Camelina and Crambe Oil Crops for Bioeconomy—Straw Utilisation for Energy

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Abstract: Agriculture can provide biomass for bioproducts, biofuels and as energy feedstock with a low environmental impact, derived from carbohydrate, protein and oil annual crops, as well from lignocellulosic crops. This paper presents the thermophysical and chemical features of camelina and crambe straw depending on nitrogen fertilisation rate with a view to their further use in a circular bioeconomy. A two-factorial field experiment was set up in 2016, with camelina and crambe as the first factor and the N fertilizer rate (0, 60 and 120 kg·ha^{-1}·N) as the second factor. Ash content in crambe straw (6.97% d.m.) was significantly higher than in camelina straw (4.79% d.m.). The higher heating value was higher for the camelina (18.50 MJ·kg^{-1}·d.m.) than for the crambe straw (17.94 MJ·kg^{-1}·d.m.). Sulphur content was also significantly higher in camelina than in crambe straw. An increase in nitrogen content with increasing fertilisation rate was visible in the straw of both species (from 1.19 to 1.33% d.m., for no fertilisation and for a rate of 120 kg·ha^{-1}·N, respectively). Crambe straw contained more than five times more chlorine than camelina straw. In conclusion, despite certain adverse properties, camelina and crambe straw can be an alternative to other types of biomass, both for direct combustion, gasification and in the production of second-generation biofuels.

Keywords: biomass; bioenergy; circular bioeconomy; oil crops; agricultural residues; thermophysical and chemical features

1. Introduction

The European Union is taking on increasingly ambitious challenges concerning a sustainable bioeconomy and closing the circulation of energy and materials used in production. It is estimated that the bioeconomy market is worth 2.4 billion euros and employs approx. 22 million people [1,2]. Moreover, the EU has set further ambitious goals concerning bioeconomy and sustainable development. The European Commission is developing new policies concerning renewable energies and agriculture (e.g. The European Green Deal, EU Biodiversity Strategy for 2030) and expects to spend approx. 1 trillion euros over the next 10 years. Moreover, the European Commission is developing the first European Climate Law, with a binding climate neutrality target [3]. There is a need for feedstock for biobased materials and bioenergy supported by the Renewable Energy Directive (RED II). In RED II, the biofuels, bioliquids and biomass fuels produced from food or feed crops should be zero in 2030. Moreover, the directive sets a target for 3.5% advanced biofuels in 2030 (0.2% in 2022, 1% in 2025) which need to be produced from non-food crops or lignocellulosic residues to be categorized as advanced [4].

Agriculture can provide various kinds of biomass for bioproducts, biofuels and as energy feedstock with a low environmental impact, derived from carbohydrate, protein and oil annual crops, as well from dedicated lignocellulosic crops [5–8]. Camelina (*Camelina sativa*) and crambe (*Crambe abyssinica*)

are oilseed crops proposed by scientists and industry, adapted to the European climate and tested in many European research projects [9]. Their features include high oil levels in seeds and fatty acid profiles which are of interest to industry. Camelina contains 14–16% oleic acid, 15–23% linoleic acid, and 31–40% linolenic and 12–15% eicosenoic acids [10]. Crambe oil contains a high (>54%) share of erucic acid [11]. Owing to these features, oils of both these crops are used in lubricants, rubber additives, nylon, hydraulic fluids, jet fuel, biodiesel and other products [10,12–14]. Obviously, these crops are grown to obtain oil from seeds, but not only this component should be used. Crambe and camelina seeds account for 44–45% of the total harvested biomass, with straw accounting for the rest of the biomass [15]. This can be used for other energy-related purposes: thermal and electric energy and production of bioethanol and biogas, as well as in the production of biocarbon [16–18]. Considering the above, experiments concerning the yield, energy efficiency and economic efficiency, as well as the environmental aspects of, crambe and camelina production have been conducted in the University of Warmia and Mazury in Olsztyn since 2015 [5,15,19,20]. One of the experiments analysed energy input, energy output and energy efficiency indices in camelina and crambe biomass (seeds, oil, straw) production depending on the rate of mineral nitrogen (N) fertilizer application (0, 60 and 120 kg·ha^{-1}·N). The above studies focused mainly on the use of oils from the crops for chemical purposes. The research team decided to also determine the possibilities of utilising agricultural residues, i.e. straw. Therefore, the aim of this communication is to present the thermophysical and chemical properties of camelina and crambe straw depending on the nitrogen fertilisation rate with a view to its further use in a circular bioeconomy, mainly for energy.

