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Characteristic Properties of Alternative Biomass Fuels

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Abstract: Biomass is one of the most promising renewable energy sources because it enables energy accumulation and controlled production. With this, however, the demand for biofuels grows and thus there is an effort to expand their portfolio. Nevertheless, to use a broader range of biofuels, it is necessary to know their fuel properties, such as coarse and elemental analysis, or lower heating value. This paper presents the results of testing the fuel properties of several new, potentially usable biofuels, such as quinoa, camelina, crambe, and safflower, which are compared with some traditional biofuels (wood, straw, sorrel, hay). Moreover, the results of the determination of water content, ash, and volatile combustible content of these fuels are included, along with the results of the elemental analysis and the determination of higher and lower heating values. Based on these properties, it is possible to implement designs of combustion plants of different outputs for these fuels.

Keywords: biomass analysis; alternative biofuels; emissions

1. Introduction

Nowadays, there is increasing pressure on the use of renewable sources of fuel in domestic boilers. The primary renewable energy source is plant biomass [1]. A promising form of biomass is energy crops, which are usually compressed into pellets for combustion [2]. The number of pellets made of alternative non-wood material, so-called agropellets, is continuously increasing. Agropellets are produced by pressing agricultural commodities, such as energy plants, rapeseed and cereal straw, waste, oilcake, and others [3]. The combustion of agrofuels generates minimal greenhouse gases and other potentially hazardous emissions under optimal conditions relative to conventional fuels [4]. Biomass is even considered neutral from the point of view of carbon dioxide production since the amount of carbon dioxide produced by combustion is comparable to the amount consumed by plants as they grow. The amount of these substances released during combustion is influenced by the composition of the fuel, the type of combustion equipment used, the setting of the combustion process, etc. One of the factors that significantly affects the combustion efficiency and potential emissions production is the characteristics of the biomass combusted. In addition to solid biofuels, there are also liquid and gaseous biofuels that are the product of solid biofuel transformation processes; however, this study does not focus on them.

Biomass is composed of organic and inorganic substances containing mainly carbon, hydrogen, and oxygen. In addition to these essential elements, there are also often nitrogen, chlorine, iron, and alkali metals [5].

On the contrary, sulfur and heavy metals are only present in trace amounts compared to fossil fuels. The more of these elements the biomass contains, the higher the number of harmful substances will be released during its combustion. Moreover, the amount of these elements in biomass is greatly influenced by the type of biomass and the place of cultivation.

Emissions from biomass combustion can then be divided into three main groups:

- Pollutants from incomplete combustion: CO, C_xH_y, tar, soot, unburnt hydrocarbon particles, hydrogen, and incompletely oxygenated nitrogen compounds (HCN, NH_3, N_2O).
- Pollutants from complete combustion: nitrogen oxides (NO, NO_2) and CO_2.
- Pollutants from trace elements of impurities: incombustible dust particles, sulfur, chlorine compounds, and trace metals (Cu, Pb, Zn, Cd) [5].

The most monitored pollutants are carcinogenic, poisonous, and greenhouse gases. The most important pollutants are characterized in the following passage.

The quality of the combustion process determines the formation of carbon dioxide. The combustion of biomass is characterized by long-flame CO burning. Undesirable cooling results in the release of pure carbon (soot), resulting in significant heat losses. For this reason, the combustion and post-combustion chambers for biomass in the boiler bodies are much larger than for fossil fuels, and secondary or tertiary air is supplied to the flames. This results in improved combustion in terms of the chemistry of the reaction, which leads to a significant reduction in CO and unburned chemicals. In terms of sulfur oxides, biomass is considered ecological fuel compared to fossil fuels because the sulfur content from which sulfur oxides are produced during combustion processes is present only in low concentrations in biomass. Furthermore, the fuel releases large amounts of water vapor and hydrogen, with which sulfur reacts to form hydrogen sulfide (H_2S) [5,6].

Usually, about 0.5–5% of nitrogen is present in biomass [1–4]. All nitrogen content is converted into NO_x compounds during combustion. At temperatures of 700–800 °C, mainly N_2O is produced, which contributes to the greenhouse effect. At temperatures above 1000 °C the formation of NO prevails, which is unstable and oxidizes to NO_2, which is involved in the creation of photochemical smog, possibly due to a reaction with water to form acid rain (HNO_3) [7]. Domestic boilers, however, usually do not reach temperatures that lead to the formation of NO to such an extent [5]. Nevertheless, the values of NO_x emissions produced by the combustion of different biomass types with varying contents of nitrogen show an apparent effect of the increased nitrogen content in non-woody biomass on total NO_x emissions [8].

Chlorine is present in biomass in the form of inorganic and organic compounds. The fundamental problem caused by these substances in the flue gas is their reactivity and the high ability to corrode the materials they come into contact with. It is released into the environment during the combustion of fuels containing chloride (e.g., coal and some plant materials and wastes). Chlorine reacts with airborne water vapor to form hydrogen chloride. Hydrogen chloride gas is rapidly converted to hydrochloric acid, which contributes to the formation of acid rain [9].

One of the critical factors in terms of the optimization of the combustion process, construction of the fireplace, and distribution of combustion air distribution into primary, secondary, and possibly tertiary air is the proportion of volatile combustible material [10]. Increased portions of volatile combustible materials and a lack of secondary or tertiary air will lead to an increase in unburned chemicals and products of incomplete combustion (CO, C_xH_y) [3,5,10,11].

Emissions of particulate matter (PM) are also a significant problem in combustion. The formation of PM during biomass combustion is closely related to the release of inorganic substances and alkali metals from the fuel. These substances are fuel ash, and therefore the formation of PM is closely associated with the composition of fuel ash, specifically and predominantly with the number of alkali metals in the ash [12]. The polluting particles themselves are usually composed of the K, Cl, and S elements, which form aerosols and alkali metal sulfates, chlorides, and carbonates. The critical element in the composition of the dust particles is potassium, which is usually found in the form of K_2SO_4, KCl, and K_2CO_3 [13,14]. PM emissions may also be related to the phosphorus content of the fuel. Combustion of agropellets with a high phosphorus content produces PM consisting of the chlorides mentioned above, carbonates, and sulfates, plus an increased amount of phosphates [15].

Since all the emissions above and fuel behavior in combustion processes are related to the biomass composition, it is always necessary to know its properties, such as moisture, ash content, elemental composition, or lower heating value to optimize it.

