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The Analysis of the thermodynamic properties of sesame seeds, oil and products by differential scanning calorimetry

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Work accepted..

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Analiza parametrów termodynamicznych nasion, oleju i produktów z sezamu za pomocą różnicowej kalorymetrii skaningowej

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Author

MERT ATAKAN UTCU

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Summary

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Organoleptic peculiarities of traditional products have reasonable influence on the cuisine practiced around the world which is the effect of global integration between the nations or migration of people to different parts of the globe. Special product such as Halva is good example of this situation. Turkey has a big share in production of halva because of its history dating back to the ancient times. The aim of presented thesis was to investigate thermodynamic properies of seeds, oil and products made from sesame in term of distinguishing the genuine sesame oil and halva from the adulterated sesame products. In this study differential scanning calorimetry (DSC) was used to analyze sesame seeds and extracted oils originated from various countries like Turkey, Nigeria, Sudan, Ethopia, India. It was shown by DSC technique that origin of the seeds has no influence on the melting profile of sesame oil. Two extraction methods were also tested: by cold pressing and by hexane extraction. It was stated that there were no significant differences in thermodynamic properties of sesame oils between two methods of extraction. The effect of addition of 20 % of palm olein to sesame oil on thermodynamic properties was also analyzed. Statistical analysis proved that there were significant differences in thermal properties of DSC melting profile between genuine sesame oil and oil wth addition of palm olein, which proves that the DSC technique can be used to detect adulteration of sesame oil.

Keywords: Sesame, sesame oil, halva, authentification, thermodynamic properties, melting and crystalisation profile, DSC

Streszczenie

Analiza parametrów termodynamicznych nasion, oleju i produktów z sezamu za pomocą różnicowej kalorymetrii skaningowej

Organopelptyczne właściwości tradycyjnych produktów mają znaczący wpływ na kuchnię praktykowaną na całym świecie, co jest efektem globalnej integracji oraz migracji ludzi do różnych części świata. Specjalny produkt, jakim jest halwa, jest dobrym tego przykładem. Turcja ma ogromny udział w produkcji hałwy z powodu historii sięgającej czasów starożytnych. Celem przedstawionej pracy było zbadanie właściwości termodynamicznych nasion, oleju i produktów z sezamu w aspekcie odróżniania autentycznego oleju sazamowego i hałwy od produktów fałszowanych. W badaniach zastosowano różnicową kalorymetrię skaningową do analizy nasion sezamu i ekstrahowanego oleju, pochodzących z różnych krajów jak Turcja, Nigeria, Sudan, Etiopia, Indie. Za pomocą techniki DSC pokazano, iż pochodzenie nasion sezamu nie ma wpływu na profil topnienia oleju sezamowego. Testowano również dwie metody ekstrakcji: za pomocą zimnego tłoczenia i za pomocą heksanu. Stwierdzono, że nie ma istotnych statystycznie różnic we właściwościach termodynamicznych oleju sazamowego pomiędzy dwiema metodami ekstrakcji. Analizowano również wpływ dodatku 20 % oleiny palmowej do oleju sezamowego na właściwosci termodynamiczne. Analiza statystyczna dowiodła, że występują statystycznie istotne różnice w parametrach termodynamicznych pomiędzy autentycznym olejem sezamowym a olejem z dodatkiem oleiny palmowej, co dowodzi, że technika DSC może być wykorzystania do wykrywania zafałszowań oleju sezamowego.

Słowa kluczowe: Sezam, chałwa, autentyczność termodynamiczne właściwości , profil topnienia i krystalizacji, DSC

1. Introduction

Sesame is the main substance of halva production and has many varieties within the genus *Sesamum*. Within this genus, *S. indicum* seeds are the most commonly cultivated for sesame seed production. *S. indicum* species originated in India; however, they are also other species that are cultivated in the Middle East, Asia and some wild variants in sub-Saharan Afica (web source1). This product is a rich source of protein, vitamins (i.e. B, C, and E), and minerals (i.e. calcium, potassium, iron, phosphorus) (El Khier et al, 2008; Tunde-Akintunde et al., 2012). These nutritional properties make halva products more valuable for consumers. Furthermore, antioxidant properties (i.e. lignins and saponins) have a positive health effect and play an important role in giving the product a long shelf life.

Sesame products can be divided into two final product categories: halva and tahini. The main difference between the halva product and tahini is material composition. Tahini is mostly a semi-fluid colloidal pressed sesame seeds while halva is the pressed sesame seeds liquid mixed with sugar to form a butter-like final product. Depending on bakery needs or consumer preferences, tahini will most likely be used in confectionary or as an ingredient of other sweet products. Halva rich in protein, minerals, in addition, natural substances like *Semolina* seeds, a crispy texture and low in calories makes it attractive for health conscious consumers.

Halva has many different names based on the country it is consumed and some of these names include *halawa*, *halvah*, *halva*, *halava*, *helva* and *halwa* (Birer, 1985; Şavkay, 2000; Aktas and Cebirbay, 2015) Halva is considered special dessert of Middle Eastern, Eastern Medeterranean, Central Asian countries, African countries, and Turkey (Birer, 1985; Yücecan, 1992). The name halva is derived from the Arabic word “Hulv*”* that means “sweet product”. In Turkish culture, halva is a product that is consumed traditionaly in community. This food has a specific traditional importance for the community and is usually consumed on special days such as holidays, births, and funeral ceremonies. In terms of production, halva is made by using ingredients such as wheat flavour followed by the addition of *Semolina* seeds, which are roasted in butter, and then added to sugar syrup. Market demand for halva production is strong in Middle Eastern and European markets.

2. Literature Review

2.1. Halva as a traditional product from sesame

Due to globalization, cuisine culture has increasingly been shared among other countries and as a result more people have been exposed to foods that are different in organoleptic peculiarity to their own traditional food. Subsequently, the production stages of some of these food ingredients may even become incorporated into the foods of these countries. The history and cultural heritage of previous civilizations that resided in Turkey has had a significant impact in the development of Turkish cuisine culture (Baysal, 2002; Yücecan, 1992). According to the Turkish Food Codex, halva is categorized as a dessert dish, and must be prepared by cooking the proper amount of *Radix saponariae Albae sive* L. root extract and white egg together with sugar (sucrose or glucose) and some type of nut (i.e. traditionally walnut, almonds, peanuts, or pistachio) (Birer, 1985; Offical paper, 2008). In Turkey, the production volume of tahini and halva production is approximately 35,000 and 40,000 tons, which is one of the largest countries of production, and offers a large variety of halva to its consumers. That is a well-known product and consumer acceptance is very high. (Birer, 1985; Official Paper, 2008)

2.1.1 The analysis of physical and chemical composition of sesame

Sesame seed has high nutritonal value due to its high content of oil and protein. The composition is markedly influenced by genetic and environmental factors (Kinman and Stark, 1954; Lyon, 1972; Hedge, 2012). The seeds contain 6–7 % moisture, 17–32 % protein, 48–55 % oil, 14–16 % sugar, 6–8 % fibre, and 5–7 % ash. In general, Indian varieties tend to be lower in protein and higher in oil content than Sudanese varieties (e.g. such as those generally appearing in the export market) are commercially used in the USA. The hull content averages about 17 % of the sesame seed, and contains large quantities of oxalic acid, calcium, other minerals, and crude fibre. Thus, when using sesame for human food, it is advisable to remove the hull. When the seed is properly dehulled, the oxalic acid content is reduced from about 3 % to less than 0.25 % of the seed weight (Nagaraj, 1995). Screw-pressed, dehulled sesame contains about 56 % protein, while the solvent extracted meal contains more than 60 % protein. This is mostly used in feed except in India where it is used as a food. (Hedge, 2012)

Table 1.Proximate composition of whole sesame seeds (Hedge, 2012)

Constituent (%)	Joshi (1961)	Smith (1971)	Gopalan et al. (1982)	Weiss (1983)
Moisture	5.8	8.0	5.3	5.4
Protein	19.13	22.0	18.3	18.6
Fat	51.0	43.0	43.3	49.1
Carbonhydrates	21.2	21.0	25.0	21.6
Ash	5.7	6.0	5.2	5.3

2.1.2. Lipids

Sesame seeds contain more oil than many other oil seeds. Oil content varies by genetic and environmental factors. A wide range of the oil content, from 37–63%, has been reported in sesame seeds (Lyon, 1872; Swern, 1979; Bernardini, 1986; Hedge 2012). Oil content in seeds can vary considerably among different varieties and also with growing seasons (Lyon, 1972; Yen *et al.*, 1986; Hedge, 2012). The oil content is also related to the colour and size of the seeds. In general, white or light-coloured seeds usually have more oil than the dark seeds, and smaller seeds contain more oil than larger seeds (Seegeler, 1983). Rough-seeded cultivars generally have lower oil content than smooth seeded types (Yermanos *et al*., 1972; Hedge, 2012). Agronomic factors also influence the seed oil content. The oil content tends to rise with increasing length of photoperiod and early planting dates (Arzumanova; Abdel-Rahman *et al*., 1980; Hedge, 2012). The seeds from plants with a shorter growing period tend to have higher oil content than those from plants with a medium to long growing cycle (Yermanos, 1978; Hedge, 2012). Heavy application of nitrogen fertilizer reduces oil content of sesame seeds (Singh *et al.*, 1960; Hedge, 2012). The lipids of sesame seeds are mostly comprised of neutral triglycerides with small quantities of phosphatides (0.03–0.13 % with a 52:46 ratio of lecithin: caphalin respectively). The phosphatides also contain about 7 % of a fraction soluble in hot alcohol, but are insoluble when cold. However, sesame oil contains a 1.2% unsaponifiable matter, which is a relatively high percentage (Johnson and Raymond, 1964; Weiss, 1983; Hedge, 2012). The glycerides present in sesame oil are diverse and are primarily composed of oleo-dilinoleo, linoleo-dioleo triglycerides with one radical of a saturated fatty acid combined with one radical of oleic and linoleic acids. The glycerides of sesame oil are mostly triunsaturated (58 mol%) and diunsaturated (36 mol%) with small quantities (6 mol%) of monounsaturated glycerides. (Lyon, 1972; Hedge, 2012).

2.1.3. Fatty Acid Composition

Sesame oil contains about 80 % unsaturated fatty acids and the major fatty acids acids found in this group are oleic and linoleic acids that are present in approximately equal amounts (Lyon, 1972; Hedge, 2012). The saturated fatty acids account for less than 20% of the total fatty acid profile. Palmitic and stearic acids are the major saturated fatty acids present in sesame oil (see Table 2).

Table 2. Fatty acid composition of sesame oil (% percentage of total fatty acids) (Hedge, 2012)

Fatty Acid	Godin And Spensley (1971)	Yermanos(1978)	Seegeler(1983)	Maiti *et al.*(1988)
Palmitic	7-9	8.3-10.9	8.4-10.3	7.8-9.1
Stearic	4-5	3.6-6.0	4.5-5.8	3.6-4.7
Arachidic	8	-	0.3-0.7	0.4-1.1
Oleic	37-50	32.7-53.9	39.5-43.0	45.3-49.4
Linoleic	37-47	39.3-59.0	41.0-45.0	37.7-41.2

Approximately 44% linoleic, 42% oleic, and 13% saturated fatty acids are found in sesame oil (Smith, 1971; Hedge, 2012)

2.1.4. Antioxidans

Among the commonly used vegetable oils, sesame oil is known to be most resistant to oxidative rancidity (Budowski, 1950; Hedge, 2012). It also exhibits noticeably greater resistance, which is expected from its content of tocopherols (i.e. vitamin E). This high stability to oxidation is often attributed to the presence of a large proportion of unsaponifiable matter. Moreover, the unsaponifiable matter itself includes substances such as sesamol and phytosterol that are normally not found in other oils. Sesamolin, upon hydrolysis, yields sesamol. Sesame oil contans 0.5 – 1.0% sesamin, 0.3 – 0.5% sesamolin (Budowski *et al.*, 1950; Hedge, 2012), and only traces of free sesamol (Beroza and Kinman, 1955; Budowski, 1964; Hedge, 2012).

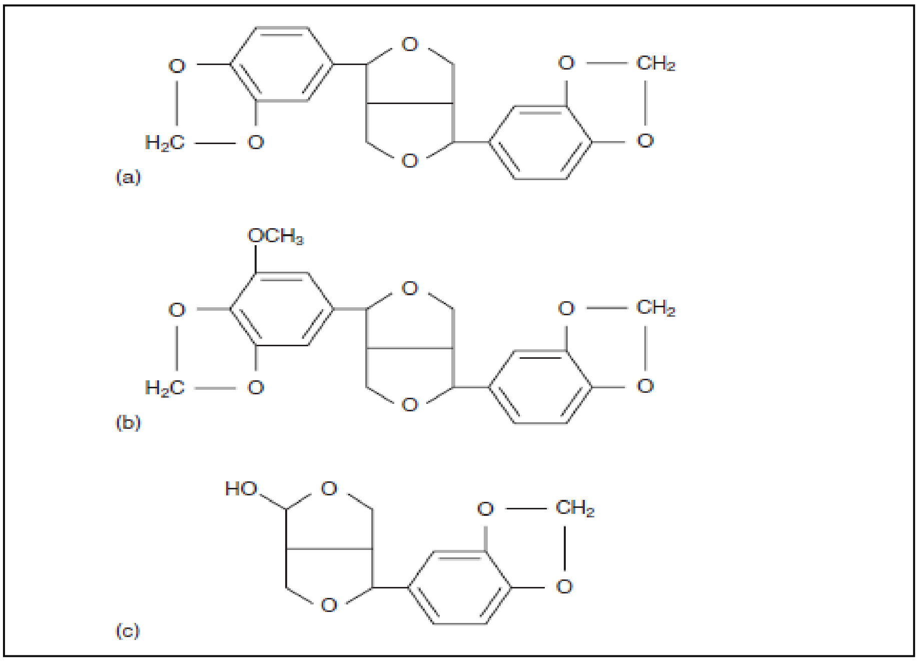


Figure 1. Structures of natural antioxidants found in sesame oil: (a) sesamin; (b) sesangolin; and (c) samin. (Hedge, 2012)

2.1.5. Proteins

Sesame seed contains 17 – 32% protein content with an average of 25% (Joshi, 1961; Lyon, 1972; Yen *et al*., 1986). Protein content of sesame seeds tends to decline with increase processing (Caliskan *et al.*, 2004; Hedge, 2012). Based on solubility, sesame proteins have been classified as albumin (8.6%), globulins (67.3%), prolamin (1.3%) and glutelin fractions (6.9%) (Rivas *et al*., 1981; Hedge, 2012). The essential amino acid composition of sesame seed proteins (see Table 3) indicates that sesame proteins are rich in sulphur-containing amino acids, particularly methionine (Smith, 1971; Brito, 1981; NarasingaRao, 1985; Hedge, 2012) and tryptophan (Johnson *et al*., 1979; Yen *et al*., 1986; Hedge, 2012).

