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Impact of differences in combustion conditions of rape straw on the amount of flue gases and fly ash properties

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Abstract. The rising trend of biomass energy usage as a renewable energy source raises issues with combustion waste products, mostly bottom ash and its potential for further use. Rape straw was selected as a fuel sample for experiments because of the fact, that this crop figures among the 10 most important crops in the world and its straw is frequently used as a source of renewable energy. The rape straw was processed in pelletizing line LSP 1800 of the company ATEA PRAHA Ltd. into pellets with diameter of 8 mm and length 15 to 30 mm. Composition of bottom ash arising during the energy utilization of biomass is primarily dependent on the composition of input raw material and next on the combustion technology. Therefore, the aim of this article is to clarify the influence of excess air amount on the composition of end products in combustion of rape straw pellets in three combustion modes (low, optimal and high excess air).
The last part of study were combustion tests and measurements on a laboratory hot-air stove – KNP from the company KOVO NOVAK. Excess air coefficient values ranged between 3.31 and 6.77. The average net calorific value of the original rape straw sample was about 15.95 MJ kg^{-1}. Input raw material may not have always been completely combusted in the device, and therefore the ash could contain elevated amounts of hazardous elements. These substances are a limiting factor for application of the ash into soil. Overall, ash from biomass not only offers a wide range of potential applications thanks to its physical and chemical properties, but also returns some of the nutrients back to the soil closing the nutrient cycle and reducing the landfill of such material. And last but not least it enables cost reduction in agricultural production spent on mineral fertilizers.

Key words: rape straw, combustion conditions, ash properties, emission concentrations, flue gas temperature.

INTRODUCTION

During energy utilization of biomass the issue of ash handling arises. Composition of these end products of combustion is largely dependent on the fuel composition and used combustion technology and its configuration (Bradna et al., 2016). Plants growing on forest or agricultural land not only create organic matter but also take nutrients required for growth, which after burning usually accumulate in the solid non-combustible residue – ashes. One option of using these residues is the application on agricultural land, to which nutrients are returned (Zemanová et al., 2014).

Combustion of solid fuels, biomass included, produces undesirable gaseous and particulate emissions in flue gases. These substances have to be subsequently removed from the flue gas to comply with emission limits for gases emitted into the atmosphere (Fournel et al., 2015). The process of solid fuels combustion should always be run at the optimal conditions and efficiency for a particular combustion plant. From available literature (Malaťák et al., 2016), (Khodaei et al., 2017) it is known that operation of combustion devices is better when the fuel is drier, because it carries more net calorific value per unit of weight and less inner space of a combustion device is needed to firstly dry the fuel. As a consequence, overall higher surface area of fuel and more material is burning simultaneously in a given combustion device and the performance is accordingly higher as well. Net calorific value of biofuels from plant biomass is primarily dependent on the water and ash content in the fuel (Bradna & Malaťák, 2016). The construction of various furnace types as well as input material preparation for combustion depends on basic properties of used biofuels.

This paper focuses on the aforementioned topic. In the first part selected rape straw pellet samples are evaluated using elemental analysis. Following is an operational measurement of emission concentrations during combustion of samples on an automatic hot-air stove KNP from the company KOVO NOVAK. In these tests effects of operational temperature and amount of combustion air are identified and analyzed for individual samples.

Different types of solid biofuels vary in their characteristics such as the net calorific value, moisture or chemical composition (Vassilev et al., 2010). Contents of hazardous elements present in the biofuel influences the final amount of these elements left in ash. The content of hazardous elements is also significantly influenced by their behavior during combustion and accordingly by separation of individual fractions of ash (Niu et al., 2010).

MATERIALS AND METHODS

Rape straw has been chosen as the most suitable biofuel for the experimental measurement. This material was transformed into the form of pellets by pelletizing line LSP 1800 (company ATEA PRAHA Ltd.). Pellets had diameter of 8 mm and length of 15–30 mm. This work firstly focus on the determination of the elemental composition of samples. Before each combustion test samples for determination of elemental analyses were taken. Pellet samples were taken at 3 points: immediately after pelletizing, after thirty days of storage and just prior to the combustion tests. During these experiments, basic parameters of fuel were examined, specifically the contents of water, ash, volatile and non-volatile combustible matter, and contents of carbon, nitrogen, oxygen, hydrogen, sulphur and chlorine.