This study aimed to investigate the fuel properties (such as coarse and elemental analysis, or lower heating value) of several new, potentially usable biofuels, such as quinoa, camelina, crambe, safflower, and compare them with some traditional biofuels (wood, straw, sorrel, hay). The obtained data can contribute to the expansion of the biofuel portfolio in energy production.

2. Materials and Methods

The section summarizes the subsections containing the description of tests, procedures of determination, processing of measured data, and formulas used for calculation of the monitored values. Determination of dry matter, water content, ash amount, and loss during annealing, determination of volatile combustible content, elemental analysis (C, H, N, S), determination of calorific value using the calorimetric method, and calculation of the lower heating value were performed.

For determination of the dry matter and water content of solid biofuels, three different gravimetric procedures were used based on standards ČSN EN ISO 18 134-1–3 [16–18], which were used depending on available sample amount. ČSN EN ISO 18 134-1 is a reference method that was used when a large amount of sample was available. The method in the calculation also included the so-called buoyancy effect on the hot sheet on which the analyzed sample was dried. The sample was weighed with an accuracy of 0.1 g. The result was calculated using the formula (1):

$$W_1 = \frac{(m_{1,2} - m_{1,3}) - (m_{1,4} - m_{1,5})}{(m_{1,2} - m_{1,1})} \times 100 \quad (\%), \tag{1}$$

where:

$m_{1,1}$—mass of empty sheet for sample (g),
$m_{1,2}$—mass of sample sheet before drying (g),
$m_{1,3}$—mass of sample sheet after drying (g),
$m_{1,4}$—reference sheet mass before drying (g), and
$m_{1,5}$—reference sheet mass after drying (g).

ČSN EN ISO 18 134-3 is a method that was used when only a limited amount of sample was available. A smaller sample volume was compensated for in this method by higher weighing accuracy requirements. The weighing was carried out only with wholly cooled samples. Both methods mentioned so far utilized oven drying at 105 °C until there was a constant mass. In the second case, the result was calculated according to Equation (2):

$$W_3 = \frac{(m_{3,2} - m_{3,3})}{(m_{3,2} - m_{3,1})} \times 100 \quad (\%), \tag{2}$$

where:

$m_{3,1}$—mass of empty crucible with lid (g),
$m_{3,2}$—mass of crucible with sample and lid before drying (g), and
$m_{3,3}$—mass of crucible with sample and lid after drying (g).

To determine the ash content of solid biofuels and the loss on annealing, a procedure based on the standard ČSN EN ISO 18 122 (Solid biofuels – Determination of ash content) [19] was used, where the sample was annealed in the furnace at 550 °C until a constant sample mass was reached. The result was then calculated as a percentage for both the raw and the anhydrous sample according to Equations (3) and (4):

Determination of ash content in the anhydrous sample:

$$A_d = \frac{m_3 - m_1}{m_2 - m_1} \times 100 \times \frac{100}{100 - M_{ad}}, \tag{3}$$

where:

m_1—mass of empty dish (g),
m_2—mass of dish with test portion (g),
m_3—mass of dish with ash (g), and
M_{ad}—the water content of the test portion used for the determination (%).
Determination of ash content in the raw sample:

$$A_r = \frac{m_3 - m_1}{m_2 - m_1} \times 100, \tag{4}$$

where:

m_1—mass of empty dish (g),
m_2—mass of dish with test portion (g), and
m_3—mass of dish with ash (g).

The determination of the volatile combustible solid biofuels content was performed gravimetrically according to the standard ČSN EN ISO 18 123 (Solid biofuels–Determination of volatile combustible content) when the biofuel sample was annealed at 900 °C for 7 min in a porcelain crucible with a lid inside an oven [20]. The resulting mass percent of volatile combustible in the sample was calculated using the following Equations (5) and (6):

Determination of volatile combustible content in an anhydrous sample:

$$V_d = \left[\frac{100(m_2 - m_3)}{(m_2 - m_1)} - M_{ad} \right] \times \left(\frac{100}{100 - M_{ad}} \right), \tag{5}$$

where:

m_1—mass of empty crucible with lid (g),
m_2—mass of crucible with sample and lid before heating (g),
m_3—mass of crucible with sample and lid after heating (g), and
M_{ad}—the percentage of the mass of the sample water content (%).
Determination of volatile combustible content in a raw sample:

$$V_d = \left[\frac{100(m_2 - m_3)}{(m_2 - m_1)} - M_{ad} \right], \tag{6}$$

where:

m_1—mass of empty crucible with lid (g),
m_2—mass of crucible with sample and lid before heating (g),
m_3—mass of crucible with sample and lid after heating (g), and
M_{ad}—the percentage of the mass of the sample water content (%).

Furthermore, the percentage of carbon, hydrogen, nitrogen, and sulfur in the sample was determined using elemental analysis and the oxygen content was calculated. The elementary analyzer Vario Macro cube CHNS (Elementar company) was used for the analysis, working on the principle of sample combustion in a catalytic tube, separation of different gases from monitored components by adsorption-desorption on columns, and subsequent detection using a thermal conductive detector [21]. The measured concentrations of individual elements in the original sample were also recalculated for combustible and dry matter according to the following Equations (7)–(9):

Determination of elemental content in a biofuel sample:

From the measured concentration values in the original sample (wt%) of carbon C^a, hydrogen H^a, nitrogen N^a, and sulfur S^a in the raw sample, the oxygen concentration O^a was calculated assuming that the elements C, H, N, S, and O constituted all the combustible content in the sample:

$$O^a = 100 - (C^a + H^a + N^a + S^a) - A^a, \tag{7}$$

where A^a is the ash content in the original sample (wt%).

When determining the concentrations of C, H, N, S, and O in a combustible content, it was necessary to assume that these elements together made up all the combustible content and water in the original sample. The water in the original sample consisted of only the elements H and O. From the molar masses of H and O, it was possible to determine the mass fraction of the given elements in water (H_2O):

$$H_{H_2O} = \frac{2 \times M(H)}{2 \times M(H) + M(O)} \times 100 = \frac{2 \times 1.0079}{2 \times 1.0079 + 15.999} \times 100 = 11.19, \tag{8}$$

$$O_{H_2O} = 100 - H_{H_2O} = 100 - 11.19 = 88.81, \tag{9}$$

where:

H_{H_2O}—hydrogen mass content in water (-),

O_{H_2O}—oxygen mass content in water (-),

$M(H)$—hydrogen molar mass (kg·mol^{-1}), and

$M(O)$—oxygen molar mass (kg·mol^{-1}).

