EFFECTS OF DIFFERENT AIR DRYING TEMPERATURE ON SUNFLOWER SEEDS OIL AND ASH CONTENT

UTICAJ RAZLIČITIH TEMPERATURA VAZDUHA ZA SUŠENJE NA SUNCOKRETOVO ULJE I SADRŽAJ PEPELA

Ana MATIN, Tajana KRIČKA, Vanja JURIŠIĆ, Neven VOĆA, Julijana ŽUNIĆ, Mateja GRUBOR
University of Zagreb Faculty of Agriculture, Svetošimunska cesta 25, 10 000 Zagreb, Hrvatska
e-mail: amatin@agr.hr

ABSTRACT

The aim of this paper was to determine the impact of different air temperature (60 °C, 80 °C and 100 °C) at air drying velocity of 1.0 ms⁻¹ during convection drying thermal process on the sunflower seeds oil and ash content. The research was conducted at 4 different sunflower seeds hybrid Apollo, NK Brio, PR 63 and PR 90 A 63 D 82, which by their characteristics are early and medium early hybrids. Based on the results, the curve of water speed release from the sunflower seeds, the activation energy, as well as changes in oil content and ash content before and after the convective drying was obtained. It was established that the NK Brio hybrid fastest release water compared to other hybrids during drying which is confirmed by minimum value of activation energy and that the increasing of air drying temperature increases oil content, while reduces ash content.

Key words: sunflower seed, convection drying, activation energy, nutritional properties.

REZIME

Suncokret (*Helianthus annuus* L.) je najznačajnija uljarica u Republici Hrvatskoj za proizvodnju jestivog ulja. Sjemenke suncokreta moraju se termički doraditi kako bi skladištenje bilo što kvalitetnije. Stoga je cilj ovog rada utvrditi utjecaj različitih temperatura zraka termičkog procesa konvekcijskog sušenja (60°C, 80°C i 100°C) na sadržaj ulja i pepela sjemenki suncokreta. Istraživanje je provedeno na 4 različita hibrida sjemenki suncokreta Apolon, NK Brio, PR 63 A 90 i PR 63 D 82, koji su po svojim svojstvima rani i srednje rani hibridi. Na temelju dobivenih rezultata, određene su krivulje brzine otpuštanja vode iz sjemenki suncokreta i energija aktivacije E_a , kao i promjene sadržaja ulja i pepela prije te nakon konvekcijskog sušenja. Istraživanjem je utvrđeno da hibrid NK Brio najbrže otpušta vodu iz sjemenki suncokreta, pri svim temperaturama. Također je utvrđeno da kod svih eksponencijalnih ednadžbi koeficijent determinacije iznosi između 0.850 i 0.973 što pokazuje da su istraživanja otpuštanja vode iz sjemenki suncokreta vođena precizno te da su dobiveni rezultati međusobno usporedivi i ponovljivi. Iz dobivenih rezultata može se utvrditi najveća energija aktivacije kod hibrida PR 63 D 82 (23.66 kJ/mol) te najmanja kod hibrida NK Brio (18.79 kJ/mol). Istraživanjem je također utvrđeno da postoji značajna razlika u količini pepela u prirodnim uzorcima sjemenki suncokreta te se kretala u rasponu od 2.86 do 4.60%, dok se količina pepela nakon sušenja nije se značajno promijenila. Količina ulja u prirodnim uzorcima sjemenki istraživanih hibrida kretala se u rasponu od 45.26 do 58.12%, dok je nakon sušenja količina ulja rasla.

Ključne riječi: sjemenka suncokreta, konvekcijsko sušenje, energija aktivacije, nutritivna svojstva.

INTRODUCTION

Human nutrition today is unimaginable without the production of oil and solid plant fats, and buckshot and cake that arise during the oil preparation are by-products necessary in livestock (Krička *et al.*, 2009). Sunflower (*Helianthus annuus* L) is the most important oleaginous crop for production of edible oil in the Republic of Croatia. According to the State Bureau of Statistics (2015) the sunflower production in Croatia in 2015 was 94.075 tonnes. The sunflower yield depends on quantity of water in the intensive growing phase and oil synthesis phase, so that in the years with abundant precipitations, which stimulate the development of diseases, there is a significant reduction of sunflower seed yield, and consequently of oil yield.

By botanical definition, the sunflower is a fruit or seed consisting of two main parts. The hull or pericarp is a visible outer component that protects the inner kernel. Information about sunflower seed and kernel physical and mechanical properties are necessary for seeding, harvesting, handling, drying, storage and further processing. Sunflower fruit is the raw material used for sunflower oil production for human consumption, and its defatted meal, as a feed for livestock, has advantages over other oilseed farm crops (Babić *et al.*, 2012).

