

Article

Exploring the Prospective of Weed *Amaranthus retroflexus* for Biofuel Production through Pyrolysis

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Abstract: *Amaranthus retroflexus* or redroot pigweed is a second generation lignocellulosic fuel. Each biomass sample (leaves, inflorescences and stems) was pyrolyzed in a lab-scale furnace, in a nitrogen atmosphere under non-isothermal conditions at heating rates of 10 °C/min until the furnace temperature reached 550 °C. The pyrolysis characteristics of the three major components were also studied through thermogravimetric analysis. The thermal decomposition of the biomass samples is similar to the process of pyrolysis of lignocellulosic materials and proceeds in three main stages: dehydration, devolatilization, and carbonation. The highest bio-oil yield was obtained for inflorescences (55%) and leaves (45%). Gas chromatography—mass spectrometry analysis was carried out for oil fractions of the pyrolysis liquid from *Amaranthus retroflexus*. The composition of the pyrolysis oil fraction from the leaves had an overbearing aliphatic hydrocarbon nature whereas the oil fraction from inflorescences and stems was composed mainly of oxygen-containing components. The use of *Amaranthus retroflexus* biochars can lead to slag formation in power equipment, so it is advisable to use them to produce composite fuel, for example, mixed with coal. The results would help to better understand the thermal behavior of *Amaranthus retroflexus* biomass and its utilization for fuels or chemicals.

Keywords: biomass; *Amaranthus retroflexus*; pyrolysis; thermogravimetric analysis; bio-oil; biochar



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1. Introduction

Second generation biofuels are produced from lignocellulosic biomass derived from agricultural waste, forest waste, municipal and industrial waste, and grass and aquatic plants. All of these types of biomass have one common property; they are formed from non-food resources [1]. *Amaranthus retroflexus* (AR), or redroot pigweed, is a second-generation lignocellulosic biomass. This plant is a fast growing herb of class C4, consisting of 60–70 species [2,3]. AR is a cosmopolitan plant capable of growing in any climatic zone, including the cryolitic zone [4]. The plant can reach 1.5–3 m in height, thus, it is possible to obtain huge biomass resources with little water and fertilizer consumption [2].

Pyrolysis is the most promising technology for thermal utilization, since it allows for the procurement of gaseous, liquid, and solid products, and is also the first stage of all thermochemical processes [5]. The quantity, properties, and application of these three main products depend on the parameters of the feedstock, the type of reactor and the technological conditions for the implementation of the process (the heating rate, final pyrolysis temperature, pyrolysis atmosphere, etc.) [6].

From a practical point of view, bio-oil and biochar are of the greatest interest, since pyrolytic gas is most often used for its own technological needs. The rich chemical composition of bio-oil allows it to be used as renewable fuels and value-added chemicals [7,8].

Biochar has the following applications: soil amendment, nutrient and microbial carrier, immobilizing agent for remediation of toxic metals and organic contaminants in soil and water, catalyst for industrial applications, porous material for mitigating greenhouse gas emissions and odorous compounds, and feed supplement to improve animal health and nutrient intake [9,10]. Due to its low thermal conductivity, it can also be mixed with soil and used as a thermal backfill [11]. In addition, biochar-derived activated carbon is suitable for batteries and electrode material for supercapacitor applications [12].

There are known studies on the pyrolysis of weeds *Ageratum conyzoides* (goat weed) [13], *Ageratina adenophora* (Crofton weed) [14], *Alternanthera philoxeroides* (alligator weed) [15], *Parthenium hysterophorus* [16], and *Cannabis sativa* [16] to obtain biochar, bio-oil, and biogas. It should be noted that there are studies on the pyrolysis of invasive plants, such as: *Acacia Holosericea* [17], water hyacinth [18], *Prosopis juliflora* [12], and *Eupatorium adenophorum* [19]. However, there are no reports on the utilization of AR as a feedstock for pyrolysis. Therefore, the use of pyrolysis for the use of weeds and invasive plants with the production of bio-oil and biochar can contribute to the formation of a circular economy and increase the profitability of the agricultural industry [20].

For a detailed study of the process of thermochemical conversion, the plant can be divided into fractions. For example, leaves and stems [21], seeds [22–24], flowers, leaves, and stems [25], leaves, hurds, and roots [26], pseudo-stems [27], stem, leaves, fiber, chaff, and seed husks [28], and inflorescences [29,30]. This will make it possible to understand the contribution of each fraction to the material balance of the pyrolysis process. The content of hemicellulose, cellulose, and lignin differs in all constituent parts of the plants, so the quantity and quality of the resulting gaseous, liquid, and solid products varies significantly.

The aim of the work is to study the possibilities of thermal utilization of the AR weed plant, to study in detail the prospects for using its aboveground biomass to obtain new liquid and solid products with high added value. In this research, the authors studied the pyrolytic process of the leaves, stems, and inflorescences. Conventional pyrolysis was performed in combination with a thermogravimetric analysis. Therefore, the present study aims to solve the following problems: (a) determine the material balance of the AR pyrolysis of leaves, inflorescences, and stems of AR; (b) analysis the characteristics of the features of thermal decomposition of leaves, inflorescences, and stems according to TGA data, at a heating rate of 10 °C/min in an inert atmosphere; (c) study of the composition and quality of the chemical composition of the oil fraction of the pyrolysis liquid; and (d) analyze the possibility of using biochar for combustion both as an independent fuel and as part of a mixed fuel, taking into account the parameters of slag formation.

2. Materials and Methods

2.1. Sample Materials

The object of the study was the aerial part of the weed plant AR (Figure 1). The plants were grown in a field with cultivated plants (55°63' N, 48°73' E). In addition, they were divided into leaves, inflorescences (partially with seeds), and stems. Leaves and inflorescences were dried at room temperature, crushed, and sieved to obtain a mass with a particle size of less than 5 mm. The stems were crushed immediately, then dried and additionally ground; the particle size also did not exceed 5 mm.

2.2. Physicochemical Characterization

Moisture, ash content, and volatile matter (VM) were measured in accordance with ASTM E1755-01, ASTM E1756-08, GOST R 56881-2016, and GOST 32990-2014. Elemental analysis of the samples was carried out on a EuroEA3000 CHNS analyzer (Eurovector, S.p.A., Milan, Italy). The samples were weighed on a Sartorius CP2P microbalance (Germany) in tin capsules. Callidus 4.1 software was used to evaluate the obtained data.

