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Otpuštanje vode konvekcijskim sušenjem različitim temperaturama iz sjemenki uljane repice

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RELEASE OF WATER BY CONVECTIVE DRYING FROM RAPESEED AT DIFFERENT TEMPERATURES

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SUMMARY

Rapeseed is one of the most important oil plants in the world. The objective of this research was to analyse the influence of thermal treatment temperature on rapeseed quality, i.e. to investigate the content of oil and free fatty acids in chosen rapeseed hybrids: Turan, Traviata, NK Toccata, NK Petrol, PR 46 W 14 and PR 46 W 15. By their characteristics, these varieties are early, medium-early and medium-late hybrids. The initial moisture content of the investigated hybrids ranged from 11.28% to 11.69%. The hybrids were subjected to thermal process of thin-layer convective drying, at temperatures of 40°, 60° and 80°C and air velocity of 1.0 m/s. During the investigation, decomposition of oil due to drying at 80°C and increase of free fatty acids concentration above permitted 2% were observed. Furthermore, based on the obtained results, velocity of water release from seed have been determined, and the drying process was mathematically modelled, whereby determination coefficient (R²) and activation energy were also determined.

Key-words: rapeseed, free fatty acids, convective drying, mathematical modelling, activation energy

INTRODUCTION

Rapeseed is one of the industrial plants whose economic importance is increasing in Croatia and in the European Union (Kachel-Jakubowska and Szpryngiel, 2008). Only the EU member states (EU-28) produce more than 20 million tonnes of rapeseed making 31% of the global production (FAOSTAT, 2016). The main factor, which determines usability of rapeseed as animal feed, as raw material for food production and other non-food purposes, can be researched with the aim of improving varieties, seed yield, oil content, proteins and active substances. Changes in the composition and fatty acids content as well as to reduce anti-nutritional components in seeds by treatments can also determinate rapeseed usability (Podkówka, 2004; Bomb et al., 2007; Wakowski, 2006). Factors that significantly influence the oilseeds yield and oil content are hybrid or variety (Gunasekera et al., 2006; Marjanović-Jeromela et al., 2011). High rapeseeds quality can be ensured by an adequate post-harvesting treatment in order to minimise the adverse effects of storing, e.g., high water activity or temperatures and drying times which affects the com-

mercial quality of oil, flours and other derivatives (Gely and Santalla, 2000).

For determination of quality drying process, it is crucial to gather a bigger number of information about rapeseed varieties and the influence of chemical properties on drying kinetics (Gely and Santalla, 2000). Different moisture content and changes in chemical composition during drying process influence on drying kinetics (Gupta and Das, 1997; Brooker et al., 1992). The speed and drying quality of agricultural products depend on environment physical characteristics, physical characteristics of the raw material, and the layer thickness (Krička et al., 2007). Drying can be defined as one of the oldest methods for food preservation (Doymaz, 2007). It is probably the main and the most expensive step in post-harvest operations (Cohen and Yang 1995; Mirzaee et al., 2009). The main purpose of drying is to separate excessive water from the product

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without deteriorating its quality in the process. This procedure provides certain time for preserving the products unchanged and the possibility of using the products throughout the year.

The essential factors for a successful drying process are moisture diffusion, activation energy (E_a), heat and mass transfer, as well as specific energy consumption (Aghbashlo et al., 2008). These factors can be changed by convective drying process and they are influenced by materials and drying parameters (Chayjan et al., 2011). Modelling of the drying process is the most important aspect of the drying technology (Khazaei and Daneshmandi, 2007). In optimisation of dryers the most important factor is prediction of agricultural products drying kinetics under various conditions (Aghbashlo et al., 2008).

In order to optimize the procedure of any thermal treatment method, mathematical models are used to describe the drying kinetics of agricultural products (Karim and Hawlader, 2005). Drying kinetics is significantly influenced by air temperature, air velocity, material size, and drying time (Khazaei et al., 2008).

The researchers describe mathematical modelling of the kinetic process of drying in theoretical, semi-empirical and empirical mathematical models of drying of any biological material, depending on drying layer property, namely whether it is an elementary, thin or thick layer (Akpinar and Bicer, 2005). The moisture content of drying materials can be anticipated using drying equations, especially if the drying constant "k" is calculated. Activation energy calculation can be through drying temperature (T) and water release constant (k). Bala (1997) defined the reaction activation energy (E_a) of water release from rapeseed as the energy which must be brought to the water molecules to stir their inter-reactions.

