Energy Value of Yield and Biomass Quality in a 7-Year Rotation of Willow Cultivated on Marginal Soil

Mariusz Jerzy Stolarski *, **Stefan Szczukowski**, **Michał Krzyżaniak** and **Józef Tworkowski**

Centre for Bioeconomy and Renewable Energies, Department of Plant Breeding and Seed Production, Faculty of Environmental Management and Agriculture, University of Warmia and Mazury in Olsztyn, Plac Łódzki 3, 10-724 Olsztyn, Poland; stefan.szczukowski@uwm.edu.pl (S.S.); michal.krzyzaniak@uwm.edu.pl (M.K.); jozef.tworkowski@uwm.edu.pl (J.T.)
* Correspondence: mariusz.stolarski@uwm.edu.pl; Tel.: +48-89-5234838

Abstract: Bioenergy plays a major role as a renewable energy source in the European Union. Solid biomass is derived mainly as wood from forests and wood processing plants. Willow plantations set up on marginal lands can be a supplementary source of wood for energy generation. This study aimed to determine the energy value of yield and the thermophysical properties and elemental composition of the biomass of 7-year rotation willow harvested on marginal soil. Three varieties and three clones were cultivated in the Eko-Salix system on three marginal soils in northern Poland: riparian, alluvial soil, classified as heavy complete humic alluvial soil (Obory); organic, peat–muck soil formed from peat (Kocibórz); very heavy mineral clay soil (Leginy). Favourable conditions for obtaining high energy value biomass were at Kocibórz and Obory with a high groundwater level. The energy value of biomass at Leginy was lower than at Kocibórz and Obory (by 33% and 26%, respectively). The Ekotur variety had the significantly highest yield energy value (217 GJ ha^{-1} year^{-1}) among the varieties and clones under study. This feature at Kocibórz and Obory was 288 and 225 GJ ha^{-1} year^{-1}, respectively, and 139 GJ ha^{-1} year^{-1} at Leginy. Moreover, the biomass of this variety contained less ash (1.1% d.m.), sulphur (0.03% d.m.) and nitrogen (0.28% d.m.), which is beneficial from the energy-use perspective. Notably, the yield energy value of the UWM 095 clone biomass was also high (167 GJ ha^{-1} year^{-1}). This study showed that willow grown in the Eco-Salix system can be a significant source of energy contained in good-quality woody biomass.

Keywords: willow wood; marginal land; biomass; yield energy value; elemental composition

1. Introduction

Due to the growing priority in the European Union (EU) for renewable energy sources (RES), the demand for energy from biomass is also increasing. This is due to (among others) the need to reduce energy dependence, the need to protect the environment and increasing prices of fossil energy carriers. This is a consequence of the fact that bioenergy plays a major role as a renewable energy source in the EU as it accounts for 61.7% of all RES, with solid fuels accounting for 43% of this amount [1]. Solid biomass is derived mainly as wood from forests and the wood processing industry. Additionally, energy crop plantations set up on agricultural land can be a supplementary source of wood for power plants, heating plants and combined heat and power plants [2–8]. From lignocellulosic biomass, second-generation bioethanol can be also produced [9–12]. Since it should be assumed that the demand for woody biomass will increase in the future, willow grown in short, 2–10-year harvest rotations has been the focus of many studies [13–17].

Willow (*Salix* spp.) is grown in the SRC (short rotation coppice) system on 19,378 ha in the EU [18]. The largest portion of this area is in Sweden and Poland: 8587 and 7832 ha, respectively.

Willow plantations are usually set up in the SRC system, in which the soil must be ploughed and prepared properly for planting short (ca. 20 cm) cuttings obtained from 1-year shoots. Such plantations are usually set up at a density of 13–20 thousand per 1 ha, while biomass is generally harvested in short, 3–4-year rotations. The biomass yield and quality, and as a consequence, the yield energy value from 1 ha of an SRC willow plantation depends on several factors, such as the species and variety, soil and climate conditions, fertilisation type and rate, agrotechnical procedures, planting density and harvest frequency, as well as the technology applied [19–26]. For example, the yield energy value for different SRC species (willow, poplar and black locust) ranged from 29 to 177 ha^{-1} year^{-1} [27], depending on the soil enrichment method, and it exceeded 280 GJ ha^{-1} year^{-1} in other studies for willow [28,29]. The thermophysical properties and elemental composition of biomass of agricultural (e.g., straw, perennial energy crops) or forest (e.g., woodchips, sawdust, pellet) origin are significantly differentiated depending on the factors mentioned above [25,30].

A significant novelty of this study is that it proposes the production of willow biomass, as a solid biofuel, in the Eko-Salix system, which—unlike traditional SRC willow production—applies a different technology in setting up and running a plantation. The main differences in Eko-Salix system willow production are: (1) soil does not have to be ploughed; (2) long cuttings (200–250 cm), so-called long rods, obtained from 2–3-year old shoots, are used as planting material; (3) the long rods are planted at the depth of 40–50 cm; (4) the planting density can be small and range from ca. 2 to 7 thousand long rods per 1 ha; (5) weed control is limited as the long rods jutting out of the ground for 200 cm defeat competition from weeds; (6) fertilisation rates are reduced; (7) plant are harvested in longer, 5–8-year rotations. Therefore, the Eko-Salix system enables setting up extensive willow plantations on marginal soils, which cannot be ploughed for technical or environmental reasons (humid, very heavy soil or peatland), with long rods and obtaining the energy accumulated in biomass in a longer harvest rotation. However, like SRC willow production, new varieties and clones should also be sought in the Eko-Salix system. Such new varieties and clones should have a high yield energy value and good biomass properties from the perspective of conversion plants. Therefore, the current study aimed to determine the yield energy value as well as the thermophysical properties and elemental composition of willow biomass obtained in the Eko-Salix system from three types of marginal soils and harvested in a 7-year rotation.

2. Materials and Methods

2.1. Field Experiments

The study included three field experiments which involved Eko-Salix willow cultivation on marginal soils in the north of Poland in the villages of Obory (53°59′ N, 18°53′ E), Kocibórz (54°00′ N, 21°10′ E) and Leginy (53°59′ N, 21°08′ E). A different type of marginal soil was present at each site. The experiment at Obory was set up on riparian, alluvial soil, classified as heavy complete humic alluvial soil. It is noteworthy that it was good quality soil with neutral pH$_{KCl}$ 7.2, and a high groundwater level (40–81 cm), which made it periodically marshy. The experiment at Kocibórz was set up on organic, peat–muck soil formed from peat with neutral pH$_{KCl}$ 6.8. This site was periodically excessively wet, and the groundwater table was 10–50 cm. The last experiment at Leginy village was set up on very heavy mineral clay soil with neutral pH$_{KCl}$ 7.0. This soil was fertile and very heavy, but cultivation was very difficult, and the groundwater table was the lowest (150–200 cm). The climatic conditions with respect to average annual temperature were similar at all the three sites (ca. 8 °C), and the growing season lasted 200–210 days. The annual total rainfall at Obory (average 500 mm) was lower compared to Leginy and Kocibórz by ca. 200 mm.