By subtracting water from the original sample, the concentrations of H and O were reduced, while the concentrations of C, N, and S were maintained, as seen in Equations (10) and (11):

$$H^{a,red} = H^a - \left(H_{H_2O} - w_w \right) \tag{10}$$

$$O^{a,red} = O^a - \left(O_{H_2O} - w_w \right) \tag{11}$$

where:

$H^{a,red}$—reduced hydrogen concentration (wt%),

$O^{a,red}$—reduced oxygen concentration (wt%),

O^a—oxygen concentration in the original sample (wt%),

H^a—hydrogen concentration in the original sample (wt%),

H_{H_2O}—percentage by mass of hydrogen content in water (-), and

O_{H_2O}—percentage by mass of oxygen content in water (-).

Concentrations C^a, N^a, and S^a in the original sample, along with the reduced concentrations $H^{a,red}$ and $O^{a,red}$, together form real ratios related to the combustible content. These have to be recalculated to make up 100% of the combustible content; for a calculation example, see Equations (12) and (13):

$$C^{daf} = \frac{C^a}{C^a + H^{a,red} + N^a + S^a + O^{a,red}} \times 100, \tag{12}$$

$$H^{daf} = \frac{H^{a,red}}{C^a + H^{a,red} + N^a + S^a + O^{a,red}} \times 100, \tag{13}$$

where:

C^{daf}—the concentration of carbon in the combustible content (wt%),

H^{daf}—hydrogen concentration in the combustible material (wt%),

C^a—carbon concentration in the original sample (wt%),

$H^{a,red}$—reduced hydrogen concentration (wt%),

N^a—nitrogen concentration in the original sample (wt%),

S^a—sulfur concentration in the original sample (wt%), and

$O^{a,red}$—reduced oxygen concentration (wt%).

Subsequently, the remaining concentrations were calculated for N^{daf}, S^{daf}, and O^{daf} in the combustible content similarly.

A simple relation was used to convert the concentrations of the elements C, H, N, S, and O in the combustible content to the concentrations of individual elements in the dry matter (only the sample relation for C is described here):

$$C^{dr} = \frac{w_{daf}^{dr} \times C^{daf}}{100},$$ (14)

where:

C^{dr}—the concentration of carbon in dry matter (wt%),

C^{daf}—carbon concentration in the combustible content (wt%), and

w_{daf}^{dr}—combustible content in dry matter (wt%).

The concentrations H^{dr}, N^{dr}, S^{dr}, and O^{dr} in the dry matter were subsequently calculated.

Subsequently, the calorific value of the selected materials was determined using an IKA C 200 calorimeter (IKA company) or a 6100 Compansated Calorimeter (Parr Instrument Company) following the standard ČSN EN ISO 18125 (Solid biofuels – Determination of higher and lower heating values). The principle was to burn the weighed analytical sample in an oxygen atmosphere at high pressure in a calorimeter vessel. The measured higher heating values determined by both calorimetric methods indicate the higher heating value of the original sample HHV^a. The following Equations (15) and (16) were used to convert the higher heating value of the original sample HHV^a to the higher heating value of dry matter HHV^{dr} and the higher heating value of the combustible content HHV^{daf} [22]:

$$HHV^{dr} = \frac{HHV^a}{W_{dr}} \times 100,$$ (15)

$$HHV^{dr} = \frac{HHV^{daf}}{w_{daf}^{dr}} \times 100,$$ (16)

where:

HHV^{daf}—the higher heating value of the combustible content (kJ·kg^{-1}),

HHV^{dr}—higher heating value of dry matter (kJ·kg^{-1}),

HHV^a—higher heating value of the original sample (kJ·kg^{-1}),

w_{daf}^{dr}—combustible content in dry matter (= loss by annealing in dry matter) (wt%), and

W_{dr}—dry matter content in the sample (wt%).

The lower heating value could then be calculated from the higher heating value using Equation (17). The lower heating value is defined as the higher heating value released by burning 1 kg of fuel minus the condensation heat of the water produced by combustion. In accordance with ČSN EN ISO 18 125 [23], Equation (17) was chosen to determine the lower heating value of the original sample LHV^a:

$$LHV^a = HHV^a - r_{H_2O}^{20°C} \times \left(W + 8.94 \times x_H^a\right),$$ (17)

where the concentration of combustible hydrogen in the original sample x_H^a was calculated using Equation (18):

$$x_H^a = \frac{H^{daf} \times w_{daf}^a}{100},$$ (18)

where:

LHV^a—lower heating value of the original sample (kJ·kg^{-1}),

HHV^a—higher heating value of the original sample (kJ·kg^{-1}),

$r_{H20}^{20°C}$—the evaporation heat of water at 20 °C has a value of 2454 (kJ·kg^{-1}),

W—concentration of water in the sample (wt%),

x_H^a—concentration of combustible hydrogen in the original sample (wt%),

H^{daf}—concentration of hydrogen in the original sample (wt%), and

w_{daf}^a—combustible content in the original sample (wt%).

For the calculation of the lower heating value of the dry matter LHV^{dr}, Equation (19) was used:

$$LHV^{dr} = HHV^{dr} - r_{H_2O}^{20°C} \times 8.94 \times x_H^{dr}, \tag{19}$$

where the concentration of hydrogen in dry matter x_H^{dr} was calculated using Equation (20):

$$x_H^{dr} = \frac{H^{dr}}{100}, \tag{20}$$

where:

LHV^{dr}—lower heating value of dry matter (kJ·kg^{-1}),

HHV^{dr}—higher heating value of dry matter (kJ·kg^{-1}),

$r_{H20}^{20°C}$—the evaporation heat of water at 20 °C has a value of 2,454 (kJ·kg^{-1}), and

x_H^{dr}—concentration of hydrogen in dry matter (wt%).

The following Equation (21) was used for the conversion from the lower heating value of dry matter to the lower heating value of the combustible content:

$$LHV^{daf} = \frac{LHV^{dr}}{w_{daf}^{dr}} \times 100, \tag{21}$$

where:

LHV^{daf}—the lower heating value of the combustible content (kJ·kg^{-1}),

LHV^{dr}—the lower heating value of the dry matter (kJ·kg^{-1}), and

w_{daf}^{dr}—combustible content in the dry matter (wt%).

