Annals of Warsaw University of Life Sciences – SGGW
Forestry and Wood Technology No 111, 2020: 13-20
(Ann. WULS–SGGW, For. and Wood Technol. 111, 2020)

Selected problems concerning volatile organic compounds emission reduction from thick-veneer pine plywood

MARTYNA DYRWAL, PIOTR BORYSIUK
Warsaw University of Life Sciences – SGGW Institute of Wood Sciences and Furniture

Abstract: *Selected problems concerning volatile organic compounds emission reduction from thick-veneer pine plywood*. The paper presents results of research conducted on volatile organic compounds emissions, considering two different production parameter sets for thick-veneer pine plywood, manufactured in industrial conditions. Both types of plywood were produced from raw wood material, which was hydrothermally treated under two different variants of parameters (I – 47˚C, 19 h; II – 55˚C, 24 h). Based on the results it was stated that severe hydrothermal treatment of raw wood material (longer soaking time, higher temperature) had impact on reduction of plywood VOC emission rates. Main VOCs emitted from pine plywood were monoterpenes and carbonyl compounds. Of the monoterpenes, α-pinene and 3-carene had the highest emission. Of the carbonyl group of compounds, the highest emission had hexanal and caproic acid.

Keywords: VOC, thick-veneer pine plywood, HDPE, hydrothermal treatment

INTRODUCTION

Even though it has been present on the market for a long period of time, plywood is still an important construction material used globally across many different industries. In 2018, more than 163 million m^3 of plyboards were produced globally, with almost 10 million m^3 in Europe, which only confirms its popularity (http://www.fao.org/faostat). In the last 10 years, plywood global production volume has increased by 80% and by 40% in Europe only. In 2018, Poland's annual production volume was approximately 555 000 m^3, which gives it 14th place globally and 3rd place in Europe. Companies from Poland produce both softwood and hardwood plywood, which are mainly used in furniture, construction, automotive, boatbuilding and packaging industries (Fierek *et al.* 2013). Just as any other wood material, regardless of its application, plyboards should have not only appropriate resistance parameters but it also needs to conform to different health quality standards by providing a low rate of Volatile Organic Compounds (VOC) emission.

VOCs are a group of organic compounds, which (WHO 1989, https://goodair.pl):

- can easily change their forms to gas or steam,
- characterize with high vapour pressure and low solubility in water,
- boiling point amounts to temperatures between 50–250˚C (measured at normal pressure level of 101.3 kPa).

VOCs are present in various production processes as by-products and conduce to environment pollution. The most significant consequence is secondary pollution, which is a result of chemical reaction between VOCs and other substances in the environment. It is also worth mentioning that 60% of atmosphere polluting substances are VOCs and 73% of them are carcinogenic (Zabiegała 2009). The most common VOCs are aliphatic hydrocarbons, olefines, aromatic hydrocarbons, aldehydes, ethers, organic nitrogenous and organic sulphur compounds.

For wood materials, which are a common intermediate product in interior design elements, VOC emission comes from both lignocellulosic materials and chemical additives. Formaldehyde and other compounds have significant impact on the interior air condition and pollution (Cakmak *et al.* 2014, Liang *et al.* 2014, Harb *et al.* 2018, Qi *et al.* 2019). Moreover,

they could also have negative effects on one's health and wellbeing (Gminski *et al.* 2011a, Gminski *et al.* 2011b). Specific level of harmfulness depends on VOC concentration in the indoor air (Table 1). Types of compounds emitted from wood-based panels and their emission levels are subjects to many researches, conducted all over the world (Koontz and Hoag 1995, Baumann *et al.* 1999, Baumann *et al.* 2000, Jiang *et al.* 2002, Kim *et al.* 2006, Xiong *et al.* 2019).

