

Pretreatments and temperature effects on the drying kinetics of peas

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In this study, peas were dried in convection dryer at a temperature range of 55-75°C with a constant air velocity of 2 m/s. The peas were pre-treated with ethyl oleate and blanched with hot water at 85°C before drying. Drying process continued until sample moisture fell down to 0.11 kg water/kg dry matter. The blanched samples dried faster than the other pre-treatment and control conditions. Besides, drying rate increased with increasing temperature. The experimental results illustrated the absence of constant-rate drying period and drying took place in the falling-rate period. Four well-known mathematical models were used to predict drying kinetics by nonlinear analysis of regression. Midilli and Kucuk model best fitted the experimental data for the whole range of temperatures. The moisture diffusivity coefficient at each temperature was determined by Fick's second law of diffusion, in which their value varied from 7.66×10^{-11} m²/s to 2.44×10^{-10} over the mentioned temperature range. The dependence of effective diffusivity coefficient on temperature was expressed by an Arrhenius type equation. The calculated values of the activation energy of moisture diffusion were 36.75, 38.11 and 43.25 kJ/mol for pre-treated with ethyl oleate, blanched samples and control samples, respectively.

Keywords: Activation energy, Drying, Effective diffusivity, Pea, Pre-treatments.

INTRODUCTION

Pea (*Pisum sativum* L.) is one of the most commonly grown food legumes in the world. The worldwide pea production in 2014 was 17426421 tons. The major producer countries include China, India, USA, France and Egypt. According to Food and Agriculture Organization of United Nations (FAO) agriculture data, Pea is grown on 15300 ha areas in Turkey with a production of 105279 tons in 2014 [1]. Pea has been widely used in the human diet for a long time due to it being an excellent source of protein, vitamins, minerals and other nutrients, while being low in fat, high in fiber and containing no cholesterol [2, 3]. Because of its high moisture content, drying is one of alternative method of pea preservation. Dried peas are gaining popularity because they offer the advantage of longer self life, palatability and convenience during transport and handling [4]. Like other legumes, dried peas can be used in meals or soups [5].

Drying is an established method of food processing. It is used to extend the self-life of vegetables and to reduce the mass transportation. The low water activity of the products prevents growth of microorganisms, enzymatic reactions, and other deteriorative reactions [6]. Hot-air drying is the most widely used method for preservation of food in processing industry. The applied drying conditions and pre-treatments highly influence the resulting physical, chemical, microbial, functional and organoleptic properties of the agricultural products. Sodium and potassium hydroxide, sodium

bicarbonate, potassium meta bisulphate, potassium carbonate, methyl and ethyl ester emulsions, ascorbic and citric acids, the most common and commercially used some pre-treatments [7-9]. Blanching is one of the pre-treatment methods that are used to stop some physiological processes before drying vegetables and fruits. It helps to inactivate enzymes that leads to some quality degradations and improves the acceptability of the final products. Moreover, it can accelerate drying rate and prevent quality deterioration by expelling intercellular air from the tissues and softening the texture [10].

In this study, the main objectives were to investigate the effect of pre-treatment and air temperature on the drying time, fit the experimental data to four drying models, and compute effective moisture diffusivity and activation energy.

EXPERIMENTAL

Materials and methods

Good quality fresh green peas (*Pisum sativum*) were purchased from a local market in Istanbul, Turkey. The damaged, immature, and dried pods were removed manually by visual inspection. The pea pods were shelled manually. The average diameter of the peas was 0.7 ± 0.1 cm. Pea samples were divided in three sample groups. One sample group were blanched (BLANCH) in water at $85 \pm 1^\circ\text{C}$ for 1 min. Other one sample group was dipped in solution of 2% ethyl oleate and 3% potassium carbonate (EO) at $20 \pm 1^\circ\text{C}$ for 1 min. Another sample group dried as a control group (Control).

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The initial moisture content of peas was determined using a standard method [11], by vacuum drying at 70°C for 24 h over a magnesium sulphate desiccant. This was repeated three times to obtain a reasonable average. The initial moisture content of the samples was found as %77.25, wet basis (3.494 kg water/kg dry matter).

