DOI 10.7251/JEPM1901024D
UDC 664.34>549.67

Journal of
Engineering & Processing
Management

ORIGINAL SCIENTIFIC PAPER

Removing Products of Thermal Degradation from Edible Oils by Zeolite and by Clinoptilolite - Comparison of Results

Sanja Dobrnjac[1] | Ljubica Vasiljević[2] | Stevan Blagojević[3] | Miladin Gligorić[2] | Zoran Obrenović[4] | Vesna Cvijetinović[2] | Dragan Tošković[2]

[1]Krebs+Kiefer Eastern Europe, Trg Republike Srpske 1, 78 000 Banja Luka, Bosnia and Herzegovina
[2]University of East Sarajevo, Faculty of Technology, Karakaj, 75400 Zvornik, Bosnia and Herzegovina
[3]Institute of General and Physical Chemistry, Studentski trg 12, 11000 Belgrade, Serbia
[4]Alumina Ltd, Karakaj, 75400 Zvornik, Bosnia and Herzegovina

Corresponding Author:
Sanja Dobrnjac, Krebs+Kiefer Eastern Europe, Trg Republike Srpske, Banja Luka, Bosnia and Herzegovina

Email: sanjadob@gmail.com

Keywords:
edible oil, free fatty acids, acid number, peroxide number, adsorbent

Abstract
When edible oils are heated above 150°C, they undergo thermo-oxidative changes depending on a variety of factors, such as temperature, heating time, type of oil, etc. These changes cause a series of chemical reactions (hydrolysis, oxidation, polymerization, etc.) resulting in the formation of free fatty acids, an increase in the peroxide number and the acid number, a change of color and a decrease in the iodine number. This study investigates changes of the content of free fatty acids, the acid number, and the peroxide number in edible sunflower oil when heating at the temperature range from 110°C to 190°C for 30 minutes, as well as after the adsorption by a natural and a synthetic adsorbent (clinoptilolite and zeolite 4A). The results of the research show that these adsorbents are effective in removing the products of chemical reactions occurring in thermal degradation, which is particularly evident after the adsorption of oil heated at 190°C. Somewhat better results were achieved after the adsorption using clinoptilolite, with a 72 % reduction in the content of free fatty acids, 83 % reduction in the acid number, and 43 % reduction in the peroxide number. After the adsorption by zeolite 4A, the content of free fatty acids was reduced by 65%, the acid number by 76 %, and the peroxide number by 39 %. The results obtained open the possibilities of further research aiming at discovering the adsorbents which would be most suitable for the regeneration of used edible oils, after which they could be applied safely for different purposes.

1. INTRODUCTION

Edible oils and fats belong to a group of compounds of lipids and organic materials of different chemical compositions. They are insoluble in water, but soluble in organic solvents (diethyl ether, hexane, benzene, chloroform, methanol). Oils and fats consist most commonly of triglycerides and triacylglycerols which are esters of trihydroxy alcohol glycerol and fatty acids.Vegetable oils contain a higher proportion of unsaturated fatty acids and, therefore, unlike fats, are liquid at room temperature. Edible vegetable oils are products with a limited shelf life. Due to various enzymatic and microbial processes, as well as chemical reactions, they undergo undesirable changes very quickly, which results in spoilage. The processes causing spoilage depend on the type and quality of oils, as well as their storage conditions. Oil spoilage leads to the formation of compounds which have negative effects on the organoleptic properties and reduce the nutritive value of oil due to the loss of biologically active substances (essential fatty acids, pro-vitamins, vitamins, etc.) and the formation of harmful substances (peroxides and polymers). Spoilage results in degradable products (particularly volatile carbonyl compounds and lower molecular fatty acids) giving the oil its unpleasant smell and taste. Certain degradable products can also cause health risks (peroxides, polymers, malondialdehydes), so these lipids are used for industrial purposes only (Čorbo, 2008).

Chemical processes causing spoilage of vegetable oils are the following:

- autoxidation,
- thermal oxidative changes,
- reversion.