Three willow varieties bred at the University of Warmia and Mazury in Olsztyn (UWM) and registered at Research Centre for Cultivar Testing in Słupia Wielka (Poland) were grown in each experiment: Turbo (*Salix viminalis* L.), Tur (*Salix viminalis* L.), Ekotur (*Salix viminalis* L.) and three willow clones: UWM 046 (*Salix viminalis* L.), UWM 095 and UWM 200 (*Salix alba* L.) were also from the

UWM collection. Unrooted long rods (240 cm) were used as planting material. They were obtained from three-year-old shoots and were planted at the depth of 40 cm, i.e., the remaining 200 cm jutted out of the ground. Additionally, two variants of the long rods' planting density were examined when the experiments were first set up: 5200 and 7400 plants ha^{-1}. However, this manuscript concerning the yield energy value and biomass quality from the 7–year rotation does not consider this factor (planting density) because of potentially small feature differentiation and the cost of laboratory analyses. More detailed data on the soil quality, climate conditions and the experiment procedure are provided by Stolarski et al. [31].

2.2. Determination of the Biomass Quality and the Energy Value of Willow Yield

Seven-year-old willows were harvested with chainsaws and the fresh biomass yield was determined. Each variety and clone was cut up and chipped and representative samples (ca. 2 kg) were taken for laboratory analyses. The biomass moisture content was determined at 105 °C (FD BINDER, Tuttlingen, Germany) by drying and weighing (EN ISO 18134–1:2015). Subsequently, the dried chips from two initial planting densities were combined to make one collective sample and the biomass quality was analysed for six willow varieties and clones from three different sites. Biomass samples were ground with a 1 mm sieve (Retsch SM 200, Haan, Germany) and kept in closed laboratory containers for further analyses. The higher heating value (HHV) of the biomass was analysed using the dynamic method in calorimeter (IKA C2000, Taufen, Germany). Subsequently, the moisture content and HHV were used to calculate the lower heating value (LHV) for each willow from each site (PN–EN ISO 18125:2017–07). The ash, fixed carbon and volatile matter were determined (Eltra Tga–Thermostep, Neuss, Germany) (PN–EN ISO 18122:2016–01). Examination of the elemental composition of the biomass was completed using an Eltra CHS 500 analyser (Neuss, Germany) (PN–EN ISO 16948:2015–07 and PN–EN ISO 16994:2016–10) and included carbon (C), sulphur (S) and hydrogen (H) content. Moreover, a total nitrogen (N) assay in the willow biomass was performed with Kjeldahl's method using a K-435 mineraliser and a B-324 Buchi distiller (Flawil, Switzerland).

The yield energy value of the willow biomass was calculated as the product of the mean yield of fresh biomass for each willow variety and clone from three sites, and the biomass LHV was calculated from Formula (1). Moreover, the willow biomass yield energy value was also converted to one year of plantation use.

$$Y_{ev} = Y_b \cdot LHV \tag{1}$$

where:

　　Y_{ev}—biomass yield energy value (GJ ha^{-1}),
　　Y_b—fresh biomass yield (Mg ha^{-1}),
　　LHV—lower heating value of fresh biomass (GJ Mg^{-1}).

2.3. Statistical Analysis

A two–way analysis of variance was carried out to determine the effects of site (factor A), variety and clone (factor B), and all interactions between the main factors for the yield energy value and the thermophysical properties as well as the willow biomass elemental composition. The significance level was established at $p < 0.05$. Homogeneous groups for all features were determined by Tukey's (HSD) multiple-comparison test. The arithmetic mean and standard deviation (SD) were calculated for each of the analysed features. Additionally, simple correlation coefficients were calculated for the thermophysical properties and the willow biomass elemental composition. All statistical analyses were performed using STATISTICA software (version 13.3).

3. Results and Discussion

3.1. Energy Value of Yield

The energy value of Eko-Salix willow biomass yield was significantly differentiated by the type of soil site and by the varieties or clones and by their interactions as shown in Table 1. The yield energy value for the 7-year rotation willow was 957 GJ ha^{-1} (Table 2). The energy value of the yield at Kocibórz was the significantly highest: 1119 GJ ha^{-1}. It was higher than at Obory and Leginy by 114 GJ ha^{-1} and by 372 GJ ha^{-1}, respectively. The Ekotur variety had the significantly highest biomass energy value (1522 GJ ha^{-1}) among the varieties and clones in the study. This value was significantly higher than for the UWM 095 clone and for the Turbo (homogeneous group b and c) and Tur (homogeneous group d) varieties. However, the lowest biomass yield energy value was determined for the UWM 200 clone (541 GJ ha^{-1}, homogeneous group f).

Table 1. Results of analysis of variance (ANOVA) for studied biomass properties.

| Item	Yield Energy Value	Moisture	Ash	Volatile Matter	Fixed Carbon	HHV	LHV	C	H	S	N
					P Value for						
Site (A)	<0.001 *	0.857	0.318	<0.001 *	<0.001 *	0.001 *	0.455	<0.001 *	<0.001 *	<0.001 *	<0.001 *
Variety or clone (B)	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *
A × B	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *	<0.001 *

* asterisk indicate statistically significant values at *p < 0.05*.

Table 2. Energy value of yield and higher and lower heating value of the 7-year willow rotation.

Item		Yield Energy Value (GJ ha^{-1})	Higher Heating Value (MJ kg^{-1} d.m.)	Lower Heating Value (MJ kg^{-1})
Site	Obory	1004.9 ± 392.9 B	19.5 ± 0.1 B	8.6 ± 0.4
	Kocibórz	1118.6 ± 457.0 A	19.5 ± 0.2 B	8.6 ± 0.6
	Leginy	746.7 ± 149.5 C	19.6 ± 0.1 A	8.6 ± 0.5
Variety or clone	Turbo	880.9 ± 132.1 c	19.6 ± 0.1 a	8.9 ± 0.2 b
	Tur	842.7 ± 162.5 d	19.6 ± 0.1 a	9.2 ± 0.1 a
	UWM 095	1167.0 ± 242.9 b	19.6 ± 0.1 a	8.0 ± 0.1 d
	UWM 200	541.3 ± 18.8 f	19.4 ± 0.1 b	8.0 ± 0.3 d
	Ekotur	1521.7 ± 453.0 a	19.4 ± 0.2 b	8.5 ± 0.2 c
	UWM 046	786.8 ± 132.9 e	19.6 ± 0.1 a	8.9 ± 0.3 b
Mean		956.8 ± 385.1	19.5 ± 0.1	8.6 ± 0.5

± standard deviations; A.B.C ... homogenous groups for sites; a.b.c ... homogenous groups for varieties or clones.

