Analysis of raw and refined sunflower oil from Macedonia

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ABSTRACT

Following writing is analysis of raw and refined sunflower oil, produced in a food factory "Blagoj Djorev" in Veles, Republic of Macedonia. To determine whether refining is well done and good quality is obtained, analyzed were certain parameters like: moisture and volatile matter, sediment and insoluble substances, soaps, phosphatide and specific weight. In analyzed oil determined are: iodine, peroxide, acid and saponification value. The percentage of sediment and the relative density of the oil are also determined. The refined oil does not contain mechanical impurities and sediment which are removed with processes of degumming, neutralization and filtration. Presence of moisture and volatile substances in sunflower oil is also determined. The analyses showed that with refining, completely removed are: moisture, volatile matters, sediment and insoluble substances which were present in raw oil. The phosphatides in raw oil are 200 mg/kg and after refining 0 mg/kg, which means that during refining process they are completely removed.
There are major differences in acid value. Acid value in the raw oil is 2.26 g / kg, while in the refined oil it is only 0.15 g/kg. Presence of soaps and saponification value in refined oil were also analysed. The results show that analysed refined sunflower oil is produced with cutting edge technology, excellent stability and the quality is preserved.

Keywords: raw oil; refined oil; sunflower oil; analysis;

INTRODUCTION

Sunflower (*Helianthus annuus L.*,) is the most important resource for oil production, originating from North America and is one of four the most important oilseeds in the world. It was brought in Europe at the beginning of 16th century as a decoration plant. In 1716, sunflower was patented as resource for oil production in England (Dimić, 2005). Science development and its hybrid creation have increased the seed production and the quality of this kind of oil. In the beginning of the first half of 20th century, the sunflower was cultivated on large areas and was used as food oil.
Today the commercial hybrid can contain up to 50 % oil. The sunflower is cultivated on area of 14, 5 million hectares. The largest manufactures of sunflower are Russia, Ukraine, Argentina, combined with Europe Union and South Africa.
The largest part, from 40-60 % of the oil is found in the seed (% dry matter), kernel 50-70 % and shell 2, 5-4, 5 %. However, the percentage depends of hybrid type location, condition and the way of cultivation (Balalić et al., 2008).
The sunflower oil is valued because of its pleasant sensory characteristic and high quantity of vitamin E (Dimić, 2005) and tocopherol (Tasan et.al 2005). The most dominated fatty acids in sunflower oil are: linoleic, oleic, stearic and palmitic acid (Dimić, 2000). Sunflower oil is widely used in nutrition as a source of essential linoleic (9-cis, 12-cisoctadecadienoic) acid (Poiana, 2012).

In this paper, we have analyzed the sunflower oil "Kristal", manufactured by food industry "Blagoj Gjorev" in Veles, Macedonia which is produced with cutting edge technology of classic alkaline refining of raw oil. This raw oil is obtained from high quality seed grown on Macedonian fields.
The technology for obtaining raw oil includes technological process starting with acceptance of raw material until its house storage. The technological scheme for obtaining raw and refining oil is shown on figure 1.

