

The Effect of Deep Heating on Rheological Behavior of Edible Vegetable Oils

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Abstract — In this study, sunflower, soybean and canola oils were heated by oven in 190°C, while the oxidation period was passed before in oven with 110°C. The rheological analyzes were done every 24 hr at 10°C while measurements were done by viscometer.

Temperature was controlled using water bath with precision of 0.1°C. Measurements were done in different speed ramps (resulting in different shear rates), during heating. The viscosities of samples were investigated as a function of the shear rate and also shear stress as a function of shear rate at 10°C. The related Herschel–Bulkley Model equations were identified at the specific temperatures. Peroxide index has been determined during investigation. As a result, peroxide reduction during polymerization of the samples, which happen with heating at 190, showed viscosity increase. Deep heating of oils happens in frying process, in which fats and oils are repeatedly used at very high temperatures in the presence of air and moisture. This causes a conversion of fats and oils to dimeric and polymeric, or cyclic and volatile compounds affecting the viscosity of them as well as foods fried in them. Additionally, these undesirable constituents produced may also lead in health hazards. Surprisingly, very few reports have been reported on the rheological behaviors of edible vegetable oils. Besides, they are mostly on temperatures below 100°C. The present work, therefore, has made an attempt to report the effects of deep temperature and polymerization happening after, on viscosity of sunflower, soybean and canola oils.

Keyword — vegetable oils, Deep heating, Peroxide index

1. INTRODUCTION

According to the importance of edible vegetable oils and their effects on the quality and texture of food, the factors affecting the rheological parameters of them must be considered. About three quarter of total world vegetable oil supplies are soybean oil, Canola oil, Sunflower and palm oils. High temperatures is one of the most important parameters affecting viscosity that might happen when they are used for frying. Vegetable oils are liquid plant products mainly composed of the glycerides of the fatty acids. They are termed triglycerides and are esters of glycerol (O. Igwe, 2004). Disregarding the realm of food manufacture, vegetable oils are widely used in a diversity of industries. They are mainly used in manufacturing soap (which is by far the most important) and are actively utilized in the production of paints, varnishes, lubricants and plastics. Vegetable oils with negligible sulfur, nitrogen and metal contents are renewable, available and non-polluting energy resources. Due to these important characteristics, they are regarded as suitable materials for purposes other than food. For instance, alternative uses, like biodiesel production, are being investigated (Kim et al., 2010; Karaosmanoglu & Kurt, 1998). However, currently, vegetable oils are mainly employed in nutrition. Sunflower is rich in linoleic acid content. Soybean contains high portion of linolenic acid and Canola are rich in linolenic and oleic acid (Bailey, 2005). According to the importance of these oils and their effects on the quality and texture of food, the factors affecting their rheological parameters must be considered. Rheology is concerned with the way materials respond to applied forces and deformations. Basic parameters of stress (force per area) and strain (deformation per length) are keys to all rheological evaluations (Gipsy Tabilo-Munizaga and Gustavo V. Barbosa-Ca'novas, 2005). Simply talking, Rheology is an

analysis being applied in order 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 (Rao, 1977). According to Valde's and Garcia's study on the two original vegetable oils, Sunflower oil was reported to be more sensitive to thermal treatment, undergoing greater changes in its properties, especially in viscosity, potential to increase considerably (F. Valde's & B. Garcia, 2005). On the other hand, regarding the importance of oil industry, unfortunately there have not been enough researches on edible vegetable oils rheology. So the necessity of working on this subject stands clear by itself. A number of factors affecting the viscosity of vegetable oils include the physical and chemical properties of oils such as the density, molecular weight, melting point and degree of un-saturation. Temperature is the factor that greatly affects oils' viscosity (O. Igwe, 2004). Deep heating of oils happens in frying process. Also, fats and oils are repeatedly used at high temperatures in the presence of air and moisture. This has partially caused conversion of fats and oils to oxidized derivatives, and dimeric, polymeric, or cyclic compounds (Chang et al., 1978), which affects the viscosity of the solutions. In addition, these undesirable constituents produced may also be sources for health hazards (Tyagi and Vasishtha, 1996). Surprisingly, very few reports have been carried on the rheological behaviors of edible vegetable oils and are mostly on temperatures below 100°C. The present work attempted to report the effects of deep temperature and polymerization happening after, on viscosity of sunflower, soybean and canola oils.

2. MATERIAL AND METHODS

2.1. Experimental materials

Pure refined deodorized edible vegetable oil samples were purchased from Nahan Gol factory of Boroudjen. Importantly, Samples were antioxidant free and kept in polyethylene triphthalate containers during the experiment.

2.2. Measurement of fatty acid composition

As the fatty acid composition affects the rheological behavior of oils (Kim et al., 2010), Fatty acid composition of fresh vegetable oils was investigated by using GC-MS (table 1).

