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Torrefaction as a Way to Remove Chlorine and Improve the Energy Properties of Plant Biomass

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Abstract: This study characterizes and compares the physicochemical parameters of three types of biomass: giant miscanthus, wheat straw, and white willow. An analysis of the chlorine content in the biomass was determined using a 5E-FL2350 fluorine and chlorine analyzer. In addition, energy parameters characterizing the biomass were determined, such as the content of ash and volatile matter in the tested materials, using the LECO TGA 701 thermogravimetric analyzer. The carbon and hydrogen contents were tested using the LECO TruSpec CHN elementary organic analyzer. The calorific value was determined using the LECO AC 500 isoperibolic calorimeter. Based on the research results, it was concluded that the use of the biomass torrefaction process improves its energy parameters. In the long term, this will affect the maintenance of the technical and operational efficiency of devices, installations, and power boilers compared to the co-combustion of fresh biomass. The greatest differences in results were recorded in the case of chlorine content. Carrying out detailed tests on the material immediately after its harvest showed that the content of this element was about 70% higher than in the case of torrefied raw material. The presence of chlorine in alternative fuels is responsible for the formation of chloride corrosion. Its content can be up to five times higher compared to conventional energy sources. The degree of risk of chloride corrosion of the selected elements of devices and installations is assessed on the basis of the so-called "chlorine corrosion index".

Keywords: biomass; torrefaction; energy production

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1. Introduction

One of the problems with using biomass for energy purposes is the high chlorine content in its composition. This negatively affects the condition of the combustion installation, degrading various elements of the installation [1,2]. A characteristic feature of biomass is its heterogeneity and fibrous structure, which has a negative impact on dust separators, causing them to frequently become blocked. The second disadvantage is the lower energy value of solid biofuels compared to fossil fuels. It is related to the need to introduce a larger stream of fuel mixture into the process than in the case of only burning fossil fuels [3]. Another example of the degradation of some elements of a heat block are heated surfaces, where corrosion and corrosion–erosion processes are intensified. Some substances that are contained in ashes and exhaust gases, e.g., chlorine and sulfur, are the direct cause of these processes. Moreover, deposits are formed on the heating surfaces of the boiler elements, which results in an increase in failure rates and a reduction in the durability of the materials used [4]. They accumulate on the internal and external walls of pipes and contribute to reducing the efficiency of the entire installation. The accumulation of impurities on the outer surfaces of pipes leads to a change in the shape of the heat-absorbing area, which consequently affects the temperature and stress field in the pipe [5]. The co-combustion

of biomass is generally associated with the occurrence of sulphate–sulfide and chloride corrosion. The first type of corrosion occurs in the presence of sodium and potassium, which together with sulfur form sulfates. The rapid progress of sulfation and the formation of multiphase scales are components of the corrosion process of metals in sulfur-containing environments [6]. Chloride corrosion is related to the presence of chlorine and alkali metals in solid biofuels, which increase the risk of damage to devices and installations. A significant problem is the formation of deposits that influence corrosion during the combustion of biomass fuels, which are rich in sulfur (S), chlorine (Cl), and potassium (K) [7]. The chlorine content in alternative fuels can be up to five times higher than in coal. Chlorine bound in solid fuels is classified into inorganic and organic chlorine. Inorganic chlorine consists of mainly chlorides of sodium or potassium [8]. The initial stage of this type of corrosion is the formation of gaseous alkali metal chlorides, which condense on colder elements, e.g., on heat exchangers. Then, as a result of chemical reactions, chlorine is released and reaches metal surfaces through the layers of sediment. There, it interacts with iron to form iron(II) chloride. Diffusing again into the outer layer, it is oxidized, and the produced chlorine molecule may participate in a further corrosion process [9]. The co-combustion of biomass with traditional fuel significantly affects the combustion process in boilers. Solid biofuels are characterized by a high moisture content, which affects the stability and temperature of the flame. Significant operational problems are caused by the dynamic and continuous process of supplying the fuel mixture to the boiler, which leads to erosion of the screen pipes and contributes to accelerating the corrosion of the installation. They also cause an increase in the heat load on steam superheaters and an uneven distribution of combustion zones both in the combustion chamber and in the convection sequence [10]. The use of biomass with good physicochemical parameters allows for a reduction in carbon monoxide emissions, nitrogen oxides, and harmful dust into the atmosphere [11].