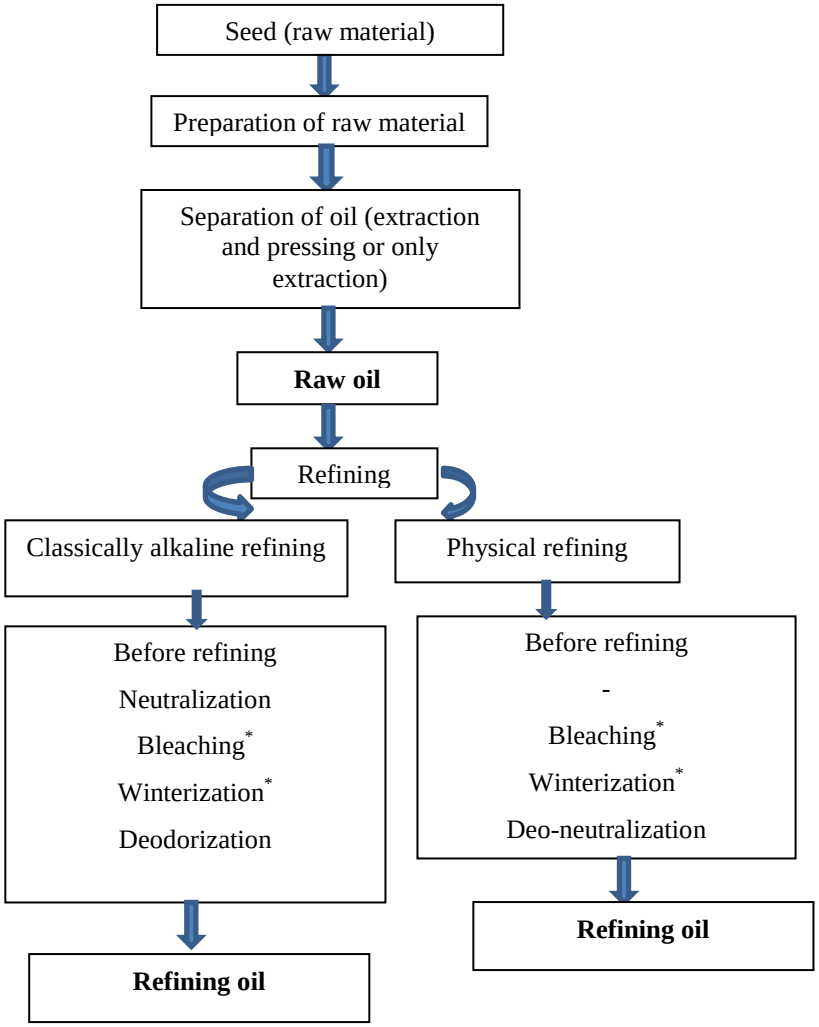

Fig.1. Technological scheme of obtaining raw and refined oil (Dimić et al., 2003, a)

*These phases of refining are applied when necessary depending on the type and quality of raw oil

MATERIALS & METHODS

We have analyzed raw sunflower oil, stored in vertical cylindrical storage tanks. From the tanks taken were three samples, from “top", "middle" and "bottom “of the tank. Sampling is done in accordance to JUS E.K8.020/1991 standard and all samples were homogenized.
The analyzed oil is refined oil "Kristal" produced by food industry "Blagoj Gjorev" AD Veles with classical alkaline refining process. In this process continuous neutralization is applied. Bleaching and winterization on raw oil, was not done, due to the type and quality of raw oil. The deodorization applied in this food industry is done with semi continuous process.

In order to determine the quality of refined sunflower oil, analyzed are the following parameters: moisture and volatile matter, sediment and insoluble substances, soaps, phosphatide, acid value, iodine value, saponification value, peroxide value and specific weight.

For determination of moisture and volatile matter in the oil following methods are used ISO 662: 1987 and JUS E.K8.024.

Insoluble substances in oil are determined with the standard method JUS ISO 663:1993 and petroleum ether is used as a solvent.
In classical alkaline refining of oils, free fatty acids are removed by using NaOH, in the form of soluble soaps, Na-oleate. Determination of the soap was made with the method of Wolff.
Phosphatides are determined on the basis of phosphorus, which originated from the esters bond of phosphoric acid linked to their composition. The content of phosphatides is obtained by calculation i.e. by multiplying the amount of phosphorus in a percentage whit conversion factor (Chapman et al., 1980).
One of the parameters for monitoring the quality of raw and refined oil is acid value, or determination of free fatty acids and that value is law regulated. For determinations of acid value is used method ISO 660: 1983, JUS E.K8.026 1991.
Parameters which are specific to the identification of oils are: iodine value, specific weight and saponification value (Dimić et al., 2003, b).
The specific weight of oil is determined with the method ISO 6883:1995, JUS E. KB.022/1991.
Iodine value is an important characteristic of the oil because it indicates its unsaturation i.e. the presence of double bonds of fatty acids in the triglyceride molecule (Hamilton et al., 1986). Iodine value of raw and refined oil is analyzed with the method ISO 3961: 1989, JUS E.K8. 027 1991.
Saponification value is determined with the method JUS E. K8.028/1991.
Occurrence of oil oxidation and creating peroxides are monitored through peroxide value. In raw oils peroxide value, as a measure of quality, is not limited by legislation and therefore does not analyze (Official Journal of Macedonia. 2012). Peroxide value of raw and refined oil is determined by the standard method ISO 3960: 1998, JUS E.K8.034/1991

RESULTS & DISCUSSION

The results for the analyzed parameters of raw and refined sunflower oil are presented in Table 1.
The contents of moisture (water) and volatile substances is an important indicator of the quality of raw and refined oil (Hamilton, 1986). The presence of water may result in hydrolytic changes with increasing acidity i.e. content of free fatty acids and reduce the quality of the oil (Dimić, Turkulov, 2000). Moisture and volatile substances in raw oil are 0.6%, while in the refined oil is 0% because oil deodorization is done on 230°C, all volatile substances, including moisture are removed (Saba et al., 2014).

Table 1. Analysis of raw and refined sunflower oil

Parameters	Raw sunflower oil	Refined sunflower oil	Refined sunflower oil according to a Rulebook of Macedonia
Moisture and volatile matter (%)	0,6	0	max 0,2
Sediment and insoluble substances (%)	0,2	0	/
Soaps (mg/kg)	/	10	max 50
Phosphatide (mg/kg)	200	0	/
Acid value (g/kg)	2,26	0,15	max 0,3
Iodine value	128	130	118-141
Saponification value (mg KOH/g)	190	190	188-194
Peroxide value (mmol O_2/kg)	/	1	max 5
Specific weight (g/ml) (ºC/20)	0,925	0,921	0,918 -0,923

In raw oil, sediment and insoluble substances are 0.2%. They can originate from mechanical impurities in the raw material or equipment and machinery for processing raw material, dust in raw

material in the form of sand or soil and various products of chemical reactions that take place in oil and raw material itself (Dimić, Turkulov, 2000).

