CONTRIBUTIONS FOR EVALUATION CHARACTERISTICS PHYSICO-CHEMICAL OF SOME TYPES OF OILS

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Abstract: *The food industry is increasingly studying the oxidation of oils stability question the purpose of seeking ways to improve the physico-chemical parameters for increasing the oxidation stability of oils, because oils degraded hazardous to human health. Oil degradation occurs in the preparation of food but can occur in conditions of inadequate custodians, and transport. Most current research is headed if oil oxidation at high temperatures, which require testing times in laboratory conditions up to an hour. This study presents physical-chemical evaluations of oxidation in oils under laboratory conditions at lower temperatures up to 100 ° C, analysis of unfolding times having more than* up to 72 hours.

Keywords: *oxidation, acids, peroxides, saponificatin, storage*

Introduction

Degradation of the oil changes are: *autooxidation* resulting in temperatures below 100 ° C, *thermal polymerization*, which occurs at temperatures between 200-300 ° C, in the absence of air, *thermal oxidation*, which occurs at a temperature of 200 ° C in the presence of air.

Autooxidation lead to the formation of various byproducts, including products oxidation, cleavage, dehydration and polymerization of hidroperoxids trained in first stage autooxidation. Cyclic polymers are an important part of the oxidized material. Heating oil leads to important physical and chemical changes, the intensity of these changes is dependent on temperature, heating duration, type of oil (and thus the degree of unsaturation unsaturated fatty acids), predicts some catalysts (Cu, Fe), mode of heating (in the absence or this air and light). The heated oils accumulate unsaponified materials (peroxides, aldehydes, ketones, etc) Monomers cyclic, acyclic and cyclic dimers, trimer, cetoesters saturated and unsaturated, saturated and unsaturated monohydroxiesters, esters di-, trihydroxy. The ratio of these components is depending on the mode of heating.

In the case of thermal polymerization in the absence of air, the main reactions are type Diels-Alder (Banu, 1982). Are formed mainly dimer and trimer, but monomers or polymers tall. Thermal oxidation is more complex in terms of chemical reactions as occurring simultaneously two factors: heat and oxygen. It is thought that thermal oxidation of oils involving a chained reaction mechanism. Recent studies show the influence of thermal oxidation in the field of heat treatment of some biochemical parameters of oils (Avramiuc, 2008).

This paper aims to present research results, having as an objective phenomenon of oxidation of oils, above 100 ° C. This type of oxidation characterized stages of storage and transport of edible oils.

To extend the shelf life of oils using antioxidants and synergists, and sometimes vegetable oils are trnsformate in margarine by hydrogenation.

Antioxidants inhibit oxidation of fats in foods, by inhibiting the effects of oxygen, act and as a preservative (Gutt, S. and Gutt, Gh., 2006). The following vitamins have antioxidant effects: β :-carotene (carrots, broccoli), ascorbic acid (lemon, oranges), vitamin E or tocofenol (nuts, cereals), selenium (fish, garlic). Other important sources of antioxidants are green tea and berries. Recent studies show the effect of stabilizing the natural plant extracts on sunflower oil (Popovici, 2008).

In the category of substances synergistic remember: citric acid, the mixture of isopropyl citrate, phosphoric acid. Hydrogenation of vegetable oils is used for the manufacture of margarine and other vegetable fats. It is necessary to modify the melting temperature of the oil glycerides fluids additives double hydrogen bonds of unsaturated fatty acid radicals in triglycerides.

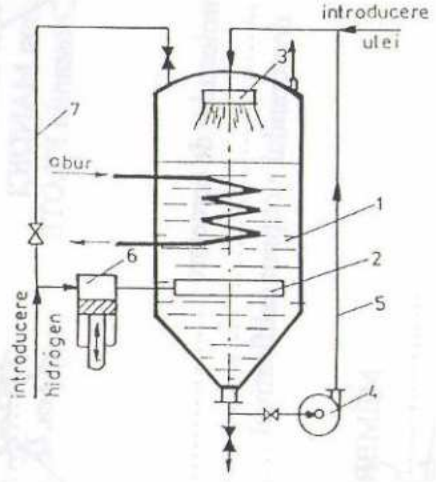


Figure 1 Istallation view bubbling and recycling for hydrogenation of oils:
1-vessel; 2-barbotor; 3-distributor of oil; 4-pump oil; 5-ecycling, oil circuit; 6-ompressors; 7-oreign circuit for hydrogen.

