Open Journal of Applied Sciences, 2021, 11, 264-272
https://www.scirp.org/journal/ojapps
ISSN Online: 2165-3925
ISSN Print: 2165-3917

Attempt to Polymerize *Cucurbita pepo* Oil by Temperature Action and Photolysis

Aristide H. W. Nakavoua[1*], Louis Okotaka Ebale[2], Bertin Mikolo[3], Vincent Verney[4], Gilles Figuérédo[5]

[1]Laboratory of Chemistry of Natural Substances (IRSEN), Brazzaville, Congo
[2]Laboratory of Mechanics, Energetics and Engineering, Unesco Chair in Engineering Sciences Ecole Nationale Supérieure Polytechnique, Marien Ngouabi University, Brazzaville, Congo
[3]Marien Ngouabi University, National Polytechnic High School (ENSP), Laboratory for the Valorisation of Agri-Resources, Brazzaville, Congo
[4]Institute of Chemistry of Clermont-Ferrand (ICCF), UMR 6296 Team Design of Polymers and Macromolecules Scientist Set Cézeaux24 Avenue des Landais, Clermont Ferrand, France
[5]LEXVA Analytical, 460 rue du Montant, 63540 Romagnat, France or Henri Mondor Street Biopole Clermont-Limagne 63360 Saint Beauzire, Clermont Ferrand, France
Email: *a.nakavoua@lycee-saintexbrazza.org

How to cite this paper: Nakavoua, A.H.W., Ebale, L.O., Mikolo, B., Verney, V. and Figuérédo, G. (2021) Attempt to Polymerize *Cucurbita pepo* Oil by Temperature Action and Photolysis. *Open Journal of Applied Sciences*, **11**, 264-272.
https://doi.org/10.4236/ojapps.2021.113019

Received: January 10, 2021
Accepted: March 12, 2021
Published: March 15, 2021

Abstract

The study of the polymerization of a vegetable oil has a double interest; industrial but especially food. Industrial because polymers based on vegetable oil are in line with sustainable development; food because an oil which polymerizes easily is a danger for human consumption. Three situations of *Cucurbita pepo* oil polymerization are carried out in the course of time, the factor retained being temperature. A monitoring of the evolution of the enthalpy by temperature variation by the DSC method allows to report the polymerization of this oil. It happens that a polymerization is triggered in the oil matrix but it seems to fade very quickly, this behavior is general because after sweeping a temperature range of 80˚C; 100˚C and 150˚C adding different amounts of Irgacure: the *Cucurbita pepo* oil resists polymerization through its antioxidant compounds. However, a photolysis of this oil carried out over 8 days shows that it effectively polymerizes after 144 hours, which proves the great capacity of antioxidant compounds to protect this oil. The analyses carried out at 25˚C aim to simulate the behavior of the oil at room temperature. The results reveal good resistance to both thermochemical and photochemical polymerization, which opens up great prospects for its development in the food industry and in nutrition.

Keywords

Cucurbitea pepo, DSC, Polymerization, Antioxidants, Irgacure and Photolysis

1. Introduction

At present, two major challenges are facing researchers in the field of natural substance chemistry in developing countries, namely:

- To comply with a logic of replacing petroleum-derived products because they are non-renewable and therefore in opposition to the policy of sustainable development and environmental protection.
- To create conditions for valorizing local resources known as "from home" through clean chemical processes.

USDA [1] has shown that the use of so-called conventional oils in the world has reached record levels, however non-conventional oils such as *Cucurbitea pepo* oil, although having a composition [2] [3] almost identical to rapeseed for example, is not part of this dynamic [4] hence the need to develop it. Desroches *et al.* [5] have shown that 14 billion tonnes of vegetable oils per year are used in the production of polymers, while pumpkin seed oil is likely to polymerize under certain conditions. The aim is therefore to put the oil in a situation where the temperature favors radical reactions in order to evaluate the polymerization of pumpkin seed oil, which precedes many compounds with strong antioxidant power [3]. Photolysis of *Cucurbitea pepo* oil in a petri dish under a mercury filament lamp produces a thin, transparent film that adheres easily to glass [6]. Monitoring by gas chromatography allowed to know which fatty acids were impacted. The power of the lamp having considerably damaged the antioxidant compounds, their action could unfortunately not be followed.

