

# Article

# Emission Factors and Energy Properties of Agro and Forest Biomass in Aspect of Sustainability of Energy Sector

# Grzegorz Maj

Department of Power Engineering and Transportation, University of Life Sciences in Lublin, Gleboka 28, 20-612 Lublin, Poland; grzegorz.maj@up.lublin.pl; Tel.: +48-81-531-97-20

Received: 4 May 2018; Accepted: 8 June 2018; Published: 11 June 2018



**Abstract:** The paper presents the possibility of managing forest and agricultural biomass for energy purposes in the aspect of environmental protection and sustainable development. The results of experimental studies of physicochemical properties of four types of plant biomass, i.e., a wheat straw, oat grains, larch needles and rapeseed pods are shown. The study consisted of determining the energy parameters in the form of gross and net calorific values of the test material. In addition, the ash and moisture content of the material was tested. Moreover, an elementary analysis for the tested materials by determining the content of carbon, hydrogen and nitrogen was performed. The studies have shown energy potential for the examined materials, in particular oat grains, where the gross calorific value amounted to 17.16 MJ·kg<sup>-1</sup>, net calorific value to 15.37 MJ·kg<sup>-1</sup> and ash content to 2.71%. Larch needles are characterised by the highest carbon content of 45.73%, oat grains by hydrogen at 6.53%, 1.53% nitrogen and sulphur 0.11%. Determined emission rates indicate a reduction of 31–41% CO, 30–39% CO<sub>2</sub>, 22–55% NO<sub>x</sub>, 95–97% SO<sub>2</sub>, 47–97% dust depending on the type of used biomass in relation to hard coal.

Keywords: biomass; energy; emission factors

## 1. Introduction

One way of implementing the principles of sustainable development is the use of low-emission fuels. It is believed that biomass represents a source of low-emission fuels [1,2]. The entire energy contained in the biomass comes from the Sun and it is processed and retained in plants through photosynthesis. This energy can be used for very different purposes, including the production of heat by burning. Of course, when burning biomass, carbon dioxide and other pollutants are released, but it is a gas that has been absorbed into the primary growth of combusted biomass and that will be absorbed during the photosynthesis processes carried out by new plants [3–5]. Surely, the assumption that the total emission is zero would be a mistake, because the cultivation of plants used for biomass requires some energy expenditure. During activities such as the collection and transport of biomass, pollutants are released from the use of natural resources but the total emission index using biomass is many times lower than in the case of fossil fuels [6,7]. For the countries whose economy is based on natural resources it is a good idea to produce composite fuels from the combination of biomass and a fossil resource or to find solutions for transforming greenhouse gases into new energy carriers [8,9]. The above-mentioned fuel can be produced by mixing both the components and briquetting or torrefaction of the composite. This solution allows for reducing carbon dioxide emissions, thus being in line with the assumptions of eco-development and low-emission economy as well as the principles of sustainable development [10]. However, it should be remembered that the emissions generated during the combustion of fuels containing biomass are related both to the process parameters during combustion and the type of



biomass that is used as biofuel [11–13]. The implementation of low-emission economy principles is a long-term process, requiring many new investments and thus involving significant financial outlays [14,15], which is why in the countries where energy is still produced mainly on the basis of burning minerals a good solution is the introduction of composite fuels consisting of both biomass and non-renewable fuels. The consumption of such fuel pollutes the environment to a lesser extent, thus contributing to the goals of a low-emission economy [6,16]. This approach contributes to achieving sustainable economic growth through the introduction of an energy policy that reduces dependence on fossil resources and minimises environmental damage [17]. The production of biofuels, in comparison with the use of conventional energy carriers based on minerals, is really beneficial for environmental, economic and energy security reasons [18]. The most important environmental benefits include a significant reduction of greenhouse gas emissions, primarily of methane and carbon dioxide, biomass biodegradability and thus no problem with the storage of toxic waste as well as the possibility of effective management of organic waste from various industry sectors [16,19]. Among the economic benefits the most important are: the activation of rural communities, impact on reducing unemployment through the creation of new jobs and increase in the wealth of farmers (the production is a completely new source of income). The co-products in the production of bioethanol may be used as animal feed, thus reducing the financial outlays for running farms [20]. Biomass production also entails increased investment in agriculture and farm modernization, which contributes to the improvement of production efficiency [21]. The use of biomass allows for a partial independence from energy supplies from imports, resulting in the energy sector decentralization and an increase in competitiveness among local suppliers, which is a favourable phenomenon from the point of view of energy security as well as the principles of sustainable development [9].

The aim of the research was to perform a physicochemical analysis of selected agricultural and forest biomasses and determination of the emission indicators for individual gases and dusts in terms of their availability for energy purposes and environmental protection in the aspect of sustainable development.

## 2. Materials and Methods

#### 2.1. Biomass Sample

The object of research in the form of: larch needles, rapeseed pods, oat grain, wheat straw, were used as the reference biomass feedstock. The studied agro-biomass was obtained from farms plots in Lublin province (Poland) and the larch needles were obtained from a forest in the Jastków area (Lublin province, Jastków, Poland). The plants were harvested once in 2017. Agro-biomass in its various forms that is widely available in Poland was chosen for research. Larch needles were used in research due to the lack of detailed results in terms of energy use and emissivity of this material. In order to obtain homogeneous samples in research, ca. 1 kg portions of each biomass type were dried.

#### 2.2. Physical Properties of Biomasses

The dried biomass samples were pulverised and ground (0.5 mm) in a laboratory grinder (IKA A 11, Warsaw, Poland) prior to analysis. The physical characteristics of biomass samples such as proximate, calorific values, carbon (C), hydrogen (H), nitrogen (N), sulphur (S) content and thermogravimetric (TG) analysis were obtained by using International Organization for Standardization (ISO) methods. The research was carried out at the Department of Power Engineering and Transportation of the University of Life Sciences in Lublin, Poland. Ten replications were performed for all measurements.