In the professional power industry, despite the use of appropriate structures, systems, and devices, in many cases, it has not been possible to find the ideal technology to effectively prevent progressive corrosion or the accumulation of sediments on the surfaces of heating units [12]. In order to protect equipment and energy blocks, corrosion inhibitors are increasingly used, which reduce the destructive effect of certain chemical compounds contained in fuels. They are usually introduced into the combustion chamber via spraying onto a previously loaded fuel material [13]. During the exothermic reaction, anti-corrosion layers are deposited on the elements of power boilers. Depending on the inhibitor used, they may take the form of active or passive layers. The first type allows for the partial cleaning of the boiler heating surfaces and the transformation of hard sediments into those that can be easily and quickly removed. Anti-corrosion passive layers act as shields and protect the metal against the penetration of aggressive elements causing corrosion and erosion processes into its structure. The greatest interest among the electricity industry is aroused by preparations that, in addition to their properties, also improve fuel combustion processes [14,15]. This is an extremely important issue when damp agricultural biomass is introduced into the combustion chamber, which reduces the efficiency and optimal operation of the entire power unit [16]. The most frequently used inhibitors in the commercial power industry for the co-combustion of solid biofuels are calcium compounds in the form of carbonates, oxides, and hydroxides; phosphorus and aluminum compounds; aluminosilicates; and copper oxychloride. The formation of slag can be reduced by adding calcium compounds to the combustion process [17]. Due to their physicochemical properties, they also significantly reduce sulfur oxide emissions [18]. The participation of phosphorus enables the formation of calcium–potassium phosphates, which have a very high melting point. It is usually given in the form of phosphoric acid, acidic calcium phosphate, or sewage sludge with a significant phosphorus content. Aluminosilicates are a group of chemical compounds that help to minimize the risk of high-temperature corrosion in power boilers and devices associated with them [19]. It is important to properly identify areas exposed to chlorine, the appropriate selection of construction materials, and appropriate fuel preparation methods [20].

A good way to improve the energy use of biomass and to remove harmful compounds is to use the torrefaction process [21,22]. This thermal treatment technology is mainly used for plant biomass, i.e., lignocellulosic biomass, in order to convert it into solid fuel [23]. The temperatures used in this process are in the range of 200–300 °C. Torrefaction is carried out in an oxygen-free, inert atmosphere and at a pressure close to or equal to atmospheric pressure [24]. Changes in the structure of biomass result from the destruction of its fibrous skeleton structure as a result of the decomposition of polymer structures, which leads to a reduction in the mechanical strength of the obtained material. Moreover, it allows for a reduction in the costs related to the preparation of fuel in its final form, e.g., in the form of pellets [25]. In the classic torrefaction process, the material is partially degassed, which leads to mass loss, but the simultaneous energy loss is lower compared to the mass loss [26]. This biomass-processing technology allows for a 30% reduction in mass while retaining 90% of the original energy [27].

The use of the biomass torrefaction process to remove chlorine is a very important research topic that creates new opportunities for the development of biomass combustion technology. This research has been conducted by many researchers, although they differ in the scope of the torrefaction process and the types of biomass. The torrefaction process is not commonly used in the professional or commercial power industry. The development of this technology will certainly influence its widespread use. Studying different types of biomass will allow us to learn more about this process.