This paper investigates thermal oxidative changes in oil and the possibility of removing products of thermal degradation by natural and synthetic zeolite. At higher temperature (above 150°C) oxidation of oil accelerates abruptly. After a certain period of heating, apart from the products of oxidation (hydroperoxides and their degradable products), thermal oxidation products are also formed: cyclic fatty acids, dimers and polymers of fatty acids and triglycerides, oxypolymers and other volatile and nonvolatile compounds (Choe and Min, 2007) (Wonglamom and Rakariyatham, 2014).

Since food is fried at the temperatures between 170°C and 180°C, the oil used must undergo certain physical and chemical changes. Heating of oil leads to an increase in viscosity, in the refractive index and specific weight, an increase in the content of free fatty acids, saponification number, an increase in the peroxide number, and a decrease in the iodine number. Therefore, the increase in the content of free fatty acids (FFA) and the peroxide number (PN) can be taken as a measure of the degree of degradation of edible oils (Rossell, 2001).

The acid number is a measure of the degree of hydrolysis. It is defined as the number of milligrams of KOH required to neutralize free fatty acids in 1g of oil or to neutralize 1g of fatty acids. The acidity of fats is often expressed as the percentage of free fatty acids. The higher the content of free fatty acids (FFA), the lower the quality of oil and degradation processes are the more intensive and inversely proportional to the content of all other components which make up for the quality of oil (aromatic compounds, vitamins, polyphenols, etc.), as well as its nutritional value. The content of FFA depends on the preparation method, the quality of raw materials and storage conditions. Freshly prepared refined oils have a low content of free fatty acids; with the passing of time and use, the content of FFA increases due to oil hydrolysis (degradation of oil) together with the formation of higher fatty acids as components of esters of higher fatty acids. According to the Regulations for edible vegetable oils, edible vegetable fats and mayonnaise, the content of free fatty acids in edible vegetable oils must not exceed 0.3% (expressed as oleic acid) (Pravilnik, 2011).

Peroxide number (PN) refers to the level of primary oxidation of fatty acids and indicates the quantity of hydroperoxides as primary products of autoxidation, expressed in mmol of O_2 per 1kg. Peroxide number depends largely on storage conditions. Oxidation of fats is one of the fundamental reactions affecting health safety of triglycerides, due to the fact that the products of oxidation are hazardous. The commonest form of oil and fat spoilage is the unpleasant taste and smell, or rancidity, which is most often caused by oxidation. Primary products of oxidation are hydroperoxides and peroxides, and their presence is primarily identified by calculating the peroxide number. Considering the fact that peroxides are at the same time precursors for secondary products of oxidation, they are very important indicators of oil quality and durability. Consequently, determination of the peroxide number in oils and fats is a standard procedure of quality control. According to the Regulations, the peroxide number in edible refined oils must not exceed 7mmol of O_2 per 1kg of oil. The peroxide number of a high-quality edible oil immediately after deodorization is 0, and usually remains very low in normal storage conditions. Peroxide number is also widely applied in determining the efficiency of various antioxidants, as well as in rapid tests for determining oil durability. Apart from that, it is often used for determining the overall oxidative conditions or the "oxidative history" of oils (Dimić and Turkulov, 2000).

Adsorption is being used increasingly as an efficient surface method for removing undesirable substances from oils and improving the quality of used heated edible oil (Vasiljević et al., 2017). In this respect, modern research, technology and industry are particularly focused on the possibilities of using zeolites as adsorbents. Zeolites have significant adsorption properties and are therefore increasingly used as surface-active materials to remove dissolved, mainly organic materials. The process uses adsorption as a very simple and efficient method (Penavin Škundrić et al., 1979) (Levi, 2010.) (Penavin Škundrić et al., 2005).