3. Results and Discussion

Table 1 summarizes the measured water content values W, which was determined using the gravimetric method described in the previous section. The water content is an important parameter that affect fuel quality. Above all, it directly affects its lower heating value by reducing the dry matter content and by consuming heat to evaporate water during combustion [24]. During combustion, the combustion temperature may fall below the optimum value due to evaporative heat consumption.

Consequently, there is a risk of incomplete combustion of fuel and the generation of above-the-limit emissions [25]. If the flue gas temperature drops below the dew point, water condensation will occur, leading to an acceleration of the flue gas corrosion of the combustion device [26]. Ideally, the moisture of the material to be combusted is less than 15% in the case of pellets or less than 20% in the case of loose material. As can be seen from Table 1, the water content ranged from 3.82% to 11.92%, which meant the materials were suitable for combustion. The pellets had very low moisture contents, which partially caused the pellets to crumble and break. Low moisture in a very narrow range of values is influenced by storage in a dry and warm fuel storage environment. The standard deviation and the confidence interval were calculated for the average water content. From the moisture content, the dry matter content in the sample was found range between 88.08% and 96.18%.

After determining the moisture content and dry matter content, the ash contents of the raw and anhydrous samples were determined, and the loss during annealing and the ballast fraction were calculated from these data. After finding the water content, the ash content is another important parameter that characterizes the examined fuel sample. Table 2 shows that the lowest ash content of 0.3% was found in a wood pellet sample, which corresponded to the fact that only wood mass was present almost entirely in this sample. By contrast, in the case of agro-materials, the ash content is higher: hay 4.83%, sunflower 3.92%, and safflower 6.6%. An increased content of ballast substances was evident, which also corresponded to the increased value of the calculated ballast portion. The highest ash content was determined in samples with a high percentage of waste sludge present due to the increased occurrence of heavy metals and other hazardous elements contained in the combusted

material. This phenomenon is disadvantageous for the material to be burned because the increased ash content during the combustion makes the boiler operation more challenging in terms of removing the ash from the boiler body and faster filling of the ashbin.

Table 1. Results of the determination of water and dry matter contents in samples of biofuels.

Sample	Water Content W (wt%)	Dry Matter Content W_{dr} (wt%)	Standard Deviation	Confidence Interval
Digestate	8.43	91.57	0.07	0.08
Softwood pellets (spruce)	7.67	92.33	0.04	0.04
Hardwood pellets (beech)	7.84	92.16	0.07	0.08
Composite wood	9.49	90.51	0.05	0.06
Energo compost	9.35	90.65	0.24	0.27
Rape straw	10.62	89.38	0.08	0.09
Wheat straw pellet	7.16	92.84	0.02	0.02
Hay	7.96	92.04	0.08	0.09
Straw 60% + sludge 40%	3.86	96.11	0.03	0.03
Straw 70% + sludge 30%	3.82	96.18	0.02	0.02
Straw 80% + sludge 20%	4.39	95.61	0.04	0.04
Straw 90% + sludge 10%	4.79	95.21	0.09	0.1
Sunflower—peel	7.71	92.29	0.05	0.06
Sunflower—after the oil press	6.09	93.91	0.06	0.07
Sunflower—whole plant	10.58	89.42	0.32	0.36
Mix—seeds rape, sunflower, mustard, husks	11.92	88.08	0.05	0.06
Mustard—seed	5.88	94.12	0.17	0.19
Spruce sawdust + digestate	6.44	93.56	0.09	0.10
Safflower—seed	5.41	94.59	0.09	0.10
Safflower—peel	5.49	94.51	0.09	0.10
Safflower—after the oil press	7.08	92.92	0.12	0.13
Amaranth	6.69	93.31	0.02	0.02
Flax—waste	5.42	94.58	0.08	0.09
Crambe abyssinica	5.49	94.51	0.04	0.04
Camelina—seed	5.95	94.05	0.01	0.01
Camelina—after the oil press	7.10	92.90	0.08	0.09
Spelt—waste	8.06	91.94	0.04	0.04
Cocoa—peel	7.34	92.66	0.03	0.03
Sorrel pellet (whole plant)	8.64	91.36	0.05	0.05
Rye straw	7.69	92.31	0.12	0.13
Quinoa—waste	8.43	91.57	0.03	0.03

Notes: The accuracy of the determination methods were below 0.5%$_{abs}$

The ash content for the selected commodity may also vary depending on the different regions from which it is extracted. In plant and woody materials, the ash content is greatly influenced by the content and composition of substances derived from the soil, whose composition varies in different locations. For this reason, the ash content can only be compared approximately. For example, in Barbanera and Cotana [27], the ash content in the dry matter of the digestate was 12.38%, whereas in the sample digestate we analyzed, 11.31% ash was found. Similar values were found in safflower seed (3.0%) [28], sunflower peel (2.7%) [29], and wheat straw (6.72%) [30].

Another variable characterizing the fuel is the ballast portion *B*. As mentioned, it is the proportion of substances reducing the lower heating value of the fuel. The ballast ratio values largely correspond to the ash value. As can be seen in Table 2, low amounts of ballast were observed in the case of wood material, with increased values found in the analyzed agro-materials and the highest values were reached for the material containing waste sludge. It was precisely in the waste sludge that the non-combustible components were concentrated, which in turn significantly reduced the lower heating value of the material. For this reason, waste sludge is often used in mixed pellets with varying proportions of woody or plant biomass.

Table 2. Results of the determination of ash content, loss on annealing, and ballast ratio in samples.