The yield energy value as converted to a year of plantation use ranged from 74 to 288 GJ ha^{-1} year^{-1} as shown in Figure 1. The Ekotur gave the highest yield energy value at all three sites, whereas this value was significantly different at each site. The highest energy value for this variety was determined at Kocibórz, where the plants grew on organic, peat−muck soil (average 288 GJ ha^{-1} year^{-1}). It was lower by 64 GJ ha^{-1} year^{-1} at Obory (riparian, heavy complete humic alluvial soil) and was lower by 149 GJ ha^{-1} year^{-1} at Leginy (very heavy mineral clay soil). The UWM 095 clone biomass energy value was higher at Obory than at Kocibórz (homogeneous groups c and d, respectively) and was significantly lower at Leginy (homogeneous group g). The Tur variety gave a low biomass yield with a low energy value both at Obory and at Kocibórz (homogeneous group f) at both sites). The UWM 200 clone gave a biomass yield with a very low energy value (74–78 GJ ha^{-1} year^{-1}) at all three experiment sites (homogeneous groups l and k).
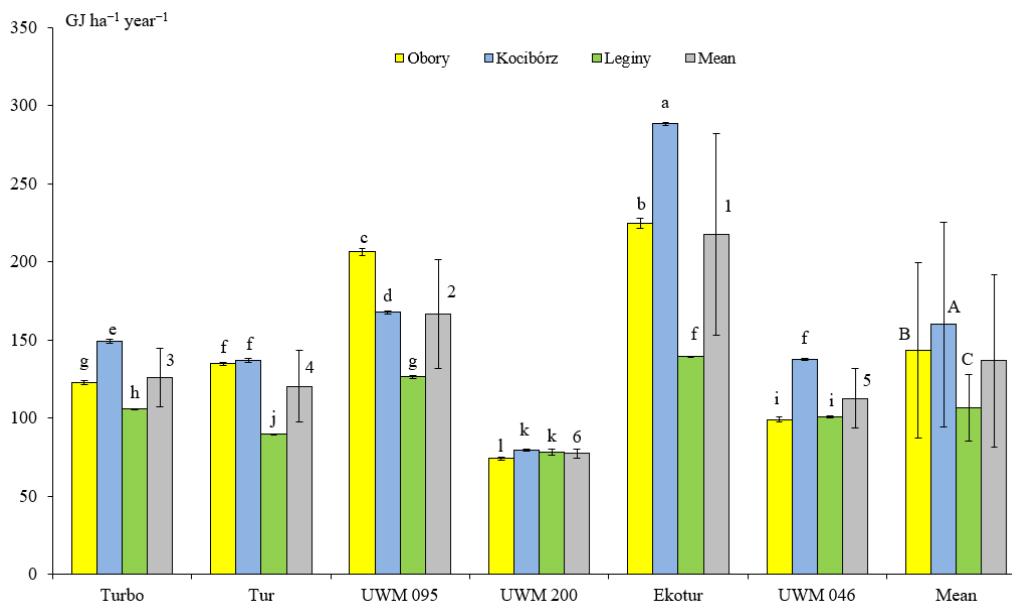
Figure 1. Yield energy value of the 7-year rotation willow depending on site and variety (GJ ha^{-1} year^{-1}); A.B.C . . . homogenous groups for sites; 1.2.3 . . . homogenous groups for varieties or clones; a.b.c . . . homogenous groups for interactions between sites and varieties or clones; error bars represent standard deviations.

It is noteworthy that the yield energy value obtained in the experiment from Eko-Salix willow grown on marginal soils and harvested in a 7-year-long rotation was highly varied, both by the soil site, variety and clone. Ekotur and UWM 095 had much higher yield energy value of wood compared to the other willow varieties or clones. Moreover, the high yield energy value for these two varieties was a consequence of much higher biomass yield compared to the yield of the other varieties and clones because the yield energy value was calculated based on the fresh willow biomass yield and its LHV. Furthermore, the yield differentiation between the willow varieties and clones had a genetic foundation as all clones were grown in a similar manner. Moreover, other studies, where SRC willow was grown in 2–4-year rotations, also showed that the yield energy value varied depending on factors such as species, variety or clone, harvest cycle, fertilisation and other agrotechnical factors. For example, the biomass energy value for *Salix viminalis* harvested in a 2-year rotation in Canada ranged between 73–290 GJ ha^{-1} year^{-1} [28], which was similar to the current results in the Eko-Salix system. Meanwhile, the average annual gross energy yields for 3-, 4- and 5-year rotation willow in Sweden (depending on the nitrogen fertilisation rate: N–high, N–medium, and N–zero) were: 185, 138 and 88 GJ ha^{-1} year^{-1}, respectively [32]. In a different study with willow production in a 3-year harvest rotation in Poland, the yield energy value ranged from 46 to 242 GJ ha^{-1} for UWM 155 and UWM 006 clone, respectively [33]. The biomass energy value in the cultivation of a 4-year rotation of willow on poor quality soil depended on the method of soil enrichment and ranged from 88 to 175 GJ ha^{-1} year^{-1}, for a nonfertilisation site and for a site where lignin, mycorrhiza and mineral fertilisation were applied simultaneously, respectively [27]. On the other hand, in the cultivation of willow in 4-year rotation on very good soil, the average yield energy value was much higher (243 GJ ha^{-1} year^{-1}) [29]. An equally high yield energy value was obtained in Italy in a study with poplar grown in different harvest rotations with mineral fertilisation and irrigation: 257 GJ ha^{-1} year^{-1} [34] and 270 GJ ha^{-1} year^{-1} [35]. Furthermore, very high yield energy value (450 GJ ha^{-1} year^{-1}) was achieved in another study, in the first three-year harvest rotation for poplar with mineral fertilisation [36]. A much lower yield energy value (70.9 GJ ha^{-1} year^{-1}) was achieved in an extensive poplar cultivation in a 4-year harvest rotation [4]. In another study, in which poplar was also obtained in a 4-year harvest rotation, the yield energy value ranged between 93–177 GJ ha^{-1} year^{-1} depending on the soil enrichment method [27]. The poplar yield energy value was also high (ca. 190 GJ ha^{-1} year^{-1}) in a 24-year-long plantation life