Table 1. Relation between TVOC concentration (Total Volatile Organic Compounds) in the indoor air and potential health hazards (Zabiegała 2009)

Pollution level	Level of health hazard
< 100 μg/m^3	Harmless
200 – 300 μg/m^3	Potentially harmful
300 – 5000 μg/m^3	Harmful, causing unpleasant smell

After plywood testing, Jóźwiak and Czajka (2013) noted that the level of VOC emission depends on veneer storage time and plywood seasoning. Main VOCs emitted from pine plywood and veneer were monoterpenes and carbonyl compounds. From monoterpenes the highest emission had α-pinene and 3-carene. From the carbonyl group, hexanal had the highest emission. Nonetheless, wood materials VOC emission can be reduced by applying appropriate finishing materials (Liu and Zhu 2014, Cao *et al.* 2019). However, according to the research conducted by Liu and Zhu (2014) and also Cao *et al.* (2019), the mentioned solution can reduce the emission rate of one compound but increase the emission rate of another. Jua *et al.* (2020) indicated that it is possible to reduce VOC emission from birch plywood glued with phenol formaldehyde resins by partially substituting phenol with bio-oil. Although authors noted a statistically significant reduction of the total emission of VOC, they also confirmed that the formaldehyde emission rate had increased.

Many research are currently conducted to describe what impact production processes, starting from raw material preparation to further wood-based panels manufacturing technology, have on the final VOC emission rate. While examining MDF, He *et al.* (2012) indicated that the VOC emission rate can be reduced by applying appropriate drying and pressing parameters. Most of such research is aimed only at finding possible new solutions to reduce formaldehyde emissions. For example, Bekhta *et al.* (2020) stated that applying higher temperature during drying process of birch veneer in an industrial veneer steam dryer can reduce formaldehyde emission of plywood.

The aim of present research is to determine the impact of hydrothermal processing of raw pine wood on VOC emission of plywood, made from tested material.

MATERIALS AND METHODS

The assay of volatile organic compounds emission was made on pine thick veneer plyboards, produced in industrial conditions. Raw pine wood material (Pinus sylvestris L.), used in production process of the plywood, was hydrothermally treated, concerning two different technological parameter sets:

- Variant I (standard) – soaking raw wood material in temperature of 47˚C ±1˚C for 19 h ±1 h;
- Variant II (modified) – soaking raw wood material in temperature of 55˚C ±1˚C for 24 h ±1 h.

During application of both variant factors, which could influence hydrothermal treatment (such as log diameter, season) were maintained on the same range of variations.

After hydrothermal treatment, the plasticized wood material was peeled into veneer sheets with thickness of 2.6 mm, ±0.2 mm. The material was peeled using Raute peeling line. Drying process was made using Raute drying line VTS6 and applying following parameters:

temperature – 192˚C ±3˚C, drying time – 90 minutes, final humidity – 8% ±1%. Plywood produced from treated veneer sheets had 8 and 9 veneer layers and were glued with phenol-formaldehyde-based resin. Characteristics of produced plywood and parameters used during production processes are shown in table 2.

Table 2. Characteristics and parameters used for pressing process of plywood

Plywood structure*		Glue ingredients and composition	Pressing parameters	
Variant I (starting)	9-layer plywood with 21 mm of thickness	resin – 720 kg filler – 100 kg water – 70 kg spread rate – 165 g/m^2	time – 15 min	temperature – 132^{o}C ±2˚C pressing pressure – 1.1 MPa
Variant II (modified)	8-layer plywood with 18 mm of thickness		time – 12 min	

* Variations in structure of analysed plywood resulted from necessity of producing items for different purchase orders while conducting the research.

For the VOC emission analysis two samples were obtain from the above-mentioned types of plywood with 450 mm of length, 200 mm of width and thickness as follows:

- Variant I (starting) – 42 mm (2 × 21 mm) with sample density of 11416 g/m^2 (Figure 1);
- Variant II (modified) – 36 mm (2 × 18 mm) with sample density of 10137 g/m^2 (Figure 2);

Analysis of volatile organic compounds emission was made in accordance with EN 16516:2017 and EN 717-1:2006 standards in laboratory certified by MPA Eberswalde Materialprüfanstalt Brandenburg GmbH. Present assay was compliant with German AgBB-scheme (Committee of Health-related evaluation of construction products), according to French regulations “decret n˚2011-321 du 23 mars 2011” and “arrête du 19 avril 2011” and according to Finnish M1/M2- assessment.

Before testing side surfaces of the samples were covered using low-carbon aluminium tape. Samples were placed in test chambers (Figure 1 and 2), which enabled to maintain following testing parameters:

- Temperature: 23˚C (±1˚C).
- Humidity: 50% (±3%).
- Air-flow velocity: 0.5 AC/h (±0.5 AC/h).

