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Valorization of sunflower husk after seeds convection drying for solid fuel production

Valorizacija ljuske suncokreta nakon konvekcijskog sušenja sjemenki za proizvodnju krutog goriva

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Abstract

Since the initial moisture content in sunflower seeds after the harvest is rather high, seeds must be processed by convection drying so that their quality can be maintained for as long as possible a period of time. Sunflower is an oilseed crop, which can be used as food and as a feedstock for solid fuels production. The aim of this paper is to determine the influence of the convection drying process (at 60 °C, 80 °C and 100 °C) on energy characteristics of seeds of four sunflower hybrids (Apolon, NK Brio, PR 63 A 90 and PR 63 D 82), which by their characteristics belong to early and medium-early hybrids. It will also be determined if the energy used in the drying process can be recovered through utilisation of energy from husk. On the basis of the obtained results, the changes in energy characteristics were identified, namely, the content of non-combustible matters (water, ash, coke, fixed carbon and nitrogen) and of combustible matters (carbon, sulphur, hydrogen, oxygen, volatile matter), as well as higher and lower heating values of sunflower seeds. The resulting data prove that convection drying of sunflower husk has a positive influence on its energy characteristics and that it can be used for solid fuel production.

Keywords: convection drying, energy, sunflower husk

Sažetak

Zbog povišene početne vlažnost nakon žetve, sjemenke suncokreta moraju se doraditi konvekcijskim sušenjem kako bi im se očuvala kvaliteta kroz što dulje vrijeme. Suncokret je uljarica kojoj se osim za prehrambene svrhe može koristiti i u proizvodnji krutih goriva. Cilj ovog rada je utvrditi utjecaj termičkog procesa konvekcijskog sušenja (60 °C, 80 °C i 100 °C) na energetske karakteristike sjemenki 4 različita hibrida suncokreta (Apolon, NK Brio, PR 63 A 90 i PR 63 D 82) koji su po svojim svojstvima rani i srednje rani hibridi. Također će se utvrditi može li se utrošena energija u procesu sušenja vratiti kroz energetsku iskoristivost ljuske. Temeljem dobivenih rezultata određene su promjene energetskih karakteristika, odnosno sadržaj negorivih tvari (voda, pepeo, koks, fiksirani ugljik i dušik) te gorivih tvari (ugljik, sumpor, vodik, kisik, hlapiva tvar), kao i gornja i donja ogrjevna vrijednost sjemenki suncokreta. Dobiveni podaci dokazuju da konvekcijsko sušenje ljuske suncokreta pozitivno utječe na dobra energetske karakteristike ljuske te se može koristiti za proizvodnju krutog goriva.

Ključne riječi: energija, konvekcijsko sušenje, ljuske suncokreta

Introduction

Sunflower (*Helianthus annuus* L.) is an oilseed crop. In Croatia, it is the main crop for production of edible oil (Pospišil et al., 2006). It is also one of the major feedstock for production of vegetable oil in the world (Kaya, 2005). By its morphology sunflower seed consists of core and husk. According to literature sources (Gupta and Das, 2000) sunflower husk generally makes 20 - 30% of total mass of sunflower seed, pending on the variety. Industrial production of vegetable oil generates a large amount of waste during the entire production process, including the husks of the seeds used as raw material (Quaranta et al., 2011). Edible oil is produced only from seed core, with cake or grit as by-products and sunflower husk as a residue from the production process.

Due to elevated initial moisture after the harvest, sunflower seeds must be processed by convection drying in order to maintain their quality as long as possible. Drying is the oldest method of preserving agricultural products. The drying procedure ensures that sunflower seeds remain unchanged for a certain period of time and that seeds can be used throughout the year (McLean, 1980; Krička et al., 2003; Matin et al. 2013; Matin et al., 2017). The efficiency of drying is influenced by heat intensity of the air, relative humidity, airflow rate and dryer construction. In the drying process water is moved from the seed's interior towards its surface and then from the surface in to the drying air (Mujumdar, 2000). After drying the sunflower seeds must pass through the cleaning line and husk must be separated from the core. Most often, the dried husk remain unused, although it represents usable agricultural biomass. In many European countries, agricultural residues represent an important energy potential (around 250 million tonnes per year) for development of the bio-energy industry (Voća et al., 2016).