2.1.6. Carbonhydrates

Sesame seeds contain 14–25% carbohydrates. The seeds contain about 5% sugars, which most are of simple type. Defatted sesame seed meal contains more sugars. Sesame seeds are reported to contain 3–6% crude fibre (Ramachandra *et al*., 1970; Gopalan *et al*., 1982; Taha *et al*., 1987; Hedge, 2012). Wankhede and Tharanathan (1976) reported 0.58–2.34% and 0.71–2.59 % hemicellulose A and B in defatted flour, respectively. Hemicellulose A was found to contain galacturonic acid and glucose in the ratio of 1:12.9 while hemicellulose B contained galacturonic acid, glucose, arabinose and xylose in the ratio of 1: 3.8: 3.8: 3.1 (Hedge, 2012).

2.1.7. Minerals

Elleuch *et al.* (2007) have evaluated the prospects of sesame coat as a source of dietary fiber, polyphenols, and essential minerals (i.e. potassium, magnesium, phosphorus, and iron). They studied the chemical composition of the coat, the importance of each component within the sesame seed coat, and the results were that dietary fiber and polyphenol content was reduced to a considerable extent after roasting. In addtion, they found that the mineral content of the roasted hull increased (Das *et al*., 2015). Sesame seed is a good source of certain minerals, particularly calcium (e.g. mostly present in the seed coat but lost after dehulling), phosphorus, and iron. The seeds contain a total of 4 – 7% minerals. Deosthale (1981) reported 1% calcium and 0.7% phosphorus in the seeds

Table 3. Minerals content of sesame whole seeds (mg/100 g)

Mineral	**Joshi (1961)**	**Agren And Gibson (1968)**		**Gopalan et al. (1982)**	**Weiss (1983)**
		White Seeds	**Brown Seeds**		
Calcium	1000	1017	1483	1450	1160
Phosphorus	700	732	578	570	616
Iron	20	56	----	10.5	10.5
Total	5700	5600	6200	5200	5300

2.1.8. Vitamins

Sesame seeds are also a source of certain vitamins particularly niacin, folic acid, and tocopherols (Gopalan *et al.*, 1982; Weiss, 1983; Hedge, 2012). The vitamin A content of seeds is, however, very low and the vitamin E group includes several tocopherols, isomers, and derivatives that differ in their biological activity. The biological activity of vitamin E activities of α-, β-, γ-, δ-tocopherols, and tocotrienol are in the ratio of 100: 40: 10: 1: 30 respctively (McLaughlan and Weihraugh, 1979; Hedge, 2012).

Table 4. Vitamin content of whole sesame seeds (Hedge, 2012)

Mineral	**Agren And Gibson (1968)**		**Gopalan et al. (1982)**	**Weiss (1983)**	**Seegeler(1983)**
	White Seeds	**Brown Seeds**			
Vitamin A(IU)	-	-	60*	30	Trace
Thiamin(mg/100g)	0.22	0.14	1.0	0.98	1.0
Riboflavin(mg/100g)	0.02	0.05	0.34	0.24	0.05
Niacin (mg/100g)	7.3	8.7	4.4	5.4	5.0
Pantothenic acid (mg/100g)	---	---	---	---	0.6
Folic acid (µg/100g)	---	---	---	---	---
Free	---	---	5.1	---	---
Total	---	---	134	---	---
Ascorbic acid(mg/100g)	---	---	---	---	0.6
***µg carotene(100g)**					

2.1.9. Antinutritional factors

In general, sesame seeds contain about 1 - 2% oxalic acid and articles by Gopalan *et al.* (1982) and Hedge (2012) reported that their sesame seeds contained 1.7% oxalic acid. The high proportion of oxalate reduces the physiological availability of calcium from the seeds. The oxalic acid in sesame seeds is mostly present in the testa (i.e. the hull portion). The slightly bitter taste comes from the testa apart of the seed. The testa imparts to the whole seed or the processed meal because of chelation of calcium by oxalic acid. Although the dehulling process reduces the oxalic acid content of the seeds, the oxalic acid may also be removed from the sesame meal by treating it with very basic hydrogen peroxide (i.e. 9.5 pH). Sesame oil contains two minor constituents, namely sesamin (0.5 - 1.0%) and sesamolin (0.3 - 0.5 %). Sesamolin upon hydrolysis yields sesamol (Godin and Spensley, 1971). Although the nutritional significance of sesamin and sesamolin is not clear, sesamol has been reported to be partially responsible for the resistance of sesame oil to oxidation (Weiss, 1983; Kim *et al.*, 2006; Hedge, 2012). Sesame plants seem to have an unusual capacity for accumulating lead in the seeds which is a point of concern for human consumption as lead poisioning over time would be possible to the consumer if the consumption of sesame seed based products are very high.

2.2. Oil extraction methods for the sesame seeds and halva product

In comparision to the most well-known seed oils, sesame seeds have higher oil content (50%) than other oil seeds (Hwang, L.S., 2005; Elkhaleef and Shigidi, 2015). Sesame oil is generally regarded as high-priced and high-quality oil. It is one of the most stable edible oil despite its high degree of unsaturation (Hwang, L.S., 2005; Elkhaleef and Shigidi, 2015). Sesame oil is rich in monounsaturated and polyunsaturated fatty acids. (Elleuch et al., 2011; Elkhaleef and Shigidi, 2015). The most abundant fatty acids in sesame oil are oleic, linoleic, palmitic, and stearic acids, which together comprise about 96% of the total fatty acid profile of the seed. According to the simulation results and the essential criteria, acetone is superior to other solvents; but under certain conditions where oil extraction takes place, hexane is a superior catalyst. Usually meal or medicinal oils are obtained from plant or animal fats. Plant fats are liquid at room temperature and are often derived from vegetables or plant seeds. In contrast, animal fats are derived from animal sources (i.e fish, insects, mammals, etc.) and are solid at room temperature (Safari et al., 2011).

Edible sesame seed *(Sesamum indicum* Linn.) has high oil content *(ca.* 50%) with superior oxidative stability compared to several other vegetable oils both at storage temperatures (Beroza et al., 1955; Yen, 1991; Kamal-Edin et al., 1995) and during frying (Yen, 1991; Kamal-Edin et al., 1995). Due to difficulties and low yield of production, sesame oil is considered a minor oil (Robbelen G. et al., 1989; Kamal-Edin et al, 1995). Its use is restricted to the areas of production and is considered as a “gourmet oil" in industrialized countries (Terrones, 1990; Kamal-Edin et al., 1995). Because the sesame seeds are mainly products of developing countries, full technological optimization of seed processing and/or oil extraction has not yet been achieved. Sesame oil is obtained from unroasted seeds by simple mechanical pressing of the seeds or by presshigh-pressure methods followed by solvent extraction from which the oil is extracted. Oxidative stability, an important characteristic of the oil, is expected believed to be influenced by the method of extraction as well as seed treatment prior to extraction. Extractions of oils by Soxhlet method were comparable to stability of oils from extraction by pressing. Extraction methods involving effective seed crushing and cold solvents (steel tubes and homogenizer) yielded considerably more-stable sesame oils than methods for coarsely crushed seeds and heat (pressing and Soxhlet)(Kamal-Edin et al., 1995).

2.2.1. Hexane extraction method for sesame seeeds and halva products

Solvent extraction method providing higher yields (i.e. 98 - 99%) is the most commonly used extraction process technique in industrial settings (see figure 2). Presently, n-hexane is the preferred solvent throughout the world due to its extraction efficiency and ease of availability (Saxena at al., 2011; Elkhaleef and Shigidi, 2015). In comparison between the most globally used solvent extractions with hexane, the result is the removal of all but 0.5% of the residual oil using less power and requiring less maintenance. Hence, it is relatively efficient and reliable. Studies have shown that optimization of n-hexane extraction is defined by studying the parameters which affect the process (Elkhaleef and Shigidi, 2015). The weighted sesame seeds are sieved to have equal size and are then washed to remove any particulates that may be deposited during harvesting that may contaminate the final product. The seeds are then crushed to increase the surface area, thus improving the extraction process. Döker et al. (2010) examined the impact of sesame particle size Elkhaleef and Shigidi, 2015 on oil extraction and concluded that the extraction yield increased as the particle size decreased depending on decreasing intraparticle diffusion resistance. The particle size from 45% of the maximum extraction yield obtained was about 300 - 600 μm (Elkhaleef and Shigidi, 2015).

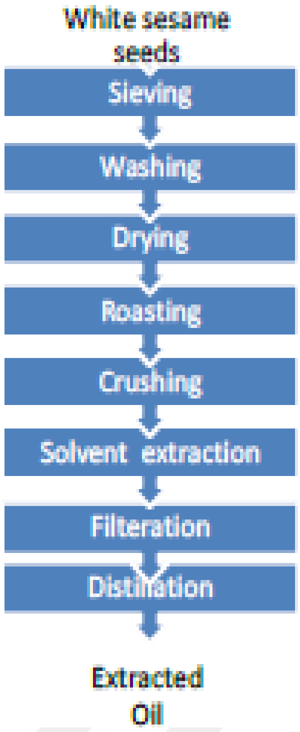


Figure 2. Extraction process description of sesame seeds (Elkhaleef and Shigidi, 2015)

Hexane is a solvent obtained from petrochemical source and is generally used as an oil extraction solvent. This solvent can be emitted during extraction and has been identified as an air pollutionant since it can react with other pollutants to produce an ozone precursor and photochemical oxidants (Wan *et al.*, 1995; Hanmoungjai *et al.*, 2000; Ferrera-Dias *et al.*, 2003). The solvent extraction is the key point-operation. Extraction takes place due to the affinity of solvent towards oil and the affinity is mainly chemically based. Various researchers studied the impact of different solvents on sesame oil extraction. Majority of researchers found that n-hexane yields in higher extraction percentages making it the optimum solvent (Elkhaleef and Shigidi, 2015). Elkhaleef and Shigidi (2015) referred that the extraction process has been studied under heating. The seeds were roasted to 150˚C and added to the n-hexane with the optimized ratio defined earlier of 6:1. All of this was completed under a pre-defined contact and stirring speed. The mixture was left under room temperature where other samples were heated to up to 55˚C with increasing temperature increment of 5˚C. Figure 3 demonstrates the work completed by National Research Instutue (1995), Warra (2011), and Elkhaleef and Shigidi (2015) that the maximum extraction of 42.5% was achieved at only 40˚C. Furthermore, the increasing temperature is merely an operational cost and has no impact on extraction yield percentages.

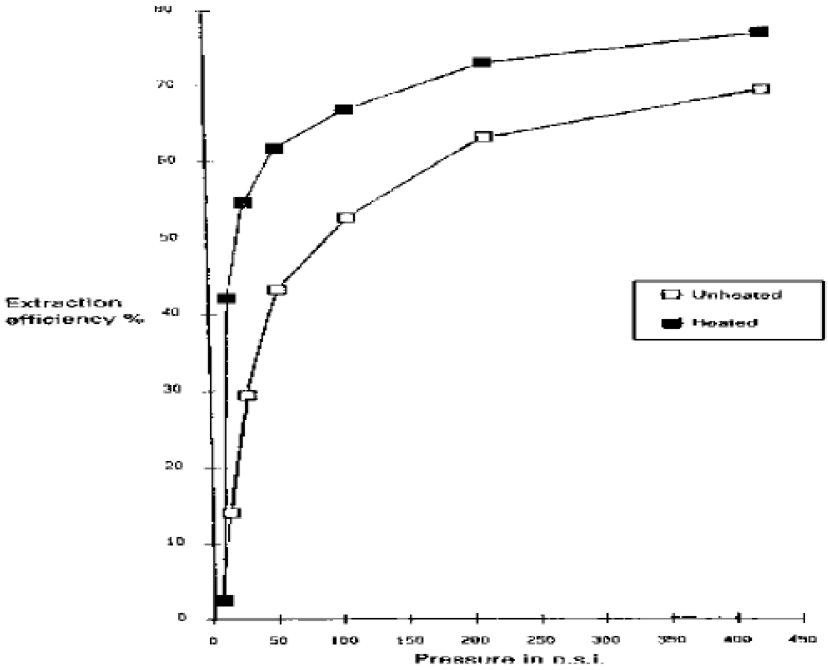


Figure 3. Extraction efficiencies of sesame seed paste at 12.7% moisture heated to 50°C and unheated before pressing (National Research Instutue, 1995; Warra, 2011).

2.2.2. Cold press extraction method for sesame seeeds

Extraction of sesame oil has developed significantly over the last few years. Primer lipid library stated that the mechanical method was an early means of separation, which was applying physical pressure to "squeeze the oil out". The most energy efficient and practical embodiment of that method is the modern screw press. More than half of the oil is easily removed with this method, but perhaps 7 - or 8% residual oil is left in the cake solid. The process uses considerable power and requires more maintenance. In addition, it also requires more machine setup for higher capacity. In summary, such techniques are no longer the prevailing method of extraction due to the higher cake oil content.

The extraction process is one of the most critical stages in the oil production from vegetable oilseeds. The most important techniques for vegetable oil extraction are solvent extraction and mechanical pressing (Koubaa et al., 2016; Delfan-Hosseini et al., 2017). Oil extraction by organic solvents is the most efficient approach; however, it has several disadvantages such as problems of plant security, emissions of volatile organic compounds into atmosphere, high operational costs, lower quality of products, which is a result of high processing temperatures, and a relatively high number of processing steps (Azadmard-Damirchi et al., 2010; Yang *et al.*, 2013; Delfan-Hosseini et al., 2017).

Mechanical pressing oil extraction is usually applied to seeds with high oil content. This method is easier and safer thus resulting in lower operational cost and relatively good quality of extracted oil, which is preferred for oil extracted by solvents (Oyinlola, Ojo, and Adekoya, 2004; Delfan-Hosseini et al., 2017).