Figure 1. Variant I sample

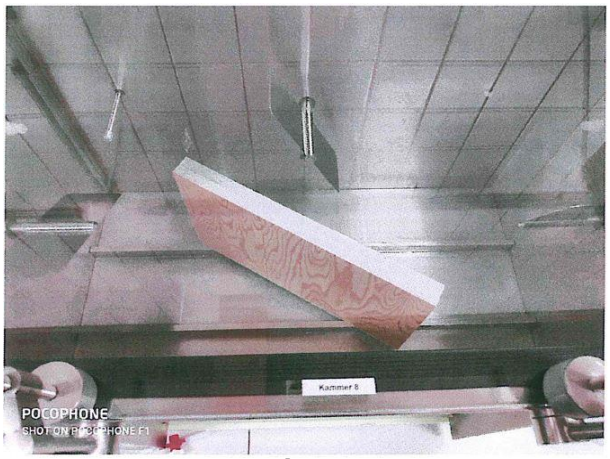

Figure 2: Variant II sample

The VOC emission rate and formaldehyde concentration in air were measured twice, 3 and 28 days after the plywood was produced.

RESULTS AND DISCUSSION

The analysis of thick-veneer pine plywood enabled to determine total volatile organic compounds, total semi-volatile organic compounds, carcinogenic, mutagenic, or toxic volatile compounds to reproduction (CARC 1A and CARC 1B) content levels and also formaldehyde emission rate. The results of the analysis were presented in tables 3, 4, 5 and 6.

Table 3. VOC and formaldehyde content levels after 3 days – variant I (standard)

	Concentration after 3 days [μg/m^3]	SER$_a$ [μg/m^{2}h]*
TVOC**	2984	1492
TSVOC***	< 5	< 2.5
Volatile carcinogens of act. CARC 1A and CARC 1B	< 1	< 0.5
Formaldehyde	57	28.5
*specific emission rate related to area **total volatile organic compounds (sum of concentrations of VOC) ***total semi-volatile organic compounds (sum of concentrations of SVOC)		

Table 4. VOC and formaldehyde content levels after 3 days – variant II (modified)

	Concentration after 3 days [μg/m^3]	SER$_a$ [μg/m^{2}h]*
TVOC**	399	199.5
TSVOC***	< 5	< 2.5
Volatile carcinogens of act. CARC 1A and CARC 1B	< 1	< 0.5
Formaldehyde	11	5.5
*specific emission rate related to area **total volatile organic compounds (sum of concentrations of VOC) ***total semi-volatile organic compounds (sum of concentrations of SVOC)		

According to above-mentioned results, applying changes in hydrothermal treatment, applied on raw material, had a positive impact on reducing VOC emission rate of final products, taking eventual influence of different plywood structures into consideration. 3 days after the day of manufacture, the plywood produced from the material treated in more severe hydrothermal conditions (longer soaking time, higher temperature) had over 7 times lower TVOC emission rates and over 5 times lower formaldehyde emission rate. Corresponding results were obtained 28 days after the day of manufacture. What is more, 3 days after the manufacture day it was noted that TVOC emission rate was reduced by 40% and formaldehyde emission rate was reduced by 60%, regardless of the used production variant. No difference was noticed in the concentration values of total semi-volatile organic compounds and volatile carcinogens of act. CARC 1A and CARC 1B between the applied variants after both 3 and 28 days after day of manufacture.

While analysing the obtained results it can be firmly stated that the plywood produced using variant I (starting) parameters, regardless of time duration between the day of manufacture and testing, had such high TVOC emission rate that it can be regarded as non-indifferent (Zabiegała 2009). On the other hand, the plywood produced using variant II (modified) parameters had TVOC emission rate reduced to 300 μg/m^3 28 days after the day of manufacture, which allows to classify it as potentially harmful (Zabiegała 2009).

What is important, the reduced TVOC emission rate of plywood produced from raw wood material using severe hydrothermal treatment (variant II) did not result only from a difference in structure (fewer veneer sheets and glue joints) in comparison with the standard plywood (variant I).

It was also confirmed by Jóźwiak and Czajka (2013), whose research results showed that 4 days after the day of manufacture three-ply pine plywood, glued with MUF-based resin,

had 5700 μg/m^3 of TVOC emission rate. However, the content level of heartwood and sapwood had a significant impact on the VOC emission rate (Czajka and Fabisiak 2012). Taking those factors into account it should be stated that plywood produced in the purpose of this research using both, variant I and II, were manufactured from raw wood material with a similar macroscopic structure (comparable heartwood content).