cycle [37]. Furthermore, black locust as the third SRC species achieved lower yield energy value between 29 and 95 GJ ha^{-1} year^{-1} in a 4-year rotation depending on the soil enrichment method [27]. This index was much higher in the 6-year harvest rotation (190 GJ ha^{-1} year^{-1}) [38]. The yield energy value for other perennial herbaceous crops, e.g., *Sida hemaphrodita* varied and lay within the range of 79–226 GJ ha^{-1} year^{-1} [20,39–41]. *Miscanthus × giganteus* is often mentioned as a species with the highest potential of yield energy value of all perennial grasses, which can reach 235–479 GJ ha^{-1} year^{-1} [42,43]. However, it was demonstrated in other studies that its yield energy value was much lower in the first years of cultivation and it reached 118 GJ ha^{-1} year^{-1} in the fourth year [20]. On the other hand, the much higher yield energy value in the study cited above was achieved for another grass species, *Miscanthus sacchariflorus* – 175 GJ ha^{-1} year^{-1}. It must be stressed that such a large diversity of the yield energy value in the literature reports was mainly caused by the species and variety choice, soil quality, climatic conditions, fertilisation and agrotechnical measures, harvest cycle, etc. These factors affected the biomass yield and, in consequence, the yield energy value. Compared to these data, the yield energy value of Eko-Salix willow, achieved in the current experiment for the Ekotur variety and the UWM 095 clone should be regarded as high and satisfactory.

3.2. Thermophysical Properties and Elemental Composition of Biomass

The higher heating value determined in the willow dry matter obtained in the 7-year rotation in this experiment was 19.5 MJ kg^{-1} d.m. on average, as shown in Table 2. This value was slightly (although significantly) lower in the biomass obtained at Obory and Kocibórz (homogeneous group B) than at Leginy (homogeneous group A). The higher heating value determined in biomass of the Ekotur variety and the UWM 200 clone was the same (homogeneous group b) and significantly lower than in the other varieties in the study (all—homogeneous group a). On the other hand, the lower heating value of fresh Eko-Salix willow biomass at the three sites was not significantly different at 8.6 MJ kg^{-1}, as shown in Tables 1 and 2. The value of this feature in the Tur variety (*Salix viminalis*, homogeneous group a) was 9.2 MJ kg^{-1} and it was higher by 1.2 MJ kg^{-1} than in the UWM 095 and UWM 200 clones (both *Salix alba* species, homogeneous group d). In a different study, the lower heating value for willow harvested in a 4-year rotation ranged from 8.3–8.5 GJ Mg^{-1} [27]. A similar value for willow harvested in the same rotation was found by Monedero et al. [44]. The lower heating value for willow harvested in a 3-year rotation ranged from 7.7–9.3 GJ Mg^{-1}, depending on the clone [45]. Moreover, the LHV depends on the moisture content for each biomass type. A very strong negative correlation between the biomass moisture content and LHV (−0.99) was also demonstrated in the current experiment as shown in Table 3. Furthermore, the biomass moisture content depends on its type, plant species, harvest date and weather conditions during the harvest. Three groups are identified among perennial energy plants: (1) SRC, which give woody biomass and included willow; (2) herbaceous crops, which give semiwoody biomass; (3) grasses which give biomass as straw [25]. The highest moisture content at harvest as determined in the studies cited above was observed in poplar, which is why the heating value for this species was lower and ranged from 6–7 GJ Mg^{-1}. In contrast, LHV for black locust was much higher and exceeded 10 GJ Mg^{-1}. Delaying the harvest of herbaceous crops and grasses from November to March had a significant, beneficial effect on the biomass moisture content decrease and, in consequence, it increased the biomass heating value to as much as 15 GJ Mg^{-1}. Such a high LHV was also achieved for cereal straw, which is production waste in grain production, and is obtained in summer after plants have naturally dried [30]. On the other hand, woody biomass of agricultural origin (willow, poplar) or obtained from forests (pine, birch) can have high LHV, provided that their moisture content was reduced by natural or forced drying, e.g., during biomass storage [30,46,47].

The average moisture content determined in the biomass of 7-year old Eko-Salix willows was 49.8% as shown in Table 4. The values of this feature for biomass obtained at the three sites in the study did not differ significantly, as displayed in Table 1. The biomass moisture content for the UWM 095 and UWM 200 clones did not differ (homogeneous group a) and was significantly higher than that determined in the biomass of the Ekotur (homogeneous group b), Turbo and UWM 046 (c) and Tur (d).

In other studies, the moisture content of willow biomass harvested in 3- and 4-year rotations exceeded 50% [44,45]. As mentioned above, in the discussion of LHV, among the SRC species, lower moisture content compared to willow was observed in black locust (ca. 40%), and higher moisture content was observed in poplar (ca. 60%) [25]. High moisture content (40–60%) was determined in the fresh biomass of forest trees or production residues (e.g., sawdust) produced in the processing of fresh wood. The moisture content in sawdust, shavings, etc. produced in the processing of naturally seasoned or thermally dried wood can be below 10%. Low moisture content, usually below 15–20%, was also determined for the straw of cereals and oily crops harvested in summer [30] and biomass of herbaceous crops and grasses obtained just before the start of a new growing season (March–April) [25].

Table 3. Simple correlation coefficient between the analysed properties.

Item	Moisture	Ash	Volatile Matter	Fixed Carbon	HHV	LHV	C	H	S	N
Moisture	1.00									
Ash	0.12	1.00								
Volatile matter	0.29 *	−0.58 *	1.00							
Fixed Carbon	−0.34 *	0.44 *	−0.99 *	1.00						
HHV	−0.19	0.26	−0.27 *	0.25	1.00					
LHV	−0.99 *	−0.08	−0.32 *	0.37 *	0.32 *	1.00				
C	−0.50 *	−0.07	−0.08	0.10	0.02	0.48 *	1.00			
H	−0.42 *	−0.27 *	0.21	−0.18	0.05	0.41 *	0.71 *	1.00		
S	−0.21	0.52 *	−0.63 *	0.59 *	0.56 *	0.28 *	0.16	0.06	1.00	
N	−0.26	0.26	−0.07	0.03	0.17	0.28 *	0.23	0.09	0.22	1.00

* asterisk indicate statistically significant values at *p < 0.05*.

Table 4. Moisture, ash, volatile matter and fixed carbon content in biomass of 7-year-old willow.