2. Materials and Methods

2.1. Field Experiment

A two-factorial split-plot design field experiment in four replicates was set up in 2016, with camelina and crambe species as the first factor and nitrogen fertilizer rate (0, 60 and 120 kg·ha^{-1}·N) as the second factor. The experiment was set up at the Didactic and Research Station in Łężany (N:53°57′, E:21°08′), owned by the University of Warmia and Mazury in Olsztyn (UWM). The soil was classified as Eutric Cambisols soil formed from silt founded on weakly loamy, silty sand. It was classified as quality class IVa. The sowing density was 500 plants·m^{-2} for camelina and 200 plants·m^{-2} for crambe. The plants were sown in the first week of April. Seeds and straw of both crops were harvested with a Wintersteiger plot harvester in the third week of August. Immediately after the harvest, straw was taken for laboratory analyses as bulk samples for each species and fertilisation rate (from four replicates).

2.2. Laboratory Analyses

Representative 300 g samples of straw were placed in tightly-sealed plastic bags to prevent any changes in their moisture content in transport. After the samples were delivered to the laboratory, their moisture content was determined by drying at 105 °C until a constant weight was achieved followed by weighing [21]. Dried straw was ground in a mill and reduced from the collective sample to a laboratory sample (ca. 50 g) in accordance with PN-EN 14780:2011 [22]. The obtained samples were ground in an analytic mill to a diameter of under 1.0 mm for further analyses.

The ash content, fixed carbon and volatile matter content was determined with a TGA THERMOSTEP thermogravimetric oven manufactured by ELTRA, used in accordance with PN-EN ISO 18123:2016-01 [23].

A C-2000 calorimeter (IKA WERKE) was used to determine the higher heating value by the dynamic method [24]. The nitrogen content in the biomass was determined by Kjeldahl's method as per the norm modified by Zinneke, on a K-435 mineraliser and a B-324 BUCHI distilling device. The contents of carbon, hydrogen and sulphur were determined with an ELTRA CHS 500 automatic

analyser [25,26]. Chlorine in the biomass was determined with an Eschka mixture by Mohr's method. All analyses were performed in three replicates.

2.3. Statistical Analysis

A two-way analysis of variance was carried out to determine the effects of species, nitrogen fertilization rate and the interactions between these factors for all analysed features of straw. The level of significance of the analysis was established at $p < 0.05$. Homogeneous groups for the examined features were determined by Tukey's multiple-comparison test (HSD). All analyses were done with STATISTICA 13.3 software (Tibco Inc.).

3. Results and Discussion

Table 1 presents p-values of the camelina and crambe straw depending on the experimental factors, including species (factor A), fertilisation level (0; 60; 120 kg·ha^{-1}) (factor B) and interaction between these factors (A × B). Based on the results, it was found that all the traits (dependent variables) significantly differed by at least one experimental factor or factor interaction. The camelina and crambe straw (factor A) did not only differ with respect to their moisture and nitrogen contents. For the fertilisation rate, no significant differences were noted in the straw quality (fixed carbon, elemental carbon and sulphur content). Only two traits, i.e. the fixed carbon and elemental carbon contents, were not changed by the A × B interaction. Detailed differences in the studied traits are presented in further in the study results, tables and figures.

Table 1. p-value of tested traits for camelina and crambe (factor A) straw depending on nitrogen fertilisation rate (0, 60, 120 kg·ha^{-1}·N) (factor B); fixed carbon (FC), volatile matter (VM), higher heating value (HHV), lower heating value (LHV). Significance at $p < 0.05$.

