





## Article

# Influence of Thermal Decomposition of Wood and Wood-Based Materials on the State of the Atmospheric Air. Emissions of Toxic Compounds and Greenhouse Gases

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**Citation:** Rybiński, P.; Syrek, B.; Szwed, M.; Bradło, D.; Żukowski, W.; Marzec, A.; Śliwka-Kaszyńska, M. Influence of Thermal Decomposition of Wood and Wood-Based Materials on the State of the Atmospheric Air. Emissions of Toxic Compounds and Greenhouse Gases. *Energies* **2021**, *14*, 3247. <https://doi.org/10.3390/en14113247>

Academic Editor: Rajender Gupta

Received: 19 April 2021

Accepted: 31 May 2021

Published: 2 June 2021

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**Abstract:** This paper presents the energy characteristics of wood and wood-based materials in the form of commercially available pellets, furniture board (MDF) and OSB. Toxicometric indices were determined for gaseous destructs arising from thermal decomposition and combustion of the materials studied. The paper proves that combustion conditions are crucial in terms of toxic destructive emissions. It has been shown that the combustion of wood-based materials under controlled conditions can lead to equally low emissions of toxic wastes as the combustion of traditional wood materials. The paper also presents the index of greenhouse gas emission, the so-called CO<sub>2</sub> equivalent, for the examined wood and wood-based materials.

**Keywords:** toxicity; fire hazard; air pollution; fluidized bed; CO<sub>2</sub> equivalent; toxic greenhouse gases

## 1. Introduction

Recently, the problem of air pollution, commonly called “smog”, in the face of enormous health, social and economic costs has become an absolute priority. Numerous studies conducted in many parts of the world indicate that there is a link between exposure to air pollution and the occurrence of various adverse health effects. Particularly vulnerable groups are children, people with existing cardiovascular and respiratory disease, diabetes, obesity and the elderly. It has now been proven that exposure to air pollution is associated with increased mortality and reduced life expectancy [1–4].

Particularly important, from the point of view of protection of human health and life, is particulate matter, whose particles have an aerodynamic diameter of less than 2.5 micrometers. In addition to the size of the dust particles, the effects of dust pollution on human health may also depend on its chemical composition. Dust from combustion processes may include various substances harmful to health, e.g., polycyclic aromatic hydrocarbons and their derivatives, azaarenes and other polycyclic aromatic compounds, compounds from the dioxin group (PCDD/F), as well as heavy and transition metals and their compounds [5–22]. Gaseous pollutants such as carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>) and tropospheric ozone, which is formed by nitrogen dioxide in photochemical reactions, also have a harmful effect on health. Reactions between gaseous substances (ammonia, sulfur oxides and nitrogen oxides) may also result in the

formation of so-called secondary dusts, and the chemical composition of primary dusts may be modified.

Studies conducted in many parts of the world clearly show the relationship between ambient air pollution and cancer incidence. Cohort studies performed to date, carried out in groups of several hundred thousand people followed for several years, show a clear, statistically significant relationship between exposure to dust pollutants and nitrogen oxides and lung cancer incidence and mortality [6,7].

Elevated nitric oxide exposure has been shown to be associated with a higher risk of brain tumors and cervical cancer in adults [8]. Furthermore, exposure of pregnant mothers to nitric oxides is associated with a higher risk of cancer in their children in early childhood [9]. Strong carcinogenic effects are also demonstrated by compounds from the PAH group, as well as some compounds from the PCDD/F group.

It should also be clearly emphasized that the available analytical results clearly indicate an increased risk of death or hospitalization for stroke as a result of increased exposure to air pollutants such as: CO, SO<sub>2</sub>, NO<sub>2</sub>, O<sub>3</sub> and PM and that a short-term increase in PM<sub>2.5</sub> concentrations of 10 µg/m<sup>3</sup> translates into an 11% increase in the risk of death from stroke [10]. Long-term exposure to pollutants, such as those found in the most polluted cities, has a cumulative effect on adverse cardiovascular health effects, including an increase in the frequency of myocardial infarctions.

Poland is at the forefront of the Member States of the European Union in terms of air pollution with PM<sub>2.5</sub> [11].

Using risk factors for long-term exposure recommended by WHO, it can be estimated that over 44 thousand people die in Poland annually due to air polluted with PM<sub>2.5</sub> (data for 2012). In comparison with other European countries, the influence of air pollution on the occurrence of cancer, including lung cancer, is particularly strongly accentuated in the case of Poland, where typical long-term exposures to PM<sub>2.5</sub> are 20–30 µg/m<sup>3</sup>, and in the most polluted places of southern Poland even over 40 µg/m<sup>3</sup>. Thus, in localities with the highest concentrations of dust pollutants, the risk of lung cancer associated with exposure to such pollutants may be even 20–40% higher than in areas with very low pollutant concentrations [4].

The studies carried out indicate that particulate matter in Poland contains a dozen or even several dozen times more carcinogenic compounds from the group of polycyclic aromatic hydrocarbons, including derivatives of PAH, such as nitro-WPAH, as well as compounds from the dioxin group, as compared to Western European countries. Many of these compounds are more carcinogenic than benzo[a]pyrene, whose carcinogenic and mutagenic nature is well understood. Converting the amount of benzo[a]pyrene inhaled into the air to the equivalent number of cigarettes that an adult of average physical activity would have to smoke to supply the same amount of this substance to the body, is appealing to the imagination. Depending on the locality and the year considered, this equivalent can range from a few hundred to even three thousand cigarettes per year [4–24].

There are many reasons for the poor or very poor quality of air in cities, but one of the most important reasons for the condition of air in Poland, especially in large urban agglomerations, is undoubtedly the combustion of high-energy municipal waste in domestic furnaces, which includes glued boards (OSB), furniture boards, varnished furniture, etc. Incineration of such waste is a source of emission of many harmful substances, including highly toxic compounds such as hydrogen cyanide, hydrogen chloride, nitrogen oxides, hydrogen sulfide and sulfur oxides as well as carcinogenic substances such as aromatic hydrocarbons, polycyclic aromatic hydrocarbons, chlorinated biphenyls and PCDD/F compounds [25,26].