## 2.2.1. Proximate Analysis

In the test samples the moisture (W) was determined according to EN-ISO 18134-1:2015-11 [22] and the ash content (A) according to the EN-ISO 18122:2016-01 [23] using a thermogravimetric analyser

(Leco TGA701, Saint Joseph, MO, USA). Determination of volatile matter (V) was based on the determination of loss on heating of the material for seven minutes under a nitrogen atmosphere at a temperature of 900 °C (EN-ISO 18123:2016-01 [24]). Samples were concurrently analysed, placing samples of approximately 1 g in net weight in ceramic melting pots, placed on a plate inside an incinerator. Samples were automatically weighed by the device, and ash content and water content were measured on the basis of the weight loss of the matter after it had been heated up when being strictly controlled in the conditions of ambient oxygen. The ambient oxygen and temperature of the incinerator was controlled automatically and steered by means of computer software (TGA 701 Series, Version 1.31 2013). W of the sample was computed in analytical terms in conformity with the EN-ISO 18134-2:2017 [25] standard, according to the following formula (Equation (1)):

$$W = (m_1 - m_2/m_1 - m_3) \times 100, \tag{1}$$

where: *W*—moisture content in analytical terms (%),  $m_1$ —weight of the pot containing the sample before drying (g),  $m_2$ —weight of the pot containing the sample after drying (g),  $m_3$ —weight of an empty pot (g).

Whereas *A* was measured in analytical terms in conformity with [23], according to the formula (Equation (2)):

$$A = (m_3 - m_1/m_2 - m_1) \times 100, \tag{2}$$

where: *A*—ash content in a sample in analytical terms (%),  $m_1$ —weight of a calcined pot (g),  $m_2$ —weight of the pot containing a sample (g),  $m_3$ —weight of a pot containing ash (g).

## 2.2.2. Calorific Value

The gross calorific value (GCV) and net calorific value (NCV) were determined in a static bomb calorimeter, a sealed Leco AC 600, using EN 14918:2010 [26] standard. Samples of 1.0 g were used for each analysis. A cotton thread was attached to the steel ignition wire and placed in contact with the sample. The bomb was filled with oxygen at 25 °C with 1.0 cm<sup>3</sup> of water added to the bomb. The calorimeter was placed in an isothermal jacket with an air gap separation of 10 mm between all surfaces. The bomb calorimeter was submerged in a calorimeter cane filled with distilled water. The calorimeter jacket was maintained at constant temperature by circulating water at 25 °C.

Calculation of the sample NCV followed Equation (3):

$$Qi = Q - 24.42 \times (W + 8.94 \times H),$$
 (3)

where: Qi—net calorific value (condensed water vapour contained in exhaust gases), Q—gross calorific value (non-condensed water vapour contained in exhaust gases) (GCV); 24.42—heat of water evaporation in standard conditions per 1% (m·m<sup>-1</sup>) of water formed during the combustion or present in the analysed sample, 8.94—coefficient of conversion of the hydrogen content into water, W—moisture content in the sample (%), and H—hydrogen content (%).

## 2.2.3. Combustible Solid Fractions (Fixed Carbon)

The content of other combustible solid fractions *FC* (%) was determined from the difference (Equation (4)):

$$FC = 100 - W - A - V, (4)$$

where: W—moisture content (%), A—ash content (%), V—content of volatile matter (%).

#### 2.3. Fuel Ratio

The fuel ratio (FR, %) was calculated according to Equation (5):

$$FR = FC/V, \tag{5}$$

#### 2.4. CHNSO Analysis

In turn, the elemental analysis was carried out using a Leco CHNS 628 automated analyser in accordance with the EN-ISO 16948:2015-07 [27] and EN-ISO 16994:2016-10 [28] standards. It is comprised of the main unit and a module used for measuring coal, hydrogen, and nitrogen content as well as an analytical weighing machine and a computer with a software used for the process steering purposes. The process of measuring *C*, *H*, and *N* content was performed in the temperature of 950 °C. The matter of 0.1 g in net weight was weighed by means of the analytical weighing machine. Then it was placed in an air-tight aluminium foil in order to prevent from oxygen access. That sample was later placed in a carousel container and automatic measurements were made. *C*, *H* and *N* content were measured automatically by means of a computer software (CHNS 628 Series, Version 1.46 2013). The S content was analysed in separate module in the temperature of 1350 °C, placing a ceramic boat with 0.3 g in net weight of sample in combustion chamber. Oxygen (*O*) in the samples was determined using the indirect method specified in Equation (6):

$$O = 100 - C - H - N - S - W - A,$$
(6)

where: C, H, N, S, O—content of elemental carbon, hydrogen, nitrogen, sulphur, and oxygen in the fuel (%).

#### 2.5. Determination of Emission Factors

The determination of emission levels of individual gases and dust was based on the factor's emission method. The  $CO_2$  emission factor was calculated using the calculation method based on the carbon content and calorific value of fuels. The Equations (7)–(16) were used for the calculation the amount of emission of CO,  $CO_2$ ,  $NO_x$  and  $SO_2$  [29]:

$$SO_2: E = B \times w \times S,$$
 (7)

$$NO_{x}/CO/CO_{2}: E = B \times w,$$
(8)

Dust: 
$$E = B \times w \times A \times 100/(100 - K)$$
, (9)

where: *E*—amount of emission (kg), *B*—fuel consumption (Mg), *S*—sulphur content in fuel (%), *A*—ash content in fuel (%), *K*—combustible components content in dust (5% for biomass) (%), *w*—emission factor gas/dust.

The CO emission factor was calculated from Equation (10):

$$CO = \frac{28}{12} \times E_c \times (C\_CO/C), \tag{10}$$

where: *CO*—carbon monoxide emission factor (kg·kg<sup>-1</sup>), 28/12—molar mass ratio of carbon monoxide and carbon, *EC*—emission factor of chemically pure coal (kg·kg<sup>-1</sup>), *C*\_*CO*/*C*—part of the carbon emitted as *CO* (for biomass 0.06).

The emission factor of chemically pure coal was calculated according to the Equation (11):

$$E_c = c \times u_c, \tag{11}$$

where: *c*—carbon content in biomass in working condition (kg·kg<sup>-1</sup>),  $u_c$ —part of carbon oxidised in the combustion process (for biomass 0.88).