Sample	Ash Content in the Raw Sample A_r (wt%)	Ash Content in the Anhydrous Sample A_d (wt%)	Loss on Annealing the Raw Sample W_{LOR} (wt%)	Loss on Annealing the Anhydrous Sample W_{LOD} (wt%)	Ballast Ratio in the Raw Sample B_r (wt%)
Digestate	10.36	11.31	89.64	87.65	18.79
Softwood pellets (spruce)	2.77	3.01	97.23	96.99	10.44
Hardwood pellets (beech)	2.25	2.44	97.75	97.56	10.09
Composite wood	0.30	0.33	99.70	99.67	9.79
Energo compost	19.92	21.97	80.08	75.76	29.27
Rape straw	3.82	4.27	96.18	95.23	14.44
Wheat straw pellet	6.16	6.64	93.84	93.36	13.32
Hay	4.83	5.25	95.17	94.30	12.79
Straw 60% + sludge 40%	27.93	29.05	72.07	69.77	31.79
Straw 70% + sludge 30%	25.07	26.07	74.93	72.90	28.89
Straw 80% + sludge 20%	17.24	18.03	82.76	81.14	21.63
Straw 90% + sludge 10%	10.24	10.75	89.76	88.71	15.03
Sunflower — peel	3.92	4.20	96.08	95.50	10.60
Sunflower— fter the oil press	5.67	6.04	94.33	93.96	11.76
Sunflower—whole plant	3.93	4.39	96.07	95.10	14.51
Mix—seeds rape, sunflower, mustard, husks	6.98	7.93	93.02	91.00	18.90
Mustard—seed	14.68	15.58	85.32	84.42	20.56
Spruce sawdust + digestate	2.53	2.70	97.47	97.11	8.97
Safflower—seed	6.60	7.00	93.40	93.00	12.01
Safflower—peel	2.69	2.97	97.31	97.03	8.18
Safflower–after the oil press	3.68	3.96	96.32	96.04	10.76
Amaranth—whole plant	7.13	7.70	92.87	92.30	13.82
Flax—waste	17.05	17.90	82.95	82.10	22.47
Crambe abyssinica	5.82	6.16	94.18	93.84	11.31
Camelina—seed	12.57	13.36	87.43	86.64	18.52
Camelina—after the oil press	10.09	10.87	89.92	89.14	17.18
Spelt—waste	4.43	4.82	95.57	95.18	12.49
Cocoa—peel	5.92	6.39	94.08	93.10	13.26
Sorrel pellet (whole plant)	4.73	5.18	95.27	94.33	13.37
Rye straw	12.51	13.67	87.49	86.33	20.19
Quinoa—waste	4.76	5.20	95.24	94.80	13.19

Notes: The accuracy of the determination method was below 2.5%$_{abs}$.

The evaluation of the rough analysis of the selected samples is subsequently shown in Figure 1 and Table 3. The content of water, ash, and combustible content in the chosen materials varied greatly, as can be seen from the table below.
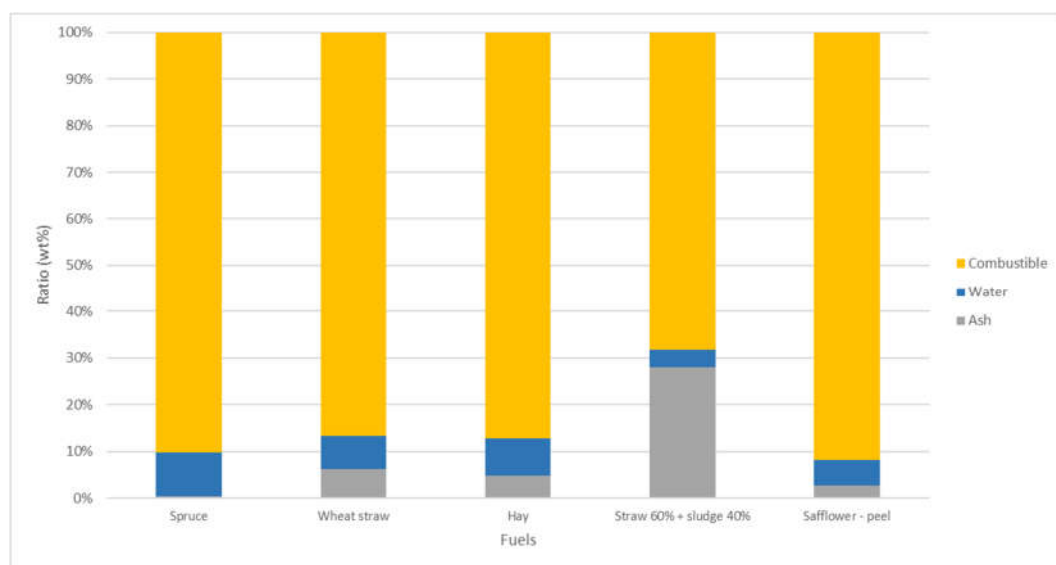
Figure 1. Total ratio of combustible content, water, and ash in the selected materials.

Table 3. Evaluation of the rough analysis of the selected samples.

Proximate Analysis		Spruce	Wheat Straw Pellets	Hay	Straw:Sludge 60:40	Safflower—Peel
Combustible	(wt%)	90.21	86.68	87.21	68.21	91.82
Water	(wt%)	9.49	7.16	7.96	3.86	5.49
Ash	(wt%)	0.3	6.16	4.83	27.93	2.69

After carrying out and evaluating the rough analysis of the materials intended for combustion, the determination of the volatile contents in the raw and anhydrous samples was carried out. The volatile content, together with the solids, make up the total combustible content in the samples. An example is given in the following Table 4.

Table 4. Ratio of volatile content to solids in the combustible.

Ratio of Combustible	Wood	Straw Pellets	Safflower—Peel
Combustible (wt%)	90.21	86.68	91.82
Volatile content (wt%)	75.45	71.37	79.15
Solids (wt%)	14.76	15.31	12.67

As can be seen in Table 5, the volatile content value ranged from 47.49wt% to 81.30wt% for the raw sample and 51.45wt% to 88.42wt% for the anhydrous sample, with average values of 74.4wt% and 79.4wt%, respectively. The volatile content value may vary within one material, as was noted for the safflower. For whole seeds, the value was 73.4wt%. On the other hand, for peels, the volatile content was higher (79.15wt%). In the safflower pellets after the oil press, the volatile content was 74.3wt%. This pellet contained both the seed and the peels. The values of the determined safflower volatile content approximately corresponded to the 83wt% found in another study [28]. A similar trend was observed in the case of camelina.

Table 5. Results of the determination of volatile content.

Sample	Volatile Content in Raw Sample V_r (wt%)	Volatile Content in Anhydrous Sample V_d (wt%)
Softwood pellets (spruce)	76.44	82.79
Hardwood pellets (beech)	76.34	82.84
Composite wood	75.45	83.36
Wheat straw pellet	71.37	76.88
Hay	78.39	89.99
Sunflower—peel	47.49	51.45
Sunflower—after the oil press	75.73	80.64
Mustard—seed	78.16	83.05
Safflower—seed	73.38	71.86
Safflower—peel	79.15	78.85
Safflower—after the oil press	74.34	80.00
Amaranth—whole plant	73.58	78.85
Flax—waste	72.41	76.56
Crambe abyssinica	78.82	83.40
Camelina—seed	80.36	85.45
Camelina—after the oil press	74.15	79.82
Spelt—waste	81.30	88.42
Rye straw	77.02	83.43
Quinoa—waste	74.77	81.65

Notes: The accuracy of the determination method was below 1%$_{abs}$.