In this paper, toxicometric indices of gaseous products of thermal decomposition and combustion of wood-based materials have been determined. Furniture board (MDF), OSB and commercially available pellets were used for testing. Determined values of toxicometric indices allowed to estimate the influence of uncontrolled combustion of such

materials (household furnaces) on the state of atmospheric air. Beech wood was used as reference material.

## 2. Materials and Methods

### 2.1. Test Methodology

#### Materials

Commercially available pellets from Stelmet (Poland) as well as OSB from SWISS KRONO (Poland) and MDF from EGGER Biskupiec (Poland) board waste were used for the tests. Beech wood was used as reference material. Prior to testing, all materials were ground to obtain samples that were homogeneous in terms of physicochemical properties. For toxicity testing, pellets were prepared from the crushed samples.

### 2.2. Methodology

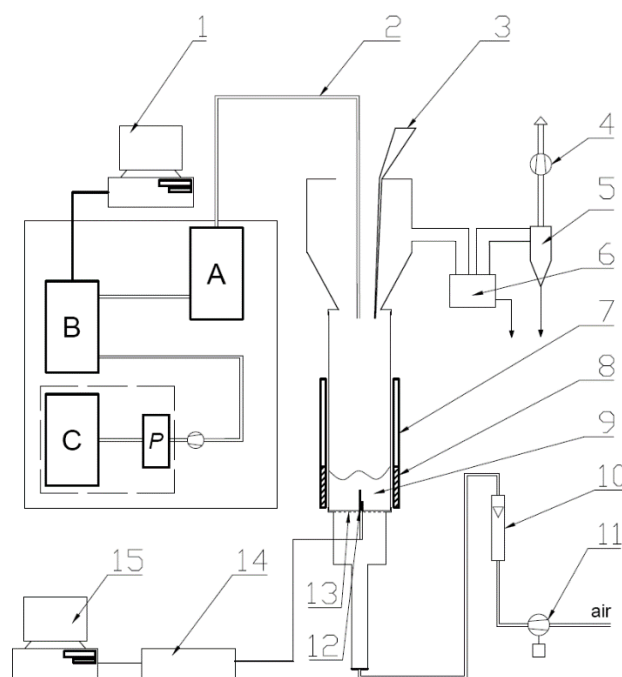
**Thermal analysis:** The thermal properties of the tested materials were examined in the air atmosphere, in the temperature range of 25–700 °C, using a Jupiter STA 449 F3 thermal analyzer from Netzsch.

**Flammability:** Flammability tests were performed with the use of PCFC calorimeter (pyrolysis combustion flow calorimeter). Parameters such as: maximum heat emission rate ( $HRR_{max}$ ), total heat emitted (HR) and heat capacity (HC) were recorded during test. During measurement, gaseous products from thermal decomposition sample were transferred from the pyrolysis chamber to the tubular furnace, where after mixing with oxygen, were completely burned. The temperature of the pyrolyzer was 750 °C, while that of combustor 900 °C [12].

**Toxicity:** Toxicity: Quantitative and qualitative analyses of toxic gaseous products were performed with the use of fluidized bed reactor. Air was used as a fluidized gas, and aluminosilicate microspheres as a fluidized bed. The analysis was carried out at five temperatures: 400, 500, 600, 700 and 800 °C. The mass of the studied sample was selected experimentally. A sample by mass from 0.015–0.114 g was placed in the reactor after which the concentration of evolved gases was analyzed. The presented below results are the arithmetic means obtained from four samples of a given type of tested material.

Quantitative and qualitative data were obtained with the use of the Gasmeter DX-400 (FTIR spectrum of exhaust gases), Horiba PG250 analyzer (for measurement of the CO, CO<sub>2</sub> and SO<sub>2</sub> concentration the NDIR detectors were used, the sum of NO<sub>x</sub> were detected and analyzed with the use of chemiluminescence method, whereas the O<sub>2</sub> volume fraction was measured by the electrochemical detector (Figure 1).

Method of quantitative and qualitative analysis of toxic gaseous products, in detail was described in previous authors publication [13–31].



**Figure 1.** Scheme of the fluidized bed reactor: 1—computer storing data from FTIR analyzer; 2—heated probes for sampling the flue gases; 3—batcher; 4—exhaust fan; 5—cyclone; 6—ash trap for coarser particles; 7—movable radiation shield; 8—heating jacket; 9—bubbling bed; 10—air rotameter; 11—blower, for fluidizing air; 12—two thermocouples; 13—flat, perforated metal plate distributor; 14—A/D convertor for thermocouple signals; 15—computer storing chemical analyses quantities and temperature; A—mobile conditioning system of Gasetm DX-4000, B—analyzer FTIR (Gasetm DX-4000), C—Horiba PG250, P—Peltier’s cooler [31].

### 3. Results

#### 3.1. Thermal Analysis of Wood and Wood-Based Materials

The first stage of thermal decomposition of beech wood takes place in the temperature range of  $\Delta T = 50\text{--}110\text{ }^{\circ}\text{C}$ . This decomposition is accompanied by an endothermic transition, registered on the DSC curve, associated with the evaporation of water physically bound to the biomass. The intense exothermic decomposition of the sample takes place in the temperature range of  $\Delta T = 210\text{--}400\text{ }^{\circ}\text{C}$ . A maximum decomposition rate of  $16.36\%/ \text{min}$  is recorded at  $T_{\text{RMAX}} 330\text{ }^{\circ}\text{C}$ . The residue after thermal decomposition is burned in the range of  $\Delta T = 410\text{--}460\text{ }^{\circ}\text{C}$ . The residue after combustion at  $T = 600\text{ }^{\circ}\text{C}$  is only  $1.78\%$  of the initial sample weight (Figure 2, Table 1).