In the recent studies, modelling of the drying kinetics of food has been widely investigated, with focus on rapeseed (Crisp and Woods, 1994), strawberry (Doymaz, 2008), coconut (Madhiyanon et al., 2009), olive pomace (Meziane, 2011), and seed grape (Çakmak and Yıldız, 2011).

The main objective of this work was to investigate the water release in rapeseed hybrids (Turan, Traviata, NK Toccata, NK Petrol, PR 46 W 14, PR 46 W 15) during the thin-layer convective drying at three different drying temperatures (40°, 60° and 80°C) and to calculate the activation energy of the samples; 3) to match the drying data with two mathematical models (Henderson and Pabis and Lewis) and to determine the traits of rapeseed (oil and free fatty acids content) as main indicators of drying precision and quality.

MATERIAL AND METHODS

This investigation was performed on six rapeseed hybrids grown in the Zagreb County area in the Republic of Croatia. The investigation included early hybrid Turan (KWS), medium-early hybrids Traviata (KWS),

NK Toccata and NK Petrol (Syngenta), and medium-late hybrids PR 46 W 14 as well as PR 46 W 15 (Pioneer). The hybrids were harvested in late June 2017, when samples had moisture level of 11%.

Thermal processing of rapeseeds was conducted in a laboratory dryer where large-scale industrial dryer conditions can be replicated in a thin layer. The laboratory dryer was made in the Agricultural Faculty's Department for agricultural technology, storing and transport in Zagreb. The dryer consists of three units: the dryer's lower section is a 300x350x120 mm bed-plate, housing a fan with 1 kW heater. The electric heater is fed with alternative current with adaptable voltage, thus, allowing for adjusting air drying temperature as well. Voltage is adapted manually on the regulation transformer, whereas voltmeter, ammeter, and wattmeter are connected in electric circuit. Airflow velocity, or fan regulation, is also controlled manually by using a regulation transformer. Measurements of the air temperature were taken by a PT 100 probe immediately prior to air entering the sample. Air velocity, after passing through the sample layer, was measured by a digital anemometer. Air velocity in the dryer was maintained at 1.0 ms⁻¹, and the samples were dried at three different air temperatures: 40°, 60° and 80°C.

Based on the obtained values for water release during convective drying, the effective diffusion coefficient was determined, and by using mathematical models *Henderson and Pabis* and *Lewis* the drying kinetics of rapeseed was described. The drying data were expressed in terms of the moisture ratio (MR) versus drying time. The activation energy value was obtained by using the equation for calculating drying constant which Henderson and Pabis (1961) proposed based on Arrhenius equation, depending on a temperature, drying constant and activation energy.

Determination of rapeseed moisture content is a method which is based on sample drying in laboratory dryers (INKO ST - 40, Croatia) at 105°C in three hours duration, according to the protocol HRN ISO 6540:2002. The oil content was determined using a Soxhlet extractor R 304 Behr Labortechnik GmbH, Germany, according to the protocol HRN ISO 6492:2001. The free fatty acid content was determined by using a gas chromatograph CP-3800, Varian, Palo Alto, CA, according to the protocol HRN EN ISO 5983-2:2010.

Statistical data processing was performed using SAS package in 9.3 version (SAS Institute, Cary, NC, USA) applying the GLM procedure with significance level of $P \geq 0.05$.

RESULTS AND DISCUSSION

At the harvest time, the seeds' moisture content was above the equilibrium level, around 11.28% in hybrid Traviata and up to 11.69% in hybrid NK Toccata.

The results of water release from rape oilseeds are shown in Table 1.

Table 1. Exponential equations of water release from rapeseed up to reaching constant equilibrium moisture of the investigated hybrids at three drying temperatures

Tablica 1. Eksponencijalne jednačbe otpuštanja vode iz sjemenki uljane repice do konstantne ravnotežne vlažnosti istraživanih hibrida na tri temperature sušenja