The  $CO_2$  emission factor was calculated from Equation (12):

$$CO_2 = \frac{44}{12} \times \left( E_c - \frac{12}{28} \times CO - \frac{12}{16} \times E_{CH_4} - \frac{26.4}{31.4} \times E_{NMVOC} \right), \tag{12}$$

where:  $CO_2$ —carbon dioxide emission factor (kg·kg<sup>-1</sup>), 44/12—molar mass ratio of carbon dioxide and pure coal, 12/28—molar mass ratio of carbon dioxide and carbon monoxide, 12/16—molar mass ratio of carbon and methane,  $E_{CH_4}$ —methane emission factor,  $E_{NMVOC}$ —emission index of non-methane VOCs (for biomass 0.009).

The methane emission factor was calculated according to Equation (13):

$$E_{CH_4} = \frac{16}{12} \times E_c \times (C_C H_4 / C), \tag{13}$$

where:  $E_{CH_4}$ —methane emission factor (kg·kg<sup>-1</sup>), 16/12—molar mass ratio of methane and coal,  $C_{CH_4}/C_{-}$  part of the carbon emitted as  $CH_4$  (for biomass 0.005).

The  $NO_x$  emission factor was calculated from Equation (14):

$$NO_x = \frac{46}{14} \times E_c \times N/C \times (N_NO_x/N), \tag{14}$$

where:  $NO_x$ — $NO_x$  emission factor (kg·kg<sup>-1</sup>), 46/14—molar mass ratio of nitrogen dioxide to nitrogen. The molar mass of nitrogen dioxide is considered due to the fact that nitrogen oxide in the air oxidises very soon to nitrogen dioxide, N/C—nitrogen to carbon ratio in biomass,  $N_NO_x/N$ —part of nitrogen emitted as  $NO_x$  (for biomass 0.122).

The SO<sub>2</sub> emission factor was determined according to Equation (15):

$$SO_2 = \frac{2S}{100} \times (1 - r),$$
 (15)

where:  $SO_2$ —sulphur dioxide emission factor (kg·kg<sup>-1</sup>), 2—molar mass ratio of  $SO_2$  and sulphur, *S*—sulphur content in fuel (%), *r*—coefficient determining the part of total sulphur retained in the ash.

Rising factor and dust emission factor  $E_{dust}$  was calculated according to Equation (16):

$$E_{dust} = 1.5 \times A \times \frac{100 - \eta_0}{100 - k},$$
(16)

where:  $E_{dust}$ —dust emission factor (kg·Mg<sup>-1</sup>), 1.5 × *A*—rising index, indicating the amount of dust formed during combustion (kg·Mg<sup>-1</sup>), 1.5—coefficient denoting 15% of the ashes rising in the form of volatile dust, *A*—ash content in fuel (%),  $\eta_0$ —dust removal efficiency (for biomass 20%), *k*—content of flammable parts in the dust (for biomass 5%).

#### 2.6. Statistical Analysis

The results underwent the statistical analysis conducted by means of the STATISTICA (data analysis software system) software (Version 13.1, Tulsa, OK, USA, 2016). The normality of distribution of the properties under consideration was checked by means of the Shapiro—Wilk compliance test. The impact of a certain matter upon the value of incineration GCV and NCV, A, V, C, H, N, S content was assessed by means of the ANOVA test. Homogeneity of variance was checked by Lavene's test. In case of heterogeneity of variance, the F Welch test (Fw) was performed. The significance level of the diversity was also confirmed by means of the Tukey (HSD) test. All the statistical analyses were conducted at the significance level of  $\alpha = 0.05$ .

### 3. Results

#### 3.1. Results of Technical and Elemental Analysis

The research showed that in terms of calorific value the analysed biomass displayed different values (Table 1). The analysed biomass types exhibited similar technical parameters, as evidenced by

similar the fuel ratio (FR). The low ratio suggests that the fuels were characterised by low content of combustible solids (FC) and high content of volatiles (V), which is characteristic for the biomass.

A comparison of the technical and elemental composition of the biofuels examined showed differences between biofuels, what shows i.e., different the oxygen content in biomass. Due to the lower coalification in relation to fossil fuels (hard coal), the examined biomass indicated the lower NCV. The highest NCV among the analysed raw materials was shown for oat grain and it was 9.5% higher than the lowest value for rapeseed pods. As to ash content (A), the lowest amount of ballast was recorded for larch needles whereas the highest A was recorded for rapeseed pods and it was 94.5% higher than in the case of larch needles. The analysis of volatile substances (V) showed the highest content of non-flammable substances in larch needles, followed by oat grain, wheat straw and rapeseed pods with the lowest content. It was found out that the level of V was different in all the tested raw materials and the maximum difference did not exceed 3.45%. However, high levels of V may also be an advantage for biomass. Fuels of this type are characterised by flame stability and improved ignition of the air-fuel mixture. Determination of solid carbon content (FC) and V allows for indicating the degree of ignition and gasification, or biomass oxidation, (the higher V, the lower A and easier ignition). It can also indicate the energy efficiency of the material (the higher the ratio of hydrogen and oxygen to carbon content the less energy can be produced, due to the fact that chemical bonds between carbon and hydrogen as well as carbon and oxygen are weaker than the bonds between carbon atoms). The carbon content (C) in the analysed raw materials was at a different level. The highest content of this element was found in larch needles, the lowest in rapeseed pods and the difference was 14.21%. The highest percentage of hydrogen (H) was recorded for oat grain, followed by larch needles, rapeseed pods and, with the lowest value, wheat straw. The difference between the highest and lowest hydrogen content was 13.9% in the raw materials tested. The highest share of nitrogen (N) in the analysed raw materials was determined for oat grain and larch needles. The lowest and thus the most agreeable contents of these elements were determined for rapeseed pods and wheat straw. As to sulphur, its highest content was recorded for rapeseed pods and it was 86.53% higher than the lowest content, found in wheat straw.

