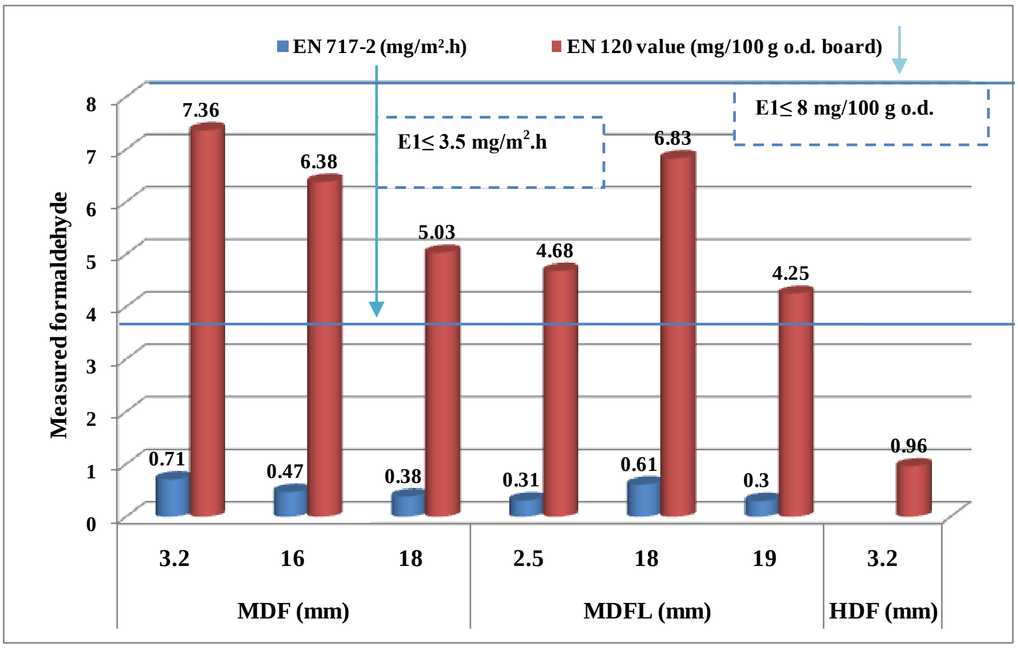


Figure 15: Values of formaldehyde release of fiberboards measured by EN 120 and EN 717–2 in comparable with the standard limitation.

5.2.2 Relationship between Gas Analysis and Perforator Values of Formaldehyde from Fiberboards.

The polynomial regression in Figure 16 for MDF without coating 3.2–18 mm shows a good positive correlation coefficient of 0.86 between the gas analysis and perforator values. Although the weight (100 g) of the wooden board is used in the perforator method, the dimensions of the wooden board are taken into consideration in the gas analysis method.

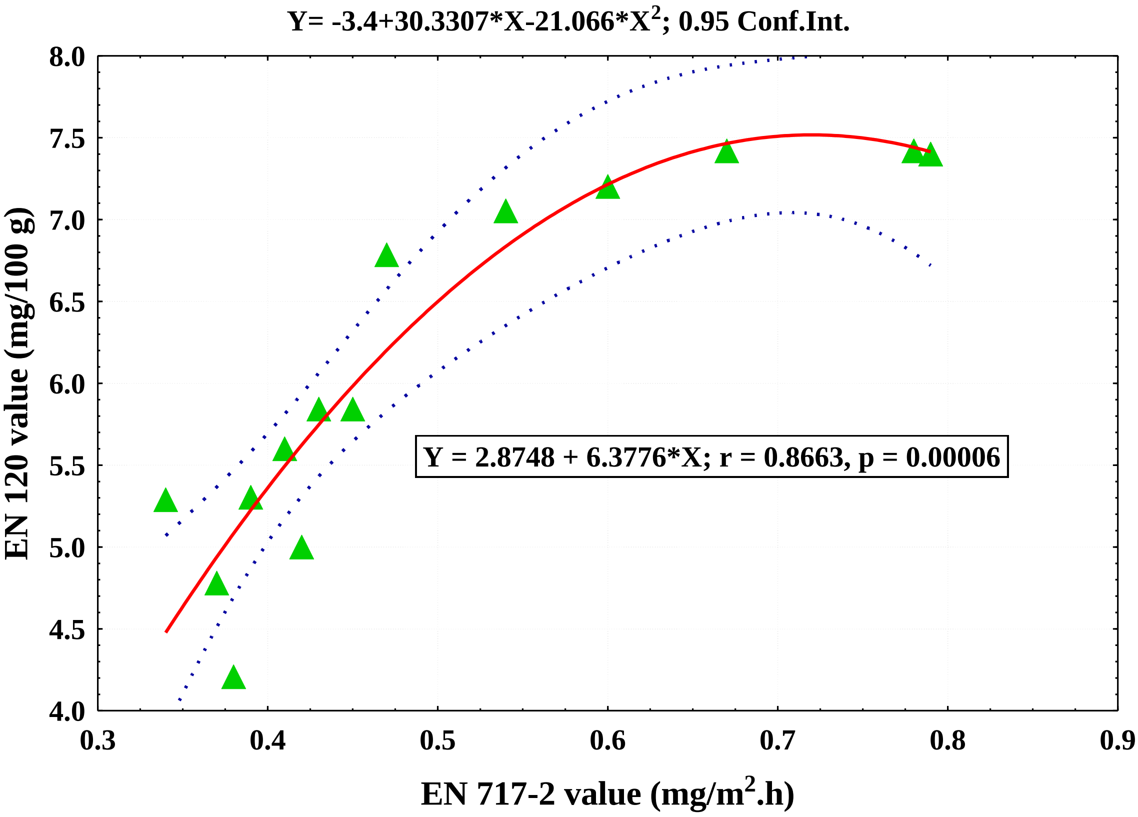


Figure 16: Polynomial correlation between EN 717–2 and EN 120 for uncoated MDF, 3.2–18 mm thick.

5.2.3 Effect of Board Type and Thickness on Formaldehyde Release from Fiberboards

For the fiberboards [uncoated MDF (MDF) and laminated MDF (MDFL)] samples used in this study, the significant analysis was done using one way ANOVA, to study the effect of board type and thickness on the formaldehyde release from fiberboards. It seen that from Table 28 there were a significant differences between the boards used in this study.

The board MDF18 mm was highly significant effect on the formaldehyde release measured by EN 717–2 and EN 120 (0.68 mg/m^2.h and 7.36 mg/100 g o.d. board, respectively), followed by MDFL 18 mm (0.61 mg/m^2.h and 6.83 mg/100 g o.d. board, measured by EN 717–2 and EN 120, respectively.

Table 28: Values for the emitted formaldehyde measured by EN 717–2 and EN 120 for different types of fiberboards.

Board type	EN 717–2 value	EN 120 value
	(mg/m^2.h)	(mg/100 g o.d.)
MDF 3.2 mm	0.38 ± 0.03^{d}	5.03 ± 0.49^{c}
MDF 16 mm	0.47 ± 0.05^{c}	6.38 ± 0.63^{b}
MDF 18 mm	0.68 ± 0.09^{a}	7.36 ± 0.11^{a}
MDFL 2.5 mm	0.31 ± 0.01^{e}	4.68 ± 0.03^{c}
MDFL 18 mm	0.61 ± 0.02^{b}	$6.83 \pm 0.01^{a,b}$
MDFL 19 mm	0.30 ± 0.03^{e}	4.25 ± 0.04^{c}

Values (mean± SD).
Means with the same letter are not significantly different ($P > 0.05$), Duncan's multiple range test.

These results was in agreements with Kim *et al.,* (2009) who examined the FE behavior of MDF overlaid with three types of uncoated lignocellulosic surface materials (oak decorative veneer, LPM impregnated paper and high pressure melamine impregnated paper) and four types of coated surface materials (coated paper, two types of finishing foils, and PVC) using the FLEC method and a 20 L small chamber method. The uncoated lignocellulosic surface materials exhibited lower FE levels. Coated surface materials in the 20 L small chamber test reduced the FE. In the FLEC test, both the uncoated lignocellulosic surface materials and coated surface materials showed lower FE from MDF.

5.2.4 European Small Chamber value

The chamber values were ranged from 0.042 to 0.065 (MDFL) and 0.05–0.087 mg/m^3 (MDF) from the fiberboards. The formaldehyde concentrations shown in Table 29 were below the E1–emission class (E1 ≤ 0.124 mg/m^3).

Table 29: Values of formaldehyde emission of fiberboards (12–18 mm) measured by chamber method (mg/m^3).

Wood product	Board type	Thickness (mm)		
		T12	T16	T18
MDF	Uncoated	0.050	0.077	0.087
	Laminated	0.042	0.052	0.065

5.3 Plywood Panels

5.3.1 Gas Analysis Values from Plywood Panels

The PLW used for interior uses (*i.e.,* PLY) were bonded with MUF with reduced melamine content levels. The PLW used for the construction uses (*i.e.,* PLYs) were bonded with PF. All the PLY boards emitted more formaldehyde than the PLYs.

Table 30 showed that the formaldehyde concentrations from all samples measured by the gas analysis ranged from 0.13 to 0.49 mg/m^2.h were below the E1–class emission. Mean levels for each PLW type were measured by averaging the concentrations measured in the each repetitions for the same thickness. Figure 17 shows that all values measured for the two types of PLW were below the standard limit E1 from EN 717–2. As a general, the values of FE from PLY (ranged from 0.21 to 0.49 mg/m^2.h) were higher than those from PLYs (ranged from 0.13 to 0.24 mg/m^2.h) and it can be explained in the using of different glue types.

As discussed below there are many different in the behavior of the formaldehyde emitted from wood–based products as well as between the types of resins used.

Table 30: Values of formaldehyde emission from plywood panels measured by EN 717–2.

Method	15 mm		18 mm		21 mm		25 mm
	PLY	PLYs	PLY	PLYs	PLY	PLYs	PLY
EN 717–2 (mg/m².h)	0.21	0.13	0.31	0.24	0.35	0.15	0.49

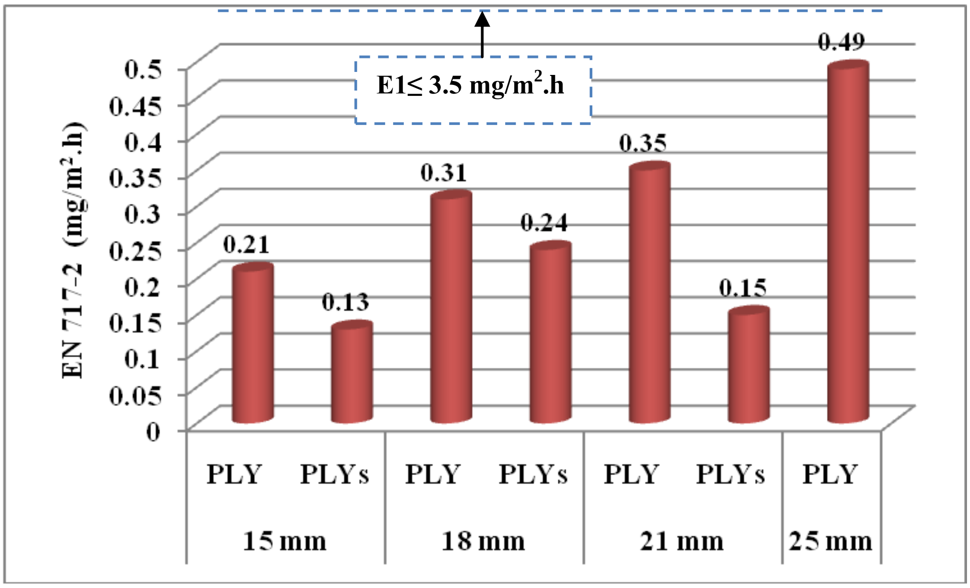


Figure 17: Values of formaldehyde emission of plywoods measured by EN 717–2 in comparable with the standard limitation.

5.3.2 European Large Chamber Value

Three panels of PLY (5–ply, 1 m x 2 m, 8 mm thickness, and UF glued beech veneer) were evaluated in the chamber. During this chamber test, the steady–state formaldehyde concentration in the chamber, obtained under constant temperature, relative humidity, loading factor and air exchange rate, expressed by (mg/m^3). At 23 °C and 1013 hPa, the following relationship exists for formaldehyde: 1 ppm = 1.24 mg/m^3 or 1 mg/m^3 = 0.81 ppm.

Table 31 and Figure 18 are summarized the results of the chamber test for FE rates from the 1st day values as well as the steady–state emission rates after exposure for the boards. Figure 18 shows the instantaneous concentration in the 12 m^3 chamber for the PLY material.

As shows in the figure, the equilibrium concentrations obviously drop over time until the steady–state emission rate of the PLY boards is reached. The formaldehyde initial concentrations for the PLY material C_1 is listed in Table 30. It is seen that the C_1 (0.19 mg/m^3 or 0.15 ppm) of the 8 mm 5–ply boards is high (E > 0.12 mg/m^3) and may cause indoor air pollution.

On the other hand, in accordance with the European standard (EN 717–1) the final formaldehyde concentration ($C_{S–S}$) was 0.03 ppm (0.033 mg/m^3) as the steady–state concentration is reached after 18 days.

Table 31: Steady–state formaldehyde emission rate (mg/m^3 or ppm) of 8 mm plywood panels tested in chamber.

Time (h)	**Sample**	**A_s**	**A_b**	***f* (mg/ml)**	**V_{sol} (ml)**	**G_{tot} mg**	**V_{air} (m^3)**	***C* (mg/m^3)**	***C* (ppm)**	
6 (1st day)	1	0.351	0.100	0.0024	30	0.023	0.12	0.19	0.15	C_1
	2	0.163	0.100	0.0024	30					
426 (18 days)	1	0.103	0.095	0.0024	30	0.004	0.122	0.033	0.03	$C_{S–S}$[a]
	2	0.143	0.095	0.0024	30					

[a] Days to reach steady–state emission rate as defined in EN 717–1 standard.

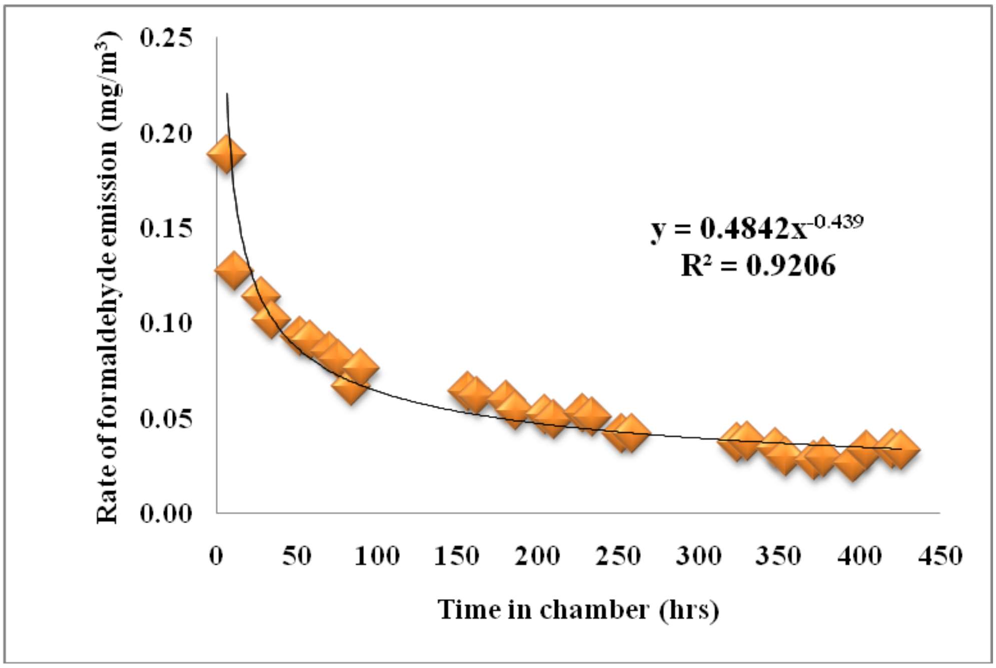


Figure 18: Formaldehyde emission data from a large chamber test (EN 717–1) on 8 mm beech plywood.