Post-extraction seed processing gives protein-rich grits or cake which represents a high quality feed for animal nutrition and a valuable resource in animal farming.

However, sunflower seed must be thermally processed in order to preserve the seed quality during the period of storage and to prevent negative physical and chemical changes on the seed. Classical drying technology, only convective drying with heated air, is one of the most common procedures (Pavkov *et al.*, 2011).

Consequently, drying is only a sequence and a finalizing stage of natural seed maturation, which was somehow prevented. In order to enable the longest possible period of storage of sunflower seed, drying process has to preserve the quality of seed and ensure the normal conditions which they require (Krička *et al.*, 1998). During the drying process, the seed in contact with environmental air releases water up to the point of equilibrium moisture content.

The seed moisture level at which the equilibrium moisture content will be established depends on air condition, air temperature and relative humidity (Matin, 2013). The equilibrium moisture depends on relative humidity and air temperature in the environment. The equilibrium moisture content in the same conditions of the environmental air varies from one crop to another (Katić, 1997).

The efficiency of drying is influenced by air, its heat intensity, relative humidity, air flow velocity and dryer design (Krička, 1993; Katić et al., 1994). The drying method, or drying air temperature and the temperature to which the product is exposed, should be adjusted to the product's characteristics and its future use (Katić, 1997). In the drying process, water moves from the seed's interior toward its surface and then is transferred from the fruit surface (product) to the drying air (Mujumdar, 2000). Drying is an old process and as such is directly a subject of various innovations. If it had not been permanently improved and advanced, it would have probably disappeared, because today a great number of different materials is dried in the drying processes (Babić et al., 2006). As one of the preservation methods, drying enables the seeds to reduce the moisture content, and contributes to creation of the product with new quality features and new dietary and economic values (Akpınar et al., 2003; Babalis and Belessiotis, 2004). This procedure ensures that the product can be preserved for certain period of time without changes as well as the possibility of its use year-around (McLean, 1980; Krička and Pliestić, 1994; Krička et al., 2001; Krička et al., 2003; Matin et al., 2007).

Bala (1997) defined the activation energy or activation energy (E_a) for a reaction of seed water release as energy that must be supplied to trigger water molecules to interact. In order to interact, water molecules must collide, but only those molecules can interact which have energy higher than activation energy. Activation energy is brought to molecules by conversion of their kinetic energy into potential energy. Because of this, if kinetic energy of seed water molecules is not sufficiently high, it can fully convert into potential energy by their collision, but it will not create an activated complex and the molecules will only move apart from each other as soon as potential energy falls. The higher potential energy barrier, i.e., the higher the activation energy for a reaction, the lesser the number of reactants' molecules that can cross the energy barrier and in such case, the reactions are slower. Activation energy value for most of agricultural products comes in a ratio 12.7 to 110 kJ/mol (Chayjan et al., 2011). According to literature references, activation energy needed for hazelnut drying is 22.5 kJ/mol (Demir and Cronin, 2005), mushrooms 30.80 kJ/mol to 48.47 kJ/mol (Babalis and Belessiotis, 2004), berry fruit 110.84 kJ/mol to 130.61 kJ/mol (Aghbashlo et al., 2008), seedless grapes 44.81 kJ/mol to 46.30 kJ/mol (Chayjan et al., 2011).

On the basis of this the objective of this work is to determine the influence of temperature on water release before and after thermal process of convection drying on the activation energy values and water, ash and oil content in sunflower seeds.

MATERIAL AND METHOD

The samples of sunflower seed hybrids (Apolon, NK Brio, PR 63 A 90, PR 63 D 82) were cultivated during 2015. The samples were first coalesced and then separated in a separator in two procedures, each of them comprising of eight sub-separations, in accordance to the Rulebook on methods of sampling and quality control 137/2004 (Official Gazette, 2004). The seeds were manually cleaned to remove all foreign matter. The analysis of sunflower seed was conducted before and after convection drying in three sample groups.

Drying was conducted in a laboratory dryer in a 15 cm thick stationary layer. Air speed in the dryer was maintained at 1.0 m s^{-1} , and the samples were dried at air temperatures 60 °C, 80 °C and 100 °C. Just before drying, water content in the sunflower seed samples was determined. Mass loss was determined by use of a digital scale every 5 minutes until 7.5 % equilibrium moisture content was reached.

For each group of samples water content was determined by standard methods in the laboratory dryer (INKO ST-40, Croatia) (HRN EN ISO 2171:2010), ash content was determined in a muffle oven (HRN EN ISO 712:2010) and oil content on an extractor Soxhlet R 304 (Behr Labortechnik GmbH, Germany) (HRN EN ISO 6492:2011).