The thermal transformations associated with the decomposition of pellets, OSB and MDF are not significantly different from the thermal transformations recorded for beech wood. On the other hand, clear differences can be observed in the thermal decomposition of OSB as well as MDF in relation to the reference material (beech wood) (Figure 3, Table 1). A significant reduction in the thermal decomposition rate parameter was recorded for both OSB and MDF. In the case of OSB, the value of the  $dm/dt$  parameter was reduced by  $27.9\%$ , while in the case of MDF, it was reduced by  $28.6\%$  compared to beech wood. The reduction of  $dm/dt$  parameter unambiguously indicates the reduction of the amount of gaseous destructs entering the flame, which can be a consequence of cyclization reactions, especially carbonization occurring in the boundary layer between the flame and the sample. The cyclization and charring reactions are also indicated by an increase of nearly  $174\%$  in the residue after thermal decomposition of OSB relative to beech wood and by more than  $200\%$  relative to pellets. The thermal decomposition residue of MDF is  $138\%$  greater than that of beech wood and over  $160\%$  greater than that of pellets [30].

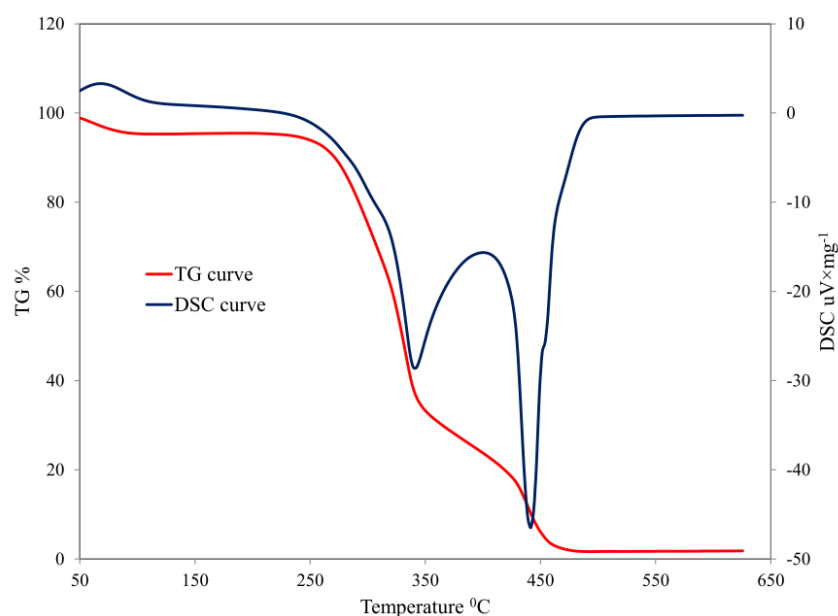


Figure 2. TG and DSC curves of beech wood.

Table 1. Thermal analysis of tested wood and wood-based materials.

Material	T <sub>5</sub> /°C	T <sub>50</sub> /°C	T <sub>RMAX</sub> /°C	dm/dt/%/min	ΔTs/°C	P <sub>600</sub> /%
Beech	110	330	330	16.36	410–460	1.78
PELLET	104	340	337	15.30	420–480	1.54
OSB	115	337	331	11.79	390–555	3.10
MDF	108	337	328	11.68	435–560	2.47

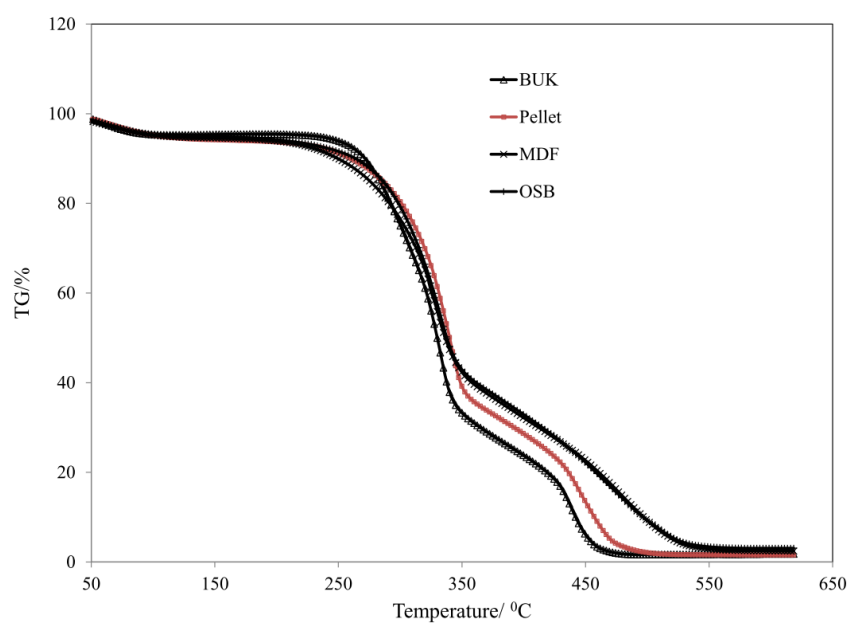


Figure 3. TG curves of beech wood, pellets, OSB and MDF.

It should also be noted that in the case of both OSB and MDF, the combustion of residues after thermal decomposition occurs in a much wider temperature range than in the case of beech wood and pellets, which may indicate an intensification of cyclization and carbonization processes (Figure 3).

### 3.2. Flammability of Tested Wood and Wood-Based Materials

The results obtained using PCFC (pyrolysis combustion flow calorimeter) clearly show that the pellets studied exhibit higher combustibility ( $HRR_{MAX}$  and THR parameters) and calorific value (heat capacity, HRC parameter) than the reference material in the form of beech wood. For OSB, the  $HRR_{max}$  parameter was reduced by 27%, while the THR parameter was reduced by 14.5% compared to beech wood. MDF is also less flammable than both beechwood and pellets (Table 2).

**Table 2.** Flammability of wood and wood-based materials.

Sample	$HRR_{MAX}/W/g$	$THRR_{MAX}/^{\circ}C$	THR/kj/kg	HRC/J/gK
Beech	195	361	14.5	171
PELLET	210	371	16.8	204
OSB	142	354	12.4	140
MDF	167	345	14.2	164

The reduction in flammability of both OSB and MDF in relation to the reference material (beech wood) results directly from their chemical composition. In the production process of both OSB and MDF, urea-formaldehyde and melamine-urea-formaldehyde resins are used. In the case of OSB, the middle layer consists of mainly pine chips bonded with polyurethane glue. The melamine-urea-phenol-formaldehyde resins are used for bonding the outer layers of OSB [32]. The presence of synthetic adhesives in the composition of OSB and MDF directly results in lowering their flammability in relation to beech wood (parameter  $HRR_{MAX}$ , THR, but also  $dm/dt$ ). The reduction in flammability results directly from the intensification of cyclization and charring reactions under the influence of synthetic adhesives.

