TEMPERATURE - DEPENDENCE OF EDIBLE OIL VISCOSITY

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Abstract

This work has been undertaken to investigate the effect of heat treatment on the edible oil, corn oil viscosity used in frying and cooking. Our study is conducted on this product, since corn oil is one of the most inexpensive, popular and plays an important role in health and in life. Viscosity and temperature of corn oil samples were measured using the Digital Viscometer Model NDJ-5S with accuracy ±1%. The viscosity behavior of the corn oil has been identified in the range of 20 to 60 °C. The Electric model L-81 was used to increase the temperature of the oil samples to a specific temperature. The studied parameters were: density, moisture content, free acidity, electrical conductivity and dynamic viscosity. In addition to the dynamic viscosity and density, kinematic viscosity and fluidity of the formulas were also determined. The dependence on the oil viscosities to temperature was mathematical modeled using two and multi constant equations. We noticed that, viscosity of corn oil decreases non-linearly with increasing temperature. Fitting of the experimental data in some theoretical models was performed in order to describe the temperature dependence of the viscosity of oil. Hence, a Clement model was found to best describe this dependence.

Key words: *Corn oil, heating, dynamic viscosity, mathematical model.*

Përmbledhje

Kjo punë është ndërmarrë për të studiuar efektin e trajtimit termik në viskozitetin e vajit ushqimor, vajit të misrit të përdorur në skuqje dhe gatim. Studimi ynë është kryer mbi këtë produkt, pasi vaji i misrit është më ekonomik, më i përdorur dhe luan një rol të rëndësishëm në shëndet dhe në jetë. Viskoziteti dhe temperatura e mostrave të vajit të misrit u matën duke përdorur Viskometrin Dixhital Model NDJ-5S me saktësi ±1%. Viskoziteti i vajit të misrit është studiuar në intervalin nga 20 deri në 60 °C. Modeli

Elektrik L-81 u përdor për të ngrohur mostrat e vajit në një temperaturë specifike. Parametrat e studiuar ishin: dendësia, përmbajtja e lagështirës, aciditeti i lirë, përcjellshmëria elektrike, viskoziteti dinamik dhe viskoziteti kinematik. Përveç viskozitetit dinamik dhe densitetit, u përcaktuan me anë të ekuacioneve viskoziteti kinematik dhe rrjedhshmëria. Varësia nga viskoziteti i vajit ndaj temperaturës u modelua matematikisht duke përdorur ekuacione dy dhe shumë konstante. Vërejmë se, viskoziteti i vajit zvogëlohet jo-linearisht me rritjen e temperaturës. Vendosja e të dhënave eksperimentale në disa modele teorike është kryer në mënyrë që të përshkruhet varësia e viskozitetit të vajit ndaj temperaturës. Kështu që, modeli Clement, paraqet më së miri këtë varësi.

Fjalë kyçe: *vaj misri, ngrohje, viskozitet dinamik, model matematikor*

Introduction

Corn oil (maize oil) is oil extracted from the seeds of maize (Sea mays L.) a plant grown in large areas of the U.S.A, China, Brazil and Mexico. It is the largest cereal crop in the world. Corn germ contains about 85% percent of the total oil of the kernel. The rest is dispersed in endosperm and hull fractions and is generally utilized in feed products. Corn oil is generally less expensive than most other types of vegetable oils. Almost all corn oil is expeller-pressed, then solvent-extracted using hexane or 2 isohexane. The solvent is evaporated from the corn oil, recovered, and re-used. After extraction, the corn oil is then refined by degumming and/or alkali treatment, both of which remove phosphatides. Alkali treatment also neutralizes free fatty acids and removes color (bleaching). Final steps in refining include the removal of waxes, and deodorization by steam distillation of the oil at 232–260 °C under a high vacuum. (Corn Oil Association, 2006) The oil content of the seeds ranges from 20 to 50% depending on the variety. Corn oil contains about 25 to 30 percent monounsaturated, 10 to 15 percent saturated fats and 60 percent polyunsaturated.