Item		Moisture Content (%)	Ash Content (% d.m.)	Volatile Matter (% d.m.)	Fixed Carbon (% d.m.)
Site	Obory	49.8 ± 1.8	1.3±0.3	80.2 ± 1.2 A	18.6 ± 1.0 B
	Kocibórz	49.7 ± 2.7	1.3 ± 0.2	80.0 ± 1.6 A	18.7 ± 1.5 B
	Leginy	49.7 ± 2.3	1.3 ± 0.2	79.0 ± 0.4 B	19.7 ± 0.4 A
Variety or clone	Turbo	48.7 ± 0.9 c	1.4 ± 0.3 a	78.8 ± 0.4 b	19.8 ± 0.4 a
	Tur	47.1 ± 0.4 d	1.1 ± 0.2 c	79.9 ± 1.1 a	19.0 ± 0.9 b
	UWM 095	52.6 ± 0.4 a	1.3 ± 0.1 b	79.9 ± 1.4 a	18.8 ± 1.3 b
	UWM 200	52.2 ± 1.3 a	1.4 ± 0.2 a	80.2 ± 1.3 a	18.5 ± 1.1 c
	Ekotur	49.7 ± 0.6 b	1.1 ± 0.1 c	80.5 ± 1.1 a	18.4 ± 1.1 c
	UWM 046	48.2 ± 1.5 c	1.4 ± 0.2 a	79.1 ± 1.5 b	19.5 ± 1.4 a
Mean		49.8 ± 2.2	1.3 ± 0.2	79.7 ± 1.3	19.0 ± 1.2

± standard deviations; A.B.C … homogenous groups for sites; a.b.c … homogenous groups for varieties or clones.

Shown in Table 1, the mean ash content in the biomass of 7-year old willow obtained at the three sites in the study did not differ significantly and was 1.3% d.m., as displayed in Table 4. A beneficial, significantly lower ash content was found in the biomass of the Tur and Ekotur varieties (homogeneous group c) than in the biomass of the Turbo variety (homogeneous group a). A higher ash content (1.9% d.m.) was found in the biomass of 4-year rotation willow [44]. An even higher ash content in willow biomass (more than 3%) was found in another study [48]. Nevertheless, the ash content in woody SRC biomass was usually lower (1–2% d.m.) compared to the ash content in biomass of perennial herbaceous crops (semiwoody biomass, 2–4% d.m.) and grasses (straw, 2–4% d.m.) [25]. An even higher ash content, often exceeding 5% d.m., was determined in the straw of cereals and oily crops. The lowest ash content was determined in clean, debarked wood (below 0.5% d.m.), and the value did not exceed 1% d.m. in non-debarked wood obtained from a forest [30]. The average ash content in residue biomass from palm kernel shell (PKS) in the studies cited above was 2.35% d.m.,

and other data show that the ash content in PKS ranged from 1.3–10.8% d.m. [49]. Due to mineral contaminations of biomass, such as sand, clay, etc., which may be present at various stages of the logistic process, the ash content in solid biofuels received by the end recipient may be higher than given above.

The average content of volatile matter as determined in the current study in the willow biomass was 79.7% d.m., as shown in Table 4. A slightly lower volatile matter content was found in biomass at Leginy (homogeneous group B) than at Obory and Kocibórz, where the content was similar (homogeneous group A). The value of this feature in the UWM 046 clone biomass was slightly lower (homogeneous group B) than in the other varieties and clones, whose values did not differ (homogeneous group a). A higher volatile matter content (83.6% d.m.) was found in the biomass of a 4-year willow rotation [45]. Furthermore, the fixed carbon content, as determined in biomass obtained at Leginy in this study, was slightly higher (homogeneous group A) than at the other two sites, where the values were similar (homogeneous group B). The highest fixed carbon content was found in biomass of the Turbo variety (19.8% d.m.). The same fixed carbon content was found in the biomass of a 3-year willow rotation [46]. The fixed carbon content in the current study was significantly positively correlated with LHV and with the sulphur content, as shown in Table 3.

The elemental composition of a 7-year Eko-Salix willow rotation biomass was significantly differentiated by the soil site and the varieties or clones and their interactions, as displayed in Table 1. The average carbon content in the biomass was 51.1% d.m., shown in Table 5. A slightly higher content of this element was determined in the biomass obtained at Obory (homogeneous group A) than in the biomass obtained at the other two sites (similar values, homogeneous group B). The carbon content determined in the biomass of the Tur variety was the highest (homogeneous group a), and the significantly lowest content of this element was found in biomass of the Ekotur variety and the UWM 095, UWM 200 clones (homogeneous group c). The carbon content in willow biomass was significantly and positively correlated with the hydrogen content and with the LHV, as shown in Table 3.

Table 5. Content of carbon, hydrogen, sulphur and nitrogen in the biomass of 7-year-old willow (% d.m.).

Item		C	H	S	N
Site	Obory	51.5 ± 0.7 A	6.0 ± 0.1 A	0.039 ± 0.013 B	0.34 ± 0.03 B
	Kocibórz	50.9 ± 0.7 B	5.9 ± 0.1 B	0.038 ± 0.009 C	0.35 ± 0.06 A
	Leginy	50.8 ± 0.9 B	5.8 ± 0.1 B	0.041 ± 0.007 A	0.26 ± 0.02 C
Variety or clone	Turbo	51.1 ± 0.4 b	5.9 ± 0.1 a	0.052 ± 0.005 a	0.32 ± 0.04 b
	Tur	51.8 ± 0.9 a	6.0 ± 0.2 a	0.038 ± 0.005 d	0.31 ± 0.04 b
	UWM 095	50.7 ± 0.8 c	5.8 ± 0.1 b	0.045 ± 0.007 b	0.32 ± 0.04 b
	UWM 200	50.6 ± 0.6 c	5.8 ± 0.1 b	0.029 ± 0.003 f	0.29 ± 0.04 c
	Ekotur	50.7 ± 1.1 c	6.0 ± 0.2 a	0.030 ± 0.002 e	0.28 ± 0.03 d
	UWM 046	51.4 ± 0.4 b	5.9 ± 0.1 a	0.040 ± 0.009 c	0.37 ± 0.07 a
Mean		51.1 ± 0.8	5.9 ± 0.1	0.039 ± 0.010	0.32 ± 0.05

± standard deviations; A.B.C . . . homogenous groups for sites; a.b.c . . . homogenous groups for varieties or clones.