According to the Rulebook of the quality of vegetable oils in the RM in refined oil it is not allowed any presence of sediment and insoluble substances (Official Journal of Macedonia. 2012). After conducting refining, sediment and insoluble substances are completely removed from the analyzed oil and amount is 0%. The overall amount of sediment and mechanical impurities are removed during the refining processes by bleaching, neutralization and filtration (Reddy et al., 2001).

During the classical alkaline refining, free fatty acids from the raw oil are removed using a base NaOH, in the form of soaps that are soluble in water (Dimić, Turkulov, 2000). Refined oil that is released for sale under Rulebook of quality for vegetable oils should contain a maximum up to 50 mg/kg soaps. The resulting value of 10 mg/kg soap in refined sunflower oil showed in table 1 meets the criteria for quality oil. Soaps in raw oil are not determined, because soaps are crated during neutralization process of refined oil.

Phospholipids, as an important indicator of quality, appear only in raw oils. For refined oils they are not significant, because they completely removed during refining. During the processing of sunflower seed by extraction and extrusion, under the influence of heat, moisture or solvent, phosphatides converted into oil (Dimić, Turkulov, 2000). Their content depends on the amount of phospholipids in seeds, the level of maturity and storage conditions of the seeds and the method of technological separation of oil. Phosphates are removed during the process of neutralization and bleaching and quality refined oil should not contain any phosphates. Our analysis of raw and refined oil showed that phosphatides of 200 mg / kg in raw oil are completely removed during refining and refined oil amount to 0 mg/kg.

Acid value is an important parameter for determining the quality of refined oil. In the process of neutralization and deodorization of oil, a substantial part of the free fatty acids present in the oil is removed. The results presented in table 1 show that there is a substantial neutralization of free fatty acids from 2,26 g / kg in raw oil to 0,15 g/kg in refined oil.

Iodine value depends on the nature of the oil, and hybrid variety of the raw material from which oil is extracted, the climate, soil quality, etc. (Karlović, Andrić, 1996). According to the Rulebook on the quality of vegetable oils RM, value of iodine value of refined sunflower oil ranges from 118-141. Iodine value of the analyzed raw sunflower oil is 128 and analyzed for refined sunflower oil is 130, which means that these values are in the allowed limits.

Saponification value is usually a characteristic of raw oil and its value depends on the composition of fatty acids in the oil and the chain length of the fatty acids in the triglyceride molecule. Saponification value in refined sunflower oil under Rulebook of quality vegetable oils should range from 188-194. As seen in table, the resulting value of 190 for saponification number as identification parameter, shows that the sunflower oil is in allowable limits.

Peroxide value is characteristic parameter and uses as indicators for the primary oxidation of sunflower oil. Hydroperoxides are the primary products of lipid oxidation. They are odorless and colorless, but are labile species that can undergo both enzymatic and non-enzymatic degradation to produce a complex array of secondary products. Determination of peroxide value can be used as oxidation index for the early stages of lipid oxidation (Talal et. al., 2013; Rehab, 2010; Zhang, 2010). According to the Rulebook of Macedonia the peroxide value higher than 5 mmol O_2 / kg are considered as an unacceptable. From the resulting value for peroxide value 1 mmol O_2 / kg shown in table 1 it can be concluded that the oxidation has not happen or an adulteration of the oil, meaning there are no peroxides as the primary product of oxidation, which means that this refined oil is acceptable for use.

Table 1 show that there is a difference in the density of the analyzed raw and refined sunflower oil. Refined oil is rarely with a specific weight 0,921 g/ml, and the specific weight of raw oil is 0,925 g/ml. The difference in specific weight is because with refining of oil, disposed substances which are part of raw oil such as mucous substances, phosphates, waxes, moisture and volatile solids, sediment and mechanical impurities, some pigments and saturated triglycerides are removed.

CONCLUSION

Sunflower oil from “Blagoj Gjorev” AD Veles, Macedonia is analyzed before and after refining. In order to conclude whether refining is quality made and whether the resulting oil is within quality frame, we have analyzed certain parameters. The oil before refining is called “raw” and after refining is called “refined”. Raw sunflower oil contains a small amount of moisture and volatile matter (0.6%) and a small amount of sediment and insoluble substances (0.2%) which are completely removed during the process of refining oil. Soaps which are created during neutralization are present in refined oil with10 mg/kg, which amount is allowed so the refined oil the quality criteria. The phosphatides and acid number has largest change in value during refining process. Phosphatides found in the raw oil are 200 mg /kg, and they are completely removed with neutralization and bleaching. Acid value or free fatty acids in raw oil is present in a high concentration of 2,26 g/kg and in the refined oil only 0,15 g/kg, as a result of good refining process. The iodine and saponification value of raw and refined oil is not much different and is in accordance with the Rulebook of the quality of vegetable oils in RM. The low value for peroxide number of refined oil 1 mmol O_2/kg shows that refined oil has high stability, there is no auto-oxidation and no peroxide is produced. The lower value of the density of refined oil compared with raw oil is result of removing substances that are part of raw oil. All analyzed parameters are within the limits in the Rulebook for quality of vegetable oils in Macedonia. Obtained refined sunflower oil is produced using cutting edge technology and it has excellent stability and quality preserved.

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