Corn oil is characterized by high content of linoleic acid (34-61%), lower amount of oleic acid (21-48%), slightly linolenic acid and high content of unidentifiable substances reaching up to 2-9% of which about 1% are phytosterols (α, β and γ sitosterol). Corn oil as a concentrated source of energy (calories), is highly digestible and provides essential fatty acids and Vitamin E to the body. It is also a rich source of poly-unsaturated fatty acids which help regulate blood cholesterol levels and lower elevated blood pressure. (Erickson, 2006) (Hauman, 1985) (Dupont et al., 1990)

The principal food uses of corn oil include: salad and cooking oil, margarine, blends of butter, mayonnaise and emulsion type salad dressings. Its main use is in cooking, where its high smoke point makes refined corn oil valuable frying oil. Corn oil is also a feedstock used for biodiesel. (Esteban et al., 2012) Other industrial uses for corn oil include soap, salve, paint, rust proofing for metal surfaces, inks, textiles, nitroglycerin, and insecticides Physicochemical and rheological data on vegetable oils serve a number of practical uses: assessment of nutritional values; quality control and monitoring of refining and food manufacturing processes and background information for chemical, biological and medical research involving fats. Rheology is a simple analysis that is applied to determine the physical behavior of solutions, suspensions and mixtures.

The basic parameter obtained in the rheological study of liquid foods, is viscosity, used to characterize the fluid texture. (Alonso et al., 1990) (Bower et al., 1990) (Rao, 1977) Viscosity is one of the most important properties of a liquid system; the change of viscosity is linked to physicochemical oil properties. (Fasina & Colley, 2008) This parameter can change under temperature, pressure, and concentration influence and all these changes can be modeled by some theorical equations (Ramakrishna et al., 1987). Corn oil was found to be more sensitive to thermal treatment, undergoing greater changes in its properties, especially in viscosity. The variation of the dynamic viscosity of corn oil with the temperature (20 to 60°C) is analyzed applying the different mathematical models, two, three and multi constant equations. The correlation coefficient for all the models obtained from the non-linear regression procedure was greater than 0.99.

Material and methods

The edible vegetable oil, corn oil available in Albanian market has been monitored. All the measurements were made in Chemical Process Engineering laboratory, Department of Industrial Chemistry. Corn oil samples were stored at room temperature and in a dark place before analysis. In the first phase, following the analytical methods described in Albanian Standard (General Directorate of Standardization Albania, 2017) were determined: moisture content, free fatty acidity and electrical conductivity. The moisture was calculated by sample weight loss at 105°C for a period of 24 h, according to standard method (SSH EN ISO 662:2000). Also, we measured the electric conductivity with DDS-120W Microprocessor Conductivity Meter. Free Fatty Acids determination was carried out according to standard method (SSH EN ISO 660:2009). Five grams of the oil were weighed accurately into 250 ml conical flask. Fifty ml mixture of 95% alcohol and ether solvent (1:1) were added.

The contents of the flask were then heated with caution until the oil was completely dissolved; the solution was neutralized after addition of one ml of phenolphthalein indicator. The contents of the flask were then titrated with 0.1N KOH with continuous shaking until a pink color persisted for 15 seconds. The number of ml of 0.1N KOH required was recorded. Acid value of a oil is a quantities indication of the acidity of the oil due to the formation of free fatty acids from rancidity, oxidation or decomposition of the constituent triglycerides of the oil. Acid number is expressed as the milligrams of potassium hydroxide required neutralizing 1 gram of the oil. The higher the acid number, the greater the formation of free fatty acids and the more acidic the oil.

In the second phase of the study, density and dynamic viscosity were experimentally determined as a function of temperature from 20 to 60^{o}C. For the determination of the density, the pycnometric method was used. For this purpose, pycnometers with a volume of 50 ml and an analytical balance with an accuracy of 0.0001 g were used. Since the oil was assumed to be a Bingham fluid and creating of internal textures was not expected, no special pre-experiment treatment was performed. (Santos et al, 2005) Viscosity and temperature of corn oil samples were measured using the Digital Viscometer Model NDJ-5S with accuracy ±1%. T

he SP-1 spindle was operated at different rpm. The Electric model L-81 was used to increase the temperature of the oil samples to a specific temperature. All values were below the limits, were within the range established by European Guidelines. All measurements were performed in three repetitions. The dependence of the oil viscosities to temperature was modeled using two and multi constant equations. The relationship between density and temperature can be expressed mathematically, while density decreases linearly with increasing temperature (Rodenbush et al., 1999).