### 3.3. Toxicity of Gaseous Products of Thermal Decomposition and Combustion of Wood and Wood-Based Materials

At present, four types of tests are used to test the toxicity of gaseous products of thermal decomposition and combustion: analytical, biological, biological-analytical and computational-analytical. Due to the cost of experiments, biological and biological-analytical tests are rarely used, while computational-analytical methods are gaining importance. In the calculation and analytical tests to assess toxicity of gaseous destructs, data are used in relation to the thermal decomposition process, i.e., the amount of thermal exposure (heat flux), volume of the volatile phase formed as a result of thermal decomposition and combustion of the sample, qualitative and quantitative composition of the volatile phase, assumed time of human exposure to a given toxin, maximum permissible concentration of individual components of the volatile phase, including e.g., the limiting concentration of a given product of thermal decomposition, causing death of 50% of the population with a 30-minute exposure. As a result of the obtained data, the so-called toxicological profile is developed, which is the basis for estimating the toxicity of gases formed during the thermal decomposition of the tested material.

The effect of poisonous substances on living organisms depends on many factors, such as: the type of toxic substance, the route of penetration of the toxin into the body, the dose, the physical and chemical properties of poisons, as well as the transformations they undergo in the body and the susceptibility of the body to poisoning [27,28].

In Poland, toxicity testing of gas destructs is carried out based on the methodology described in the PN-88/B-02855 standard.

The principle of the method is the quantitative, chemical, selective determination of toxic gases that are primarily responsible for fatal accidents. The test enables determination of  $CO$ ,  $CO_2$ ,  $HCl$ ,  $NO_x$ ,  $HCN$ ,  $SO_2$ , depending on the chemical composition of the tested material. Toxic effects of gases forming toxicological profile according to PN-88/B-02855 methodology are well known.



For example: Carbon monoxide (CO) combines with hemoglobin to form carboxyhemoglobin, causing oxygen deficiency in the body. The concentration of CO at the level of 6000–8000 ppm in the air already after about five minutes causes significant changes in human body, as a result of which it loses its ability to function efficiently. Concentrations of about 12,000–16,000 ppm cause death after five minutes.

By irritating the airways, carbon dioxide (CO<sub>2</sub>) causes increased breathing, which increases the risk of absorbing other dangerous substances. In low concentrations, it does not exhibit toxic properties, but at concentrations higher than 5000 ppm, its harmful effects on the body are clearly visible.

Nitrogen dioxide (NO<sub>2</sub>). Concentrations less than 1.5 ppm generally do not cause any symptoms. Depending on the time of exposure, higher concentrations of NO<sub>2</sub> cause respiratory distress leading to hypoxia, lung damage and death.

Hydrogen chloride (HCl). It is characterized by a pungent, suffocating aroma. Irritating to mucous membranes and respiratory system. The hazardous concentration is 140 mg/m<sup>3</sup>.

Hydrogen cyanide (HCN). It paralyzes the respiratory system at the first moment of contact, causing tissue respiration to be impaired. A concentration of 120–200 ppm causes incapacitation after about five minutes, while 250–400 ppm causes death.

In the method according to the PN-88/B-02855 standard, the results are given in specific emission units (E (g/g) mass of a given product arising from a unit mass of the initial sample under given test conditions). By combining the emission results with the limit concentrations, the toxicometric indices  $W_{LC50}$ ,  $W_{LC50M}$  and  $W_{LC50SM}$  are obtained.

The toxicometric index  $W_{LC50}$  is defined as the mass of a given material whose decomposition or combustion under the test conditions produces limiting concentrations of toxic gaseous destruction.

$$W_{LC50,i} = \frac{LC_{50,i}}{E_i}$$

$$\frac{1}{W_{LC50M}} = \sum_{i=1}^n \frac{1}{W_{LC50,i}}$$

The  $W_{LC50SM}$  toxicometric index is defined as the arithmetic mean of the  $W_{LC50}$  indices from individual temperatures, e.g., (400, 500, 600, 700, 800 °C). This index is used to classify the toxicity of materials (Table 3).

**Table 3.** Toxicity classification of gas destructs.

$W_{LC50SM}$	Toxic Properties of Thermal Decomposition and Combustion Products of Materials
$\leq 15$	Very toxic
$>5, \leq 40$	Toxic
$>40$	Moderately toxic

Table 4 shows the emissions of gaseous destructs at T = 400, 500, 600, 700 and 800 °C from the decomposition of beech wood, pellets, OSB and furniture board (MDF). (Mean and standard deviations based on four replicates).

From the results of the analyses in Table 4, it is clear that the highest emission values are recorded, irrespective of the decomposition temperature and type of sample, for carbon dioxide and carbon monoxide. It should be noted that OSB as well as MDF have noticeably higher carbon dioxide emissions, especially at T = 400, 500, 600 and 700 °C than beech wood or pellets.

**Table 4.** Specific emission for selected, according to the standard, gas destructs formed during the decomposition of beech wood, pellet, OSB and MDF at 400, 500, 600, 700 and 800 °C [14].

