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THERMAL STABILITY OF COMMERCIAL VEGETABLE OILS IN AIR

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Abstract. *The studies carried out in this paper aim at describing certain edible oils by the thermal analysis under dynamic and isothermal conditions. For this purpose, we applied the thermal analysis (TG, DTG) and the evaluation of the thermogravimetric data obtained by using the STAR^e software. The results highlight a degradation which takes place in three or four stages, according to a complex mechanism, with different weight losses, depending on the type of oil. We established the thermal stability range for 8 types of edible oils, taking as criterion the temperature at which their thermal decomposition starts. The tests carried out under isothermal conditions, in the air, showed a better thermal stability for the extra virgin olive oil and for the pumpkin seed oil as compared to the sunflower oil found in stores.*

Keywords: thermal stability, vegetable oils, dynamic and isothermal conditions

1. Introduction

The vegetal oils are used in households in order to cook by different procedures, but also in the food industry as ingredient in a wide range of products [1]. Their use is preferred by the consumers as compared to the animal fats, as it is considered that they do not contain cholesterol and that they are rich in unsaturated fats [2]. Even though the main usage of the vegetal oils is in the food industry, because of the increase of the petrol price, researchers focus their attention on their use as industrial fluids, as they are obtained from renewable and ecologic sources [3]. Therefore, the vegetal oils are used more and more frequently in order to obtain eco-lubricants [4] and fuels (biodiesel) [5, 6]. Regardless of the field of use of the vegetal oils, it is important to know their thermal stability both under dynamic and isothermal conditions. The thermal (TG) and thermal differential (DTG) analyses are methods that researchers frequently use in order to analyze the thermal stability of different types of vegetal oils [7-16].

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In this paper, we aim at comparatively analyzing the thermal stability under dynamic and isothermal conditions for a range of eight vegetal oils. For some of them, respectively: the pumpkin seed oil, hazelnut oil, pistachio oil and saffron oil there aren't in the specialty literature studies regarding the thermal stability, neither under dynamic conditions, nor under isothermal conditions.

2. Materials and methods

The thermal analysis was carried out by means of a Mettler Toledo 851^e derivatograph in dynamic conditions, in the air with the flow of 20ml/min, with the heating rate of 10ºC/min, in the 25-700ºC temperature interval and sample mass between 2 and 5mg. The used device presents a temperature accuracy ±0.25 °C and a mass resolution of ±1μg. We considered as indicator of the thermal stability the temperature at which the thermal decomposition starts (T_{onset}).

The materials subject to the thermogravimetric analysis were eight edible oils bought from stores: extra virgin olive oil (sample 1), sunflower oil (sample 2), pumpkin seed oil (sample 3), hazelnut oil (sample 4), pistachio oil (sample 5), saffron oil (sample 6), nut oil (sample 7) and linseed oil (sample 8).

For the commercial edible oils, tests were carried out at constant temperature too (180ºC) by means of the same Mettler Toledo 851^e derivatograph. In this situation, we considered as an indicator of the thermal stability the weight loss percentage.

3. Results and discussion

The thermogravimetric (TG) and derivative thermogravimetric (DTG) curves obtained for the eight types of edible oils are presented in Figure 1. They provided information on the thermal stability of the analyzed edible oils. The main thermogravimetric characteristics obtained based on the thermogravimetric curves: T_{onset} – temperature at which the degradation starts; T_{peak} – temperature at which the degradation rate is maximum; T_{endset} – temperature at which the degradation process ends; W- the weight loss percentage and the residue quantity are presented in Table 1. The analysis of the obtained results show that the thermal degradation of the edible oils is almost completely performed, the resulted residue quantity being lower than 2.5%. We can notice in the DTG curves the existence of three or four degradation stages, according to the analyzed type of oil. In fact, according to the specialty literature, the first thermal decomposition stages are related to the content of polyunsaturated, monosaturated and saturated fat acids, which can be present in the composition of the vegetal oils [4, 8, 17]. The last decomposition stage which starts at temperatures of about 450°C is related to carbonaceous waste oils [4].