2.3. Heating experiment

The collected samples were heated at 110°C for 19 days and oxidation process happened. The temperature was increased to 190°C from the 20th day to 25th day. Temperature increasing to 190°C results in polymerization of oils (Bailey, 2005). Peroxide value was determined daily by the use of Iodometric (visual) endpoint determination method to get aware of oxidation

process. The point is that this process is not frying and is definitely a very deep heating of edible vegetable oils.

2.3. RHEOLOGICAL MEASUREMENT

The flow behaviors of vegetable oils were measured by the use of viscometer (model LV DVIII-Brookfield, Middleboro, MA, USA), with a UL adapter permitting the use of only 20-30 ml of oil in each analysis. Temperature was controlled by the use of a water bath (Brookfield TC5 ± 0.1 °C). Also, in order to investigate the effect of temperature on oil viscosity, the oils were sheared at a range of speed ramp over temperatures ranging from 10 to 90°C and their viscosity was then measured. The two main indexes, consistency index and flow index, as well as yield stress were identified at 10°C for each day. Based on the main flow equation above, consistency index indicates viscosity, flow index and yield stress indicate the type of flow behavior of fluid.

2.4. STATISTICAL ANALYSIS

SPSS and Excel system were used in carrying out all the experiments followed by Duncan's multiple range tests. Secondly, the rheological curves were analyzed and the viscosity values were checked. The main curves of this study show consistency index as a function of peroxide value. These curves indicate the correlation between deep heated oil peroxide index (as a heating indicator) and rheological behavior.

3. RESULT AND DISCUSSION

The fatty acid compositions of three different vegetable oils were analyzed as shown in Table 1. The main component of canola oil was oleic acid (18:1) whilst the others were rich in linoleic acid (18:2). The presence of linolenic acid was found in soybean (5.3%) and canola (5.4%) oils which were relatively higher than sunflower. The results of another research demonstrated a high correlation between oil viscosity and fatty acid composition suggesting that the oils with more double bonds appeared to have lower viscosity due to their loose structure (Kim et al. 2010). So it is expected to see lower viscosity of soybean oil in comparison to canola and sunflower oils at specific temperature. It has also been investigated by Santos et al. that fresh vegetable oils show Newtonian flow behaviors because of their long chain molecules (Santos et al., 2004). Also it has been recognized by Maskan that temperature increasing, affects the viscosity at frying temperature and that is due to polymerization of oils (Maskan, 2003). However, the effect of chemical changes on physical behavior of vegetable oils is a new subject to discuss. Peroxide value is the sign of oxidation (chemical changes) while viscosity is an indicator of rheological behavior (physical changes). Because the samples have passed oxidation before deep heating, the data of control sample and the two main oxidation stages (before peroxide pick and after the pick) are shown in table 2 too.

Table(1) Fatty acid composition (%) of edible vegetable oils

Fatty acid	Sunflower	Soybean	Canola
C14	0.1123	0.0707	0.0746
C16	7.0406	8.9354	4.8552
C16:1	0.111	0.2081	0.2502
C17	-	-	0.1171
C18	3.7865	4.64	2.5837
C18:1cis9	25.1956	22.7953	57.671
C18:1cis11	1.0565	1.433	3.1824
C18:2trans	0.2113	0.2299	0.3204
C18:2cis	61.309	54.9011	20.0903
C20	0.3274	0.4457	0.8483
C18:3trans	-	-	0.5597
C20:1	0.1927	0.331	2.4802
C18:3cis	0.2727	5.3193	5.4084
C22	0.3844	0.6906	0.08
C20:2	-	-	0.4813
C22:1	-	-	1.0164

Table (2) Peroxide value and consistency index changes of 3 oils during oxidation and polymerization period (10°C)

Day	Canola		Soybean		Sunflower	
	PV*	k	PV	k	PV	K
		96		12 7.8		89. 6
0	0.6	13 1.9	0.7	10 0.7	0.9	11 9.6
5	15.15	11 9.7	37.43	11 6.4	37.43	11 6.4
6	13.42	10	27.6	10	38.4	10
7	11.28	7.5	21.29	3.2	25.56	9.7
19	8.11	24 7	12.64	11 8.5	17.76	68 2
21	1.73	15	1.73	21	1.93	16
23	1.39	3	1.73	7.3	1.66	3.3
25	1.06	34 8.4	1.19	55 6.2	1.39	11 56
		41 3		67 7.8		32 91

*meq O2/ Kg oil

As mentioned before, consistency index (k) is the viscosity indicator and its changes as a function of peroxide value is evaluated. Temperature of this study is considered 10°C, because the best change observing

could be observed at it. Canola and soybean oils peroxide value was at the pick on 5th day of oxidation and sunflower pick peroxide value was on 6th day of oxidation. So as was expected from high linolenic content of canola and soybean oil, they got through the second phase earlier than sunflower (table 2). The consistency index changes can show the viscosity change process. Canola has the lowest and sunflower has the highest CI at the end of deep heating among the three samples. That could be for fatty acid content of samples as well. It shows a good agreement with Kim et al. research when the results are compared (Kim et al., 2010). The curves of consistency index (CI) versus peroxide value (PV) are shown in following.