Figure 1 presents a facility for the hydrogenation of oils (Gutt, S., 2002). Fluid brought to the upper part of the installation is spread by the distributor 3. Hydrogen is fed to the bottom and liquid mass distributed by barbotor 2. Required pressure is achieved with bubling compressor 6.

At the beginning of 2004/2005 season vegetable oil prices have seen an upward trend due to low production and stocks of soya beans in the U.S., as well as sustained demand from importing countries (the seeds of the current economic crisis).

Table 1 Structure of production and export of edible (million tonnes)

	2002/2003		2003/2004		2004/2005	
	Prod.	Exp.	Prod.	Exp.	Prod.	Exp.
Total uleiuri comestibile	94,83	36,07	100,63	37,24	106,21	39,11
din care						
- de soia	30,31	9,17	30,26	9,04	32,80	9,90
- de palmier	27,26	19,67	28,67	20,26	29,46	20,78
- de floarea soarelui	8,22	2,29	9,15	2,42	8,85	2,24
- de rapita	12,04	0,90	14,17	1,28	14,91	1,23
- de masline	2,39	0,46	2,82	0,48	2,60	0,48

Soybean oil is the main range of the structure of edible oils, table 1. Brazil and Argentina have a share of 40% of production and about 80% of exports of soybean oil on the world market. China became the third producer of soybeans with a production of 4.97 million tonnes of vegetable oils (CAMIB, 2005).

Experiemental

Oxidation of oils, the theory chained reaction takes place in three stages: 1) *Initiation.* This stage is probably the induction period of oxidation of oils. At this stage the oil molecules are transformed into free fatty unstable radicals that can catalyze the formation of free radicals in the substrate.

$$\underset{\text{Oil moleccules}}{RH} \xrightarrow{\text{Initiators } (K_I)} \underset{\text{Radical free fatty}}{R\cdot + H\cdot}$$

Agency initiators of the process can be: light and especially ultraviolet UV radiation, heat, heavy metals (particularly Cu and Fe).

b) *Propagation*. Fatty free radicals, which formed the first stage, are combined with molecular oxygen (air) to form peroxide free radicals that can react with substrate to form free fatty and more radical and hidroperoxides:

$R\cdot + O_2 \xrightarrow{K_2} ROO\cdot$ (Peroxide free radical)

$ROO\cdot + RH \xrightarrow{K_3} ROOH$ (Hidroxide)

$ROOH \rightarrow RO\cdot + \cdot OH$

$\cdot OH + RH \rightarrow R\cdot + H_2O$ etc.

During the propagation phase, especially in the presence of catalysts, decomposition of hidroperoxides lead to aldehydes, ketones, acids, substances responsible for taste and smell rancid.

c) *Termination*. Ending chain reaction occurs when free radicals (autocatalizatorii) are inactivated or destroyed:

$R\cdot + R\cdot \rightarrow RR$

$R\cdot + ROO\cdot \rightarrow ROOH$ etc.

In choosing an antioxidant should keep in mind the following: *the potential antioxidant, solubility and antioxidant dispersability, change the color of the product, or alakalinity acid food, such as food processing and application of antioxidants.*

Aldehyde is subject to rancidity some physico-chemical factors. Oxidation increases as the speed doubles the number of molecules related unsaturated fatty acids is higher. In this area, three double bond fatty acids are oxidised to four times faster than those with one double bond.

Moreover, free fatty acids are oxidised by two times faster than their esters, the effect being due to the decomposition of carbonyl group hyperperoxids. High temperature enhances autooxidation through the activation of reactant molecules and the decomposition of hiperperoxids trained. Light accelerates autooxidation initiating the formation of free radicals, ultraviolet radiation (UV) is most active. Heavy metals, in particular the versatile of autooxidation increase speed by reducing the induction period, increasing to a maximum speed stage of initiation, propagation and termination of chain reactions and possibilities of branching chain reactions (Gutt, Gh., 2000). Oxidative enzymes and crude fat hurry autooxidation, raw or processed from seeds heated.