Hybrid Hibrid	Drying air temperature Temperatura sušenja (°C)	Moisture Vlaga (%)	Exponential equations Eksponencijalna jednačba	R ²
Turan	40	11.38	$y = 10.055e^{-0.0069x}$	0.945
	60		$y = 10.800e^{-0.0251x}$	0.962
	80		$y = 10.851e^{-0.0434x}$	0.965
Traviata	40	11.28	$y = 10.050e^{-0.0065x}$	0.929
	60		$y = 10.374e^{-0.0172x}$	0.951
	80		$y = 10.614e^{-0.0431x}$	0.951
NK Toccata	40	11.69	$y = 10.383e^{-0.0082x}$	0.948
	60		$y = 10.218e^{-0.014x}$	0.953
	80		$y = 10.958e^{-0.0457x}$	0.945
NK Petrol	40	11.53	$y = 10.313e^{-0.0064x}$	0.947
	60		$y = 10.411e^{-0.0182x}$	0.933
	80		$y = 10.977e^{-0.0438x}$	0.965
PR 46 W 14	40	11.38	$y = 10.356e^{-0.0078x}$	0.963
	60		$y = 10.810e^{-0.0207x}$	0.949
	80		$y = 10.823e^{-0.0427x}$	0.961
PR 46 W 15	40	11.40	$y = 10.137e^{-0.0073x}$	0.947
	60		$y = 10.565e^{-0.0224x}$	0.965
	80		$y = 10.799e^{-0.0444x}$	0.963

Legend: y-seed moisture, x-time of water release from seeds, R²- coefficient of determination

Legenda: y-vlaga sjemenki, x-vrijeme otpuštanja vode iz sjemenki, R²-koeficijent determinacije

The analysis of the results shows the differences in water release rates between drying temperatures and in the observed hybrids as such. According to the obtained data it can be determined that hybrid NK Toccata releases water faster at all temperature levels, while hybrid Traviata had the lowest water release rate. The deter-

mination coefficients were between 0.929 and 0.965. Similar results were obtained by Kumar et al. in 2010.

Mathematical modelling of rapeseed drying is described by using two most frequent thin layer drying models: *Henderson and Pabis* and *Lewis* (Table 2).

Table 2. Mathematical modelling of water release from rapeseed of the investigated hybrids at three drying temperature levels

Tablica 2. Matematičko modeliranje otpuštanja vode iz sjemenki uljane repice istraživanih hibrida na tri temperature sušenja

Hybrid Hibrid	T°C	Coefficient a Koeficijent a	Exponent k	Model			
				Henderson and Pabis MR = a exp (-kt)		Lewis MR = exp (-kt)	
				MR	R ²	MR	R ²
Turan	40°C	0.36699	0.06302	0.05305	0.952	0.17622	0.937
Traviata		0.36601	0.14256	0.04131	0.904	0.13933	0.887
NK Toccata		0.37599	0.06618	0.05556	0.952	0.18348	0.939
NK Petrol		0.37378	0.06474	0.0540	0.951	0.17819	0.939
PR46W14		0.37263	0.06884	0.05295	0.946	0.18791	0.932
PR46W15		0.36477	0.06353	0.05415	0.953	0.18303	0.941
Turan		60°C	0.39581	0.12122	0.05302	0.935	0.17511
Traviata	0.38004		0.24833	0.04222	0.846	0.14342	0.833
NK Toccata	0.36966		0.07865	0.05784	0.956	0.19656	0.946
NK Petrol	0.37747		0.09492	0.05603	0.951	0.18920	0.937
PR 46 W 14	0.39552		0.11428	0.05185	0.932	0.17005	0.907
PR 46 W 15	0.33811		0.10352	0.05509	0.944	0.18998	0.926
Turan	80°C		0.40015	0.13105	0.05488	0.931	0.18695
Traviata		0.39154	0.33594	0.04799	0.939	0.16541	0.923
NK Toccata		0.40242	0.12187	0.05918	0.937	0.20396	0.927
NK Petrol		0.40558	0.13142	0.05650	0.930	0.19126	0.916
PR 46 W 14		0.40094	0.13320	0.05554	0.929	0.18820	0.917
PR 46 W 15		0.39620	0.12777	0.05616	0.934	0.19384	0.916

Higher values of moisture ratio (MR) were obtained by changing the Lewis model, in all the observed hybrids and with all applied temperatures. The Lewis equation assumes that the drying rate is proportional to the difference between actual medium moisture content and equilibrium moisture level in the given conditions. Unlike Lewis, Henderson and Pabis introduce the coefficient in the calculation which is directly related to the time of water release and, as such, it gives a more accurate modelling and a significantly better drying curve. Introduction of this parameter allowed for better matching of the experimental and computational data. Hence, the higher values of moisture content ratio (MR)

and determination coefficient R² by application of these drying models were obtained in thermal treatment of the hybrid NK Toccata. Based on the obtained values, it is proposed to use the Henderson and Pabis formula for a more accurate presentation of drying because the received coefficients are applicable to the investigated hybrids regardless of seeds' moisture. Simulation of thin layer drying, i.e., of diffusion model, is far more appropriate.