Biomass from agricultural production is a very acceptable fuel in terms of environmental impact, especially because it diminishes the atmospheric burden of greenhouse gases (Miller, 1992; Kiš et al., 2013). It is the main energy source for more than a half of world population and provides about 1.25 billion tonnes (tonne of oil equivalent) of primary energy, or covers about 14% of global annual energy consumption (Purohit et al., 2006; Zeng et al., 2010; Bilandžija et al., 2012).

Biomass contains lower sulphur and ash than non-renewable sources, such as coal, and, therefore, generates lower SOx and volatile particles emissions (Van den Broek, 2000; Klason and Bai, 2007). The interest for use of biomass for energy production has been growing recently, due to the fact that biomass is considered CO_2 neutral and because the ability of biomass to regenerate makes it highly available (Raclavska et al., 2011).

Biomass can be converted in to useful energy forms by means of several types of processes. The choice of the conversion process depends on the type, properties and quantity of available biomass, on desired final energy form, environmental standards and economic conditions (Krička et al., 2012).

The utilization of renewable agro-industrial residues has been attracting interest because of high petrol prices and depletion of fossil fuel reserves and, more recently, increasing environmental and political pressures (Davis et al., 2005; Okur and Saraçoĝlu, 2007). Environmental pollution and proper disposal of organic agricultural wastes have prompted studies on developing technologies that will downscale that problem.

Bilandžija et al. (2018) state that sunflower production yield is 2.77 $t*ha^{-1}$, mass ration 1:0.19 ($t*t^{-1}$), biomass yield 0.526 $t*ha^{-1}$ and average potential per hectar 9.37 MJ what makes sunflower husk one of most significant agro-industrial biomass.

Therefore, the aim of this paper is to examine sunflower husk as fuel treated at different temperatures and to determine the influence of those temperatures on husk's energy properties, namely, to determine usability of sunflower husk after drying for the purpose of energy utilisation in various forms.

Materials and methods

Materials

For the purpose of investigating the usability of sunflower seed husk for energy the analyses were carried out of the contents of non-combustible and combustible matters and heating values using standard methods in three repetitions. The investigations were conducted on sunflower hybrids (Apolon, NK Brio, PR 63 A 90, PR 63 D 82), which by their properties are early and medium-early hybrids. The early hybrids are Apolon and PR 63 A 90, while NK Brio and PR 63 D 82 are medium-early hybrids.

The sampling was carried out in accordance with the Ordinance on the methods for sampling and seed quality inspection 99/2008 (Ministry of Agriculture, 2008).

Treatment

Drying was conducted in a lab-scale dryer (Department of Agricultural Technology, Storage and Transport, Croatia) at air temperatures of 60 °C, 80 °C, 100 °C and air flow of 1 $m*s^{-1}$ in a stationary layer 15 cm thick. The dryer consisted of a centrifugal fan to supply the air flow, an electric heater, air filter and an electronic proportional controller. Air temperatures were controlled by a proportional controller and air flow-rate for all drying runs was measured with anemometer (Edra five). Drying was conducted until the moisture level of 8.5% was reached. All measurements were carried out in triplicates.

Analytical methods

The analytical investigation was conducted in the laboratory of the Department of Agricultural Technology, Storage, and Transport of the Faculty of Agriculture, University of Zagreb.