DRYING PROCEDURE

Drying experiments were performed in a cabinet type dryer (API & PASILAC Limited of Carlisle, Cumbria, UK.), and described by Doymaz [12]. Samples dried with air of 55, 65 and 75°C, and a constant air velocity of 2 m/s. The experiments were conducted with about 60±0.5 g of peas. The moisture losses were recorded at 15 minute intervals during the drying process, using a digital balance (Mettler-Toledo BB3000, AG, Grefensee, Switzerland) with a sensitivity of 0.1 g. Drying process was carried out until a moisture content of about 0.11±0.02 kg water/kg dry matter. The dried product was cooled, to normal temperature in a desiccator containing silica gel and then packed in polyethylene bags, which were then heat-sealed and stored in incubators at ambient temperature. The experiments were repeated twice and the average of the moisture ratio at each value was used for the drawing of the drying curves.

Mathematical modeling and data analysis

The moisture ratio (MR) of the pea was calculated using the following equation:

$$MR = \frac{M_t - M_e}{M_0 - M_e} \quad (1)$$

where M_t , M_0 and M_e are the moisture content at any time of drying (kg water/kg dry matter), initial moisture content (kg water/kg dry matter) and equilibrium moisture content (kg water/kg dry matter), respectively. The moisture ratio (MR) was simplified to M_t/M_0 instead of $(M_t - M_e)/(M_0 - M_e)$ (Ismail et al. 2014) because of the values of M_e small compared with M_t or M_0 for long drying time.

The drying rate (DR) was calculated using Eq. (2):

$$DR = \frac{M_t - M_{t+\Delta t}}{\Delta t} \quad (2)$$

where $M_{t+\Delta t}$ is moisture content at $t + \Delta t$ (kg water/kg dry matter), and t is time (min).

The regression analysis was performed by using the STATISTICA computer program. The determination of coefficient (R^2), reduced chi-square (χ^2) and root mean square error ($RMSE$) were used in this study to evaluate the goodness of fit. These parameters can be calculated by using the following equations:

$$R^2 = 1 - \frac{\sum_{i=1}^N (MR_{pre,i} - MR_{exp,i})^2}{\sum_{i=1}^N (\overline{MR}_{pre} - MR_{exp,i})^2} \quad (3)$$

$$\chi^2 = \frac{\sum_{i=1}^N (MR_{exp,i} - MR_{pre,i})^2}{N - z} \quad (4)$$

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^N (MR_{pre,i} - MR_{exp,i})^2 \right]^{1/2} \quad (5)$$

In these equations, N is the number of observations, z is the number of constants, MR_{exp} and MR_{pre} are the experimental and predicted moisture ratios, respectively. The best model describing the drying characteristics of pea samples is chosen as the one with the highest R^2 values and the lowest χ^2 and $RMSE$ values [13].

Determination of effective moisture diffusivity

The values of effective moisture diffusivity (D_{eff}) of dried peas are determined by using the Fick's second law of diffusion equation:

$$\frac{\partial M}{\partial t} = D_{eff} \nabla^2 M \quad (6)$$

The analytical solution of Fick's second law (Eq. 6) unsteady state diffusion in a spherical coordinates with the assumptions of moisture migration being by diffusion, negligible shrinkage, constant effective diffusivity and temperature during the drying process is given as follows [14]:

$$MR = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-n^2 \pi^2 \frac{D_{eff} t}{r^2}\right) \quad (7)$$

For long drying periods, Eq. (7) can be further simplified to only the first term of the series. Thus, Eq. (7) is written in a logarithmic form as follows:

$$\ln(MR) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff} t}{r^2}\right) \quad (8)$$

The effective moisture diffusivity is obtained by plotting the experimental drying data in terms of $\ln(MR)$ versus time (min). From Eq. (8), a plot of $\ln MR$ versus *time* gives a straight line with a slope of (K), in which:

$$K = \frac{\pi^2 D_{eff}}{r^2} \quad (9)$$

Computation of activation energy

The dependence of the effective diffusivity on temperature is generally described by the Arrhenius equation:

$$D_{eff} = D_0 \exp\left(-\frac{E_a}{R(T + 273.15)}\right) \quad (10)$$

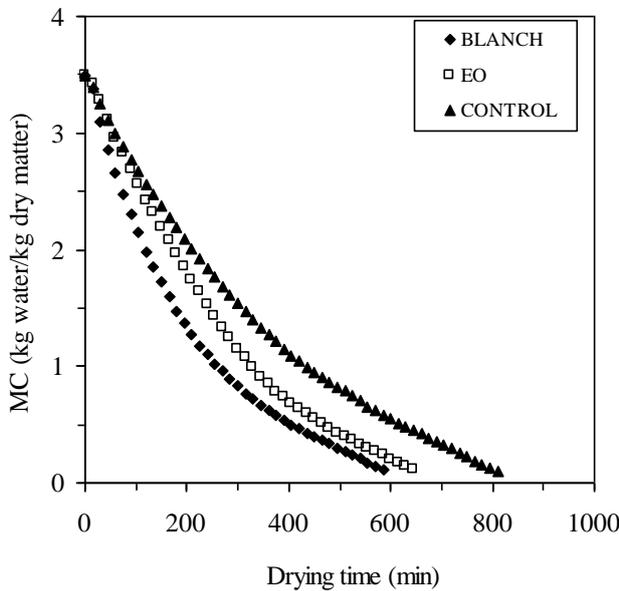
Here D_0 is the pre-exponential factor of Arrhenius equation (m^2/s), E_a is the activation energy (kJ/mol), R is the universal gas constant (kJ/(mol.K)), and T is temperature ($^{\circ}C$).

RESULTS AND DISCUSSION

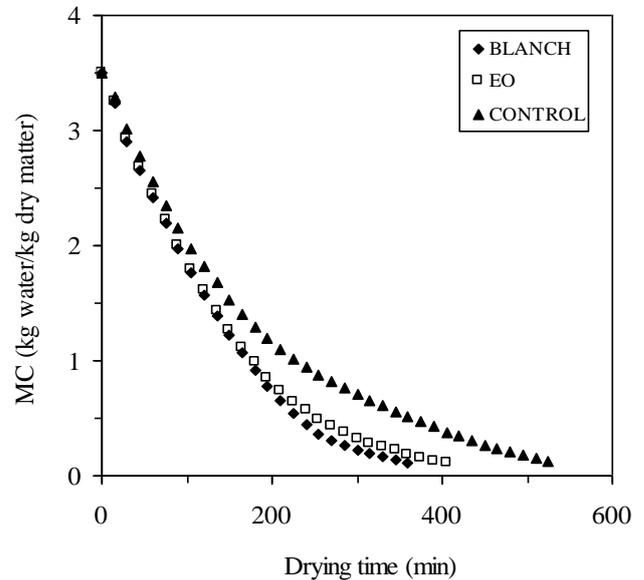
Effect of pretreatment and air drying temperature

Figures 1 presents variations in the moisture content as a function of drying time at 55, 65 and

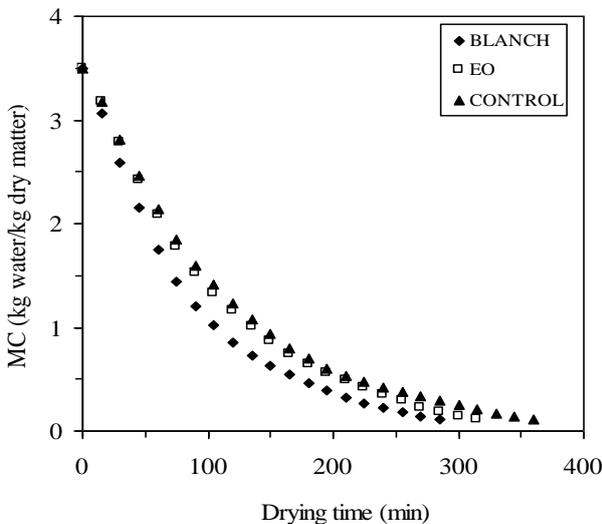
75 $^{\circ}C$. It is clear that the moisture content decreases continuously with drying time. The pre-treatments affected the drying time. The peas dipped in pre-treatment solutions before the drying process was found to have a shorter drying time compared to the control ones. From Figures 1, it is observed that the drying times required for reducing the moisture content of pre-treated samples were 585, 360 and 285 for BLANCH samples, and 645, 405, and 315 min for EO samples. Corresponding values for the control samples were 810, 525 and 360 min at same temperatures, respectively. As a result, the experimental results demonstrate the importance of the blanched in reducing the mass-transfer resistance of the peas. A similar effect of blanching has been found in the drying of various vegetables [9,13,15].