The CHN analyzer Perkin-Elmer 2400 was used for determination of the elements carbon, hydrogen and nitrogen. Chlorine and sulphur were determined by burning of samples in oxygen-hydrogen flame in Wickbold apparatus. The amount of ash and total water content (non-combustible substances) were determined by burning, respectively drying of the sample. Gross calorific value was determined by calorimetric method in the calorimeter IKA 2000.

The net calorific value of fuel as well as the amount of oxygen required for complete combustion of fuel, quantity and composition of flue gas and flue gas density

were calculated by stoichiometric calculations. These calculations were converted to normal conditions, i.e. temperature0 °C and pressure = 101.325 kPa. After the theoretical analysis, practical measurements of combustion process were carried out focusing on emission concentrations. These tests were carried out on an automatic hot-air stove KNP made by company KOVO NOVAK. This stove has a burner with automatic ignition and is equipped with automatic fuel supply by a screw conveyor. The transport of pellets was performed from the pellet hopper with a capacity of 50 litres.

During combustion experiments combustion process could be influenced by adjusting the combustion air intake and by the rate of fuel supply. During experimental tests varying excess air coefficients were used in order to determine combustion characteristics.

Three combustion modes were selected:

1) Combustion under low excess of air - the device was set to maximum fuel supply and the quantity of combustion air was regulated to the lowest possible amount.

2) Combustion under optimum excess air coefficient – fuel and combustion air supply rate were set to a level, when the emission concentrations of carbon dioxide reached maximum value and the concentrations of carbon monoxide reached minimum.

3) Combustion under high excess air coefficient – the combustion device was fed with low fuel supply rate and high supply of combustion air simultaneously.

A multifunction analyzer of flue gas Madur GA-60, based on the principle of electrochemical converters, was used to monitor emission concentrations. Concentrations of carbon monoxide and dioxide, oxygen, nitrogen monoxide and dioxide, sulfur dioxide, hydrogen chloride were measured as well as excess air coefficient. Madur GA-60 also enables the measurement of ambient and flue gas temperature. Based on these temperatures and chemical parameters this device performs calculation of combustion characteristics. The emission concentration values are converted for normal conditions of dry flue gas and reference oxygen content in flue gas. The results of measurements were processed by statistical regression analysis for expressing the mathematical relationship of carbon monoxide and dioxide, flue gas temperature and total nitrogen oxides depending on excess air coefficient.

The elemental analysis of solid combustion end products with different excess air coefficients were carried out at the end of laboratory tests. The concentration of individual elements in the samples were determined by flame atomic absorption spectrophotometry on the device Varian-400 SpectrAA. The mineral compositions, with regard to samples utilization as soil amendment, were determined according to Száková et al. (2013) and available metal fractions were determined by extraction (Trakal et al., 2013).

RESULTS AND DISCUSSION

The results of elemental analyses are shown in Table 1 and 2. The results are divided into 3 analyses of samples from rape straw after pelletizing and one sample of uncompressed rape straw for comparison. The average values of pellets used for stoichiometric calculations are at the bottom of tables. The results show that the dependence of net calorific value on the ash and water content in the fuel in its original state is not clearly confirmed, which confirm also Müller et al. (2015) and Niu et al. (2010).

Table 1. Elemental analysis of the rape straw samples (in original state)

Sample	Water Content (% wt.)	Ashes (% wt.)	Volatile Combustible (% wt.)	Non-volatile Combustible (% wt.)	Gross Calorific Value (MJ kg^{-1})	Net Calorific Value (MJ kg^{-1})
	W	A	V	NV	Q_s	Q_i
Rape straw before processing	9.37	4.98	68.85	16.80	16.71	15.34
Rape straw pellets 1 (diameter 8 mm)	7.85	5.64	71.11	16.40	16.75	15.23
Rape straw pellets 2 (diameter 8 mm)	8.80	4.13	71.19	15.88	17.98	16.47
Rape straw pellets 3 (diameter 8 mm)	7.45	4.83	72.28	17.44	17.36	16.15
Average values of pellet samples	8.03	4.87	71.53	16.57	17.36	15.95
Statistical dispersion	0.57	0.62	0.53	0.65	0.50	0.53

Table 1 shows that the total water content in all samples was quite low. After pelletizing it ranged from 7.45 to 8.80 (% wt.). This had a positive effect on the net calorific value of samples. When considering the ash content, the samples from rape straw had higher content than e.g. pure wood samples. This fact confirm also Shen & Xue (2015) who carried out elemental analyses on samples of pure wood and the amount of ash in pure wood stayed under 1% wt. Combustion of rape straw in small combustion devices produces relatively higher amount of solid residue after combustion and increases the amount of solid particles in the flue gas. On the other hand, it produces a substantial amount of ash usable as a soil amendment (Mollon et al., 2016).