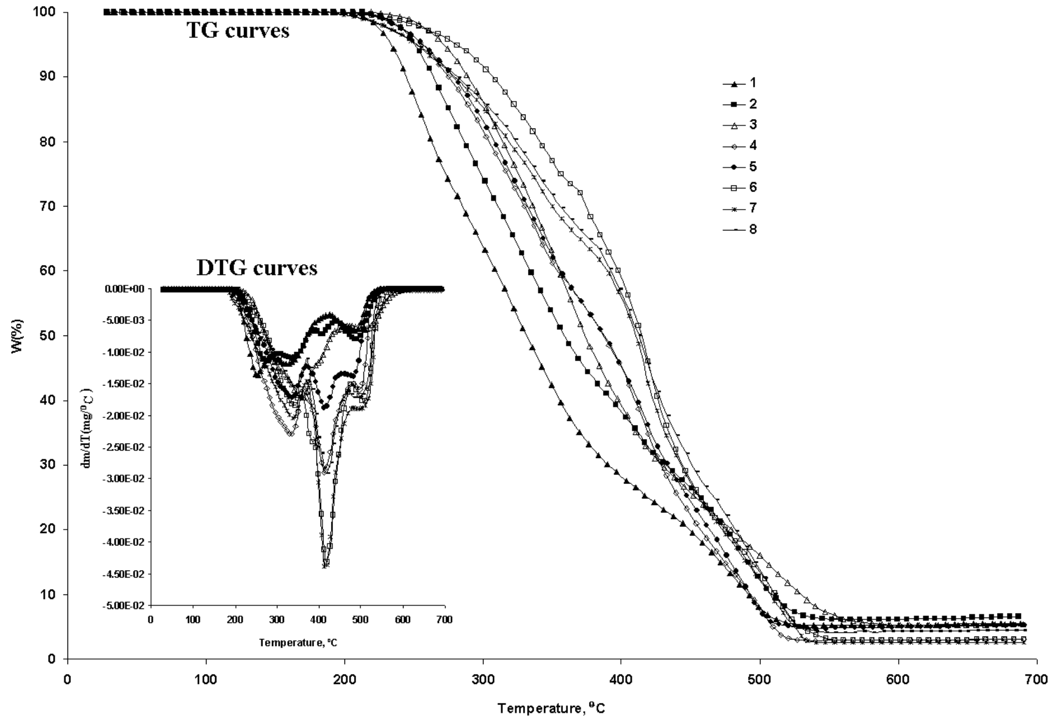

Fig. 1. TG and DTG curves of: **1**- extra virgin olive oil, **2**- sunflower oil, **3**- pumpkin seed oil, **4**- hazelnut oil, **5**- pistachio oil, **6**- saffron oil, **7**- nut oil and **8** – linseed oil

Considering as criterion of the thermostability the initial temperature at which the thermal degradation starts, we obtain the following series for the thermal stability:

$$1 < 7 < 8 < 5 < 2=4=6 < 3$$

The pumpkin seed oil (sample 3) has the best stability, so that the recordings are performed with the heating rate of 10°C/min, in air atmosphere, the temperature at which this type of oil starts to decompose being around the value of 263°C. We also notice that the sunflower oil has the same thermal stability as the hazelnut oil (sample 4) and the saffron oil (sample 6), the temperature at which these samples start to decompose in the mentioned conditions being of 245°C. The nut and the linseed oils (samples 7 and 8) decompose by a succession of three stages, starting from almost 230°C, and the pistachio one (sample 5) from 240°C. The lower thermal stability in dynamic conditions is the one of the extra virgin olive oil (sample 1), which starts its degradation from 220°C.

Table 1. Thermogravimetric characteristics of commercial vegetable oils

Sample	*Stage of thermal degradation*	T_{onset} (ºC)	T_{peak} (ºC)	T_{endset} (ºC)	*W* (%)	*Residue* (%)
1	I	220	252	266	36.44	2.07
	II	266	326	377	44.02	
	III	437	488	509	17.47	
2	I	245	272	322	37.13	2.41
	II	322	337	376	25.34	
	III	376	405	455	17.46	
	IV	455	490	522	17.66	
3	I	263	301	344	35.31	2.41
	II	344	360	378	20.66	
	III	378	402	443	21.13	
	IV	443	510	568	20.49	
4	I	245	367	353	43.05	1.07
	II	380	413	441	34.32	
	III	441	498	514	21.56	
5	I	240	341	361	47.23	2.24
	II	389	414	434	26.34	
	III	434	487	505	24.19	
6	I	245	342	370	28.13	1.02
	II	370	381	407	18.37	
	III	407	418	492	33.83	
	IV	492	511	543	18.65	
7	I	230	340	355	37.57	1.04
	II	398	415	445	33.57	
	III	445	504	533	27.82	
8	I	231	341	373	35.44	1.63
	II	387	415	443	38.97	
	III	472	497	525	23.96	

Considering the manner in which the cooking oils are used in the modern cuisines, we carried out thermal stability tests under isothermal conditions too. For all the types of oils, thermogravimetric curves were registered in the air, at a constant temperature (180°C), for 20 minutes. The obtained results are presented in Figure 2.

The analysis of the graphic representation in Figure 2 shows that the best thermal stability under isothermal conditions is the one of the following types of oils: the extra virgin olive oil (sample 1), the pumpkin seed oil (sample 3) and the pistachio oil (sample 5), for which the weight loss percentage is lower than 1%.

We can also notice weight losses lower than 2% for the sunflower oil (sample 2), respectively for the hazelnut oil (sample 4) and lower than 3% for the linseed oil (sample 8). The largest weight loss percentages appear in the case of the saffron oil (sample 6) and of the nut oil (sample 7).