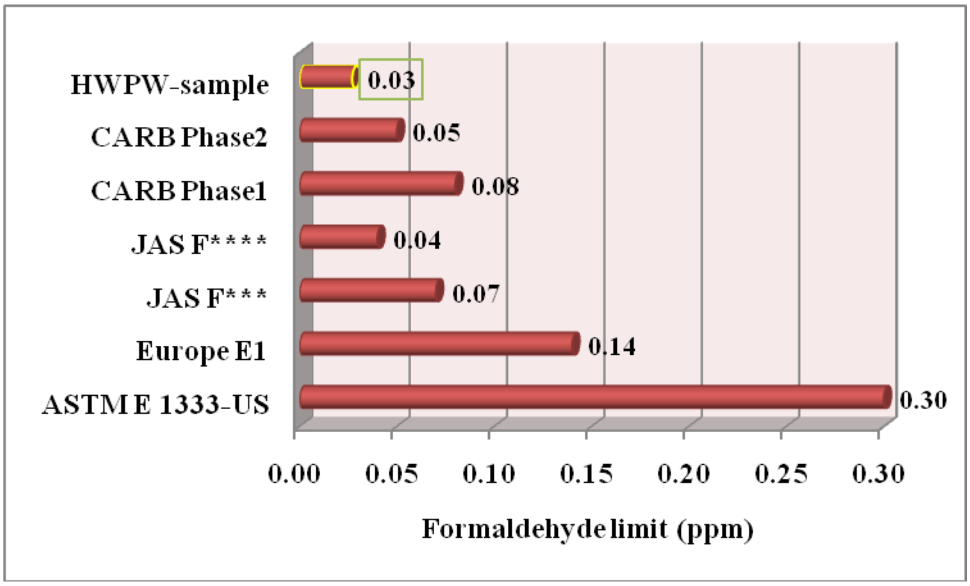


Figure 19: Formaldehyde emission line comparison for 8 mm plywood sample with the other normalized standards.

The FE test data showed that the PLY panels below the E1 classification requirement of the European requirements (E1 ≤ 0.1 ppm). Moreover, this value (0.03 ppm) is below the other emission limits standards, it was below the Phase 2 for CARB new regulations also below the limitations from the American large chamber and Japanese desiccator method (Figure 19).

5.3.3 The Effect of Plywood Type and Thickness on Formaldehyde Emission Measured by EN 717–2

The analysis of variance (*i.e.*, ANOVA) presented in Table 32 showed that, there were a very highly significant effect of PLW type ($P < 0.001$), board thickness ($P < 0.001$) and the interaction between the board type and thickness was highly significant ($P < 0.01$) on the formaldehyde release measured by EN 717–2.

Table 32: The ANOVA for the formaldehyde emission of plywoods measured by EN 717–2 as affected by board type, thickness and the interaction between them.

S.O.V.	*SS*	*DF*	*MS*	*F*	*Sig. Level*
Plywood type	0.08096	1	0.08096	58.0984	***
Thickness	0.039174	2	0.019587	14.0561	***
PLW type*Thickness	0.027769	2	0.013884	09.9637	***
Error	0.02787	20	0.001394		

(***) very highly significant effect ($P < 0.001$). $R^2 = 0.84$. $CV = 16.04$ %

The Duncan’s multiple comparisons followed the ANOVA test that was shown in Table 33, represents the differences between the means of PLW as affected by board type and thickness. The PLYs samples had the lowest amount of the formaldehyde release in comparable with PLY samples. The PLY sample with 21 mm had the highest amount of formaldehyde (0.31 mg/m^2.h) and the PLYs samples had the lowest amount (0.13 mg/m^2.h) from the tested boards. These results were also presented in Figure 20.

Table 33: Values of formaldehyde concentrations for different types and thicknesses of plywood (15–18 mm) measured by formaldehyde measured by EN 717–2 (mg/m^2.h).

Board type	**Thickness (mm)**			**Board mean**
	15	**18**	**21**	
PLY	0.21± 0.04^b	0.31± 0.056^a	0.35± 0.059^a	0.29*A*
PLYs	0.13± 0.007^c	0.24± 0.022^b	0.15± 0.014^c	0.17*B*
Thickness mean	0.17^B	0.27^A	0.25^A	0.23

Values (mean±SD).
Means with different letters are significantly different ($p < 0.05$) according to Duncan's multiple range Test.

5.3.4 European Small Chamber Value

From Table 34 the PLW values ranged from 0.051–0.066 mg/m^3 for PLY and 0.005 to 0.007 mg/m^3 for PLYs. All values measured under the E1–emission class (E1 ≤ 0.124 mg/m^3). The differences between the values should be related the different types of formaldehyde resins.

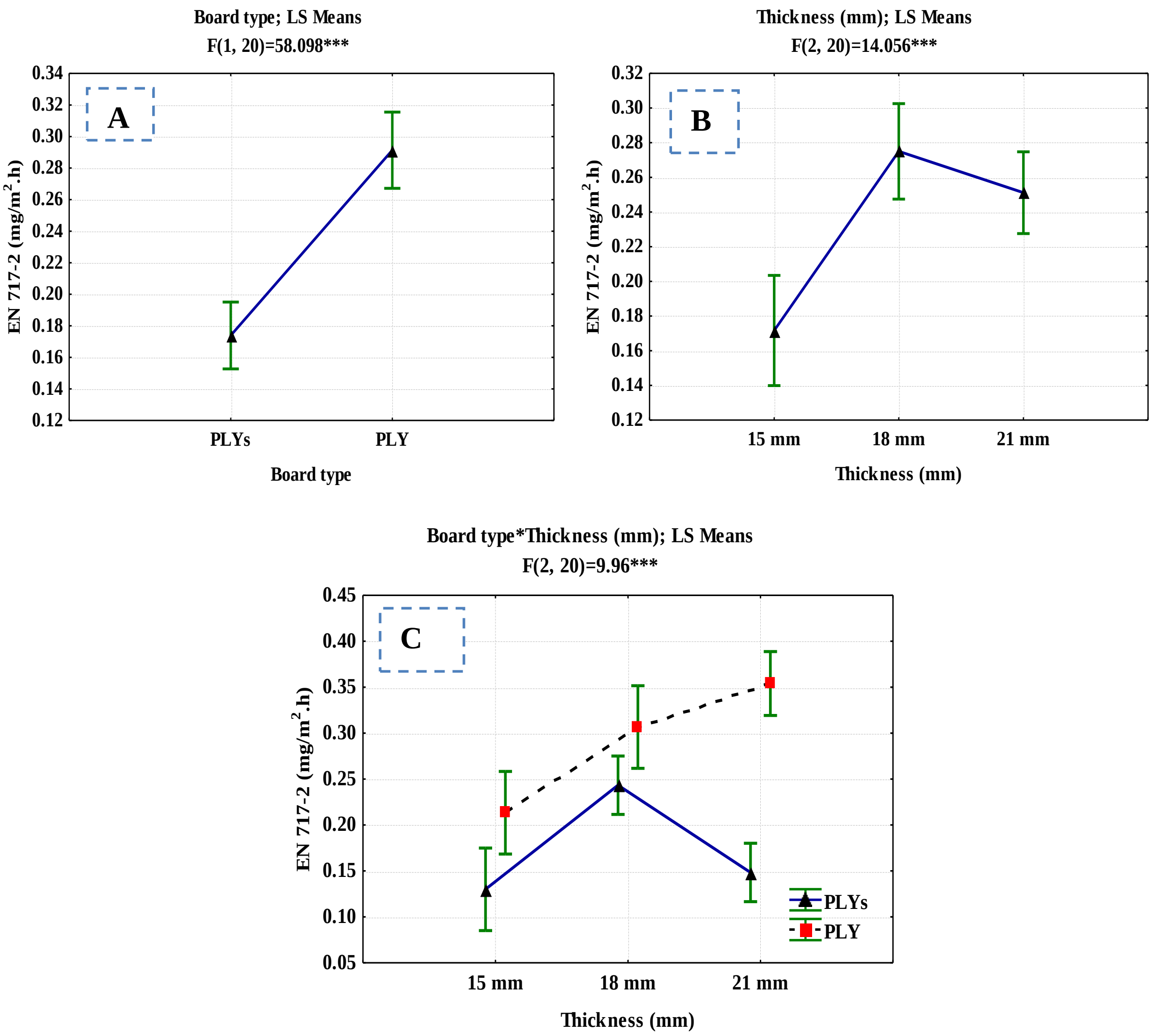


Figure 20: The effect of plywood types (A), thicknesses (B) and the interaction between them (C) on the formaldehyde release measured by EN 717–2.

Table 34: Values of formaldehyde emission of wood product (12–18 mm) measured by chamber method (mg/m^3).

Wood product	Board type	Thickness (mm)		
		12	16	18
PLW	PLY	0.051	0.063	0.066
	PLYs	0.005	0.006	0.007

From the above results about determination of FE and FC from different types of composite wood products it was found that, the perforator method was not used for PLW samples because this method has been mainly used for PB and MDF in general. The FE values of PLW samples measured by the gas analysis method were lower than those of the PB and MDF samples. These results were in agreements with Park *et al.*, 2010, which he found that in his study the FE values of PLW samples measured by the 1 m3 chamber method, was lower than those of the PB and MDF samples.

In addition, these results were in agreements with the investigation by Kolarik *et al.*, (2009) as he aimed to identify major sources of formaldehyde among construction and finishing products.

The methodology of measuring was followed by EN 717–1. The concentrations differed widely between tested materials. The initial concentration ranged from below 0.01 mg/m^3 to 0.115 mg/m^3 and it dropped below 0.01 mg/m^3 at the end of the measuring period.

In accordance with Martínez and Belanche (2000), there were two main reasons explaining the differences between the FE and FC measured by EN 717–2 and EN 120 respectively from the panels. The first one being that the formaldehyde present in the adhesive interacts in a distinct way with each wood species and the second one that FE and FC values are affected by the anatomy of the respective wood species.

There is a small amount of free formaldehyde in the liquid resin (generally less than 0.1%) which is used during the cross–linking of the resin. The free formaldehyde is present in various forms in the manufactured board. It can react with moisture present in the wood fiber to form methylene glycol, polymethylene glycol and polyoxymethylene hemiacetal etc.; it can also undergo labile binding to the wood fiber or to the polymer resin.

This free formaldehyde will in time migrate and be released into the atmosphere, especially under high temperature and when exposed in a well–ventilated environment. The FE of the CWPs is not limited to the emission of the free FC of the board. The FE can also come from the thermolysis of wood lignin and polysaccharides in the wood fiber, which will further contribute towards the FE from the manufactured board.

The hydrolysis of the partially cured and cured resin will continuously produce formaldehyde that will be emitted. Depending on the species, the wood particles can liberate acids under certain temperature and moisture conditions. These can cause a shift towards a lower pH, which may cause hydrolysis of the N–methylol group and to a lesser extent, the methylene ether linkages in the UF resin.

The majority of the formaldehyde first emitted from a new wood–based board comes from the free formaldehyde present in the material. The emission typically declines exponentially until a steady–state level is reached (Yu and Crump, 1999).

5.4 Formaldehyde Values Measurements from Flooring Panels by European Small Chamber

The European small–scale chamber (0.225 m^3) was used to measure the steady–state formaldehyde concentration from different types of flooring panels and it was found that:

1. Laminated fiberboard–flooring with:
    - 1.1. 8 mm (0.042 mg/m^3)
    - 1.2. 7 mm (0.087 mg/m^3)
    - 1.3. 12 mm (0.123 mg/m^3)

2. Multi–layer solid wood flooring with:
    2.1. 10 mm (0.035 mg/m^3) and 15.5 mm (0.125 mg/m^3) – spruce wood.
    2.2. 10 mm (0.021 mg/m^3) – oak wood
    2.3. 15 mm (three layers of oak wood) (0.041 mg/m^3)
3. PVC flooring panels with High Pressure Laminates (HPL) – with 13.5 mm (0.041 mg/m^3),
4. PVC flooring panels – with:
    4.1. 5 mm (0.025 mg/m^3).
    4.2. 2.5 mm (0.3 mm covering layer) (0.005 mg/m^3).
    4.3. 5 mm (0.5 mm layer for protecting against UV) (0.008 mg/m^3).
    4.4. 1.2 mm (0.07 mm covering layer) (0.003 mg/m^3).
5. High density fiberboard with HPL with 11 mm (0.052 mg/m^3).
6. Flooring solid bamboo with 12 mm (0.01 mg/m^3) and Multi–layer solid bamboo with 15 mm (0.082 mg/m^3).

These measurements of FE from wooden flooring were varied and in accordance with Kolarik *et al.,* (2009) who found that the concentrations measured by EN 717–1 differed widely between tested materials. The initial concentration ranged from below 0.01 mg/m^3 to 0.115 mg/m^3 and it dropped below 0.01 mg/m^3 for 7 out of 12 the investigated materials at the end of the measuring period.

5.5 Measurement of formaldehyde concentration values by perforator and converting between methods with conversion equations

As shown in Tables 35 and 36 the amount of formaldehyde measured with different methods from the PBs and fiberboards under this experiment differed according to the type and thickness of boards and the conditions of the methods used.

Table 35: Values of formaldehyde concentrations for different types of particleboards measured by EN 120 and converted to different methods.

Board Type	**Thickness (mm)**	**EN 120 (mg/100 g o.d.)^a**	**EN 717–1 (mg/m^3)**	**ASTM E 1333 (ppm)**	**JIS A 1460 (mg/L)**
P2	16	5.165±0.58^{c} (0.26)	0.067	0.066	0.508
	18	7.679±0.60^{b} (0.27)	0.097	0.095	0.715
	19	9.003±0.07^{a} (0.04)	0.113	0.111	0.824
PL	16	3.696±0.50^{d} (0.29)	0.049	0.048	0.386
	18	7.296±0.46^{b} (0.21)	0.093	0.091	0.683
	19	7.823±0.07^{b} (0.04)	0.099	0.097	0.727
***P* value**	Test method	Board type		Thickness	Board type × Thickness
	EN 120	< 0.001		< 0.001	$P = 0.07$

(*) Values are the corrected perforator value (mg/100 g o.d. board) at a moisture content of 6.5% (EN 312, 2003).
Values of EN 717–1 and EN 120 in [mean ± SD (SEM)].
Different letters represent statistical differences between the averages of the LS Means values.
Means with different letters within the column are significantly different ($P < 0.05$).

The FC ranged from 5.16 to 9.003 mg/100 g o.d. board (P2) and from 3.69 to 7.82 mg/100 g o.d. board (PL). The FC of the P2 and PL boards was under E1 grade except for the P2 of 19 mm thick (9.003 mg/100 g o.d. board). For the fiberboards, the amount of the FC were discussed in section 5.2.

Table 36: Values of formaldehyde concentrations for different types of fiberboards measured by EN 120 and converted to different methods.

Board Type	Thickness (mm)	EN 120 (mg/100 g o.d.)[a]	EN 717–1 (mg/m^3)	ASTM E 1333 (ppm)	JIS A 1460 (mg/L)
MDF	3.2	5.03 ± 0.49^{c} (0.20)	0.065	0.064	0.496
	16	6.38 ± 0.63^{b} (0.32)	0.081	0.079	0.608
	18	7.36 ± 0.11^{a} (0.05)	0.093	0.091	0.688
MDFL	2.5	4.68 ± 0.03^{c} (0.02)	0.061	0.059	0.467
	18	$6.83\pm0.01^{a,b}$ (0.01)	0.087	0.085	0.645
	19	4.25 ± 0.04^{c} (0.03)	0.056	0.054	0.432
***P* value**	Test method	Board type		Thickness	
	EN 120	< 0.001		< 0.001	

For legend, see Table 35.