The average net calorific value of the rape straw samples in the original state was around 15.95 MJ kg^{-1}. These values are comparable to wheat straw with its value around 15.55 MJ kg^{-1} (Bradna & Malaťák, 2016).

For all samples analysis of nitrogen, sulphur and chlorine contents were carried out (see. Table 2). Average concentrations of chlorine were found in examined samples of rape straw in its original state, where the average value was around 0.18% wt. Chlorine passes during the combustion process for the most part into the gaseous phase. If the chlorine concentration in the fuel is high there can arise problems. On the one hand, significance of problems with chlorine is based on the emissions of HCl and their possible influence on the formation of polychlorinated dibenzo/dioxins and furans (PCDD/F). Another issue are the corrosive effects of these elements or their derived compounds on parts of combustion devices (Niu et al., 2010).

Sulphur also leaves for the most part during combustion in the gas phase as SO_2 or SO_3. Emissions of sulphur in combustion devices for solid fuels from renewable resources generally do not present a problem regarding maximum limiting values. This fact is confirmed also in the evaluated samples (see. Table 2). A high concentration of oxygen was found in the samples – over 37% wt. in average. Oxygen is a problematic component of fuel because it binds hydrogen and partly also carbon to hydroxides, water

and oxides (particularly nitrogen and chlorine). The adverse effect is based on their interaction with the combustion device, especially the heat transfer surfaces.

Table 2. Elemental analysis of the rape straw samples (in original state)

Sample	Carbon C (% wt.)	Hydrogen H (% wt.)	Nitrogen N (% wt.)	Sulphur S (% wt.)	Oxygen O (% wt.)	Chlorine (% wt.)
	C	H	N	S	O	Cl
Rape straw before processing	41.38	5.20	0.57	0.11	38.24	0.15
Rape straw pellets 1 liameter 8 mm)	42.64	6.11	0.84	0.14	36.64	0.14
Rape straw pellets 2 (diameter 8 mm)	42.83	5.95	0.47	0.12	37.54	0.16
Rape straw pellets 3 (diameter 8 mm)	43.70	4.90	0.72	0.23	37.94	0.23
Average values	43.06	5.65	0.68	0.16	37.37	0.18
Statistical dispersion	0.46	0.54	0.15	0.05	0.54	0.04

For samples of rape straw high emissions of nitrogen (see Table 3) were evident, because this type of energy plant has quite high content of nitrogen in the combustible (see Table 2) compared to fossil or wood fuels (Vassilev et al., 2010). Dependence of emission concentrations on contents of individual elements in the samples is evident from their elemental composition given in Table 2. The values shown in Table 3 confirm that maintaining the optimum excess air coefficient is essential during combustion, because this state guarantees such combustion conditions which do not generate high emission concentrations of unburned components and do not increase the heat losses (Bradna & Malaťák, 2016).

Table 3. Average values of thermal properties and emission concentration of the rape straw pellets (diameter 8 mm)

	Average	s^2	s	V	Max.	Min.
$T_{ambient}$ (°C)	33.40	9.09	3.02	0.09	37.00	26.00
$T_{flue-gas}$ (°C)	240.36	0.35	0.59	0.00	241.30	238.34
O_2 (%)	16.72	0.38	0.62	0.04	17.90	14.66
n (-)	4.99	0.45	0.67	0.13	6.77	3.31
CO_2 (%)	3.10	0.22	0.47	0.15	4.62	1.65
CO (mg m^{-3})	1,071.48	44,810.63	211.68	0.20	1,938.00	810.00
SO_2 (mg m^{-3})	262.09	9,454.44	30.47	0.01	349.11	134.06
NO_x (mg m^{-3})	1,848.85	12,595.59	112.23	0.06	1,992.55	1,487.00

For the evaluation of combustion process quality graphs of dependencies of carbon monoxide and carbon dioxide on the excess air coefficient are shown in Fig. 1. Excess air coefficient influences behaviour of the combustion device and the combustion process itself.