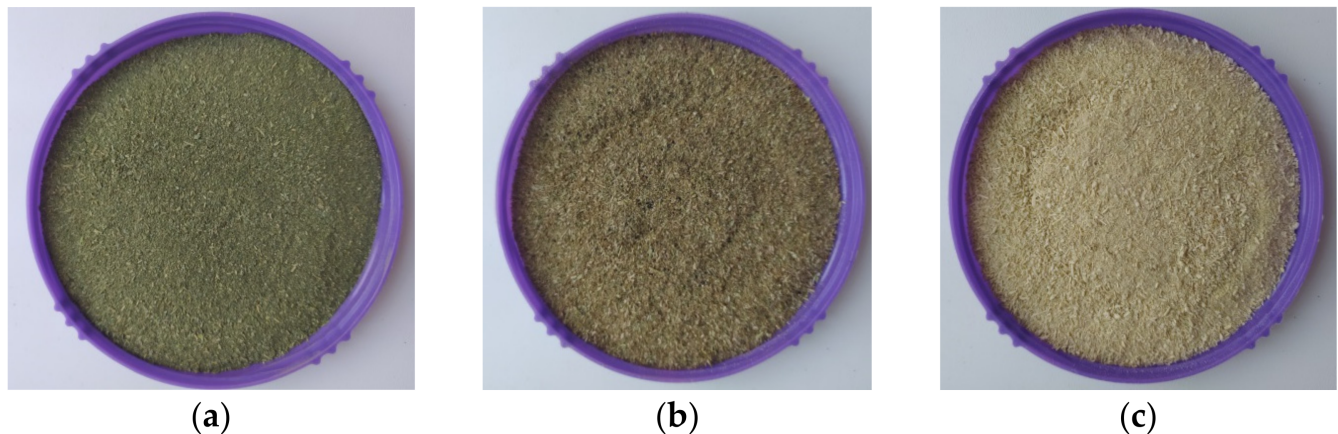


Figure 1. Photographs of the dry biomass AR: (a) leaves; (b) inflorescences; and (c) stems.

The oxygen content (O, wt%) was calculated from the difference by Equation (1):

$$O = 100 - H - C - N - \text{Ash}, \quad (1)$$

where H, C, N, and Ash are wt% of hydrogen, carbon, nitrogen, and ash content of the fuel, respectively.

Atomic H/C and O/C ratios of AR fractions and their biochars were determined with Equations (2) and (3) [31]:

$$\text{atomic } \frac{H}{C} \text{ ratio} = \frac{\text{number of H atoms}}{\text{number of C atoms}} = \frac{H/1}{C/12} \quad (2)$$

$$\text{atomic } \frac{O}{C} \text{ ratio} = \frac{\text{number of O atoms}}{\text{number of C atoms}} = \frac{O/16}{C/12} \quad (3)$$

The higher heating value (HHV, MJ/kg) of the leaves, inflorescences, and stems were determined using Equation (4) [32]:

$$\text{HHV}_{\text{AR}} = 0.3491 \cdot C + 1.1783 \cdot H + 0.1005 \cdot S - 0.1034 \cdot O - 0.0151 \cdot N - 0.0211 \cdot \text{Ash}, \quad (4)$$

where C, H, O, N, and S, are, respectively, the carbon, hydrogen, oxygen, nitrogen, and sulfur content of the fuel, wt%.

2.3. Thermogravimetric Analysis

The most common method used to study the thermal behavior and thermal stability of fuels is the thermogravimetric analysis. Thermal decomposition data were measured using an STA 449 A1 Jupiter synchronous microthermal analyzer (Netzsch, Selb, Germany). For this, the following experimental parameters were chosen:

- temperature range: from 38 to 1000 °C;
- dynamic inert atmosphere: argon;
- heating rate: 10 °C/min;
- flow rate: 75 mL/min;
- average weight—35 mg;
- atmospheric pressure.

To ensure the repeatability of the experiment with an error of 1.5%, the experimental conditions were repeated at least three times.

2.4. Experimental Pyrolysis Procedure

A laboratory setup was used to study the pyrolysis of the biomass samples. It includes a tubular reactor (Figure 2), in which various organic raw materials can be thermally treated [33,34].

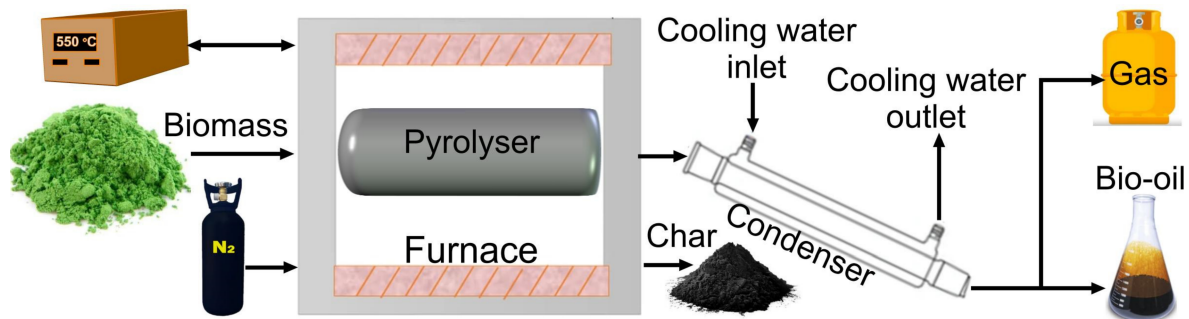


Figure 2. Experimental setup for the study of pyrolysis.

The laboratory setup was preliminarily purged with nitrogen. The prepared biomass sample (weighing about 45 g) was placed in a retort, which was installed in a preheated tubular reactor, which was hermetically sealed with lids. In the reactor, the biomass samples were subjected to a pyrolysis process. The maximum temperature of the pyrolysis process was 550 °C. The heating rate in the experiment was 10 °C/min. As a result of the experiments, three products were obtained: pyrolysis gas, pyrolysis liquid, and solid carbonaceous residue, biochar. Upon completion of the pyrolysis process, the retort was cooled, the solid residue was extracted and its mass yield was determined. Liquid pyrolysis products were collected, and their mass was determined. The gaseous product was determined by the difference in the masses of products from the material balance. Each experiment was repeated at least three times.

2.5. Expanded Measurement Uncertainty

The combined standard uncertainty of the measured value Y (Equation (5)) is obtained according to the law of propagation of uncertainties by summing the squares of the products of the standard uncertainties of all influencing quantities:

$$u(Y) = \sqrt{u^2(m_{ind}) + u^2(m_{device}) + u^2(F_{cor})} \quad (5)$$

The standard measurement uncertainty of m_{ind} is calculated assuming a normal probability distribution using Equation (6):

$$u(m_{ind}) = \sqrt{\frac{\sum_{i=1}^n (m_i - m_{ind})^2}{n(n-1)}}, \quad (6)$$

where m_i is the result of the i -th repetition of the weight measurement, m_{ind} is the arithmetic mean of m ; n is the number of repeated measurements, $n = 3$.

