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VISCOSITY AS A MEASURE OF OIL COMPOSITION CHANGES DUE TO THERMAL DEGRADATION

PILAR OLIVARES-CARRILLO[1], ANTONIA PÉREZ DE LOS RÍOS[1], JOAQUÍN QUESADA-MEDINA[1]*,
JOSÉ GINÉS HERNÁNDEZ CIFRE[2], FRANCISCO GUILLERMO DÍAZ BAÑOS[2]

[1] Department of Chemical Engineering and [2] Department of Physical Chemistry,
University of Murcia, 30071 Murcia, Spain

* Corresponding author: quesamed@um.es
Fax: x34.868.884148

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ABSTRACT:
In this work, the viscosity of soybean oil subjected to thermal degradation has been determined and related to the chemical composition of the oil. In particular, it is found a linear relationship between the viscosity value and the triglycerides content during the degradation process (an increase of the former is associated to a decrease of the latter). Thus, it is shown that viscosity provides us a reliable way of measuring oil degradation and, insofar as proportional to flow time, it allows for the design of simple devices to control the oil quality. Besides, the study of the viscosity behavior along with the changes in composition during the cooking time, i.e. the period of time that the oil is being heated, give us valuable information about the type of chemical reactions occurring within the oil.

KEY WORDS:
deep frying, polymerization, shear viscosity, soybean oil

1 INTRODUCTION

The characterization of rheological properties of edible oils is of great importance for their handling in food industry as well as a powerful tool to understand the structural changes occurring after oil processing. One important, primary rheological property is the dynamic viscosity which is a measure of the resistance of a fluid to flow. That property is closely related to the size and shape of the molecules that form the fluid. Thus, viscosity changes are indicative of structural changes within the fluid. Natural oils are triglyceride esters of fatty acids which typically comprise from 14 to 22 carbon atoms and present 1 to 3 double bonds (unsaturations). Thus, they are formed in binding three fatty acid chains to a glycerol center. It is well known that the viscosity of vegetable oils increases with both the increase of the chain length of the fatty acids and the increase of the hydrogenation degree (i.e. the decrease in the number of unsaturations) [1]. It is also well determined that the viscosity of the oil varies after heating due to the change in oil composition consequence of the chemical reactions provoked by the heating conditions [2]. Therefore, the change in viscosity is a good index to quantify the degradation of heated oil [3].

Heat has a crucial role during food preparation. In particular, frying in oil is one of the most popular methods of cooking. In deep frying, oil is heated in air and in the presence of light at temperatures of 160°C to 200°C. In public restaurants, it is usual to keep the oil at those conditions during long periods of time or, in household cooking, the same fried oil is commonly used many times. The frying conditions cause physical and chemical changes in the oil, being hydrolysis, oxidation, and polymerization common chemical reactions occurring in frying oil under the presence of moist air [4, 5]. The problem with the degradation of frying oil is not just a question of loss in organoleptic properties but the risk that reaction products has for human health. In addition, the used oil is frequently thrown away with the subsequent environmental damage (an interesting alternative being to recycle it to make biodiesel). Thus, it seems crucial to characterize the physical-chemical changes in the oil and, in particular, to acquire a good understanding of the rheological changes provoked after heating it. There are other works that illustrate the dependence of the rheological properties of some types of oil on the temperature [6]. The question elucidated in this paper is rather how the heating period affects the composition and therefore the viscosity of a type of oil, namely the soybean oil, which is widely

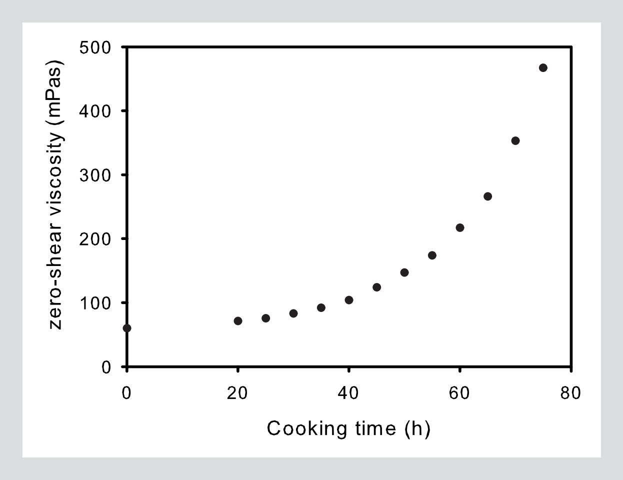

Figure 6: Evolution of the zero-shear viscosity of soybean oil with cooking time.