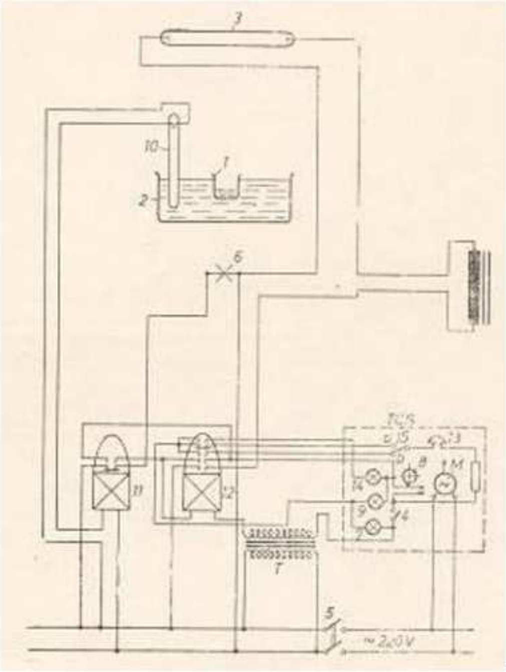


Figura 2. Device for determining the resistance to oxidation of oils

To conduct experiments we considered the conditions favorable for oxidation of oils in the stages of transport and storage, less provided on metal catalysts, because we considered that the oil is stored in plastic packs of PET (Gutt, S. and Gutt, Gh, 1992). Accordingly, for the experiments we used a plant for oxidation of oils with the principle scheme shown in Figure 2 (Sabău, 1979). The cup 1 containing the sample oil sits in the oil bath thermostat 2, irradiated with ultraviolet rays emitted by a mercury vapor lamp 3, with a power of about 400 W, arranged at a distance of 200 mm from the bottom of the cup 1.

Samples of oil were exposed the device between the hours of 9-19, for 3 days.

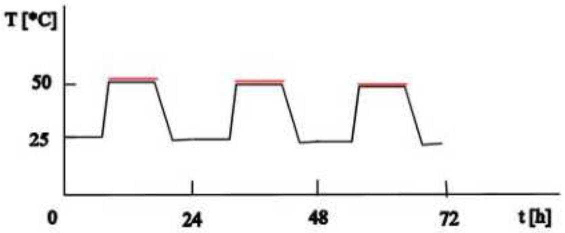


Figure 3 Chart of progress of the experiment

Moments that were performed tests are: t_0 = 0h, t_1 = 24h, t_2 = 48h, t_3 = 72h. These are moments semnificative to reproduce the diurnal and nocturnal variations of physico-chemical parameters during storage of oil, according to schedule in "saw tooth", Figure 3.

For samples of 200 ml were performed the following tests:

Acidity value determination

Metode description. Free acidity value shows acids localization in fatt. Natural fatt is neutral, but in this medium forming free acids when it is processing or has preserving.

The acids determinated by titration with KOH in alcholic solution

Acidity value is represented in mg KOH qantity which is necesary for neutralisation of free fatt in one gram of oil.

Both determination are for oils fott acids quality determination and they have a large utilization like control value in procesing technology. Between the acidity value (A.V.) and free acidity (FA) are the relation:

F.A. = 0,5041A.V. g oleic acid/100 g oil

For acidity value determination was used next formula:

$$AV = \frac{28 \cdot V \cdot f}{m} \text{ [mg KOH/g], where:}$$

V = solution volume of KOH used by titration (ml);
f = 0,8416: solution factor of KOH 0,5N;
m = sample quantity, in gram.

Saponification value determination

Metode description. Saponification value (index Köttostorfer) is determinated experimentaly, in same way reprezent KOH quantity in mg who is necessary for one gram of oil saponification and fatt acids neutralization.

For saponification value (SV) was used next formula:

$$SV = \frac{(V - V_1) \cdot 28{,}055 \cdot f}{m} \text{ [mg KOH/g],}$$

where:

V = 11,5 ml; solution volume by HCI 0,5N used by titration of referance sample, in ml;
V_1 = solution volume by HCI 0,5N used by titration of sample (ml);
f = 1,1476; solution factor by HCI 0,5N;
m = sample quantity, in gram.

Iodine value determination

Metode description. Iodine value represent iodine quantity which is absorbed by one gram of oil in conection with facts is double connexion which exist in fact acids components structure. The determination of iodine value is quite difficult because iodine has low reactivity and because the adition doesn´t have a cantitative way.

For iodine number was used next formula:

$$IV = \frac{(V - V_1) \cdot 0,01269 \cdot 100}{m} \quad [\text{g} \quad I_2/100\text{g}$$

sample],

where:

V =. 18ml; solution volume by 0.1 N sodium thiosulphate used by reference sample titration in ml;

V_1 = solution volume by 0.1 N sodium thiosulphate used by sample titration in ml;

0.01289 = quantity found in 1ml sodium iodine thiosulphate 0,1 N, g;

m = quantity of sample, g.I.

Peroxide value determination

Peroxide value means the quantity of peroxide which is found in food structure and has capacity to eliberate in one oxidative proces iodine by potasium iodine.