The uncertainty associated with the value of m_{device} (Equation (7)) is estimated using the manufacturer's data on the balance. In the laboratory scale passport for a measurement range of up to 50 g, the limits of weighing error are ± 0.001 g (Δ). Since the value is given without a confidence level, we accept a rectangular distribution of weighing error values within these limits. The standard uncertainty is estimated according to type B and is:

$$u(m_{device}) = \frac{\Delta}{\sqrt{3}}. \quad (7)$$

The standard uncertainty of the correction factor is calculated from the information on the allowable discrepancy between parallel weight determinations. The given allowable relative discrepancy is $r = 20\%$ and is considered a 95% confidence interval for the difference between two estimates of a quantity distributed according to the normal distribution law. The standard uncertainty of the correction factor will be equal to the standard deviation calculated on the basis of the specified interval, taking into account that the measurement result is taken as the arithmetic mean of the determinations of two parallel samples, according to type B and according to Equation (8):

$$u(F_{cor}) = \frac{r}{100\% \cdot 2.8 \cdot \sqrt{2}} \quad (8)$$

The expanded uncertainty U is obtained by multiplying the combined standard uncertainty by a coverage factor using Equation (9):

$$U = k \cdot u(Y), \quad (9)$$

where U is the expanded uncertainty, k is the coverage factor ($k = 2$ at a confidence level of approximately 95%, assuming a normal probability distribution of the measure), $u(Y)$ is standard uncertainty.

2.6. GC-MS Analysis of Bio-Oils

Gas chromatography–mass spectrometry (GC–MS) was carried out on a Shimadzu GCMS-QP2010 Ultra chromatate mass spectrometer on an HP-5MS column (0.25 μm , 0.32 mm, 30 m) with the following parameters: carrier gas helium “A”, temperature injector 300 $^{\circ}\text{C}$, flow rate through the column 2 mL/min, split mode (10), thermostat temperature program—gradient temperature increasing from 60 to 180 $^{\circ}\text{C}$ in steps of 10 $^{\circ}\text{C}/\text{min}$, then holding for 10 min, then increasing the temperature from 180 to 230 $^{\circ}\text{C}$ in steps of 10 $^{\circ}\text{C}/\text{min}$, then holding for 5 min, then increasing the temperature from 230 to 280 $^{\circ}\text{C}$ in steps of 10 $^{\circ}\text{C}/\text{min}$, then holding for 5 min, then increasing the temperature from 280 to 310 $^{\circ}\text{C}$ in steps of 10 $^{\circ}\text{C}/\text{min}$, then holding for 13 min, and the range of scanned masses: 35–700 m/z . The 1 μL sample was injected into a 10% wt% toluene solution.

2.7. Analysis of Biochars

The chemical analysis of the mineral part was carried out using an EDX-800HS2 energy dispersive fluorescent X-ray spectrometer (Shimadzu, Kyoto, Japan). Measurement conditions: tube: Rh-anode (50 W), voltage: 50 kV, 15 kV, current: auto, atmosphere—air, measured diameter: 10 mm, measurement time: 100 s. The sample was placed on a Mylar film (6 μm thick) in a cuvette for the X-ray fluorescence analysis, after which the cuvette was placed in the instrument and the measurement was taken.

The volatile matter (VM) and ash content were determined according to ASTM D3175-89 and ASTM D3174-04, fixed carbon (FC) was calculated from the difference and calculated by Equation (10):

$$\text{FC} = 100 - \text{VM} - \text{Ash} \quad (10)$$

The HHV (MJ/kg) of the biochars were determined using Equation (11) [35]:

$$\text{HHV}_{\text{biochar}} = (15.59 \cdot \text{VM} + 35.36 \cdot \text{FC} - 0.78 \cdot \text{Ash}) / 100 \quad (11)$$

The basic-acid ratio B/A (Equation (12)), slag viscosity index S_R (Equation (13)), and fouling index F_u (Equation (14)) were used to determine the possibility of contamination of the heating surfaces of the power equipment when using biochar as a fuel [36]:

$$B/A = (\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{P}_2\text{O}_5) / (\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2) \quad (12)$$

$$S_R = 100 \cdot \text{SiO}_2 / (\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}) \quad (13)$$

$$F_u = (B/A)/(Na_2O + K_2O) \quad (14)$$

3. Results and Discussion

3.1. Results of Proximate and Ultimate Analyses

Table 1 presents the results of the determination of the physicochemical characteristics of the AR biomass samples. Proximate and ultimate analysis results indicate the potential use of the studied samples in thermochemical conversion processes. In the structure of all parts of the plant, a high content of volatile components was found, 68.3 to 77.9 wt%. This indicates a high reactivity of the material, as well as the fact that they can be converted into pyrolysis products with a large amount of gaseous and liquid components. The samples had a moisture content of about 7 wt%, which did not exceed the permissible limit of 10 wt%. A higher moisture content can lead to an increase in drying costs due to the need for additional thermal energy and a decrease in the efficiency of the thermal conversion of biomass [37].

Table 1. Results of the proximate and ultimate analyses of the AR biomass samples.

Parameter	Leaves	Inflorescences	Stems
Moisture, wt%	7 ± 0.01	7 ± 0.01	7 ± 0.01
VM, wt%	68.3 ± 0.4	74.2 ± 0.7	77.9 ± 0.8
Ash, wt%	23 ± 0.02	8 ± 0.01	11 ± 0.01
FC, wt%	8.7	17.8	11.1
HHV _{AR} , MJ/kg	21.0	25.6	24.1
C, wt%	34.6 ± 0.22	40.9 ± 0.12	35.4 ± 0.09
H, wt%	5.14 ± 0.09	6.34 ± 0.03	6.43 ± 0.13
N, wt%	4.04 ± 0.05	5.45 ± 0.09	3.97 ± 0.1
O, wt%	33.2 ± 0.17	39.3	43.2 ± 0.18
H/C	1.8	1.9	2.2
O/C	0.7	0.7	0.9

The elemental composition of all samples and their ash content are within the limits characteristic of lignocellulosic materials [38–40]. High ash content is considered a problem in thermochemical conversion processes because it can cause fouling or aggregation, as well as lead to some disposal problems, lower energy conversion rates, and ultimately higher recycling costs. AR leaves are characterized by the highest ash content. Given that this plant was grown on unprepared soil and without fertilizing, the increased ash content in the leaves can be explained by the biological characteristics of the plant. The HHV of the samples was determined from the results of the elemental analysis. For leaves, it was the minimum value equal to 21 MJ/kg; the maximum value was 25.6 MJ/kg for AR stems. The high HHV values in this study are comparable to those for various municipal solid wastes [41–43].

3.2. Thermal Degradation Analysis

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of the AR samples are shown in Figure 3. Mass loss during thermal decomposition was recorded in an inert medium at a temperature of 10 °C/min.