Combustible matter

Samples were characterized by proximate analysis according to standard methods: moisture content (HRN EN 18134-2:2015) in a laboratory oven (INKO ST-40, Croatia), whereas ash (HRN EN ISO 18122:2015), fixed carbon (by difference) and coke (CEN/TS 15148:2009) were determined by use of a muffle furnace (Nabertherm GmbH, Nabertherm Controller B170, Germany) and nitrogen (N) (HRN EN ISO 16948:2015) by method of dry combustion in a Vario Macro CHNS analyser (Elementar Analysensysteme GmbH, Germany).

Non-combustible matter

Total carbon, hydrogen (HRN EN ISO 16948:2015) and sulphur (HRN EN ISO 16994:2015) were determined simultaneously by method of dry combustion in a Vario Macro CHNS analyser (Elementar Analysensysteme GmbH,Germany). The oxygen content was calculated by difference, as well as the content of volatile matter (EN 15148:2010).

Heating value

The heating value was determined by method (EN 14918:2010) using an IKA C200 oxygen bomb calorimeter (IKA Analysentechnik GmbH, Heitersheim, Germany). Heating value is reported in MJ*kg^{-1} on a dry basis.

Statistical analysis

All data obtained in this way were analysed according to the GLM procedure in the SAS system package version 9.3 (SAS Institute, Cary, NC, USA).

Results

The results regarding the content of non-combustible matters in sunflower husk (moisture, ash, coke, fixed carbon and nitrogen (N)), i.e., the statistical analysis of the influence of the hybrid type on naturally dried sunflower husk, are presented in Table 1, The analysis of the influence of the hybrids regarding drying temperatures is given in Table 2.

Table 1. Non-combustible matter of natural sunflower shell

Parameter/ Samples	MC (%)	AC (% db)	CK (% db)	FC (% db)	N (% db)
	<0.0001***	0.2398 NS	0.0021**	0.0282*	<0.0001***
Apolon	15.2±1.45[c]	3.12±0.1[a]	25.11±0.27[b]	18.17±0.36[b]	0.87±0.01[d]
NK Brio	18.09±0.29[b]	2.99±0.03[a]	27.36±0.8[a]	19.42±0.58[a]	1.28±0.01[a]
PR63A90	19.14±0.13[ab]	3.09±0.07[a]	28.46±1.02[a]	19.92±0.82[a]	1.13±0.01[c]
PR63D82	20.48±0.13[a]	3.09±0.08[a]	27.98±0.56[a]	19.16±0.34[ab]	1.17±0.05[b]

% db - % on dry basis; MC - Moisture Content; AC - Ash Content; CK - Coke; FC - Fixed Carbon; N - Nitrogen. [a,b,c]Different letters within a column indicate significant differences at the 5% level. Significance: *** P<0.001; ** P<0.05, NS - Non-significant.

Table 2. Non-combustible matter of dried sunflower shell

Parameter/ Samples	MC (%)	AC (% db)	CK (% db)	FC (% db)	N (% db)
	<0.0001 ***	0.0493*	<0.0001***	<0.0001***	<0.0001***
Aplon	8.03±0.49[ab]	2.72±0.09[b]	18.09±0.15[b]	13.92±0.19[b]	1.26±0.01[a]
NK Brio	7.92±0.24[b]	2.96±0.34[a]	18.57±0.82[c]	14.15±0.84[c]	1.14±0.12[a]
Pr63A90	8.36±0.49[a]	2.8±0.06[ab]	19.32±1.48[a]	14.92±1.31[a]	1.01±0.09[c]
Pr63D82	7.43±0.17[c]	2.75±0.17[b]	17.79±0.82[b]	13.72±0.68[b]	1.03±0.11[b]
Temp	0.8692 NS	0.6606 NS	0.8619 NS	0.8997 NS	0.1543 NS
60 °C	7.93±0.59[a]	2.83±0.22[a]	16.73±3.3[a]	12.59±3.18[a]	1.16±0.16[a]
80 °C	7.99±0.49[a]	2.84±0.28[a]	17.2±3.11[a]	12.98±2.95[a]	1.02±0.19[a]
100 °C	7.88±0.42[a]	2.76±0.1[a]	16.53±2.71[a]	12.46±2.49[a]	1.12±0.18[a]
Hib*Tem	<0.0001***	0.5627*	<0.0001***	<0.0001***	<0.0001***

% db - % on dry basis; MC - Moisture Content; AC - Ash Content; CK - Coke; FC - Fixed Carbon; N - Nitrogen. [a,b,c]Different letters within a column indicate significant differences at the 5% level. Significance: *** P<0.001; ** P<0.05. NS - Non-significant.