Zeolites are important aluminosilicates widely used in agriculture, industry, environment protection, etc. due to their complex properties. They are used in horticulture for retaining soil moisture, in pharmacology, as components of cosmetic products, odor control products, as mineral fillers, products for air purification and ion exchange in water preparation processes. They are also used as adsorbents in petrochemical industry, at radioactive waste landfills, for removing oil from water surfaces, in water treatment processes, etc. (Armbruster, 2001). Zeolites are classified as natural and synthetic, the most significant being those of type A, then faujasites and a series of zeolites with a low content of aluminum. They are similar to argillaceous minerals in structure, but their main advantage is that they do not affect the environment. They have a large active (specific) surface and are able to bind dispersed impurities in the process of flocculation (Grim, 1962). Physicochemical characterization of adsorbents involves a complex application of complementary methods, all of which enable insight into one aspect of the problem. The data obtained in this manner on the specific surface area, total porosity and porous structure help to understand the adsorption capacity, adsorption energy, surface density and distribution of active centers, the connection between the change in texture and adsorbent activity, etc. (Bošković, 2007). The texture of the adsorbent is defined as a network of channels, cracks and pores formed by the distribution of mutually connected primary and secondary particles with varying sizes and shapes, with empty spaces between the junctions. Adsorbent texture is defined by the following parameters: specific surface area, porosity, pore shape, the proportion of pores of specific size in total pores (pore diameter distribution), mean pore size, pore size distribution, and the shape and size of pore agglomerates (Putanov, 1995) (Dobrnjac et al., 2018).

2. MATERIAL AND METHODS

The sample used in the investigation was sunflower oil from the market of Bosnia and Herzegovina. Adsorption was carried out using the natural zeolite adsorbent called clinoptilolite, the white tuff from the area of Novakovići (Republic of Srpska, Bosnia and Herzegovina), and a synthetic zeolite 4A manufactured at "Alumina" ltd. Zvornik (Republic of Srpska, Bosnia and Herzegovina). The following methods and instruments were used for the characterization and identification of clinoptilolite and zeolite 4A:

- Particle size and mean diameter ($D_s50\%$), calculated using the laser BA Instruments "MicroSizer-201S" in the measuring range of 0-50 µm for 30 seconds at ultrasound intensity of 50W;
- Ion exchange capacity was determined by means of the ion selective electrode Ca^{2+}, on the pH ion meter Orion Aolus 720A$^+$ device.
- The specific surface area data (directly related to the structure of the adsorbent) were obtained by means of low-temperature nitrogen adsorption (BET method) using the Micromeritics, Flowsorb II 2300;
- Degree of crystallinity (XRD) was calculated using the X-ray diffractometer, PHILIPS, PW1710 with Cu anticathodes (40 V, 50 mA, K_α = 0,154056 µm). The samples were recorded in the region of 2θ from 5 to 40°; the results were analyzed using the automated diffraction software (PC–APD) and ICDD/JCPDS PDF-2 database;
- Particle morphology analysis was conducted using the scanning electron microscope (SEM) JEOL JSM 6460LV, the samples were prepared on the BAL – TEC, SCD 005 Sputer Coaltar.

2.1. Determination of FFA content and AN in edible oil

The content of FFA was determined by the method of alkalimetric titration, which is based on the principles of neutralization, and is the most suitable method for oils that are not dyed. In this case, FFA react with the alkali and produce soaps. The consumption of the alkali solution is directly proportional to the amount of FFA.

$$CH_3(CH_2)_{16}COOH + NaOH \rightarrow CH_3(CH_2)_{16}COONa + H_2O$$

stearic acid + alkali → soap (sodium stearate) + water

Acid number, expressed as the number of mg of KOH per 1g of oil, is calculated using the following formula:

$$\text{AN (mgKOH/g)} = \frac{56{,}1 \cdot V \cdot c}{m}\text{, where:}$$

- V – volume of consumed standard volumetric solution of KOH, in milliliters,
- c – accurate concentration of consumed standard volumetric solution of KOH, in mol/L,
- m – mass of the sample, in grams.

