

## Estimation of Kinetic Parameters of Walnut Oil Using Rancimat Test

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### ABSTRACT

In this paper, walnut oil at four different temperatures (353, 363, 373 And 383 ° K) were oxidized under the rancimat test conditions, it was observed that the rate of oxidation increases with increasing temperature. The natural logarithm of the reaction rate constant (k) had a linear relationship with temperature changes, according to the Arrhenius equation and activated complex theory, reaction rate constant (A), energy of activation ( $E_a$ ), Q10 value, enthalpy ( $\Delta H^{++}$ ), entropy ( $\Delta S^{++}$ ) was used to assess oxidative stability of walnut oil, the values of A,  $E_a$ , Q10,  $\Delta H^{++}$ ,  $\Delta S^{++}$  was  $2.78 \times 10^{13}$  (per hour), 80.32 (kJ /mole), 2.077, 77.27(kJ /mole), -55.76 joule per mole kelvin, respectively.

**KEYWORDS:** Kinetic parameters, oxidative stability, rancimat, walnut oil

### 1 INTRODUCTION

Foods, because of their nature, as well as a biochemical reactive system, undergo biochemical and physical changes during maintenance and processing and their quality can be changed. The study of these reactions can help identify the most influential factor in determining the quality [18]. Vegetable oils undergo desirable and undesirable changes where these changes depends on chemical compositions (fatty acid structure, the number and position of double bonds, peroxide, chelating compounds and antioxidants), and environmental factors (oxygen, moisture, heat and light) [7].

The oxidation of fats and edible oils is one of the most important reactions that may cause deterioration of the quality of the oil. Rancimat was one of tests that developed fasters for testing the resistance to oxidation of fats. All of these methods include the use of high temperatures, because it is clear that the reaction rate is correlated with temperature [13]. Among them, rancimat test, due to its ease of use and repeatability, has become a popular method used nowadays [15-14]. Rancimat test allows estimating induction period (IP) or oxidative stability index (OSI) which is the period before oil rapid oxidation [1,3].

To design an effective solution to prevent the development of oxidative reactions in food and biological systems, knowing the nature of these reactions and how they are affected by controllable chemical and physical factors is essential. This goal can be achieved through study of reaction kinetics as well as mechanism and energy aspects of these reactions. Kinetics basics deal with the rate of chemical reactions [1,9]. A good understanding of the kinetics of oxidation in vegetable oils can enhance the ability to formulate food products and minimizing undesirable products. Kinetic data are essential for prediction of oxidative stability of vegetable oils at various temperatures, storage and distribution conditions. However, regarding the oxidation of oils and fats, not enough attention is paid to these data [17]. In most of the cases, oxidative reactions have complex and unique behaviors. Therefore, for each product and oil system a separate and an appropriate model must be determined [4]. Through the kinetics of the reactions, two aspects are being studied, first is the speed at which the reaction occurs, and then the factors affecting the reaction (mainly temperature, concentration of reactants and processing and the presence of a catalyst) [12].

Rancimat device determines secondary volatile compounds resulted from lipids oxidation. Volatiles are trapped in deionized water and the increase in water conductivity is measured and is plotted versus time curve. Induction time is the elapsed time to reach the point of failure in the electrical conductivity versus time curve and is defined as an indicator of oxidative stability. [16-6] OSI is determined at different temperatures and therefore can study relative oxidative stability of edible fats and oils in a wide range of temperatures. A number of kinetic parameters can be determined under rancimat test conditions. These are very useful data, to predict the evaluation of vegetable oils under different heat treatment, storage, distribution process [10].

Temperature is the most important external factor affecting the quality and the shelf life of food. Therefore, knowing how temperature affects the reaction kinetics is essential. Many scientists use Arrhenius model and activation energy derived from it. Arrhenius model is a simple yet highly accurate method [8]. Therefore, the purpose of this study was to determine the relative oxidation of walnut oil and oxidation kinetic parameters under rancimat test.

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## 2. MATERIALS AND METHODS

### 2.1 Materials

Walnut oil extracted by solvents Merck, Germany, and without antioxidant was used.

### 2.2 Rancimat Test

To determine the oxidative stability, the rancimat device (Metrohm Ltd, model 743) was used. For this purpose, 2.5 gram oil samples were tested at 353, 363, 373 and 383 Kelvin, the air flow rate was 15 liters per hour [1].