2.3. Moisture content of seeds

Sesame seed is rich in oil and protein. The seeds contain 4.50-11.00% moisture,bdifferent reports is listed in table 5 (Badifu and Akpagher, 1996; Egbekun and Ehieze, 1997; Gandhi et al., 2007; Nzikou et al., 2009; Onsaard, 2012)

Table 5. Moisture Content of sesame seeds (Onsaard , 2012)

Moisture Content	**Badifu and Akpagher (1996)**	**Egbekun and Ehieze (1997)**	**Gandhi and Srivastava (2007)**	**Nzikou et al. (2009)**
Moisture (%)	4.50	7.00	11.00	5.70

2.4. Global production and export of sesame

According to Chemonics International Inc. (2002) data, Sudan, Uganda, Nigeria, and Tanzania were among the ten top producers of sesame. Africa. In 2009, the world production of sesame seed was 3,976,968 tons, and the major production area were Asia (2,489,518 tons) and Africa (1,316,690 tons), constituting about 62.6% and 33.1% of the total world production (FAOSTAT, 2011; Onsaard 2012.) The largest producers are China and India, each with an annual harvest around 750,000 tonnes followed by Myanmar (425,000 tonnes) and Sudan (300,000 tonnes). Figure 4 estimates the situation as sesame is a small holder crop and much of the harvest is consumed locally, without record of the internal trade and domestic processing (Chemonics International Inc., 2002; Warra, 2011).

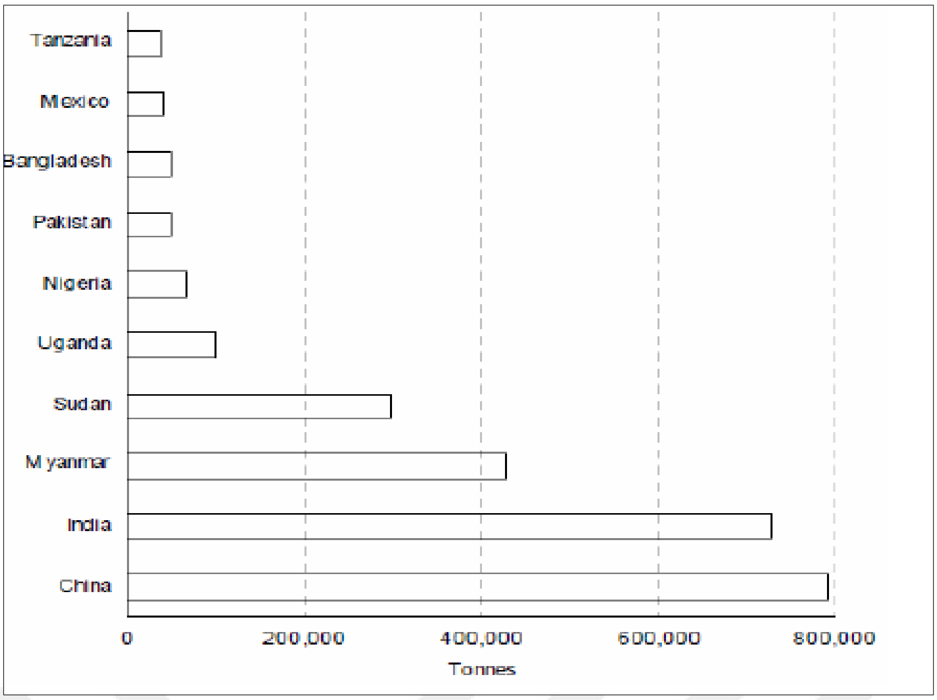


Figure 4. Top ten producers of sesame seed, 2001 (Chemonics International Inc., 2002; Warra, 2011)

Sudan, Ethiopia, Nigeria, and Tanzania were among the ten top exporters of sesame from the statistical data (Chemonics International Inc., 2002). Global exports of sesame seed are estimated to have reached 657,000 tonnes in 2000 having risen from 427,000 tonnes since 1988 figures. In 2000 exports were valued at $478 million USD. Figure 5 shows the rise of Africa over the last ten years as a supplier of sesame seed and also the growth of Indian output (Warra, 2011).

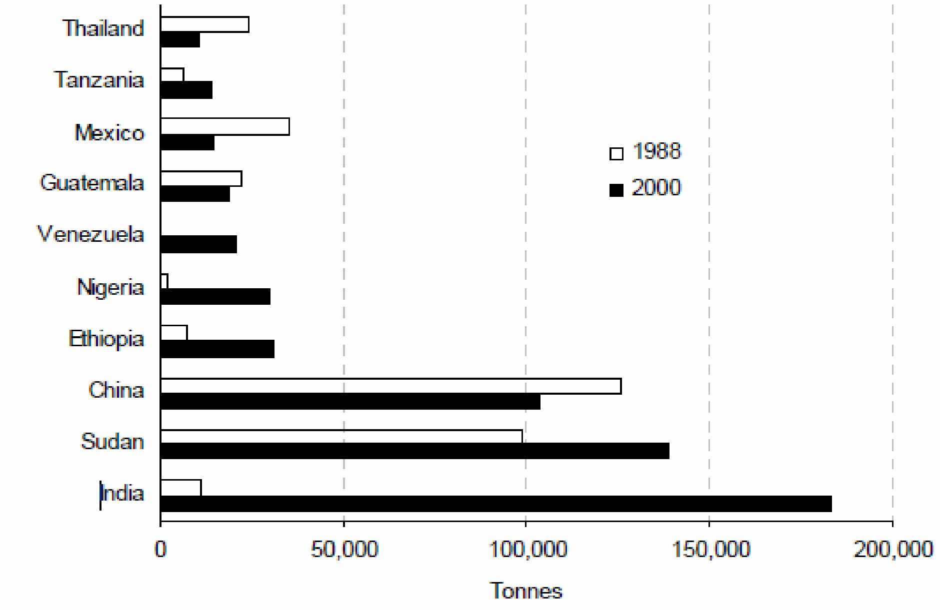


Figure 5. Top ten exporters of sesame seed in 2001. Source: Chemonics International Inc., 2002 and Warra, 2011

2.5. Differential scanning calorimetry method

The Differential scanning calorimetry method (DSC) is a thermoanalytical technique that measures the amount of energy absorbed or released by a sample when it is heated or cooled, providing quantitative and qualitative data on endothermic and exothermic process (Anderson materials, Columbia) DSC thermal analysis applications are typically designed to hold the sample temperature change is a linear function of time. Reference sample should thermally stable over the temperature range that is to be scanned.

In the 1960s, this technique was developed by E.S. Watson and M.J. O'Neill and in 1963 was commercially introduced at the Pittsburgh conference on applied spectroscopy for chemical analysis. DSC curves of heat flux over time, result in a positive or negative peak and device used this curve for the enthalpy of phase change. It does this by integrating the peak corresponding to the transfer and use of the following formula: $\Delta H = KA$ where ΔH is the enthalpy change, K is the phase constant, and A is the area under the curve. It is important to note that K may be different for each manufacture of DSC equipment (Wunderlich, 1990; Fahimdanesh et al., 2014).

This analysis can be used to measure some characteristics of an unknown sample. This technique can be used for calculating heat, freezing temperatures, and the glass transition temperature (T_g) for crystallization. Endothermic peak in the DSC curve is the result of a melting process. Ability to determine the transition temperature and enthalpy of the DSC is an invaluable tool in producing a phase diagram is constructed for different chemical substances (Wunderlich, 1990; Fahimdanesh et al., 2014). DSC analysis is performed in the laboratories for the unknown properitie measurements of samples. For this analysis some standards are necessary for the compatibility and precision of the results.

Heating and cooling

High scanning rates result in better sensitivity of the recorded transition. On the other hand, low scanning rates provide better resolution in temperature and may be appropriate in the resolution of closely overlapping transitions (PN-EN ISO STAND 11357-3).

Determination of transition temperatures

Scaling the plot is necessary so that the peak covers at least 25 % of full scale. Construct a baseline to the peak (Figure 4) by joining the peak initiation temperature, Tim, and end temperature, Tfm, at which the peak (endothermic peak for fusion, exothermic peak for crystallization) begins to deviate from the relatively straight baseline. If multiple peaks are present, a baseline should be drawn, covering all peaks. The evaluation should then be divided between each peak, in order to get the most correct enthalpy.

For a crystallization transition curve, measurement and report for each peak of the extrapolated onset crystallization temperature, (Teic); the peak crystallization temperature, (Tpc) is required. Extrapolated onset and end temperatures need to be reported if the width of the peak is of interest. ISO STAND 11357-3)

Determination of enthalpies

Enthlapy calclulation is done by measuring the area under the peak. Calculate the enthalpy of fusion, ΔHf [enthalpy of crystallization, ΔHC], in kilojoules per kilogram (kJ/kg), using the following equation:

$$\Delta H = \Delta HC \frac{m.AB.\sigma}{m.AC.BC.\sigma C}$$

Where:

ΔH is the enthalpy of fusion or crystallization of the specimen (kJ/kg)
ΔHC is the enthalpy of fusion or crystallization of the calibration material (kJ/kg)
A is the peak area for the specimen (mm^2)
AC is the peak area for the calibration material (mm^2)
m is the mass of the specimen (mg)
mC is the mass of the calibration material (mg)
σ is the y-axis sensitivity of the specimen (mW/mm)
σC is the y-axis sensitivity of the calibration material (mW/mm)
B is the x-axis sensitivity (time base) of the specimen (s/mm)
BC is the x-axis sensitivity (time base) of the calibration material (s/mm)

Figure 6. Equation for calculation of peak area in DSC method (ISO STAND 11357-3)

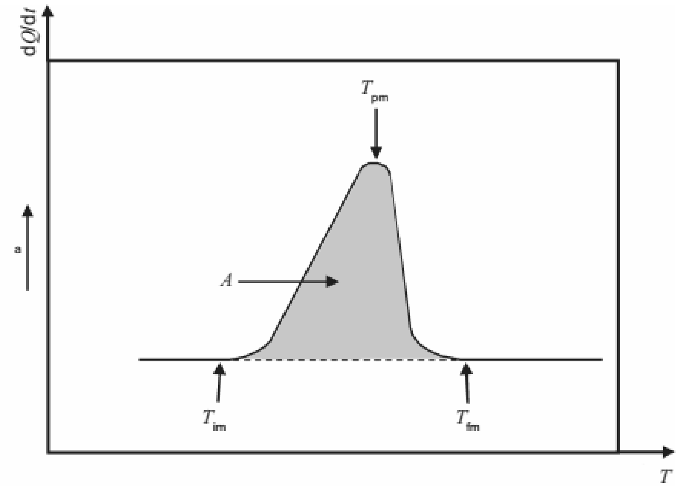


Figure 7. Determination of enthalpy of transition (ISO STAND 11357-3) . dQ/dt heat flow rate, T = temperature, A = peak area, a = endothermic direction.

2.6. Production of helva

Halva is one of the oldest sweets and traditional desserts (Abu-Jdayil 2004; Kahraman *et al*. 2010). There are many many varieties of halva, and the most famous form is consumed throughout the Middle East, Balkan, and North Africa regrions where halva is prepared from sesame paste (Sengun *et al*. 2005; Zahedi and Tahrani, 2012). This type of halva mainly consists of sesame paste (50 wt %), sucrose (25–35 wt %) and glucose syrup (12–25 wt%)(Abu-Jdayil, 2004; Sengun *et al*., 2005; Kahraman *et al*., 2010; Zahedi and Tahrani, 2012). The industrial production of halva uses sesame paste, concentrated sugar solution that is partially converted to invert sugar by citric acid, mixed with glucose, and bleached by *saponaria* extract to produce a clear syrup. Sesame paste is then blended with the syrup, kneaded, molded, and packaged (Sengun *et al*., 2005; Eissa and Zohair, 2006; Kahraman *et al*., 2010; Zahedi and Tahrani, 2012).

Tahini halva is usually made of sesame-seed paste (tahini), sugar and soapwort (*Saponaria officinalis*) extract by certain technological processes that create needle-like particles, which give a specific fiber structure to halva. Production of tahini halva was placed mostly under artisanal conditions by poorly trained staff and was based on practices (i.e. experienced and family established) for handmade production. Sesame seeds, the primary ingredient, add a nutty taste and a delicate aroma to this product. Besides making tahini and halva, sesame seeds are used for the preparation of rolls, crackers, cakes, and pastry products in commercial bakeries (Gavrilović, 2003).

Sesame in Turkey is the most important annual oil crop and there are numerous varieties and ecotypes of sesame adapted to various ecological conditions (Ercan et al., 2002). Proximate composition of Turkish sesame seeds and characterization of their oils have been investigated by (Unknown, 2012), and stated that there were very few scientific papers that deal with the specific methods of Turkish production and specific properties of tahini halva. In Bosnia and Herzegovina, this issue has never been seriously investigated. According to regulations of confectionary quality in Bosnia and Herzegovina (Unknown, 2012), tahini halvah belongs to a special group of candy products where final product quality, quality assurance, and storage of this product are poorly defined.

Halvah definines as it is a product obtained from sugar and tahini paste with soapwort root extract addition. Three kinds of product are defined: tahini halva, black halva, and white halva. Tahini halva may be yellow-white to grayish in color, have a fibrous structure, with sesame oil content at least 22% from the sesame paste. Black halvah is a dark, fibrous structure with sesame oil content at least 20% and with nut fruits and cacao powder added. White halva is a hard and sticky mass, white in color and with roasted nut fruits added; soapwort root extract is excluded. To achieve the characteristic flavor, aroma, and consistency in the production of tahini halva, citric acid, foaming agents (gelatin), egg white, soy protein extract, soapwort roots extract, chocolate and cocoa powder may be used

(Unknown, 2012). Liquid extract of soapwort is often used as a food additive in tahini halvah making (Sezgin et al., 2010).

As an active substance of soapwort liquid extract, saponin positively affects the color and consistency of the halva, thus preventing the oozing of oil from halva with time by acting as an emulsifier (Sezgin et al., 2010). Soapwort extract contains 11.58 - 19.58% total saponins, which increases the importance of soapwort (Battal, 2002). The classical definition of saponins is based on their surface activity. Many saponins have detergent properties, giving stable foams in water, showing hemolytic activity, and consequently having a bitter taste (Šošević, 2012). Turkish Standard (TS 2590) (Anonymous, 1998) is a standard of tahini halva in Turkey and total saponin level must be at a maximum content of 0.1% in tahini halva.