2. Materials and Methods

2.1. Biomass Feedstock and Torrefaction Process

Detailed laboratory tests were performed on the biomass of Miscanthus giganteus, wheat straw, and white willow. These analyses were aimed at assessing the impact of the torrefaction process on the chlorine content and comparing selected physicochemical parameters in raw and post-torrefaction biomass. The samples for testing were collected in 2022 at the plantation of the University Experimental Station in Rzeszów, and the dates of the sample collection corresponded to the typical harvest dates of energy crops. After harvesting, the raw material intended for research was dried and then crushed. One kg each of willow, miscanthus, and straw materials was prepared for laboratory tests. Half of each material was subjected to the torrefaction process. Each test used 100 g of the material (total sample weight in the measurement cycle). The method of preparing the experiment is shown in Figure 1. The torrefaction tests were performed in triplicate.

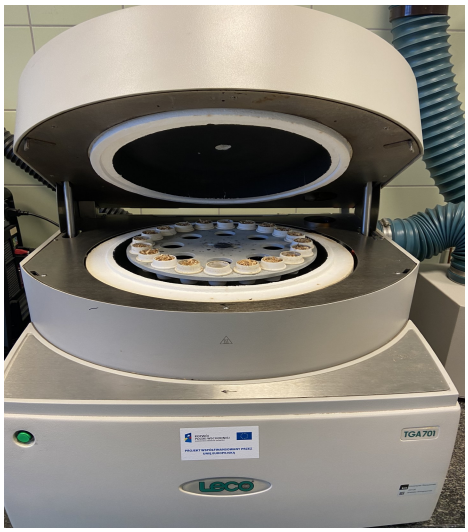


Figure 1. Experimental system of torrefaction test with LECO TGA.

The torrefaction process was carried out in the LECO TGA 701 type. Tests of the physicochemical properties and torrefaction tests using a thermobalance were performed for the raw materials with particle sizes of less than 10 mm. A study of the torrefaction process of the energy willow and rapeseed straw was carried out at temperatures of 220, 240, 260, 280, and 300 °C for 60 min in a nitrogen atmosphere of 99.99% purity, with a gas flow of 10 l/min, using temperature increases of 30 °C/min. The observed physical changes in the biomass after the torrefaction tests are shown in Figure 2.



Figure 2. Physical changes to the biomass after torrefaction tests.

2.2. Chlorine Content Analysis

The chlorine content was analyzed using the CKIC 5E-CLT2311 chlorine analyzer. This analyzer is used to automatically determine chlorine contents using the hydrolysis combustion method. The samples were analyzed directly in measuring crucibles that were transferred to the combustion chamber. A sample weighing 0.5 g was placed in the measuring crucible, which was automatically placed next to the feeder in the combustion furnace. After combustion at a temperature of 1100 °C, the solution was introduced into the titration chamber and the measurement was performed. The decomposition of the tested material took place within 35 min. The chlorine content was measured using potentiometric titration over a total time of 15 min. The share of chlorine in the elementary composition of the waste (in relation to its dry weight) in an amount of less than 0.2% allows for the failure-free operation of power boilers. Waste with a determined chlorine content of $\leq$0.2% may, in accordance with the PN-EN 15359:2012 standard, be classified as class 1, while samples with a chlorine content of $\leq$3% may be classified as class 5 [28].

2.3. Physicochemical Analyses

The material was analyzed to determine its basic physicochemical parameters, such as the total contents of carbon, ash, nitrogen, hydrogen, water, and volatile matter, as well as the calorific value of the material. The analyses were performed using a LECO TGA 701 (Leco, St. Joseph, MI, USA) thermogravimeter, a Truespec LECO CHN (Leco, St. Joseph, MI, USA) elemental composition analyzer, and a LECO AC 500 (Leco, St. Joseph, MI, USA) isoperibolic calorimeter.

2.4. Statistical Analysis

The STATISTICA12.5 PL software by StatSoft was used for the statistical calculations. A significance threshold of $\leq$0.05 was set for all analyses. The data were analyzed separately for each type of pellet. In order to verify the significance of the impact of various wastes used in pellets on their quality parameters, an analysis of variance (ANOVA) was used.