(A)



(B)

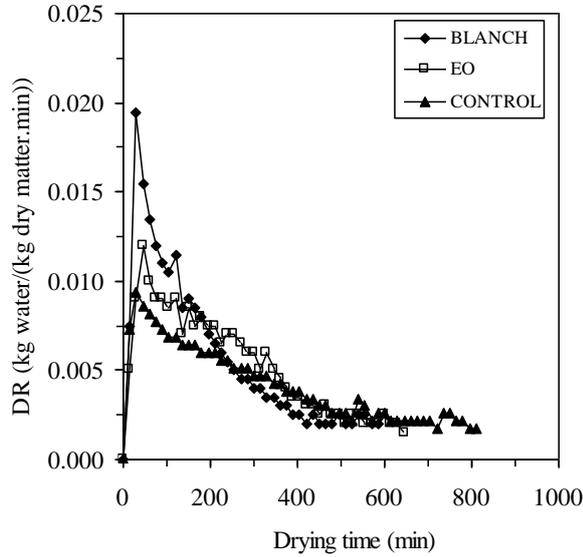


(C)

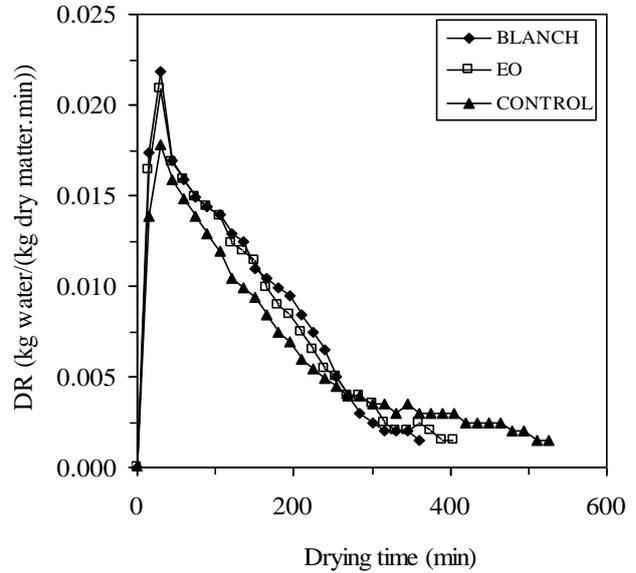
Figure 1. Effect of pre-treatments on moisture contents of peas (A: 55 $^{\circ}C$, B: 65 $^{\circ}C$, C: 75 $^{\circ}C$)

The drying times taken to reduce the moisture contents of the peas from initial moisture of 3.494 kg water/kg dry matter to final moisture of 0.11 kg water/kg dry matter are demonstrated in Figure 1. As expected, the higher air temperature of 75°C results in higher drying rate compared to 55 and 65°C. The drying air temperature of 75°C resulted in a shorter drying time than 55°C by approximately 300, 330,

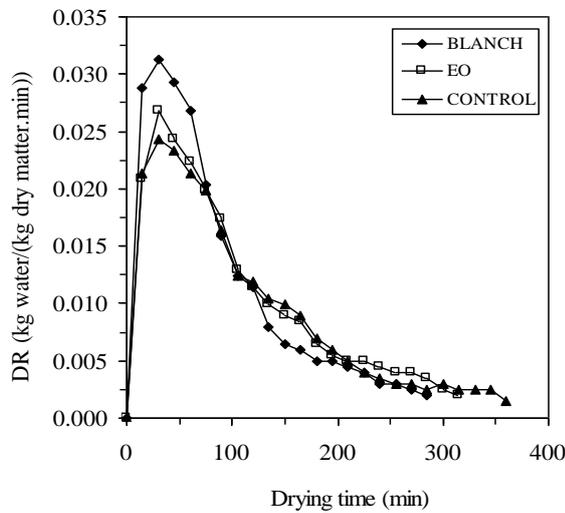
and 450 min for BLANCH, EO and CONTROL samples, respectively. The enhancement in drying rate at higher drying temperature is due to the fact that higher drying temperatures lead to the higher driving forces for heat transfer. The effect of temperature on drying time was similar, in accordance with earlier studies made on green pea [3,16], green bean [13], and bitter gourd [9].