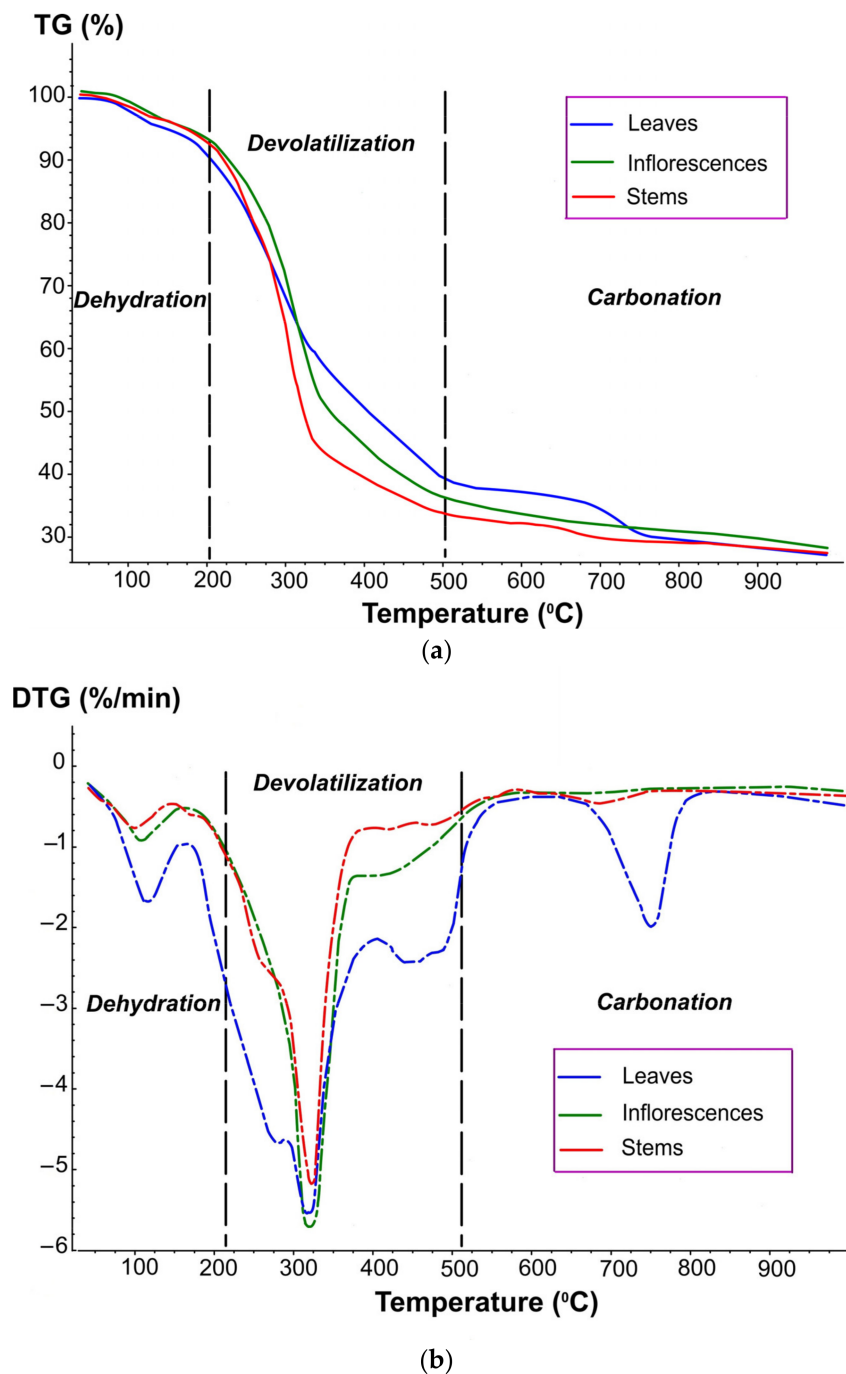


Figure 3. TG (a) and DTG (b) curves of the AR biomass at a heating rate of 10 °C/min.

The thermal decomposition of the three biomass samples studied is similar to the process of pyrolysis of lignocellulosic materials and proceeds in three main stages, which are characterized by the processes of dehydration, devolatilization, and carbonation (Table 2). The dehydration stage starts from 38 °C and proceeds on average up to 200 °C for the studied samples. Mass loss at this stage is considered to be the removal of free moisture, accompanied by evaporation from the sample surface upon heating, as well as chemically bound moisture. In addition to evaporation of the moisture, a slight release of volatile components is possible at this stage [44–46]. The average mass loss at this stage is 7.7%. At this stage, small peaks are found on the DTG curves. The first peak on the DTG curve is associated with the removal of free moisture at a temperature of about 100 °C.

Table 2. Main stages of thermal decomposition.

Sample	Heating Rate (°C/min)	Pyrolysis Stage	Starting Temperature (°C)	Ending Temperature (°C)
Leaves	10	Dehydration	38	200
		devolatilization	200	502
		carbonation	502	1000
		dehydration	38	216
Inflorescences	10	devolatilization	216	512
		carbonation	512	1000
		dehydration	38	190
		devolatilization	190	520
Stems	10	carbonation	520	1000

The main stage of thermal decomposition for all samples starts at about 200 °C and ends in the temperature range of 502–520 °C. The processes that occur at this stage are associated with the release of volatile components. Significant mass loss is reflected as a peak in the DTG curve, which is due to complex thermochemical reactions during the conversion of biomass organic matter. In addition, the peak shown on the DTG curve characterizes the maximum decomposition rate, which is due to the breakdown of hemicellulose and cellulose [47]. As is known, the thermal decomposition of hemicellulose occurs in the temperature range of 180 to 300 °C, and cellulose from 300 to 480 °C [48,49]. Hemicellulose is composed of short-chain heteropolysaccharides and has an amorphous and branched structure. Monosaccharides are the main functional groups of hemicellulose with a small amount of uronic acids and acetyl groups [50]. The behavior of hemicellulose during pyrolysis is largely reflected by the characteristics of these building blocks during the thermal conversion process. Cellulose is a linear macromolecular polysaccharide consisting of a long chain of glucose units linked by β -1,4-glycosidic bonds [50]. The decomposition of cellulose is carried out by the depolymerization of various chemical bonds with the formation of carbon monoxide and dioxide, and carbon residues, as well as by the formation of bonds at high temperature to obtain liquid pyrolysis components.

Peaks in the DTG curves at the second stage indicated the decomposition of hemicellulose, which decomposes in the temperature range of 200–340 °C. Peaks at temperatures of 320–450 °C confirmed the thermal decomposition of cellulose. However, the temperature range changed as a result of the different biochemical compositions of the samples studied. For example, during the pyrolysis of AR stems, the maxima on the DTG curves shift, probably because of the high content of hemicellulose, which decomposes before cellulose.

At the carbonation stage, the processes of thermal cracking and dehydrogenation, as well as the decomposition of the solid carbonaceous residue and inorganic substances in its composition, take place [51]. The average mass loss in the carbonation stage is 8.7% for the studied samples. The main process at this stage is the thermal conversion of the complex structure of lignin, which decomposes almost throughout the entire temperature range from 190 to 900 °C. Unlike the carbohydrate structure of cellulose and hemicellulose, lignin has an aromatic matrix that gives strength and rigidity to the cell walls. Cellulose and hemicellulose have been shown to rapidly decompose over a short temperature range, while lignin slowly decomposes over a wider temperature range up to the end temperature of the experiment with the maximum formation of solid carbonaceous residues [52–54]. At temperatures above 680 °C, apparent shoulder peaks appeared in the DTG curves, which is due to the decomposition of inorganic components with low thermal stability [55,56]. At temperatures above 750 °C, practically no mass loss was observed, and the average residual weight as a result of heat treatment was 27.5% (Table 3).