Table 5. VOC and formaldehyde emission rate after 28 days – variant I (standard)

	Concentration after 28 days [μg/m^3]	SER$_a$ [μg/m^{2}h]*
TVOC**	1804	902
TSVOC***	< 5	< 2.5
Volatile carcinogens of act. CARC 1A and CARC 1B	< 1	< 0.5
Formaldehyde	21	10.5
*specific emission rate related to area **total volatile organic compounds (sum of concentrations of VOC) ***total semi-volatile organic compounds (sum of concentrations of SVOC)		

Table 6. VOC and formaldehyde emission rate after 28 days – variant II (modified)

	Concentration after 28 days [μg/m^3]	SER$_a$ [μg/m^{2}h]*
TVOC**	231	115.5
TSVOC***	< 5	< 2.5
Volatile carcinogens of act. CARC 1A and CARC 1B	< 1	< 0.5
Formaldehyde	4	2
*specific emission rate related to area **total volatile organic compounds (sum of concentrations of VOC) ***total semi-volatile organic compounds (sum of concentrations of SVOC)		

Table 7 presents a comparison of specific VOC emission rates of pine plywood manufactured according to variant I and II parameters. The main VOC emitted from the tested plywood were monoterpenes and carbonyl compounds, regardless of variant parameters. From monoterpenes the highest emission had α-pinene and 3-carene. From the carbonyl group of compounds the highest emission had hexanal and caproic acid. Analogous results were obtained by Jóźwiak and Czajka (2013), who tested plywood and Baumann *et al.* (1999, 2000), who tested particleboards and MDF. The presence of monoterpenes could be noticed as a specific smell, which in high concentration could cause irritation of the respiratory system. (Prosiński 1984, Rowell 2005, Ek *et al.* 2009).

On the other hand, carbonyl compounds (aldehydes, ketones, carboxylic acids) exude a very unpleasant smell and have higher toxicity (Ek *et al.* 2009). It should be mentioned that aldehydes are not original wood extracts and are developed during the oxidation of unsaturated fatty acids (Baumann *et al.* 2000, Roffael 2006, Ek *et al.* 2009). The enzymatic oxidation of unsaturated fatty acids processes and change to hexanal and nonanal for non-woody plants were described by Hamilton-Kemp and Andersen (1986).

The presented analysis of changes in the emission rates of specific compounds (table 7) shows that severe hydrothermal treatment of raw material (longer soaking time, higher temperature), used in accordance with variant II parameters, reduces the concentration of every analysed substance. Depending on the compound type, the emission rate was reduced from 33% to 94%. Taking into consideration health hazard issues, the most significant changes were noted for aldehyde compounds, such as formaldehyde, propionaldehyde, acetaldehyde and hexanal, which have toxic or even carcinogenic properties.

Table 7. Selected VOC emission rates for plywood, 28 days after day of manufacture

Compound name	Concentration [μg/m^3]	
	Variant I (standard)	Variant II (modified)
Formaldehyde	21	4
Propionaldehyde	17	3
Acetaldehyde	49	10
Butyraldehyde	7	4
Pentanal	43	16
Hexanal	240	32
Heptanal	8	2
Octanal	8	5
Nonanal	9	6
Octane	19	4
1-pentanol	18	5
Toluene	6	1
1-Isopropyl-4-methylbenzene	15	2
Acetic acid	120	19
Valeric acid	34	4
caproic acid	210	16
Octanoic Acid	4	1
Acetone	120	17
2-heptanone	11	4
α-pinene	720	69
Camphene	16	1
3-carene	180	58
Verbenone	8	1
Limonene	22	2

CONCLUSION

On the basis of conducted research concerning TVOC emission rates of thick-veneer pine plywood manufactured from raw wood material which was hydrothermally treated using two different variants of parameters, it can be stated that:

1. Thick-veneer pine plywood manufactured from raw wood material, treated in severe hydrothermal conditions (longer soaking time, higher temperature) had over 7 times lower TVOC emission rates.
2. Thick-veneer pine plywood manufactured from raw wood material, treated in severe hydrothermal conditions (longer soaking time, higher temperature) had over 5 times lower formaldehyde emission rate.
3. From monoterpenes the highest emission had α-pinene and 3-carene. From the carbonyl group of compounds, the highest emission had hexanal and caproic acid.
4. The suggested changes in hydrothermal treatment of raw wood material do not influence concentration values of total semi-volatile organic compounds and volatile carcinogens of act. CARC 1A and CARC 1B emission rates, considering both mentioned types of plywood manufacturing parameter variants.