For peoxide value was used next formula:

$$PV = \frac{(V_1 - V_2) \cdot n}{g} \cdot 100 \ [\text{mEg/Kg oil}],$$

where:

V_1 = ml sodium tiosulfat used by sample titration;

V_2 = ml sodium tiosulfate used by referance sample titration;

g = quantity of sample, g;

n = solution normality.

Rezultats and discution

Table 2 Physico-chemical properties, at t_0 = 0h

Oil	IA [%]	IS [mg KOH/g]	II [g I/100g]	IP[meq/kg]
1.Sunflower	0,081	189	119	10
2.Corn	0,197	195	124	14
3.Olive	0,225	206	134	16

Table 3 Physico-chemical properties, at t_1 = 24 h

Oil	IA [%]	IS [mg KOH/g]	II [g I/100g]	IP[meq/kg]
1.Sunflower	0,5	190	121	10,2
2.Corn	2,5	253	152	15,1
3. Olive	1	244	148	18,3

Table 4 Physico-chemical properties, at t_2 = 48 h

Oil	Aciditate liberă	IS [mg KOH/g]	II [g I/100g]	IP[meq/kg]
1.Sunflower	0,6	193	124	10,5
2.Corn	3,2	295	167	16,3
3.Olive	1,1	281	159	19,2

Table 5 Physico-chemical properties, at t_3 = 72 h

Oil	IA [%]	IS [mg KOH/g]	II [g I/100g]	IP[meq/kg]
1.Sunflower	0,8	195	127	11
2.Corn	3,8	306	185	18,4
3.Olive	1,4	294	171	23,6

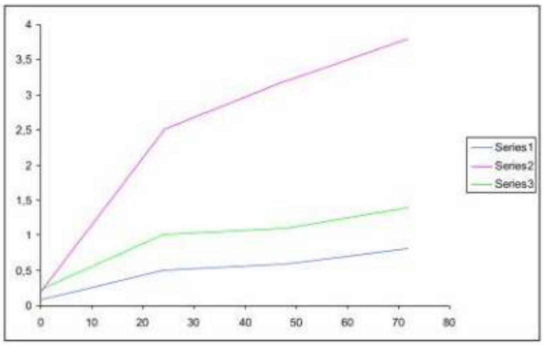


Figura 4 Variation of **IA** [mgKOH/G]

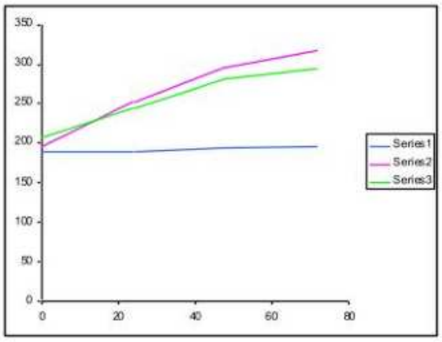


Figura 5 Variation of **SV**[mgKOH/G]

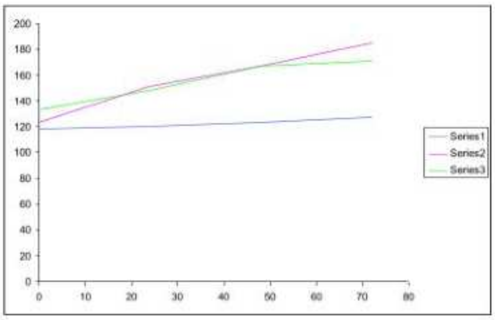


Figura 6 Variation of **IV** [g I_2/100g sample]

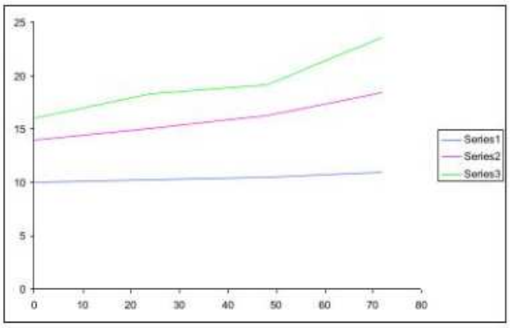


Figura 7 Variation of **PV** [mEg/Kg oil]

Following analysis of oil samples before the experiment t_0 = 0 h obtained results were shown in table 2.

Then tests were conducted at the time t_1 = 24 h, and the results are presented in table 3. The experiment continued with oil analysis at times t_3 = 48 h and 72 h, the results are presented in table 4 and respectively in table 5.