The contents of combustibles: carbon (C), sulphur (S), hydrogen (H), oxygen (O) and volatile matters, i.e. statistical analysis of the influence of specific hybrids on naturally dried sunflower husk are given in Table 3, and the analysis of the influence of hybrids types by drying temperature is shown in Table 4.

Table 3. Combustible matter of natural sunflower shell

Parameter/Samples	C (% db)	S (% db)	H (% db)	O (% db)	VM (% db)
	<0.0001***	<0.0001***	<0.0001***	<0.0001***	0.0002***
Apolon	55.83±0.96[b]	0.15±0.02[b]	4.56±0.08[d]	39.2±0.05[a]	63.51±1.25[a]
NK Brio	62.87±0.22[a]	0.15±0.01[a]	5.73±0.02[a]	29.76±0.25[c]	59.5±0.8[b]
Pr63A90	63.16±0.1[a]	0.15±0.01[c]	5.62±0.01[b]	29.93±0.12[c]	57.85±0.9[b]
Pr63D82	62.8±0.1[a]	0.14±0[d]	5.21±0.01[c]	30.62±0.05[b]	57.27±0.51[a]

% db - % on dry basis; C - Carbon; S - Sulphur; H - Hydrogen; O - Oxygen; VM - Volatile Matter.
[a,b,c]Different letters within a column indicate significant differences atthe 5% level. Significance: *** P<0.001; ** P<0.01; * P<0.05. NS - Non-significant.

Table 4. Combustible materials (carbon (C), sulfor (S), hydrogen (H), oxygen (O) and volatlle matter) of dried sunflower shell

Parameter/ Samples	C (% db)	S (% db)	H (% db)	O (% db)	VM (% db)
Hibrid	<0.0001***	<0.0001***	<0.0001***	<0.0001***	<0.0001***
Aplon	54.04±0.64[c]	0.13±0.03[b]	4.74±0.08[c]	39.83±0.64[a]	75.33±0.43[b]
NK Brio	56.37±0.4[a]	0.14±0.06[a]	5.02±0.06[a]	37.23±0.36[c]	80.96±0.87[a]
Pr 63A90	55.56±0.35[b]	0.12±0.05[c]	4.91±0.07[b]	38.54±0.39[b]	73.33±1.63[c]
Pr 63D82	55.23±1[b]	0.13±0.07[bc]	4.83±0.12[b]	38.78±1.23[b]	76.09±0.88[b]
Temp	0.0922 NS	0.6945 NS	0.6945 NS	0.07 NS	0.8366 NS
60 °C	55.83±0.62[a]	0.13±0.05[b]	4.91±0.12[c]	37.96±0.71[b]	76.67±3.14[a]
80 °C	55.08±1.3[ab]	0.12±0.08[a]	4.82±0.15[b]	38.96±1.4[a]	76.19±2.99[a]
100 °C	54.99±0.98[b]	0.13±0.01[c]	4.9±0.12[b]	38.86±1.14[ab]	76.89±2.65[a]
Hib*Tem	<0.0001***	<0.0001***	<0.0001***	<0.0001***	<0.0001***

C - Carbon; S - Sulphur; H - Hydrogen; O - Oxygen; VM - Volatile Matter; % db - % on dry basis.
[a,b,c]Different letters within a column indicate significant differences atthe 5% level. Significance: *** P<0.001; ** P<0.01; * P<0.05. NS - Non-significant.