Generally preparation of halva samples may be described through the main steps: making sesame-seed paste tahini (seed cleaning, soaking in salty water for 4-5 hours, and washing, centrifuging, roasting at 115 – 120 °C, cleaning by air stream, grinding, cooling, fine grinding, and storing), making soapwort liquid extract from soapwort root (grinding, cooking in closed tanks at 115 °C until a viscous liquid is produced with 10% of dry mater and 1,050 kg/m3 is achieved, and then filtrated), and preparing inverted sugar syrup with liquid soapwort extract added (3L on 100 kg of sugar in closed tanks under atmospheric pressure, adjustment, and mixing at 100 -120 rpm). Obtained foam is white and movable due to specific mass reduction from 1,300 to 1,100 kg/m3. Tahini halva samples generally were produced by 2 different methods (see figure 7). Final products were keept at 18 - 20 °C and 50% RH. (Oručević Žuljević et al., 2015).

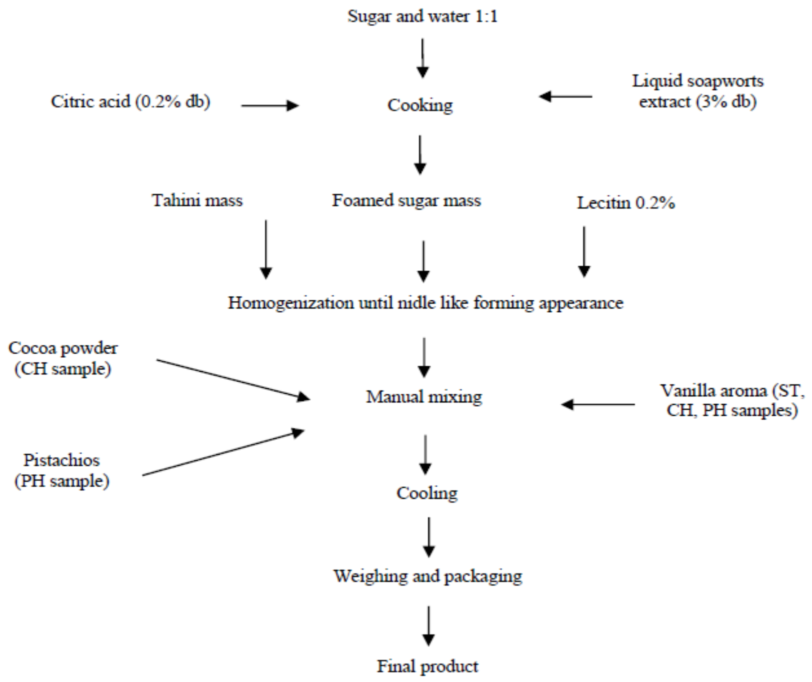


Fig 8. Making tahini halva samples SH, CH, and PH (Oručević Žuljević et al., 2015) SH= Halva, PH= Halva with pistachio, CH= Halva with cocoa

2.6.1 Codex standards and Turkish standards for halva

Regional Standard for halva Tahini according to CODEX STAN 309R-2011 described as a product ‘Halwa tehenia” designates a heat-processed food product made of tahini, natural sugars, and other ingredient with the composition is externally added to the product. Its texture is consistent or crumbly (Fibrous Halva). It is a food product made by grinding peeled and roasted sesame seeds. Unprocessed carbohydrates such as sucrose, glucose, fructose, or a mixture of them are used for sugar material in the product. A substance extracted from the bark, leaves or roots of soapwort (*Saponaria officinalis*) must also be added.

It is either called soapwort or saponin that acts like a stabilizing agent. The primary ingredients are tahini, natural sugars, soapwort extract or authorized substitutes. There are also other options for the different recipes of halva production such as adding almonds, pistachios, walnuts, dried fruits, and/or cocoa powder can be used according to standard limits.

General quality of the halva must be like all raw materials used in the production process and should meet their respective standards. The product shall be free of any rancid taste, smell, or any other foreign taste. The product shall be free of insects, their body parts, and secretions. The product shall retain its natural characteristics, particularly the non-separation of its oil never separating, and it should be free of white or dark spots. The product shall be of a consistent texture that can be easily cut into (CODEX STAN 309R-2011).

The acidity percentage expressed as citric acid shall not exceed 0.2% of the product’s weight. The percentage of acid insoluble ash shall not exceed 2% of the products dry weight. The percentage of acid insoluble ash shall not exceed 0.2% of the product weight. The percentage of fat (sesame oil) shall not be inferior to 25% of the weight.

Flavorings are acceptable for use in foods conforming to this standard when used in accordance with good manufacturing practices and in compliance with the codex guidelines for the use of flavorings (CAC/GL 66-2008). The products covered by this standard shall comply with the maximum levels of the *General Standard for Contaminants and Toxins in Food and Feed* (CODEX STAN 193-1995). The products covered by this standard shall comply with the maximum residue limits for pesticides established by the Codex Alimentarius Commission (CODEX STAN 309R-2011).

3. Aim of experiment

The aim of presented thesis was to investigate thermodynamic properies of seeds, oil and products made from sesame in term of distinguishing the genuine sesame oil and halva from the adulterated sesame products. In this purpose specific goals were set:

1. Comparison of the thermodynamic properties of sesame seeds and oils from these seeds originated from various conutries

2. Analyze the effect of extraction method of oil from sesame seeds on the thermodynamic properties

3. Analyze the effect of addition of palm olein to sesame oil on the thermodynamic parameters.

4. Comparison of the thermodynamic properties of pure sesame oil with sesame oil from sesame products (halva, tahini).

4. Materials and methods

4.1. Sample materials

For the experiment of sesame oil quality 5 different sesame samples each in 500g package with different geographical origin (Ethiopia Humera, Nigeria Masduguri, Sudan, Turkey Egean Zone) were obtained from company which exports and import sesame and other herbals and spices on international level in Turkey İZMİR, ARI SUSAM SAN. VE TIC. LTD. STI. Furthermore, 3 halva product were taken from the market which have produced by Şarkütire SAN. VE TIC. LTD. STI. İzmir Turkey. Tahini product was obtained from in a liquid form in bottled as 500dm^3 at plastic container produced by Koska SAN. VE TIC. LTD. STI İstanbul Turkey. Indian black sesame samples was obtained from Polish market produced by Helio S.A, Wyględy (Brochów Poland).

Table 6. Sesame seeds content per origin

Sesame type	**Origin**	**Amount**
Turkish sesame	Egean District	500g
Nigerian sesame	Masduguri District	500g
Sudanian sesame	Blue Nile District	500g
Ethiopian sesame	Humera District	500g
İndian Black Sesame	-	500g

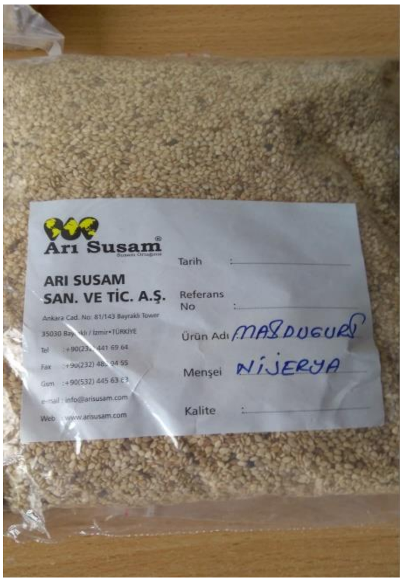
Table 7. Halva and tahini content per origin

Halva Type	**Production**	**Amount**
Halva	Turkey Izmir	500g Package
Halva with cocoa	Turkey İzmir	500g package
Halva with pistachio	Turkey İzmir	500g package
Tahini liquid	Turkey İzmir	500g Liquid

Figure 9. Sesame, halva and tahini products.

A

B



C

D

E

Figure 10. Raw sesame seed samples for analyse A. Turkish Sesame Seeds, B. Ethiopia Sesame Seeds, C.Nigeria Sesame Seeds, D. Sudan Sesame Seeds E. Indian Sesame Seeds

F G

I J

Figure 11. Halva and tahini materials for analyse F. Halva , G.Halva with cocoa, I. Halva with pistachio, J.Tahini liquid

4.1.2. Chemicals and glassware

n-Hexane CDZA was used as a solvent for determination of oil yield in raw sesame seeds produced by Polish chemical company POCH, (Gliwice Poland).

Glassware and equipments used in our experiment were produced by Sigma-Aldrich company (Missouri, ABD). Erlenmeyer flask 250cm^3, baker 500cm3, knife for slicing, magnetic stirrer, volumetric flask 1000dm^3 were used for measurements at laboratory.

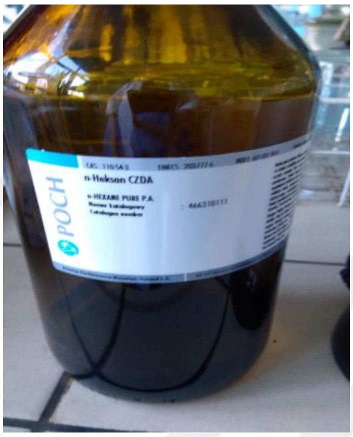


Figure 12. POCH n-hexane solvent

4.1.3. Equipments

Sieving of raw sesame seeds from foreign objects was performed by Multiserw (Brzeżnica ,Poland) automatic sieving machine. Diameter of 0.7mm, 1.0 mm, and 3.0 mm sieves has been used for sieving procedure.

Figure 13. Equipment Multiserw

Before analyte preparation, raw seed materials were homogenizated for solvent extraction by Automatic blender Magic MBR-1701 17 produced by Magic Bullet (USA).

Figure 14 . Equipment Magic Bullet MBR-1701 17

Before the extraction of raw materials sesame seeds were weighed by Sartorius MA130 produced by Sartorius, (Gottingen Germany).

Figure 15. Equipment Sartorius MA130

Dry matter analysis was performed by incubator BİNDER BD53 which has produced by Binder INC (NY USA).

Figure 16. Equipment Binder BD53

Cold pressing procedure was performed by Dulong Oil Presser DL-ZYJ06, (Nanchang, China) at cold pressing temperature.

Figure 17. Equipment Dulong DL-ZYJ06

Analytes were mixed with Chemland heating equipment produced by Chemland (Stargard Szczeciński, Poland). Stirring of analytes were performed by ENVAG stirr equipment Flocculation Tester FC65 produced by OMC ENVAG, (Warszawa, Poland).

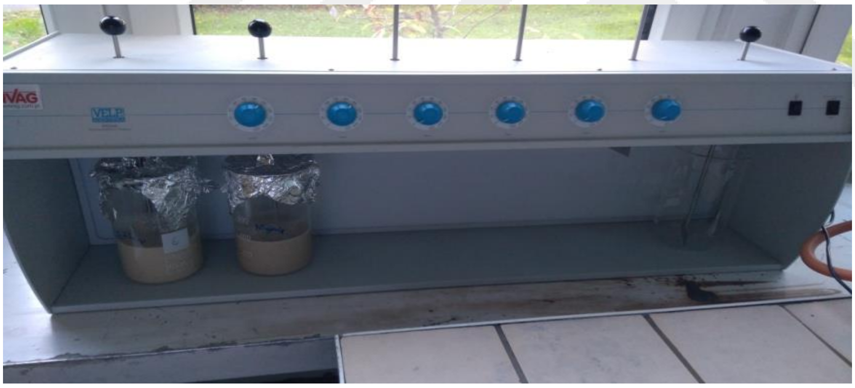


Figure 18. Equipment ENVAG stir equipment Flocculation Tester FC65

Analytes were separated and centifrugated from the sediments by Janetzki K70 centrifuge equipment.

Figure 19. Equipment Janetzki K70 Heavy Duty Centrifuge

Evaporation of n-Hexane from analyte was performed by LABAROTA 4003 equipment produced by LabX **(**Midland, ON, Canada).

Figure 20. Equipment Labarota 4003

Determination of temperature and enthalpy of melting and crystallization was performed by differential scanning calorimetry (DSC 7) which has been produced by Perkin Elmer,) and results were performed with Pyris Series software.

Figure 21. Differential Scanning Calorimeter DSC7

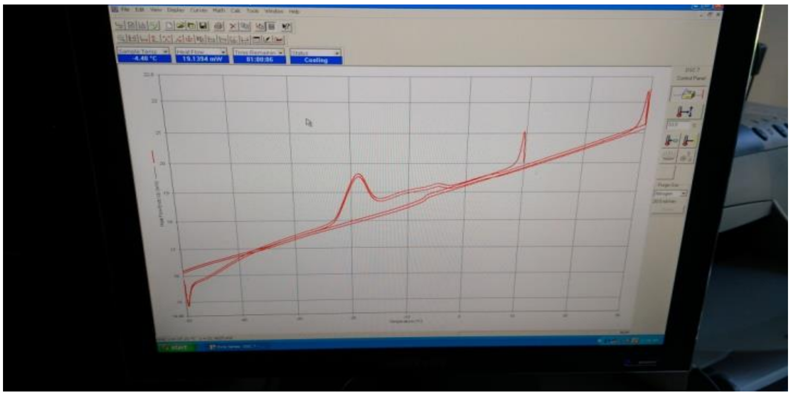


Figure 22. Software pyris series DSC 7

4.2. Methods

4.2.1. Determination of dry matter content

Sample materials were obtained from producer and sieved for elimination of foreign objects and particles. Multiserw automatic sieving machine was used to perform the process with sieve diameters of 0.7mm, 1.0 mm and 3.0 mm.