Table 3. TG-data on changes in mass.

Sample	Mass Loss, %			Residual Mass, %
	Dehydration	Devolatilization	Carbonation	
Leaves	8.6	51.8	12.5	27.1
Inflorescences	8.5	57.1	8.3	26.7
Stems	6.1	59.4	5.6	28.9
Average, %	7.7	56.1	8.7	27.5

The content of hemicellulose, cellulose, and lignin in biomass affects the yield of pyrolysis products [57]. A high content of cellulose and hemicellulose contributes to the production of bio-oil, while a higher concentration of lignin results in more biochar produced. The structural complexity and stability of lignin make it difficult to destroy it during pyrolysis, leading to a higher yield of biochar [58].

3.3. Product Distribution and Yields

As a result of the study of the pyrolysis process at a temperature of 550 °C, three products were obtained: gas, bio-oil, and biochar (Table 4). Generally, the yields of liquid, solid and gaseous products are 50–70 wt%, 13–25 wt%, and 12–15 wt%, respectively [59]. A similar trend is typical for the results obtained. For all samples, the mass fraction of bio-oil among the pyrolysis products was the largest. In a number of studies, it has already been shown that the pyrolysis temperature from 450 to 550 °C contributes to the production of liquid products [35,60]. The yield of pyrolysis products when using AR leaves is similar to pine, AR inflorescences are comparable to *Acacia cincinnata* trunk, and AR stems are similar to agricultural biomass residues [61].

Table 4. Distribution of product pyrolysis yields and uncertainty analysis.

Sample	Pyrolysis Product	Mass, g	Mass Share, %	Expanded Uncertainty
Leaves	bio-oil	20.3	45.2	0.285
	biochar	17.5	38.9	0.587
	gas	7.1	15.9	0.836
Inflorescences	bio-oil	24.9	55.3	0.385
	biochar	14.5	32.2	0.473
	gas	5.6	12.5	0.203
Stems	bio-oil	17.7	39.3	0.428
	biochar	16.6	36.9	0.539
	gas	10.7	23.8	0.710

The results obtained in this study were compared with experimental data on the pyrolysis of plant biomass. Table 5 presents data on the products of thermal decomposition obtained during the pyrolysis of various biomass, its parts, and the plant as a whole. Experiments in which the process temperature was 500–600 °C and the heating rate varied from 5 to 50 °C/min were considered as pyrolysis conditions.

Table 5. Distribution of pyrolysis products obtained from various raw materials.

Biomass	Type of Pyrolysis	Pyrolysis Products, wt%			Reference
		Bio-Oil	Gas	Biochar	
<i>Ageratum conyzoides</i>	without catalyst	30	43	23	[13]
Crofton weed	catalytic	27–29	45–49	25–28	[14]
<i>Alternanthera philoxeroides</i>	without catalyst	45	22	33	[15]
<i>Eupatorium adenophorum</i>	catalytic	29–32	36–41	28–33	[19]
<i>Acacia holosericea</i>	without catalyst	33–38	33–37	26–34	[17]
Mixture of discarded vegetables and fruits	catalytic	35	22	30	[20]
<i>Cortaderia selloana</i>	without catalyst	19–34	45–62	18–27	[21]
Banana pseudo-stem (<i>Musa acuminata</i>)	without catalyst	28	32	42	[27]
Agricultural biomass residues	without catalyst	32	32	33	[61]
<i>Acacia holosericea</i> trunk	without catalyst	47	22	31	[61]
<i>Amaranthus retroflexus</i>	without catalyst	39.3–55.3	12.5–23.8	32.2–36.9	This study

A large yield of pyrolysis liquid was observed during pyrolysis of *Alternanthera philoxeroides* biomass [15]. The authors of [15] conclude that with an increase in temperature from 350 °C to 450 °C, the bio-oil yield and the yield of gas increase while the yield of biochar decreases. An increase in temperature leads to an increase in the gas yield and a decrease in the yield of pyrolysis liquid, which is associated with the secondary cracking of pyrolysis vapors at a higher pyrolysis temperature. During the pyrolysis of the banana pseudo-stem, a high mass yield of biochar was observed [21]. During the thermochemical conversion of the mixture of discarded vegetables and fruits at 500 °C, the maximum yield of bio-oil was observed, with an increase in temperature, its yield decreased [20]. During catalytic pyrolysis, there was a tendency to increase the yield of pyrolysis liquid and pyrolysis gases [14,19,20].

The heating rate during pyrolysis also affects the product yield. With fast pyrolysis, the yield of liquid products is higher, as this technology is characterized by high heating rates [17,20]. The analysis of studies showed that the temperature of 600 °C turned out to be optimal for further research on optimization due to its highest yields [15,17,20,27]. A comparative analysis showed that the results obtained in this work are comparable with the values obtained by other authors. The difference in values is explained by the composition of the feedstock, the influence of the parameters of the pyrolysis process and the influence of catalysts.

3.4. Composition of Bio-Oils

The composition of pyrolysis products is dominated by bio-oil or pyrolysis liquid, which is associated with the rich chemical composition of AR biomass. It contains at least 15 substances of phenolic nature, pectin substances, organic acids, tannins, amino acids, flavonoids, and other chemical components [62]. Furthermore, a significant content of

hemicellulose can contribute to a higher yield of pyrolysis liquid [63]. Bio-oil consists of an aqueous fraction and an oil fraction (Figure 4). The highest yield of the aqueous fraction was obtained during the pyrolysis of AR stems, which may be due to the high content of holocellulose in them. The high content of the aqueous fraction in all bio-oil samples is due to lignin oligomers present in biomass due to the presence of hydrophilic polar functional groups [64].

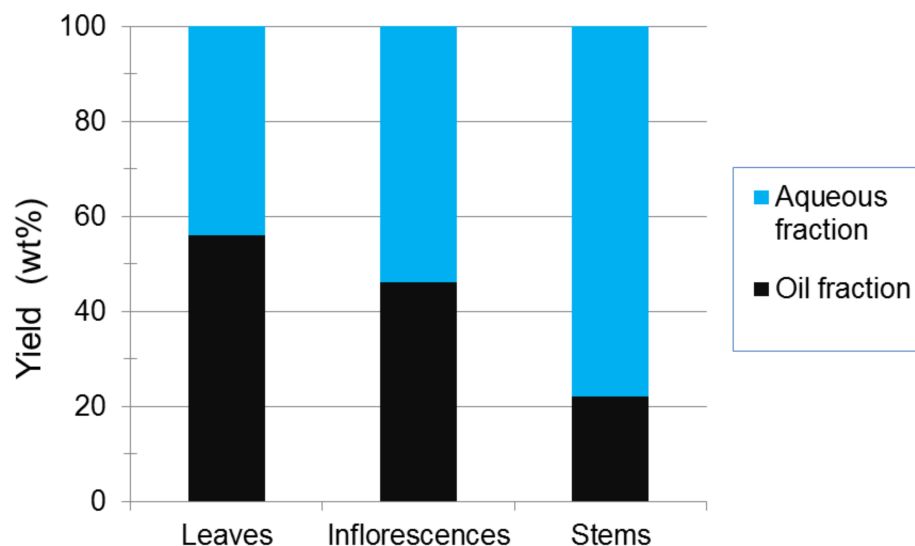


Figure 4. The content of the fractions in the pyrolysis liquid.