Statistical data processing was carried out by use of SAS package version 9.1 (SAS Institute, Cary, NC, USA) using GLM procedure with significance level $P \geq 0.05$.

RESULTS AND DISCUSSION

At the harvest time, sunflower seeds most often have a moisture above hygroscopic equilibrium. Due to this and for purpose of efficient storage the seeds must be preserved by thermal processing. In Table 1 the results of moisture, ash and oil content in dry matter in the sunflower seeds of the investigated hybrids in a natural sample are given.

Table 1. Water, fat and ash content per dry basic of natural sunflower kernel

Sample	Water (%)	Oil (%)	Ash (%)
Apolon	$18.44^a \pm 0.01$	46.07 ± 0.49^c	3.98 ± 0.03^a
NK Brio	$20.37^d \pm 0.02$	45.26 ± 0.44^c	2.86 ± 1.14^b
PR 63 A 90	$18.06^b \pm 0.04$	58.19 ± 0.90^a	4.53 ± 0.15^a
PR 63 D 82	$17.64^c \pm 0.22$	55.70 ± 0.59^b	4.60 ± 0.04^a

Mean values $\pm$ SD values marked with identical letter are not significantly different ($p < 0.05$)

According to data in Table 1, the parameters of moisture and oil content are significantly different while ash does not display significant differences except in hybrid NK Brio. The hybrid NK Brio sunflower seeds had the highest moisture of 20.32 % and the lowest ash content of 2.86 %, while hybrid PR 63 A 90 contained the highest oil of 58.19 %. The results are somewhat higher than those obtained by Flagella et al., 2002, who state that sunflower nucleus contains about 49.00 % oil at average, and Robertson et al., 1984 who quote an oil content of 45.80 %. Krizmanić et al., (2013) from their three-year investigations at two locations in Croatia (Nova Gradiška, Osijek) found statistically significant differences in oil content and fatty acid composition in sunflower seed between the years and locations, which indicates that, besides genotype, agro-ecological factors have considerable influence on these properties. Pospíšil et al., (2006), who conducted four-year investigations in Croatia (western Slavonia) also state that seed and oil yield is significantly influenced by weather conditions, hybrid type and their interaction. In Table 2 the Exponential equation for drying at air drying temperatures 60 °C, 80 °C and 100 °C and air flow speed of 1.0 m s^{-1} in hybrids Apolon, NK Brio, PR 63 A 90, PR 63 D 82 up to equilibrium moisture content of 7.5 % are presented. The analysis of the results of the investigated sunflower hybrids and air drying temperatures presented in Table 2 displays the differences in water release rates. Based on the above presented exponential equation for drying it can be determined that hybrid NK Brio has the fastest water release from sunflower seed at all temperatures. This is corroborated by shorter time needed for water release before reaching 7.5 % equilibrium moisture content and a higher exponent value. Namely, the exponents show the tendency of drying rate and with a higher exponent value the drying is faster (Krička, 1993). In all investigated exponential equations the determination coefficient between 0.850 and 0.973 was found which corroborates that the investigated seed water releases were conducted with precision and that the results are mutually comparable.

Table 2. Exponential equations of sunflower seed water release rate

Sample	Exponential equation for drying	Coefficiente of determination (R^2)
Aplon		
60 °C	$y = 14.293e^{-0.006x}$	0.850
80 °C	$y = 14.921e^{-0.015x}$	0.896
100 °C	$y = 17.264e^{-0.0592x}$	0.967
NK Brio		
60 °C	$y = 16.719e^{-0.007x}$	0.949
80 °C	$y = 17.73e^{-0.0197x}$	0.957
100 °C	$y = 18.73e^{-0.0594x}$	0.973
PR 63 A 90		
60 °C	$y = 14.538e^{-0.0063x}$	0.870
80 °C	$y = 15.499e^{-0.0121x}$	0.951
100 °C	$y = 16.265e^{-0.0346x}$	0.947
PR 63 D 82		
60 °C	$y = 15.137e^{-0.0054x}$	0.966
80 °C	$y = 14.046e^{-0.0094x}$	0.906
100 °C	$y = 16.057e^{-0.0344x}$	0.971

Due to significant differences in feedstock repetitions, the coefficient of determination in the hybrid Apolon at a temperature of 60 °C (0.850) and 80 °C (0.896) as well as the hybrid PR 63 A 90 at 60 °C (0.870) show lower drying kinetics. This is also confirmed by a comparison with literature data for hazelnut drying process (Demir and Cronin, 2005; Özdemir and Devers, 1999), corn drying (Krička, 1993; Krička and Plietić, 1994; Krička and Plietić, 1997;), and seedless grapes drying (Chayjan et al., 2011).