Acidity, expressed as the percentage of mass, is calculated from the results obtained in determining the acid number using the following formula:

$$\text{Acidity } (\%\text{ oleic acid}) = \frac{V \cdot c \cdot M}{10 \cdot m}\text{, where:}$$

- V – volume of the consumed standard volumetric solution of KOH, in milliliters,
- c - accurate concentration of consumed standard volumetric solution of KOH, in mol/L
- M – molar mass of the acid used for the representation of results,
- m - mass of of the sample, in grams

2.2. Determination of PN in edible oil

The peroxide number, or the content of hydroperoxides and peroxides in lipids, is mostly calculated using the method of iodometric titration, suggested originally by C.H. Lea. The method is based on the reaction between hydroperoxides or peroxides from oil and hydroiodic acid, liberated from potassium iodide in an acidic environment. The product of this reaction is liberated elementary iodine (Dimić and Turkulov, 2000). The peroxide value expressed as mmol/kg, is calculated using the following formula:

$$\text{PV (mmol/kg)} = \frac{(V_1 - V_0)\cdot c}{m}\cdot 500\text{, where:}$$

- V_1 – volume of the consumed sodium thiosulfate ($Na_2S_2O_3$) solution for sample titration, in milliliters,
- V_0 – volume of the consumed sodium thiosulfate ($Na_2S_2O_3$) solution for blank titration, in milliliters,
- c - molar concentration of the sodium thiosulfate ($Na_2S_2O_3$) solution, in mol/L,
- *m* - mass of the sample, in grams.

2.3. Heating of edible oil

After determining the initial reference content of FFA in oil, different samples of oil are heated in a sand bath at 110°C, 130°C, 150°C, 170°C and 190°C for 30 minutes. The FFA content, AN and PN were determined to reveal the influence of temperature. After determining the initial reference content of FFA in oil, different samples of oil are heated in a sand bath at 110°C, 130°C, 150°C, 170°C and 190°C for 30 minutes. The FFA content, AN and PN were determined to reveal the influence of temperature.

2.4. Adsorption by zeolite 4A and clinoptilolite

After heating, the oil was adsorbed by zeolite 4A and clinoptilolite under equal conditions. Adsorption was performed under the following conditions: 50g of oil sample and 1g of the adsorbents at room temperature (24°C), stirring at 500 rpm for 60 minutes. The adsorbents were separated from the adsorbate by centrifugation and filtration. The FFA content, AN and PN were determined in the filtrate of all the samples after adsorption. The tests were performed in the laboratory of the Institute for General and Physical Chemistry, Belgrade.

3. RESULTS AND DISCUSSION

The analyses of zeolite 4A and clinoptilolite involved the determination of the ion–exchange capacity, specific surface area, relative crystallinity and mean particle diameter. The results of the analyses are given in Table 1.

The X-ray diffractograms reveal the relative crystallinity of 98.90% for zeolite 4A and 48.24% for clinoptilolite, compared to the standard value. Correspondingly, the ion-exchange capacity is 158 mg of CaO/ g for zeolite 4A and 64 mg of CaO/g for clinoptilolite. The SEM analysis of the zeolite 4A sample indicates a large number of regular crystals (Figure 1), whereas the sample of clinoptilolite (Figure 2) is hypocrystalline, partly cavernous and porous.

3.1. Content of Free Fatty Acids - FFA

The analysis the FFA content in refined sunflower oil sample before heating shows that FFA content was 0.04%, expressed as oleic acid.

Table 1. Physio-chemical properties of zeolite 4A and clinoptilolite

Adsorbent	Ion-exchange capacity mg CaO g^{-1}	Specific surface m^2 g^{-1}	Oil adsorption cm^3 g^{-1}	Relative crystallinity %	Mean particle diameter D_s50%, μm
Zeolite 4A	158	2.52	0.65	98.90	4.30
Clinoptilolite	64	22.73	1.20	48.24	4.77

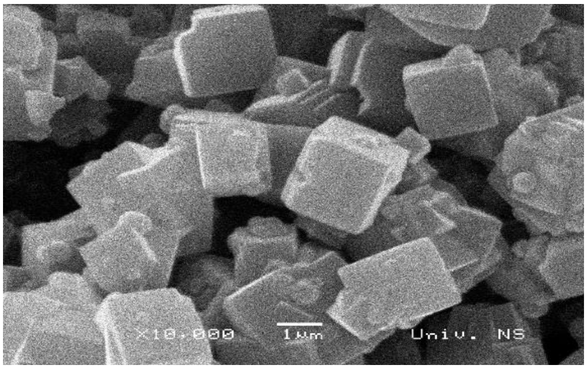

Figure 1. SEM image of zeolite 4A.