The oil fraction can be used as a fuel directly or converted into a high-quality fuel or chemical material. While the aqueous phase cannot be used directly as a fuel. As a result of the GC–MS analysis of the oil fractions of the pyrolysis liquid, their chemical composition was determined. It varies significantly depending on the part of the plant and is a complex mixture of organic compounds that contains hundreds of chemicals in total [65].

In the oil fraction from AR leaves, mass spectra of 72 substances of organic nature were determined, which were combined into four groups (Figure 5).

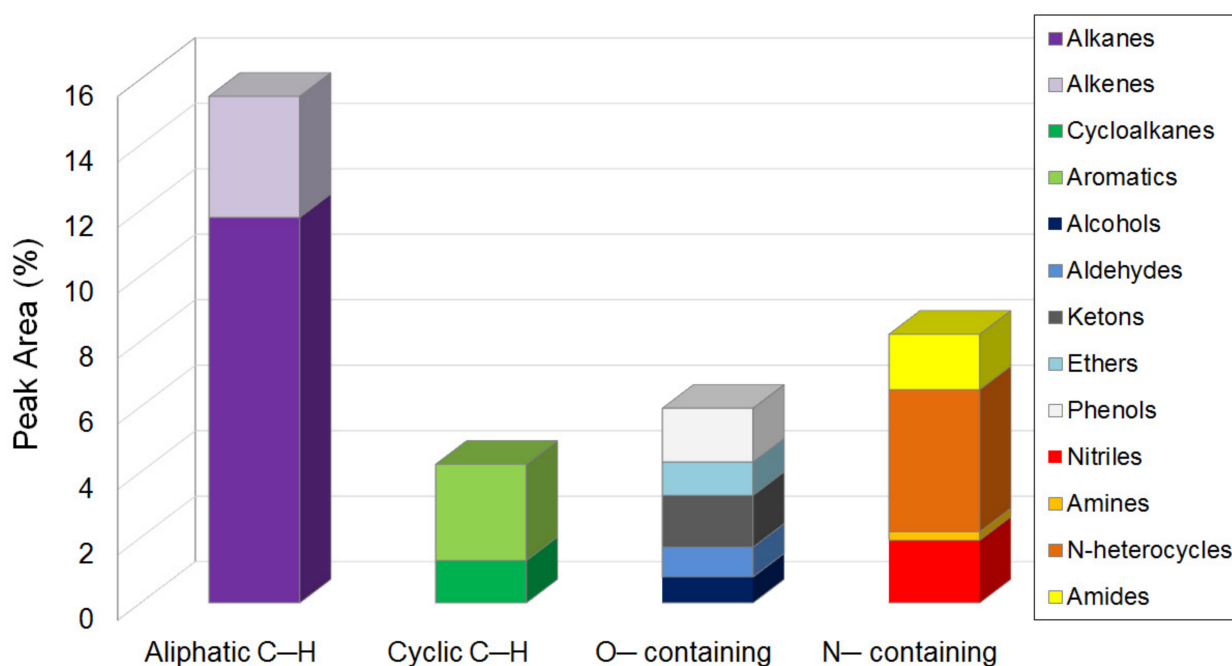


Figure 5. Chemical composition of the oil fraction from leaves.

In total, 33.8% of the total composition of the oil fraction was identified. The majority of all identified compounds are aliphatic hydrocarbons (15.5%), of which 11.8% are paraffinic hydrocarbons (C_{11} – C_{31}) and 3.7% are olefinic hydrocarbons (C_{12} – C_{23}). This carbon distribution is consistent with some bio-oils that can be used as liquid fuels in terms of carbon distribution [66,67]. A small part (4.23%) consists of cyclic hydrocarbons. The group of oxygen-containing components includes alcohols (0.79%), aldehydes (0.91%), ketones (1.58%), ethers (1.02%), and phenols (1.64%). Nitrogen-containing compounds account for 8.2%, more than half of which (4.34%) are heterocyclic in nature. The slight presence of seeds in the samples can lead to an increase in the content of hydrocarbons in bio-oil [68].

A GC–MS analysis of the oil fraction from AR inflorescences was also carried out, as a result of which the mass spectra of 80 organic substances were obtained (Figure 6). In total, 38.8% of the total composition of the liquid was identified.

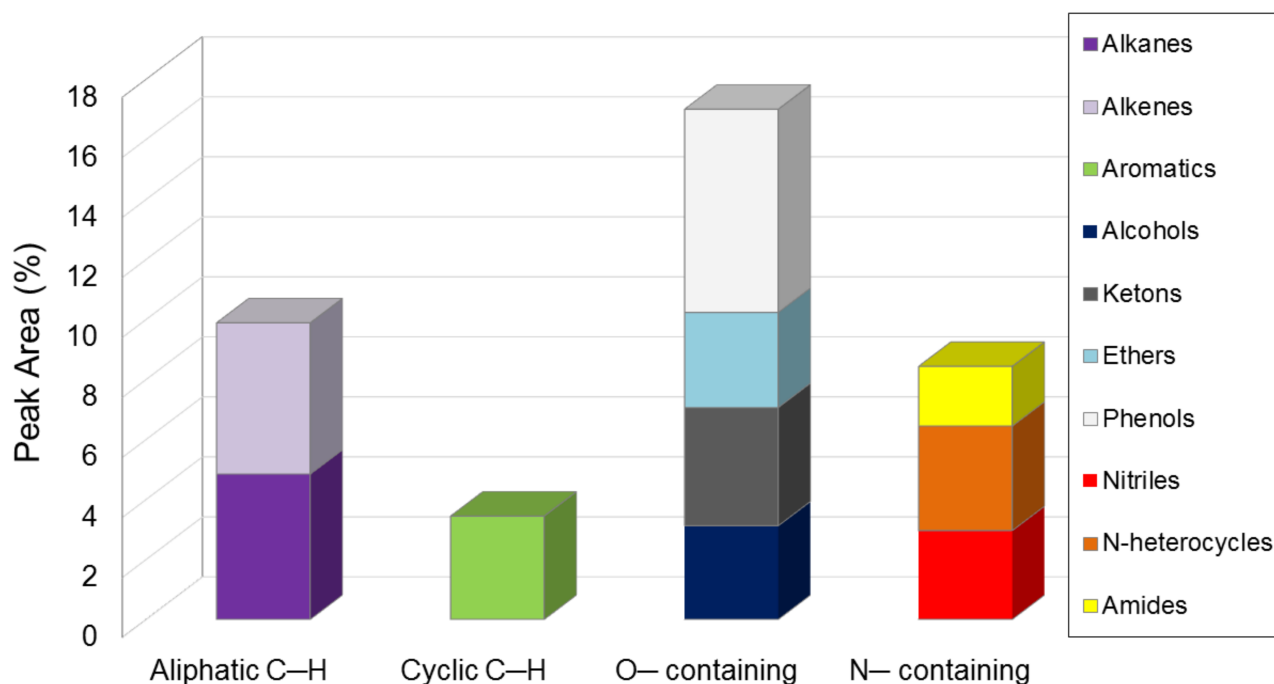


Figure 6. Chemical composition of the oil fraction from inflorescences.