(A)



(B)



(C)

Figure 2. Drying rate versus drying time of peas (A: 55°C, B: 65°C, C: 75°C)

Table 1. List of drying models used for describing the drying kinetics

Model name	Model	Reference
Henderson and Pabis	$MR = a \exp(-kt)$	Henderson and Pabis [18]
Midilli and Kucuk	$MR = a \exp(-kt^n) + bt$	Midilli and Kucuk [19]
Weibull	$MR = \exp\left(-\left(\frac{t}{b}\right)^a\right)$	Corzo et al. [23]
Aghbashlo et al.	$MR = \exp\left(-\left(\frac{at}{I+bt}\right)\right)$	Aghbashlo et al. [24]

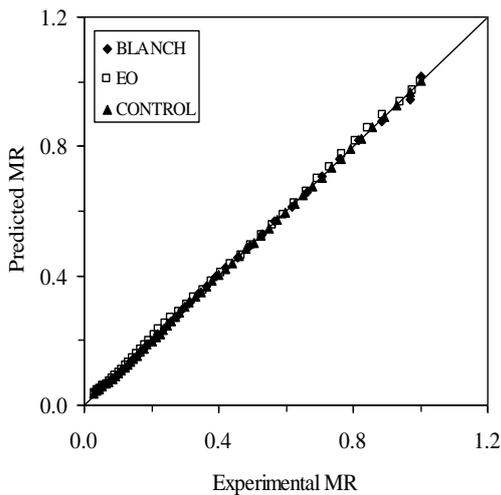
a, b, c, n : constants in drying models; k : drying rate coefficient (1/min)

DRYING RATE

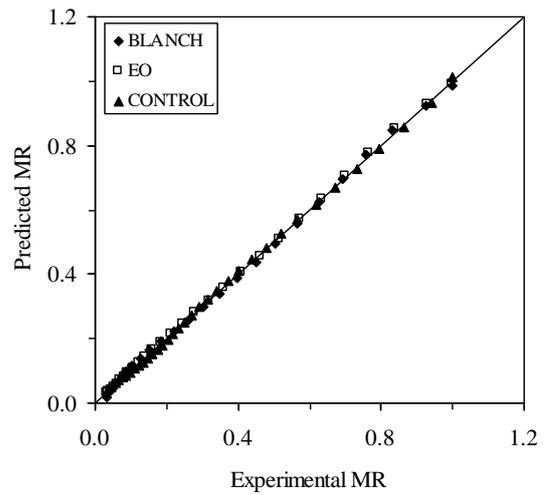
The drying rate values of peas at different temperatures were calculated using Eq. 2 and are shown in Figure 2. At the beginning of the process the drying rate is high and the diffusion resistance increases gradually during the drying process, so this leads to a continuous reduction in drying rate. Similar result has been reported previously by Ghalavand et al. [17] has been reported. Figure 2 indicates that the moisture removal inside the peas was higher at higher air temperatures. So, the migration of moisture to the surface and the evaporation rate from surface to air slows down with decreasing the moisture in the product, the drying rate clearly decreases. As can be seen no constant drying rate period was observed, and the whole drying process occurred in the falling drying rate period. This shows that diffusion is dominant physical mechanism governing moisture movement in the samples.

EVALUATION OF THE MODELS

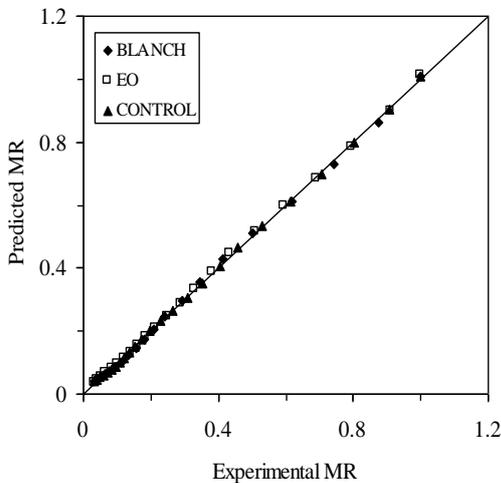
Nonlinear regression analysis was done according to the four mathematical models which are given in Table 1 after moisture content data of air drying was transferred into the moisture ratio (MR). The statistical analysis values are summarized in Table 2. In all cases, the R^2 values for the models were greater than 0.98, indicating a good fit. The Midilli and Kucuk model gave a higher R^2 and lower χ^2 and RMSE values, and were selected to represent the drying characteristics of peas. The R^2 values of the model varied between 0.9989 and 0.9998, χ^2 values between 0.000013 and 0.000060, and RMSE values between 0.020874 and 0.036854. The worst fit in this study belongs to the Henderson and Pabis model. Figure 3 compare the experimental data with the predicted ones using Midilli and Kucuk model for peas at 55, 65 and 75°C. The prediction using the model showed MR values banded along a straight line, which proved the suitability of these models in describing the drying characteristics of peas.