5.5.1 Relationship Between the Test Methods Using the Conversion Factor Equations

Table 37 shows the applied conversion factor equations for converting EN 120 test values (mg/100 g o.d. board) to EN 717–1 values (mg/m^3) for the P2 16 mm as an example and subsequently converting the EN 717–1 value to E1333 value (ppm).

Table 37: Relationship between the different standard methods for 16 mm thick particleboard

[0.012*(8 mg/100 g o.d.)] + 0.005	= 0.101 mg/m^3 ≈ E1 ≤ 0.12 mg/m^3 → (standard limit)
[0.012*(5.165 mg/100 g o.d.)] + 0.005	= 0.06 mg/m^3 (estimated value for P2 16 mm thick)
[0.101 mg/m^3]*0.98	= 0.10 ppm (estimated value for P2 16 mm thick)
[0.0825*(8 mg/100 g o.d.)] + 0.0816	= 0.74 mg/L ≈ *F*** ≤ 1.5 mg/L → (standard limit)

According to the results shown in Figure 21 A–E and from the equations used for converting between test methods, the estimated emission limit E1–class by conversion factor for EN 717–1 is nearly equivalent to those measured by EN 120. The Japanese *F*** class was more equivalent to European E1–class, while the *F**** and *F***** emission limits were much lower than the E1–class. In this regard, the emission of *F***** boards is close to the emission of solid untreated wood (*i.e.,* between 0.008–0.01 ppm or 0.5–2.0 mg/100 g o.d. board for spruce wood flakes) (Marutzky and Dix, 2004).

The resulting Phase 1 was roughly equivalent to the European E1–emission class, as was the Japanese *F*** class. Phase 2 (0.09 ppm) limits were comparable to the Japanese *F**** limits (≈ 0.07 ppm) estimated by conversion factor, the so–called E0 levels in Europe. Also from the tested samples, there was a proportionality observed within the E1–class for EN 120 and EN 717–2 using standard test procedure.

As can be observed, the PB E1–emission class had approximately the same value and showed similar behavior for each method. This demonstrates that for the same kind of material, the methods give results, which are likely to be accurate (EN 120, EN 717–1, ASTM E1333 and JIS A 1460). The EN 717–2 in contrast gives a much more pronounced difference, in spite of an intermediate correlation with EN 120.

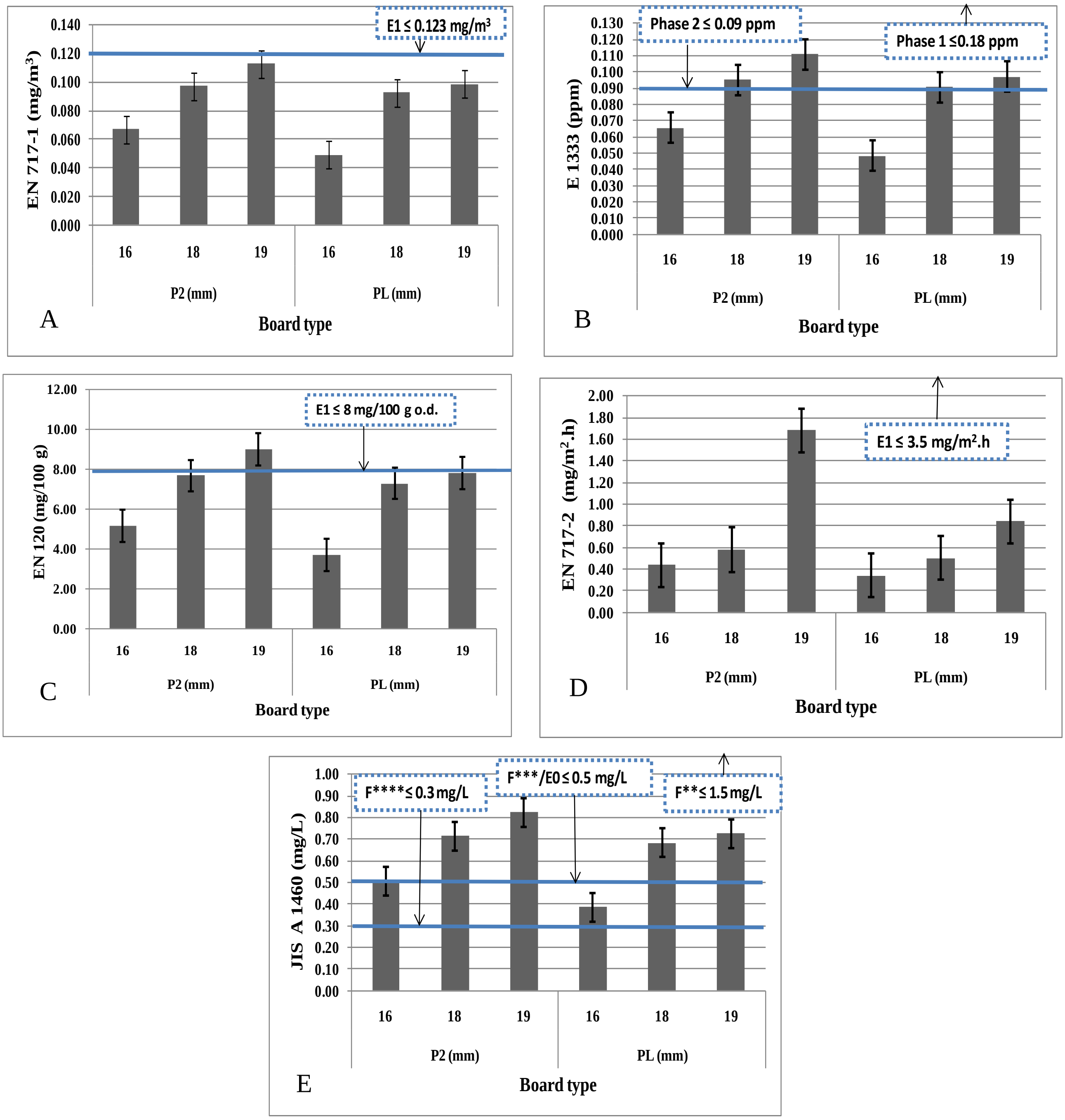


Figure 21: Relationship between the standard limits of formaldehyde emission values from the studied uncoated and laminated particleboards (16–19 mm).

At the present time, E0 is an updated version of E1 with much more stringent standards requiring FEs to be equal to or less than 0.07 ppm. Therefore, a PB that met E0 standards would be considered a safer, greener choice than one that only met E1 standards (PB with 16 mm thick).

5.6 Evaluation of the Effect of Different Types of Formaldehyde–Based Resin As Well As the Effect of Board Type and Thickness

The FE values of different wood products used in this study were subjected to two–way analysis of variance (*i.e.*, ANOVA) followed by the Duncan's multiple–range test. Outputs of the statistical analyses are given in Tables 38–41. ANOVA in Table 38 showed that the formaldehyde values measured by gas analysis method were extremely affected significantly by board type ($P < 0.001$), board thickness ($P < 0.001$) and the interactions between them ($P < 0.001$) for most of all types of wood product used in this study. For MDF boards the interaction between them had a significant effect ($P < 0.05$).

Table 38: ANOVA results for the effects of board type and thickness on the overall of formaldehyde emission values measured from particleboard, MDF and plywood panels.

EN 717–2 test	Source of Variation	Sum. of Squares	d.f.	Mean Square	*F*–value	*P*
PB	A	5.9797	2	2.9899	399.27***	< 0.0001
	B	7.9801	2	3.9900	532.84***	< 0.0001
	A × B	1.4994	4	0.3749	50.06***	< 0.0001
	Error	0.2396	32	0.0075		
	model R–Square (R^2)= 0.98			model Coefficient of Variance (*CV*)= 8.71		
MDF	A	0.1228	1	0.1228	130.48***	< 0.0001
	B	0.6073	2	0.3036	322.67***	< 0.0001
	A × B	0.0072	2	0.0036	03.81*	0.0387
	Error	0.0198	21	0.00094		
	R^2= 0.97		*CV* = 6.58			
PLW	A	0.08233	1	0.08233	76.25***	< 0.0001
	B	0.09158	2	0.04579	42.41***	< 0.0001
	A × B	0.02150	2	0.01075	09.96**	0.0018
	Error	0.01619	15	0.00108		
	R^2=0.93		*CV* =13.61			

(*) $P < 0.05$ (significant), (**) $P < 0.01$ (highly significant), (***) $P < 0.001$ (extremely significant); d.f. represent the degrees of freedom for the hypothesis; A: Board type; B: Board thickness; A x B: Interaction between board type and thickness.

Table 39 showed that, the FE of PB was high by PV T18 and PV T16 (2.52 and 1.68 mg/m^2.h, respectively) followed by PV T12 (0.96 mg/m^2.h), whereas the PL T12 had the lowest amount (0.23 mg/m^2.h) from the studied boards. As a mean effect from the board type, the PV (1.56 mg/m^2.h) presented a high amount of FE and T18 (1.68 mg/m^2.h) as a mean effect from the thicknesses. The FE from the fiberboards (Table 40) showed a high amount in uncoated MDF T18 (0.77 mg/m^2.h) followed by laminated MDF T18 (0.61 mg/m^2.h). However, the T18 and uncoated MDF had a high amount as a mean effect (0.69 and 0.53 mg/m^2.h, respectively).

The formaldehyde concentrations reported in Table 41 from the PLW showed that, the PLY T18 had a high amount of FE (0.35 mg/m^2.h) and the PLYs T12 panels had the lowest amount of FE (0.11 mg/m^2.h) from PLW panels studied. Mean levels for each PLW type were measured by averaging the concentrations measured in the each repetition for the same thickness. The values of FE from PLY (ranged from 0.16 to 0.35 mg/m^2.h) were higher than those from PLYs (ranged from 0.11 to 0.25 mg/m^2.h) and it can be explained in the using of different glue types. All values measured for the different types of wood–based panels used in this study were below the standard limit E1 from EN 717–2.

Table 39: Values of formaldehyde emission of particleboards (12–18 mm) measured by gas analysis method (mg/m^2.h).

Board type	Thickness (mm)			Board mean[1]
	T12	T16	T18	
P2	(0.67± 0.16)^{e}	(0.63 ± 0.09)^{e}	(1.68 ± 0.02)^{b}	(0.88 ± 0.45)^{B}
PV	(0.96± 0.02)^{d}	(1.19 ± 0.02)^{c}	(2.52 ± 0.02)^{a}	(1.56 ± 0.72)^{A}
PL	(0.23± 0.02)^{f}	(0.54 ± 0.08)^{e}	(0.84 ± 0.03)^{d}	(0.56 ± 0.26)^{C}
Thickness mean[2]	(0.65 ± 0.29)^{C}	(0.76 ± 0.28)^{B}	(1.68 ± 0.72)^{A}	

Values (mean ± SD) in mg/m^2.h.
Different letters represent statistical differences between the averages of the values.
Means with the same letter are not significantly different at $P < 0.05$ according to Duncan's multiple test.
Means with small letters to compare between the means of board type and thickness interaction.
[1] Capital letters within the column to compare between the board type as a mean effect.
[2] Capital letters within the row to compare between board thicknesses as a mean effect.

Table 40: Values of formaldehyde emission fiberboards (12–18 mm) measured by gas analysis method (mg/m^2.h).

Board type	Thickness (mm)			Board mean
	T12	T16	T18	
Uncoated MDF	(0.38 ± 0.03)^{d}	(0.47 ± 0.05)^{c}	(0.77 ± 0.03)^{a}	(0.53 ± 0.17)^{A}
Laminated MDF	(0.29 ± 0.02)^{e}	(0.32 ± 0.01)^{e}	(0.61 ± 0.01)^{b}	(0.40 ± 0.15)^{B}
Thickness mean	(0.33 ± 0.05)^{C}	(0.40± 0.09)^{B}	(0.69 ± 0.09)^{A}	

For legend, see Table 39.

Table 41: Values of formaldehyde emission of plywood (12–18 mm) measured by gas analysis method (mg/m^2.h).

Board type	Thickness (mm)			Board mean
	T1	T2	T3	
PLY	(0.16 ± 0.01)^{c}	(0.37 ± 0.01)^{a}	(0.35 ± 0.06)^{a}	(0.31 ± 0.09)^{A}
PLYs	(0.11 ± 0.01)^{c}	(0.25 ± 0.01)^{b}	(0.15 ± 0.01)^{c}	(0.17 ± 0.06)^{B}
Thickness mean	(0.14 ± 0.03)^{C}	(0.31 ± 0.07)^{A}	(0.26 ± 0.12)^{B}	

For legend, see Table 39.

In comparison, The European chamber values that were obtained for almost all of the boards examined from PB, MDF and PLW are shown in Table 42. Each measure is the value from the two pieces tested from boards. For PBs samples, the presented values were discussed before.

From the previous results, it was concluded that, the veneered PBs were emitted a high amount of formaldehyde more than the uncoated and laminated boards. Moreover, the PLW panels used in construction purposes had the lowest amount of FE. All the values measured were below the E1–class emission.

The FE values of PLW samples measured by the gas analysis method were lower than those of the PB and MDF samples. These results were in agreements with Park *et al.*, 2010 that he found that the emission of formaldehyde values of PLW samples measured by the 1 m^3 chamber method was lower than those of PB and MDF samples.

Table 42: Values of formaldehyde emission of wood product (12–18 mm) measured by chamber method (mg/m^3).

Wood product	Board type	Thickness (mm)		
		T1	T2	T3
PB	P2	0.074	0.076	0.083
	PV	0.082	0.087	0.123
	PL	0.048	0.049	0.079
MDF	Uncoated	0.050	0.077	0.087
	Laminated	0.042	0.052	0.065
PLW	PLY	0.051	0.063	0.066
	PLYs	0.005	0.006	0.007

For the comparisons between the formaldehyde–based resins (MUF with MDF and PLY, UF with PB and PF with PLYs), the ANOVA for the FEs from the boards measured by EN 717–2 followed by Duncan’s multiple–range test were done.

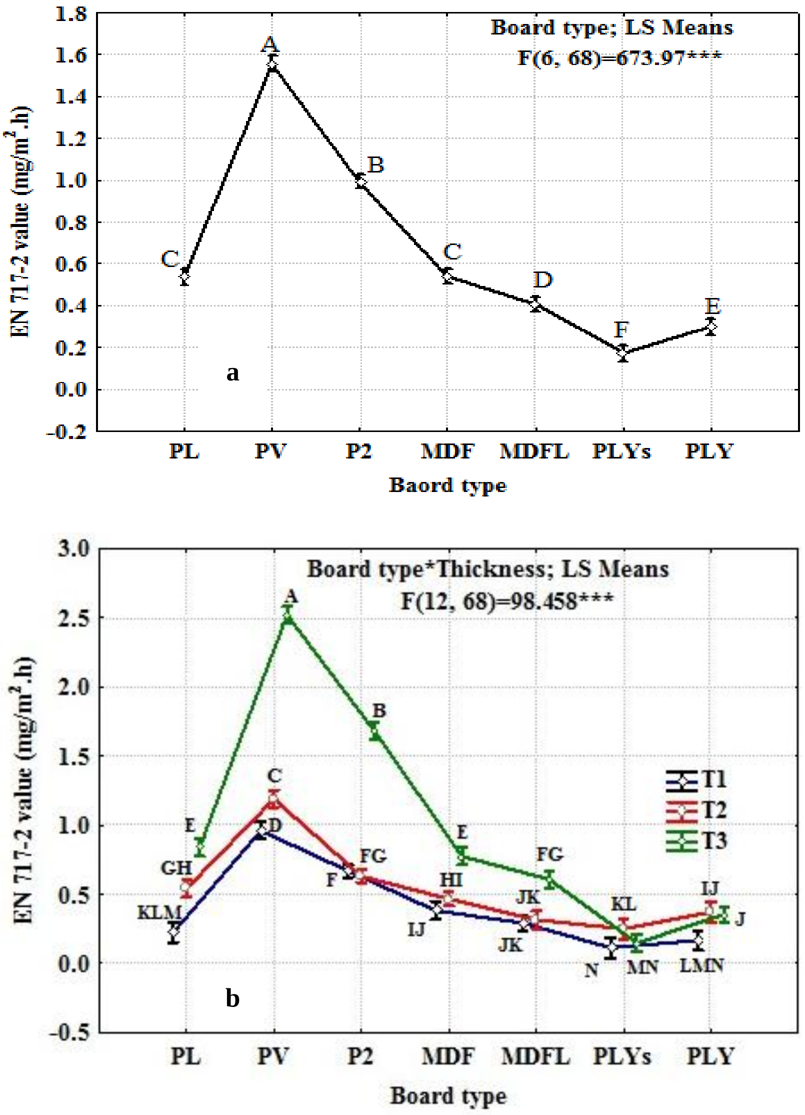
As shown in Figure 22 (a,b) the high amount of FE measured by gas analysis method was observed from PV/UF followed by P2/UF. In the middles values it was found that the uncoated MDF/MUF emitted formaldehyde with values equal PL/UF, in contrast the laminated MDF/MUF had an amount less than the values from PBs, whereas the PLW values from PLYs/PF had the lowest amount of FE. In addition, this results in comparable with the chamber values for the same board type.