### 2.3 Determination of fatty acid

The oil samples were determined by gas-liquid chromatography and were reported based on the relative percentage levels. Oil methyl esters of fatty acids were prepared by mixing the oil and hexane (0.3 g in 7 ml) with seven mL of 2- normal potassium hydroxide in methanol at 50 °C for 15 minutes. Esters of fatty acids were identified by gas chromatograph HP -5890 (Hewlett-Packard, SC, USA) equipped with a capillary column of BPX 70 Silica glass (120 m long, 250 micro meter internal diameter, 0.20 micro meter inner layer thickness) and a flame ion detector. The carrier gas was nitrogen with flow rate of 0.6 ml per minute. The temperatures of the oven, the injector and detector part were 198, 250, and 28 °C, respectively [11].

### 2.4 Calculation of Kinetic parameters of oxidative reaction

In Arrhenius model  $k$  is the kinetic rate (per hour) which is obtained through reversing the oxidative stability index (OSI).  $E_a$ , activation energies (kJ/mol), is the minimum energy that the molecule must have before the reaction takes place. 'A', the frequency factor for the reaction (per hour) is related to the frequency of molecular collisions in molecular theory. 'E<sub>a</sub>' and 'A' are determined by the slope and intercept of the regression Ln(k) respectively, against inverse temperature using Vant Hoff equation (Equation 1):

$$\ln(k) = \ln(A) - (E_a / RT) \quad (1)$$

where R is the molar gas constant (8.3143 J/ mol K) and T is the temperature (Kelvin).

The temperature coefficient ( $T_{coef}$ ) was calculated from the slope of the regression line between Ln (k) and the absolute temperature (T).

$$\ln(k) = a(T) + b \quad (2)$$

'a' And 'b' are the parameters of the model. Enthalpy and entropy are calculated using the regression equation Ln (k) against inverse temperature and the equation derived from the theory of and activation complex called Eyring's equation (Equation 3).

From the slope and intercept of the regression equation, the enthalpy and entropy are calculated, respectively.

$$\ln(k/T) = \ln(K_B/h) + (\Delta S^{++}/R) - (\Delta H^{++}/RT) \quad (3)$$

$H\Delta^{++}$  is enthalpy (kJ/ mol); h is Planck constant ( $6.626 \times 10^{-34}$ , joules per second);  $K_B$  is Boltzmann constant ( $1.384 \times 10^{-23}$ , Joule per Kelvin) and  $\Delta S^{++}$  is entropy (J/mol K) [13].

## 3 RESULTS AND DISCUSSION

The oxidation reaction rate constants (k) of walnut oil at different temperatures are given in (Table 1). The results show that the increase in temperature leads to increase in reaction rate constant of walnut oil. With respect to the reaction rate constant as a function of temperature [17], this result was to be expected. Farhush et al (2008 ), reported the reaction rate constant at temperature 100 °C (373 degree Kelvin) for refined oil (containing synthetic antioxidants), canola, soybean, sunflower, and corn as 0.025, 0.035, 0.036, 0.049 (per hour), respectively, that showed a lower rate constant compared with walnut crude oil (Table 1). The high reaction rate constant of walnut oil to the oil mentioned earlier can be attributed to the presence of antioxidants in these oils [15]. Furthermore, purification process also leads to the removal of some peroxide compounds. The presence of double bonds increases the oxidation rate and would increase the reaction rate constant [9]. The reaction rate constant in olive oil without antioxidants in 100 degree centigrade is estimated 0.044 (per hour). [3] The reaction rate constant of walnut oil to olive oil without antioxidants can be attributed to higher percentage of polyunsaturated fatty acids in walnut oil (67.34 %) in comparison with olive oil (19.53 %).

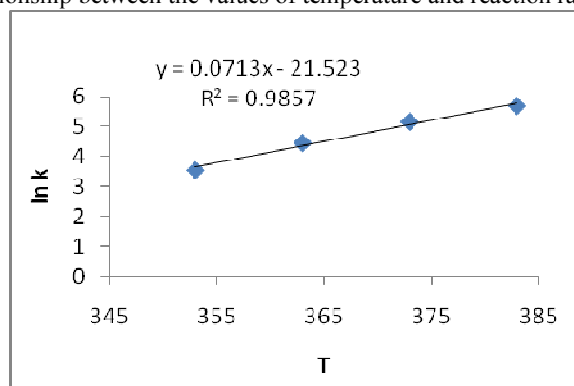
Figure 1 shows a semi-logarithmic relationship between walnut oil reaction rate constant versus temperature, as the figure shows there is a good correlation between these two parameters ( $R^2 = 0.9857$ ).

$$y = 0.0713x - 21.523 \quad (4)$$

Table 1 Values of the reaction rate constant ( k ) \* at different temperatures.

Temperature (Kelvin)	353	363	373	383
Walnut oil	0.2012	0.2197	0.2403	0.2631

Figure 1 Logarithmic relationship between the values of temperature and reaction rate of oxidation of walnut oil



Temperature coefficient ( $T_{\text{coeff}}$ ) which was calculated from the linear function in Figure 1 is 0.0089 (in Kelvin).