2. Materials and Methods

2.1. Process of Obtaining the Oil

The seeds from all sides are already stripped of their hulls bought on the market place of Brazzaville. They have been crushed using an electric crusher equipped with a rotor calibrated at 2500 rpm. The grind (powder) obtained is then placed in a cartridge and the whole is introduced into an extraction device (Soxhlet), the extraction solvent is hexane and the extraction is done during 3 hours.

2.2. Fatty Acid Composition

Fatty acid (FA) esters are obtained after direct methylation: 2 drops of oil in 1 mL hexane in the presence of 0.4 mL 1 N soda (in methanol) heated for 1 minute. Then 0.4 mL 1 N hydrochloric acid in methanol is added followed by 1 mL hexane [7]. After 144 hours the residue is scraped off and diluted in chloroform before methylation.

The AG composition is determined by GC/FID using an AGILENT 5890 apparatus equipped with a 100 m long Supelco FAMES column with an internal diameter of 0.25 mm and a thickness of 0.25 µm. This apparatus delivers hydrogen (H_2) as carrier gas at 0.7 mL·min^{-1}. It is equipped with an oven whose temperature rises to 140˚C and then continues to rise for 5 minutes at a rate of 4˚C·min^{-1} up to 240˚C. The temperature of the injector is at 280˚C according to a split of 1/30 and injecting a volume of 1 µL, that of the detector is at 300˚C at a rate of 40 mL·min^{-1} for hydrogen (H_2) and 450 mL·min^{-1} for air finally a makeup of 45 mL·min^{-1} for dinitrogen (N_2).

2.3. Temperature Action

The temperature action is performed by DSC, the sample (encapsulated) and the reference (empty capsule) are placed on platforms in the ceramic thermoelectric disc, which serves to transfer heat from the oven to the cell and capsules. The oven temperature is fixed and the differential heat flow between the sample and the reference is measured by area thermocouples fixed under the platforms [8].

Three series of measurements at different temperatures; 25˚C, 100˚C and 150˚C were carried out for 6000 seconds. A test at 80˚C was carried out to evaluate the effects of radical reactions on pumpkin seed oil, which gave results with the same profile as at 100˚C.

A first series of measurements are obtained under nitrogen followed by a second series under oxygen from the air and then finally a last series under oxygen from the air in the presence of a radical initiator: Irgacure 620 (Benzophenol). For this last series, mixtures of the oil sample with 1%, 2% and 3% of Irgacure 620 are carried out.

One bottle of compressed nitrogen and oxygen is used each time for a flow rate of 200 mL per minute.

The measurements were performed with the differential enthalpy analyzer DSC 822e from Mettler Toledo.

2.4. Photolysis

Photolysis is carried out using an accelerated aging device equipped with a mercury vapor lamp with a capacity estimated at twice the African sun at zenith [9].

It consists of a metal box that contains the entire operating mechanism of the enclosure. By integrating the curve (area under the curve) we can calculate the irradiance of a mercury vapor lamp: between 290 and 400 nm, I = 140.75 W/m^2, but for the solar spectrum we find I = 67.91 W/m^2, which corresponds to an irradiance more than twice that of the sun. The borosilicate glass lamp envelope filters out wavelengths below 290 nm (as in the earth's solar radiation). The temperature of the enclosure is set at 35˚C and is maintained by an automatic cooler (fan) placed above the control gear. To cope with any rise in temperature, the room is maintained at 18˚C by an air conditioner.

The experiment was carried out for 8 days and samples were taken at 0; 2; 4; 24; 48; 72; 96; 120; 144; 168 and 192 hours. Each sample was analyzed in GC/FID.