The PLY/MUF had low amount of formaldehyde in comparable with some PB bonded with UF. These results were in agreement with Aydin *et al.*, (2006) that he reported the FE values of poplar and spruce PLW panels decreased with melamine addition into the UF glue mixture.

The differences between the formaldehyde values emitted due to the different formaldehyde–based resins can be explained as the following; the reaction of urea with formaldehyde first produces hydroxylmethyolated urea that then condenses to yield methylene and dimethylene ether bridged urea polymers (Pizzi, 2003; Meyer, 1979).

Although these reactions are not unlike the steps to produce the other formaldehyde–containing wood adhesives, the UF polymers are distinct in that they are susceptible to hydrolysis under some normal use conditions (Myers, 1986b). The reaction shown in Figure 23 for urea and formaldehyde illustrates the problem with depolymerization in that it can yield additional free formaldehyde, especially when free water is present.

The presence of free water in the composite panel, as in the case of higher humidity, tends to drive the reverse reaction, yielding more free formaldehyde. Myers showed that formaldehyde adsorbed onto wood reaches an emission plateau in about 7 days at 80% relative humidity (RH) and 27 °C, as does PF–bonded PB.



PL: Laminated particleboard, PV: Veneered particleboard, P2: Uncoated particleboard, MDF: Uncoated MDF; MDFL: Laminated MDF; PLY: Uncoated plywood used in interior application; PLYs: Uncoated plywood used in construction application. T1: 12 mm thick; T2: 16 mm thick; T3: 18 mm thick.
Vertical bars denote 0.95 confidence intervals.
(***) extremely significant effect ($P < 0.001$).
Different letters represent statistical differences between the averages of the values.
Means with the same letter are not significantly different at $P < 0.05$ according to Duncan's multiple test.

Figure 22: Comparisons of formaldehyde emission measured by EN 717–2 of different types of wood–based panels bonded with different formaldehyde–based resins.

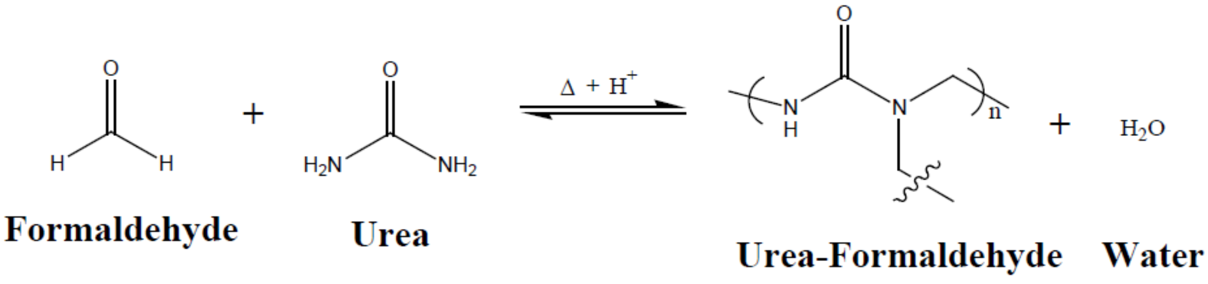


Figure 23: The reaction of urea with formaldehyde to form the urea–formaldehyde polymer.

In contrast, UF–bonded PB emitted formaldehyde for over 30 days without reaching a plateau (Myers 1986a). In addition, Myers's own data and his analysis of the literature data showed that FEs increase from UF–bonded wood composites at higher humidity and temperature conditions (Myers, 1985; Myers and Nagaoka, 1981).

Wood itself generates significant formaldehyde when exposed to certain conditions common to the composite panel manufacturing process (Schäfer and Roffael, 2000; Roffael, 2006). This so–called "native" formaldehyde has been shown to be transient and rapidly decreases to levels below those set by the standards (Birkeland *et al.*, 2010). Production of formaldehyde from wood has been shown to occur at conditions of very high heat and would not be expected to be a significant source of formaldehyde in composite wood products during service.

Aminoplastic and phenoplastic resins show differences in the hydrolysis behavior based on molecular level; this different susceptibility against hydrolysis also explains the significant difference between the aminoplastic and the phenoplastic resins in terms of their subsequent FE.

In accordance with Dunky (2005), Figure 24 shows the stability against hydrolysis is increased for the MUF due to stabilization of the C–N–bonding resulted from the quasi aromatic ring structure of the melamine and slower decrease of the pH in the bond line due to the buffer capacity of melamine. In addition, the C–C bonding in the PF resins is very stable against hydrolytic attack.

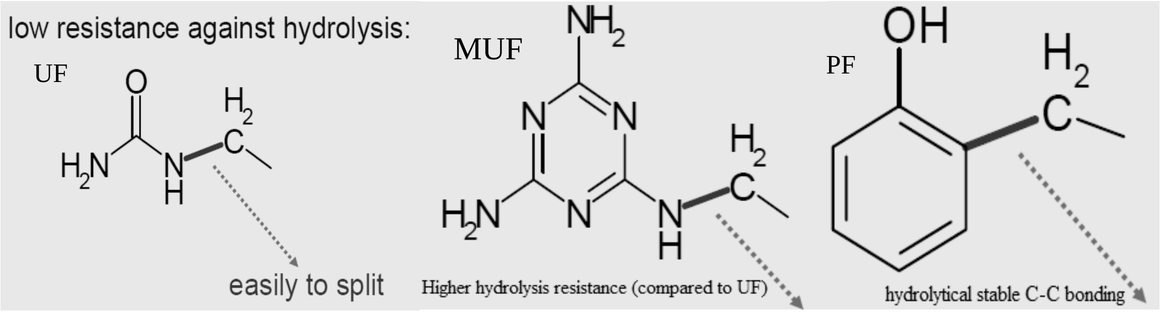


Figure 24: The differences in hydrolysis between UF, MUF and PF adhesive resins.

As discussed above there are many different in the behavior of the formaldehyde emitted from wood–based products as well as between the types of resins used. Furthermore, as can be seen, the boards, E1, have approximately the same value for each method. This shows that for the same kind of material, the methods show similar results.

Furthermore, a linear correlation analyses made between gas analysis concentrations (Y) and the corresponding average chamber values (X) were significant as affected by different types and thicknesses of PB (Figure 25), MDF (Figure 26) and PLW (Figure 27) panels (Y = 24.74 X – 1.21, R^2 = 0.82, P < 0.001 for PB panels as measured at P2, PV and PL), (Y = 9.47 X – 0.16, R^2

= 0.76, $P < 0.05$ for the influences of uncoated and laminated MDF) and (Y = 2.64 X – 0.15, R^2 = 0.52, $P < 0.05$ for the effect of PLY and PLYs).

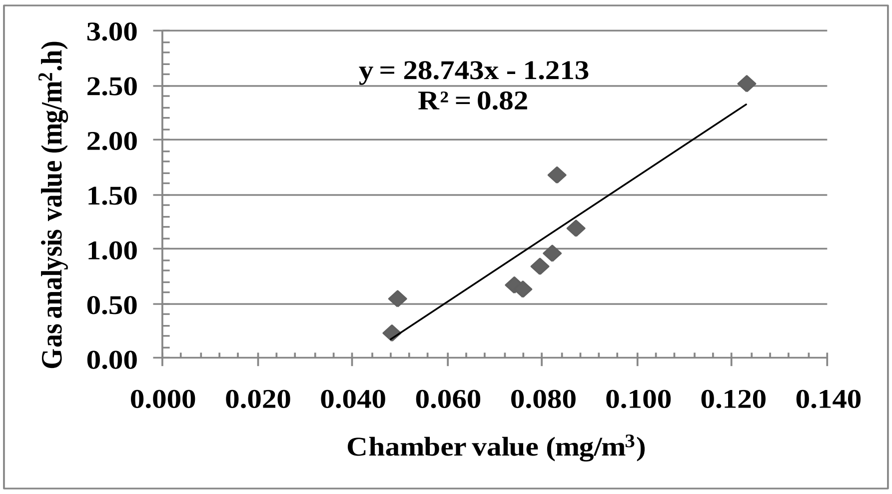


Figure 25: Correlation between EN 717–1 and EN 717–2 values for particleboards, thickness 12–18 mm.

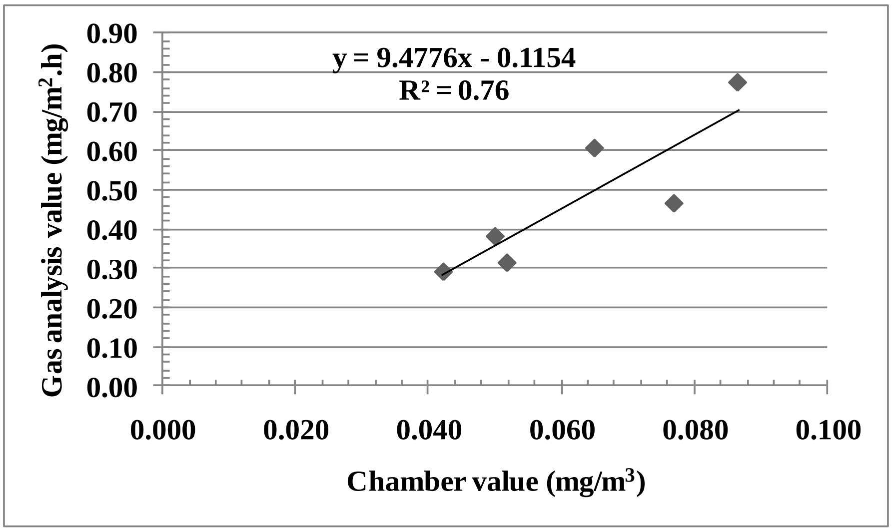


Figure 26: Correlation between EN 717–1 and EN 717–2 values for fiberboards, thickness 12–18 mm.

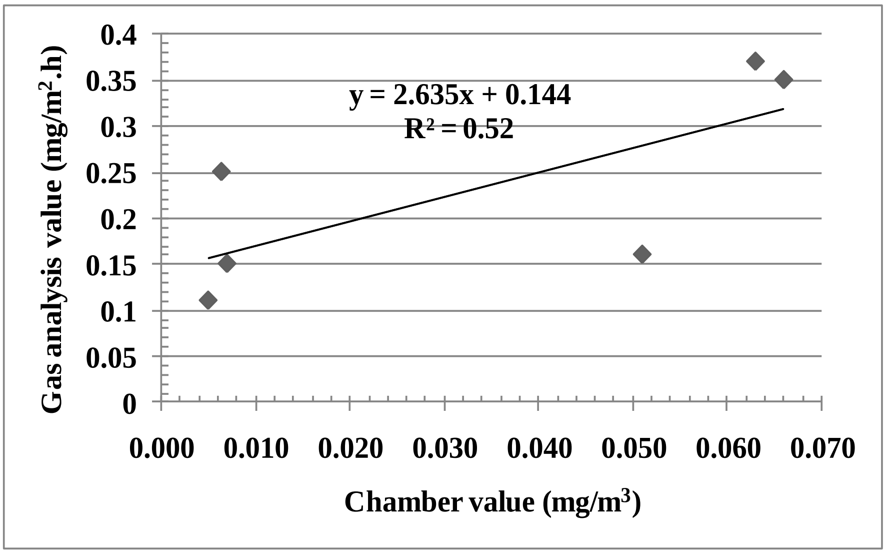


Figure 27: Correlation between EN 717–1 and EN 717–2 values for plywoods, thickness 12–18 mm.

So that the emissions of formaldehyde resulting from the free formaldehyde or from hydrolysis of the cured resin might be attributed to the board type and thickness levels. The correlation between the formaldehyde values of the gas analysis and the European chamber methods was not convincing for PLW panels, the R^2 values obtained was 0.52 (see Figure 27), and it possibly related to the differences in the resins used.

5.7 Evaluation the inter–laboratory comparison of formaldehyde emission from particleboard using American small chamber (ASTM D 6007–02)

The inter–laboratory comparison of FE from PB used for non–structural and interior application as furniture materials supplied from a commercial wood products plant in the Czech Republic was performed by the American small–scale test chamber (ASTM D 6007–02) in two laboratories.

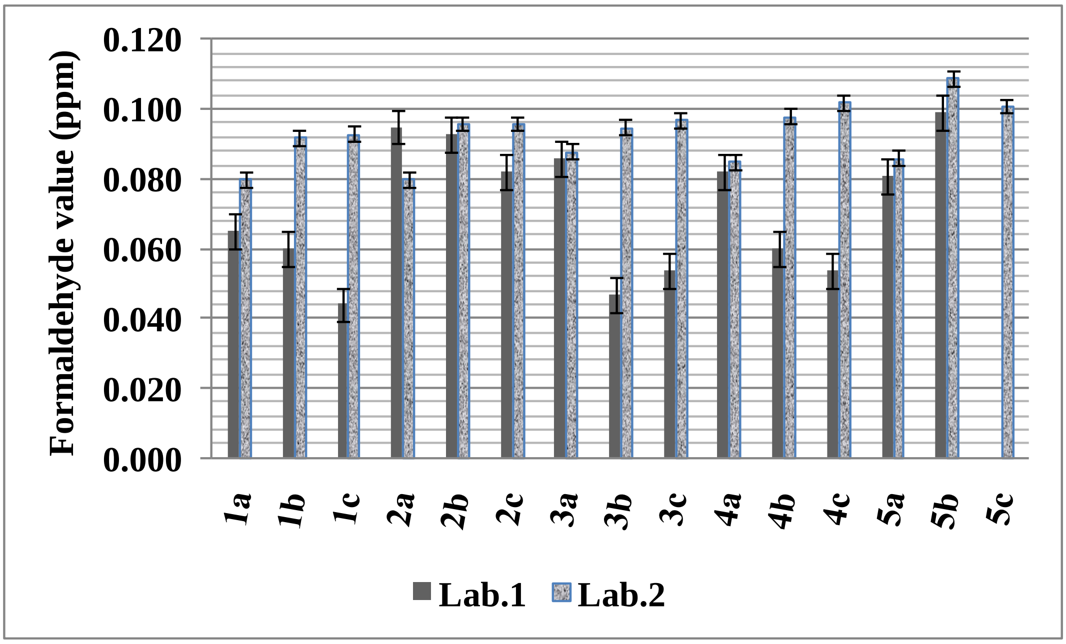
The evaluation of the differences between the values of FE from PL and between P2 boards measured in two laboratories were presented in Table 43. The summary of statistics for the FE, showing average values of observed parameters between both laboratories. These data were represented graphically in Figures 28–30.

Table 43: Descriptive statistics results of the concentration of formaldehyde from particleboard in groups 1 and 2.