Material	Wheat Straw	Oat Grain	Larch Needles	<b>Rapeseed Pods</b>	F Test	<i>p</i> -Value	Fw Test	pw-Value
$GCV \pm Sx (MJ \cdot kg^{-1})$	$16.6a \pm 0.00$	$17.16ab \pm 0.00$	$16.83b\pm0.00$	$15.48b\pm0.00$	7.71	0.02	-	-
$NCV \pm Sx (MJ \cdot kg^{-1})$	$15.32a\pm0.22$	$15.73 ab \pm 0.00$	$15.3b\pm0.00$	$14.25b\pm0.00$	7.71	0.02	-	-
$C \pm Sx$ (%)	$41.04\mathrm{c}\pm0.08$	$41.86b\pm0.23$	$45.73a\pm0.03$	$39.23d \pm 0.13$	871.47	< 0.01	3616.17	< 0.01
$H \pm Sx$ (%)	$5.59b\pm0.13$	$6.53a\pm0.06$	$5.81b\pm0.02$	$5.62 \mathrm{c} \pm 0.03$	90.7	< 0.01		
$N \pm Sx$ (%)	$0.52d\pm0.01$	$1.53a\pm0.04$	$0.91b\pm0.06$	$0.61 \mathrm{c} \pm 0.04$	376.37	< 0.01	665.83	< 0.01
$S \pm Sx$ (%)	$0.07d\pm0.00$	$0.11b\pm0.00$	$0.09c \pm 0.00$	$0.54a\pm0.00$	45.50	< 0.01	-	-
O ± Sx (%)	$36.36a \pm 011$	$35.46b \pm 0.31$	$32.52c \pm 0.10$	$31.67d \pm 0.48$	175.93	< 0.01	-	-
W (%)	8.05	11.81	14.41	12.39	-	-	-	-
$A \pm Sx$ (%)	$8.37b\pm0.23$	$2.71\mathrm{c}\pm0.02$	$0.54d\pm0.02$	$9.94a\pm0.34$	91797.3	< 0.01	75079.1	< 0.01
$V \pm Sx$ (%)	$68.65 \mathrm{c} \pm 0.47$	$69.71b \pm 0.22$	$71.72a \pm 0.25$	$68.27d\pm0.68$	70.13	< 0.01	65.48	< 0.01
FC (%)	$15.08a\pm0.47$	$15.77a\pm0.24$	$13.34b\pm0.24$	$9.40c \pm 0.39$	192.74	< 0.01	156.61	< 0.01
FR	0.22	0.23	0.19	0.14	-	-	-	-

Table 1. Results of technical and elemental analysis of examined biomass.

GCV—gross calorific value, NCV—net calorific value, W—moisture content, A—ash content, V—volatile matter content, FC—combustible solid content, Sx—standard deviation; \*—Significant value of the F test at significance level  $\alpha = 0.05$ ; a, b, c, d—Significant difference at the level of significance of  $\alpha = 0.05$ ; F—F test; Fw—Welch's F test, pw—*p*-value for Welch's F test.

The ANOVA test proved that the kind of matter under consideration did have an impact indeed upon of all tested characteristics (Table 1). The Tukey HSD test proved that the properties under consideration are substantially diversified in those groups for the majority of the values of p < 0.05. The statistical analysis showed that there were significant differences between all the groups concerning the contents of C, N, S, O, A and V. In the case of GCV and NCV, no significant differences were found for larch needles and rapeseed pods as well as wheat straw and oat grains. As to GCV of oat grain, no significant differences were found in relation to wheat straw, larch needles or rapeseed pods. The Tukey HSD test did not show any significant differences in H only between the wheat straw

and larch needles biomass. In other cases, significant differences in the content of this element were demonstrated.

#### 3.2. Emission Factors

On the basis of technical and elementary analysis, using the factor's method (Equations (7)–(16)), the assessment of CO,  $CO_2$ ,  $NO_x$ ,  $SO_2$  and dust emission indices was performed for the examined biomass. Table 2 shows the results of estimated emission factors for tested materials and hard coal.

CO	CO <sub>2</sub>	NO <sub>x</sub>	$SO_2$	E <sub>Dust</sub>
50.57	1238.24	1.83	0.14	10.56
51.58	1262.98	5.39	0.16	3.43
56.34	1379.53	3.20	0.18	0.68
48.33	1183.53	2.16	0.21	12.56
82.01	1969	4.09	5.2	23.57
	CO 50.57 51.58 56.34 48.33 82.01	CO         CO2           50.57         1238.24           51.58         1262.98           56.34         1379.53           48.33         1183.53           82.01         1969	CO         CO2         NOx           50.57         1238.24         1.83           51.58         1262.98         5.39           56.34         1379.53         3.20           48.33         1183.53         2.16           82.01         1969         4.09	COCO2NOxSO250.571238.241.830.1451.581262.985.390.1656.341379.533.200.1848.331183.532.160.2182.0119694.095.2

**Table 2.** Emission factors for analysed biomass and coal (in kg·Mg<sup>-1</sup>).

It can be noticed that carbon monoxide emission levels were similar for all the raw materials. In the case of carbon dioxide, the highest emission rate was recorded for the biomass of larch needles, while the lowest for rapeseed pods and the difference was 14.21%. In relation to hard coal, the  $CO_2$ emission level was on average 40% lower for the biomass studied. However, it should be noted that in nature the  $CO_2$  cycle during biomass burning is closed. While analysing the  $NO_x$  emissions among biomass of different origins, the highest was recorded for oat grain, while the lowest for wheat straw. In relation to hard coal, only oat grain showed a higher emission index. The use of the tested biomass as a fuel would reduce NO<sub>x</sub> emissions and the attempt to create composite fuels based on coal and biomass would greatly contribute to the reduction of emissions of nitrogen oxides to the environment. During the research larch needles showed the highest index of  $SO_2$  emissions. The lowest emission was recorded for rapeseed pods and it was over 95% lower in comparison to hard coal. High dust emission indices were recorded for wheat straw and rapeseed pods, although they were about 50% lower than in the case of hard coal. The lowest dust emission was demonstrated for larch needles, and was over 97% lower in relation to hard coal emission. In the case of the studied biomass sources only for nitrogen oxides there was an increase in their level per unit of energy in relation to hard coal (Table 3).