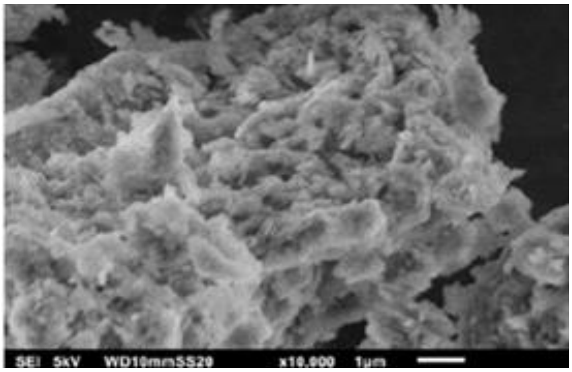

Figure 2. SEM image of clinoptilolite.

Experimental results after heating of the oil samples show that the influence of heating temperature on the FFA content in 30-minutes period is evident at 110°C (Table 2). By decomposition of triglycerides, the FFA content increases from 0.04 to 0.78% for the continued heating (30 minutes at 190°C). The analysis of the FFA content after heating at 190°C for 30 minutes shows a decrease by 72% (0.78 to 0.22%) after oil regeneration by adsorption by clinoptilolite. The analysis of the FFA content after heating at 190°C for 30 minutes shows a decrease by 65% (0.78 to 0.27%) after oil regeneration by adsorption on zeolite 4A.

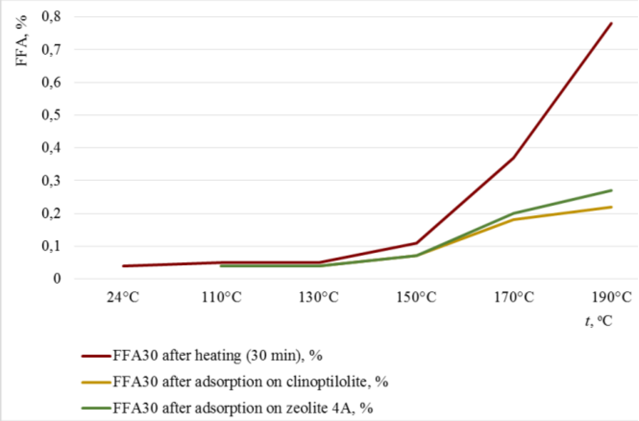

Figure 3. Effects of 30-minutes warming on FFA content in sunflower oil and recovery of oil after adsorption.

3.1. Acid number - AN

The acid number of the sample of refined sunflower oil prior to heating was 0.30 mg KOH/g. Experimental results after heating show that the effect of heating temperature on the acid number for a 30-minute period was evident at 110°C (Table 3). The acid number increased from 0.30 to 1.70 mg KOH/g for the continued heating (30 minutes at 190°C). Adsorption by clinoptilolite resulted in the decrease in the acid number 82% (1.70 to 0.30 mg KOH/g) in the oil previously heated at 190°C for 30 minutes. The analysis shows that the acid number in the oil previously heated at 190°C for 30 minutes decreased by 76% (1.70 to 0.40 mg KOH/g) after the adsorption by zeolite 4A.