(A)



(B)



(C)

Figure 3. Experimentally determined and predicted moisture ratios of peas (A: 55°C, B: 65°C, C: 75°C)

Table 2

Code	T (°C)	Model name	R ²	χ ²	RMSE
BLANCH	55	Henderson and Pabis	0.9990	0.000074	0.032247
		Midilli and Kucuk	0.9994	0.000050	0.030621
		Weibull	0.9991	0.000067	0.035008
		Aghbashlo et al.	0.9990	0.000074	0.036845
	65	Henderson and Pabis	0.9885	0.001109	0.145978
		Midilli and Kucuk	0.9995	0.000044	0.026595
		Weibull	0.9981	0.000183	0.056078
		Aghbashlo et al.	0.9990	0.000104	0.041357
	75	Henderson and Pabis	0.9981	0.000122	0.038276
		Midilli and Kucuk	0.9994	0.000105	0.036854
		Weibull	0.9993	0.000124	0.040970
		Aghbashlo et al.	0.9987	0.000161	0.040648
AEEO	55	Henderson and Pabis	0.9900	0.000888	0.167948
		Midilli and Kucuk	0.9997	0.000027	0.028956
		Weibull	0.9992	0.000656	0.038987
		Aghbashlo et al.	0.9991	0.000080	0.048052
	65	Henderson and Pabis	0.9942	0.000533	0.105072
		Midilli and Kucuk	0.9997	0.000026	0.020874
		Weibull	0.9996	0.000036	0.023688
		Aghbashlo et al.	0.9994	0.000049	0.031104
	75	Henderson and Pabis	0.9986	0.000173	0.041025
		Midilli and Kucuk	0.9989	0.000060	0.028295
		Weibull	0.9986	0.000063	0.030103
		Aghbashlo et al.	0.9982	0.000111	0.034312
CONTROL	55	Henderson and Pabis	0.9927	0.000574	0.139895
		Midilli and Kucuk	0.9998	0.000013	0.023374
		Weibull	0.9973	0.000209	0.080979
		Aghbashlo et al.	0.9991	0.000064	0.041372
	65	Henderson and Pabis	0.9991	0.000069	0.038666
		Midilli and Kucuk	0.9994	0.000052	0.036212
		Weibull	0.9991	0.000068	0.040487
		Aghbashlo et al.	0.9991	0.000069	0.041805
	75	Henderson and Pabis	0.9989	0.000087	0.030678
		Midilli and Kucuk	0.9998	0.000034	0.021831
		Weibull	0.9993	0.000046	0.026832
		Aghbashlo et al.	0.9987	0.000098	0.036768

EFFECTIVE MOISTURE DIFFUSIVITY

The determined values of the effective moisture diffusivity are shown in Figure 4 and were found to range between 7.66×10^{-11} m²/s and 2.44×10^{-10} m²/s. The moisture diffusivity was affected by the pre-treatment solution and air temperature. It can be seen

that D_{eff} values for blanched samples are greater than those obtained for the other samples under the same drying conditions. Moreover, D_{eff} was increased with increasing temperature. The values of D_{eff} were in the range 10^{-11} to 10^{-10} m²/s and are comparable with reported values in literature for peas [4,15,20].

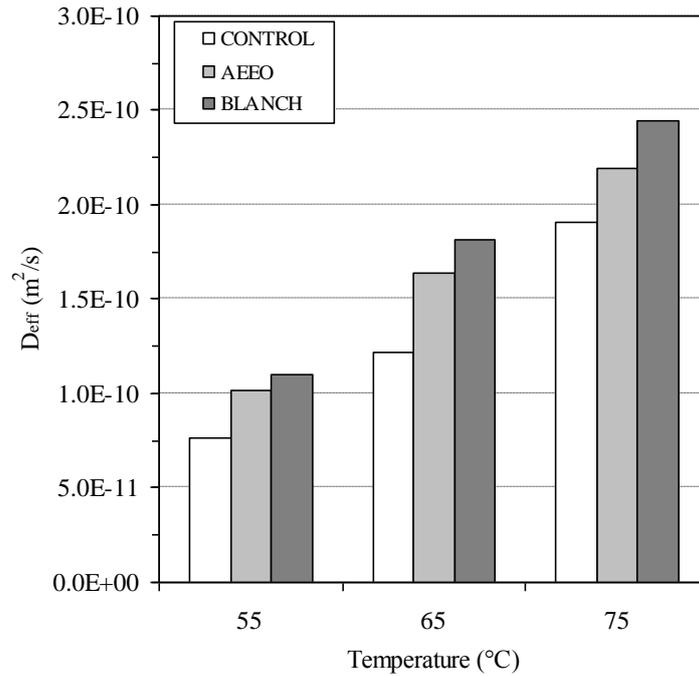


Figure 4. Variation of effective diffusivity with drying temperature.