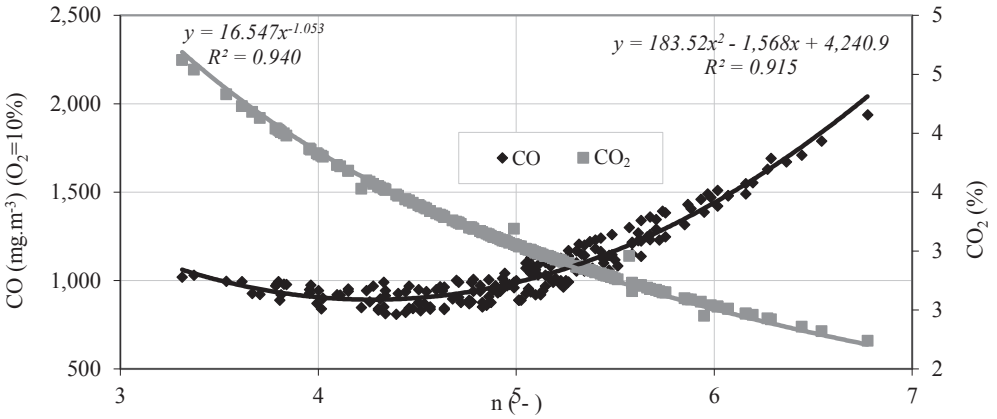

Figure 1. Dependence of carbon monoxide and carbon dioxide on the excess air coefficient – combustion of the rape straw pellets in diameter 8 mm.

When burning pellets from rape straw (see Fig. 1), increasing excess air coefficient *n* increased the emission concentrations of carbon monoxide according to the equation:

$$CO = 183.52n^2 - 1{,}568n + 4{,}240.90 \text{ (mg m}^{-3}\text{)} \quad (1)$$

With confidence level of $R^2 = 0.9159$, when increasing *n* in the range from 3.31 to 6.77, this also leads to reduction in the carbon dioxide concentration according to the equation:

$$CO_2 = 16.547n^{-1.053} \text{ (\%)} \quad (2)$$

When increasing excess air coefficient $n > 5$ (see Fig. 2) dampening of combustion process starts and flue gas temperature goes below 240 °C. This flue gas cooling can be defined by the equation:

$$T_{flue\text{-}gas} = -0.2545n^2 + 1.6943n + 238.36 \text{ (°C)} \quad (3)$$

With confidence level of $R^2 = 0.9571$.

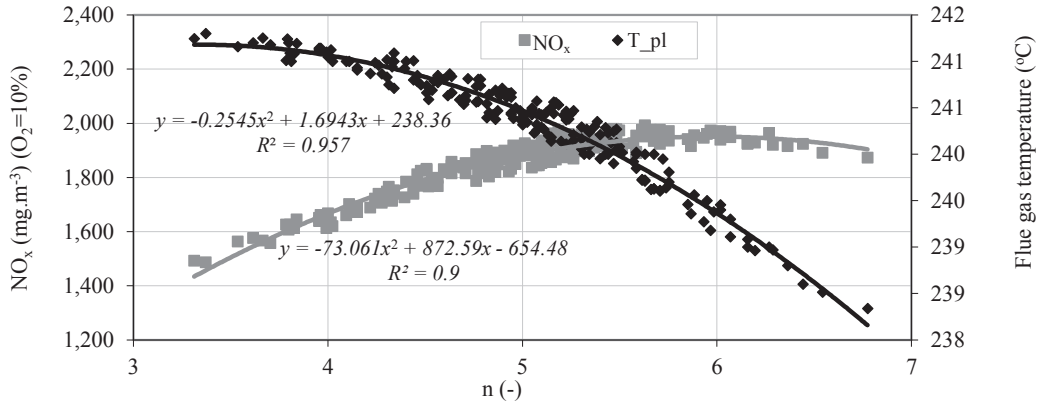

Figure 2. Dependence of nitrogen oxides and flue gas temperature on the excess air coefficient - combustion of the rape straw pellets in diameter 8 mm.

Increase in NO_x emissions while increasing the amount of supplied combustion air was likely mainly caused by nitrogen reacting with oxygen and produced nitrogen oxides (see Fig. 2). Dependence of concentration of nitrogen oxides on the excess air coefficient is described by the equation:

$$NO_x = -73.061n^2 + 872.59n - 654.48 \text{ (mg m}^{-3}\text{)} \quad (4)$$

With confidence level of $R^2 = 0.9368$.