Source of Variation	Moisture	FC	Ash	VM	HHV	C	H	S	N	Cl
Species (A)	0.06	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.06	<0.001
N rate (B)	<0.001	0.20	<0.001	0.007	<0.001	0.08	0.02	0.18	<0.001	<0.001
A × B	<0.001	0.10	<0.001	<0.001	<0.001	0.19	0.004	<0.001	<0.001	<0.001

The moisture content of freshly harvested straw was not differentiated by crop species and was 55.68% (Table 2). The moisture content in straw obtained at the rate of 120 kg·ha^{-1}·N variant (57.06%) was significantly higher than at the other two rates. The crop × N-rate interaction also significantly differentiated the biomass moisture content, which ranged from 51.75% to 57.64%, for Camelina N0 and Camelina N120, respectively. High moisture content in straw after biomass harvest is caused by the fact that camelina pods and crambe fruits dry faster than the rest of the plant. Moreover, seed shattering is weaker when the crops are harvested at an early phase of ripeness [10,27]. Delaying seed harvest results in large losses, especially in the case of crambe (more than 25%) [20]. Therefore, plants should be collected earlier and straw should be left to dry naturally in swaths before being baled.

The mean fixed carbon content was 20.23% d.m. and was differentiated only by the crop species (Table 2). Its content in camelina straw was higher than in crambe straw—20.90% and 19.56% d.m., respectively. Volatile matter was significantly differentiated both by the principal factors and by the interaction. A significantly higher content of these compounds was found in the straw of camelina (74.32% d.m.) than in crambe (Table 2). An increase in the nitrogen fertilisation rate also brought about a significant decrease in volatile matter content compared to no fertilisation, by 0.20 and 0.35 p.p., respectively. On the other hand, considering the interaction of both these attributes, one can claim that the straw of camelina contained more volatile matter than crambe (range 73.27–74.74% d.m.).

Table 2. Moisture content, fixed carbon (FC), volatile matter (VM) and ash content of camelina and crambe straw depending on the nitrogen rate.

Source of Variation		Moisture (%)	FC (% d.m.)	VM (% d.m.)	Ash (% d.m.)
Species (A)	Camelina	55.48 ± 2.8	20.90 ± 0.1 [a]	74.32 ± 0.4 [a]	4.79 ± 0.4 [b]
	Crambe	55.87 ± 0.5	19.56 ± 0.2 [b]	73.47 ± 0.2 [b]	6.97 ± 0.1 [a]
N rate (B)	0	53.72 ± 2.2 [b]	20.32 ± 0.7	74.08 ± 0.7 [a]	5.60 ± 1.4 [c]
	60	56.26 ± 1.0 [b]	20.20 ± 0.7	73.73 ± 0.5 [ab]	6.07 ± 1.1 [a]
	120	57.06 ± 0.7 [a]	20.16 ± 0.9	73.87 ± 0.2 [b]	5.96 ± 1.0 [b]
A × B	Camelina 0	51.75 ± 0.2 [d]	20.97 ± 0.1	74.74 ± 0.1 [a]	4.30 ± 0.01 [d]
	Camelina 60	57.05 ± 0.7 [ab]	20.78 ± 0.02	74.19 ± 0.1 [b]	5.03 ± 0.1 [c]
	Camelina 120	57.64 ± 0.03 [a]	20.94 ± 0.2	74.03 ± 0.2 [bc]	5.03 ± 0.06 [c]
	Crambe 0	55.68 ± 0.2 [c]	19.67 ± 0.2	73.42 ± 0.2 [cd]	6.91 ± 0.003 [b]
	Crambe 60	55.47 ± 0.2 [c]	19.62 ± 0.2	73.27 ± 0.05 [d]	7.11 ± 0.1 [a]
	Crambe 120	56.47 ± 0.5 [b]	19.39 ± 0.07	73.72 ± 0.07 [c]	6.90 ± 0.02 [b]
Mean	-	55.68 ± 2.0	20.23 ± 0.7	73.89 ± 0.5	5.88 ± 1.2

± standard deviation; [a], [b], [c], . . . letters means that values are statistically different (Tukey's test at $p < 0.05$).