There were marked changes in the composition of the oil fraction obtained from inflorescences relative to the composition of the oil fraction obtained from leaves. The main mass fraction of all identified compounds here is represented by an oxygen-containing group of substances (17%): alcohols (3.12%), ketones (3.94%), ethers (3.17%), and phenols (6.77%). At the same time, the proportion of phenols increased markedly. The content of aliphatic hydrocarbons decreased to 9.88%, mainly due to a decrease in the content of paraffinic hydrocarbons to 4.84%. The fractions of hydrocarbons also changed: paraffinic (C_{16} – C_{44}) and olefinic (C_{14} – C_{30}), respectively. Cyclic hydrocarbons make up 3.44%. Nitrogen-containing compounds account for 8.43%, of which less than half are heterocycles (3.48%).

The chemical composition of the pyrolysis liquid from the AR stems is mainly relatively simple and is represented by phenolic compounds (Figure 7). The data obtained are consistent with [4]. Phenolic compounds in bio-oil are a typical conversion product of lignocellulosic biomass, obtained mainly from the decomposition of lignin [69].

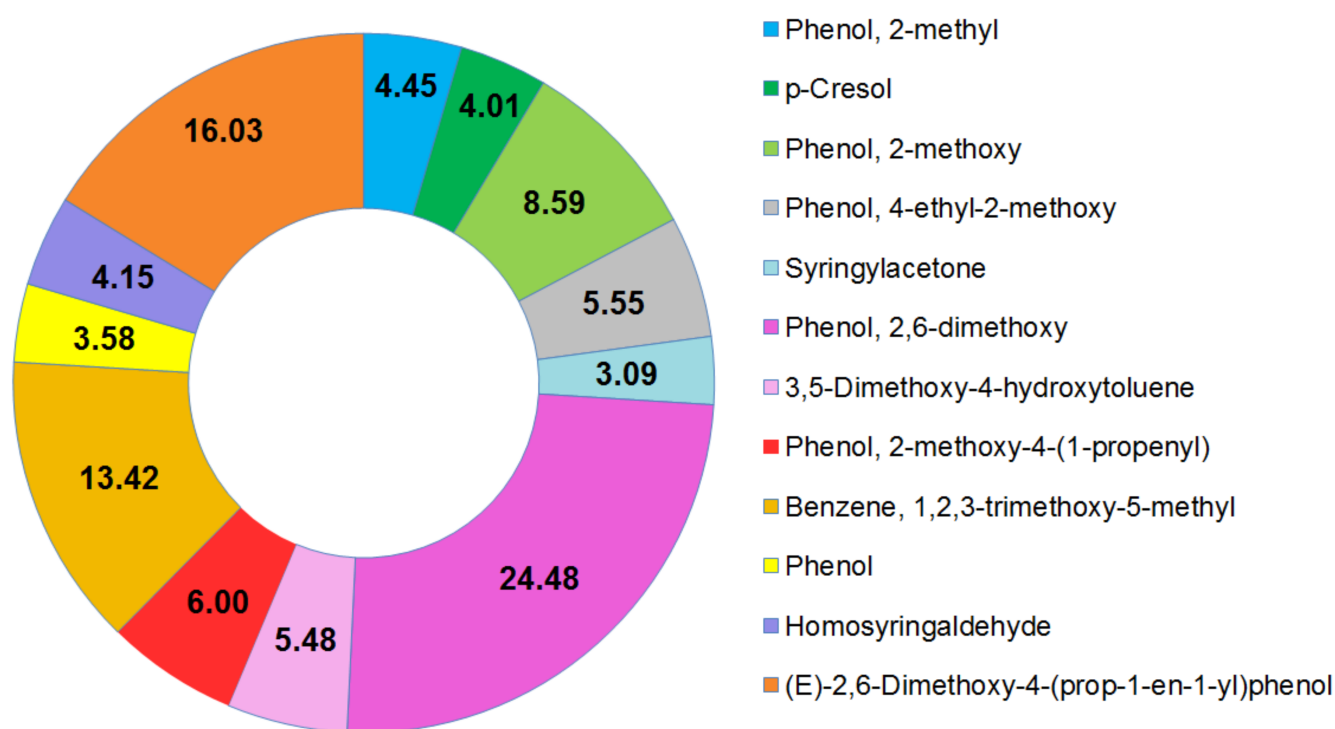


Figure 7. Chemical composition of the oil fraction of the stems.

Mass spectra of 12 organic substances were obtained. Phenolic compounds from AR stems have great potential to produce valuable chemical compounds.

3.5. Composition of Biochars

Biochar is a form of stable carbon and is a viable option for minimizing climate change and carbon footprint reduction. The pyrolysis process significantly increases the carbon content in the feedstock and converts it into stable aromatic compounds, increasing their number and density. The main characteristics of biochars obtained from AR are presented in Table 6. The highest amount of fixed carbon is found in samples from inflorescences, and the lowest from leaves. The ash content of the studied biochars varies from 31.9 to 46.8%. Leaves are characterized by the maximum ash content, and inflorescences are characterized by the minimum. The higher calorific value naturally decreases with the growth of the ash residue. The comparison of biochars obtained from inflorescences of AR weed and cultivated plants [70] showed that they have a similar composition; they contain a lot of calcium and potassium.

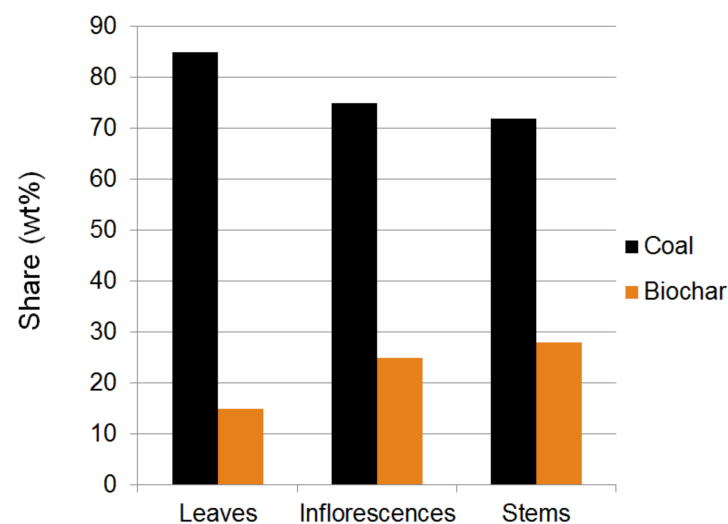
The study of the mineral part of biochar is a top priority when considering it as a fuel for power plants. Since most of the chemical elements contained in the samples have high melting and boiling points, after the pyrolysis process, they are concentrated in a solid carbonaceous residue. In the case of intensive slag formation processes, there is a high probability of not only unscheduled equipment shutdowns but also its failure due to the accumulation of uncontrolled amounts or forms of deposits. To predict the slag-forming and polluting properties of biochars, we determined the values of B/A , S_R , and F_u .