The obtained results were analyzed individually for each type of material and the number of repetitions was $n = 3$.

3. Results

3.1. Total Chlorine Content Analysis

The percentage of chlorine in the raw and torrefied biomass after harvesting is shown in Figure 3. The analysis showed that wheat straw had the highest chlorine content among the fresh biofuels—0.78%. The percentage indicator for the other types of biomass reached the following values: giant miscanthus—0.55%, willow—0.12%. Willow had the lowest chlorine content; this value was almost 85% lower than in the case of wheat straw. The chlorine content in the solid biofuels that were subjected to the torrefaction process demonstrates the validity of this process. The obtained results clearly show significant changes. Wheat straw had the highest content of this element—0.24%. The results of the other energy raw materials were as follows: giant miscanthus—0.18%, willow—0.05%. This research shows that the use of the torrefaction process allowed the chlorine content in the biomass to be reduced to a safe level in the case of miscanthus. Safe values were present in all willow samples. In the case of wheat straw, the recorded values classified the fuel as of lower quality. Straw torrefaction at a temperature of 300 °C allowed us to obtain a value close to 0.2% of chlorine.

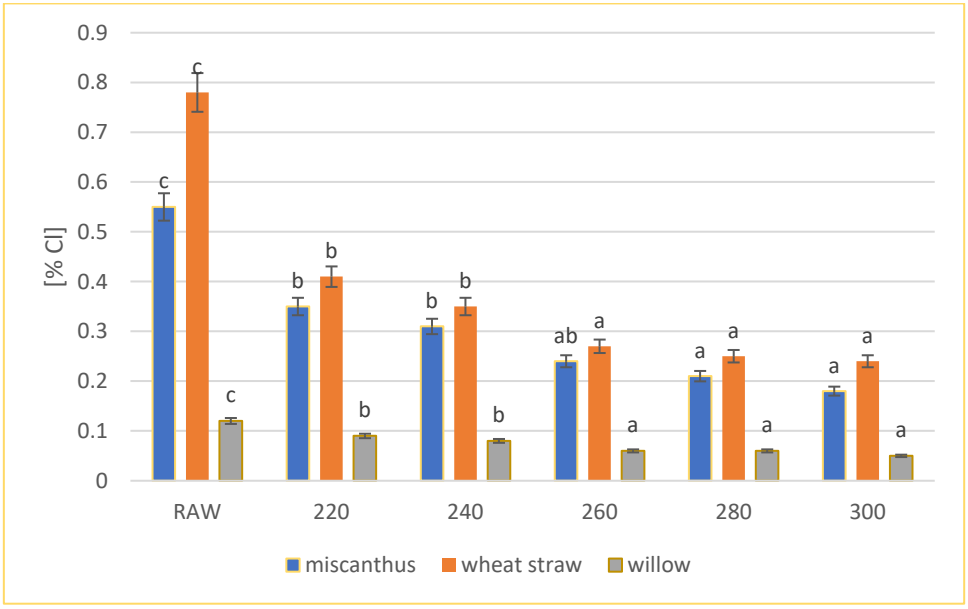


Figure 3. Comparison of total chlorine content in raw and torrefied biomass as a function of the temperature of the torrefaction process. x—arithmetic mean; SD—standard deviation according to Duncan's test; means marked with the same letter are not significantly different at $\alpha \leq 0.05$.

3.2. Determination of Energy Properties in the Tested Biomass

This research involved an analysis of the biomass of energetic willow, wheat straw, and giant miscanthus. Energy willow and giant miscanthus are types of biomass grown for energy purposes. Wheat straw, on the other hand, is a waste product from agricultural production. The thermogravimetric, calorimetric, and elemental composition of the raw biomass and torrefied materials were assessed depending on the process temperature. The results are presented in Table 1. By analyzing specific parameters, it can be concluded that the torrefaction process increases the content of carbon, volatile matter, and the calorific value of the material. A comparison of the raw biomass and torrefied products shows differences that are significantly influenced by the process temperature.