REFERENCES

1. BAUMANN M.G.D., BATTERMAN S.A., ZHANG G.Z., 1999: Terpene emissions from particleboard and medium-density fiberboard products. Forest Products Journal, 49, 49–56.
2. BAUMANN M.G.D., LORENZ L.F., BATTERMAN S.A., ZHANG G.Z., 2000: Aldehyde emissions from particleboard and medium density fiberboard products. Forest Products Journal, 50, 75–82.

3. BEKHTA P., SEDLIAČIK J., BEKHTA N., 2020: Effect of veneer-drying temperature on selected properties and formaldehyde emission of birch plywood. Polymers 12, 593, doi:10.3390/polym12030593.
4. CAKMAK S., DALES R.E., LIU L., KAURI L.M., LEMIEUX C.L., HEBBERN C., ZHU J., 2014: Residential exposure to volatile organic compounds and lung function: results from a population-based cross-sectional survey. Environmental Pollution, 194, 145–151.
5. CAO T., SHEN J., WANG Q., LI H., XU C., DONG H., 2019: Characteristics of VOCs released from plywood in airtight environments. Forests 10, 709, doi:10.3390/f10090709.
6. CZAJKA M., FABISIAK E., 2012: Emission of volatile organic compounds from cross section of pine wood (Pinus sylvestris L.). Annals of Warsaw University of Life Sciences – SGGW, Forestry and Wood Technology 77, 150–154.
7. EK M., GELLERSTEDT G., HENRIKSSON G., 2009: Pulp and Paper Chemistry and Technology Volume 1 Wood Chemistry and Wood Biotechnology. Walter de Gruyter GmbH & Co. KG, Berlin.
8. EN 16516:2017 Construction products: Assessment of release of dangerous substances – Determination of emissions into indoor air; Determination of the emission of volatile organic compounds (VOC) and Formaldehyde from construction products.
9. EN 717-1:2006 Wood-based panels. Determination of formaldehyde release Formaldehyde emission by the chamber method.
10. FIEREK A., WNOROWSKA M., BORYSIUK P., HIKIERT M. A., KOWALUK G., 2013: Przewodnik po płytach drewnopochodnych. Stowarzyszenie Producentów Płyt Drewnopochodnych w Polsce.
11. GMINSKI R., MARUTZKY R., KEVEKORDES S., 2011a: Chemosensory irritations and pulmonary effects of acute exposure to emissions from oriented stand board. Human & Experimental Toxicology, 30,1204–1221.
12. GMINSKI R., MARUTZKY R., KEVEKORDES S., 2011b: Sensory irritations and pulmonary effects in human volunteers following short-term exposure to pinewood emissions. Journal of Wood Science, 57, 436–445.
13. HAMILTON-KEMP T.R., ANDERSEN R.A., 1986: Volatile Compounds from Wheat Plants: Isolation, Identification and Origin. ACS Symposium Series Vol. 317, Biogeneration of Aromas, 193–200, DOI: 10.1021/bk-1986-0317.ch016.
14. HARB P., LOCOGE N., THEVENET F., 2018: Emissions and treatment of VOCs emitted from wood-based construction materials: impact on indoor air quality. Chemical Engineering Journal, 354, 641–652.
15. HE Z., ZHANG Y., WEI W., 2012: Formaldehyde and VOC emissions at different manufacturing stages of wood-based panels. Building and Environment 47, 197–204.
16. http://www.fao.org/faostat/en/#data/FO (dostęp 25.06.20220 r.).
17. https://goodair.pl/blog/lzo-co-to (dostęp 26.06.20220 r.).
18. JIA L., CHU J., LI J., REN J., HUANG P., LI D., 2020: Formaldehyde and VOC emissions from plywood panels bonded with bio-oil phenolic resins. Environmental Pollution 264, 114819. https://doi.org/10.1016/j.envpol.2020.114819.
19. JIANG T., GARDNER D.J., BAUMANN M.G.D., 2002: Volatile organic compound emissions arising from the hot-pressing of mixed-hardwood particleboard. Forest Products Journal, 52, 66–77.
20. JÓŹWIAK M., CZAJKA M., 2013: Investigation of VOC emissions from pine plywood. Annals of Warsaw University of Life Sciences – SGGW, Forestry and Wood Technology 83, 29–31.