Emissions g/g T = 400 °C						
Product	CO <sub>2</sub>	CO	NO <sub>2</sub>	SO <sub>2</sub>	HCl	HCN
Beech	0.724 ± 0.031	0.153 ± 0.007	0.004 ± 0.00	0.0004 ± 0.00	0.0002 ± 0.00	0.00 ± 0.00
PELLET	0.686 ± 0.067	0.155 ± 0.008	0.006 ± 0.001	0.0004 ± 0.00	0.0002 ± 0.00	0.00 ± 0.00
OSB	1.393 ± 0.041	0.136 ± 0.011	0.004 ± 0.003	0.0002 ± 0.00	0.000 ± 0.00	0.0013 ± 0.00
MDF	1.871 ± 0.068	0.141 ± 0.013	0.005 ± 0.002	0.0001 ± 0.00	0.0001 ± 0.00	0.0018 ± 0.00
Emission, g/g T = 500 °C						
Beech	1.183 ± 0.062	0.232 ± 0.026	0.0019 ± 0.001	0.0002 ± 0.00	0.00 ± 0.00	0.0001 ± 0.00
PELLET	1.159 ± 0.094	0.267 ± 0.016	0.0019 ± 0.001	0.0005 ± 0.00	0.0001 ± 0.00	0.00 ± 0.00
OSB	1.557 ± 0.141	0.274 ± 0.011	0.0032 ± 0.001	0.0009 ± 0.00	0.00 ± 0.00	0.0030 ± 0.00
MDF	1.778 ± 0.097	0.307 ± 0.010	0.0027 ± 0.001	0.0007 ± 0.00	0.00 ± 0.00	0.0055 ± 0.00
Emission, g/g T = 600 °C						
Beech	1.386 ± 0.04	0.312 ± 0.018	0.0001 ± 0.00	0.0003 ± 0.00	0.00 ± 0.00	0.0003 ± 0.00
PELLET	1.366 ± 0.108	0.329 ± 0.032	0.0003 ± 0.00	0.0004 ± 0.00	0.00 ± 0.00	0.0002 ± 0.00
OSB	1.681 ± 0.101	0.301 ± 0.043	0.0007 ± 0.00	0.0009 ± 0.00	0.00 ± 0.00	0.0039 ± 0.00
MDF	1.751 ± 0.134	0.269 ± 0.115	0.0011 ± 0.00	0.0007 ± 0.00	0.00 ± 0.00	0.0063 ± 0.002
Emission, g/g T = 700 °C						
Beech	1.558 ± 0.085	0.314 ± 0.025	0.0007 ± 0.00	0.0004 ± 0.00	0.00 ± 0.00	0.0002 ± 0.00
PELLET	1.481 ± 0.073	0.373 ± 0.085	0.0007 ± 0.00	0.0003 ± 0.00	0.00 ± 0.00	0.0001 ± 0.00
OSB	1.949 ± 0.014	0.152 ± 0.088	0.0007 ± 0.00	0.0005 ± 0.00	0.00 ± 0.00	0.0018 ± 0.00
MDF	1.829 ± 0.001	0.182 ± 0.073	0.0007 ± 0.00	0.0004 ± 0.00	0.00 ± 0.00	0.0037 ± 0.00
Emission, g/g T = 800 °C						
Beech	2.129 ± 0.096	0.101 ± 0.003	0.0002 ± 0.00	0.0011 ± 0.00	0.00 ± 0.00	0.0001 ± 0.00
PELLET	2.176 ± 0.057	0.0089 ± 0.002	0.0008 ± 0.00	0.0005 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
OSB	2.109 ± 0.246	0.0092 ± 0.002	0.0004 ± 0.00	0.0004 ± 0.00	0.00 ± 0.00	0.0003 ± 0.00
MDF	2.103 ± 0.207	0.0081 ± 0.002	0.0004 ± 0.00	0.0003 ± 0.00	0.00 ± 0.00	0.0004 ± 0.00

Undoubtedly, the emission of NO<sub>2</sub> as well as HCN influences the value of toxicometric index for both OSB and MDF. It should be clearly noted that both NO<sub>2</sub> and HCN are emitted in the temperature range of 500–600 °C, which is in the range of combustion of thermal decomposition residues of both OSB and MDF (Table 1). The range of decomposition temperature values clearly indicates that the emission of volatile nitrogen compounds is related to the thermal decomposition of the binder used in the production of OSB and MDF [29,30].

In the production process of both OSB and MDF, urea-formaldehyde and melamine-urea-formaldehyde resins are used, which are a potential source of NO<sub>x</sub>, HCN and toxic formaldehyde. Additionally, polyurethane adhesives, used for bonding the middle layer of OSB, which are a precursor of toxic HCN, and melamine-urea-phenol-formaldehyde resins used for bonding the outer layers of OSB, which are a source of NO<sub>x</sub> and HCN emissions [32].

The data in Table 5 clearly show that the volume of gases formed during the thermal decomposition of OSB and MDF at 400, 500 and 600 °C is much larger than that of beech wood and pellets. For example, in the temperature range of 500 °C, the volume of emitted gases during OSB decomposition is 22.5% higher than for beech wood and 21% higher



than for pellets. For MDF, the volume of emitted gases at  $T = 500\text{ }^{\circ}\text{C}$  is as much as 32% higher than for beech wood, and 30% higher than for pellets.

**Table 5.** Volume of gaseous destructs ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HCN}$ ) formed during thermal decomposition of the tested materials.

	V, $\text{cm}^3/\text{g}$ of Sample				
	400 $^{\circ}\text{C}$	500 $^{\circ}\text{C}$	600 $^{\circ}\text{C}$	700 $^{\circ}\text{C}$	800 $^{\circ}\text{C}$
Beech	$529.3 \pm 22.5$	$848.8 \pm 54.2$	$1027.0 \pm 33.4$	$1126.0 \pm 43.0$	$1177.2 \pm 53.3$
PELET	$511.7 \pm 43.0$	$865.7 \pm 61.7$	$1031.9 \pm 48.1$	$1134.8 \pm 66.4$	$1200.1 \pm 32.9$
OSB	$883.5 \pm 23.1$	$1094.2 \pm 67.8$	$1184.9 \pm 20.9$	$1202.7 \pm 102.5$	$1165.5 \pm 134.4$
MDF	$1150.9 \pm 40.5$	$1242.4 \pm 60.2$	$1197.3 \pm 49.2$	$1164.3 \pm 91.6$	$1161.2 \pm 116.0$

On the basis of the results presented in Table 5 concerning the volume of the gaseous wastes emitted ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HCN}$ ), taking into account similar values of  $\text{CO}_2$  and  $\text{CO}$  emissions for all the materials studied, especially in the temperature range  $T = 500$  and  $600\text{ }^{\circ}\text{C}$ , it should be stated that the increase in the volume of the gases emitted during the decomposition of OSB and MDF in comparison with beech wood and pellets is mainly due to the formation of nitrogen oxides and hydrogen cyanide.