Ash content was also differentiated by the crop species, N rate and the interaction of these factors (Table 2). Ash content in crambe straw (6.97% d.m.) was significantly higher than in camelina straw (4.79% d.m.). It was significantly the lowest in non-fertilised straw (5.60% d.m.), and significantly the highest in fertilised straw (at the rate of 60 kg·ha^{-1}·N). Nitrogen fertilisation (both rates) significantly increased the ash content in camelina straw by 0.73 p.p. However, the ash content in crambe straw was significantly higher and ranged from 6.90% d.m. to 7.11% d.m. In general, nitrogen fertilisation brought about a slight, though significant, increase in ash content in the straw of both crop species, although the species-related differentiation of the attribute was more noticeable in this case. The ash level in camelina straw was much lower. This is important from an energy generation and industrial perspective because of the adverse effect of ash on further biomass use, especially for combustion. According to some studies, ash deposition decreases the combustor utilization efficiency, damages the combustor equipment and causes maintenance problems [28,29]. However, the ash content in biomass is usually much lower than in fossil fuels, especially in the biomass of dedicated energy crops, followed by straw and agricultural residues [30,31].

The higher heating value (HHV) was differentiated significantly by the main factors of the experiment and their interaction. The value of this attribute for the camelina straw was significantly higher (18.50 MJ·kg^{-1}·d.m.) than for crambe straw (17.94 MJ·kg^{-1}·d.m.) (Figure 1). Non-fertilised straw and straw of both species fertilised at 60 kg·ha^{-1}·N had significantly higher HHVs than straw fertilised at 120 kg·ha^{-1}·N. For interactions of both factors, the two highest HHVs were, significantly, for camelina straw non-fertilised and fertilised at a lower rate (18.80 and 18.54 MJ·kg^{-1}·d.m., respectively). Significantly, the lowest value of the attribute was determined for crambe straw in variants with no fertilisation and with fertilisation at 120 kg·ha^{-1}·N: 17.76 and 17.94 MJ·kg^{-1}·d.m., respectively.

Since camelina and crambe straw contain high moisture levels at harvest, they should be left to dry naturally in swaths before baling to achieve higher LHV, and, in consequence, higher energy gain per 1 ha. In the authors' other studies, it was found that the energy gain from naturally dried straw can be 32.8–36.3 and 37.9–41.4 GJ·ha^{-1}, depending on the fertilisation rate, and is ca. 54% and 52% of the energy present in total harvested biomass (harvested straw and seeds), for camelina and crambe, respectively [15].

The mean elemental carbon content was 50.72% d.m. and it was significantly differentiated by the crop species (Table 3). The element content in camelina straw (51.70% d.m.) was higher than in crambe straw (49.73% d.m.). However, hydrogen content was significantly differentiated by both the main factors and by their interaction. The hydrogen content was higher by 0.22 p.p. in camelina straw than in crambe straw. Significantly higher hydrogen content was found in straw from plots with no

