CIMAD

Madrid, España
10-14 de Junio

24

III Congreso Ibero-Latinoamericano de la Madera en la Construcción

LIBRO DE ACTAS DE RESÚMENES EXTENDIDOS

Anfitriones:

Montes

ARQUITECTURA

POLITÉCNICA

CIMAD 24

Madrid, España

10-14 de Junio

III Congreso Ibero-Latinoamericano de la Madera en la Construcción

LIBRO DE ACTAS DE RESÚMENES EXTENDIDOS

Organizado por el Grupo de Investigación Construcción con Madera

CONSTRUCCION CON MADERA
GRUPO DE INVESTIGACIÓN
UNIVERSIDAD POLITÉCNICA DE MADRID

Web del congreso:
https://www2.montes.upm.es/CIMAD2024/

Editada en Madrid el 26 de junio de 2024

1105

INFLUENCE OF THE USE OF UNDERUTILISED TREE AND SHRUB SPECIES ON FORMALDEHYDE EMISSIONS FROM PARTICLEBOARD

Tamara Coello-García[1]; Eduardo Bordallo[1]; Irene Mediavilla[2]; Werner Gerwin[3]; Steffi Schillem[3]; Ciprian Palaghianu[4]; Luis Saúl Esteban[2]

[1] *CESEFOR*
[2] *CEDER-CIEMAT*
[3] *Brandenburg Univ. of Technology Cottbus-Senftenberg*
[4] *Universitatea Ștefan cel Mare*

Palabras clave / Palavras-chave:

Wood extractives, Flask method, Perforator method, Lignin, Acetyl groups, PH

Resumen / Resumo:

The demand for wood for use in construction will multiply in the coming years with the emergence of new European policies pushing for a more carbon-efficient sector, but wood prices are increasing and availability is periodically threatened by different factors such as bark beetle outbreaks, climatic events and spruce decline. It becomes necessary to incorporate new wood species into engineered wood-based products to supply the industry, which is especially appealing in products such as particleboard, with less stringent requirements than other wood products in terms raw materials' quality. However, there is scarce knowledge on 1) how the introduction of new species affects formaldehyde emissions from boards (one of the main industry's sticking points), and 2) what is the role of the wood's main components (cellulose, hemicellulose, acetyl groups, lignin, extractives) in these emissions. Within the scope of the BeonNAT project, we manufactured particleboards from ten different tree & shrub species from Germany, Romania and Spain, we evaluated their formaldehyde emissions (EN-717-3) and we compared them with the emissions from particleboard made with the biomass used in a manufacturing plant. Besides, we explored the relationship between formaldehyde emissions and the biomass main components. Most of the boards made from the species under study produced less emissions than the boards from industrial biomass ($F(12,26)=15.02$, $p<0.05$), suggesting that all of them could be introduced as raw material without entailing an increase of formaldehyde emissions. Besides, we found a strong correlation ($p<0.01$) between wood extractives (%) and formaldehyde emissions.

1. Introduction

Formaldehyde (HCOH) emission is one of the main challenges of the wood-based panels industry. Current emission limit for low formaldehyde wood-based panels is ≤ 8 mg HCOH/ 100 g of dry board (measured using the "perforator method" UNE-EN ISO 12460-5), and will be reduced by half as of 2026[1]. At the same time, there is a growing interest in the industry to introduce alternative woody biomass resources to face wood's increasing demand and prices as well as low availability, but there is scarce information on how the introduction of these alternative species will affect formaldehyde emissions from particleboards. While there is a deep understanding on the influence of process parameters and environmental variables on emissions, there is little information on the influence of the main components of the wood (cellulose, hemicellulose, acetyl groups, lignin, extractives and ash). It has been proposed that some wood extractives can act as HCOH scavengers by reacting with the HCOH from the adhesive[2], but this has not been investigated across a wide range of species. In the context of the BeonNAT project, and from the perspective of the cascade use of materials in a biorefinery approach where several underutilised tree & shrub species are grown and used for the manufacturing of different products (e.g., essential oils, herbal extracts), we have: 1) Produced particleboards from ten different species from different origins (twelve samples), measured their HCOH emissions and compared them with the emissions from boards manufactured with biomass used by a particleboard manufacturer; and 2) Investigated the relationship between HCOH emissions from the boards and the biomass main components.