Table 5 gives the data of higher (HHV) and lower (LHV) heating values for the naturally dried sunflower husk, and Table 6 gives the equivalent data for the convection-dried samples.

Table 5. Heating values of natural sunflower shell

Parameter/Samples	HHV ($MJ*kg^{-1}$)	LHL ($MJ*kg^{-1}$)
Hybrid	0.0013**	0.0014**
Apolon	$22.46±0.38^{b}$	$21.47±0.36^{ab}$
NK Brio	$23.19±0.47^{b}$	$21.94±0.48^{b}$
Pr 63 A 90	$22.12±0.12^{b}$	$20.89±0.2^{b}$
Pr 63 D 82	$21.19±0.4^{c}$	$20.05±0.4^{c}$

HHV - Higher Heating Values. LHV - Lower Heating Values. ^{a,b,c}Different letters within a column indicate significant differences at the 5% level. Significance: *** P<0.001; ** P<0.01; * P<0.05. NS - Non-significant.

Table 6. Heating values of dryed sunflower shell

Parameter/Samples	HHV ($MJ*kg^{-1}$)	LHL ($MJ*kg^{-1}$)
Hibrid	0.7927 NS	0.7617 NS
Aplon	$20.16±0.24^{a}$	$19.13±0.25^{a}$
NK Brio	$20.19±0.06^{a}$	$19.1±0.06^{a}$
Pr 63 A 90	$20.07±0.42^{a}$	$18.99±0.41^{a}$
Pr 63 D 82	$20.12±0.25^{a}$	$19.07±0.26^{a}$
Temperature	0.6945 NS	0.7491 NS
60 °C	$20.2±0.33^{a}$	$19.12±0.33^{a}$
80 °C	$20.11±0.2^{a}$	$19.06±0.21^{a}$
100 °C	$20.11±0.27^{a}$	$19.04±0.27^{a}$
Hib*Tem	<0.0001***	<0.0001***

HHV - Higher Heating Values. LHV - Lower Heating Values. ^{a,b,c}Different letters within a column indicate significant differences at the 5% level. Significance: *** P<0.001; ** P<0.01; * P<0.05. NS - Non-significant.

Discussion

The analysis of the data in Tables 1 and 2 shows that the values of non-combustible matters in husk, i.e., water, ash, coke, and fixed carbon and nitrogen (N) are significantly diminished, and nitrogen (N) is the only element that increases in the dried husk. The moisture content was significantly lowered, from average 18.23% in the natural samples down to 7.94% in dried sample; ash content drops from 3.07% to 2.81%; coke from 27.23% to 18.44%; fixed carbon from 19.17% to 14.18%.

Nitrogen (N) was slightly higher, from 1.11% in the natural sample to 1.14% after drying. For all investigations of non-combustible matters, the temperature of 80 ºC proved to be the most favourable, because at this temperature the largest amount of coke is obtained, and higher coke content largely contributes to the quality of a fuel (Boboulos, 2010). As for other non-combustibles, nitrogen (N) content is also important because it lowers heat value of the combustion; the presence of ash determines the quality of fuel, since with a lower ash content the quality of fuel increases. Ash has a catalytic influence on thermal decomposition and with ash concentration increasing, coal and gases also increase (McKendry, 2002). When a percentage share of ash is higher, the quantity of combustible matter is lower, as is the case with mositure content (Sluiter et al., 2005). The content of ash is most often between 0.5 and 3%, depending on the type of agricultural biomass and parts of biomass, although it can vary in a very wide range from 0.1% to 46% (Vassilev et al., 2010). According to literature, the moisture content in sunflower husk is between 18% and 20%, fixed carbon about 19% (Vassilev et al., 2010), while Demirbas (2006) states fixed carbon content of 19.8%, and nitrogen (N) of 1.4%. According to Khan et al. (2009), in general, biomass contains 30 – 60% of carbon (C); 5 – 6% of hydrogen (H); and 30 – 45% of oxygen (O), while nitrogen (N), sulphur (S) and chlorine (Cl) can be found in quantities usually below 1%. The results are consistent with the literature references. The variance analysis showed a very significant interaction ($P<0.001$) of the investigated parameters (hybrid x temperature) with the water, coke, fixed carbon, and nitrogen (N) contents, while it had a significant influence on the ash content.