3. Results and Discussion

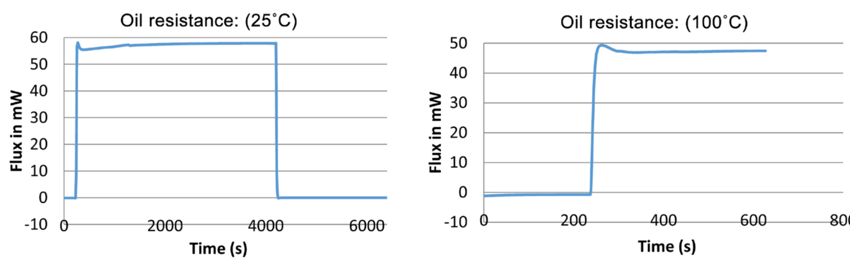
3.1. Temperature Action

600 seconds after the start of the temperature action, the oil displays two phases;

a first one which corresponds to a peak followed by a second one which corresponds to a bearing (**Figure 1**). The peak represents a spontaneous polymerization of the pumpkin seed oil. Indeed, the chemical composition of this oil reveals that it consists of 80% unsaturated fatty acid with less than 1% of C18:3 which would probably be at the origin of this polymerization. This behavior is observed throughout the experiment. However, at 100˚C **Figure 1** on the right, there is a latency time of 250 seconds which explains the high resistance of pumpkin seed oil to the action of temperature [10]. This result confirms the resistance of pumpkin seed oil and proves at the same time that there are compounds in pumpkin seed oil that undergo the action of heat very quickly. Once the adaptation is made, the oil resists as long as possible because the bearing already observed at room temperature settles during the next 4000 seconds.

This result shows that at 25˚C and in the absence of oxygen from the air, the pumpkin seed oil is sufficiently resistant. This means that at this temperature, pumpkin seed oil can be stored for a fairly long time in the absence of oxygen. This result is consistent with the high presence of antioxidant compounds in this oil [3].

At 150˚C, the small peak corresponding to a pseudo-polymerization visible at 25˚C and at 100˚C disappears, but the adaptation time of the pumpkin seed oil remains 250 seconds (**Figure 2**). It is noted that the expected polymerization is still not real, which allows us to prove that pumpkin seed oil like peanut oil resists well to heat [11] [12]. This result confirms the resistance of pumpkin seed oil and in particular the action of antioxidants of chain breakage that this oil has [3].



(a) (b)

Figure 1. Attempted polymerization of pumpkin seed oil at 25˚C (left: (a)) and 100˚C (right: (b)) under nitrogen.

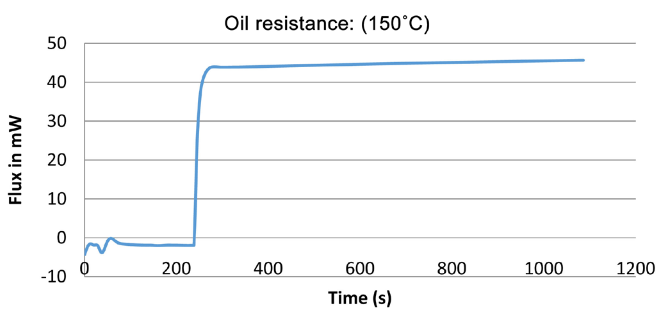


Figure 2. Attempted polymerization of pumpkin seed oil at 150˚C under nitrogen.

However, the fact that the curve increases shows that there is an obvious polymerization initiation when the experiment is carried out in the presence of oxygen [13].

We notice after 4000 seconds at 100˚C in the presence of oxygen from the air that the pumpkin seed oil does not polymerize. It should however be noted that the enthalpy is negative so the system releases energy [9]. A steep slope at the beginning indicates a strong release of energy which therefore corresponds to a predominance of bond formation over homolytic cuts. The new links becoming more and more numerous generating a reticular network [14] hence the slowing down of the energy supplied by the system (slope becoming weak). This behavior can be interpreted by the formation of branching within carbon chains due to the incorporation of fatty acids (FA) released during Soxhlet extraction (**Figure 3**).

However, at 150˚C, the enthalpy obtained is positive and grows very rapidly up to a threshold, which proves a significant increase in homolytic cuts in carbon chains. This result is in agreement with the clear brittleness of the double bonds with respect to the temperature [15]. Above the threshold, the enthalpy slowly decreases showing a reorganization of the oil matrix by the formation of new chemical bonds without polymerization. This phase represents an increase in the intramolecular bonds and thus molecular rearrangements which may possibly be an extension of the carbon chains of the fatty acids [13].

This observation suggests that these two phenomena follow one another in the matrix, firstly an increase in cross-linkages by incorporation of free FA in the oil at moderate temperature, then homolytic cuts and chain lengthening at high temperature [14]. However, the polymerization of the oil is still not observed, which suggests that pumpkin seed oil undergoes little significant degradation after 4000 seconds in the presence of oxygen, which is an encouraging result for the recovery of this oil [3].