**Table 3.** Gas-dust emission indices for biomass per unit of energy (in kg·GJ<sup>-1</sup>).

Material	CO	CO <sub>2</sub>	NO <sub>x</sub>	$SO_2$	E <sub>Dust</sub>
wheat straw	2.87	60.35	0.10	0.01	0.60
oat grain	2.93	61.76	0.31	0.01	0.19
larch needles	3.20	68.38	0.18	0.01	0.04
rapeseed pods	2.75	57.25	0.12	0.01	0.71
hard coal [29]	3.83	70.87	0.04	0.28	1.14

For the larch needles, the highest emission rates per unit of energy were observed for CO (25.1% lower than hard coal), CO<sub>2</sub> (3.51% lower than hard coal), SO<sub>2</sub> (69.4% lower than hard coal also for all biomass). The highest dust emission rate per unit of energy was determined for rapeseed pods and it was 37.72% lower than hard coal. The highest NO<sub>x</sub> emissions were reported for the oat grain (87.1% higher than hard coal).

## 4. Discussion

The search for new energy sources in terms of their neutral or minimal impact on the environment with high energy potential is an important element of sustainable development, in particular of the the renewable energy sector.

energy sector. In order to reduce the emission of gases generated during the combustion of fuels, such biofuels are sought that will reduce or eliminate emissions potentially dangerous and harmful for the natural environment, including man. The determination of emission indices also for biomass is quite significant due to the assumptions about its zero-emission. Very often in the literature on the subject one can encounter theses about the neutral impact of biomass in the combustion process on the natural environment, which is not entirely consistent with reality. The examined biomass showed a high energy potential in relation to other types of biofuels. Thus, it can be observed that, compared to other energy raw materials, the ones analysed here can contribute to increasing the diversification of energy in the fuel and energy balance of the economy as well as to the sustainable development of

Li et al. [30] suggest that in order to alleviate contradictions between the economic development, energy and environment, it is necessary to find bioenergy technology that has the best potential for sustainable development. It should not be forgotten that flame combustion involves a quick reaction of oxygen with gases emitted from solid biomass fuel [31]. In the flame combustion, C, H, N and S are converted into highly oxidised gases, such as CO<sub>2</sub>, H<sub>2</sub>O, NO<sub>x</sub> and SO<sub>2</sub>, also, the majority of black (or elemental) carbon particles are produced. The presented factor's emission method in determining the level of emissions of individual gases and dusts allows the assessment of the impact of biomass on the environment in its use for energy purposes without the need for analytical equipment. Thanks to this method, it is possible to easily determine the emissivity of biofuels, which is often omitted in assessing the suitability of biomass for energy purposes, which was done in this work.

On the basis of the estimated emission factors compared to the literature data, it can be pointed out that among the analysed biomass, the rapeseed pods in particular are characterised by low emissivity. Larch needles also deserve attention. The emission and energy evaluation of this material has not been widely discussed in the literature yet. It should be emphasised the relatively low emission intensity of this material in the dust range. The obtained results of CO and  $CO_2$  emissions for wheat straw were similar to those obtained by Zhang et al. [32]. Literature data show that much higher CO and  $CO_2$ emissivity in relation to the examined biomass has been recorded for rice straw and rapeseed straw, so the use of obtained biomass as an energy source in the energy industry may contribute to a significant reduction in greenhouse gas emissions. According to Cereceda-Balic et al. [33] similar levels of CO emissions for the tested materials can be seen in relation to Pinus radiata, Eucalyptus globulus, or Nothofagus obliqua, whereas much lower  $CO_2$  (30% on average) as well as  $SO_2$  (50% on average) emissions occur, which also confirms the pro-ecological advantages of studied material. A 50% reduction in SO<sub>2</sub> emissions using wheat straw in relation to the above materials indicates this biofuel as low-emission and environmentally friendly. The studied biomass is characterised by high  $NO_x$ emission indices, which coincides with the emission levels for straw pellets, sunflower stalk pellets, corn stalk pellets and wood pellets obtained by Krugly et al. [34], which is a disadvantage of these biofuels and excessive use of this type of biomass, may contribute to the formation of acid rain.

The presented emission rates indicate a reduction of 31-41% CO, 30-39% CO<sub>2</sub>, 22-55% NO<sub>x</sub>, 95-97%% SO<sub>2</sub>, 47-97% dust depending on the type of used biomass in relation to hard coal. Only in the case of oat grains, a NO<sub>x</sub> emission ratio increases by 24% in relation to hard coal. It should be noted that the use of agro and forest biomass as fuel significantly reduces the emission of harmful compounds to the natural environment. Hence, the possibility of developing this type of fuel gives real environmental benefits, which is very important for the environment. Table 4 presents literature data on physicochemical properties of selected biomass species.

Parameters	Acacia	Pine	Rape Straw	Miscanthus	s Wheat Straw	Sunflower Husk
C (%)	49.1	51.2	41.38	46.30	48.5	43.87
H (%)	6.40	6.77	5.20	5.93	5.5	6.29
N (%)	0.121	0.0134	0.57	0.362	0.3	1.57
S (%)	0.01	0	0.11	0.09	0.1	0.03
O (%)	44.38	38.66	38.24	45.57	3.9	-
V (%)	82.26	71.34	68.85	84.10	59	-
A (%)	0.22	0.13	4.98	2.55	4	2.12
FC (%)	10.36	5.68	-	6.77	21	-
GCV (MJ⋅kg <sup>-1</sup> )	18.1	19.2	16.71	17.5	17.3	17.9
NCV ( $MJ \cdot kg^{-1}$ )	-	-	15.34	-	12.3	16.27

Table 4. Comparison of physicochemical properties of selected biomass species [35–38].