After determination of the volatile content, the elemental analysis was carried out to determine the carbon, hydrogen, nitrogen, and volatile sulfur content of the sample, and the calculation of the oxygen content was added. The measured concentrations of individual elements in the original sample were also converted to the content in the combustible and dry matter. The measured and calculated values of the elemental analysis are summarized in the following Tables 6–8.

Table 6. Percentages of carbon, nitrogen, hydrogen, sulfur, and oxygen in the raw (original) samples of combusted material.

Sample	Raw (Original) Sample—Elements (wt%)				
	N^a	C^a	H^a	S^a	O^a
Digestate	1.91	41.68	5.45	0.04	39.60
Softwood pellets (spruce)	0.43	46.65	6.37	0.00	43.79
Hardwood pellets (beech)	0.60	46.33	6.17	0.00	44.65
Composite wood	0.80	48.30	6.08	0.00	44.50
Energo compost	2.13	38.22	4.79	0.33	32.56
Rape straw	0.69	41.72	6.10	0.02	47.02
Wheat straw pellet	0.76	43.81	6.09	0.11	43.07
Hay	0.68	42.20	5.98	0.05	45.84
Straw 60% + sludge 40%	0.40	36.04	4.23	0.01	30.27
Straw 70% + sludge 30%	0.44	37.19	4.36	0.00	31.93
Straw 80% + sludge 20%	0.67	39.10	4.83	0.00	37.37
Straw 90% + sludge 10%	0.39	41.88	5.52	0.00	41.46
Sunflower—peel	0.80	46.48	5.96	0.04	42.51
Sunflower—after the oil press	3.67	50.85	7.97	0.20	31.63
Sunflower—whole plant	0.90	45.24	5.87	0.03	43.57
Mix—seeds rape, sunflower, mustard, husks	2.12	40.32	5.86	0.16	43.58
Mustard—seed	5.02	52.37	8.04	1.08	18.80
Spruce sawdust + digestate	0.61	46.23	6.12	0.00	43.34
Safflower—seed	2.29	52.55	7.52	0.01	31.02
Safflower—peel	1.67	50.82	7.19	0.01	37.61
Safflower—after the oil press	2.70	48.14	6.87	0.04	38.57
Amaranth—whole plant	0.89	40.16	5.71	0.09	46.03
Flax—waste	3.41	46.78	6.75	0.17	25.83
Crambe abyssinica	3.13	54.48	8.28	0.67	27.61
Camelina—seed	4.66	54.81	8.45	0.66	18.06
Camelina—after the oil press	6.17	47.21	7.41	0.90	28.23
Spelt—waste	0.68	44.98	6.05	0.19	43.67
Cocoa—peel	2.39	45.49	6.19	0.11	39.43
Sorrel pellet (whole plant)	1.31	43.28	5.86	0.09	44.29
Rye straw	2.81	41.74	6.79	0.05	36.10
Quinoa—waste	2.87	42.99	6.84	0.18	42.34

Notes: The accuracy of the determination method was below 0.5%$_{abs}$.

Table 7. Percentages of carbon, nitrogen, hydrogen, sulfur, and oxygen in the combustible content.

Sample	Combustible—Elements (wt%)				
	N^{daf}	C^{daf}	H^{daf}	S^{daf}	O^{daf}
Digestate	2.38	51.94	5.62	0.05	40.02
Softwood pellets (spruce)	0.48	52.08	6.15	0.00	41.28
Hardwood pellets (beech)	0.66	51.53	5.88	0.00	41.92
Composite wood	0.85	51.17	5.82	0.00	42.16
Energo compost	3.10	55.65	5.45	0.48	35.32
Rape straw	0.81	49.12	5.78	0.02	44.26
Wheat straw pellet	0.88	50.54	6.10	0.12	42.35
Hay	0.78	48.62	5.86	0.06	44.67
Straw 60% + sludge 40%	0.60	53.72	5.66	0.01	40.01
Straw 70% + sludge 30%	0.63	53.05	5.61	0.00	40.71
Straw 80% + sludge 20%	0.86	50.40	5.59	0.00	43.14
Straw 90% + sludge 10%	0.46	49.59	5.90	0.00	44.05
Sunflower—peel	0.90	52.16	5.85	0.04	41.05
Sunflower—after the oil press	4.16	57.63	8.26	0.23	29.72
Sunflower—whole plant	1.06	53.20	5.51	0.04	40.19
Mix—seeds rape, sunflower, mustard, husks	2.65	50.32	5.65	0.20	41.18
Mustard—seed	6.32	65.93	9.30	1.36	17.09
Spruce sawdust + digestate	0.68	51.45	6.01	0.00	41.87
Safflower—seed	2.60	59.73	7.86	0.02	29.79
Safflower—peel	1.82	55.35	7.16	0.01	35.65
Safflower—after the oil press	3.03	53.94	6.81	0.04	36.17
Amaranth—whole plant	1.03	46.60	5.76	0.10	46.52
Flax—waste	4.40	60.34	7.92	0.22	27.11
Crambe abyssinica	3.53	61.43	8.64	0.76	25.64
Camelina—seed	5.78	67.94	9.64	0.82	15.83
Camelina – after the oil press	7.45	57.00	7.98	1.08	26.49
Spelt—waste	0.78	51.40	5.89	0.21	41.72
Cocoa—peel	2.77	52.73	6.22	0.13	38.15
Sorrel pellet (whole plant)	1.52	50.21	5.68	0.10	42.48
Rye straw	3.52	52.30	7.43	0.07	36.68
Quinoa—waste	3.30	49.47	6.80	0.21	40.22

Notes: The accuracy of the determination method was below 0.5%$_{abs}$.

Table 8. Percentages of carbon, nitrogen, hydrogen, sulfur, and oxygen in the dry matter.