The hydrogen content in biomass at the three sites ranged from 5.8% to 6.0% d.m. (homogeneous group B and A), as displayed in Table 5. A lower content of the element was found in biomass of the UWM 095 and UWM 200 clones (homogeneous group b) than in the other varieties and clones (similar values, homogeneous group a). The average sulphur content in biomass obtained from the 7-year rotation willow in this experiment was 0.039% d.m. The highest element content was found in the biomass at Leginy (homogeneous group A); it was significantly higher than at Obory (homogeneous group B) or Kocibórz (homogeneous group C). The sulphur content in the biomass of the clones and varieties in the study differed significantly and ranged from 0.029% d.m. in UWM 200 to 0.052% d.m. in the Turbo variety. The nitrogen content in the willow biomass at Leginy was significantly lower

(homogeneous group C) than at Obory (homogeneous group B) and Kocibórz (homogeneous group A). The nitrogen content in the biomass of UWM 046 (0.37% d.m.) was significantly higher than in the Ekotur variety (0.28% d.m.). The sulphur content was significantly negatively correlated with the volatile matter content and was significantly positively correlated with ash and fixed carbon content, HHV and LHV, as shown in Table 3.

The elemental composition of biomass depends (among others) on the species, rotation length and harvest date as well as on the soil chemical composition. Therefore, for example, in a different study [44], willow biomass harvested in a 4-year rotation contained less carbon, more hydrogen and nitrogen and similar sulphur content compared to the current study. In another study, willow biomass was also found to contain less carbon and more nitrogen [45,48]. Considering the elemental composition of different biomass types, it should be noted that the carbon content in cereal or rape straw is usually lower (below 50% d.m.) compared to woody biomass, which usually contains over 50% d.m. of carbon. Moreover, the carbon content in old wood, especially that obtained from forests, can exceed 54% d.m., whereas it ranges from 50–52% d.m. in younger wood from energy SRC crops [30]. Moreover, the studies cited above show that woody biomass of forest origin is a fuel of higher quality than other solid fuels due to its low content of sulphur and chlorine (below 0.02% d.m.) and nitrogen (below 0.2% d.m.). Much higher content of sulphur, chlorine and nitrogen was determined in wheat straw—0.13, 0.20 and 1.2% d.m., respectively. Even larger amounts of these undesirable elements were found in rape straw (0.32, 0.42 and 1.3% d.m., respectively). Therefore, it can be claimed that the willow biomass obtained in the current experiment in a 7-year harvest rotation was a fuel of much better quality in terms of its elemental composition compared to straw. Moreover, the content of these elements in willow wood was slightly higher, but also more similar to their content in forest wood.

The findings of this study can be applied in commercial production of Eko-Salix willow biomass, especially on soil where ploughing before setting up a plantation is difficult or impossible. However, one should emphasise that it is a challenge in setting up an Eko-Salix plantation to prepare long cuttings (more than 2 m long) from two- or three-year-old shoots of properly selected willow clones or varieties. Therefore, in order to set up an Eko-Salix plantation, one should identify the origin of the planting material and agree on the time and form of its preparation. Harvesting willow in a 7-year rotation is also a challenge because of a large shoot diameter, as well as the plants' height and weight. Manual harvest is possible in small-area plantations. On the other hand, harvesters with cutting heads, used for obtaining forest wood, can be used in large plantations. However, soil must be frozen in winter or the soil load-bearing capacity in winter must be sufficient so that it is possible for heavy equipment to enter the plantation. It should also be noted that in the future, one must examine and analyse the intensity of growing of new shoots out of stumps after the willow harvest and determine the productivity and biomass quality from successive rotations. It will be an interesting issue and a challenge to analyse and determine the number of harvests and the total biomass yield energy value for the whole use period for Eko-Salix plantations.

4. Conclusions

This experiment demonstrated that it is possible to obtain large amounts of energy accumulated in good quality biomass from a 7-year rotation of Eko-Salix willow grown on marginal soils. However, the type of soil and the choice of willow clone or variety also affected the yield energy value and thermophysical properties and elemental composition of the biomass. Favourable conditions for obtaining high yield energy value were in organic, peat–muck soil and riparian, humic alluvial soil with a high groundwater level (but not stagnant). On the other hand, the conditions on unscarified and unploughed very heavy mineral clay soil, with a low groundwater level, were not suitable for willow. The high yield energy value in Ekotur and UWM 095 was a consequence of the higher biomass yield compared to the yield of the other varieties. Furthermore, the yield differentiation between the willow varieties and clones had a genetic foundation. It must be stressed that all the clones and varieties were cultivated in the same manner, and the Ekotur variety had the best yield energy value in all

conditions while the UWM 200 clone was always the worst. These results indicate that the cultivation of properly selected varieties or clones of willow in the Eko-Salix system on marginal land can be a significant source of energy contained in good-quality woody biomass. This applies mainly to riparian alluvial soils, organic soils and soils which are difficult to cultivate, often covering large areas. Due to their high yield energy value, it can be assumed that willow production in the Eko-Salix system can be also profitable in some cases. However, further studies are needed to verify the economic and environmental soundness of Eco-Salix willow cultivation over a longer period.

Author Contributions: Conceptualization, M.J.S., S.S., M.K. and J.T.; data curation, M.J.S.; formal analysis, M.J.S. and M.K.; funding acquisition, M.J.S.; investigation, M.J.S. and M.K.; methodology, M.J.S. and S.S.; project administration, M.J.S.; validation, M.J.S.; visualization, M.J.S.; writing—original draft, M.J.S. and S.S.; writing —review & editing, M.J.S., M.K. and J.T. All authors have read and agreed to the published version of the manuscript.

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

Nomenclature

RES	renewable energy sources
EU	European Union
UWM	University of Warmia and Mazury in Olsztyn
d.m.	dry matter
HHV	higher heating value
LHV	lower heating value of fresh biomass (GJ Mg^{-1})
Y_{ev}	biomass yield energy value (GJ ha^{-1})
Y_b	fresh biomass yield (Mg ha^{-1});
C	carbon
H	hydrogen
S	sulphur
N	nitrogen

References

1. Eurostat. Energy. Energy statistics—Quantities (nrg_quant). Available online: https://ec.europa.eu/eurostat/web/energy/data/database (accessed on 28 January 2020).