fertilisation and from those fertilised at 120 kg·ha^{-1}·N (6.44% d.m. in both variants) than from the plot fertilised at 60 kg·ha^{-1}·N (6.34% d.m.). An analysis of the species × N rate interaction shows a significantly higher hydrogen content in straw from camelina plots with no fertilisation and fertilised at the higher rate. The other values made up a second homogeneous group with the element content ranging from 6.29% d.m. to 6.34% d.m.
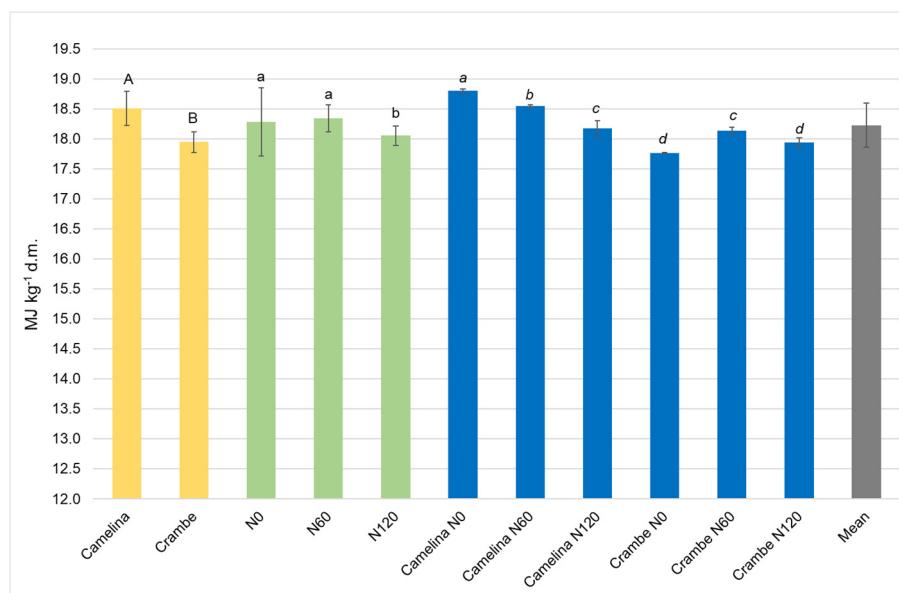
Figure 1. Higher heating value of camelina and crambe straw depending on fertilization rate; error bars-standard deviation; letters indicate that values are statistically different (Tukey's test at *p* < 0.05).

Sulphur content was significantly higher in camelina straw (0.284% d.m.) than in crambe straw (0.216% d.m.) (Table 3). Nitrogen fertilisation alone did not change this attribute for the straw of these species, and the mean value was 0.250% d.m. However, significant differences were observed when interactions of both factors were taken into account. Camelina straw contained more sulphur, with its content decreasing with increasing fertilisation rates, whereas sulphur content in crambe was significantly lower and not differentiated by the fertilisation rate (the last homogeneous group, with a sulphur content of 0.210–0.222% d.m.).

Table 3. Elemental composition of camelina and crambe straw depending on nitrogen rate (carbon, hydrogen, sulphur, nitrogen and chlorine).

Source of Variation		C (% d.m.)	H (% d.m.)	S (% d.m.)	N (% d.m.)	Cl (% d.m.)
Species (A)	Camelina	51.70 ± 0.7 [a]	6.50 ± 0.1 [a]	0.284 ± 0.013 [a]	1.27 ± 0.03	0.097 ± 0.01 [b]
	Crambe	49.73 ± 0.4 [b]	6.32 ± 0.05 [b]	0.216 ± 0.006 [b]	1.27 ± 0.14	0.531 ± 0.06 [a]
N rate (B)	0	51.03 ± 1.4	6.44 ± 0.1 [a]	0.249 ± 0.038	1.19 ± 0.1 [a]	0.312 ± 0.3 [b]
	60	50.34 ± 0.9	6.34 ± 0.04 [b]	0.254 ± 0.048	1.29 ± 0.06 [b]	0.343 ± 0.3 [a]
	120	50.79 ± 1.2	6.44 ± 0.2 [a]	0.246 ± 0.028	1.33 ± 0.04 [c]	0.288 ± 0.2 [c]
A × B	Camelina N0	52.21 ± 0.6	6.56 ± 0.02 [a]	0.284 ± 0.008 [ab]	1.29 ± 0.01 [b]	0.083 ± 0.006 [d]
	Camelina N60	51.02 ± 0.6	6.34 ± 0.01 [b]	0.297 ± 0.008 [a]	1.23 ± 0.01 [c]	0.095 ± 0.006 [d]
	Camelina N120	51.88 ± 0.02	6.59 ± 0.1 [a]	0.271 ± 0.008 [b]	1.29 ± 0.01 [b]	0.112 ± 0.006 [b]
	Crambe N0	49.85 ± 0.2	6.33 ± 0.02 [b]	0.215 ± 0.003 [c]	1.09 ± 0.01 [d]	0.540 ± 0.006 [b]
	Crambe N60	49.67 ± 0.7	6.33 ± 0.06 [b]	0.210 ± 0.002 [c]	1.35 ± 0.01 [a]	0.590 ± 0.006 [a]
	Crambe N120	49.69 ± 0.5	6.29 ± 0.05 [b]	0.222 ± 0.004 [c]	1.36 ± 0.01 [a]	0.463 ± 0.006 [b]
Mean	-	50.72 ± 1.2	6.41 ± 0.1	0.250 ± 0.037	1.27 ± 0.10	0.314 ± 0.2