Index values acidity (IA) increased is present in all types of oil, as shown in Figure 4. Also, note that sunflower oil acidity index was within the acceptable limits: max 4% (STAS 12/1- 84).

As regards the saponification index (SV) is observed also increases the allowed limits (181-198 mg KOH / g) although the values are increasing, Figure 5.

Changes in iodine index (IV) for the three types of oils subjected to selfoxidation sample are shown in Figure 6. The values recorded are increasing without exceeding the allowed limits (119-135 g I/100g). About index peroxide can say that is an increase in the accepted limits (max 12 mEq / kg). Peroxide index variation is shown in Figure 7. Laboratory results can be used for storage and transportation phase of the oil.

Conclusions

Experiments show degradation of edible oil (sunflower, corn, olive) in conditions of inadequate storage. Chimical and physical parameters considered were: oxygen from the atmosphere through ventilation (O_2), light in particular ultraviolet radiation (UV) and excess temperature (50 ° C). Samples were analyzed at times: 0h, 24h, 48h, 72h. Was observed physico-chemical modification of oils analyzed as follows: free acidity growing, saponification value growing, and iodine colour increasing so, growing peroxide index.

This development is reflected in all types of edible oil under the experiment building an aseptic area for sterilizing air that's filled PET content in order to eliminate potential biological oxidizing agents, is another pursue cutting-edge technology, the plant is automated based on sensors of different types (Gutt, Gh , 2001).

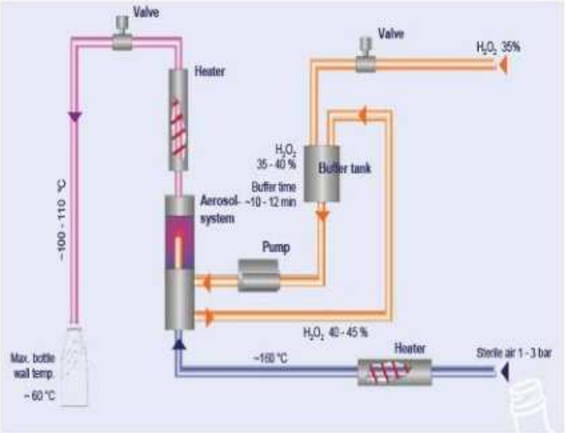


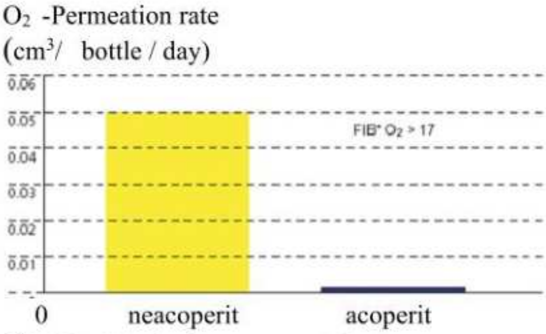
Figure 8 aseptic filling valve

Figure 8 shows an installation diagram of PET filling with air sterilization. The supply of empty bottles, clean and the car is by keeping the support ring of the bottle (the neck manipulation).

Aseptic area above the car is protected by a positive displacement of sterile air.

Aseptic filling valve is located in the top of the car. Only filling nozzles are within the aseptic area. SIP module is integrated for steam sterilization in aseptic valve assembly. A battery of sterile filters for sterile air is located above the car and connected to the SIP module for steam sterilization. H_2O_2 separate power unit is able to manage container storage including 4 x 65 l H_2O_2. Car transport chain is located outside the aseptic.

Diagram of Figure 9 shows the improvement in oxygen barrier bottle cover and reduce the amount of air (khsplasmax, 2009).



* FIB = Barrier improvement factor

Figure 9 Improved barrier-O2 by PLASMAX
(1 liter bottle with cold filling)

Corn oil **Sunflower oil** **Olive oil**

Figure 10 Packaging PET dark

An interesting option is the edible oil manufacturers use lemon juice as a natural antioxidant in olive oil in following proportions: 98% olive oil, natural lemon flavor 2% (Extra virgin olive oil and lemon product of Quattrociocchi). Note that were studied and other natural antioxidants (Popovici, 2008; Bipă, 2007), and attempt to edible oil fortification (Haritonov, 2006). The light serves to initiate the oxidation reaction. Ordinary producers of edible oil use dark PET packaging in order to block the penetration of ultraviolet radiation in the mass of oil (biomania, 2009). Examples are shown in Figure 10.

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