The results regarding activation energy in rapeseed water during the drying process, i.e., statistical analysis of influence of the investigated hybrids are shown in Table 3.

Table 3. Values of activation energy in all investigated hybrids

Tablica 3. Vrijednosti energije aktivacije svih istraživanih hibrida

Hybrid Hibrid	Turan	Traviata	NK Toccata	NK Petrol	R 46 W 14	PR 46 W 15
Activation energy Energija aktivacije (kJkg ⁻¹)	17.07 ^a ±2.10	19.80 ^a ±1.58	14.08 ^a ±2.08	16.28 ^a ±2.30	15.31 ^a ±2.68	16.30 ^a ±2.23

Linear relations and the Arrhenius equation were used to define the curves of rapeseed water release constants for each investigated hybrid. The obtained activation energy values showed that the highest energy needed for initiating the water release process was found out in hybrid Traviata (19.80 kJmol⁻¹), while hybrid NK Toccata had the lowest activation energy (14.08 kJmol⁻¹). According to various authors who investigated other crops, the obtained values are somewhat lower

than the values of drying activation energy. For example, energy of activation in mushrooms ranges from 30.80 kJmol⁻¹ to 48.47 kJmol⁻¹ (Babalís and Belessiotis, 2004), in berries from 110.84 kJmol⁻¹ to 130.61 kJmol⁻¹ (Aghbashlo et al., 2008).

The content of initial moisture in hybrids Turan, Traviata, NK Toccata, NK Petrol, PR 46 W 14, PR 46 W 15, as well as the content of oil and free fatty acids (FFA) are shown in Table 4.

Table 4. Moisture content, oil and free fatty acids contents (FFA) in natural samples of all investigated hybrids

Tablica 4. Sadržaj vlage te ulja i slobodnih masnih kiselina (SMK) u prirodnom uzorku svih istraživanih hibrida

Hybrid Hibrid	Moisture (%) Vlaga (%)	Oil (%) Ulje (%)	FFA (%) SMK (%)
Turan	11.38 a ± 2.09	42.95 a ± 2.75	1.45 a ± 0.59
Traviata	11.28 a ± 2.42	40.05 b ± 3.08	1.85 b ± 0.17
NK Toccata	11.69 b ± 0.69	41.35 a ± 3.18	1.83 a ± 0.29
NK Petrol	11.53 a ± 0.81	40.35 a ± 3.01	1.98 a ± 4.02
PR 46 W 14	11.38 b ± 1.23	36.08 a ± 3.16	1.58 a ± 2.10
PR 46 W15	11.40 a ± 1.41	41.28 b ± 2.32	1.88 a ± 2.77

It is evident that there are significant differences among the investigated parameters, and these differences enable the obtained results to be compared. The moisture content was in a range from 11.28% in hybrid Traviata to 11.69% in hybrid NK Toccata. The oil content was from 36.08% in hybrid PR 46 W 14 to as high as 42.95% in hybrid Turan, which meets the Croatian buy-out standard. Namely, according to this standard, good quality rapeseed should have the oil content of 40% (NN 88/2010). Pospisil et al. (2014) determined the average

oil content at 45.41%. Kis et al. (2004) state that the oil synthesis is most commonly influenced by climate factors, air temperature, quantity of available moisture in soil at time of soil wetting, and the length of this phase. The FFA content is below the allowed 2% level for all the investigated hybrids and it is between 1.45% in Turan and the marginal 1.98% in NK Petrol.

Table 5 shows that the oil and FFA contents in most hybrids, after thermal treatment, increased in relation to the relevant contents in natural samples.

Table 5. Contents of moisture, oil and free fatty acids (FFA) of the all investigated rapeseed hybrids after thermal treatment by convective drying

Tablica 5. Sadržaj vlage te ulja i slobodnih masnih kiselina (SMK) svih istraživanih hibrida nakon termičke dorade konvekcijškoga sušenja