Table 1. Summary of the tested parameters of raw and torrefied biomass depending on the variable temperature of the process.

Parameters		Raw Willow	220 °C	240 °C	260 °C	280 °C	300 °C
		x ± SD					
C	%	48.24 ^{c} ± 0.1	48.31 ^{c} ± 0.31	49.19 ^{bc} ± 0.21	52.44 ^{b} ± 0.35	54.03 ^{ab} ± 0.18	55.27 ^{a} ± 0.11
H	%	5.48 ^{ab} ± 0.02	5.92 ^{a} ± 0.02	5.99 ^{a} ± 0.06	4.37 ^{c} ± 0.1	3.99 ^{cd} ± 0.04	3.31 ^{d} ± 0.01
N	%	0.51 ^{d} ± 0.01	1.24 ^{a} ± 0.04	1.21 ^{b} ± 0.03	1.07 ^{c} ± 0.02	1.01 ^{c} ± 0.04	0.91 ^{b} ± 0.03
Moisture content	%	10.64 ^{a} ± 0.12	9.01 ^{b} ± 0.04	8.61 ^{bc} ± 0.03	8.02 ^{bc} ± 0.1	7.98 ^{c} ± 0.11	7.76 ^{c} ± 0.1
Ash content	%	3.03 ^{b} ± 0.1	3.07 ^{b} ± 0.1	3.31 ^{ab} ± 0.05	3.49 ^{a} ± 0.1	3.6 ^{a} ± 0.1	3.69 ^{a} ± 0.12
Volatile matter	%	22.51 ^{c} ± 0.22	23.14 ^{d} ± 0.16	24.85 ^{bc} ± 0.16	29.3 ^{b} ± 0.32	37.71 ^{a} ± 0.24	40.14 ^{a} ± 0.25
HHV	**MJ·kg^{-1}**	17.22 ^{c} ± 0.16	19.05 ^{b} ± 0.05	20.03 ^{b} ± 0.1	21.19 ^{a} ± 0.14	21.72 ^{a} ± 0.1	21.77 ^{a} ± 0.1
		Raw Wheat Straw	**220 °C**	**240 °C**	**260 °C**	**280 °C**	**300 °C**
C	%	44.22 ^{d} ± 0.06	47.34 ^{c} ± 0.1	49.61 ^{c} ± 0.12	50.94 ^{b} ± 0.16	51.4 ^{ab} ± 0.11	53.26 ^{a} ± 0.08
H	%	6.94 ^{a} ± 0.07	5.55 ^{b} ± 0.06	4.91 ^{bc} ± 0.08	4.32 ^{c} ± 0.1	3.96 ^{c} ± 0.07	3.44 ^{d} ± 0.02
N	%	0.26 ^{d} ± 0.03	1.01 ^{c} ± 0.03	1.05 ^{c} ± 0.02	1.24 ^{b} ± 0.04	1.3 ^{b} ± 0.1	1.16 ^{a} ± 0.08
Moisture content	%	10.05 ^{a} ± 0.1	8.24 ^{b} ± 0.1	7.69 ^{bc} ± 0.1	6.55 ^{c} ± 0.13	5.94 ^{c} ± 0.15	4.12 ^{d} ± 0.1
Ash content	%	3.95 ^{d} ± 0.1	4.88 ^{c} ± 0.11	6.72 ^{c} ± 0.17	8.84 ^{b} ± 0.16	9.32 ^{a} ± 0.1	9.41 ^{a} ± 0.1
Volatile matter	%	14.1 ^{d} ± 0.09	18.62 ^{c} ± 0.22	22.37 ^{bc} ± 0.16	31.33 ^{b} ± 0.23	40.58 ^{ab} ± 0.2	44.77 ^{a} ± 0.2
HHV	**MJ·kg^{-1}**	17.43 ^{d} ± 0.1	18.12 ^{c} ± 0.1	19.01 ^{c} ± 0.1	19.65 ^{b} ± 0.24	20.01 ^{b} ± 0.13	20.87 ^{a} ± 0.26
		Raw Miscantus	**220 °C**	**240 °C**	**260 °C**	**280 °C**	**300 °C**
C	%	43.16 ^{d} ± 0.05	45.31 ^{c} ± 0.1	47.12 ^{c} ± 0.11	50.12 ^{b} ± 0.2	51.75 ^{ab} ± 0.24	53.01 ^{a} ± 0.31
H	%	6.55 ^{a} ± 0.06	5.31 ^{b} ± 0.03	4.87 ^{bc} ± 0.08	4.02 ^{c} ± 0.1	3.34 ^{c} ± 0.06	3.03 ^{d} ± 0.02
N	%	0.18 ^{d} ± 0.01	0.92 ^{c} ± 0.03	1.01 ^{c} ± 0.02	1.06 ^{b} ± 0.02	1.13 ^{b} ± 0.02	1.1 ^{a} ± 0.05
Moisture content	%	9.06 ^{a} ± 0.1	8.63 ^{b} ± 0.1	7.58 ^{bc} ± 0.2	6.23 ^{c} ± 0.1	5.03 ^{c} ± 0.1	4.75 ^{d} ± 0.1
Ash content	%	4.06 ^{d} ± 0.09	5.62 ^{c} ± 0.1	6.37 ^{c} ± 0.11	7.12 ^{b} ± 0.1	8.08 ^{a} ± 0.1	9.07 ^{a} ± 0.1
Volatile matter	%	12.73 ^{d} ± 0.22	18.37 ^{c} ± 0.21	23.12 ^{bc} ± 0.17	31.54 ^{b} ± 0.22	40.14 ^{ab} ± 0.16	42.54 ^{a} ± 0.16
HHV	**MJ·kg^{-1}**	17.51 ^{d} ± 0.1	18.34 ^{c} ± 0.11	19.36 ^{c} ± 0.21	20.16 ^{b} ± 0.21	21.11 ^{b} ± 0.1	21.62 ^{a} ± 0.16