The fact that a pseudo-polymerization occurs at 25˚C under nitrogen, it is therefore interesting to catalyze this polymerization with a compound that generates free radicals, in this case Irgacure 620 (Benzophenol) [16].

For more certainty, we had put up to 3% because, 1% and 2% give the same results as without Irgacure. We notice that the peak becomes more and more pointed, this is due to the Irgacure which undergoes a polymerization, on the other hand, the bearing remains constant which is a satisfactory result.

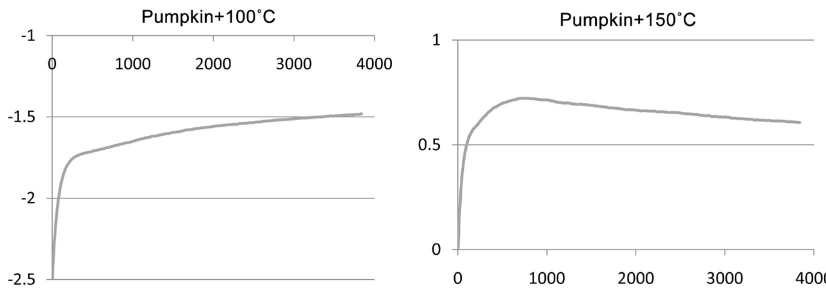


Figure 3. Attempt to polymerize pumpkin oil under O_2 at 100˚C (left) and 150˚C (right).

The action of oxygen at 25˚C seems completely non-existent because these results are identical to those obtained under nitrogen (**Figure 4**) despite the presence of 3% irgacure [6]. This means that pumpkin oil can be left in the open air and at room temperature without any polymerization beginning.

At 80˚C, which is a range conducive to radical reactions, the observation is the same as shown in **Figure 4**.

The pumpkin seed oil is quite resistant to heat in the presence of a generator of free radicals causing chain reactions, it turns out that the expected behavior is not observed which supports the conclusion already obtained in previous work that pumpkin seed oil contains chain-breaking antioxidants that act during the initiation phase by reducing the rate of peroxidation and trapping the radicals involved in this phase which results in a more or less continuous slowing of the oxidative process [12].

At 100˚C under the same conditions, the results are identical to those at 80˚C (**Figure 5**). Obviously, as the temperature increases, the peak corresponding to pseudo-polymerization is more pronounced.

At 150˚C under the same conditions, the slope becomes steeper, indicating a weakening of the oil resistance (**Figure 5**). To see the impact of the oxygen we had twice decreased the flow rate of this gas. Each time the slope was reduced. This means that pumpkin seed oil resists better to heat in the absence of oxygen.

3.2. Photolysis

The photolysis of pumpkin seed oil provides a great deal of information, particularly on the stability of this oil. Indeed, the results in **Figure 6** allow us to note

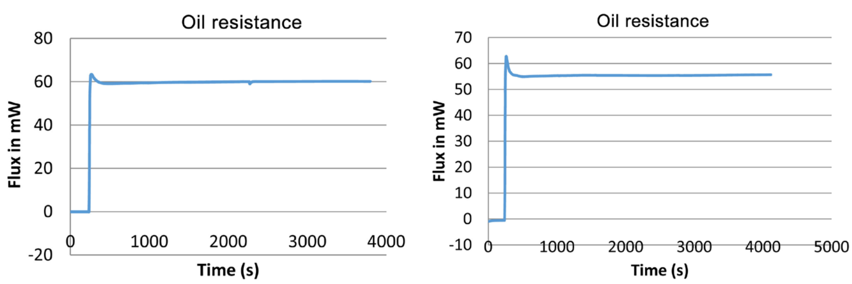


Figure 4. Attempted polymerization at 25˚C (left) and 80˚C (right) under oxygen of pumpkin seed oil in the presence of 3% irgacure.