Parameter	Formaldehyde value (ppm)			
	Group 1 (PL)		Group 2 (P2)	
	Lab. 1	Lab. 2	Lab. 1	Lab. 2
$\bar{x}$	0.071	0.093	0.170	0.179
Median	0.073	0.095	0.171	0.182
S	0.019	0.008	00.04	0.009
CV %	26.18	8.79	24.23	05.36
n	14	15	15	15
min.	0.044	0.080	0.101	0.160
max.	0.099	0.109	0.273	0.192
SEM	0.005	0.002	00.01	0.002
Lower quartile	0.054	0.086	0.139	0.173
Upper quartile	0.086	0.098	0.199	0.188
Variance	$3.51\text{x}10^{-4}$	$6.7\text{x}10^{-5}$	$1.71\text{x}10^{-3}$	$9.3\text{x}10^{-5}$

Figure 28 shows the variation between the average of three measurements for all samples except for the sample 5c which was measured only by laboratory 2 (*i.e.,* Lab. 2), and the other measurement from the first laboratory (*i.e.,* Lab. 1) was not available. The relative coefficient of variation for the FE values from PL was 26.18% and 8.79%, and for P2 was 24.23% and 5.36%, from Lab. 1 and Lab. 2, respectively.

Furthermore, the outliers of the measured FE values presented in Figure 29 from both laboratories as in groups 1 and 2 showed that there were differences between the values from both laboratories, which indicated that the Lab. 1 had a high number of numerically distant from the rest of the data than Lab. 2. The normal quantile plot showed in Figure 30 represents that the distribution of FE values measured from the Lab. 2 had a high homogeneity that from the Lab. 1.



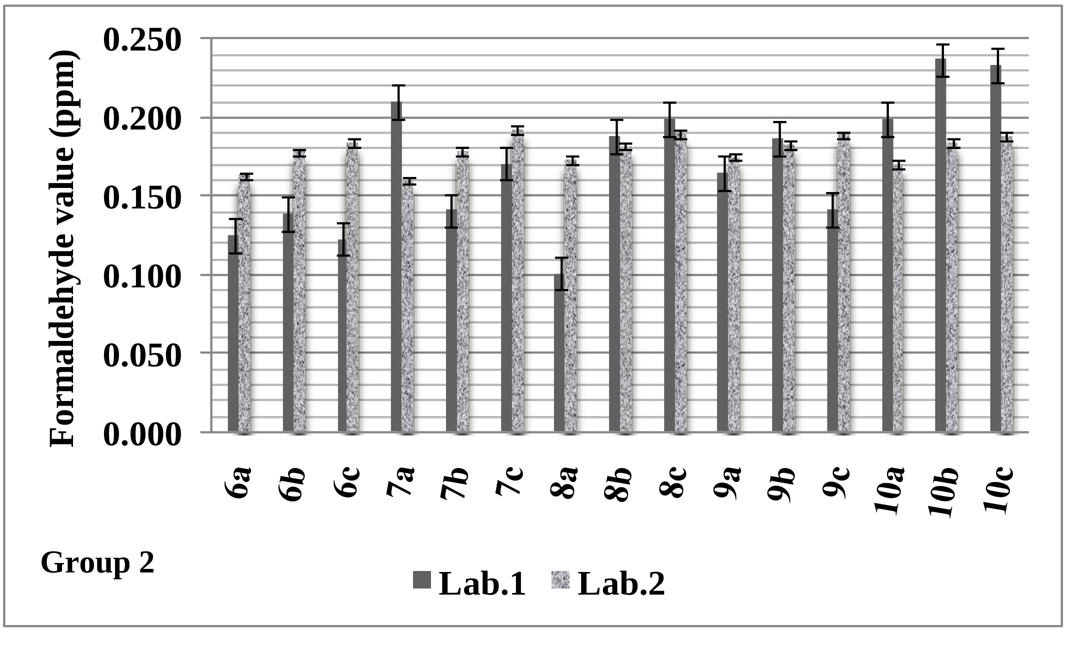
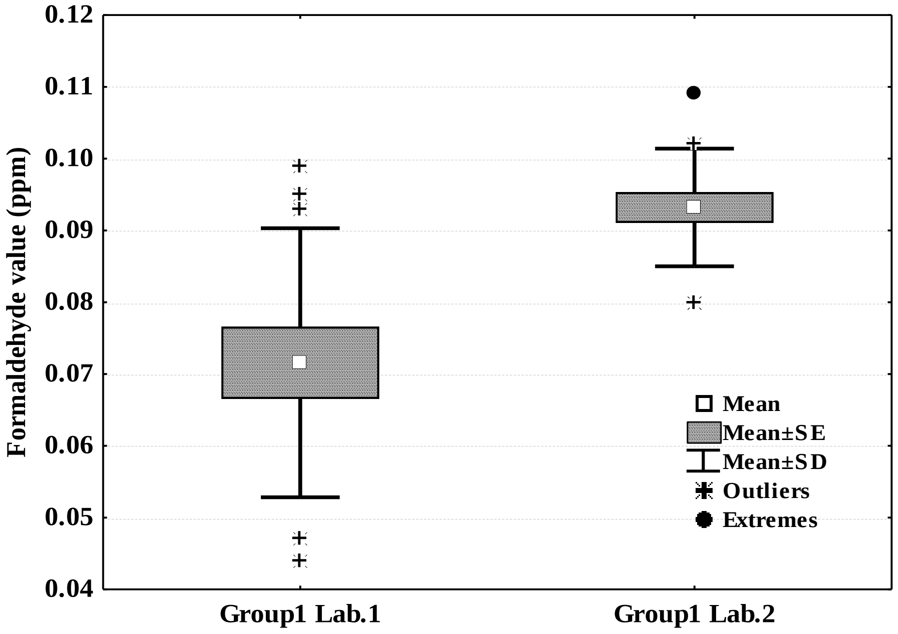


Figure 28: Concentration of formaldehyde from the two laboratories in group 1 and group 2.



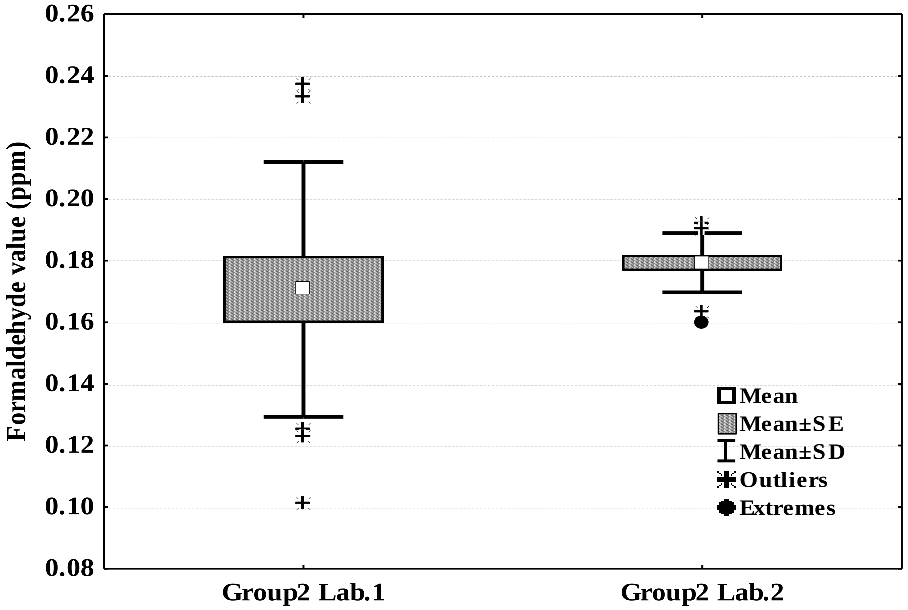


Figure 29: The variations of the formaldehyde concentration between the two laboratories.

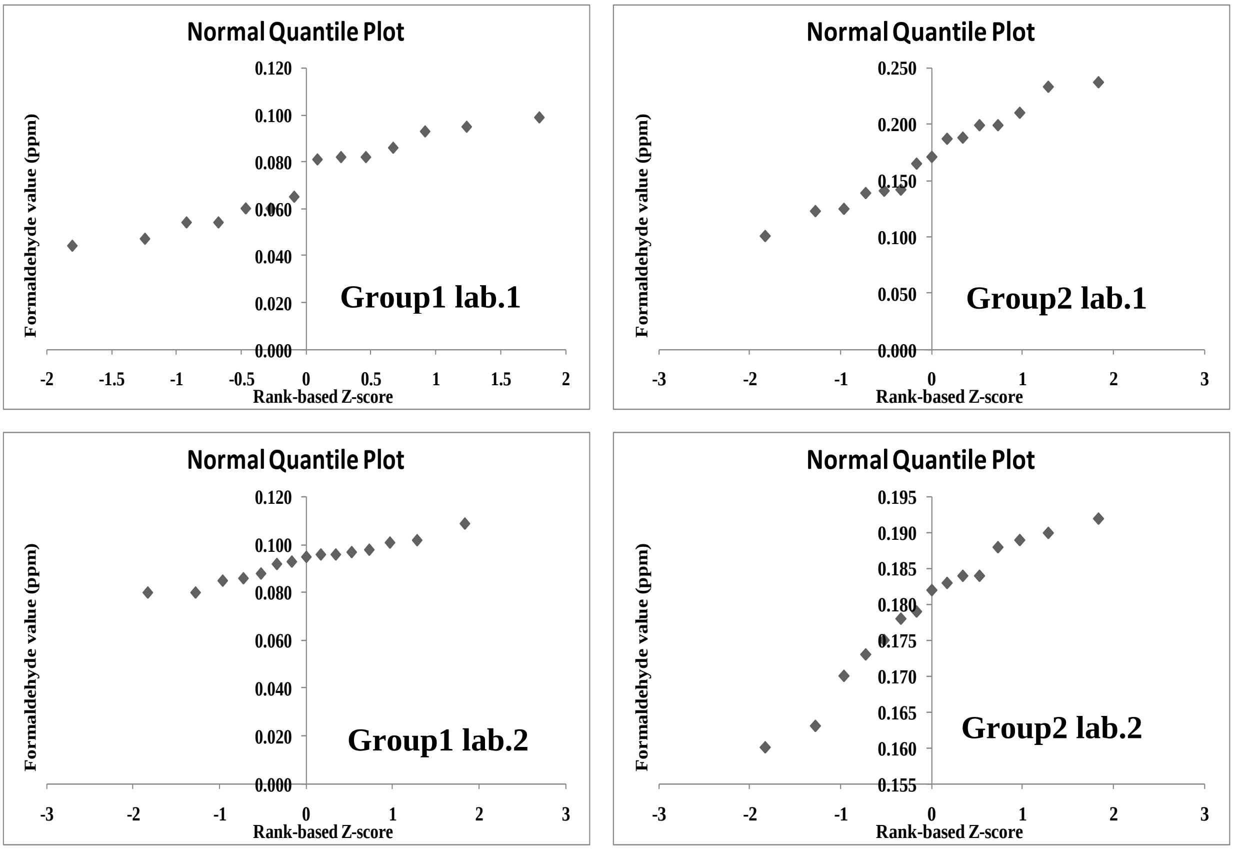


Figure 30: Normal Quantile plot of small–scale chamber data.

Two–way ANOVA analysis for group 1 and group 2 (Table 44) showed that, the differences between samples were significant in both groups ($P < 0.05$) and between laboratories were high significant for the first group ($P < 0.001$) and not significant for the second group ($P = 33$), also the interactions between the samples and laboratories for both groups of PBs were not significant. The variability between the values of FE due to the sample heterogeneity was presented in Table 45, which it was seen that the sample number 5 PL had a high amount of FE measured in the two laboratories, also there were no differences between the values of FE from the PL samples measured in Lab. 2. On the other hand, there were differences between FE values the same samples when it measured in the Lab. 1. Also the same trends of measurements were found between the FE values from P2 samples measured in the two laboratories, even thought that there were no significant differences between the two laboratories ($P = 0.33$).

Thus, these results suggested that there were a high homogeneity between the samples in Lab. 2 than in Lab. 1 and the most important source of variation is inter–laboratory bias due to heterogeneity of chamber conditions and probably sampling air (Wiglusz *et al.*, 2000).

Taking into account, the received samples in the two laboratories were distributed throughout the PB bundle, which performs it unlikely that the observed variations were due to inter–panel variability, there were some variations in average formaldehyde concentrations between the boards (Figure 28).

Table 44: Significant levels for the effects of sample and laboratories on the overall of small chamber values (ppm).

Group	Source of Variation	*F* Value	*Pr.* > *F*	whole R^2	whole *CV* %
1	**Laboratory (Lab)**	22.14***	0.0002	0.71	14
	Sample	3.40*	0.03		
	Lab*Sample	2.32^{ns}	0.09		
2	**Lab**	0.99^{ns}	0.33	0.56	13.62
	Sample	3.32*	0.03		
	Lab*Sample	2.78^{ns}	0.055		

(^{ns}) $P > 0.05$ (not significant); (*) $P < 0.05$ (significant); (***) $P < 0.001$ (highly significant).

Table 45: Differences between formaldehyde emission values of two groups of particleboard measured by ASTM D 6007–02 (ppm) in two laboratories.

Sample	Group 1*		Sample mean*
	Lab.1	**Lab.2**	
1	0.056 ± 0.01^{b}	0.088 ± 0.007^{a}	0.072 ± 0.02^{c}
2	0.090 ± 0.007^{a}	0.090 ± 0.009^{a}	0.090 ± 0.007^{ab}
3	0.062 ± 0.02^{b}	0.093 ± 0.005^{a}	0.078 ± 0.02^{bc}
4	0.065 ± 0.01^{b}	0.095 ± 0.009^{a}	0.080 ± 0.02^{bc}
5	0.090 ± 0.01^{a}	0.099 ± 0.01^{a}	0.095 ± 0.01^{a}
Mean of lab.*	0.072 ± 0.02^{B}	0.093 ± 0.008^{A}	
Sample	**Group 2***		**Sample mean***
	Lab.1	**Lab.2**	
6	0.129 ± 0.009^{c}	0.175 ± 0.01^{b}	0.152 ± 0.03^{b}
7	0.174 ± 0.03^{b}	0.177 ± 0.02^{b}	0.175 ± 0.03^{ab}
8	0.163 ± 0.05^{bc}	0.182 ± 0.008^{ab}	0.172 ± 0.04^{ab}
9	0.165 ± 0.02^{bc}	0.182 ± 0.007^{ab}	0.174 ± 0.02^{ab}
10	0.223 ± 0.02^{a}	0.181 ± 0.009^{ab}	0.201 ± 0.03^{a}
Mean of lab.*	0.171 ± 0.04^{A}	0.179 ± 0.009^{A}	

Values (mean ± SD).
Different letters represent statistical differences between the averages of the values.
(*) Means with the same letter are not significantly different at 0.05 level of probability according to Duncan's multiple range test.

Although, these differences between the formaldehyde values in Lab. 1 and Lab. 2, a good positive acceptable correlation between the values of formaldehyde from both groups of boards (16 mm thick) had an R^2 value of 0.84 as measured by ASTM D 6007–02 (Figure 31).

Regarding to the one way ANOVA observed in Figure 32, the mean value of formaldehyde measured from PL in Lab. 1 (0.072 ppm) was lower than in Lab. 2 (0.093 ppm) and correspondingly, there were a significant differences between the means. On the other hand, there were no significant differences between means of the formaldehyde emitted from P2 as measured in Lab. 1 (0.171 ppm) and Lab. 2 (0.179 ppm).

Simultaneously, the formaldehyde concentrations values from almost of PL samples measured in Lab. 1 and Lab. 2 ranged from 0.056 to 0.099 ppm, and these values were in agreement of CARB regulation for PB Phase 2 limit (≤ 0.09 ppm). Furthermore, most of FE, values from P2 were ranged from 0.129 to 0.182 and these values in the requirements of CARB Phase 1 limit (≤ 0.18 ppm), except the sample 10 P2 had a high amount of formaldehyde (0.223 ppm).