The optimal value of B/A , at which the fuel will not be slagged, should be less than 0.6. The value of this parameter indicates that the biochar ash of AR will be highly prone to slagging. The slag viscosity index S_R (>72) corresponds to a high viscosity and therefore a low tendency to slagging. The optimal value of the fouling index F_u should be less than 0.6. The parameters obtained indicate extreme slag formation in power equipment when using AR biochars.

Table 6. Results of the proximate analysis, oxide compositions of biochars, and slagging parameters.

Parameter	Leaves	Inflorescences	Stems
VM, wt%	35.1 ± 0.6	19.7 ± 0.7	20.4 ± 0.6
Ash, wt%	46.8 ± 0.4	23.3 ± 0.5	31.9 ± 0.5
FC, wt%	18.1 ± 0.4	57.0 ± 0.6	47.7 ± 0.5
HHV, MJ/kg	11.5	23.0	19.8
CaO, wt%	49.9	27.9	22.6
K ₂ O, wt%	27.6	51.1	64.2
MgO, wt%	8.3	3.34	3.6
P ₂ O ₅ , wt%	5.58	5.65	3.84
SO ₃ , wt%	4.58	2.68	1.64
SiO ₂ , wt%	2.51	4.21	0.54
Cl, wt%	0.75	3.89	3.11
Fe ₂ O ₃ , wt%	0.4	0.81	0.28
MnO, wt%	0.15	0.13	-
Br, wt%	0.08	0.02	0.01
SrO, wt%	0.08	-	0.02
ZnO, wt%	0.05	0.06	-
CuO, wt%	0.04	0.25	0.09
B/A	36.5	21.1	176
S _R	4.11	11.6	1.99
F _u	1009	1076	11,291

A promising solution to the problem is the use of composite fuel from a mixture of coal and biochar [71]. When using Krasnogorskiy coal (south of west Siberia) [72] in a mixture with biochars, one can obtain high-quality fuel with optimal *B/A* and *S_R* values (Figure 8).

**Figure 8.** Composite fuel composition.

If biochar is planned to be used without mixing with high-quality fuel, then it is advisable to use it as a soil additive. Adding biochar to the soil not only captures carbon, but also reduces greenhouse gas emissions from the soil, is a promising option for managing agricultural waste, increases soil resilience, reduces the need for fertilizers, and also has a number of other environmental benefits [73]. Thus, the use of biochar promotes carbon sequestration [74]. Mild conditions of thermochemical conversion (at temperatures below 600 °C) make it possible to avoid the melting of ash and retain nutrients in a form accessible to microorganisms and plants [75]. The removal of biomass from the biocenosis should not lead to the disruption of the biogeochemical cycle of substances, so it is advisable to use

biochars as soil additives. This use of biochar can also improve soil fertility by increasing its cation exchange and water retention capacity, as well as microbial activity [73,76,77].

A study [78] showed that biochar increased soil pH and improved its electrical conductivity, aggregate stability, water retention, and micronutrient content. In this case, it is necessary to take into account: soil type, seasonality, application rates, and characteristics of cultivated crops. In the study [76], it was noted that, depending on the feedstock and pyrolysis conditions, biochars have the most favorable effect on acidic and neutral soils. The authors of [79,80] proved that the introduction of biochar is of great importance for clay, sandy, and shale soils. The high content of calcium, potassium, magnesium, and phosphorus suggests that AR-derived biochars can not only improve soil structure, but also provide plants with essential nutrients. Thus, AR weed has a promising potential as a raw material for the production of soil additives.

4. Conclusions and Future Perspectives

In this study, an analysis was made of the possibilities of the thermal utilization of the aboveground biomass of the AR weed plant. The results of the proximate and ultimate analysis confirm the potential use of the studied samples in thermochemical conversion processes. TGA showed that the thermal decomposition of the studied AR biomass is similar to the process of pyrolysis of lignocellulosic materials and proceeds in three main stages, which are characterized by the processes of drying, release of volatile components, and carbonation. As a result of the study of the pyrolysis process in a laboratory setting at a temperature of 550 °C, three products were obtained: gas, bio-oil, and biochar. The composition of pyrolysis products is dominated by bio-oil or pyrolysis liquid, which is associated with the rich chemical composition of AR biomass. The main part of the oil fraction of AR leaves is aliphatic hydrocarbons (15.5%). The pyrolysis liquid from the inflorescences is represented by oxygen-containing compounds (17%). The chemical composition of the liquid product from AR stems is relatively simple and mainly by phenolic compounds. The results obtained allow us to conclude that the oil fractions of the pyrolysis liquid of AR parts can be used both as a fuel and as a source of valuable chemicals. An analysis of the characteristics and microelement composition of biochars showed that they can be used to produce composite fuel, for example, mixed with coal. It should be noted that all obtained biochars have a high potential as a raw material for the production of soil additives. The results of the study made it possible to study in detail the potential of using AR from its aboveground biomass to produce new liquid and solid products with high added value.

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Nomenclature

List of abbreviations and symbols

Letters of the Latin alphabet

C	carbon atom
H	hydrogen atom
C-H	hydrocarbons

Abbreviations

AR	<i>Amaranthus retroflexus</i>
ASTM	American Society for Testing and Materials
B/A	basic-acid ratio
C	carbon content (wt%)
°C	degree Celsius
DTG	differential thermogravimetric
FC	fixed carbon (wt%)
F_u	fouling index
g	gram
GC-MS	Gas chromatography—mass spectrometry
H	hydrogen content (wt%)
HHV	higher heating value (MJ/kg)
k	coverage factor
kV	kilovolt
m	weight (g)
m	meter
mg	milligram
MJ/kg	megajoule per kilogram
mL/min	milliliter/minute
mm	millimeter
n	number of repeated measurements
N	nitrogen content (wt%)
O	oxygen content (wt%)
r	given allowable relative discrepancy
s	second
S	sulfur content
S_R	slag viscosity index
TG	thermogravimetric
VM	volatile matter (wt%)
W	watt
μm	micrometer
u	uncertainty

Greek symbols

Δ	limit of weighing error
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Superscripts and subscripts

AR	<i>Amaranthus retroflexus</i>
i	sequence number of the experiment

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