Taking into account the experimentally determined  $\text{LC}_{50}^{30}$  values (Table 6), toxicometric indices  $W_{\text{LC}50}$  and  $W_{\text{LC}50\text{SM}}$  were calculated, depicting the toxicity level of gaseous destructs emitted during thermal decomposition of the studied materials (Table 7) [15–17].

**Table 6.**  $\text{LC}_{50}^{30}$  concentration limits of gaseous thermal decomposition products ( $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{HCl}$ ,  $\text{HCN}$ ) [14,31].

Compound	Formula	$\text{LC}_{50}^{30}$ , $\text{g}/\text{m}^3$
Carbon dioxide	$\text{CO}_2$	196.4
Carbon monoxide	$\text{CO}$	3.750
Hydrogen cyanide	$\text{HCN}$	0.160
Nitrogen dioxide	$\text{NO}_2$	0.205
Hydrogen chloride	$\text{HCl}$	1.000
Sulfur dioxide	$\text{SO}_2$	0.700

On the basis of the  $W_{\text{LC}50\text{SM}}$  index value, gaseous destructs formed during the decomposition of beech wood, pellets, as well as OSB and MDF board should be considered toxic. However, the analysis of the  $W_{\text{LC}50\text{M}}$  index values, especially in the temperature range  $T = 500$  and  $600\text{ }^{\circ}\text{C}$ , indicates significant differences in the toxicity of the gaseous destructs formed from the decomposition of the materials studied.

The  $W_{\text{LC}50\text{M}}$  value for beech wood at  $T = 500$  and  $600\text{ }^{\circ}\text{C}$  is 14.78 and 10.82, respectively. For pellets 12.35 and 10.45, for OSB 9.48 and 8.73, and for MDF 7.82 and 8.71. It should be clearly emphasized that the higher the value of toxicometric index, the lower the toxicity of gas destructs. In the temperature range  $T = 500\text{ }^{\circ}\text{C}$ , the  $W_{\text{LC}50\text{M}}$  index for OSB is 35% lower than for beech wood, in the case of MDF, the  $W_{\text{LC}50\text{M}}$  value at  $T = 500\text{ }^{\circ}\text{C}$  is as much as 47% lower than for beech wood. In the range  $T = 600\text{ }^{\circ}\text{C}$ , the  $W_{\text{LC}50\text{M}}$  both for OSB and MDF is 19% lower compared to beech wood. The values of determined toxicometric indices clearly indicate higher toxicity of gas destructs originating from the decomposition of OSB and MDF, compared to the toxicity of gas destructs originating from the decomposition of the reference material in the form of beech wood. It should also be clearly stated that commercially available pellets do not generate gaseous destructs with significantly higher toxicity than beech wood. The higher toxicity of gaseous products

of thermal decomposition of both OSB and MDF results from the use of polymeric glues based on formaldehyde, urethane or melamine for board production.

**Table 7.** Values of toxicometric indices for beech wood, pellets, OSB and MDF.

Sample	Tr/°C	W <sub>LC50</sub> [g/m <sup>3</sup> ]						W <sub>LC50M</sub>	W <sub>LC50SM</sub>
		CO <sub>2</sub>	CO	NO <sub>2</sub>	SO <sub>2</sub>	HCl	HCN		
Beech	400	273 ± 12	24 ± 1	100 ± 5	-	-	-	18.32 ± 0.84	25.75
	500	166 ± 8	16 ± 2	-	-	-	-	14.78 ± 1.59	
	600	142 ± 4	12 ± 1	-	4449 ± 544	-	495 ± 119	10.82 ± 0.65	
	700	126 ± 7	12 ± 1	-	-	-	848 ± 136	10.79 ± 0.72	
	800	92 ± 4	388 ± 113	-	-	-	-	74.04 ± 5.64	
PELLET	400	288 ± 30	24 ± 1	82 ± 8	1368 ± 309	-	-	17.33 ± 1.06	25.20
	500	170 ± 14	14 ± 1	318 ± 69	1513 ± 315	-	-	12.35 ± 0.72	
	600	145 ± 11	11 ± 1	-	7290 ± 2715	-	696 ± 121	10.43 ± 0.92	
	700	133 ± 7	10 ± 2	-	-	-	1584 ± 454	9.50 ± 2.03	
	800	91 ± 4	486 ± 114	-	-	-	-	76.40 ± 4.82	
OSB	400	141 ± 4	28 ± 2	152 ± 26	-	-	127 ± 12	17.27 ± 0.95	22.78
	500	127 ± 12	14 ± 1	239 ± 44	888 ± 224	-	53 ± 2	9.48 ± 0.17	
	600	117 ± 7	13 ± 2	591 ± 85	1662 ± 213	-	41 ± 6	8.73 ± 1.07	
	700	102 ± 12	21 ± 9	450 ± 99	9158 ± 2937	-	77 ± 25	13.76 ± 4.84	
	800	94 ± 20	370 ± 44	-	4818 ± 209	-	553 ± 123	64.68 ± 6.05	
MDF	400	105 ± 4	27 ± 2	171 ± 16	-	-	89 ± 10	15.51 ± 0.94	20.81
	500	111 ± 6	12 ± 0	383 ± 21	1098 ± 213	-	29 ± 5	7.82 ± 0.56	
	600	113 ± 9	16 ± 7	293 ± 116	2062 ± 361	-	28 ± 12	8.71 ± 3.25	
	700	107 ± 10	18 ± 1	939 ± 592	-	-	39 ± 3	10.79 ± 0.63	
	800	90 ± 2	411 ± 73	-	-	-	365 ± 58	61.21 ± 4.41	

As shown above, the toxicometric index  $W_{LC50M}$  is the harmonic mean of the  $W_{LC50}$  indices calculated on the basis of the LC value  $\frac{30}{50}$  i.e., the limiting concentration of a given thermal decomposition product causing death of 50% of the test animal population at 30 min exposure.