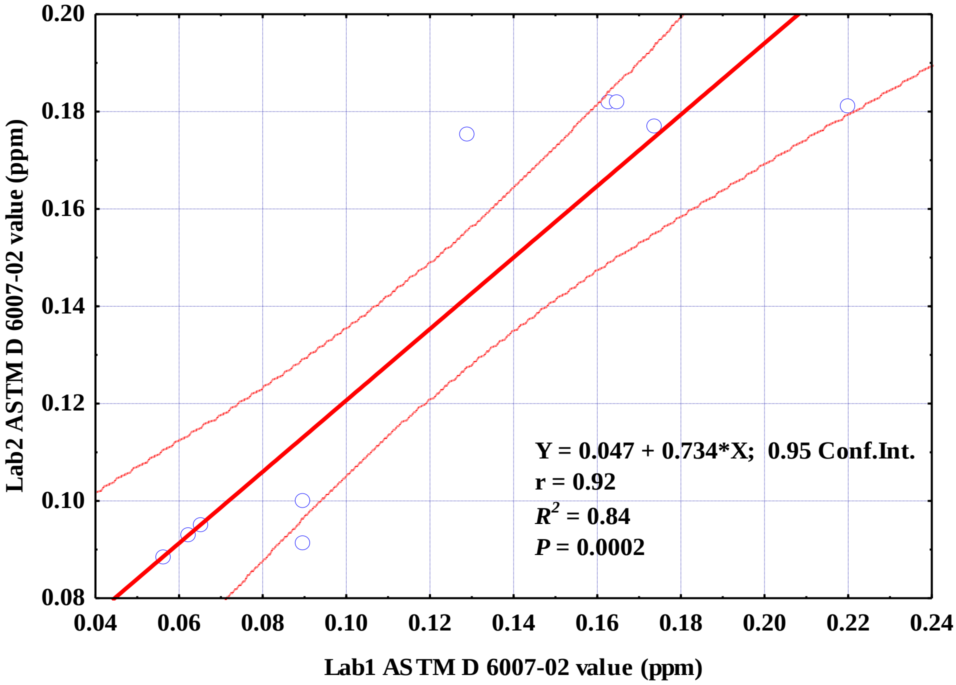


Figure 31. Correlation between the formaldehyde values for 16 mm particleboards measured in two laboratories.

Also the FE values from PBs were decreased due to the lamination of boards with melamine–impregnated paper (Figure 32) and this result was in agreements with Nemli (2003) who found that the melamine–impregnated papers coating decreased the FE of PB, or by other coats like decorative vinyl film and melamine impregnated paper (Groah *et al.*, 1984; Grigoriou, 1987).

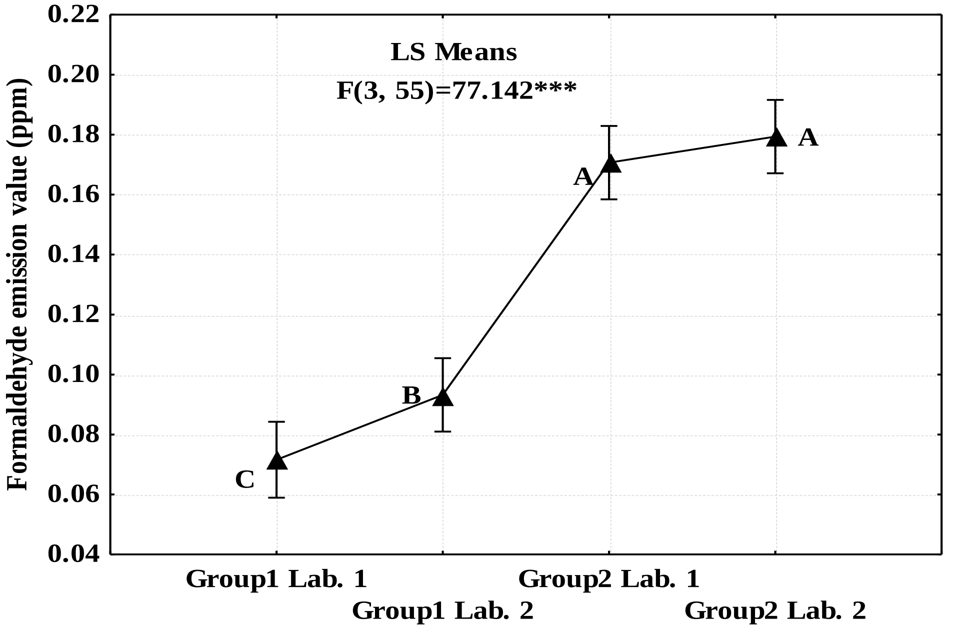


Figure 32: Comparison between the means of formaldehyde emission from two groups of particleboard (16 mm) measured in two laboratories.

The inter–laboratory results showed significant variations between both laboratories, most of them caused by sample heterogeneity and the inconsistency of the values was related to the chamber condition and sampling. These results recommended the necessity of using identical experimental conditions in chambers.

In accordance with the results mentioned above about the variation between the FE values from uncoated and laminated PBs measured in two laboratories for E1–16 mm, the comparison was showed that laboratory 2 gave better accuracy than laboratory 1.

As a general for further studies, the laboratories deemed outliers, or whose results were identified as a concern, CARB recommends that these laboratories should calibrate their small chamber in accordance with large chamber.

6. SUMMARY AND CONCLUSION

Since its discovery in the last half of the nineteenth century, formaldehyde has become an industrial chemical of outstanding importance since it is one of the substances most used by various economic sectors (Walker, 1962). In consequence, the formaldehyde emission (*i.e.,* FE) is today one of the key issues in the chemical industry, by its synthesis or by the synthesis of its derivatives (synthetic resins, plastics, medicines, coloring agents), in the wood industry, the textile industry, etc. (Urdea *et al.,* 2008). Some information about the possible implications of this substance as an industrial toxic in the manufacturing of wood particleboard (*i.e.,* PB) was available since 1962, while the first regulations in this domain regarding the FE are dating back to 1980 (Marutzky, 2008).

In this study, the formaldehyde release from different types of composite wood products such as PB, medium density fiberboard (*i.e.,* MDF), high density fiberboard (*i.e.,* HDF) and plywood (*i.e.,* PLW) and different types of flooring panels were measured well using one or more than one of the following methods: 1) European chamber (EN 717–1), 2) gas analysis (EN 717–2), 3) perforator (EN 120) and 4) American small–scale chamber (ASTM D 6007–02) methods. The European testing and evaluation system is based in principle on chamber testing but in practice, it is executed by derived test methods. Because of formaldehyde's reactivity and pungent odor, formaldehyde has been regulated in the workplace for many years in many countries. Although regulations within Central and East Europe, especially in the Czech Republic, have some way to go before uniformity is achieved and further changes are anticipated, the situation and trends are becoming clearer.

Based on the results, the following conclusion can be summarized:

1. For the thicknesses 8–24 mm, the gas analysis values were ranged from 0.24–1.68, from 0.23–1.38 and 0.98–3.06 mg/m^2.h for uncoated PB (*i.e.,* P2), laminated PB (*i.e.,* PL) and veneered PB (*i.e.,* PV), respectively. In comparison, the perforator values were 3.83–7.53 and from 4.19 to 8.3 mg/100 g o.d. board for P2 and PL, respectively. Most of the values met the E1 requirements.
2. The gas analysis and perforator values for the thicknesses 2.5–19 mm were 0.38–0.71 mg/m^2.h and 5.03–7.36 mg/100 g o.d. board for the uncoated MDF (*i.e.,* MDF) and 0.3–0.61 mg/m^2.h and 4.25–6.83 mg/100 g o.d. board for the laminated MDF (*i.e.,* MDFL), respectively. According to both standards, the formaldehyde release level for MDF and MDFL was at the E1–class emission. The perforator value for HDF with 3.2 mm was 0.95 mg/100 g o.d. board.
3. As a general the values of FE from plywood used in interiors (*i.e.,* PLY) ranged from 0.21 to 0.49 mg/m^2.h, were higher than those from plywood used in construction (*i.e.,*

PLYs) that ranged from 0.13 to 0.24 $mg/m^2.h$ and it can be explained in the using of different glue types.

4. For the thicknesses 12, 16 and 18 mm, the chamber method was applied to measure the emission of formaldehyde from different types of PB (P2, PL and PV). The values ranged from 0.048 (PLT12) to 0.123 mg/m^3 (PVT18). The chamber values were ranged from 0.042 to 0.065 (MDFL) and 0.05–0.087 mg/m^3 (uncoated MDF) from the fiberboards. The PLW values ranged from 0.051–0.066 mg/m^3 for PLY and 0.005 to 0.007 mg/m^3 for PLYs. All values measured under the E1–emission class (E1 ≤ 0.124 mg/m^3). The differences between the values should be related the different types of formaldehyde resins.
5. A positive good correlation with R^2 values of 0.87 and 0.88 was found between the gas analysis concentrations and the corresponding average perforator values from the P2 with 12–18 mm and P2 with 18 mm. An empirical polynomial correlation between gas analysis and the perforator values for PL panels with 8–19 mm was presented, the observed correlation showed that, a good relationship between the two methods with a positive R^2 0.97 with nearly no measurements were outside the 95% confidence interval of the polynomial regression. The polynomial regression for uncoated MDF 3.2–18 mm shows a good positive correlation coefficient of 0.86 between the gas analysis and perforator values.
6. The correlation between the gas analysis and the chamber for the PB and MDF were good (R^2 = 0.82 and 0.76, respectively) and for PLW (R^2 = 0.52), however, was not convincing, so that the FE resulting from the free formaldehyde or from hydrolysis of the cured resin might be attributed to the board type and thickness levels.
7. From the above results about determination of FE and content from different types of composite wood products it was found that, the perforator method was not used for PLW samples because this method has been mainly used for PB and MDF in general. The FE values of PLW samples measured by the gas analysis method were lower than those of the PB and MDF samples. These results were in agreements with Park *et al.*, 2010, which he found that in his study the FE values of PLW samples measured by the 1 m3 chamber method, was lower than those of the PB and MDF samples.
8. In accordance with Martínez and Belanche (2000), there were two main reasons explaining the differences between the FE and FC measured by EN 717–2 and EN 120 respectively from the panels. The first one being that the formaldehyde present in the adhesive interacts in a distinct way with each wood species and the second one

that FE and content values are affected by the anatomy of the respective wood species.

9. The FE values of PLW samples measured by the gas analysis method were lower than those of the PB and MDF samples. These results were in agreements with Park *et al.,* 2010, which he found that the FE values of PLW samples measured by the 1 m3 chamber method, was lower than those of PB and MDF samples.
10. According to the results shown from the equations used for converting between test methods, the estimated emission limit E1–class by conversion factor for EN 717–1 is nearly equivalent to those measured by EN 120. The Japanese *F*** class was more equivalent to European E1–class, while the *F**** and *F***** emission limits were much lower than the E1–class. In this regard, the emission of *F***** boards is close to the emission of solid untreated wood (*i.e.*, between 0.008–0.01 ppm or 0.5–2.0 mg/100 g o.d. board for spruce wood flakes) (Marutzky and Dix, 2004).
11. The resulting Phase 1 was roughly equivalent to the European E1–emission class, as was the Japanese *F*** class. Phase 2 (0.09 ppm) limits were comparable to the Japanese *F**** limits (≈ 0.07 ppm) estimated by conversion factor, the so–called E0 levels in Europe. Also from the tested samples, there was a proportionality observed within the E1–class for EN 120 and EN 717–2 using standard test procedure.
12. As can be observed, the PB E1–emission class had approximately the same value and showed similar behavior for each method. This demonstrates that for the same kind of material, the methods give results, which are likely to be accurate (EN 120, EN 717–1, ASTM E1333 and JIS A 1460). The EN 717–2 in contrast gives a much more pronounced difference, in spite of an intermediate correlation with EN 120.
13. The high amount of FE measured by gas analysis method was observed from PV/UF followed by P2/UF. In the middles values it was found that the uncoated MDF/MUF emitted formaldehyde with values equal PL/UF, in contrast the laminated MDF/MUF had an amount less than the values from PBs, whereas the PLW values from PLYs/PF had the lowest amount of FE. In addition, this results in comparable with the chamber values for the same board type.
14. The PLY/MUF had low amount of formaldehyde in comparable with some PB bonded with UF. These results were in agreement with Aydin *et al.,* (2006) that he reported the FE values of poplar and spruce PLW panels decreased with melamine addition into the UF glue mixture.
15. The inter–laboratory comparison of FE from PBs used for non–structural and interior application as furniture materials supplied from a commercial PB plant in the Czech

Republic was performed by the American small test chamber (ASTM D 6007–02) in two laboratories. The inter–laboratory results showed significant variances between laboratories, caused by formaldehyde analysis or sample heterogeneity. The discrepancy was related to the chamber condition and sampling. These results support the necessity of using identical experimental conditions and including air speed measurements in chambers. The results from suggested that participating laboratory 2 have sufficient experience in the formaldehyde analysis.

16. The analysis of variance showed that there were highly significant effects of board type and thickness ($P < 0.01$) on the FE. It was statistically proven that the application of surface coatings helps significantly decrease the FE of the panels the laminating of PB and MDF surfaces and the thickness had a great influence on FE. For the production of E1 grade boards, all of the process parameters should be taken into account together.
17. From the present work, laminating and decreasing the board thickness had a significant effect on reducing the FE from PBs. This result and previous studies demonstrate that in the production of E1 type PB, low emission adhesive use was is insufficient in this regard and all of the production parameters such as resin formulation, formaldehyde to urea ratio, particle geometry, board moisture content, particle drying temperature, raw material type, board density, formaldehyde scavengers, aging, hardener type and amount, coatings and laminates should be taken into account for the technological properties of E1 type PB (Aston, 1987).
18. The measurements of FE from flooring panels as measured by European small–scale chamber (0.225 m^3) were varied, but almost of the values were under the E1–emission class.

Finally, emissions of formaldehyde are expected to decrease as the product coated and board thickness is decreased. Results reported in this study apply to freshly manufactured materials. A wide variation in the quantity of formaldehyde was observed among the product types. It was clear that the variations between the different values of formaldehyde emissions measured with different methods were resulted from the board type and thickness as well as the resin type. In addition, the other factors like edge sealing and test temperature, which have a large effect on the final emission result, should be taken in consideration.

7. REFERENCES

Akzo Nobel (2005). Kenocatch 4315L. Product information, Casco Adhesives, Sundsvall, Sweden. 2 pp.

Akzo Nobel (2006). Look at the Possibilities! Presentation by Ulf Odda at the 20 June 2006 Composite Wood Products ATCM Workshop. Acc. From: http://www.arb.ca.gov/toxics/compwood/odda.pdf.

Analyscentrum (2006). Determination of formaldehyde emission according to the European chamber method. Factsheet, 1 pp. Downloaded from: http://www.analyscentrum.com/GLP.htm.

ASHRAE (1981). ANSI/ASHRAE Standard 62–1981, Ventilation for Acceptable Indoor Air Quality, Atlanta: American Society of Heating, Refrigerating, and Air–Conditioning Engineers, Inc.

AS/NZS 4266–16 (2001). Australian and New Zealand standards for all wood panel products.

ASTM (2002a). Standard test method for determining formaldehyde concentration in air from wood products using a small–scale chamber. Method D 6007–02. American Society for Testing and Materials, West Conshohocken, PA. 8 pp.

ASTM (2002b). Standard test method for determining formaldehyde concentrations in air and emission rates from wood products using a large chamber. Method ASTM E 1333–96. American Society for Testing and Materials, West Conshohocken, PA. 12 pp.

ASTM D5582–00 (2006). Standard Test Method for Determining Formaldehyde Levels from Wood Products Using a Desiccator.

Aston, R. (1987). Remedial treatments to control formaldehyde emission from panel products. Unpublished Rep. Forintek Canada Corp. Ottowa.