Table 2. FFA content in sunflower oil after heating for 30 minutes and after adsorption on clinoptilolite and zeolite 4A

Heating temperature	24°C	110°C	130°C	150°C	170°C	190°C
FFA_{30} after heating (30 min), %	0.04	0.05	0.05	0.11	0.37	0.78
FFA_{30} after adsorption by clinoptilolite, %		0.04	0.04	0.07	0.18	0.22
FFA_{30} after adsorption by zeolite 4A, %		0.04	0.04	0.07	0.20	0.27

Table 3. Acid number in sunflower oil after heating for 30 minutes and after adsorption by clinoptilolite and zeolite 4A

Heating temperature	24°C	110°C	130°C	150°C	170°C	190°C
AN_{30} after heating (30 min), mg KOH/g	0.30	0.50	0.50	0.90	1.30	1.70
AN_{30} after adsorption by clinoptilolite, mg KOH/g		0.20	0.20	0.20	0.30	0.30
AN_{30} after adsorption by zeolite 4A, mg KOH/g		0.20	0.20	0.20	0.30	0.40

3.2. Peroxide number - PN

The analysis of the peroxide number in sunflower refined oil sample before heating shows that it was 0,02 mmol/kg. Experimental results after heating oil samples show that the influence of heating temperature on peroxide number in 30-minutes period is evident at 110°C (Table 4). Peroxide number increases from 0.02 to 1.22% for the continued heating (30 minutes at 190°C). Adsorption by clinoptilolite resulted in the decrease in the peroxide number by 43% (1.22 to 0.70 mmol/kg) in the oil previously heated at 190°C for 30 minutes. The analysis shows that the peroxide number decreased by 39% (1.22 to 0.74 mmol/kg) in the oil previously heated at 190°C for 30 minutes after the adsorption by zeolite 4A.

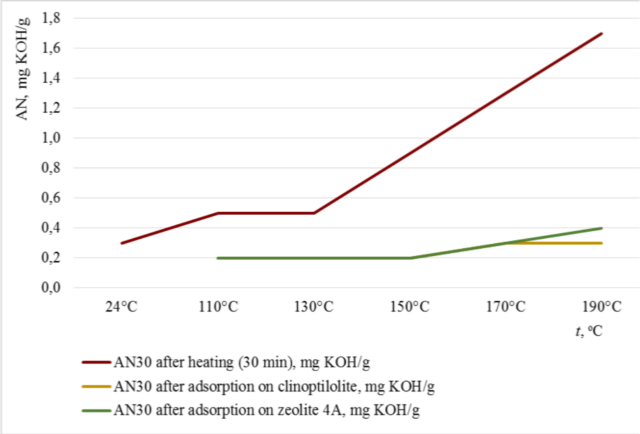

Figure 4. Effects of 30-minutes warming on acid number in sunflower oil and recovery of oil after adsorption.

Table 4. Peroxide number of sunflower oil after heating for 30 minutes and after adsorption by clinoptilolite and zeolite 4A

Heating at temperature	24°C	110°C	130°C	150°C	170°C	190°C
PN_{30} after heating (30 min), mmol/kg	0,02	0,10	0,10	0,70	0,95	1,22
PN_{30} after adsorption on clinoptilolite, mmol/kg		0,05	0,05	0,50	0,50	0,70
PN_{30} after adsorption on zeolite 4A, mmol/kg		0,05	0,05	0,50	0,65	0,74

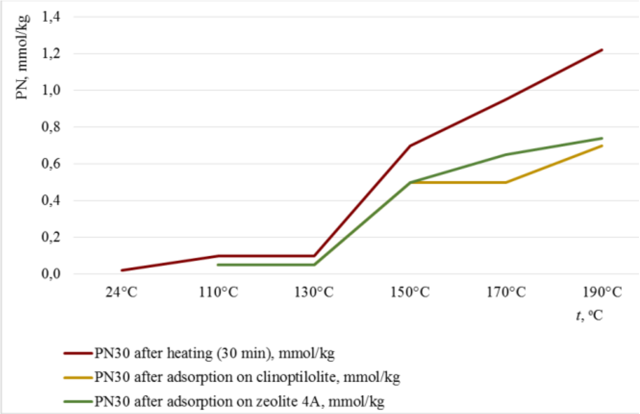

Figure 5. Effects of a 30-minute heating on the peroxide number in sunflower oil and oil recovery after adsorption.