Sample	Dry Matter—Elements (wt%)				
	N^{dr}	C^{dr}	H^{dr}	S^{dr}	O^{dr}
Digestate	2.27	46.06	4.98	0.04	35.49
Softwood pellets (spruce)	0.47	50.64	5.98	0.00	40.14
Hardwood pellets (beech)	0.65	50.37	5.75	0.00	40.98
Composite wood	0.85	51.00	5.80	0.00	42.02
Energo compost	2.42	43.42	4.25	0.37	27.56
Rape straw	0.78	47.03	5.54	0.02	42.37
Wheat straw pellet	0.83	47.42	5.73	0.12	39.75
Hay	0.74	46.07	5.56	0.05	42.33
Straw 60% + sludge 40%	0.42	38.11	4.02	0.01	28.39
Straw 70% + sludge 30%	0.46	39.22	4.15	0.00	30.10
Straw 80% + sludge 20%	0.71	41.31	4.58	0.00	35.37
Straw 90% + sludge 10%	0.41	44.26	5.27	0.00	39.32
Sunflower—peel	0.86	49.97	5.60	0.04	39.32
Sunflower—after the oil press	2.72	37.68	5.40	0.15	19.43
Sunflower—whole plant	1.01	50.87	5.27	0.03	38.43
Mix—seeds rape, sunflower, mustard, husks	2.44	46.33	5.20	0.18	37.91
Mustard—seed	5.39	56.25	7.93	1.16	14.58
Spruce sawdust + digestate	0.66	50.06	5.85	0.00	40.74
Safflower—seed	2.43	55.79	7.34	0.01	27.83
Safflower—peel	1.77	53.86	6.97	0.01	34.69
Safflower—after the oil press	2.92	51.96	6.56	0.04	34.84
Amaranth—whole plant	0.96	43.27	5.35	0.09	43.20
Flax—waste	3.65	50.06	6.57	0.19	22.49
Crambe abyssinica	3.32	57.64	8.11	0.71	24.06
Camelina—seed	5.00	58.86	8.35	0.71	13.71
Camelina—after the oil press	6.40	49.00	6.86	0.93	22.77
Spelt—waste	0.75	49.12	5.62	0.20	39.88
Cocoa—peel	2.59	49.36	5.83	0.12	35.71
Sorrel pellet (whole plant)	1.44	47.61	5.38	0.10	40.28
Rye straw	3.08	45.76	6.50	0.06	32.09
Quinoa—waste	3.14	47.11	6.48	0.20	38.29

Notes: The accuracy of the determination method was below 0.5%$_{abs}$.

It is apparent from Table 6 that wood materials reached very similar values for all monitored elements. The values from the wood samples were close to the measured percentages of elements in the samples of hay and straw, which in terms of elemental analysis, seems to be a suitable fuel that could replace wood pellets. However, a slightly increased sulfur content (up to 0.11wt%) was observed with these samples. The increased sulfur content was also observed for some oilseed samples, such as mustard (1.08wt%), sunflower (up to 0.2wt%), camelina (up to 0.9wt%), and cocoa (0.11wt%). This was similar to information found in other literary sources [29–32]. The combustion of sulfur-containing material releases its volatile content, which subsequently reacts with hydrogen to form hydrogen sulfide, or with oxygen to form sulfur dioxide. The low presence of sulfur in the raw material monitored only meant the formation of a negligible amount of these gaseous emissions in the combustion process.

In Table 7, the contents of the monitored elements in the combustible were recorded. The conversions given in Section 2 were used to obtain these values. Compared to the elements in the raw sample, a slight increase in nitrogen and carbon content, and a decrease in the amount of hydrogen and oxygen, were observed for the combustible content. The change of these values was influenced by the reduction of water and ash in the combustible content.

In the case of Table 7, there was a significant decrease in other elements to the detriment of hydrogen and oxygen. However, as already mentioned, the final concentration of sulfur and nitrogen in the material was mainly influenced by the particular soil composition in which the biomass was grown and the use of fertilizers. Higher sulfur concentrations in pellets increase the SO_2 emissions and may also cause corrosion when sulfur compounds condense on the exchanger surfaces of the boiler [33]. The content of elements in the combustible was converted to the content of elements in the dry matter. The results are summarized in Table 8 below.

After elementary analysis, the higher heating values of individual materials were determined using the calorimetric method. From the higher heating value of the original HHV^a sample, the higher heating value was then calculated in the combustible HHV^{daf} and dry matter HHV^{dr}. The measurement was performed at least three times, and the mean result was calculated from the measured values. The measured and calculated higher heating values fluctuated in a relatively wide range. The amount of woody mass greatly influenced these values in the sample. It is also evident from Table 9 that the presence of oily substances in the material had a significant influence on the value of the higher heating value. This was observed, for example, in the case of camelina and safflower samples. In the case of camelina samples obtained from the same sources, the effect of the oil content was noticeable. The whole seeds reached a significantly higher value of the higher heating value of 25.154 MJ·kg^{-1}, as opposed to the already pressed seeds, which had a value of 20.942 MJ·kg^{-1}. The tables also show that the higher heating value of the combustible was greater than that of the original sample. In fact, in the case of fuel, the carrier of energy was only combustible. The remaining fuel, ash, and water only reduced this energy of combustible content. This was evident, for example, with digestate having a high higher heating value of combustible and a low higher heating value of the original sample. This significant difference was due to the high content of ballast, i.e., ash and water, in the sample.

Table 9. Higher heating value in the original sample of HHV^a, dry matter HHV^{dr}, and combustible HHV^{daf}.

Sample	Higher Heating Value (MJ·kg^{-1})		
	HHV^a	HHV^{dr}	HHV^{daf}
Digestate	15.769	17.222	19.649
Softwood pellets (spruce)	18.207	19.718	20.330
Hardwood pellets (beech)	18.044	19.579	20.069
Composite wood	18.235	20.148	20.215
Energo compost	14.684	16.199	21.382
Rape straw	15.572	17.422	18.292
Wheat straw pellet	17.238	18.567	19.888
Hay	15.790	17.155	18.192
Straw 60% + sludge 40%	13.559	14.150	20.280
Straw 70% + sludge 30%	13.947	14.500	19.891
Straw 80% + sludge 20%	14.467	15.131	18.648
Straw 90% + sludge 10%	15.744	16.535	18.640
Sunflower—peel	17.699	18.966	19.861
Sunflower—after the oil press	22.319	23.766	25.294
Sunflower—whole plant	16.925	18.928	19.904
Mix—seeds rape, sunflower, mustard, husks	15.246	17.308	19.021
Mustard—seed	24.131	25.639	30.369
Spruce sawdust + digestate	17.565	18.773	19.331
Safflower—seed	23.221	24.550	26.397
Safflower—peel	22.677	23.994	24.728
Safflower—after the oil press	20.125	21.658	22.551
Amaranth—whole plant	16.309	17.478	18.937
Flax—waste	20.318	21.483	26.167
Crambe abyssinica	25.351	26.824	28.583
Camelina—seed	25.154	26.746	30.871
Camelina—after the oil press	20.942	22.542	25.289
Spelt—waste	16.947	18.432	19.365
Cocoa—peel	18.078	19.504	20.948
Sorrel pellet (whole plant)	16.211	17.744	18.809
Rye straw	16.835	18.237	21.126
Quinoa—waste	17.700	19.329	20.389

Notes: The accuracy of the determination method was below 0.5%$_{abs}$.