Aydin, I., Colakoglu, G., Colak, S. and Demirkir, C. (2006). Effects of moisture content on formaldehyde emission and mechanical properties of plywood. Building and Environment. 41(10):1311–1316.

Ballerini, A., Despres, A. and Pizzi, A. (2005). Non–toxic, zero emission tannin–glyoxal adhesives for wood panels. Holz als Roh– und Werkstoff. 63(6):477–478.

Battelle (1996). Determination of formaldehyde and toluene diisocyanate emissions from Indoor residential sources. Final Report, CARB Contract No. 93–315, Research Division, Sacramento, CA. 119 pp.

Baumann, M.G.D., Lorenz, L.F., Batterman, S.A. and Zhang, G.–Z. (2000). Aldehyde Emissions from Particleboard and Medium Density Fiberboard Products. Forest Products Journal. 50(9):75–82.

Baumann, M.G.D. (1997). Volatile organic chemical emissions from composite wood products. Technology summary, 8pp. From: http://www.fpl.fs.fed.us/documnts/pdf1997/bauma97a.pdf.

Birkeland, M.J., Lorenz, L., Wescott, J.M. and Frihart, C.R. (2010). Determination of native (wood derived) formaldehyde by the desiccator method in particleboards generated during panel production. Holzfoschung. 64(4):429–433.

Boehme, C. and Roffael, E. (1990). Influence of the different methods in the production of low–formaldehyde chipboard. Adhasion. 32(10):38–45.

Buyuksari, U., Ayrilmis, N., Avci, E. and Koc, E. (2010). Evaluation of the physical, mechanical properties and formaldehyde emission of particleboard manufactured from waste stone pine (*Pinus pinea* L.) cones. Bioresource Technology. 101(1):255–259.

CARB (1992). California Air Resources Board. Identification of Formaldehyde as a Toxic Air Contaminant. Part A. Exposure Assessment. Technical Support Document, Stationary Source Division, Sacramento, CA. 103 pp.

CARB (2003). Composite Wood Survey Package. Accessed: 18 January 2007. From: http://www.arb.ca.gov/toxics/compwood/Survey2002.pdf.

CARB (2007). Composite Wood Products. ATCM (homepage). California Air Resources Board, Sacramento, CA. Accessible at http://www.arb.ca.gov/toxics/compwood/compwood.htm.

CARB (2008). California Air Resources Board. http://www.arb.ca.gov/regact/2007/compwood07/fro–final.pdf.

Connor, A.H. (2001). Wood: Adhesives. In: Buschow KHJ (ed). Encyclopedia of Materials: Science and Technology, p. 9583–9599. Elsevier Science Ltd., Amsterdam. ISBN: 0–08–0431526.

Connor, A.H., Lorenz, L.F. and Hirth, K.C. (2002). Accelerated cure of phenol–formaldehyde resins: Studies with model compounds. Journal of Applied Polymer Science. 86(13):3256–3263.

Cremonini, C., Pizzi, A. and Tekely, P. (1996). Influence of PMUF resins preparation method on their molecular structure and performance as adhesives for plywood. Holz als Roh– und Werkstoff. 54(2):85–88.

Çolak, S. and Çolakoğlu, G. (2004). Volatile acetic acid and formaldehyde emission from plywood treated with boron compound. Building and Environment. 39(5):533–536.

Çolak, S., Çolakoğlu, G., Kalaycioglu, H. and Aydin, I. (2009). Effects of log storage conditions and steaming process on the formaldehyde emissions of particleboard manufactured from eucalyptus (*E. camaldulensis*) wood. Holz als Roh– und Werkstoff. 67(4):379–382.

Çolakoğlu, G. (1993). The effects of plywood manufacturing factors on the formaldehyde emission and technological properties. PhD. dissertation, Karadeniz Teknik University, Trabzon, Turkey (in Turkish).

Çolakoğlu, G., Çolak, S. and Tüfekçi, M. (1998). Einfluß der Dämpfung und Trocknung von Furnieren auf deren Acetylgruppengehalt und die Formaldehydabgabe von Sperrholz. Holz als Roh– und Werkstoff. 56(2):121–123.

Çolakoğlu, G., Aydın, I. and Çolak, S. (2002). The effects of waiting time of alder (*Alnus glutinosa subsp. barbata*) veneers before drying on shear and bending strength of plywood. Holz als Roh– und Werkstoff. 60(2):127–129.

Çolakoğlu, G. and Demirkir, C. (2006). Characteristics of plywood panels produced with urea formaldehyde resin (UF) containing borax. Holz als Roh– und Werkstoff. 64(3):250–251.

Despres, A., Pizzi, A., Vu, C. and Pasch, H. (2008). Formaldehyde–free amino resin wood adhesives based on dimethoxyethanal. Journal of Applied Polymer Science. 110(6):3908–3916.

Despres, A., Pizzi, A., Vu, C. and Delmotte, L. (2010). Colourless formaldehyde–free urea resin adhesives for wood panels. Holz als Roh– und Werkstoff. 68(1):13–20.

Duncan, D.B. (1955). Multiple range and multiple *F* tests. Biometrics. 11:1–42.

Dunky, M. (1995). Wood adhesives: Research and development in Europe. Invited presentation, IUFRO XX World Congress Meeting, 6–12 August 1995, Tampere, Finland. From: http://www.metla.fi/iufro/iufro95abs/d5pap50.htm. Accessed: 7 February 2007.

Dunky, M. (1998). Urea–formaldehyde (UF) adhesive resins fro wood. Int J Adhes Adhes 18:95–107. Eckelman, C.A. 1997. Brief survey of wood adhesives. FNR 154, Forestry & Natural Resources, Purdue University, Cooperative Extension Service, West Lafayette, IN. 10 pp.

Dunky, M. (2005). Resins for ultra low formaldehyde emission according to the Japanese *F***** quality. Wood Adhesives, November 4, 2005, San Diego.

EN 120 (1993). Wood–based panels – determination of formaldehyde content–extraction method called perforator method. European Standard, September 1993.

EN 312 (2003). Particleboard–Specifications. European Standard.

EN 322 (1993). Wood–based panels – determination of moisture content.

EN 622–1 (2003). Fibreboards. Specifications. General requirements.

EN 717–1 (2004). Wood–based panels–determination of formaldehyde release–Part 1: formaldehyde emission by the chamber method. European Standard, October 2004.

EN 717–2 (1994). Wood–based panels–determination of formaldehyde release–Part 2: formaldehyde release by the gas analysis method. European Standard, November 1994.

EN 717–3 (1996). Wood–based panels–determination of formaldehyde release–Part 3: formaldehyde release by the flask method. European Standard, March 1996.

EN 13986 (2002). Wood–based panels for use in construction. Characteristics, evaluation of conformity and marking.

EN 13419–1 (1999). Building products. Determination of the emission of volatile organic compounds. Emission test chamber method.

Eom, Y–G., Kim, S., Baek, I–C. and Kim, H–J. (2005). Comparison of Formaldehyde Emission of Wood–based Panels with Different Adhesive–hardener Combinations by Gas Chromatography and Standard Methods. Mokchae Konghak. 33(2):29–39.

Eom, Y–G., Kim, J–S., Kim, S., Kim, J–A, and Kim, H–J. (2006). Reduction of Formaldehyde Emission from Particleboards by Bio–Scavengers. Mokchae Konghak. 34(5):29–41.

ETB–Richtlinie (1981). German Guideline for the Application of Particleboard with Regards to Avoiding Build–Up of Formaldehyde Concentration in the Indoor Air. Berlin, Auschuss für Einheitliche Technische Baubestimmungen (ETB)/Beuth.

EUWID (2007). Europäischer Wirtschaftsdienst GmbH. Wood–based panels industry wants to end talks on emissions soon. Wood Products and Panels. 81(31):1–13.

Faix, O., Fortmann, I., Bremer, J. and Meier, D. (1991). Thermal degradation products of wood: Gas chromatographic separation and mass spectrometric characterization of polysaccharide derived products. Holz als Roh– und Werkstoff. 49(5):213–219.

Faix, O., Meier, D. and Fortmann, I. (1990). Thermal degradation products of wood: Gas chromatography separation and mass spectrometric characterization of monomeric lignin derived products. Holz als Roh– und Werkstoff. 48(7–8):281–285.

Flentge, A. and Meyer, B. (1990). Extruded particleboards–formaldehyde release–ageing. WKI Short Rep; 7/90.

Frihart, C.R. (2005). Wood adhesion and adhesives. In: Rowell RM (ed). Handbook of Wood Chemistry and Wood Composites. Chapter 9, p. 215–278. CRC Press, Inc., Boca Raton.

Groah, W.J., Gramp, G.D. and Trant, M. (1984). Effect of decorative vinyl overlay on formaldehyde emission. Forest Products Journal. 34(4):27–29.

Groah, W.J., Bradfield, J., Gramp, G., Rudzinski, R. and Heroux, G. (1991). Comparative response of reconstituted wood products to European and North American test methods for determining formaldehyde emissions. Environmental Science & Technology. 25(1):117–122.

Groah, W.J., Gramp, G.D., Heroux, G.L. and Haavik, D.W. (1998). Two procedural aspects of measuring formaldehyde release from wood panel products using the large chamber. Forest Products Journal. 48(9):75–80.

Grigoriou, A. (1987). Formaldehyde emission from the edges and faces of various woods based materials. Holz als Roh– und Werkstoff. 45(2):63–70.

Hamilton–Kemp, T.R. and Andersen, R.A. (1986). Volatile compounds from wheat plants: Isolation, identification, and origin. *In:* ACS Symposium Series 317. Biogeneration of Aromas. Am. Chem. Soc. Washington. DC pp 193–200.

Hatanaka, A., Kajiwara, T. and Sekiya, J. (1976). Biosynthesis of trans–2–hexenal in chloroplasts from *Thea sinesis*. Phytochemistry. 15(7):1125–1126.

IARC (2004). International Agency for Research on Cancer. Overall Evaluations on Carcinogenicity to Humans. As Evaluated in IARC Monographs, Vol. 1. International Agency for Research on Cancer, Lyon, France.

ISO/CD 12460–4 (2007). Wood–based panels–Determination of formaldehyde release–desiccator method. The European committee for standardization.

Jiang, T., Gardner, D.J. and Baumann, M.G.D. (2002). Volatile organic compound emissions arising from the hot–pressing of mixed–hardwood particleboard. Forest products journal. 52(11/12):66–77.

Jin–shul, S., Jian–zhang, L., Yong–ming, F. and Hong–xia, M. (2006). Preparation and properties of waste tea leaves particleboard. Forestry Studies in China. 8(1):41–45.

JIS A 1901 (2003). Determination of the emission of volatile organic compounds and aldehydes for building products–small chamber method. Japanese Standard, January 2003.

JIS A 1460 (2001). Building boards. Determination of formaldehyde emission–desiccator method. Japanese Industrial Standard, March 2001.

JIS A–5908 (1994). Japanese Industrial Standard. JIS standard specification for particleboard.

Jobson, B.T. and McCoskey, J.K. (2010). Sample drying to improve HCHO measurements by PTR–MS instruments: laboratory and field measurements. Atmospheric Chemistry and Physics. 10:1821–1835.

Kavvouras, P.K., Koniditsiotis D. and Petinarakis J. (1998). Resistance of cured urea–formaldehyde resins to hydrolysis: a Method of evaluation. Holz als Roh– und Werkstoff. 52(1):105–110.

Kelly, T.J., Smith, D.L. and Satola, J. (1999). Emission rates of formaldehyde from materials and consumer products found in California homes. Environmental Science & Technology. 33(1):81–88.

Kim, S. and Kim, H.–J. (2004). Evaluation of formaldehyde emission of pine and wattle tannin–based adhesives by gas chromatography. Holz als Roh– und Werkstoff. 62(2):101–106.

Kim, S. and Kim, H.–J. (2005a). Comparison of standard methods and gas chromatography method in determination of formaldehyde emission from MDF bonded with formaldehyde–based resins. Bioresource Technology. 96(13):1457–1464.

Kim, S. and Kim, H.–J. (2005b). Comparison of formaldehyde emission from building finishing materials at various temperatures in under heating system; ONDOL. Indoor Air. 15(5):317–325.

Kim, S. and Kim, H.–J. (2005c). Effect of addition of polyvinyl acetate to melamine–formaldehyde resin on the adhesion and formaldehyde emission in engineered flooring. International Journal of Adhesion and Adhesives. 25(3):456–461.

Kim, S., Kim J.–A., Kim, H.–J. and Kim, S.D. (2006a). Test method. Determination of formaldehyde and TVOC emission factor from wood–based composites by small chamber method. Polymer Testing. 25(8):605–614.

Kim, S., Kim, J.–A., Kim, H.–J., Lee, H.H. and Yoon, D.–W. (2006b). Test Method. The effects of edge sealing treatment applied to wood–based composites on formaldehyde emission by desiccator test method. Polymer Testing. 25(10):904–911.

Kim, S., Kim H.–J., Kim, H.–S. and Lee, H.H. (2006c). Effect of Bio–Scavengers on the Curing Behavior and Bonding Properties of Melamine–Formaldehyde Resins. Macromolecular Materials and Engineering. 291(9):1027–1034.

Kim, S., An, J.–Y., Kim, J.–A., Kim H.–S., Kim, H.–J. and Kim, H.–G. (2007). Physico–mechanical Properties and Formaldehyde/TVOC Emission of Particleboards with Volcanic Pozzolan. Mokchae Konghak. 35(2):39–50.

Kim, K.–W., Kim, S., Kim, H.–J. and Park, J.C. (2010). Formaldehyde and TVOC emission behaviors according to finishing treatment with surface materials using 20 L chamber and FLEC. Journal of Hazardous Materials. 177(1–3):90–94.

Kim, S. (2009a). The reduction of indoor air pollutant from wood–based composite by adding pozzolan for building materials. Construction and Building Materials. 23(6):2319–2323.

Kim, S. (2009b). Environment–friendly adhesives for surface bonding of wood–based flooring using natural tannin to reduce formaldehyde and TVOC emission. Bioresource Technology. 100(2):744–748.

Kim, S. (2009c). Control of formaldehyde and TVOC emission from wood–based flooring composites at various manufacturing processes by surface finishing, Journal of Hazardous Materials. 176(1–3):14–19.

Kim, S. (2010). The reduction of formaldehyde and VOCs emission from wood–based flooring by green adhesive using cashew nut shell liquid (CNSL). Short communication. Journal of Hazardous Materials. 182(1–3):919–922.

Kolarik, B., Gunnarsen, L. and Funch, L.W. (2009). Emission of formaldehyde from indoor surface materials. Proceedings of Healthy Buildings 2009, Paper 160.

Kramer, C.Y. (1956). Extension of multiple range tests to group means with unequal number of replications. Biometrics. 12(3):307–310.

Kramer, C.Y. (1957). Extension of multiple range tests to group correlated adjusted means. Biometrics. 13(1):13–18.

Lei, H., Pizzi, A. and Du, G. (2006). Coreacting PMUF/isocyanate resins for wood panel adhesives. Holz als Roh– und Werkstoff. 64(2):117–120.

Levendis, D. (1992). The correlation of strength and formaldehyde emission with the crystalline amorphous structure of UF resin. Holzforschung. 46(3):263–269.

Li, Q., Sritharathikhun, P. and Motomizu, S. (2007). Development of Novel Reagent for Hantzsch Reaction for the Determination of Formaldehyde by Spectrophotometry and Fluorometry. Analytical Sciences. 23(4):413–317.

Liles, W.T., Koontz, M.D. and Hoag, M.L. (1996). Comparison of Two Small Chamber Test Methods used to Measure Formaldehyde and VOC Emission Rates from Particleboard and Medium Density Fiberboard. Source: STP1287–EB, pp. 11.

Lin, Q., Yang G., Liu, J. and Rao, J. (2006). Property of nano–SiO_2/urea formaldehyde resin. Frontiers of Forestry in China. 1(2):230−237.