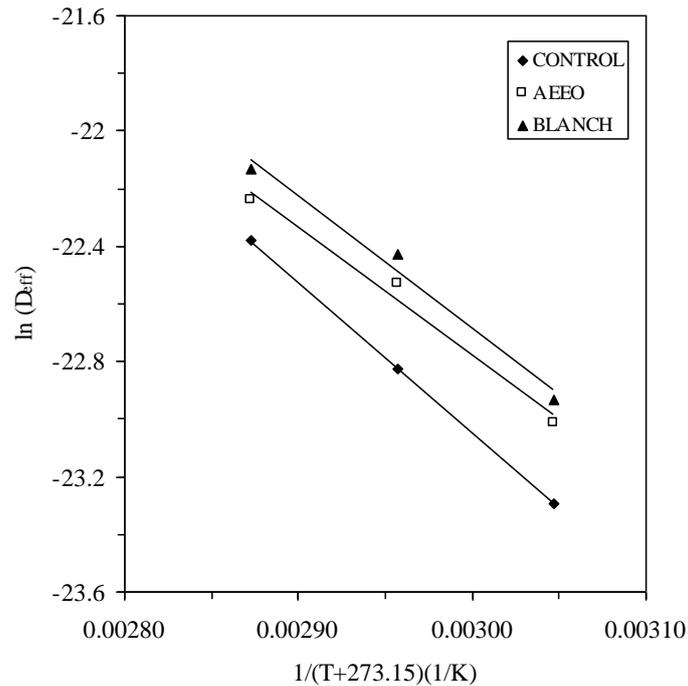


Figure 5. Arrhenius-type relationship between effective diffusivity and reciprocal absolute temperature

ACTIVATION ENERGY

The activation energy was calculated by plotting $\ln(D_{eff})$ versus the reciprocal of the temperature

For AEE0 samples:

$$D_{eff} = 7.3914 \times 10^{-5} \exp\left(-\frac{4420.9}{(T + 273.15)}\right) \quad (R^2: 0.9846) \quad (11)$$

For BLANCH samples:

($1/(T+273.15)$), and presented in Figure 5. Eqs. (11), (12) and (13) show the effect of temperature on D_{eff} of the pre-treated and the control samples with following coefficients:

$$D_{eff} = 1.3186 \times 10^{-4} \exp\left(-\frac{4584}{(T + 273.15)}\right) \quad (R^2: 0.9822) \quad (12)$$

For CONTROL samples:

$$D_{eff} = 5.8887 \times 10^{-4} \exp\left(-\frac{5203.1}{(T + 273.15)}\right) \quad (R^2: 1) \quad (13)$$

The activation energy values were found to be 36.75, 38.11, and 43.25 kJ/mol for the AEE0, BLANCH and CONTROL samples, respectively. These values are similar to those proposed by other authors for green pea and different products: 28.4 kJ/mol in green pea [14], 22.48 kJ/mol in green peas [4]; 43 kJ/mol for green beans [21], and 40.08 kJ/mol for bean grains [22].

CONCLUSIONS

Drying characteristics of peas were investigated in a cabinet dryer at various temperatures of 55, 65 and 75°C and constant air velocity of 2 m/s. Air temperature was important factor in drying of peas. High drying temperature resulted in a shorter drying time. Also, the blanched samples had shorter drying times than other pre-treated and control samples. The drying process of pea occurred in the falling drying rate period. To explain the drying kinetics of peas, four drying models were applied and fitted to the experimental data. According to the results of statistical analysis, the experimental data were well predicted by the Midilli and Kucuk model. The values of effective diffusivity of the pre-treated and control samples were in the range 7.66×10^{-11} m²/s to 2.44×10^{-10} m²/s. The activation energy values found to be between 36.75 and 43.25 kJ/mol.

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