In view of the lack of  $LC_{\frac{30}{50}}$  values for each toxic substance detected with the use of the research methodology applied in this study, in order to more precisely estimate the level of toxicity of gas destructs formed during the decomposition of the tested materials, the universal toxicometric indicator TLV<sup>®</sup>-TWA was used, i.e., the highest permissible concentration during an 8-hour exposure at the workplace, which does not adversely affect the health of a given employee and the health of his future generations (Threshold Limit Values in order of 8-hour time weighted averages) [18].

The average toxicometric index is defined as:

$$W_{\text{mean}} = \sum^n W$$

$$W = \frac{E}{\text{TLV} - \text{TWA}}$$

According to the methodology used to implement the study, the  $W_{\text{mean}}$  index in addition to gas destructs such as: CO<sub>2</sub>, CO, NO<sub>2</sub>, SO<sub>2</sub>, HCl, HCN, it also includes nitric oxide NO and nitrous oxide N<sub>2</sub>O, water vapor H<sub>2</sub>O, hydrocarbons (methane, ethane,

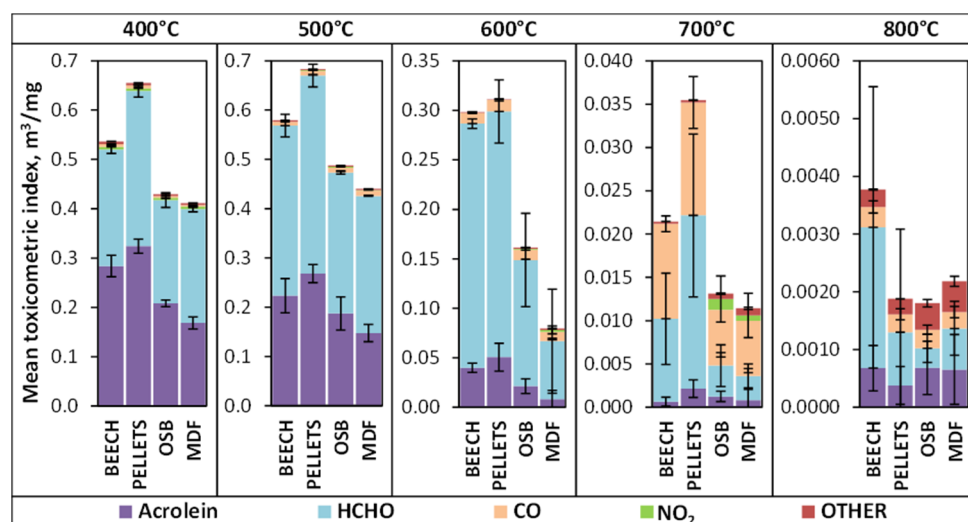
ethylene, acetylene), as well as: aldehydes and ketones (formaldehyde, acetaldehyde, acrolein, acetone) and carboxylic acids (formic acid, acetic acid).

Based on the data in Table 8, it was unexpectedly found that the gaseous destructs from burning OSB as well as furniture board were less toxic compared to the destructs from burning beech wood and pellets.

**Table 8.**  $W_{\text{mean}}$  toxicometric index determined in the temperature range 400–800 °C.

Sample	$W_{\text{mean}}$ ( $\text{m}^3/\text{mg}$ )				
	400 (°C)	500 (°C)	600 (°C)	700 (°C)	800 (°C)
Beech	$0.54 \pm 0.03$	$0.58 \pm 0.05$	$0.30 \pm 0.01$	$0.02 \pm 0.01$	$0.004 \pm 0.002$
Pellets	$0.66 \pm 0.02$	$0.68 \pm 0.01$	$0.31 \pm 0.04$	$0.04 \pm 0.01$	$0.002 \pm 0.002$
OSB	$0.43 \pm 0.02$	$0.49 \pm 0.03$	$0.16 \pm 0.06$	$0.01 \pm 0.00$	$0.002 \pm 0.000$
MDF	$0.41 \pm 0.02$	$0.44 \pm 0.03$	$0.08 \pm 0.07$	$0.01 \pm 0.00$	$0.002 \pm 0.001$

The research results presented in Table 8 and Figure 4 may lead to erroneous conclusions that domestic combustion of OSB and MDF is less harmful to the environment than traditional fuels such as beech wood or pellets. However, it should be clearly emphasized that the testing conditions in the laboratory are significantly different from those in domestic furnaces. In the adopted testing methodology, the fuel sample is given in a small amount in relation to the mass of the bed (0.1 g/200 g). Moreover, the amount of air in the reaction zone is in considerable excess, so that the amount of oxygen is not a limiting factor for the thermal transformation process. The large bed volume relative to the sample also allows the temperature to remain constant regardless of the heat released from the test sample.



**Figure 4.**  $W_{\text{mean}}$  toxicometric index determined for beech wood, pellet, OSB and MDF at 400, 500, 600, 700 and 800 °C.

Combustion in domestic furnaces is not subject to such controls, in particular with regard to maintaining a minimum temperature and the necessary amount of oxygen. Thus, under uncontrolled conditions of excess fuel relative to the oxidizer, numerous compounds can be formed that are rapidly released from the high temperature zone and do not degrade further, with particulate matter emitted as particulate matter (PM) being particularly hazardous.

The analysis showed that combustion conditions are crucial in terms of toxic emissions. Despite the unquestionable harmfulness of wood-based materials, their combustion under



controlled conditions leads to equally low emissions of toxic waste as the combustion of traditional wood materials [19–22].

From the environmental point of view, an important issue is also the amount of greenhouse gases emitted as a result of thermal decomposition and combustion of the tested materials. For this purpose, the emission index of greenhouse gases emitted during thermal decomposition and combustion of the sample, the so-called CO<sub>2</sub> equivalent, was calculated (Figure 5). CO<sub>2</sub> equivalent is the sum of carbon dioxide, nitrous oxide and methane emissions per gram of sample mass.