2. Methodology

2.1. Biomass processing and characterization

Lignocellulosic biomass from three different origins (Ulmus pumila, Cistus ladanifer, Juniperus communis and Rosmarinus officinalis from Spain, Rubus fruticosus, Cytisus scoparius, Betula pendula and Robinia pseudoacacia from Germany; and Robinia pseudoacacia, Betula pendula, Populus nigra and Carpinus betulus from Romania) (Table 1) was harvested and processed as follows: all samples were first crushed (20 mm); next, the samples of C. ladanifer, J. communis and R. officinalis were steam distilled to produce essential oils; next, all samples (extracted and non-extracted) were sieved and blowed, and the coarse fraction from sieving (with a higher proportion of wood without bark) was milled (8 mm) and blowed again to remove dust. The remaining fraction was analysed in terms of moisture content, particle size and geometry, bulk and basic density, pH and bark content, and used for particleboard manufacturing. On the other hand, samples were also characterized in terms of cellulose, hemicellulose, acetyl groups, lignin and extractives in water and ethanol, and ash.

2.2. Particleboard manufacturing

Triplicate particleboards from each species were manufactured. Biomass particles were dried at 65 °C overnight to ensure a moisture content of 2-4% and blended in a paddle mixer to reach an adhesive load of 8% on a solid adhesive to oven dry wood basis. The adhesive mix consisted of 76% commercial urea-formaldehyde resin, 8% NH_4NO_3 as hardener, 8% paraffin and 9% water according to the typical resin addition levels[3]. 1.5 kg of resinated particles were used to manually produce one-layer particleboards using a 415 x 415 x 12 mm mould and then hot-pressed (2.5 MPa, 200 °C, 5 min). Upon conditioning for 6-7 days, the particleboards were sanded to a 10 mm thickness. Next, 25 x 25 x 10 mm test pieces were produced to measure HCOH emissions. The time elapsed between panel cutting and HCOH emissions measuring was always <72 h. For the sake of comparison, we asked for a sample of biomass from an industrial particleboard manufacturer (SAMPLE I.P., 75% recycled wood, 25% pine wood) and we followed the same procedure.

2.3. Formaldehyde emissions analysis

Formaldehyde emissions were measured following the standard method EN-717-3, "the flask method". Triplicate 20 g of board samples were suspended on top of 50 ml of distilled water in closed bottles and incubated at 40°C for three hours, and formaldehyde was determined using the acetylacetone method. Results are expressed in g of HCOH per kg of dry board. While this method is widely adopted by research institutions because of its convenience and low cost, no official limits are published for it, so in order to know if the boards met the ≤ 8 mg HCOH/100 g of dry board limit, we established a comparison between the flask method and the perforator method (UNE-EN ISO 12460-5). Thus, a new set of triplicate particleboards per species were manufactured and measured with both methods. The measurement with the perforator method were outsourced to an industrial partner. Briefly, HCOH was extracted by boiling the test pieces in toluene at 110 °C for 2h, then extracted to water and detected photometrically with the acetylacetone method. Results are expressed in g of HCOH per 100 g of dry board and is corrected for a moisture content of 6.5%.

2.4. Statistical analysis

Data were analysed using RStudio. Variables and relationships between them were first inspected using boxplots, qqplots and scatterplots. One-way independent ANOVA was used to assess if particleboard manufactured from the studied species emitted less HCOH than particleboard manufactured with biomass from a particleboard manufacturer.

3. Results

3.1. Formaldehyde emissions

Measured formaldehyde emissions ranged between 19.80 and 50.20 g HCOH/ kg of dry board across samples (Figure 1).