Determination of dry matter content was performed by incubator model Binder BD 53 and weighed by Sartorius MA130 sensitive laboratory scale. Samples of 2 grams has been weighed into a Petri dishes before drying into incubator for 2 days at 130 ℃ . Two replication of each sample were performed.Water and dry matter content have been calculated after measurements.

$$\text{Dry Matter \%} = \frac{\text{Dry sample weight (g)}}{\text{Wet sample weight (g)}}\ x\ 100$$

Figure 23. Dry matter content formula

4.2.2. Determination of oil yield

Determination of oil yield and extraction of oil samples were performed by cold press and hexane extraction methods. Oil yield was calculated according to formula which is given below.

$$\text{Percentage yield of oil} = \frac{\text{Weight of oil (g)}}{\text{Weight of sample (g)}}\ x\ 100$$

Figure 24. Oil yield formula (Nkafamiya, I. I. at all., 2010)

4.2.3. Hexane extraction method of oil for sesame seeds and halva products

Sesame seeds were weighed by equipment Sartorius MA130 laboratory scale. Oil from seeds of different origin was extracted. For each extraction 50 grams of seeds were weighed. Subsequently they have been blended by the automatic blender Magic MBR-1701 17 for 2 minutes. After blending it was transferred into 500 dm^3 baker and n-Hexane was added 1:3 (w/v) into blended sample. Analytes were heated on Chemland heating equipment approximately at 40-50 °C for 1-2 minutes. Samples were stirred under 30-45 rpm rotation for an hour (Ferreria-Dias at al, 2003) with equipment ENVAG Flocculation Tester FC65. After the process was done, analytes were separated from the sediments and transferred into centrifugation tubes. Equipment Janetzki K70 has been used for 20 minutes at 20000 rpm rotation. Final extract was obtained and transferred into flask of 500 ml for evaporation of the n-hexane from oils under the 330 mbar pressure at 40-45 °C (by Heidolph LABAROTA 4003 equipment). Oils have been obtained respectively at the end of the work. This method of extraction was used also for analysis of halva products and tahini liquid sample.

4.2.4. Cold press extraction method of oil from sesame seeds

Samples 150 grams of seeds were weighed (by equipment Sartorius MA130). Samples were pressed with Dulong oil presser DL-ZYJ06 at 39-45 ^{0}C cold pressing temperature. Extraction was measured with thermometer instantly. After the extraction of samples, they were bottled into light resistant brown glass bottles and stored in a refrigerator at -20 ^{0}C for a week for the analysis to be performed.

4.2.5. Differential scanning calorimetry (DSC) method

A Perkin Elmer DSC 7 differential scanning calorimeter (Perkin Elmer, Norwalk) equipped with an Intracooler II and running under Pyris software was used to examine the melting properties of sesame oils, seeds and sesame products. Nitrogen (99.999% purity) was the purge gas. The DSC calorimeter was calibrated using indium (m.p. 156.6 °C, ΔHf=28.45 J·g^{-1}) and n-dodecane (m.p. -9.65 °C, ΔHf=216.73 J·g^{-1}). Samples of sesame oil, groud seeds or sesame product (5-10 mg) were weighed into aluminum pans of 20 μL (Perkin Elmer, No. 0219-0062) and hermetically sealed. The reference was an empty, hermetically sealed aluminum pan. The sample pan was placed in the calorimeter at 10 °C were analyzed according to the temperature program:

1) Cooling from + 10 °C to -50 °C at +20°C/min.
2) Isotherm at -50°C for 1 minute.
3) Heating from -50°C to +30°C at 5°C /min
4) Isotherm 1min at +30°C
5) Cooling from +30°C to -50°C at 5°C/min
6) Isotherm for 1 min at -50°C
7) Heating from -50 °C to 30 °C at 5°C/min

Two replicates were analyzed for each sample. The following parameters were analyzed from the first and second melting DSC curve: T- peak temperature, enthalpy of melting ΔH ($J \cdot g^{-1}$) determined as the area limited by the melting curve and the base line. International standard method (ISO 11357-3:2011) was used for analysis of determination of temperature and enthalpy of melting and crystallization in sesame oil and (*Sesamum İndicum L.*) seed samples.

4.2.5.1. Preparation of sesame oil samples blended with palm olein for DSC analysis

Twenty percent (20 %) of palm olein was added into each sesame oil extracted by hexane sample tubes up to 1g. Tubes were vortexed at 2000 rpm rotation by instrument Velp Scientifica Wizard Advanced IR vortex (Usmate ,Italy) and stored at +4ºC refrigerator temperature for 2-3 days before the analysis. Before the DSC analysis samples were heated by Falc Instruments (Treviglio, Italy) model Thermo-E 2013.

4.3. Statistical analysis

Statistical analyse is a method which is used extensively in science for precision of results.In this experiment method of Tukey test had chosen for analyzing the samples results. This method can provide an approximation for differences between the samples. 5 type of seed samples was obtained from different origin of seeds. Sesame seeds extracted by two different method, sesame seeds and oils from these extractions was analysed by DSC hardware. Results of DSC was interpreted in DSC software. Datas from DSC software were collected. Standard deviations and mean values were calculated after two times repetition. Mean values was analysed by Statsoft Statistica 13.3 software.

Analysis of variance was performed (ANOVA) for evaluate whether there were any evidence that the mean values of the sesame seeds differed. When the mean values of samles differs Tukey's test compares the difference between each pair of means with appropriate adjustment for the multiple testing. The results are presented as a matrix showing the result for each pair, either as a P-value or as a condence interval (Crichton, 1999). Tukey's multiple comparison test is one of several tests that can be used to determine which means amongst a set of means differ from the rest. Tukey's multiple comparison test is also called Tukey's honestly signifcant difference test or Tukey's HSD (Crichton, 1999)

Tukey's test was performed on sesame pure seed oils for comparision of different method of extraction. Thermodynamic parameter datas after first and second heating of sesame seeds were collected and results were analysed also by statistical software. Pure oil and palm olein additional sesame seed oils compared with Tukey's test and results interpreted on tables at results section.

5. Results

5.1. Characterisation of composition of sesame seeds

Dry matter and water content results are shown in the table 8. Origin of sesame seeds has not statistically significant influence on the dry matter and water contents of seeds. Differentiation was not observed via origin of seeds.

Table 8. Dry matter and water content of sesame seeds

Origin of seeds	**DM %**	**Water content %**
Turkish Sesame Seed	95.09 ^{a}±0.45	4.91 ^{a}±0.45
Sudan sesame seed	94.75 ^{a}±0.50	5.25 ^{a}±0.50
Nigeria sesame seed	94.84 ^{a}±3.32	5.16 ^{a}±3.64
Ethiophia sesame seed	93.89 ^{a}±0.97	6.11 ^{a}±0.97
İndian sesame seed	94.16 ^{a}±0.44	5.83 ^{a}±0.44
Total Mean Value	95.01±1.70	4.90 ±0.66

a,b, - small letters indicate significant differences between values in columns , α=0,05
A, B- big letters indicate significant differences between values in rows , α=0,05

Results of dry matter and water content dose not show big differences between the seeds with various origin. Highest percentage of dry matter was observed in Nigerian seed and lowest was in Ethiophian seed. Water content of Ethiophian seed was highest and lowest was Turkish seed.

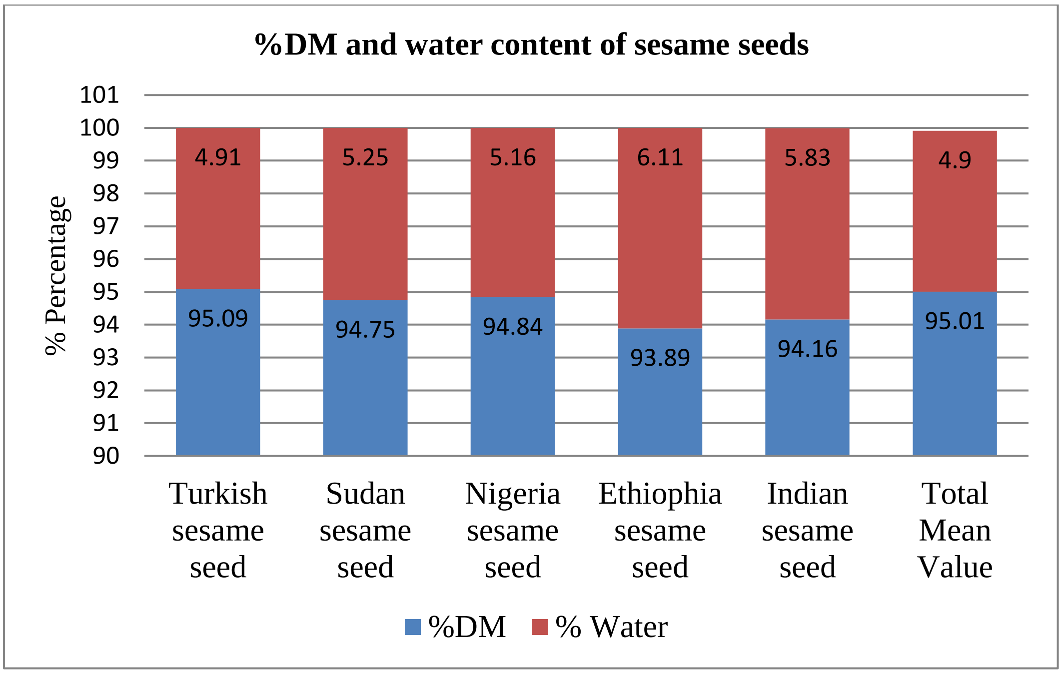


Figure 25. Dry matter and water content of sesame seeds in percentages

Results of table 8 were demonstrated as percentage % at figure 25. Ethiophian variety has shown highest water content in turn lowest water content was observed in Turkish sesame seeds.

Yield of oil via two different extraction methods were demonstrated at figure 26. Method of extraction may affect the oil yield. Results showed that lower oil yield was obtained from the cold pressing method. Cold pressing method has shown lower oil yield than hexane method. Temperature of extraction about 40 °C and time of extraction of 2h are the factors increasing efficiency of extraction, because n-hexane was interfered with the oil in the seeds more sufficiently. Highest yield of cold pressing has been observed at Nigeria variety and lowest were at Sudan variety. Highest yield of hexane extraction was observed at Indian variety and lowest were at Ethiopian variety.

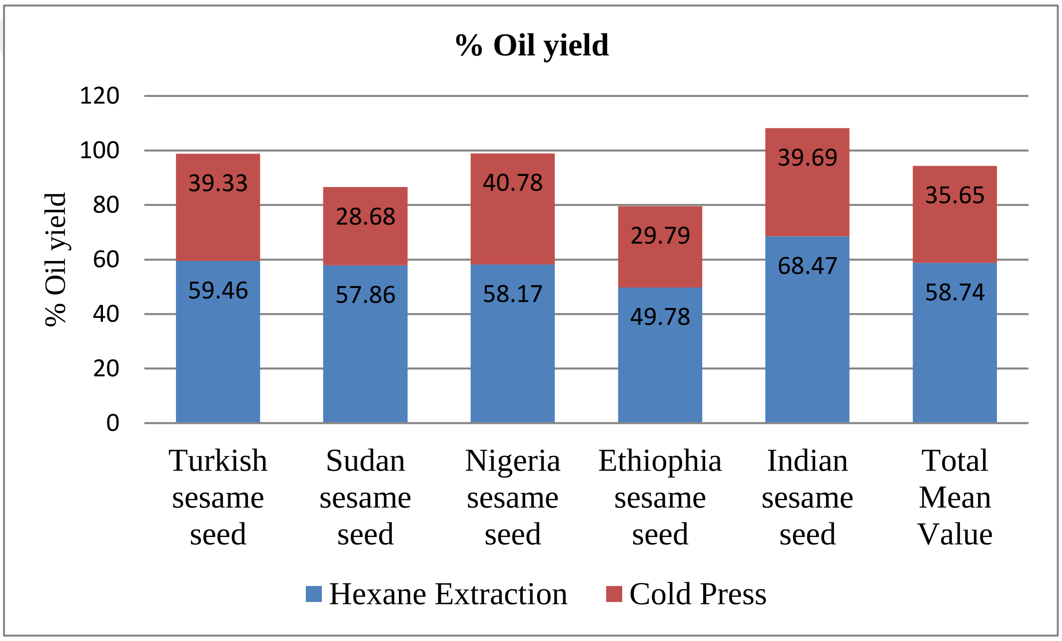


Figure 26. Oil yield of sesame seeds by cold pressing and hexane extraction

5.2 Fatty acid content of sesame seeds

Fatty acid content of oils was also analyzed. Saturated, monounsaturated and polyunsaturated fatty acid composition of oils was obtained and shown.

5.2.1. Saturated fatty acid content of sesame seeds and sesame products oils

Saturated fatty acid content of products was described at this section which was detected by fatty acid analysis.

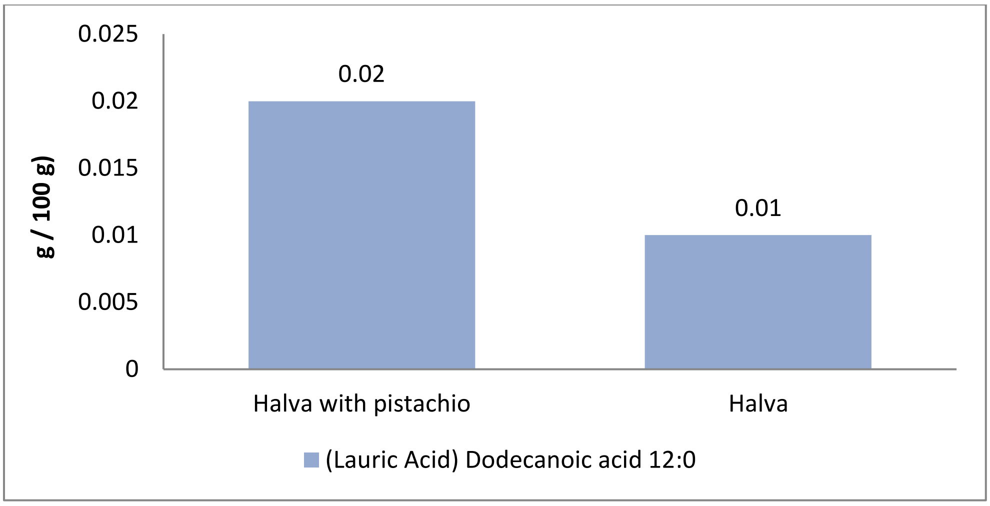


Figure 27. Lauric acid content of sesame seeds and sesame products oils

Lauric acid content of the sesame products was demonstrated at figure 27. Lauric acid was detected only in sesame products samples: halva with pistachio and halva. Consequently results of halva with pistachio showed the highest amount of lauric acid profile than halva. In others samples of pure sesame oils content of lauric acid was not detected.