According to the data presented in Tables 3 and 4, the content of combustible matters carbon (C), sulphur (S) and hydrogen (H) significantly decreases after thermal processing, while the contents of oxygen (O) and volatile matters significantly rises after drying. In average, carbon (C) was decreased from 61.17% in the natural sample to 55.3% in the dry sample, sulphur (S) from 0.15% to 0.13%, and hydrogen (H) from 5.28% to 4.88%. After drying, oxygen (O) was increased from average 32.38% in the natural sample to 38.35%, and volatile matters from 59.53% up to considerable 76.42%. The best temperature for the combustible matters content proved to be 60 ºC as this is a temperature at which the highest amount of carbon (C) and hydrogen (H) were obtained. Carbon is a critical combustion property because it determines the quality of fuel: the higher the carbon content (C) in a fuel the higher the heating value. Carbon in biomass is bound in complex compounds and during combustion process it oxidises releasing energy (Brown, 2011). Hydrogen represents the second most important combustion property in a fuel. It increases its heating value and creates flame and is most responsible for developing gases. Sulphur is an undesirable element and is present in biomass in traces; if it is bound to organic matters it is highly detrimental for the environment (Obernberger and Thek, 2004). The presence of oxygen in a fuel is also undesirable because it may affect the combustion by replacing a part of oxygen from the air which is indispensable for burning (Vasillev et al., 2010). By increasing fixed carbon the heating value of fuel is also increased; in biomass it is found in a range from 7 to 20% (Yao et al., 2005). The obtained values are consistent with the literature where Haykiri – Acma i Yaman (2009) and Yin (2011) state that sunflower husk contains 51.7% carbon and as much as 6.2% hydrogen. Friedl et al. (2005) state the content of carbon (C) of 50.5% and sulphur (S) of 0.1%, which are the values consistent with this investigation. The study by Antal et al. (2007) states the content of carbon (C) of 50.48%, sulphur (S) of 0.11%, hydrogen (H) of 5.82% and oxygen (O) of 43.33%. The variance analysis showed a highly significant interaction ($P<0.001$) of the investigated parameters (hybrid x temperature) with the contents of carbon (C), sulphur (S), hydrogen (H), oxygen (O) and volatile matters.

The analysis of these data shows that after drying heating value considerably diminishes, and the smallest reduction in heating value is found at the lowest drying temperature of 60 ºC. Thus, higher heating value HHV dropped from average 22.24 $MJ*kg^{-1}$ in the natural sample to 20.14 $MJ*kg^{-1}$ in the dried sample; lower heating value (LHV) diminished from 21.09 $MJ*kg^{-1}$ in the natural sample to 19.07 $MJ*kg^{-1}$ in the dried sample. Based on the results quoted by Yin (2011) who found higher heating value (HHV) of sunflower husk of Hg 19.5 $MJ*kg^{-1}$ and Zabanitou et al. (2008) who found lower heating value (LHV) of the same material of 17.35 $MJ*kg^{-1}$, it can be determined that the results of this investigation are in line with the literature references. The variance analysis revealed a high interaction ($P<0.001$) of the investigated parameters (hybrid x temperature) with higher heating value (HHV) and lower heating value (LHV).

Conclusions

Following the analysed data it can be determined that convection drying of sunflower seed husk has a positive effect on energy (combustion) properties, which is confirmed by high carbon (C) content, and by higher (HHV) and lower heating value (LHV). The obtained data proved that sunflower husk carries high energy potential and is potentially a very valuable feedstock for energy production when compared to other agricultural biomass. Furthermore, it was proved that drying has a positive effect on the energy value and enhances the energy potential of husk.

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