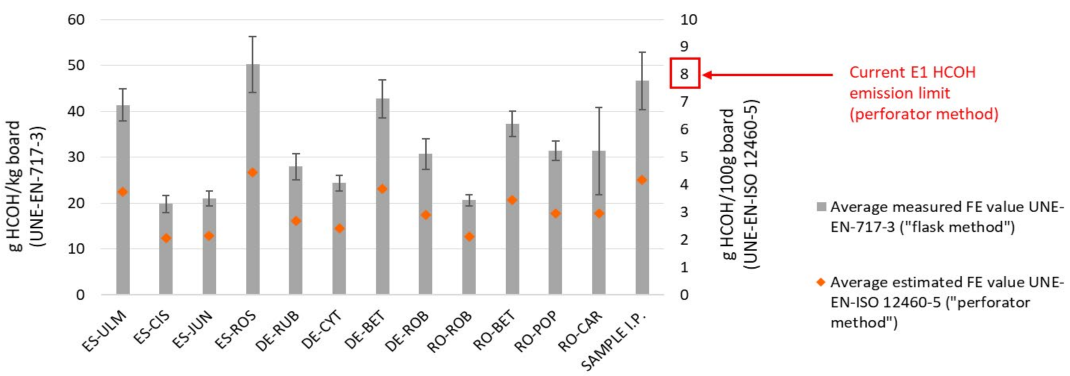

Figure 1. Formaldehyde emissions from particleboards from biomass samples of underutilized tree & shrub species.

Most of the boards from the species under study emitted significantly less formaldehyde (ANOVA, $F(12,26) = 15.02$, $p<0.05$) than the boards made of woodchips from the industrial manufacturer. Only the emissions from the boards from *U. pumila*, *R. officinalis*, the German sample of *B. pendula* and

C. betulus were not significantly different from the one from the industrial partner's biomass. This suggests that, in principle, all the species studied could be used as raw material for particleboard manufacturing without entailing an increase of formaldehyde emissions, and that, for the same manufacturing conditions and adhesive mix, the use of some of the studied species could actually reduce them. Besides, we used the correlation equation we obtained from comparing the flask method and the perforator method (1):

$$Fv\ perforator\ method = 0.079\ Fv\ flask\ method + 0.49 \quad (1)$$

(R^2=0.8596), where *Fv perforator method* is the estimated value for HCOH emissions according to UNE-EN ISO 12460-5 (g of HCOH/100 g of dry board) and *Fv flask method* is the measured value for HCOH emissions using EN-717-3 (g of HCOH/kg of dry board), to estimate HCOH emissions for the perforator method, and we found that they would be well under the current E1 limit in all cases.

3.2.Formaldehyde emissions and biomass main components

Formaldehyde emission from wood-based panels is a complicated process which can be affected by factors related to the materials, the environment and the manufacturing process[4]. The presence of moisture in particleboard made with amino resins is directly related to HCOH emissions, since water molecules can break the methylene bridges formed between urea and HCOH during adhesive curing [5]. However, there is not much information on the influence of the wood main components on HCOH emissions from particleboard. We found a weak correlation between the board moisture content and HCOH emissions (Pearson coefficient, $r = 0.49$, $p < 0.01$). This means that board moisture content accounted for 24% of the variability in formaldehyde emissions ($R^2 = 0.24$) and suggests that there must be other variables that account for the remaining variability. Therefore, as an exploratory work, we carried on looking for associations between the wood composition (Table 1), and we found a moderate positive association between the % of lignin and HCOH emissions (R^2=0.47, $p<0.05$), a moderate positive association between the % of acetyl groups and HCOH emissions (R^2=0.60, $p<0.05$), a moderate negative association between pH and FE (R^2=0.52, $p<0.05$) and a strong negative association between the % of extractives and FE emissions (R^2=0.69, $p<0.01$). These results agree with previous research [6], [7] and suggest that the role of wood composition, especially extractives, on reducing formaldehyde emissions from particleoard made with amino resins should not be overlooked.