21. KIM S., KIM J.A., KIM H.J., KIM S.D., 2006: Determination of formaldehyde and TVOC emission factor from wood-based composites by small chamber method. Polymer Testing, 25, 605–614.
22. KOONTZ M.D., HOAG M.L., 1995: Volatile organic compound emissions from particleboard and medium density fiberboard. In: Proceedings of measuring and controlling volatile organic compound and particulate emissions from wood processing operations and wood-based products. Weinheim: Wiley-VCH, 76–87.
23. LIANG W., WANG C., YANG C., YANG X., 2014: Volatile organic compounds in different interior construction stages of an apartment. Building and Environment, 81, 380–387.
24. LIU Y., ZHU X., 2014: Measurement of formaldehyde and VOCs emissions from wood-based panels with nanomaterial-added melamine-impregnated paper. Construction and Building Materials, 66, 132–137.
25. PROSIŃSKI S., 1984: Chemia drewna. PWRiL, Warszawa.
26. QI Y., SHEN L., ZHANG J., YAO J., LU R., MIYAKOSHI T., 2019: Species and release characteristics of VOCs in furniture coating process. Environmental Pollution, 245, 810-819.
27. ROFFAEL E., 2006: Flüchtige organische Verbindungen (VOC) und Formaldehyd in der Natur, im Holz und in Holzwerkstoffen. Holz als Roh-und Werkstoff 64:144–149.
28. ROWELL R.M., 2005: Handbook of wood chemistry and wood composites. CRC Press, Taylor & Francis Group, Boca Raton.
29. WHO, 1989: Indoor air quality: organic pollutants. Environmental Technology Letters, 10 (9), 855-858, https://doi.org/10.1080/09593338909384805.
30. XIONG J., CHEN F., SUN L., YU X., ZHAO J., HU Y., WANG Y., 2019: Characterization of VOC emissions from composite wood furniture: parameter determination and simplified model. Building and Environment 161, 106237, https://doi.org/10.1016/j.buildenv.2019.106237.
31. ZABIEGAŁA B., 2009: Jakość powietrza wewnętrznego – lotne związki organiczne jako wskaźnik jakości powietrza wewnętrznego = Indoor air quality – volatile organic compounds as an indicator of the quality of indoor air. In Polska Inżynieria Środowiska pięć lat po wstąpieniu do Unii Europejskiej, t. 2/ ed. red. J. Ozonek; A. Pawłowski, Komitet Inżynierii Środowiska PAN, Wydział Inżynierii Środowiska Politechniki Lubelskiej, Lublin, 303–315.

Streszczenie: *Wybrane zagadnienia ograniczenia emisji lotnych związków organicznych ze sklejki sosnowej grubowarstwowej*. Przedstawiono wyniki badań emisji lotnych związków organicznych z dwóch wariantów sklejek sosnowych grubowarstwowych wytworzonych w warunkach przemysłowych. Poszczególne warianty sklejek wykonano z surowca poddanego zróżnicowanym pod względem parametrów procesom obróbki hydrotermicznej (I – 47˚C, 19 h; II – 55˚C, 24 h). Na podstawie przeprowadzonych badań stwierdzono, że intensywniejsza obróbka hydrotermiczna surowca (wydłużony czas, wyższa temperatura) wpływa na ograniczenie emisji VOC ze sklejki. Głównymi związkami VOC emitowanymi ze sklejki sosnowej były monoterpeny oraz związki karbonylowe. Najwyższą emisją wśród monoterpenów charakteryzował się α-pinen i 3-karen, a w grupie związków karbonylowych heksanal i kwas kapronowy.

Corresponding author:
Martyna Dyrwal
Nowoursynowska Str. 159
02-787 Warszawa, Poland
e-mail: martynadyrwal@gmail.com
phone: +48 519 422 620