When comparing C, H, N and S content for wheat straw, similar values have been reported, according to Li et al. [39], Maj [9] and McKendry [37], whereas in the case of oxygen content, according to McKendry's [37] data, the difference is in the order of 90% and it is linked to a different moisture and ash content. Larch needles, on the other hand, have shown a high C content similar to acacia or *Miscanthus* which leads to low NCV and lower energy potential in relation to pine or rape straw. Wheat straw, oat grain or rapeseed pods have shown a lower content of coal than both wood and agricultural biomass. For rapeseed pods, the lowest carbon content, reaching even 24% of the difference in relation to pine and 5.5% in relation to rape straw, has been recorded [36]. When comparing the hydrogen content in the analysed biomass with the literature data, a similar level of content can be observed for most of the biomass kinds, both of the forest and agricultural origin. In contrast, in the case of nitrogen, oat grain is characterised by a similar content in relation to the sunflower husks, and wheat straw and rapeseed pods to rape straw. Noteworthy is the high nitrogen content in the larch needles, which is close to the nitrogen content in the acacia wood. Therefore, the use of larch needles in the power industry will lead to increased NO<sub>x</sub> emissions. The lowest sulphur content was recorded for wheat straw and it is at a comparable level for literature data. It should be emphasised that the sulphur content in rapeseed pods is high, compared to other biomass kinds, as it is about 80% higher than in rapeseed straw, wheat straw or *Miscanthus* and about 60% higher in relation to apple, cherry, plum or peach wood [40], hence the use of rapeseed pods in the energy industry may contribute to increased  $SO_2$  emissions in relation to the mentioned above biomass.

A similar content of volatile parts in the studied biomass was recorded as in the case of rape straw and pine wood in the literature on the subject. Noteworthy is the low content of volatile matter obtained for wheat straw by McKendry [37], as it is 14% lower than that shown in the studies. When comparing the V parameter for all the plants studied, one should notice a far lower content of volatile parts compared to acacia or *Miscanthus*, reaching about 15%, and to wheat straw, by 5%, according to McKendry [37]. In the case of fixed carbon (FC), the obtained indices are lower in the examined biomass from acacia, pine or *Miscanthus* by about 10% and comparable to sorgum, reed canary grass, wheat straw pellet, or tall fescue ecotype, according to Lalak et al. [41]. It should be noted that the gas-solid combustion reactions are slower than the gas-gas reactions and the high solid carbon content indicates that the coal will require a long burning time. In the studies the lowest ash content was found in larch needles and this is the content comparable to acacia and pine. The oat grain showed similar ballast contents in relation to the sunflower husk, Miscanthus [37,41], Virginia mallow pellets [42], or Rosa multiflora [43]. Similar values of ash content in relation to rapeseed pods and wheat straw were noted in the literature for Sudan grass, corn stover [44], reed canary grass, brome grass [41], and bean husk [45]. The analysed biomass is characterised by low ballast content and the associated low dust emission in relation fossil fuels, e.g., using larch needles as fuel leads to dust reduction by about 85% in relation to hard coal [29], what is undoubtedly a pro-environmental benefit when using this biofuel. Further research is needed to understand the different biomass feedstocks.

This knowledge will allow the use of low-emission fuels in the energy sector or the use of composite fuels containing raw materials with low emission based on biomass.

According to McKendry et al. [37] the net calorific value for the wheat straw in their research was lower by  $3.02 \text{ Mg} \cdot \text{kg}^{-1}$  than obtained in studies. It could be also noticed that analysed oat grains had gross calorific value of  $2.37 \text{ Mg} \cdot \text{kg}^{-1}$  lower [46] and the similar net calorific value as determined by Magdziarz et al. [47]. By comparing the gross calorific value all the other materials from the literature it can be concluded that the highest value characterised the pine 19.2 Mg \cdot \text{kg}^{-1} and it is the value of  $2.04 \text{ Mg} \cdot \text{kg}^{-1}$  higher than the one obtained for the oat grains, which was the highest value in the studies. Both analysed materials of the wheat straw and larch needles are characterised by a gross calorific value at a similar level as rape straw. However, in the case of rapeseed pods the gross calorific value is the lowest among analysed materials. Currently, it is necessary to look for biofuels with high energy potential and with low-emission of gases and dust. Biomass meets the above criteria, however, it is not a homogenous fuel and in particular its application in the energy sector must be preceded by an assessment of the energy and ecological suitability of this type of energy carrier.

## 5. Conclusions

The examined biomass of forest and agricultural origin indicates both good energy properties and low emission potential. When comparing the examined biomass in terms of emissions to hard coal it was noticed that for practically all the tested raw materials the emission levels were much lower (except for  $NO_x$ ). On the basis of the study of literature and research carried out, the following conclusions can be drawn:

- 1. The highest calorific value in the research was recorded for oat grain 15.73 MJ·kg<sup>-1</sup> and then for wheat straw, larch needles and rapeseed pods (14.25 MJ·kg<sup>-1</sup>). Research has shown that such a distribution is mainly related to the content of carbon in biomass. In addition, the examined biomass showed the FR indicator at a similar level, which allows to conclude on the similarity of the studied biofuels as well as the high content of volatile parts and low content of fixed coal.
- 2. The research showed that the analysed biomass had an ash content of 0.54% for larch needles up to 9.94% for rapeseed pods. Such ballast content allows for a positive evaluation of the examined biomass in the context of its use for energy purposes and contribution to sustainable development, combining the high energy potential of the tested materials with low emission levels.
- 3. Estimated emission factors for the studied biomass show lower emissions of 31–41% CO, 30-39% CO<sub>2</sub>, 22–55% NO<sub>x</sub>, 95–97% SO<sub>2</sub> and 47–97% dust relative to hard coal. This provides the basis for a positive assessment of this kind of biomass as green fuel and confirms that the tested biofuels will be included in the assumptions of sustainable development.

Funding: This research received no external funding.

Conflicts of Interest: The authors declare no conflicts of interest.