The effect of temperature on the dynamic viscosity of liquid is described by means of the Arrhenius equation as:

$$\mu = \mu_0 \exp\left(\frac{E_a}{RT}\right) \qquad (1)$$

Where μ is the dynamic viscosity in mPa.s, μ_0 is the viscosity at infinite-temperature in mPa.s, E_a is the exponential constant that is known as activation energy (J/mol); R is the gas constant (8.31 J/mol.K) and T is the absolute temperature Kelvin. (Clements C. et al.; 2006) (Ahmad, 2009) (Giap, 2010) The activation energy can be obtained from the slope of the regression equation (Diamante & Lan, 2014). Power Law Model:

$$\mu = k(T - T_{ref})^n \tag{2}$$

Where k and n are constants, T_{ref} is reference temperature of 273.15 K (Fasina O.O. and Colley Z., 2008). Multi-constant formula known as Abramovic (three constant) and Clements (four constant) models that are represented in the following equations (Abramovic & Klofutar, 1998) (Clements et al., 1992):

$$Ln\mu = A + \frac{B}{T} + \frac{C}{T^2}; \qquad Ln\mu = A + \frac{B}{T} + \frac{C}{T^2} + \frac{C}{T^3} \tag{3}$$

Where μ is the dynamic viscosity in mPa.s, T is the temperature in Kelvin. A, B and C are constants. In addition to the dynamic viscosity and density, kinematic viscosity and fluidity by the formula were also determined. Kinematic viscosity ($m^2 \cdot s^{-1}$) is defined as a ratio of dynamic viscosity to density of fluid ρ ($kg \cdot m^{-3}$) at the same temperature. Reciprocal value of dynamic viscosity is called fluidity φ and unit of fluidity is $mPa^{-1} \cdot s^{-1}$ (Hlaváč et al., 2016).

The mean absolute percentage error, which indicates the deviance of the observed values from the calculated, was calculated using the following formula:

$$MAPE^a = \frac{\left| \sum_{1=1}^{n} \left(\frac{A_0 - A_C}{A_0} \right) \right|}{n} \cdot 100 \tag{4}$$

Where A_0 is the observed value, A_C is the calculated value, and n represents the number of pairs of samples.

Results and disccusion

The corn oil available in Albanian market is light yellow, bright and almost odorless. According to the Albanian Standard (SSH 2108:1987), this product can be consumed with these characteristics. (General Directorate of

Standardization Albania, 2017) The limit values of physicochemical and rheological parameters in corn oil available on the market must comply with the national law of the Albanian Food Law and EU Food legislation. By comparing our experimental data with standard value, we can see that they are roughly the same, with very little difference. This may come as a result of many factors that affect the quality of the corn oil and therefore the experimental results.

Factors can be numerous, but we can mention the area of seed origin, storage conditions and stages of production of the final product. The density values of corn oil sample were measured at 20ºC and found to be 0.9215 g/cm^3, within the European range 0.920-0.928 g/cm^3. Moisture of corn oil sample was 0.18%. Electric conductivity of corn oil sample was 0.427 mS, at 20ºC, respectively. The free fatty acid content and the acid value are important parameters used for the characterization and the quality assessment of edible oils. The higher the acid value and free fatty acid content, the lower the quality of the oil. The acid value additionally increases with the age of oil as triglycerides decompose into fatty acids and glycerol as an effect of time.