2. Heller, M.C.; Keoleian, G.A.; Volk, T.A. Life cycle assessment of a willow bioenergy cropping system. *Biomass Bioenergy* **2003**, *25*, 147–165. [CrossRef]

3. Volk, T.A.; Abrahamson, L.P.; Nowak, C.A.; Smart, L.B.; Tharakan, P.J.; White, E.H. The development of short-rotation willow in the northeastern United States for bioenergy and bioproducts, agroforestry and phytoremediation. *Biomass Bioenergy* **2006**, *30*, 715–727. [CrossRef]

4. Vande Walle, I.; Van Camp, N.; Van de Casteele, L.; Verheyen, K.; Lemeur, R. Short-rotation forestry of birch, maple, poplar and willow in Flanders (Belgium) II. Energy production and CO_2 emission reduction potential. *Biomass Bioenergy* **2007**, *31*, 276–283. [CrossRef]

5. Stolarski, M.J.; Krzyżaniak, M.; Warmiński, K.; Niksa, D. Energy consumption and costs of heating a detached house with wood briquettes in comparison to other fuels. *Energy Convers. Manag.* **2016**, *121*, 71–83. [CrossRef]

6. Stolarski, M.; Krzyzaniak, M.; Warminski, K.; Tworkowski, J.; Szczukowski, S. Willow biomass energy generation efficiency and greenhouse gas reduction potential. *Pol. J. Environ. Stud.* **2015**, *24*, 2627–2640. [CrossRef]

7. Stolarski, M.J.; Szczukowski, S.; Tworkowski, J.; Krzyżaniak, M. Cost of heat energy generation from willow biomass. *Renew. Energy* **2013**, *59*, 100–104. [CrossRef]

8. Dias, G.M.; Ayer, N.W.; Kariyapperuma, K.; Thevathasan, N.; Gordon, A.; Sidders, D.; Johannesson, G.H. Life cycle assessment of thermal energy production from short-rotation willow biomass in Southern Ontario, Canada. *Appl. Energy* **2017**, *204*, 343–352. [CrossRef]

9. Wang, Z.; Dunn, J.B.; Wang, M.Q. GREET Model Short Rotation Woody Crops (SRWC) Parameter Development. Center for Transportation Research. Argonne National Laboratory. 2012. Available online: Greet.es.anl.gov/files/greet-SRWC-Development,Lemont,Illinois,UnitedStates (accessed on 5 May 2018).

10. Gonçalves, F.A.; Sanjinez-Argandona, E.J.; Fonseca, G.G. Cellulosic ethanol and its co-products from different substrates, pre-treatments, microorganisms and bioprocesses: A review. *Nat. Sci.* **2013**, *5*, 624–630.

11. Krzyżaniak, M.; Stolarski, M.J.; Waliszewska, B.; Szczukowski, S.; Tworkowski, J.; Załuski, D.; Śnieg, M. Willow biomass as feedstock for an integrated multi-product biorefinery. *Ind. Crops Prod.* **2014**, *58*, 230–237. [CrossRef]

12. Stolarski, M.J.; Krzyżaniak, M.; Łuczyński, M.; Załuski, D.; Szczukowski, S.; Tworkowski, J.; Gołaszewski, J. Lignocellulosic biomass from short rotation woody crops as a feedstock for second-generation bioethanol production. *Ind. Crops Prod.* **2015**, *75*, 66–75. [CrossRef]

13. Stolarski, M.; Szczukowski, S.; Tworkowski, J.; Klasa, A. Productivity of seven clones of willow coppice in annual and quadrennial cutting cycles. *Biomass Bioenergy* **2008**, *32*, 1227–1234. [CrossRef]

14. Stolarski, M.J.; Niksa, D.; Krzyżaniak, M.; Tworkowski, J.; Szczukowski, S. Willow productivity from small- and large-scale experimental plantations in Poland from 2000 to 2017. *Renew. Sustain. Energy Rev.* **2019**, *101*, 461–475. [CrossRef]

15. Guidi Nissim, W.; Pitre, F.E.; Teodorescu, T.I.; Labrecque, M. Long-term biomass productivity of willow bioenergy plantations maintained in southern Quebec, Canada. *Biomass Bioenergy* **2013**, *56*, 361–369. [CrossRef]

16. Rodias, E.; Berruto, R.; Bochtis, D.; Sopegno, A.; Busato, P. Green, Yellow, and Woody Biomass Supply-Chain Management: A Review. *Energies* **2019**, *12*, 20. [CrossRef]

17. Von Cossel, M.; Lewandowski, I.; Elbersen, B.; Staritsky, I.; Van Eupen, M.; Iqbal, Y.; Mantel, S.; Scordia, D.; Testa, G.; Cosentino, S.L.; et al. Marginal agricultural land low-input systems for biomass production. *Energies* **2019**, *12*, 3123. [CrossRef]

18. Bioenergy Europe. *Bioenergy Europe Statistical Report*; Bioenergy Europe: Brussels, Belgium, 2018.

19. Stolarski, M.J.; Szczukowski, S.; Tworkowski, J.; Krzyżaniak, M.; Załuski, D. Willow production during 12 consecutive years—The effects of harvest rotation, planting density and cultivar on biomass yield. *GCB Bioenergy* **2019**, *11*, 635–656. [CrossRef]

20. Stolarski, M.J.; Śnieg, M.; Krzyżaniak, M.; Tworkowski, J.; Szczukowski, S. Short rotation coppices, grasses and other herbaceous crops: Productivity and yield energy value versus 26 genotypes. *Biomass and Bioenergy* **2018**, *119*, 109–120. [CrossRef]

21. Larsen, S.U.; Jørgensen, U.; Lærke, P.E. Willow Yield Is Highly Dependent on Clone and Site. *BioEnergy Res.* **2014**, *7*, 1280–1292. [CrossRef]

22. Serapiglia, M.; Cameron, K.; Stipanovic, A.; Abrahamson, L.; Volk, T.; Smart, L. Yield and Woody Biomass Traits of Novel Shrub Willow Hybrids at Two Contrasting Sites. *BioEnergy Res.* **2012**, *6*, 1–14. [CrossRef]

23. Sevel, L.; Nord-Larsen, T.; Ingerslev, M.; Jørgensen, U.; Raulund-Rasmussen, K. Fertilization of SRC Willow, I: Biomass Production Response. *BioEnergy Res.* **2014**, *7*, 319–328. [CrossRef]

24. Vanbeveren, S.P.P.; Spinelli, R.; Eisenbies, M.; Schweier, J.; Mola-Yudego, B.; Magagnotti, N.; Acuna, M.; Dimitriou, I.; Ceulemans, R. Mechanised harvesting of short-rotation coppices. *Renew. Sustain. Energy Rev.* **2017**, *76*, 90–104. [CrossRef]

25. Stolarski, M.J.; Śnieg, M.; Krzyżaniak, M.; Tworkowski, J.; Szczukowski, S.; Graban, Ł.; Lajszner, W. Short rotation coppices, grasses and other herbaceous crops: Biomass properties versus 26 genotypes and harvest time. *Ind. Crops Prod.* **2018**, *119*, 22–32. [CrossRef]