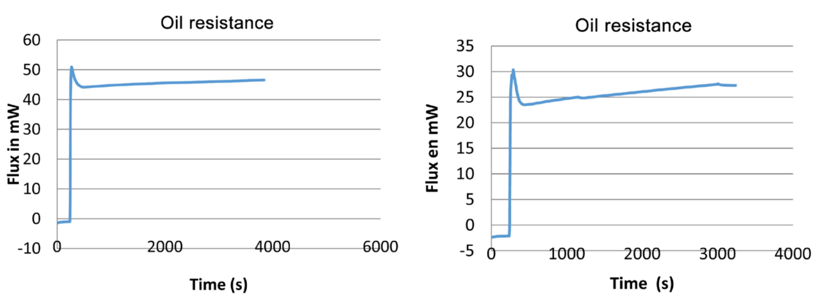


Figure 5. Attempted polymerization at 100˚C (left) and 150˚C (right) under oxygen of pumpkin oil in the presence of 3% irgacide.

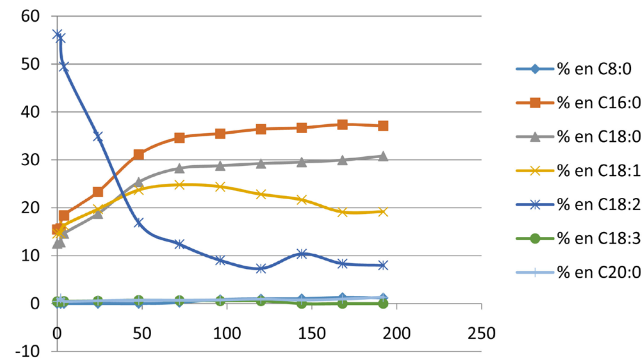


Figure 6. Fatty acid behavior during photolysis of pumpkin seed oil.

an overall increase in the contents of the SFA while the IFA decrease considerably until disappearing in the oil [17].

After 2 hours of exposure, the pumpkin seed oil does not undergo any major changes except for an increase in C20:0. This result may suggest that there are compounds with very short carbon chains in the oil which extend the FA already existing in the oil. It is the same observation made during thermo-oxidation under oxygen at 100˚C [18].

2 hours later the oil shows an increase in C16:0 and C18:0, during the same period a decrease in unsaturated fatty acids is observed. This result suggests at first glance that the increase in SFA levels is only the result of the decrease in IFA levels. Thus, all these changes are only due to the relative levels of FA. However, the appearance of C8:0 after 72 hours of exposure to UV light coincides with the disappearance of C18:3. This result is proof that a certain number of changes are taking place within the pumpkin seed oil matrix. There is a correlation with the thermoxidation under oxygen at 150˚C [19].

4. Conclusions

In conclusion, pumpkin seed oil, like peanut oil, resists the effects of temperature and does not immediately undergo polymerization, however, it settles in the oil matrix gradually because it is stopped by the many antioxidant compounds present in this oil [20].

With regard to its composition rich in unsaturated fatty acids pumpkin seed oil will have the status of seasoning oil like rapeseed oil according to French standards. However its great capacity to resist to alteration thanks to a high content of antioxidant compounds, this oil like peanut oil can be used as frying oil [20].

From the point of view of current consumption, the results of this work give reassuring information because pumpkin seed oil used in conditions of temperature below 150˚C will not polymerize. This result shows that the polymerization of pumpkin seed oil is linked to the rise in temperature. This result confirms a conclusion already reached that pumpkin seed oil, like peanut oil, cannot be used for long frying as the temperatures during these operations sometimes rise up to 250˚C.

Acknowledgements

I sincerely thank Dr. Gilles Figueredo for his involvement in the analysis and discussions in gas chromatography. I would like to add these thanks to Dr. Louis Okotaka Ebale for his expertise in thermodynamics and Dr. Bertin Mikolo for his multiple contributions. Without forgetting Professor Vincent Verney for his many contributions in DSC analysis.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

[1] USDA (2010).