Hybrid <i>Hibrid</i>	Moisture (%) <i>Vlaga (%)</i>	Oil (%) <i>Ulje (%)</i>	FFA (%) <i>SMK (%)</i>
40°C			
Turan	5.83a ± 0.32	45.07 a ± 0.65	1.60 a ± 1.60
Traviata	5.91a ± 0.44	41.23 a ± 0.79	2.63 a ± 2.08
NK Toccata	5.97a ± 0.46	43.80 a ± 0.65	1.87 a ± 0.59
NK Petrol	5.98a ± 0.38	43.20 a ± 0.80	1.83 a ± 2.01
PR 46 W 14	5.93a ± 0.42	45.23 a ± 0.05	1.40 a ± 1.56
PR 46 W 15	5.82a ± 0.36	44.23 a ± 0.04	1.57 a ± 1.51
60°C			
Turan	5.97a ± 0.28	45.80 b ± 0.57	1.73 a ± 0.05
Traviata	5.99a ± 0.32	40.63 a ± 0.72	2.73 a ± 0.05
NK Toccata	5.82a ± 0.32	43.87 b ± 0.37	2.17 b ± 0.08
NK Petrol	5.84a ± 0.42	43.47 b ± 0.89	1.60 b ± 0.39
PR 46 W 14	5.97a ± 0.38	43.27 a ± 0.68	1.67 a ± 0.79
PR 46 W 15	5.64a ± 0.40	42.33 a ± 0.72	2.33 a ± 0.39
80°C			
Turan	5.77a ± 0.44	44.90 b ± 2.01	2.13 b ± 0.08
Traviata	5.85a ± 0.32	41.40 b ± 1.39	2.73 b ± 0.03
NK Toccata	5.84a ± 0.36	43.63 a ± 1.69	2.20 a ± 2.13
NK Petrol	5.93a ± 0.36	42.47 a ± 1.11	1.83 a ± 1.03
PR 46 W 14	5.97a ± 0.42	43.40 a ± 1.28	1.70 a ± 1.98
PR 46 W 15	5.75a ± 0.48	41.97 a ± 1.54	2.60 a ± 0.89

The statistical data processing determined that the oil and FFA contents were significantly influenced by temperature levels of 60° and 80°C. In drying at temperature of 80°C the process of decomposition of fats and development of free fatty acids occurs: the level of free fatty acids exceeds the allowed 2% in most of the investigated hybrids. This is especially present in hybrid Traviata with the FFA level as high as 2.73%. Lauten and Niepenberg, 1988, state that rapeseed drying, in relation to seed humidity, indicates the problems of an increased free fatty acids content. Kachel-Jakubowska and Szpryngiel, 2008 quote the pre-drying oil content of 40.61%, while thermally treated rapeseed contained 40.36% oil. These values are in line with this investigation.

CONCLUSION

1. Rapeseed hybrid Traviata had the fastest, and hybrid NK Toccata the slowest water release rate, which is also corroborated by a higher activation energy value in hybrid NK Toccata.
2. Kinetic curve of drying demonstrates the anticipated trends regarding the conditions in which the process was performed. With increasing temperature levels, the duration times of the process become shorter. The obtained results correlated with the Henderson and Pabis dual-parameter model of thin layer drying.

3. The moisture content was found out to be in the range from 11.28% in hybrid Traviata to 11.69% in hybrid NK Toccata. The oil content of the investigated hybrids was between 36.08% in hybrid PR 46 W 14 up to as much as 42.95% in hybrid Turan, which meets the Croatian buyout standard.
4. In most hybrids, the oil and FFA contents increased after thermal treatment in relation to natural samples, which is mostly the temperatures influence of 60° and 80°C.

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OTPUŠTANJE VODE KONVEKCIJSKIM SUŠENJEM RAZLIČITIM TEMPERATURAMA IZ SJEMENKI ULJANE REPICE

SAŽETAK

Uljana repica pripada najznačajnijim svjetskim uljaricama. Cilj istraživanja bio je istražiti utjecaj termičke dorade na kvalitetu uljane repice, odnosno analizirati sadržaj ulja i slobodnih masnih kiselina u izabranim hibridima uljane repice: Turan, Traviata, NK Toccata, NK Petrol, PR 46 W 14 i PR 46 W 15. Po svojim karakteristikama, nabrojani su hibridi rani, srednje rani i srednje kasni hibridi. Početna vlaga istraživanih hibrida kretala se od 11,28 do 11,69%. Hibridi su podvrgnuti termičkoj doradi konvekcijskim sušenjem u tankome sloju, pri temperaturama 40, 60 i 80°C i brzini strujanja zraka 1,0 m/s. Tijekom istraživanja, uočeno je raspadanje ulja tijekom sušenja na 80°C te povećanje slobodnih masnih kiselina preko dopuštenih 2%. Nadalje, temeljem dobivenih rezultata, određena je brzina otpuštanja vode te je postupak sušenja matematički modeliran, gdje su određeni koeficijent determinacije (R^2) i energija aktivacije vode.

Ključne riječi: uljana repica, slobodne masne kiseline, konvekcijsko sušenje, matematičko modeliranje, energija aktivacije

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