26. Feledyn-Szewczyk, B.; Matyka, M.; Staniak, M. Comparison of the Effect of Perennial Energy Crops and Agricultural Crops on Weed Flora Diversity. *Agronomy* **2019**, *9*, 695. [CrossRef]

27. Stolarski, M.J.; Krzyżaniak, M.; Tworkowski, J.; Szczukowski, S.; Niksa, D. Analysis of the energy efficiency of short-rotation woody crops biomass as affected by different methods of soil enrichment. *Energy* **2016**, *113*, 748–761. [CrossRef]

28. Labrecque, M.; Teodorescu, T.I.; Daigle, S. Biomass productivity and wood energy of Salix species after 2 years growth in SRIC fertilized with wastewater sludge. *Biomass Bioenergy* **1997**, *12*, 409–417. [CrossRef]

29. Stolarski, M.J.; Szczukowski, S.; Tworkowski, J.; Klasa, A. Yield, energy parameters and chemical composition of short-rotation willow biomass. *Ind. Crops Prod.* **2013**, *46*, 60–65. [CrossRef]

30. Stolarski, M.J.; Rybczyńska, B.; Krzyżaniak, M.; Lajszner, W.; Graban, Ł.; Peni, D.; Bordiean, A. Thermophysical properties and elemental composition of agricultural and forest solid biofuels versus fossil fuels. *J. Elemntol.* **2019**, *24*, 1215–1228. [CrossRef]

31. Stolarski, M.J.; Szczukowski, S.; Tworkowski, J.; Krzyżaniak, M. Extensive willow biomass production on marginal land. *Pol. J. Environ. Stud.* **2019**, *28*, 4359–4367. [CrossRef]

32. Nordborg, M.; Berndes, G.; Dimitriou, I.; Henriksson, A.; Mola-Yudego, B.; Rosenqvist, H. Energy analysis of willow production for bioenergy in Sweden. *Renew. Sustain. Energy Rev.* **2018**, *93*, 473–482. [CrossRef]

33. Stolarski, M.J.; Krzyżaniak, M.; Tworkowski, J.; Szczukowski, S.; Gołaszewski, J. Energy intensity and energy ratio in producing willow chips as feedstock for an integrated biorefinery. *Biosyst. Eng.* **2014**, *123*, 19–28. [CrossRef]

34. Manzone, M.; Calvo, A. Energy and CO_2 analysis of poplar and maize crops for biomass production in north Italy. *Renew. Energy* **2016**, *86*, 675–681. [CrossRef]

35. Manzone, M.; Bergante, S.; Facciotto, G. Energy and economic evaluation of a poplar plantation for woodchips production in Italy. *Biomass Bioenergy* **2014**, *60*, 164–170. [CrossRef]

36. Nassi, O.; Di Nasso, N.; Guidi, W.; Ragaglini, G.; Tozzini, C.; Bonari, E. Biomass production and energy balance of a 12-year-old short-rotation coppice poplar stand under different cutting cycles. *GCB Bioenergy* **2010**, *2*, 89–97. [CrossRef]

37. Nordborg, M.; Berndes, G.; Dimitriou, I.; Henriksson, A.; Mola-Yudego, B.; Rosenqvist, H. Energy analysis of poplar production for bioenergy in Sweden. *Biomass Bioenergy* **2018**, *112*, 110–120. [CrossRef]

38. Manzone, M.; Bergante, S.; Facciotto, G. Energy and economic sustainability of wood chip production by black locust (*Robinia pseudoacacia* L.) plantations in Italy. *Fuel* **2015**, *140*, 555–560. [CrossRef]

39. Jankowski, K.J.; Dubis, B.; Budzyński, W.S.; Bórawski, P.; Bułkowska, K. Energy efficiency of crops grown for biogas production in a large-scale farm in Poland. *Energy* **2016**, *109*, 277–286. [CrossRef]

40. Šiaudinis, G.; Jasinskas, A.; Šarauskis, E.; Steponavičius, D.; Karčauskien, D.; Liaudanskienė, I. The assessment of Virginia mallow (*Sida hermaphrodita* Rusby) and cup plant (*Silphium perfoliatum* L.) productivity, physic-mechanical properties and energy expenses. *Energy* **2015**, *93*, 606–612. [CrossRef]

41. Szempliński, W.; Parzonka, A.; Sałek, T. Yield and energy efficiency of biomass production of some species of plants grown for biogas. *Acta Sci. Pol. Agric.* **2014**, *13*, 67–80.

42. Angelini, L.G.; Ceccarinia, L.; Nassi o Di Nasso, N.; Bonari, E. Comparison of *Arundo donax* L. and *Miscanthus × giganteus* in a long-term field experiment in Central Italy: Analysis of productive characteristics and energy balance. *Biomass Bioenergy* **2009**, *33*, 635–643. [CrossRef]

43. Felten, D.; Fröba, N.; Fries, J.; Emmerling, C. Energy balances and greenhouse gas–mitigation potentials of bioenergy cropping systems (Miscanthus, rapeseed, and maize) based on farming conditions in Western Germany. *Renew. Energy* **2013**, *55*, 160–174. [CrossRef]

44. Monedero, E.; Hernández, J.J.; Collado, R. Combustion-related properties of poplar, willow and black locust to be used as fuels in power plants. *Energies* **2017**, *10*, 997. [CrossRef]

45. Krzyzaniak, M.; Stolarski, M.J.; Szczukowski, S.; Tworkowski, J. Thermophysical and chemical properties of biomass obtained from willow coppice cultivated in one- and three-year rotation cycles. *J. Elem.* **2015**, *20*, 161–175. [CrossRef]

46. Afzal, M.T.; Bedane, A.H.; Sokhansanj, S.; Mahmood, W. Storage of comminuted and uncomminuted forest biomass and its effect on fuel quality. *BioResources* **2010**, *5*, 55–69.

47. Krzyżaniak, M.; Stolarski, M.J.; Niksa, D.; Tworkowski, J.; Szczukowski, S. Effect of storage methods on willow chips quality. *Biomass Bioenergy* **2016**, *92*, 61–69. [CrossRef]

48. Bajcar, M.; Zaguła, G.; Saletnik, B.; Tarapatskyy, M.; Puchalski, C. Relationship between torrefaction parameters and physicochemical properties of torrefied products obtained from selected plant biomass. *Energies* **2018**, *11*, 2919. [CrossRef]

49. Jagustyn, B.; Patyna, I.; Skawińska, A. Evaluation of physicochemical properties of Palm Kernel Shell as agro biomass used in the energy industry. *Chemik* **2013**, *67*, 552–559.