For the extra virgin olive oil (sample 1), sunflower oil (sample 2) and the pumpkin seed oil (sample 3) we carried out thermal resistance and time resistance tests. Therefore, they were maintained for 20, 30, 40, respectively 50 minutes at a constant temperature (180°C). Figure 3 presents the variation of the weight loss percentage, according to the time. We can notice higher weight loss percentages for the sunflower oil found in stores (sample 2) than in case of the extra virgin olive oil (sample 1**)**, respectively of the pumpkin oil (sample 3). In case of the pumpkin seed oil (sample 3), the weight loss percentage increases if the maintenance time at a constant temperature (180°C) is higher than 45 min, even exceeding the obtained values for the sunflower oil in trade.

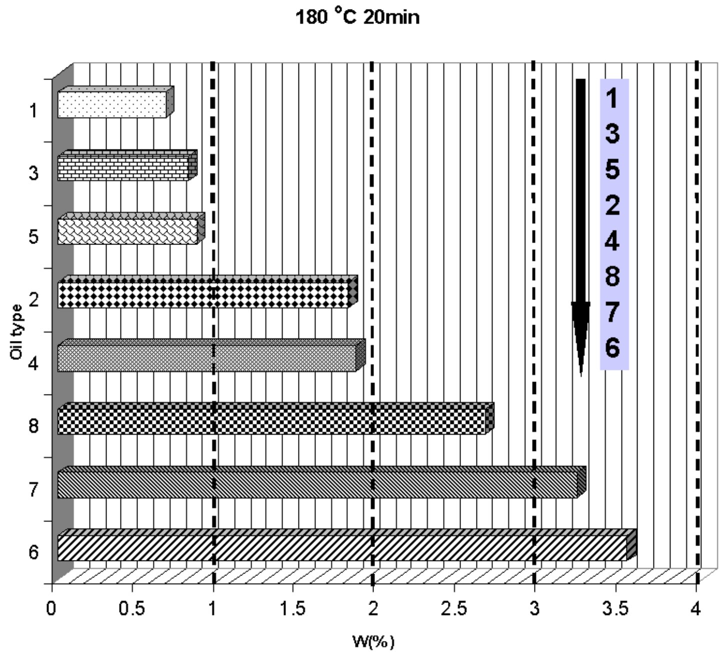

Fig. 2. The weight loss percentage for different types of oil maintained for 20 minutes at a constant temperature (180°C)

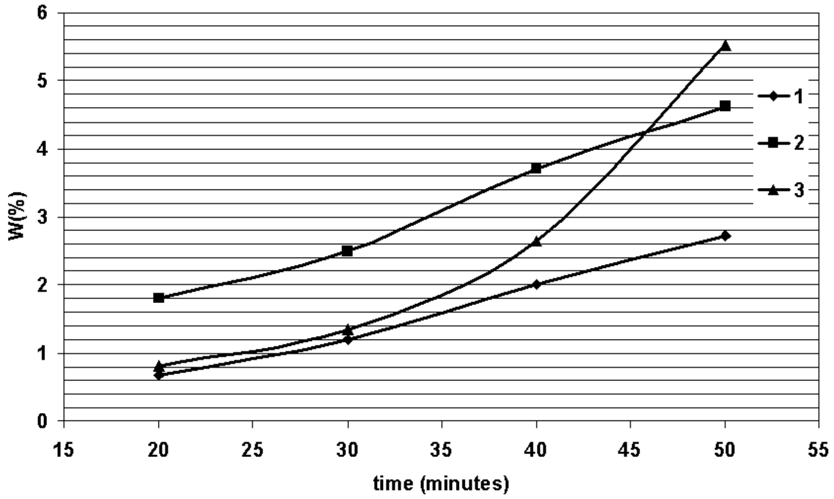

Fig. 3. Variation of the weight loss percentage with the duration of sample maintenance at a constant temperature (180°C)

The carried out study allowed the determination of the thermal stability series for 8 types of edible oils. The tests carried out under isothermal conditions, in the air, have shown a better thermal stability for the extra virgin olive oil and for the pumpkin seed oil (up to 45 minutes only) as compared to the sunflower oil in trade. We can sum up that when the roasting period of the food is longer, it is preferable to use extra virgin olive oil, resulted in compliance with the aspects established in their studies by other researchers too [7]. Even though it has an initial decomposition temperature in the air (dynamic conditions) lower by almost 20°C than the sunflower oil one, under isothermal conditions (180°C), this oil is more stable.

Conclusions

After the thermogravimetric analysis study carried out for different types of edible oils we obtained important information regarding their thermostability.

Considering as criterion of the thermostability the initial temperature at which the thermal degradation starts, we obtained the following series: $1 < 7 < 8 < 5 < 2=4=6 < 3$.

The tests carried out in isothermal conditions, in the air, have shown a better thermal stability for the extra virgin olive oil and for the pumpkin seed oil (up to 45 minutes only) as compared to the sunflower oil in trade. We can sum up that when the roasting period of the food is longer, it is preferable to use extra virgin olive oil.

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