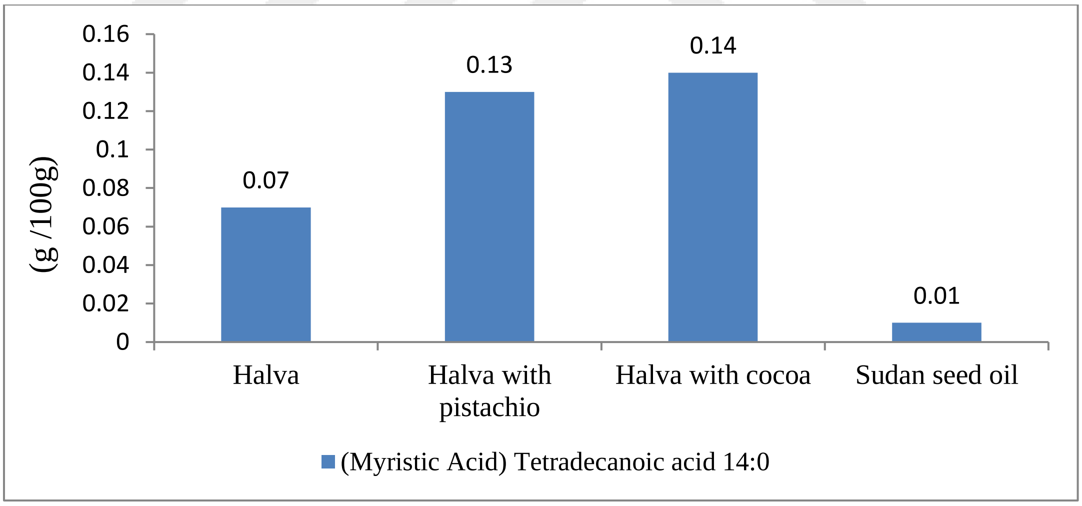


Figure 28. Myristic acid content of Sesame seeds and sesame products oils

Myristic acid content in the sesame products was demonstrated at figure 28. Myristic acid was detected only in samples of halva, halva with pistachio, halva with cocoa and Sudan seed oil. Consequently a result of halva with cocoa showed highest amount of myristic acid and lowest amount was in Sudan oil sample.

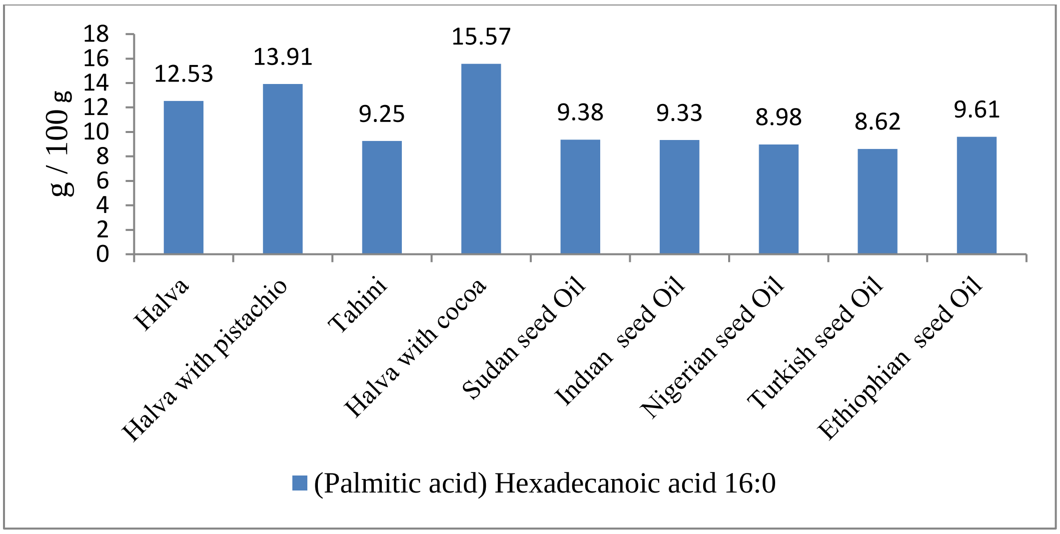


Figure 29. Palmitic acid content of sesame seeds and sesame products oils

Palmitic acid content in the sesame oils and sesame products was demonstrated at figure 29. Palmitic acid was detected in all samples. Consequently a result of halva with cocoa showed highest amount of palmitic acid and lowest amount was in Turkish sesame oil.

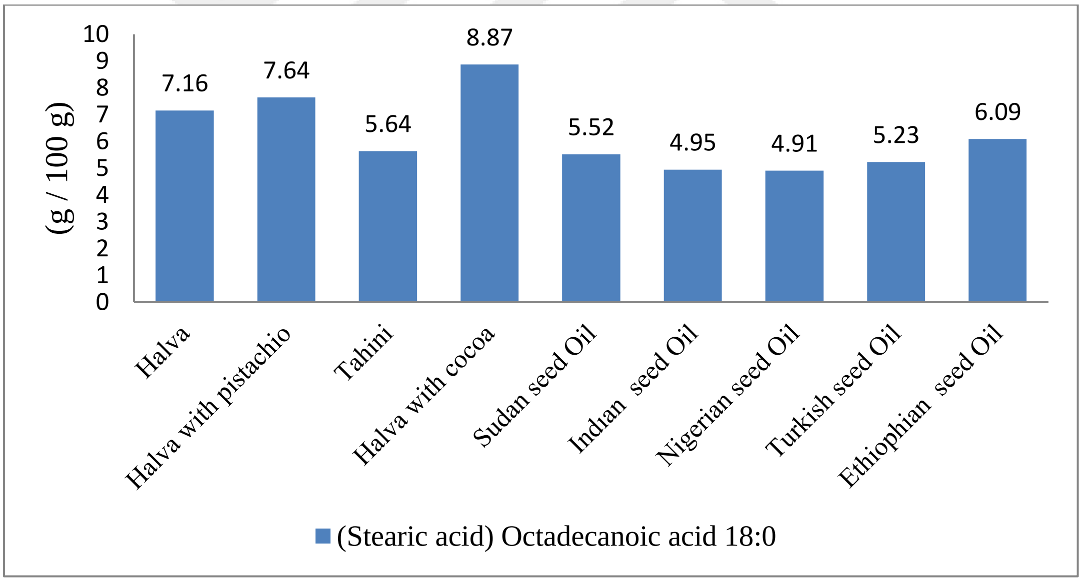


Figure 30. Stearic acid content of sesame seeds and sesame products oils

Stearic acid content of the sesame oils and products was demonstrated at figure 30. Stearic acid was detected in all samples of oils and sesame products. Consequently results of halva with cocoa showed highest amount of stearic acid and lowest amount was in Nigerian sesame oil.

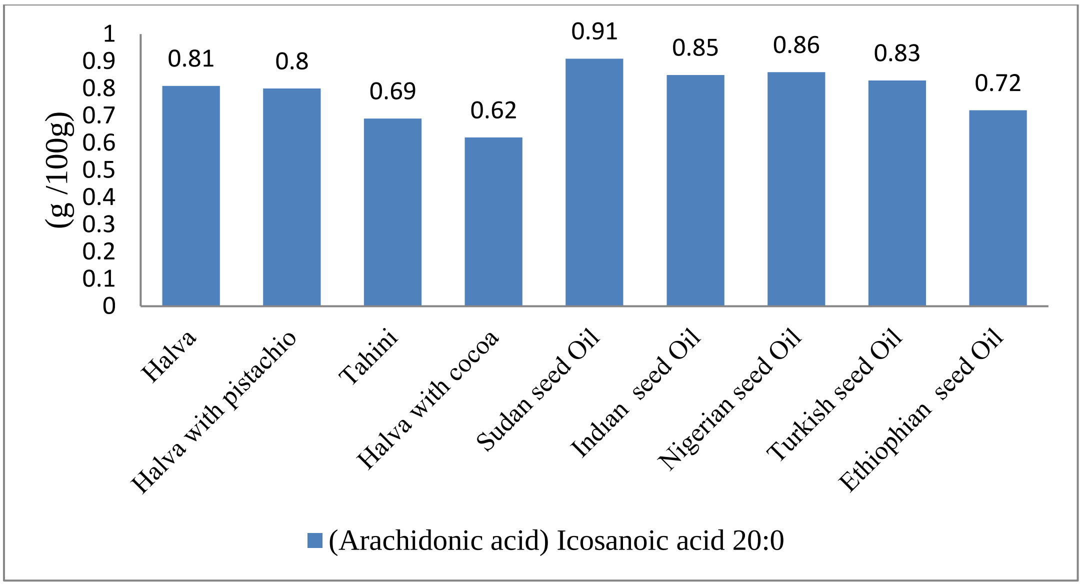


Figure 31. Arachidic acid content of sesame seeds and sesame products oils

Arachidonic acid content of the sesame oils and sesame products was demonstrated at figure 31. Arachidonic acid was detected in all samples of oils and products. Results of Sudan sesame oil showed the highest amount of arachidonic acid and lowest amount was in halva with cocoa.

5.2.2. Monounsaturated fatty acid content of sesame seed oil and sesame products oils

Monounsaturated fatty acid content of sesame seeds and sesame products oils is demonstrated in this section.

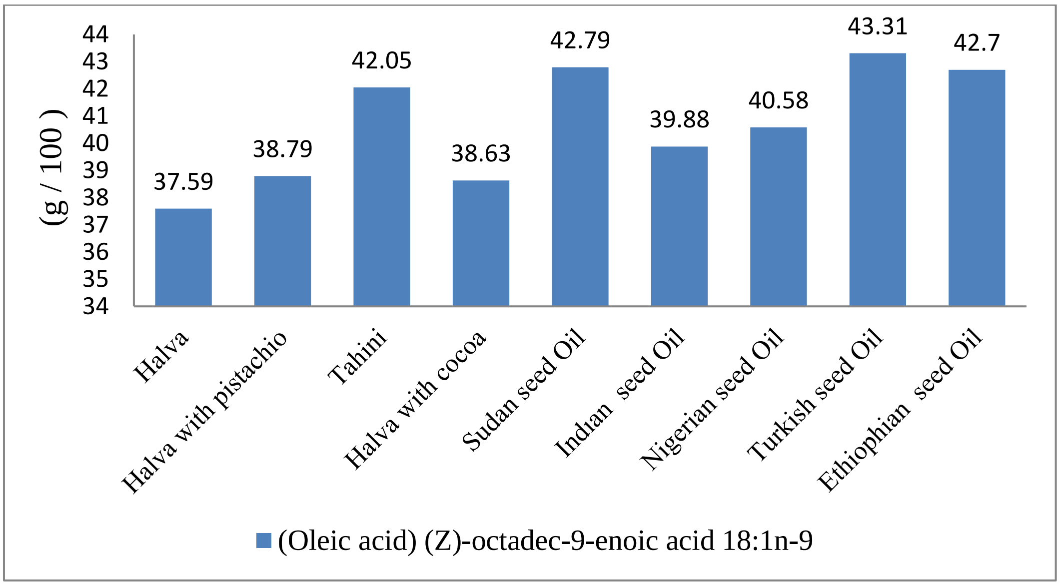


Figure 32.Oleic acid content of sesame seed and sesame products oils

Oleic acid content of the sesame seeds is demonstrated at figure 32. Oleic acid acid was detected in all samples. Consequently results of Turkish seed oil showed the highest amount of oleic acid and lowest amount was in halva.

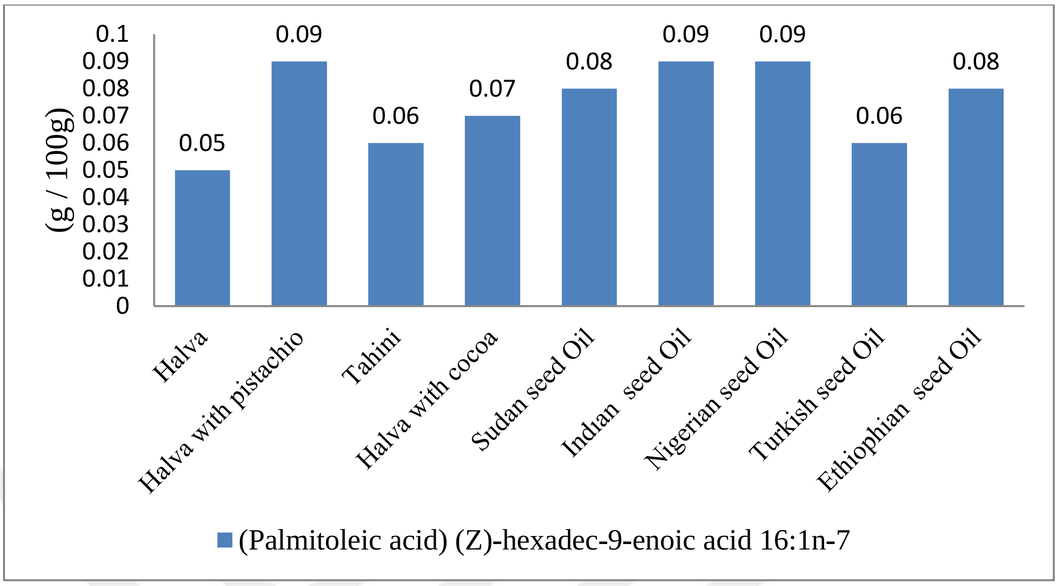


Figure 33. Palmitoleic acid content of sesame seed and sesame product oils

Palmitoleic acid content of the sesame seeds was demonstrated at figure 33. Palmitoleic acid has been detected in samples. Consequently results of halva with pistachio, Indıan seed oil and Nigerian seed oil showed the highest amount of palmitoleic acid and lowest amount was in halva sample.