x—arithmetic mean; SD—standard deviation according to Duncan's test; means marked with the same letter are not significantly different at $\alpha \leq 0.05$.

This research showed that torrefaction carried out at temperatures ranging from 220 to 300 °C for 60 min allows for the processing of many types of lignocellulosic biomass. Due to structural differences in biomass, changes in chemical composition occur in different ways during the process, which was demonstrated by changes in, e.g., the mass of the material during the process. For this reason, it is extremely important to optimize the process for each material to ensure the best energy parameters of the obtained biofuels and to reduce process costs. By analyzing the results, it can be concluded that the calorific value may be such a parameter.

4. Discussion

Nowadays, the main problem of our civilization is the protection of the natural environment while ensuring energy security [29]. The constant increase in energy demand and the burning of only non-renewable energy sources lead to the irreversible reduction in fossil fuel resources, and their excessive exploitation contributes to the emission of harmful substances and chemical compounds into the atmosphere [30]. The widespread use of renewable energy sources, such as sun, wind, water, geothermal energy, or solid biofuels,

is one of the ways that can reduce the destructive impact of conventional energy sources on the natural environment [31].

In many countries, the most important and most frequently used ecological fuel in the professional power industry is biomass [32]. The forecasts of demand for this type of biofuel in the coming years have increasing trends [33]. This is conditioned not only by the technical potential of biomass, but primarily by the implementation of obligations regarding the share of renewable energy sources in electricity production [34]. The co-combustion of biomass in thermal power units within the commercial power industry generates a number of technological and organizational problems [35]. The physicochemical properties of solid biofuels differ significantly from those of fossil fuels. They contain elements such as sulfur, potassium, and chlorine [36]. Their presence leads to the risk of high-temperature corrosion on the heating elements of power units. Moreover, they have a high moisture content, which negatively affects the combustion process and the stability of the flame in the combustion chamber [37]. Obtaining optimal co-combustion parameters also depends on the method of transport and storage of biomass, as well as the preparation and appropriate fragmentation of the raw material [38]. An important aspect is the selection of combustion technology and its proper adaptation to the thermal units without the need for their excessive modernization [39].