4. CONCLUSIONS

The decomposition of triglycerides resulted in an increase of the FFA content from 0.04 to 0.78% for continued heating (30 minutes at 190°C). The content of FFA decreased by 72% after the adsorption by clinoptilolite, and 65% after the adsorption by zeolite 4A. The acid number increased from 0.30 to 1.70 mg KOH/g for continued heating (30 minutes at 190°C). The acid number decreased by 82% after the adsorption by clinoptilolite, and 76% after the adsorption by zeolite 4A. The peroxide number increased from 0.02 to 1.22% for continued heating (30 minutes at 190°C). The peroxide number decreased by 43% after the adsorption by clinoptilolite, and 39 % after the adsorption by zeolite 4A. Both adsorbents exhibited good adsorption results. Gas chromatography and thermogravimetric analysis of thermally treated oils could give a more accurate estimation of hydrolysis and thermal degradation products. Further research should be continued on the regeneration of used edible oil by testing other quality parameters, as well as the application of other adsorbents.

REFERENCES

Armbruster, T. (2001). Natural Zeolites: Cation Exchange, Cation Arrangement and Dehydratation Behavior, Minerals as Advanced Materials I, Springer, 1-6. https://doi.org/10.1007/978-3-540-77123-4_1

Bošković, G. (2007). Heterogena kataliza u teoriji i praksi. Univerzitet u Novom Sadu, Tehnološki fakultet

Choe, E. & Min D.B. (2007). Chemistry of Deep-Fat Frying Oils, 77-86. https://doi.org/10.1111/j.1750-3841.2007.00352

Čorbo S. (2008). Tehnologija ulja i masti, Poljoprivredno-prehrambeni fakultet Sarajevo

Dimić, E. & Turkulov, J. (2000). Kontrola kvaliteta u tehnologiji jestivih ulja, Tehnološki fakultet, Novi Sad

Dobrnjac, S., Dobrnjac, M., Penavin, Skundric, J., Vasiljevic, Lj., Blagojevic, S. & Sandic Z. (2018). Possibility for Removing Products of Thermal Degradation of Edible Oil by Natural Aluminosilicates, Experimental and Numerical Investigations in Material Sciences and Engineering, Belgrade, Serbia, Springer, 59-71, https://doi.org/10.1007/978-3-319-99620-2_5 .

Grim, R.E. (1962). Applied Clay Mineralogy. New York: McGraw-Hill Book Company, https://doi.org/10.1126/science.136.3519.870-a

Levi, Z. (2010). Ponašanje nekih alumosilikata i njihovih katjon modifikovanih formi pri adsorpciji fenola iz vodene sredine. Doktorska disertacija. Banja Luka: Tehnološki fakultet Univerziteta u Banjaluci.

Penavin, J. (1979). Izomerizacija 3,3 dimetilbutena-1 na zeolitima, Magistarski rad. Zagreb: Sveučilište u Zagrebu.

Penavin, Škundrić, J., Levi Z., Sladojević S. , Škundrić B., Čegar N., Šušnjar Lj. & Sredić S. (2005). Mogućnost primjene tufova sa lokaliteta Republike Srpske kao adsorbenasa za kiselo-bazne primjese u otpadnim vodama. EcoIst'05, Ekološka istina,. Bor.

Putanov, P. (1995). Uvod u heterogenu katalizu. Novi Sad: Srpska akademija nauka i umetnosti.

Rossell, J.B. (2001) Frying - Improving quality, Cambridge, England, Ed. Woodhead Publishing, https://doi.org/10.1533/9781855736429

Službeni glasnik BiH br. 21/11. (2011). Pravilnik o jestivim biljnim uljima, jestivim, biljnim mastima i majonezama,

Vasiljević Lj., Gligorić M., Dobrnjac S., Aleksić V., (2017). Uticaj prženja suncokretovog ulja na sadržaj slobodnih masnih kiselina, V međunarodni kongres „Inženjerstvo, ekologija i materijali u procesnoj industriji", Jahorina https://doi.org/10.7251/EEMSR15011428V

Wonglamom J., Rakariyatham N. (2014). Recovery of used vegetable frying oil by two step adsorbents. 26th Annual Meeting of the Thai Society for Biotechnology and International Conference, 330-337.