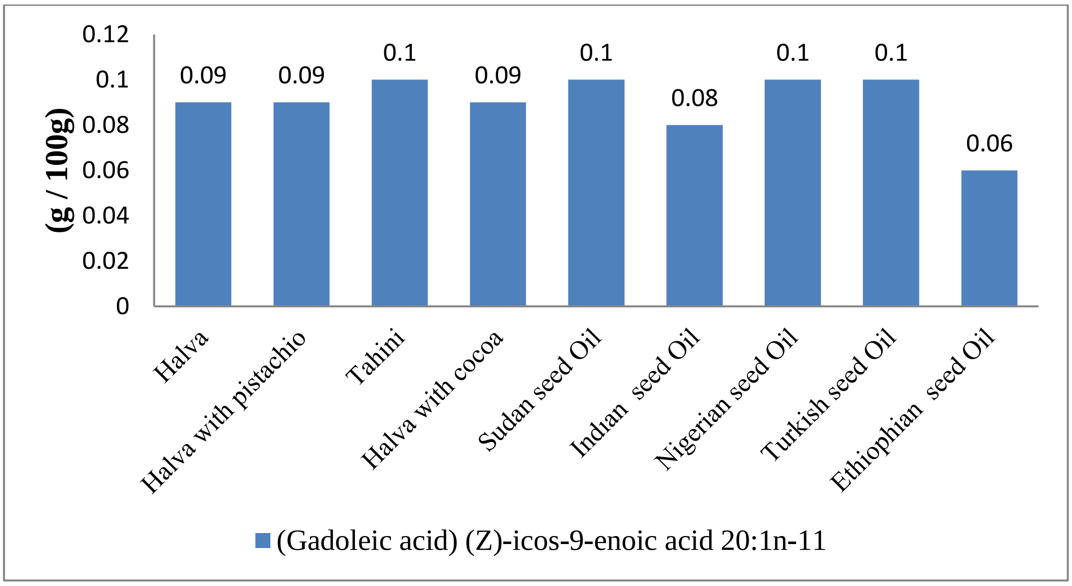


Figure 34. Gadoleic acid content of sesame seed oil and sesame product oils

Gadoleic acid content of the sesame seeds was demonstrated at figure 34. Gadoleic acid was detected in samples. Consequently results of tahini, Sudan seed oil, Nigerian seed oil and Turkish seed oil showed the highest amount of gadoleic acid and lowest amount was in Ethiophian seed oil.

5.2.3. Polyunsaturated Fatty Acid Content Of Sesame Seed Oil and Sesame Product Oils

Polyunsaturated fatty acid contents of sesame seed and sesampe product oils are demonstrated in this section.

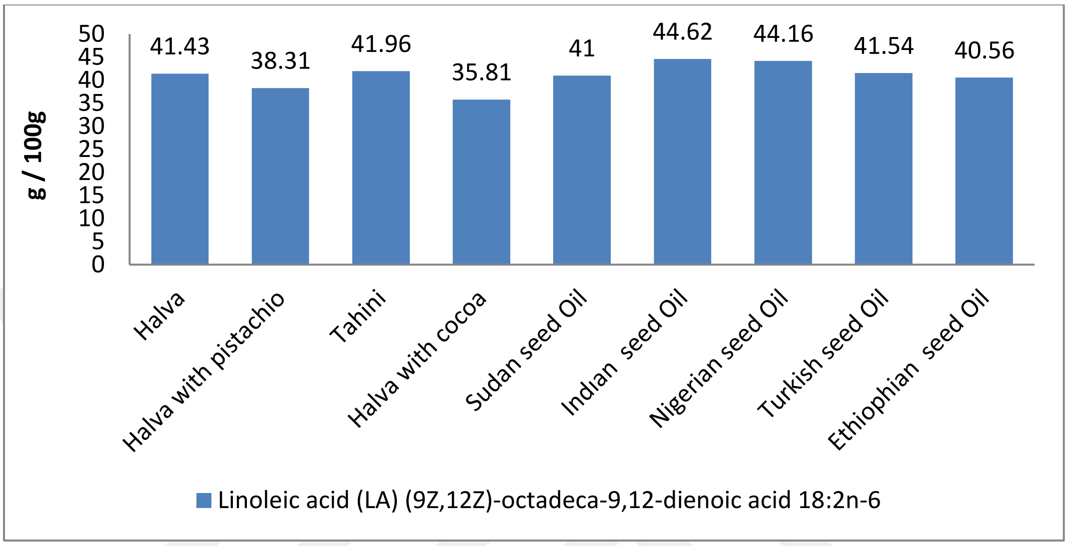


Figure 35. Linoleic acid content of sesame seed oil and sesame product oils

Linoleic acid content of the sesame seeds is demonstrated at figure 35. Linoleic acid was detected in all samples. Results of Indian oil showed the highest amount of linoleic acid and lowest amount was in halva with cocoa sample.

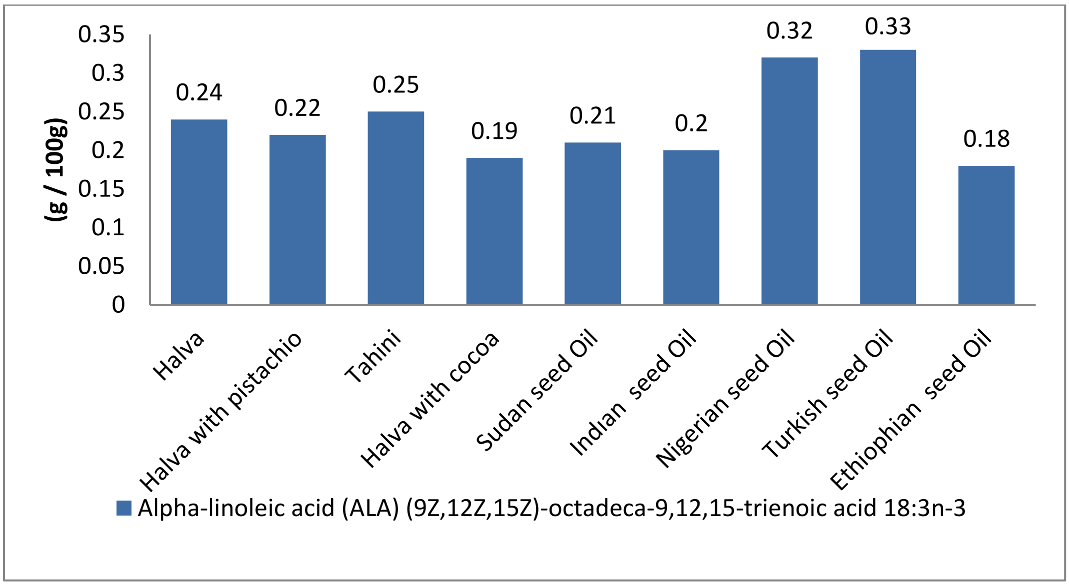


Figure 36. Alpha-linolenic acid content of sesame seed oil and sesame product oils

Alpha-linoleic acid content of the sesame seeds is demonstrated at figure 36. Alpha-linoleic acid was detected in all samples. Results of Turkish seed oil showed the highest amount of alpha-linoleic acid and lowest amount was in Ethiopian oil sample.

5.3. Thermodynamic properties of sesame seeds

Method of differential scanning calorimetry (DSC) was used to analyse thermodynamic properties of crushed sesame seeds. In Table 9 the results of first and second cycle of heating (first and second melting) are presented. It is showed that those thermodynamic properties (peak temperature and enthalpy) didn’t differ significantly between oil samples of various origin both for the first and second melting. In sesame seeds oils triacyloglicerols are the major important chemical components which has an effect on melting profile Significant differences have not been observed also between the mean values of the first heating peak temperatures and enthalpies and second heating peak temperatures and enthalpies.

Table 9. Thermal properities of sesame seeds

Origin of Seed	**1st Heating**		**2nd Heating**	
	Tpeak (▫C)	**Enthalpy ΔH (J/g)**	**T peak (▫C)**	**Enthalpy ΔH (J/g)**
Turkish Sesame Seed	-19.67^{a} ± 0.92	20.34^{a} ± 7.42	-20.61^{a} ± 1.30	22.51^{a} ± 4.31
Indian Sesame Seed	-19.11^{a} ± 0.79	23.66^{a} ± 1.78	-19.27^{a} ± 0.39	24.04^{a} ± 2.25
Nigerian Sesame Seed	-19.62^{a} ± 0.38	26.97^{a} ± 1.19	-20.17^{a} ± 0.36	27.27^{a} ± 2.25
Ethiophian Sesame Seed	-18.4^{a} ± 0.63	24.67^{a} ± 1.32	-19.33^{a} ± 0.70	23.76^{a} ± 0.02
Sudan Sesame Seed	-19.1^{a} ± 0.87	24.05^{a} ± 1.15	-19.54^{a} ± 1.61	24.41^{a} ± 1.56
Total Mean Value	-19.17^{A} ±0.74	23.91^{A} ±3.34	-19.64^{A} ±0.87	24.58^{A} ±2.52

a,b, - small letters indicate significant differences between values in columns , $\alpha=0,05$

A, B- big letters indicate significant differences between values in rows , $\alpha=0,05$

Results wasn’t shown differences between the ethalpies and T peak temperatures of seeds at first and second cycle of heating.

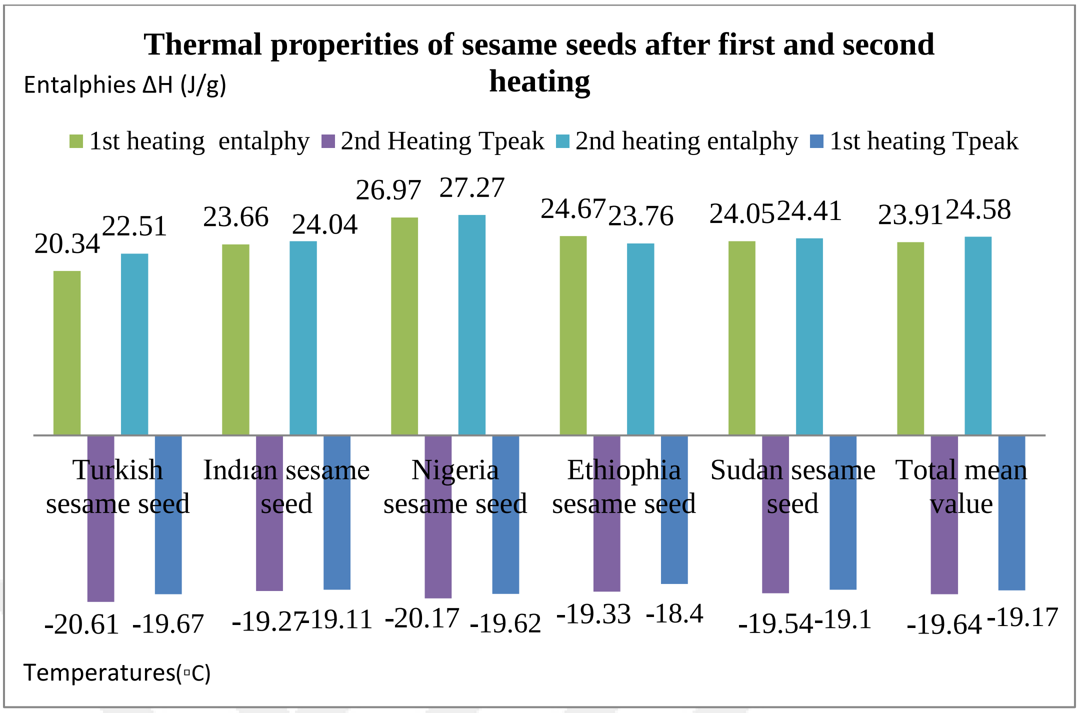


Figure 37. Thermal properities of sesame seeds

Results of thermal properties of sesame seeds shown in table 9 were also demonstrated as graph at figure 37 (Entalphies and temperatures of first and second heating).

5.4.Thermal properities of oils extracted from sesame seeds

Technique of differential scanning calorimetry (DSC) was used also to compare thermodynamic properties of sesame oils extracted by two different method. Hexane extraction and cold pressing method were applied to samples of different origin seeds to obtain pure oil. In table 9 results of comparison of both methods of thermodynamic properties obtained after first heating are shown. Generally there were no diffrences between parameters of peak temperature for sesame seeds of diffrenet origin for both methods. In case of enthalpy significant diffreneces were observed between samples of different origin, in turn for enthalpy analyzed for oils samples extracted by hexane differences were not significant. Origin of seeds had no significant influence on temperature values of first heating with different methods. Enthalpies of hexane extraction method didn’t show difference via origin seeds, but results of enthalpy obtained for cold pressing extraction samples were divided into 4 differentgroups. By hexane extraction method pure oil is obtained and, by cold pressing other than triacylglycerols substances are extracted which might be reason for the diffreneces. Comparing mean values of peak temperatures and enhalpies obtained for both methods of extraction significant diffrenecs were observed, so it could be geneally stated that extraction method has significant influence on thermodynamic properties of extracted oils.

Table 10. Thermal properities obtained after first heating of oils extracted by two different methods.

Origin of oils	**Cold pressed sesame seed oil**		**Hexane extracted sesame seed oil**	
	Temperature T peak (▫C)	**Enthalpy ΔH (J/g)**	**Temperature T peak (▫C)**	**Enthalpy ΔH (J/g)**
Turkish sesame Oil	-18.89^{a} ± 0.33	41.88^{c} ± 1.30	-19.41^{a} ± 0.19	43.80^{a} ± 0.45
Indıan sesame Oil	-19.30^{a} ± 0.38	33.94^{a} ± 0.23	-19.54^{a} ± 0.72	40.78^{a} ±2.38
Nigerian sesame Oil	-19.24^{a} ± 0.62	39.60^{b,c} ± 0.60	-19.25^{a} ± 0.31	40.74^{a} ± 0.45
Ethiophian sesame Oil	-19.20^{a} ± 0.80	39.48^{b,c} ± 0.49	-20.25^{a} ± 1.15	42.36^{a} ± 3.45
Sudan sesame Oil	-18.63^{a}± 0.14	35.68^{a,b} ±2.25	-21.00^{a}± 0.35	42.63^{a} ± 1.10
Total Mean Value	-19.01^{B}± 0.46	37.89^{A} ±3.18	-19.83^{A}± 0.82	41.83^{A} ±1.95

a,b, - small letters indicate significant differences between values in columns , α=0,05
A, B- big letters indicate significant differences between values in rows , α=0,05

Results of first heating thermal properities of oils samples obtained by two extraction methods are demonstrated also at figure 38.