By comparing the physicochemical properties of the analyzed solid biofuels, the energy parameters of torrefied biomass were improved compared to raw biomass. In studies by other authors, similar trends in changes in the analyzed parameters were observed. The differences result from the origin of the material, which do not significantly change the main conclusion. It can be concluded that the co-combustion of torrefied biomass will have a positive impact on maintaining the longer operating efficiency of devices, installations, and power boilers compared to the co-combustion of fresh biomass [40–42]. The largest differences in test results were noticeable in the case of the chlorine content. In the analyzed material of miscanthus and wheat straw, the content of this element was over three times higher than in the case of the torrefied raw material. The chlorine content in willow was more than twice as high compared to biofuels subjected to the torrefaction process. This is undoubtedly an important feature of the torrefaction process that characterizes this process [43,44].

Depending on the material analyzed, the intensity of the changes varied significantly. In the case of miscanthus, the greatest decrease in chlorine content compared to the raw biomass was recorded at a temperature of 220 °C. As the process temperature increased, significant changes in this parameter were recorded. At temperatures of 260 °C and above, the declines were not so significant. A similar trend of changes was noted for wheat straw, where the largest chlorine loss occurred at the lowest temperature of the torrefaction process. In the case of willow, these decreases were nominally not so large because the share of chlorine in raw willow was not high. In the case of this material, dechlorination can be carried out at low temperatures of the torrefaction process.

Similar results and trends in changes were observed in studies by other authors. A comparison of selected features is presented in Table 2. The parameter values vary, which results from the variability of the analyzed material. Elemental analysis and energy properties confirmed the positive impact of torrefaction on the obtained parameters of the torrefied materials [45,46].

Table 2. Comparison of selected results with those of other authors.

Torrefied	Torrefaction Temperature	Cl	Ash	HHV	References
	°C	%		$MJ \cdot kg^{-1}$	
Wheat straw	220	0.41	4.88	18.12	This work
	240	0.35	6.72	19.01	
	260	0.27	8.84	19.65	
	280	0.25	9.32	20.01	
	300	0.24	9.41	20.87	
Wheat straw	200	-	3.85	18.55	[47]
	250	-	4.68	19.94	
	300	-	8.98	27.22	
Eucalyptus	240	0.05	1.02	-	[48]
	280	0	1.1	-	
	320	0	2.52	-	
Wheat straw	220	-	9.33	18.9	[49]
	240	-	10.26	20.11	
	260	-	13.44	22.36	
	280	-	17.15	23.33	
	300	-	17.52	23.58	

5. Conclusions

The physicochemical properties of biomass affect the efficiency and optimal course of the combustion process, and also affect the operation of thermal units, devices, and installations, which is described in numerous publications. One way to eliminate these phenomena is to use corrosion inhibitors that reduce the destructive effect of some chemical compounds contained in biofuels. These additives minimize the risk of chloride and sulfate–sulfide corrosion.

A less invasive solution is the biomass torrefaction process, which allows for significant reductions in the content of hazardous chemicals for devices and installations. Moreover, this process increases the calorific value of solid biofuels, which has been demonstrated in studies using the example of chlorine compounds. The use of the torrefaction process reduced the share of chlorine in the tested biomass to a safe level, below 0.2%. These values were obtained at a temperature of 280 °C in the case of miscanthus. For straw, this value was approached at a temperature of 300 °C. In willow, at a torrefaction temperature of 220 °C, a safe value was obtained in the combustion process. In future research, it is worth optimizing the temperature parameters and the duration of the torrefaction process.

The possibility of reducing the undesirable effects of burning ecological biofuels, as well as the development of scientific research and technological processes in this area, should become a priority.

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