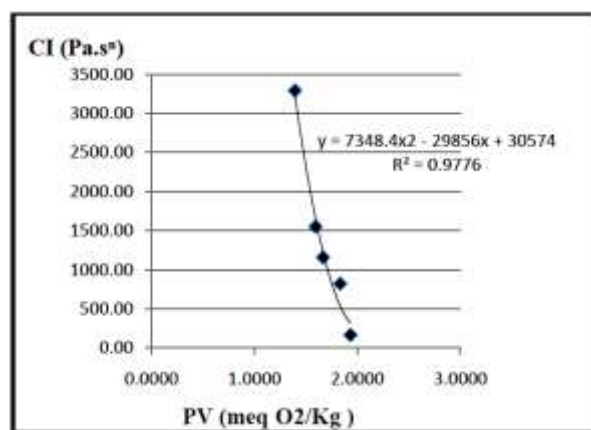


Fig 1. Curve of consistency index vs. peroxide value of Sunflower at 10 °C

The dependence of viscosity on the oxidative changes in polymerization period of vegetable oils was investigated by correlating the oil consistency index with peroxide value. So, an effort was made to investigate how the degree of peroxide value affected oil viscosity. Highly positive correlation was observed between viscosity and peroxide value in sunflower oil as shown in Fig.1 (R2 = 0.977). It means to have, as the peroxide index decreases in polymerization period, a nonlinear increase in viscosity. The rheological equation of this correlation is mentioned near the curve. Highly positive correlation was observed between viscosity and peroxide value in soybean oil too as shown in Fig.2 (R2 = 0.902). So, this graph also indicates a high nonlinear correlation between consistency index and peroxide value. Canola shows a different behavior compared to 2 other oils. As it is shown in fig. 3 canola oil shows the lowest correlation between CI and PV (R²=0.709). Therefore, there is a nonlinear correlation between PV and CI. A decrease in the oil viscosity was distinctly observed with increasing portion of 18:3. The presence of double bond does not allow fatty acid molecules to stack closely together, consequently interfering with packing in the crystalline state. Therefore, fatty acids with more double bonds do not have a rigid and fixed structure which are loosely

packed and more fluid-like (Kim et al., 2010). Although canola is rich in oleic acid, but it has the lowest viscosity during polymerization at 10°C and it does not show agreement when is compared with the results in Kim et al. The reason may rest in the importance of high content of linolenic acid that is more in higher oleic acid content.

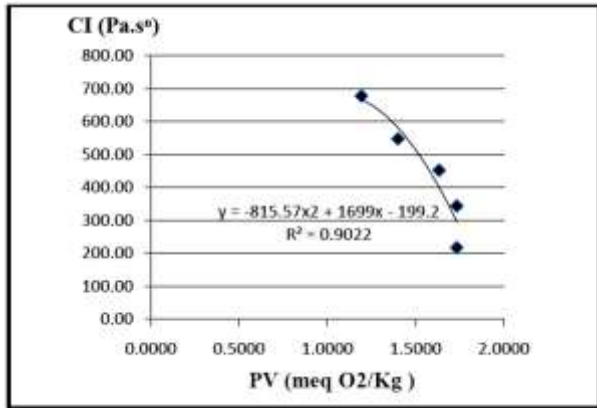


Fig 2. Curve of consistency index vs. peroxide value of Soybean at 10°C

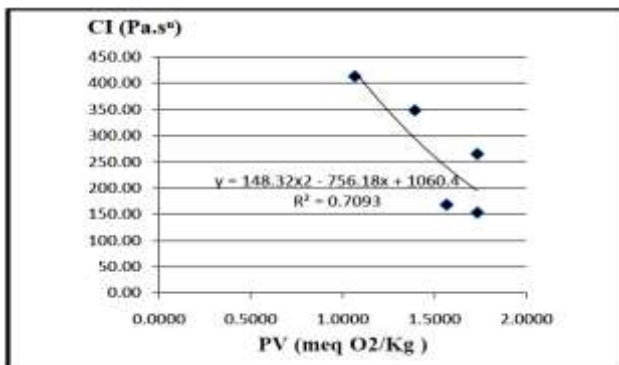


Fig.3. Curve of consistency index vs. peroxide value of Canola at 10°C

4. CONCLUSION

As a principal and essential frying component, edible vegetable oils were analyzed in terms of their polymerization effect on their viscosity. The results demonstrated that there was a high correlation between oil viscosity and peroxide value in polymerization period after oxidation stage. Also the type of oil can be effective. Less correlation between PV and CI was observed in canola in comparison with soybean and sunflower. It was demonstrated that as the peroxide value decreases in polymerization stage, oils appeared to have higher viscosity due to produced dimmers and polymers. Thus, as long as fresh vegetable oils are used for frying applications, it seems that the effect of the oil type and behavior in deep heating could be important. Since the rheological behavior of edible vegetable oils is a quiet new subject in food technology and also because

rheology plays a very important role in oils quality during deep heating process, further research would be necessary to investigate how oils chemical changes can affect their viscosity in frying conditions and repeated use.

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