## References

- Dhillon, R.S.; von Wuehlisch, G. Mitigation of global warming through renewable biomass. *Biomass Bioenergy* 2013, 48, 75–89. [CrossRef]
- 2. Nunes, L.J.R.; Matias, J.C.O.; Catalão, J.P.S. Mixed biomass pellets for thermal energy production: A review of combustion models. *Appl. Energy* **2014**, *127*, 135–140. [CrossRef]
- 3. Jahirul, M.I.; Rasul, M.G.; Chowdhury, A.A.; Ashwath, N. Biofuels production through biomass pyrolysis—A technological review. *Energies* **2012**, *5*, 4952–5001. [CrossRef]
- 4. Tumuluru, J.S.; Lim, C.J.; Bi, X.T.; Kuang, X.; Melin, S.; Yazdanpanah, F.; Sokhansanj, S. Analysis on storage off-gas emissions from woody, herbaceous, and torrefied biomass. *Energies* **2015**, *8*, 1745–1759. [CrossRef]
- Fournel, S.; Palacios, J.H.; Morissette, R.; Villeneuve, J.; Godbout, S.; Heitz, M.; Savoie, P. Influence of biomass properties on technical and environmental performance of a multi-fuel boiler during on-farm combustion of energy crops. *Appl. Energy* 2015, 141, 247–259. [CrossRef]

- 6. Morison, J.; Matthews, R.; Miller, G.; Perks, M.; Randle, T.; Vanguelova, E.; White, M.; Yamulki, S. *Understanding the Carbon and Greenhouse Gas Balance of Forests in Britain;* Forestry Commission Research Report; Forestry Commission: Edinburgh, UK, 2012.
- Suzuki, K.; Tsuji, N.; Shirai, Y.; Hassan, M.A.; Osaki, M. Evaluation of biomass energy potential towards achieving sustainability in biomass energy utilization in Sabah, Malaysia. *Biomass Bioenergy* 2017, 97, 149–154. [CrossRef]
- 8. Krzaczek, P.; Maj, G.; Piekarski, W.; Nazimek, D. Study on catalytic activity of bimetallic Pd-Ag/Al<sub>2</sub>O<sub>3</sub> catalysts for the oxidation of methane. *Przem. Chem.* **2016**, *95*, 2200–2205. [CrossRef]
- 9. Maj, G. Diversification and Environmental Impact Assessment of Plant Biomass Energy Use. *Pol. J. Environ. Stud.* 2015, 24, 2055–2061. [CrossRef]
- 10. Promotion of the Use of Energy from Renewable Sources and Amending and Subsequently Repealing Directives 2001/77/EC and 2003/30/EC. Directive 2009/28/EC. 2009. Available online: https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=celex%3A32009L0028 (accessed on 23 October 2017).
- 11. Szyszlak-Barglowicz, J.; Zajac, G.; Slowik, T. Research on Emissions from Combustion of Pellets in Agro Biomass Low Power Boiler. *Rocz. Ochr. Srodowiska* **2017**, *19*, 715–730.
- Zajac, G.; Szyszlak-Bargłowicz, J.; Słowik, T.; Wasilewski, J.; Kuranc, A. Emission characteristics of biomass combustion in a domestic heating boiler fed with wood and Virginia Mallow pellets. *Fresenius Environ. Bull.* 2017, 26, 4663–4670.
- Konieczyński, J.; Komosiński, B.; Cieślik, E.; Konieczny, T.; Mathews, B.; Rachwał, T.; Rzońca, G. Research into properties of dust from domestic central heating boiler fi red with coal and solid biofuels. *Arch. Environ. Prot.* 2017, 43, 20–27. [CrossRef]
- 14. Nakomcic-Smaragdakis, B.; Cepic, Z.; Dragutinovic, N. Analysis of solid biomass energy potential in Autonomous Province of Vojvodina. *Renew. Sustain. Energy Rev.* **2016**, *57*, 186–191. [CrossRef]
- 15. Herbert, G.J.; Krishnan, A.U. Quantifying environmental performance of biomass energy. *Renew. Sustain. Energy Rev.* **2016**, *59*, 292–308. [CrossRef]
- Jegannathan, K.R.; Chan, E.S.; Ravindra, P. Harnessing biofuels: A global Renaissance in energy production? *Renew. Sustain. Energy Rev.* 2009, 13, 2163–2168. [CrossRef]
- Bilgili, F.; Öztürk, İ.; Koçak, E.; Bulut, Ü.; Pamuk, Y.; Muğaloğlu, E.; Bağlıtaş, H.H. The influence of biomass energy consumption on CO<sub>2</sub> emissions: A wavelet coherence approach. *Environ. Sci. Pollut. Res.* 2016, 23, 19043–19061. [CrossRef] [PubMed]
- 18. Pimentel, D.; Patzek, T.W. Ethanol production using corn, switchgrass, and wood; biodiesel production using soybean and sunflower. *Nat. Resour. Res.* **2005**, *14*, 65–76. [CrossRef]
- 19. Chisti, Y. Biodiesel from microalgae beats bioethanol. *Trends Biotechnol.* **2008**, *26*, 126–131. [CrossRef] [PubMed]
- 20. Sanchez, O.J.; Cardona, C.A. Trends in biotechnological production of fuel ethanol from different feedstocks. *Bioresour. Technol.* **2008**, *99*, 5270–5295. [CrossRef] [PubMed]
- 21. De la Torre Ugarte, D.G. *Developing Bioenergy Economic and Social Issues: Bioenergy and Agriculture Promises and Challenges;* International Food Policy Research Institute (IFPRI): Washington, DC, USA, 2006; Volume 14.
- ISO (International Organization of Standardization). Solid Biofuels—Determination of Moisture Content—Oven Dry Method Part 1: Total Moisture—Reference Method. EN-ISO 18134-1:2015. 2015. Available online: https://shop.bsigroup.com/ProductDetail?pid=00000000030275466 (accessed on 23 October 2017).
- ISO (International Organization of Standardization). Solid Biofuels. Determination of Ash Content. EN-ISO 18122:2016-01. 2016. Available online: http://sklep.pkn.pl/pn-en-iso-18122-2016-01e.html (accessed on 23 October 2017).
- 24. ISO (International Organization of Standardization). Solid Fuels—Determination of Volatile Content by Gravimetric Method. EN-ISO 18123:2016-01. 2016. Available online: http://sklep.pkn.pl/pn-en-iso-18123-2016-01e.html (accessed on 23 October 2017).
- 25. ISO (International Organization of Standardization). Solid Biofuels—Determination of Moisture Content—Oven Dry Method—Part 2: Total Moisture—Simplified Method. EN-ISO 18134-2:2017. 2017. Available online: https://shop.bsigroup.com/ProductDetail?pid=00000000030344291 (accessed on 23 October 2017).
- 26. CEN (European Committee for Standardization). Solid Biofuels—Determination of Net Calorific Value. EN 14918:2010. Available online: http://sklep.pkn.pl/pn-en-14918-2010e.html (accessed on 23 October 2017).