A free acidity value and acid number of corn oil were 0.282% and 0.561. The acidity expresses the percentage content (in weight) of the free fatty acids in the oil under examination. Setting a free oil acidity level lower than 0.8% can provide a useful standard to ensure that growers provide high quality undamaged fruit that is not harvested too late. The dynamic viscosity and kinematic viscosity values of corn oil sample were measured at 20ºC and found to be 65.7mPa.s and 71.3mm^2/s. Our value of dynamic viscosity of corn oil at 20ºC is in good agreement with another researcher and European standard. The viscosity of vegetable oils is affected by a number of factors. These include the physical and chemical properties of oils such as the density, molecular weight, melting point and degree of unsaturation. A factor that greatly affects the viscosity of oils is temperature.

The experimental dates of corn oil versus temperature are presented in Figure 1-2. Results showed that temperature has significant influence on physical parameters.

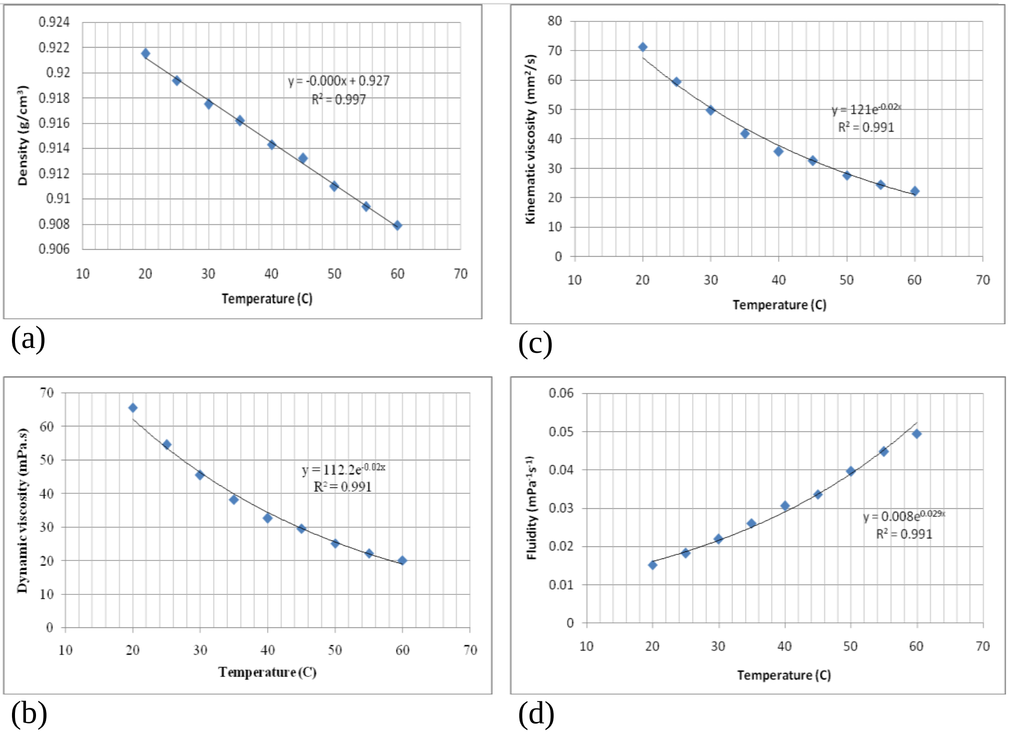
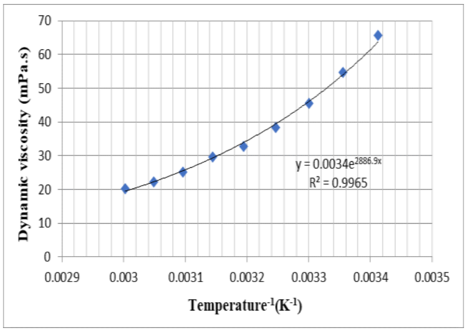


Figure 1 Effect of temperature on (a) density, (b) dynamic viscosity, (c) kinematic viscosity and (d) Fluidity of corn oil

The experimental data of corn oil, for dynamic viscosity (mPa.s) versus temperature is shown in Figure 1 (a). Density of corn oil at different temperatures ranges of 0.9215 to 0.908 g/cm^3. The dynamic viscosity of corn oil is decreasing with increasing of temperature 65.7 to 20.2 mPa.s. A temperature dependency of dynamic viscosity, described by decreasing exponential functions, is presented in figure 1(b).