The lower heating values of the original sample LHV^a, dry matter LHV^{dr}, and combustible LHV^{daf} were then calculated from the experimentally determined higher heating values. The lower heating value of the original LHV^a sample is a quantity that indicates the final energy potential of the sample during real combustion. This is the primary parameter for comparing potential fuel, whatever the type of material. The lower heating values showed a similar trend to the higher heating values, i.e., the lower heating values of wood pellets and some oil-containing pellets, such as mustard (22.363 MJ·kg^{-1}), camelina (23.280 MJ·kg^{-1}), and safflower (21.567 MJ·kg^{-1}) were high. On the other hand, digestate samples and the mixture of sawdust with a high waste sludge content showed a low lower heating value. When comparing the higher heating values and the lover heating values of these samples, it was observed that these values were influenced by the high ballast ratio. The results of the lower heating values of all analyzed samples are summarized in the following Table 10.

Table 10. Calculated lower heating values of analyzed samples.

Sample	Lower Heating Value (MJ·kg^{-1})		
	LHV^a	LHV^{dr}	LHV^{daf}
Digestate	14.559	16.129	19.860
Softwood pellets (spruce)	16.807	18.406	20.551
Hardwood pellets (beech)	16.688	18.318	20.374
Composite wood	16.848	18.876	20.925
Energo compost	13.607	15.266	21.582
Rape straw	14.223	16.207	18.942
Wheat straw pellet	15.899	17.311	19.972
Hay	14.470	15.936	18.274
Straw 60% + sludge 40%	12.615	13.269	19.453
Straw 70% + sludge 30%	12.976	13.590	19.113
Straw 80% + sludge 20%	13.396	14.125	18.023
Straw 90% + sludge 10%	14.524	15.380	18.099
Sunflower—peel	16.385	17.737	19.839
Sunflower—after the oil press	20.566	22.581	25.591
Sunflower—whole plant	15.629	17.772	20.787
Mix—seeds rape, sunflower, mustard, husks	13.946	16.167	19.936
Mustard—seed	22.363	23.898	30.083
Spruce sawdust + digestate	16.204	17.490	19.213
Safflower—seed	21.567	22.939	26.071
Safflower—peel	21.096	22.465	24.465
Safflower—after the oil press	18.614	20.219	22.656
Amaranth—whole plant	15.053	16.305	18.920
Flax—waste	18.835	20.042	25.852
Crambe abyssinica	23.530	25.044	28.237
Camelina—seed	23.280	24.913	30.578
Camelina—after the oil press	19.314	21.036	25.400
Spelt—waste	15.617	17.198	19.652
Cocoa—peel	16.711	18.226	21.012
Sorrel pellet (whole plant)	14.918	16.563	19.120
Rye straw	15.342	16.810	21.063
Quinoa—waste	16.195	17.908	20.628

Notes: The accuracy of the determination method was below 0.5%$_{abs}$.

4. Conclusions

With the increasing demand for the use of renewable energy sources, there is scope for using other biofuels as a promising energy source. However, to use a broader range of biofuels, it is necessary to know their fuel properties, such as coarse and elemental analysis or their lower heating value.

This research included 60 tested samples of different biofuels, and this publication presents only selected samples that can be expected to be of potential use, with materials and biofuels remaining as a secondary product of their primary use and processing. The selection of samples also took into account the fact that the possible availability and samples of waste materials from the processing of these crops were preferred. One of the reasons why these biofuels have not been used so far is the fact that there is insufficient knowledge about their properties and possibilities for energy use. These include, for example, crops like quinoa, camelina, cramble, safflower, amaranth, sunflowers, or parts thereof. Their fuel properties are here compared with some traditional biofuels (wood, straw, sorrel, hay). Fuels were also chosen in consultation with agricultural research institutes. These selected fuels are currently being studied intensively in the Czech Republic from an agrotechnical point of view, and they appear to be promising for their expansion in the food industry. The residual parts can then be easily used for energy processing.

Several types of analyses were carried out in the examined samples, which comprehensively characterized the given commodities within the combustion process specifics of particular crops, where the results from individual analyses are discussed directly in the text along with individual results.

The main results of the study can be summarized as follows:

- Some materials examined in this study had not been explored and analyzed yet, where some materials showed great potential for becoming a renewable and sustainable energy source for low-power boilers. A large number of these materials are of waste origin or surpluses from agriculture, and their combustion not only generates energy but also greatly facilitates the solution of disposal or possible waste management problems.
- The moisture content of the analyzed biomass significantly affected the treatment of the material itself and the amount of heat released from a unit amount of the selected material since the lower heating value of the material is reduced by a higher water content of the matrix.
- The use of biomass as fuel also affects the amount of ash formed from combustion. If the material forms a large amount of ash, it is more difficult to remove the ash from the boiler body and to quickly fill the ashpan, which is disadvantageous from a user's point of view. For small boiler bodies, it is, therefore, preferable to use biomass with low ash and low ballast contents as the energy source. This implies that materials with a high ash content (e.g., waste sludge) should be combined with, for example, a readily available woody mass that forms a minimal amount of ash.
- The volatile content and lower heating value also have a significant effect on fuel quality. These are closely related, as a higher volatile content will increase the fuel higher heating value.
- Fuel of a plant origin shows the influence of its growth location. The composition of the soil in which the plant has grown significantly affects the number of elements and their representation in all its parts. For example, increased nitrogen in plants is caused by the use of fertilizers, which directly affects the increased release of nitrogen oxides in the combustion process.

Based on the knowledge of the fuel properties of new biofuels, it is possible to realize the design of combustion devices of different outputs for these fuels, and their use can be expanded in the energy sector.

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