- ISO (International Organization of Standardization). Solid Biofuels—Determination of Total Content of Carbon, Hydrogen and Nitrogen. EN-ISO 16948:2015-07. 2015. Available online: https://www.iso.org/ standard/58004.html (accessed on 23 October 2017).
- ISO (International Organization of Standardization). Solid Biofuels—Determination of Total Content of Sulphur and Chlorine. ISO 16994:2016. 2016. Available online: https://shop.bsigroup.com/ProductDetail/ ?pid=00000000030333392 (accessed on 23 October 2017).
- 29. Borycka, B. Commodity Study on Food and Energy Utilization of Rich-Food Waste of the Fruit and Vegetables Industry. Monograph; Radom University of Technology: Radom, Poland, 2008.
- Li, M.; Luo, N.; Lu, Y. Biomass Energy Technological Paradigm (BETP): Trends in This Sector. *Sustainability* 2017, 9, 567. [CrossRef]
- Akagi, S.K.; Yokelson, R.J.; Wiedinmyer, C.; Alvarado, M.J.; Reid, J.S.; Karl, T.; Crounse, J.D.; Wennberg, P.O. Emission factors for open and domestic biomass burning for use in atmospheric models. *Atmos. Chem. Phys.* 2011, 11, 4039–4072. [CrossRef]
- Zhang, T.; Wooster, M.J.; Green, D.C.; Main, B. New field-based agricultural biomass burning trace gas, PM<sub>2.5</sub>, and black carbon emission ratios and factors measured in situ at crop residue fires in Eastern China. *Atmos. Environ.* 2015, 121, 22–34. [CrossRef]
- Cereceda-Balic, F.; Toledo, M.; Vidal, V.; Guerrero, F.; Diaz-Robles, L.A.; Petit-Breuilh, X.; Lapuerta, M. Emission factors for PM<sub>2.5</sub>, CO, CO<sub>2</sub>, NOx, SO<sub>2</sub> and particle size distributions from the combustion of wood species using a new controlled combustion chamber 3CE. *Sci. Total Environ.* **2017**, *584*, 901–910. [CrossRef] [PubMed]
- Krugly, E.; Martuzevicius, D.; Puida, E.; Buinevicius, K.; Stasiulaitiene, I.; Radziuniene, I.; Minikauskas, A.; Kliucininkas, L. Characterization of gaseous-and particle-phase emissions from the combustion of biomass-residue-derived fuels in a small residential boiler. *Energy Fuel* 2014, 28, 5057–5066. [CrossRef]
- 35. Wilk, M.; Magdziarz, A.; Gajek, M.; Zajemska, M.; Jayaraman, K.; Gokalp, I. Combustion and kinetic parameters estimation of torrefied pine, acacia and *Miscanthus giganteus* using experimental and modelling techniques. *Bioresour. Technol.* **2017**, *243*, 304–314. [CrossRef] [PubMed]
- 36. Bradna, J.; Malat'ák, J.; Velebil, J. Impact of differences in combustion conditions of rape straw on the amount of flue gases and fly ash properties. *Agron. Res.* **2017**, *15*, 649–657.
- 37. McKendry, P. Energy production from biomass (part 1): Overview of biomass. *Bioresour. Technol.* 2002, 83, 37–46. [CrossRef]
- 38. Maj, G.; Krzaczek, P.; Kuranc, A.; Piekarski, W. Energy properties of sunflower seed husk as industrial extrusion residue. *Agric. Eng.* **2017**, *21*, 77–84. [CrossRef]
- 39. Li, X.; Wang, S.; Duan, L.; Hao, J.; Li, C.; Chen, Y.; Yang, L. Particulate and trace gas emissions from open burning of wheat straw and corn stover in China. *Environ. Sci. Technol.* **2007**, *41*, 6052–6058. [CrossRef] [PubMed]
- 40. Burg, P.; Mašán, V.; Dušek, M.; Zemánek, P.; Rutkowski, K. Review of energy potential of the wood biomass of orchards and vineyards in the Czech Republic. *Res. Agric. Eng.* **2017**, *63*, 1–7. [CrossRef]
- 41. Lalak, J.; Martyniak, D.; Kasprzycka, A.; Żurek, G.; Moroń, W.; Chmielewska, M.; Wiącek, D.; Tys, J. Comparison of selected parameters of biomass and coal. *Int. Agrophys.* **2016**, *30*, 475–482. [CrossRef]
- 42. Szyszlak-Bargłowicz, J.; Zając, G.; Słowik, T. Hydrocarbon Emissions during Biomass Combustion. *Pol. J. Environ. Stud.* **2015**, *24*, 1349–1354. [CrossRef]
- 43. Kowalczyk-Juśko, A. The Influence of the Ash from the Biomass on the Power Boiler Pollution. *J. Ecol. Eng.* **2017**, *18*, 200–204. [CrossRef]
- 44. Parikh, J.; Channiwala, S.A.; Ghosal, G.K. A correlation for calculating elemental composition from proximate analysis of biomass materials. *Fuel* **2007**, *86*, 1710–1719. [CrossRef]
- 45. García, R.; Pizarro, C.; Lavín, A.G.; Bueno, J.L. Characterization of Spanish biomass wastes for energy use. *Bioresour. Technol.* **2012**, *103*, 249–258. [CrossRef] [PubMed]
- 46. Heinzel, T.; Siegle, V.; Spliethoff, H.; Hein, K.R.G. Investigation of slagging in pulverized fuel co-combustion of biomass and coal at a pilot-scale test facility. *Fuel Process. Technol.* **1998**, *54*, 109–125. [CrossRef]
- 47. Magdziarz, A.; Wilk, M. Thermogravimetric study of biomass, sewage sludge and coal combustion. *Energy Convers. Manag.* **2013**, *75*, 425–430. [CrossRef]



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