Table 1. *Main components characterization of the biomass samples.*

	Species	Sample code	Glucans	Hemicellulose		Acetyl Groups	Total Lignin	Total Extractives	Ash
				Xylan	A+G+M*				
Spain	U. pumila	ES-ULP	35.2 (0.9)	13.6 (0.3)	5.5 (0.0)	5.3 (0.0)	26.2 (0.9)	6.4 (0.8)	2.7 (0.2)
Spain	C. ladanifer	ES-CIS	23.6 (0.1)	16.4 (0.1)	4.8 (0.1)	4.8 (0.0)	24.5 (0.3)	19.4 (0.2)	3.9 (0.2)
Spain	J. communis	ES-JUN	26.9 (0.4)	5.6 (0.0)	11.3 (0.4)	2.0 (0.1)	27.6 (0.8)	21.4 (1.0)	2.0 (0.0)
Spain	R. officinalis	ES-ROS	26.9 (1.1)	17.1 (0.7)	5.3 (0.1)	4.5 (0.2)	31.2 (0.2)	9.6 (0.4)	1.9 (0.1)
Germany	*R. fruticosus*	DE-RUB	31.9 (0.8)	15.8 (0.5)	5.1 (0.1)	5.0 (0.1)	25.0 (0.0)	9.5 (0.5)	3.3 (0.3)
Germany	*C. scoparius*	DE-CYT	29.6 (0.6)	16.2 (0.0)	4.4 (0.8)	4.7 (0.1)	24.3 (0.2)	12.1 (0.1)	1.4 (0.1)
Germany	*B. pendula*	DE-BET	26.4 (0.2)	20.1 (0.0)	4.6 (0.0)	6.1 (0.0)	29.9 (0.0)	7.9 (0.4)	1.4 (0.0)
Germany	*R. pseudoacacia*	DE-ROB	35.7 (1.7)	14.1 (0.6)	4.4 (0.1)	5.1 (0.0)	24.4 (0.4)	10.7 (0.3)	2.7 (0.1)
Romania	*R. pseudoacacia*	RO-ROB	32.2 (0.5)	13.1 (0.1)	4.9 (0.2)	4.3 (0.0)	24.1 (0.4)	15.8 (0.3)	3.1 (0.2)
Romania	*B. pendula*	RO-BET	29.5 (0.4)	18.6 (0.2)	4.8 (0.0)	5.6 (0.2)	30.4 (0.1)	9.4 (0.2)	1.6 (0.2)
Romania	*P. nigra*	RO-POP	33.7 (0.3)	12.7 (0.2)	5.7 (0.0)	4.1 (0.2)	24.9 (1.0)	14.9 (0.7)	3.9 (0.1)
Romania	*C. betulus*	RO-CAR	35.9 (0.8)	23.5 (0.7)	4.1 (0.1)	7.0 (0.0)	25.8 (0.3)	5.8 (0.3)	1.6 (0.0)

4. Conclusions

The introduction of alternative under-utilized tree & shrub species can be a tool to lower formaldehyde emissions of particleboard manufactured with amino resins. Our results, besides, support the idea that some wood extractives might be acting as formaldehyde scavengers by reacting with the free HCOH in particleboard.

Acknowledgement

This research has received funding from the Bio Based Industries Joint Undertaking (JU) under grant agreement No 887917 BeonNAT. The JU receives support from the European Union's Horizon 2020 research & innovation programme and the Bio Based Industries Consortium.

References

[1] E. Comission, EUR-Lex - 32023R1464, amending Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council as regards formaldehyde and formaldehyde releasers. 2023.

[2] E. Roffael, "Significance of wood extractives for wood bonding," Appl. Microbiol. Biotechnol., vol.100, no.4, pp. 1589–1596, Feb. 2016.

[3] H. Thoemen, M. Irle, M. S.-A. I. for Specialists, and undefined 2010, "Wood-based panels," academia.edu.

[4] J. Zhang, F. Song, J. Tao, Z. Zhang, and S. Q. Shi, "Research Progress on Formaldehyde Emission of Wood-Based Panel," Int. J. Polym. Sci., vol. 2018, 2018.

[5] C. Frihart, J. Wescott, … T. C.-F. P., and undefined 2012, "Formaldehyde emissions from urea-formaldehyde–and no-added-formaldehyde–bonded particleboard as influenced by temperature and relative humidity," meridian.allenpress.com, 2012.

[6] U. Buyuksari, N. Ayrilmis, E. Avci, and E. Koc, "Evaluation of the physical, mechanical properties and formaldehyde emission of particleboard manufactured from waste stone pine cones," Bioresour. Technol., vol. 101, no. 1, pp. 255–259, Jan. 2010.

[7] J. Liang, J. Wu, and J. Xu, "Low-formaldehyde emission composite particleboard manufactured from waste chestnut bur," J. Wood Sci., vol. 67, no. 1, Dec. 2021.