[2] Güner, F.S., Yağcı, Y. and Erciyes, A.T. (2006) Polymers from Triglyceride Oils. *Progress in Polymer Science*, **31**, 633-670. https://doi.org/10.1016/j.progpolymsci.2006.07.001

[3] Nakavoua, A.H.W., Mampouya, D., Loumouamou, A.N., Silou, T., Chalard, P., Verney, V. and Figueredo, G. (2013) Accelerated Ageing Effects on Curcubitea Pepo Seed Oil. *Advance Journal of Food Science and Technology*, **5**, 806-821. https://doi.org/10.19026/ajfst.5.3144

[4] Gunstone, F.D. (2011) Supplies of Vegetable Oils for Non-Food Purposes. *European Journal of Lipid Science and Technology*, **113**, 3-7. https://doi.org/10.1002/ejlt.201000104

[5] Desroches, M., Escouvois, M., Auvergne, R., Caillol, S. and Boutevin, B. (2012) From Vegetable Oils to Polyurethanes: Synthetic Routes to Polyols and Main Industrial Products. *Polymer Reviews*, **52**, 38-79. https://doi.org/10.1080/15583724.2011.640443

[6] Zhao, Y.H. (2015) Elaboration de revêtements à base d'huile végétale par chimie thiol-X photoamorcée. Polymères. INSA de Rouen, 2015. Français.

[7] Codex Alimentarius (2017) Normes pour les huiles végétales portant un nom spécifique. Codex Stan 210.

[8] Ghettas, A. (2015) Etude du comportement thermique de polypropylène isotactique vierge et modifié par un agent réticulant en utilisant les techniques d'analyse thermique: ATD, DSC et ATG (Doctoral Dissertation).

[9] Olsson, S.K., Johansson, M., Westin, M. and Östmark, E. (2014) Reactive UV-Absorber and Epoxy Functionalized Soybean Oil for Enhanced UV-Protection of Clear Coated Wood. *Polymer Degradation and Stability*, **110**, 405-414. https://doi.org/10.1016/j.polymdegradstab.2014.09.017

[10] White, R.E., Thomas, P.S., Phillips, M.R. and Wuhrer, R. (2005) A DSC Study of the Effect of Lead Pigments on the Drying of Cold Pressed Linseed Oil. *Journal of Thermal Analysis and Calorimetry*, **80**, 237-239. https://doi.org/10.1007/s10973-005-0642-5

[11] Bacon, L. and Douville, É. (2006) Détermination du degré de détérioration d'huiles sous l'influence de la chaleur, l'oxygène et la lumière: 4e symposium des projets de

fin d'études en sciences de la nature. 20-32.

[12] Laguerre, M., Lecomte, J. and Villeneuve, P. (2007) Evaluation of the Ability of Antioxidants to Counteract Lipid Oxidation: Existing Methods, New Trends and Challenges. *Progress in Lipid Research*, **46**, 244-282. https://doi.org/10.1016/j.plipres.2007.05.002

[13] Ren, F., Zheng, Y.-F., Liu, X.-M., Yang, Q.-Q., Zhang, Q. and Shen, F. (2015) Thermal Oxidation Reaction Process and Oxidation Kinetics of Abietic Acid. *RSC Advances*, **5**, 17123-17130. https://doi.org/10.1039/C4RA16791K

[14] Laurent, S. (2014) Développement et études de l'influence des procédés d'application et de réticulation de vernis acrylates photo-polymérisables (à 100% d'extrait sec).

[15] Karak, N. (2012) Vegetable Oils and Their Derivatives. In: Karak, N., Ed., *Vegetable Oil-Based Polymers*, Woodhead Publishing, Cambridge, Chapter 3, 54-95. https://doi.org/10.1533/9780857097149.54

[16] Tehfe, M.A. (2011) Etude de nouveaux systèmes amorceurs pour des polymérisations radicalaires ou cationiques.

[17] Haynes, W.M. (2015) CRC Handbook of Chemistry and Physics. 96th Edition, CRC Press, Boca Raton. https://doi.org/10.1201/b17118

[18] Falco, G. (2016) Huiles végétales époxydées et alcool furfurylique: Deux types de monomères pour l'élaboration de thermodurcissables et de composites biosourcés (Doctoral Dissertation, Côte d'Azur).

[19] Khellaf, S. (2018) Réticulation mécanisme réactionnel du polypropylène isotactique et du polypropylène isotactique reticule (Doctoral Dissertation).

[20] Matthäus, B. and Özcan, M.M. (2017) Fatty Acid Composition, Tocopherol and Sterol Contents in Linseed (*Linum usitatissimum* L.) Varieties. *Iranian Journal of Chemistry and Chemical Engineering* (*IJCCE*), **36**, 147-152.