Further, in table 3 the activation energy needed for triggering the sunflower seed water release process in the investigated hybrids is presented.

Table 3. Values of activation energy needed for starting sunflower seeds water release process

Sample	Activation energy E_a kJ/mol
Apolon	20.09 ± 1.59^c
NK Brio	18.79 ± 0.52^b
PR 63 A 90	20.83 ± 0.94^a
PR 63 D 82	23.66 ± 2.02^c

Mean values $\pm$ SD values marked with identical letter are not significantly different ($p < 0.05$)

The results in Table 3 displays that there are significant differences of activation energy values. By calculation of the activation energy value the needed energy can be determined, which should be made available to sunflower seed by thermal procedure of convection drying with the view to incite molecules to interact in order to trigger the drying process. Namely, with higher activation energy the reaction is slower, i.e., the drying is slower. The obtained results show that hybrid PR 63 D 82 has the highest activation energy (23.66 kJ/mol) and hybrid NK Brio (18.79 kJ/mol) has the lowest activation energy. The activation energy value for most of the agricultural products is in a range from 12.7 to 110 kJ/mol (Chayjan et al., 2011). According to literature references, activation energy for hazelnut drying is 22.5 kJ/mol (Demir and Cronin, 2005), mushrooms from 30.80 kJ/mol to 48.47 kJ/mol (Babalís and Belessiotis, 2004), for berry fruit 110.84 kJ/mol to 130.61 kJ/mol (Aghbashlo et al., 2008), and for seedless grapes 44.81 kJ/mol to 46.30 kJ/mol (Chayjan et al., 2011). It results that activation energy is directly related to seeds water release rate, i.e., it is inversely proportional to water release rate (Bala, 1997).

In table 4 the results of water oil and ash content in dried sunflower seed are presented.

Table 4. Water, fat and ash content per dry basic of dried sunflower kernel

Sample	Water (%)	Oil (%)	Ash (%)
Aplon			
60 °C	2.79 ± 0.22^c	47.40 ± 1.63^b	3.98 ± 0.07^c
80 °C	2.21 ± 0.59^d	47.69 ± 1.56^a	3.85 ± 0.01^d
100 °C	2.26 ± 0.30^d	48.67 ± 0.76^a	4.02 ± 0.06^c
NK Brio			
60 °C	4.59 ± 0.20^a	46.95 ± 0.01^a	3.53 ± 0.02^f
80 °C	3.36 ± 0.01^b	47.94 ± 0.06^b	3.64 ± 0.04^e
100 °C	3.31 ± 0.02^b	49.16 ± 0.01^a	3.34 ± 0.04^g
PR 63 A 90			
60 °C	1.58 ± 0.26^c	59.79 ± 0.28^a	4.32 ± 0.02^a
80 °C	1.32 ± 0.04^e	60.87 ± 0.40^a	3.21 ± 0.12^h
100 °C	1.21 ± 0.37^e	61.34 ± 0.85^a	4.35 ± 0.06^a
PR 63 D 82			
60 °C	3.33 ± 0.43^b	56.13 ± 8.20^b	4.18 ± 0.02^b
80 °C	3.30 ± 0.02^b	56.21 ± 1.73^c	4.31 ± 0.01^a
100 °C	2.79 ± 0.18^c	59.02 ± 0.52^b	4.29 ± 0.03^a

Mean values $\pm$ SD values marked with identical letter are not significantly different ($p < 0.05$)

The analysis of the results in Table 4 displays the significant differences of the investigated parameters except in hybrid PR 63 A 90. This hybrid contained the highest oil content at all air drying temperatures compared to other investigated hybrids. It can be observed that oil is the dominant ingredient of the sunflower seed and its content grow after thermal treatment. As stated by (Babić and Babić, 2006) the changes occurring in the process of seed drying are inevitable which is visible in the results obtained.

CONCLUSION

By comparing the convection drying times by treatments (temperature 60 °C, 80 °C and 100 °C) it was determined that of all hybrids NK Brio had the highest water release rate during the drying process, which is corroborated by higher drying exponent values and the lowest activation energy values.

By monitoring the changes in water, ash and oil content in the sunflower seeds during the thermal process of drying it was determined that drying plays a significant role in increasing oil content which is a positive characteristic given the fact that sunflower is the leading crop for production of edible oil. After drying the hybrid PR 63 A 90 has proven to be the best for oil production given the amount of the resulting oil.

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