Lorenz, L.F. and Connor, A.C. (2000). Accelerated cure of phenol–formaldehyde by the addition of cure accelerators: Studies with model compounds. Accessed: 7 February 2007. From: http://www.fpl.fs.fed.us/documnts/pdf2000/loren00b.pdf.

Mansouri, H.R., Pizzi, A. and Leban, J–M. (2006). Improved water resistance of UF adhesives for plywood by small pMDI additions. Holz als Roh– und Werkstoff. 64(3):218–220.

Marra, A.A. (1992). Technology of Wood Bonding: Principles in Practice. Chapter 4, p. 61–101. Van Nostrand Reinhold Company, New York. 454 pp. ISBN: 0442007973.

Martínez, E. and Belanche, M.I. (2000). Influence of veneer wood species on plywood formaldehyde emission and content. Holz als Roh– und Werkstoff. 58(1–2):31–34.

Marutzky, R. (1989). Release of formaldehyde by wood products; in Pizzi A (ed): Wood Adhesives, Chemistry and Technology. New York, Dekker. 2:307–387.

Marutzky, R. (1994). Release of formaldehyde by wood products. Forest Product Society, 94 RS 100 R.

Marutzky, R. (2008). Technical Formaldehyde Conference–Opening and Thematic Introduction, Technical Formaldehyde Conference, Hanover, Germany, 13–14 March.

Matthews, T.G., Fung, K.W., Tromberg, B.J. and Hawthorne, A.R. (1986). Surface emission monitoring of pressed–wood products containing urea–formaldehyde resins. Environment International. 12(1–4):301–309.

Mayer, J. (1979). Aspects of the development of adhesives with low concentration of formaldehyde to be used in the wood–based materials industry, 1978. Spanplatter–Heute Morgen international Spanlatten symposium, 1979. p. 102–11; DRW–Verlag Weinbrenner K G Stuttgart, Fed. Rep. Ger.

Meyer, B. (1979). Urea–formaldehyde resins. Reading, MA: Addison–Wesley Publishing Company, Inc. pp. 128–129.

Meyer, B. and Boehme, C. (1997). Formaldehyde emission from solid wood. Forest Products Journal. 47(5):45–48.

Meyer, B. and Hermanns, K. (1985). Formaldehyde release from pressed wood products. In: Turoski V (ed) Formaldehyde: analytical chemistry and toxicology. Advances in chemistry series, vol 210. American Chemical Society, Washington, pp 101–116.

Meyer, B., Hermanns, K. and Smith, D.C. (1985). Formaldehyde Release from Urea Formaldehyde Bonded Wood Products. The Journal of Adhesion. 17(4):297–308.

Moubarik, A., Allal, A., Pizzi, A., Charrier, F. and Charrier, B. (2010). Characterization of a formaldehyde–free cornstarch–tannin wood adhesive for interior plywood. European Journal of Wood and Wood Products. 68(4):427-433.

Myers, G.E. (1983a). Formaldehyde emission from particleboard and plywood paneling: measurement, mechanism, and product standards. Forest Products Journal. 33(5):27–37.

Myers, G.E. (1983b). Bibliography: Effects of UF resin mole ratio on formaldehyde emission and other properties. Scarsdale, NY: Formaldehyde Institute.

Myers, G.E. (1984a). Effect of ventilation rate and board loading on formaldehyde concentration: a critical review of the literature. Forest Products Journal. 34(10):59–68.

Myers, G.E. (1984b). How mole ratio of UF resin affects Formaldehyde emission and other Properties: A literature critique. Forest Products Journal. 34(5):35–41.

Myers, G.E. (1985). The effects of temperature and humidity on formaldehyde emission from UF–bonded boards: a literature critique. Forest Products Journal. 35(9):20–31.

Myers, G.E. (1986a). Effects of post–manufacture board treatments on formaldehyde emission: a literature review (1960–1984). Forest Products Journal. 36(6):41–51.

Myers, G.E. (1986b). Resin hydrolysis and mechanisms of formaldehyde release from bonded wood products. In: 1986 Forest Products Research Society Proceedings, Madison, WI, USA.

Myers, G.E. and Nagaoka, M. (1981). Formaldehyde emission: methods of measurement and effects of several particleboard variables. Wood Science. 13(3):140–150.

Nash, T. (1953). The Colorimetric Estimation of Formaldehyde by Means of the Hantzsch Reaction. Biochemical Journal. 55(3):416–421.

Nemli, G. (2002). Factors Affecting the Production of E1 Type Particleboard. Turkish Journal of Agriculture and Forestry. 26(1):31–36.

Nemli, G. (2003). Effects of coating materials process parameters on the technological properties of particleboard, PhD. Dissertation Thesis, Karadeniz Teknik University, Trabzon, Turkey.

Nemli, G., Kirci, H. and Temiz, A. (2004). Influence of impregnating wood particles with mimosa bark extract on some properties of particleboard. Industrial Crops and Products. 20(11):339–344.

Nemli, G. and Colakoğlu, G. (2005a). Effects of mimosa bark usage on some properties of particleboard. Turkish Journal of Agriculture and Forestry. 29(3):227–230.

Nemli, G. and Çolakoğlu, G. (2005b). The influence of lamination technique on the properties of particleboard. Building and Environment. 40(1):83–87.

Nemli, G. and Öztürk, İ. (2006). Influences of some factors on the formaldehyde content of particleboard. Building and Environment. 41(6):770–774.

Osman, Z., Pizzi, A., Kantner, W. and Triboulot, M.C. (2005). PUF panel adhesives doped with additional urea and reinforced by isocyanates. Holz als Roh– und Werkstoff. 63(1):53–56.

Ozalp, M. (2010). Study of the effect of adding the powder of waste PET bottles and borax pentahydrate to the urea formaldehyde adhesive applied on plywood. European Journal of Wood and Wood Products. DOI 10.1007/s00107-010-0439-5.

Park, B–D., Kang, E–C., Park, S–B. Park, J.Y. (2010). Empirical correlations between test methods of measuring formaldehyde emission of plywood, particleboard and medium density fiberboard. European Journal of Wood and Wood Products. 69(12) 311–316.

Pickrell, J.A., Griffis, L.C., Mokler, B.V., Hobbs, C.H., Kanapilly, G.M. and Bathija, A. (1986). Formaldehyde release rate coefficients from selected consumer products. In: Meyer, B., Andrews, B., Reinhardt, R.M. (Eds.), Symposium Series, Formaldehyde release from wood products. American Chemical Society Symposium Series No. 385, Washington, DC, pp. 40–51.

Pizzi, A. (1994). Advanced Wood Adhesives Technology. Chapter 8, p. 273–282. Marcel Dekker, Inc., New York.

Pizzi, A., Von, L.E. and Westermeyer, C. (1995). Adhesive composition comprising isocyanate phenol–formaldehyde and tannin, useful for manufacturing plywoods for exterior application. U.S. Patent 5407980. From: http://www.freepatentsonline.com/5407980.html

Pizzi, A., Tekely, P. and Panamgama, L.A. (1996). A different approach to low formaldehyde emission aminoplastic wood adhesives. Holzforschung. 50(5):481–485.

Pizzi, A., Garcia, R. and Wang, S. (1997). On the networking mechanisms of additives–accelerated phenol–formaldehyde polycondensates. Journal of Applied Polymer Science. 66(2):255–266.

Pizzi, A. (2003). Amino resin wood adhesives. In: Handbook of adhesive technology A. Pizzi and K.L. Mittal (eds.). New York: Marcel Dekker Inc. pp. 541–572.

Que, Z., Furunoa, T., Katoha, S. and Nishino, Y. (2007). Evaluation of three test methods in determination of formaldehyde emission from particleboard bonded with different mole ratio in the urea–formaldehyde resin. Building and Environment. 42(3):1242–1249.

Risholm–Sundmana, M. (1999). Determination of Formaldehyde Emission with Field and Laboratory Emission Cell (FLEC)–Recovery and Correlation to the Chamber Method. Indoor Air. 9(4):268–272.

Risholm–Sundman, M. and Wallin, N. (1999). Comparison of different laboratory methods for determining the formaldehyde emission from three layer parquet floors. Holz als Roh– und Werkstoff. 57(5):319–324.

Risholm–Sundman, M. and Vestin, E. (2005). Emissions during combustion of particleboard and glued veneer. Holz als Roh– und Werkstoff. 63(3):179–185

Risholm–Sundman M., Larsen, A., Vestin, E. and Weibull, A. (2007). Formaldehyde emission–Comparison of different standard methods. Atmospheric Environment. 41(5):3193–3202.

Roffael, E. (1993). Formaldehyde Release from Particleboard and Other Wood Based Panels: Malayan Forest Records No. 3.

Roffael, E. (2002). On The Formaldehyde Release of Wood; Third European Panel Products Symposium.

Roffael, E. (2006). Volatile organic compounds and formaldehyde in nature, wood and wood based panels. Holz als Roh– und Werkstoff. 64(2):144–149.

Roffael, E. (2008). On the release of volatile acids from wood–based panels–chemical aspects. Holz als Roh– und Werkstoff. 66(5):373–378.

Roffael, E., Dix, B. and Schneider, T. (2007). Influence of pulping process on the emission of formaldehyde and volatile organic acids from pulps and medium density fiberboards (MDF). Holz als Roh– und Werkstoff. 65(2):145–148.

Roffael, E., Johnsson, B. and Engström, B. (2010). On the measurement of formaldehyde release from low–emission wood–based panels using the perforator method. Wood Science and Technology. 44(3):369–377.

Romeis, M. (1989). Influence of time and storage on perforators. WKI Rep No 19. Braunschweig, Fraunhofer Institute for Wood Research.

Salthammer, T. and Mentese, S. (2008). Comparison of analytical techniques for the determination of aldehydes in test chambers. Chemosphere. 73(8):1351–1356.

Salem, M.Z.M., Böhm, M. and Barcík, Š. (2009). Determination of formaldehyde emission from composite wood products with different European standard test methods: A literature review. Forest, Wildlife and Wood Sciences for Society Development Prague, 16–18 April 2009. Pages 475–488.

SAS (2001). Users Guide: Statistics (Release 8.02). SAS Inst. Inc., Cary, NC, USA.

Schäfer, M. and Roffael, E. (1996). Effect of storage of residues from saw mill processing of pine and spruce on its suitability as a raw material for particleboards and medium density fiberboards (MDF). Part 3. Effect of storage of saw mill residues derived from wood felled in winter on adhesion relevant proper–ties of chips and fibers prepared therefrom. Holz als Roh– und Werkstoff. 54(5): 341–348.

Schäfer, M. and Roffael, E. (2000). On the formaldehyde release of wood. Holz als Roh– und Werkstoff. 58(4):259–264.

Sensogut, C., Ozalp, M. and Yesil, H. (2009). The effect of borax pentahydrate addition to urea formaldehyde on the mechanical characteristics and free formaldehyde content of plywood. International Journal of Adhesion and Adhesives. 29(5):589–592.

Shinohara, N., Fujiib M., Yamasakic, A. and Yanagisawa, Y. (2007). Passive flux sampler for measurement of formaldehyde emission rates. Atmospheric Environment. 41(6):4018–4028.

Shinohara, N., Kai, Y., Mizukoshi, A., Fujii, M., Kumagai, K., Okuizumi, Y., Jona, M. and Yanagisawa, Y. (2009). On–site passive flux sampler measurement of emission rates of carbonyls and VOCs from multiple indoor sources. Building and Environment. 44(5):859–863.

SS 270236 (1988): Building boards – Determination of formaldehyde emission. Stockholm, SIS–Committee for Standardisation in Sweden.

Sundin, B. (1985). Particleboard with different content of releasable formaldehyde: A comparison of the board properties including results from four different formaldehyde tests. Proc. 21st Int. Particleboard Symp, Washington. pp 139–186.

Steel, R.G.D. and Torrie, T.H. (1989). Principles and procedures of statistics. N.Y. 2nd, McGraw–Hill, N.Y., U.S.A. 633 pp.

Tohmura, S.–I., Hse, C.–Y. and Higuchi, M. (2000). Formaldehyde emission and high–temperature stability of cured urea–formaldehyde resins. Journal of Wood Science. 46(4):303–309.

Tohmura, S.–I., Inoue, A. and Sahari, S.H. (2001). Influence of the melamine content in melamine–urea–formaldehyde resins on formaldehyde emission and cured resin structure. Journal of Wood Science. 47(6):451–457.

Uchiyamaa, S., Matsushimab, E., Kitaoa, N., Tokunagab, H., Andoc, M. and Otsuboa, Y. (2007). Technical note. Effect of natural compounds on reducing formaldehyde emission from plywood. Atmospheric Environment. 41(38):8825–8830.

Urdea, S.N., Zeleniuc, O., Petrovici, V. and Sângeorzan, L. (2008). Study on the Stable State Formaldehyde Emission for Plywood by Flask Method, Proc. of the 3rd International Conference on Environmentally Compatible Forest Products, Porto, Portugal, September, pp.25–30.

US Environmental Protection Agency (1996). Characterization of manufacturing process and emissions and pollution prevention options for the composite wood industry. EPA–600/R–96–066.

Walker, J.F. (1962). Formaldehyde. Third Edition, American Chemical Society, New York, Reinhold Publishing Corporation.

Wang, S.–Y., Te–Hsin, Y., Li–Ting, L., Cheng–Jung, L. and Ming–Jer, T. (2007). Properties of low–formaldehyde–emission particleboard made from recycled wood waste chips sprayed with PMDI/PF resin. Building and Environment. 42(7):2472–2479.

Wang, W.L., Gardner, D.J. and Baummann, M.G.D. (2003). Factors affecting volatile organic compound emissions during hot–pressing of southern pine particleboard. Forest Products Journal. 53(3):65–72.

Wang, W., Zhang, X. and Lu, R. (2006). Adhesive application method in MDI–UF particleboard manufacture. Frontiers of Forestry in China. 1(2):225–229.

Wieland, S., Pizzi, A., Hill S., Grigsby, W. and Pichelin, F. (2006). The reaction in water of UF resins with isocyanates at short curing times: A ^{13}C NMR investigation. Journal of Applied Polymer Science. 100(2):1624–1632.

Wiglusz, R., Jarnuszkiewicz, I., Sitko, E. and Nikel, G, (2000). Interlaboratory comparison experiment on the determination of formaldehyde emitted from mineral wood board using small test chambers. Building and Environment. 35(1):53–57.

Wiglusz, R., Elżbieta, S., Grażyna, N., Irena, J. and Barbara, I. (2002). The effect of temperature on the emission of formaldehyde and volatile organic compounds (VOCs) from laminate flooring–case study. Building and Environment. 37(1):41–44.

Wolcott, J.J., Motter, W.K., Daisy, N.K., Tenhaeff, S.C. and Detlefsen, W.D. (1996). Investigation of variables affecting hot–press formaldehyde and methanol emissions during laboratory production of urea–formaldehyde–bonded particleboard. Forest Products Journal. 46(9):62–68.

Yrieix, C., Dulaurent, A., Laffargue C., Maupetit F., Pacary, T., and Uhde, E. (2010). Characterization of VOC and formaldehyde emissions from a wood based panel: Results from an inter–laboratory comparison. Chemosphere 79(4):414–419.

Yu, C.W.F. and Crump, D.R. (1999). Testing for formaldehyde emission from wood–based products – A review. Indoor Built Environment. 8(5):280–286.

Yu, C.W.F., Crump, D.R. and Squire, R.W. (1999). A Bench–Top Microchamber Method for Measuring Formaldehyde Emission from Wood–Based Panel Products. Indoor and Built Environment. 8(5):287–292.

Zheng, J. (2002). Studies of PF Resole/Isocyanate Hybrid Adhesives. Ph.D. Dissertation, Virginia Polytechnic Institute and State University, Blacksburg, VA. 213 pp. Accessed: 4 February 2007.