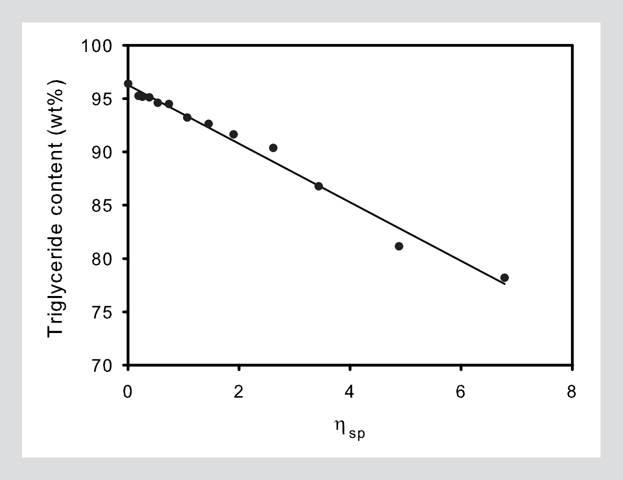

Figure 7: Relationship along cooking time between triglycerides content and "specific" viscosity of a soybean oil.

tropy. That is a kind of behavior found in dilute solutions of short and/or non-linear polymers. Otherwise, if the shear flow could significantly deform/orientate the polymeric species (or had some influence on their creation/destruction), some shear rate dependence of the viscosity would be expected. The Newtonian behavior is not unexpected if one considers that "oil polymers" are mainly formed by addition of triglycerides, which make up the vast majority of the oil at any moment (see Figure 1). Thus, the oil sample after cooking will mainly consists of some branched chains (they cannot become linear and large because of the triglyceride structure) immersed in an environment, i.e. a solvent, of triglyceride molecules. Definitely, we can consider that system like a non-linear polymer dilute solution in which all the interactions are alike since both "solvent" and "oil polymers" are of the same chemical nature.

The presence and nature of the polymerization reaction is again confirmed by the plots of Figure 4. Thus, the decrease in the amount of the fatty acids C18:2 and C18:3 is in agreement with the decrease in triglycerides shown by Figure 1 what can be explained if those acid chains (precisely the most unsaturated ones) are the main ones involved in the polymerization reaction. If we focus our attention on the time evolution of the most abundant, i.e. C18:2, we observe that it starts to strongly decrease around the cooking time 60 h in correspondence to the abrupt decrease in triglyceride content and increase in viscosity. In sum, the good correspondence between the decrease of both triglycerides curve (Figure 1) and C18:2 fatty acid curve (Figure 4) with the increase of the viscosity curve (Figure 6) indicates the presence of a polymerization reaction during the oil degradation that becomes increasingly relevant with cooking time. That way, we can think of tracking the evolution of the oil degradation by means of viscosity measurements. Moreover, we can try to relate quantitatively the change in viscosity with the change in triglyceride content which is the most apparent consequence of the thermal degradation.

Figure 7 represents the relationship between triglycerides content (wt%) and viscosity η along the cooking time. For the sake of generality, the latter is given in dimensionless form as a kind of specific viscosity, $\eta_{sp} = (\eta - \eta_o)/\eta_o$, where the reference viscosity η_o is that corresponding to the original oil sample at "zero cooking time", i.e. η_o = 60 mPas for the case under study. Thus, that quantity measures the relative increment in viscosity due to thermal degradation. In using the normalized quantities η_{sp} and wt%, the minimum attainable value in both axes is zero and possible comparison with other experimental results becomes easier. As observed, there exists a quite linear relation so that we can make a linear regression with those experimental data to obtain the following mathematical relationship: wt%(triglyceride) = 96.28 – 2.75 η_{sp}, which is obviously valid for the case of our soybean oil subjected to a thermal degradation process at 180 °C. Thus, a measure of the oil viscosity gives us straightforwardly a good estimate of the triglyceride content in wt% without any further cumbersome composition determination. Moreover, taking into account that edible oils use to behave Newtonian (see Figure 5), viscosity can be considered directly proportional to flow time under any circumstances and therefore it is feasible to design simple and cheap setups to assess the oil degradation. For example, a small recipient with well defined capacity connected to a capillary with a faucet would be an adequate device: the recipient is filled up and then the oil sample is allowed to flow while measuring the time it takes to empty. As commented above, convenient quantities to work with are the specific viscosity and the relative viscosity. The latter is just given by the ratio of the flow time of the oil to the flow time of the original oil: $\eta_r = \eta/\eta_o = t/t_o$. After proper calibration, that time ratio could be associated to the oil composition (see Figure 7). Quite practical for the oil consumer would be to dispose of tables relating oil quality with well established ranges of t/t_o. For that purpose, further studies considering many typical edible oils must be performed.

4 CONCLUSIONS

Thermal oil degradation is produced by the chemical reactions involving the oil components that occur at high temperature. That oil degradation produces, among many other measurable physical changes, a strong increase in the oil viscosity. We have subjected soybean oil at a temperature of 180 °C during several periods of time and analyzed the composition and viscosity changes, as well as the viscosity behavior under shear flow. Combining the information provided by those experimental data, one can deduce that the main chemical reactions that take place during deep frying are the rupture of some triglycerides and the addition polymerization of triglycerides containing C18:2 and C18:3 fatty acid chains, the latter reaction being responsible for the observed abrupt viscosity increment.

We have shown that viscosity, a simple physical characterization technique, provides an excellent index to follow the loss in triglycerides content caused by deep frying processes. In this work we have given a quantitative relation between the triglycerides content and the (specific) viscosity of soybean oil. We think that there is a lack of such a type of quantitative relationships in the literature. It would be desirable to study this issue systematically in order to elucidate if some general relationships between viscosity and composition can be established. In that way, considering that viscosity is proportional to flow time, which can be measured easily, it is possible to design a simple and cheap device to perform oil quality control.

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