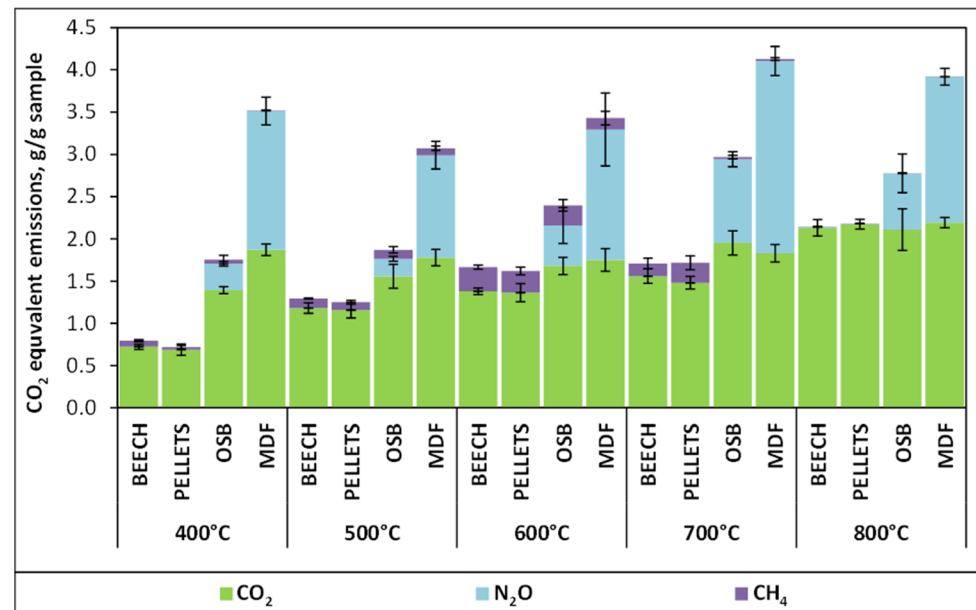


Figure 5. CO<sub>2</sub> equivalent of toxic greenhouse gases converted per gram of sample mass.

From the data in Figure 4, it is clear that during thermal decomposition and combustion of beech wood and pellets, regardless of the temperature range, greenhouse gas emissions are significantly lower than for OSB or MDF. It should also be clear that in the case of OSB and MDF, nitrous oxide, a gas with a significant impact on global warming, persisting in the atmosphere for an average of 120 years, has a very large share of CO<sub>2</sub> equivalent. Undoubtedly, N<sub>2</sub>O emission is related to the presence of polymer adhesives used as binders in the production process of both OSB and MDF board.

#### 4. Conclusions

Individual heating of single-family homes is the primary source of air pollution in larger communities. An increased concentration of gases and dusts from low emissions in certain meteorological conditions causes an exceedance of acceptable air quality standards and a threat to human health. The study showed that beech wood, pellets and waste OSB and MDF board fragments used for heating in domestic stoves have diversified toxicometric characteristics.

It was shown that the volume of gases formed during the thermal decomposition of OSB and MDF is much larger than that of beech wood and pellets. The increase in the volume of gases emitted during the decomposition of OSB and MDF in comparison with beech wood and pellets is primarily related to the formation of nitrogen oxides and hydrogen cyanide.

Higher toxicity of gaseous products of thermal decomposition of both OSB and MDF board in comparison to pellet or beech wood results from the use of polymeric glues based on formaldehyde, urethane or melamine for their production.

The results of the conducted research also indicate that the combustion conditions are of key importance for the emission of toxic wastes. Despite the unquestionable harmfulness

of wood-based materials (MDF, OSB), their combustion in controlled conditions may lead to equally low emissions of toxic wastes as the combustion of traditional wood materials.

Furthermore, it has been shown that during thermal decomposition and combustion of beech wood and pellets, regardless of the temperature range, greenhouse gas emissions are significantly lower than for OSB or MDF. It should also be made clear that in the case of OSB and MDF, nitrous oxide, a gas with a significant impact on global warming, persisting in the atmosphere for an average of 120 years, has a very large share of CO<sub>2</sub> equivalent. Undoubtedly, N<sub>2</sub>O emission is related to the presence of polymer adhesives used as binders in the production process of both OSB and MDF board.

**Author Contributions:** Conceptualization, P.R.; methodology P.R., B.S., M.S., D.B., W.Ż., formal analysis P.R., D.B., W.Ż., A.M., M.Ś.-K., investigation, P.R., B.S., M.S., D.B., W.Ż., A.M., M.Ś.-K., resources P.R., data curation P.R., D.B., writing original draft, P.R., B.S., M.S., D.B., W.Ż., A.M., M.Ś.-K., writing—review and editing P.R., B.S., M.S., D.B., W.Ż., A.M., M.Ś.-K., supervision P.R. All authors have read and agreed to the published version of the manuscript.

**Funding:** The research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** The data presented in this study are available on request from the corresponding author.

**Conflicts of Interest:** The authors declare no conflict of interest.

## Abbreviations

T <sub>5</sub> : T <sub>50</sub>	temperature 5 and 50% sample weight loss
T <sub>RMAX</sub>	temperature of maximum rate of sample decomposition
dm/dt	rate of sample decomposition
ΔT <sub>s</sub>	range of combustion temperature of the residue after thermal decomposition of the sample
P600	residue after thermal degradation at T = 600 °C
HRR <sub>MAX</sub>	maximum heat release rate
THRR <sub>MAX</sub>	temperature of maximum heat release rate
THR	total heat release
HRC	heat capacity
W <sub>LC50</sub>	toxicometric index for a single component according to the PN-88/B-02855 standard
W <sub>LC50M</sub>	toxicometric index for number components according to the PN-88/B-02855 standard
W <sub>LC50SM</sub>	mean toxicometric index according to the PN-88/B-02855 standard
LC <sub>50,i</sub>	the limiting concentration of the given i-th thermal degradation product causing death of 50% of the test animal population at 30 min exposure, g/m <sup>3</sup>
E <sub>i</sub>	specific emission, g <sub>i</sub> /g
n	number of toxic components
W	toxicometric index defined as the standardized volume of gases (m <sup>3</sup> ) emitted from the thermal decomposition or combustion of 1 mg of sample, m <sup>3</sup> /mg
W <sub>mean</sub>	average toxicometric index, m <sup>3</sup> /mg
TLV-TWA	threshold concentrations of selected gaseous effluents, mg/m <sup>3</sup>

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