Farhush et al. (2008), reported the temperature coefficient for refined oil, canola, soybean, sunflower, corn and olives in the temperature ranges from 100 to 130 °C as 0.0720, 0.0740, 0.0726, 0.0705 and 0.0695, respectively. Also pour Fallah et al. (2012), determined the temperature coefficient for refined soybean oil without synthetic antioxidants and butter oil in the temperature range of 110 to 150 degree centigrade as 0.063 and 0.081, respectively.

Table 3 shows the regression parameters for the Arrhenius, van Hoof and Eyring's equations of walnut crude oil. The activation energy ( $E_a$ ) of walnut crude oil was determined as 80.327 KJ/mol. The amount of polyunsaturated fatty acids (linoleic acid, linolenic acid and oleic acid) in vegetable oils has decisive role in their oxidative stability so that by increasing polyunsaturated fatty acids, the oil oxidative stability is reduced [16]. The presence of polyunsaturated fatty acids in vegetable oils, impact their activation energy. In general, it has been reported that high levels of polyunsaturated acids (linoleic acid and linolenic) reduces the activation energy, while the high levels of oleic acid increases it. Also an increase in saturation of the fatty acid chains increases the resistance to thermal cracking.  $E_a$  value of such systems usually is high [5]. Tan et al. (2001), calculated the  $E_a$  of canola and soybean oils 86.0 and 80.8 kilo joules per mole, respectively. The high  $E_a$  value obtained for the walnut oil can be attributed to a lower percentage of its saturation (8.2 percent) than canola and soybean oil (8.9 and 16.9 percent, respectively).

The effect of temperature on the reaction rate of oil oxidation is expressed by a number called  $Q_{10}$ . This number is determined as the ratio of the reaction rate constant at temperatures with 10 degree centigrade differences [18]. Generally, higher  $Q_{10}$  values suggest that for a given change in the rate of lipid oxidation, less temperature change is needed.  $Q_{10}$  of walnut is determined 2.077. Farhush et al. (2008) determined this number for refined oils containing antioxidants as 13.2, 18.2, 15.2, 10.2 and 2.08 respectively. Low  $Q_{10}$  of walnut oil compared to the mentioned oils can be attributed to high levels of fatty acids in walnut oil.

Table 2 Composition and percentage of fatty acids in walnut oil

Fatty acid	Walnut oil
Lauric acid (12: 0)	0.004
Myristic acid (14: 0)	0.021
Palmitic acid (16: 0)	5.186
Stearic acid (18: 0)	2.833
Oleic acid (18: 1)	23.897
Linoleic acid (18: 2)	54.543
Linolenic acid (18: 3)	12.808
Arachidic acid (20: 0)	0.175
Behenic acid (22: 0)	0.050
The total saturated fatty acids	8.4
The total unsaturated fatty acids	91.4

Table 3. Arrhenius parameters,  $Q_{10}$  value, enthalpy and entropy for lipid oxidation reaction of walnut oil

Parameters	Amount
$\text{Ln}(k) = a(1/T) + b$	
a	-9.661
b	30.988
$R^2$	90.99
A (peh hour)	$2.870 \times 10^{13}$
$E_a$ (KJ/mol)	80.327
$\text{Ln}(k/T) = a(1/T) + b$	
a	-9294
b	17.20
$R^2$	0.99
$\Delta H^{++}$ (KJ/ mole)	77.272
$\Delta S^{++}$ (J/ mole Kelvin)	-55.765
$Q_{10}$	2.077

The enthalpy, entropy and their corresponding regression parameters are given in Table 3. The amount of enthalpy and entropy of walnuts crude oil was 77.27 (kJ/ mole) and -55.76 (J/ mole K), respectively. Tan et al. (2008) stated that the oils with higher degree of unsaturation have greater enthalpy and entropy values than oils containing polyunsaturated fatty acids. The amount of negative entropy suggests that the activated complex find higher order than the reactive molecules, therefore the probability of lipid oxidation of these active complexes is less which leads to a slower reaction rates.

Farhush et al. (2008), reported the enthalpy for canola oil, soybean, sunflower, corn, and olive as 86.78, 89.20, 87.52, 84.91 and 83.64 (kJ/ mole), respectively, and the entropy as -112.99, -104.35, -107.73, -112.28 and -116.66 (J/ mole K). Due to the process of refining oil, the degree of unsaturated fatty acids is reduced, and also due to the presence of antioxidants in the oil, high enthalpy and entropy of the walnut oil is justified.

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