On Figure 1 (c) is presented kinematic viscosity decreasing versus temperature range 20 – 60^{o}C. Kinematic viscosity of corn oil at different density ranges of 71.3 to 22.2 mm/s^2. While fluidity is increasing with increasing of the temperature, is presented in Figure 1 (d). Fluitidity of corn oil at different temperature ranges of 0.015 to 0.049 (mPa.s)$^{-1}$. The values of the estimated constants and correlation coefficients are shown in each equation, set in the graphs. The R^2 for all dependence obtained was greater than 0.98.



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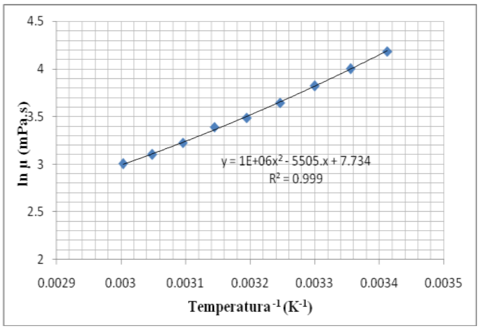

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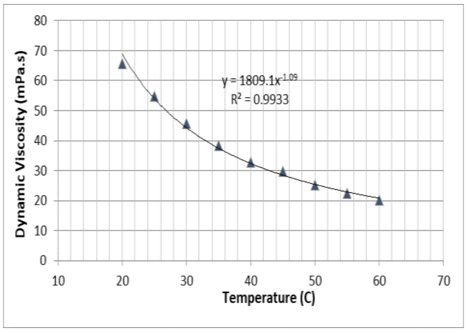

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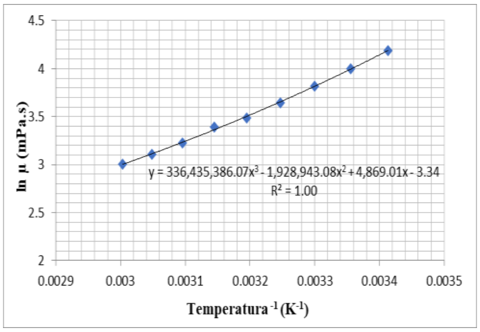

(h)

Figure 2 Effect of temperature on dynamic viscosity of corn oil by (e) Arrhenius, (f) Law Power, (g) Abramovic and (h) Clements models

The experimental data of corn oil, for dynamic viscosity fitting by Arrhenius, Law Power, Abramovic and Clements models are presented in Figure 2 (e-h), by using Equations 1 – 3, respectively. According to, the Arrhenius model result, the value of activation energy of the analyzed corn oil was 23.2 kJ/mol, which describe the sensitivity of viscosity to temperature changes. The values of the estimated constants are shown in each equation, set in the graphs. In all cases the determination coefficient (R^2) exceeded values >0.99. The experimental data are in good agreement with the theoretical prediction. The mean absolute percentage errors were below 10%: 3.2% Arrhenius model, 0.8 % Law Power model, 0.06% Abramovic model and 0.001% Clements model. All of the mean absolute percentage errors were low, which means that the viscosity values obtained were very stable. However, comparisons of the calculated data indicate that the temperature-dependence of viscosity for the corn oil samples was best described by the Clements model. An equation with lower MAPE values gives a better fit to experimental data compared to an equation with higher MAPE values.

Conclusıons

The article is focused in physicochemical parameters determination and on influence of temperature on viscosity of corn oil consumed in Albania. The physicochemical parameters results depend on corn oil nature and can be used as a way of characterizing. The limit values of physicochemical and rheological parameters in corn oil were within the Albanian and European standard values.

The dynamic viscosity versus temperature was measured and described by different mathematical models. The value of correlation coefficient and mean absolute percentage error indicates that the models fit satisfactorily to experimental data. However, comparisons of the results obtained indicate that the temperature dependence of viscosity was best described by the Clements model. More research is needed in this field to cover more types of oils other than corn.

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