± standard deviation; [a], [b], [c], ... letters means that values are statistically different (Tukey's test at *p* < 0.05).

The nitrogen content in the straw of both species was at the same level of significance and was 1.27% d.m. (Table 3). An increase in nitrogen content with increasing fertilisation rate was visible in the straw of both species (from 1.19 to 1.33% d.m.) for no fertilisation and for the rate of 120 kg·ha^{-1}·N, respectively. The interaction of both factors showed that, significantly, the highest content of the element was in the straw of crambe on fertilised plots (1.35 and 1.36% d.m., for the N rate of 60 and 120 kg·ha^{-1}, respectively), and the lowest was in the straw of non-fertilised crambe.

The chlorine content was also differentiated significantly by the crop species, N rate and the interaction of these factors (Table 3). Crambe straw contained more than five times more chlorine than camelina straw. Significantly, the highest chlorine content was found in straw from plots fertilised at 60 kg·ha^{-1}·N, whereas it was significantly the lowest on plots fertilised at 120 kg·ha^{-1}·N. For the interaction of these factors, significantly, the lowest chlorine content was determined for camelina grown with no nitrogen fertilisation (0.083% d.m.) and fertilised at the rate of 60 kg·ha^{-1}·N (0.095% d.m.). Significantly, the largest amount of this element was found in crambe straw obtained at the fertilisation rate of 60 kg·ha^{-1}·N (0.590% d.m.).

Nitrogen, chlorine and sulphur have an adverse effect on the thermal and thermochemical conversion of biomass as well as on the environment and human health. The straw of annual plants usually contains up to six times more ash and four times more chlorine and sulphur than dedicated energy crops and woody biomass. However, it contains less sulphur and nitrogen than coal, although it may contain up to twice as much chlorine [31–33]. Chlorine is undesirable in biomass as it causes corrosion, whereas sulphur and nitrogen cause the emission of sulphur and nitrogen oxides to the atmosphere in the process of biomass combustion. Shao et al. [28] reports that the water-soluble potassium and chlorine in biomass fuels are the most problematic elements during biomass combustion and can result in severe ash deposition/fouling/slagging and high-temperature corrosion.

4. Conclusions

Cereal (e.g., wheat or barley) straw is commonly used as an energy feedstock in Europe. However, it is also used for other purposes, e.g. as animal bedding or in mushroom production. Moreover, it has been pointed out in numerous studies that at least 25% of straw should return to the soil to maintain the organic substance balance and to prevent organic carbon depletion. Therefore, a shortage of cereal straw caused by competition from other sectors, as well as the needs of sustainable agricultural production, can be compensated for by camelina and crambe straw, which have similar thermophysical and chemical properties. Obviously, as in the case of cereal straw, only adequate amounts of straw should be collected and used to avoid unfavourable effects on soil properties. Both camelina and crambe straw offer similar energy values to cereal straw. Moreover, the content of compounds that are undesirable in heat generation is similar in camelina, crambe, cereal and rapeseed straws. Despite certain adverse properties, camelina and crambe straw can be an alternative to other types of biomass, both for direct combustion, gasification and in the production of second-generation biofuels. This fact is of great importance due to the increasing demand for bioproducts and bioenergy as well as the obligation to reduce the utilisation of edible parts of crops (e.g. cereal grain and oilseeds, potato tubers or sugar beet, etc.) in bioproduct production and bioenergy generation.

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