In the range of optimum excess air coefficient, the concentrations of nitrogen oxides are very low. According to the measurements of rape straw combustion the optimal setting of the combustion device is in the range of excess air coefficient from 4 to 5. This level of excess air coefficient was also studied by Shen & Xue, (2015); Bradna & Malaťák, (2016). Concentration of carbon monoxide in this range of excess air coefficient is about 1,000 mg m^{-3}. This range of the excess air coefficient prevents significant cooling of the flue gases. Combustion with low excess air is considered when of the excess air coefficient is less than 4. Combustion with high excess air coefficient is standardized at values greater than 5.

The sampling of fly ash was performed each time during measuring interval in each particular combustion mode. The sampling point for collection of fly ash was the flue duct. Analyses of the mineral composition of fly ash produced in the three different combustion modes are shown in Table 4.

Table 4. The average values of mineral composition of fly ash from rape straw pellets

	low excess air	high excess air	optimal excess air
Al (mg kg^{-1})	1,293.00	1,346.45	900.41
As (mg kg^{-1})	0.80	3.31	0.16
B (mg kg^{-1})	321.93	192.11	83.44
Cd (mg kg^{-1})	0.25	0.34	0.01
Cr (mg kg^{-1})	5.37	8.50	3.22
Cu (mg kg^{-1})	21.32	25.64	22.77
Fe (mg kg^{-1})	2,803.15	4,039.38	1,245.43
Mn (mg kg^{-1})	654.38	959.17	805.60
Mo (mg kg^{-1})	1.89	2.47	2.02
Ni (mg kg^{-1})	3.10	4.73	3.30
Pb (mg kg^{-1})	2.93	4.41	1.41
S (mg kg^{-1})	1,119.35	956.85	417.08
Zn (mg kg^{-1})	97.95	103.83	15.12
P (mg kg^{-1})	4,351.02	5,049.24	5,823.80
K (mg kg^{-1})	15,894.91	22,011.82	32,572.04
Ca (mg kg^{-1})	14,962.56	19,944.90	26,380.83
Mg (mg kg^{-1})	4,910.13	5,182.26	6,875.37

From the Table 4 it is evident that the values of cadmium in fly ash are on average significantly below 1 mg kg^{-1}. Comparing results of analyses to the limits given by valid legislation applicable for soil amendments in the Czech Republic, we find that the values of cadmium in fly ash should pose no threat when applied to soil. On the other hand, ash from wood chips generally exceeds the legal limits for cadmium set at the value of 5 mg kg^{-1}, which confirms also Berra et al. (2011).

Measured values of lead in the fly ash from rape straw was on average significantly below the limit of 10 mg kg^{-1}. Higher potassium content in ash ~~is~~ results due to higher levels of this element in the raw material itself. Higher calcium content in ash leads to increased pH values and such materials could be used for treatment of soil reaction in particular in strongly acidic or heavy soils (Obernberger & Supancic, 2009).

In the mode of optimum excess air during the combustion of rape straw pellets higher concentrations of P, K, Ca and Mg in the ash were reached. In the overall assessment, it can be said that for the use on agricultural land ashes from the combustion of rape straw are completely satisfactory in regard to the current legislation for soil amendments. The average content of hazardous elements in each sample of fly ash are fully compliant with the limits.

CONCLUSIONS

The right choice of the combustion device is very dependent on the type and form of biomass. Selection of the combustion device type is primarily influenced by the characteristics of biofuels, among which are included, in particular, moisture, ash content, net calorific value, the proportion of volatile matter, combustible carbon content and also the alkali metals content. For rape straw with an average proportion of 0.68% of the nitrogen in the fuel was measured large concentration of nitrogen oxides in the flue gas (approximately 1,848.85 mg m^{-3}), which is dependent on increasing excess air coefficient. The excess air coefficient also affect the combustion process and the overall amount of flue gas, wherein the optimal limit for rape straw combustion in the selected combustion device is in the range 3.5 to 4.5. Assessment of the suitability and optimization of solid biofuel utilization in combustion devices with regard to the quality of the solid by-products is also an integral part of other works (Niu et al., 2010; Mollon et al., 2013).

Input material may not always be completely incinerated in a combustion device, and thus the ash can contain elevated amounts of hazardous elements. These substances can be a limiting factor for application of ash on soil or any other use. Solid biofuels can be considered a renewable energy source only in the case when the energy contribution is much greater than the costs of growing, harvesting and further processing (drying, pressing etc.). Therefore, assessing the utilization options of biomass ash in the life cycle of a renewable energy source plays an important role both for the environment and the economy in the production of solid biofuels.

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