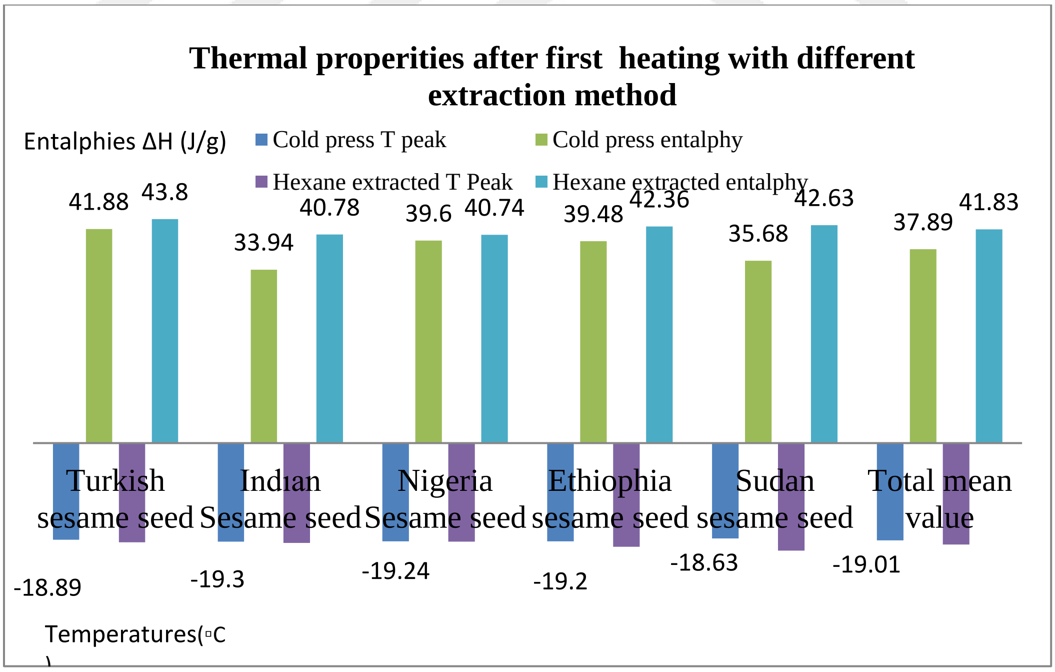


Figure 38. Comparision of thermal properities obtained after first heating of oils extracted by two different methods.

Results obtained after second heating are shown in table 11. Similarly as results in table 10, first peak temperatures and enhalpies of oils samples of diiferent origin were statistically analyzed. As in the first heating origin of seeds has no significant influence on peak temperature for both methods. Also values of enthalpy of hexane extraction method have showed no differences between seeds origin, although enhalpies for cold pressing samples were statistically divided into three different groups. Similarly as in the case of first heating method of extraction has no significant effect on the mean value of enthalpy but significant differences were observed for peak temperatures.

Table 11. Comparision of thermal properities obtained after second heating of oils extracted by different methods

Origin of oils	**Cold pressed sesame seed oil**		**Hexane extracted sesame seed oil**	
	Temperature T peak (▫C)	**Enthalpy ΔH (J/g)**	**Temperature T peak (▫C)**	**Enthalpy ΔH (J/g)**
Turkish sesame oil	-18.98 ^{a} ± 0.47	43.08 ^{b} ± 2.97	-19.49 ^{a} ± 0.01	43.51 ^{a} ± 0.26
Indıan sesame oil	-19.82 ^{a} ±0.28	34.97 ^{a} ± 0.31	-20.91 ^{a} ± 1.18	40.78 ^{a} ± 3.08
Nigerian sesame oil	-19.14 ^{a} ± 0.67	42.68 ^{b} ± 0.25	-19.38 ^{a}± 0.10	39.04 ^{a} ± 0.73
Ethiophian sesame oil	-19.19 ^{a} ± 0.81	38.47 ^{a,b} ±1.59	-20.27 ^{a} ±1.40	41.70 ^{a} ± 3.62
Sudan sesame oil	-18.44^{a} ±0.32	35.11 ^{a} ± 2.19	-20.37 ^{a} ±1.13	40.47 ^{a} ± 2.70
Total mean value	-19.05 ^{B}0.63	38.52 ^{A} ± 3.97	-20.02 ^{A} ± 0.92	40.91 ^{A} ± 2.38

a,b, - small letters indicate significant differences between values in columns , α=0,05
A, B- big letters indicate significant differences between values in rows , α=0,05

Statistical results of second heating thermal properities were also showed at figure 39 .

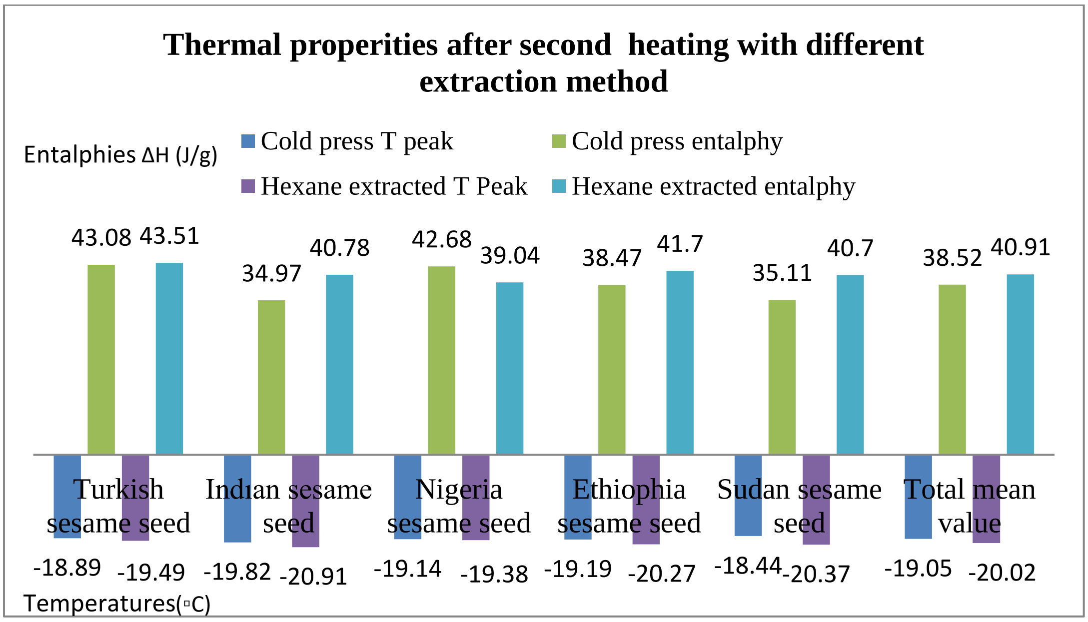


Figure 39. Comparision of thermal properities obtained after second heating of oils extracted by two different methods

5.5. Effect of addition of palm olein to sesame oil on the thermodynamic properties

Method of differential scanning calorimetry (DSC) was used to analyse first heating temperatures and enthalpies after first and second heating of hexane extracted sesame oil blended with 20 % of palm olein (w/w). Results of first heating are shown at table 12. Temperature of two peaks was detected (Tpeak, T2) and parameter of half width of first peak Tpeak (T1/2). Parameter of first peak temperature (Tpeak) didn't show significant differences in term of origin of sesame seeds and in term of addition of palm olein. However significant differences were observed for parameter of second peak temeperature (T2) and half width (T1/2) between mean values of pure sesame oil and sesame oil blended with palm olein. Addition of palm olein to sesame oil changed the melting profile of triacyloglycerols due to different fatty acids composition.

Table 12. Effect of addition 20 % of palm olein to sesame oil on first heating temperature of melting transitions properities

Origin of oils	**Hexane extracted sesame oil without palm olein**			**Hexane extracted sesame oil with %20 palm plein**		
	Temperature T peak (▫C)	Peak half width T1/2	Temperature T2	Temperature T peak (▫C)	Peak half width T1/2	Temperature T2
Turkish sesame oil	-19.37 ^{a} ± 0.24	2.95 ^{a} ± 0.29	-5.94 ^{a} ± 0.01	-19.33 ^{ab} ± 0	4.04 ^{a} ± 0.05	-5.57 ^{a} ± 0.48
Indian sesame oil	-19.54 ^{a} ± 0.72	2.30 ^{a} ± 0.47	-6.25 ^{a} ± 1.10	-20.69 ^{c} ± 0.36	4.35 ^{a} ± 0.27	-5.50 ^{a} ± 0.53
Nigerian sesame oil	-19.34 ^{a} ± 0.38	2.70 ^{a} ± 0.13	-5.36 ^{a} ± 0.09	-18.28 ^{a} ± 0.33	4.16 ^{a} ± 0.03	-3.91 ^{a} ± 0.20
Ethiophian sesame oil	-20.25 ^{a} ± 1.15	3.75 ^{a} ± 0.62	-6.35 ^{a} ± 1.01	-19.13 ^{ab}± 0.02	4.72 ^{a} ± 0.26	-5.09 ^{a} ± 1.01
Sudan sesame oil	-21.00 ^{a} ± 0.35	2.91 ^{a} ± 1.46	-7.12 ^{a} ± 0.38	-18.87 ^{ab}± 0.98	4.96 ^{a} ± 0.46	-4.86 ^{a} ± 0.57
Total mean value	-19.90^{A}± 0.83	2.92 ^{A} ± 0.75	-6.11 ^{A}± 0.85	-19.26 ^{A}± 0.91	4.52 ^{B} ± 0.36	-4.99 ^{B}± 0.78

a,b, - small letters indicate significant differences between values in columns , α=0,05
A, B- big letters indicate significant differences between values in rows , α=0,05

Effect of addition of 20 % of palm olein to sesame oil on first heating temperatures was shown at figure 40.

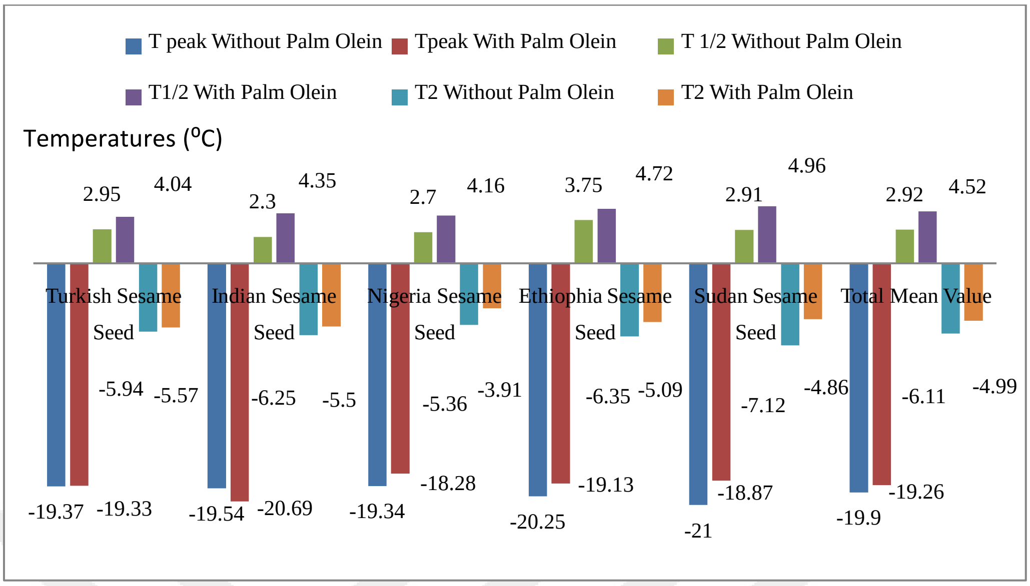


Figure 40. Effect of addition 20 % of palm olein to sesame oil on first heating temperatures of melting transitions

Method of differential scanning calorimetry (DSC) was used to analyse the enthalpies of first heating melting transition. Results were showed at table 13. Statistical data from enthalpies of the first heating of hexane oils with palm olein and without palm olein were showed at table 13 and demonstrated at fig 39. Each enthalpy type ΔH, ΔH1 and ΔH 2 were compared together with its equivalent.

Table 13. Entalphies of first heating of the pure sesame oil and with palm olein

Origin of oils	**Hexane extracted sesame oil without palm olein**				**Hexane extracted sesame oil with %20 palm olein**			
	Total Enthalpy ΔH [J/g]	**Enthalpy of first peak ΔH1[J/g]**	**Enthalpy of second peak [J/g] ΔH2**	**percent of first peak %**	**Enthalpy ΔH [J/g]**	**Enthalpy of first peak ΔH1 [J/g]**	**Enthalpy ΔH2 of second peak [J/g]**	**% ercent of first peak %**
Turkish sesame Oil	43.80^{a} ± 0.45	37.41^{a} ± 0.32	6.38^{a} ±0.78	85.43^{a} ±1.64	38.32^{a} ±1.11	28.15^{a} ±0.21	10.16^{a} ±0.89	73.49^{a} ±1.56
Indian sesame Oil	37.85^{a} ± 0.87	33.24^{a} ± 2.11	2.83^{a} ±1.24	87.78^{a} ±3.62	39.78^{a} ±1.11	30.05^{a} ±0.94	9.73^{a} ±0.17	75.52^{a} ±0.24
Nigerian sesame Oil	40.62^{a} ± 0.56	35.66^{a} ± 1.42	4.95^{a} ±0.85	87.78^{a} ±2.27	34.12^{a} ±0.44	23.85^{a} ±1.02	10.27^{a} ±0.57	69.89^{a} ±2.07
Ethiophian sesame Oil	42.36^{a} ± 3.45	37.07^{a} ± 4.07	5.29^{a} ±0.62	87.41^{a} ±2.50	36.34^{a} ±0.90	27.19^{a} ±1.43	9.15^{a} ±0.53	74.79^{a} ±2.08
Sudan sesame Oil	42.63^{a} ± 1.10	37.35^{a} ± 1.99	5.28^{a} ±0.88	87.57^{a} ±2.40	34.42^{a} ±2.85	24.92^{a} ±2.80	9.50^{a} ±0.05	72.31^{a} ±2.14

Total mean value	41.45^{B} ±2.52	36.15^{B} ±2.41	4.95^{A} ±1.39	87.20^{B} ±2.13	36.60^{A} ±2.57	26.83^{A} ±2.61	9.76^{B} ±0.59	73.20^{A} ±2.48

a,b, - small letters indicate significant differences between values in columns , α=0,05

A, B- big letters indicate significant differences between values in rows , α=0,05

There were no significant differences between enhalpies values (ΔH, ΔH1, ΔH2) in term of origin of sesame seeds for both: pure oil and oil with palm olein). Compariing mean values of enhalpies in can be seen that for all parameters of enhalpies there were significant differences samples of pure sesame oil and oil with palm olein what means that addition of palm olein has significant effect on the enthalpies of melting transition, Palm olein addition has changed the melting profile of triacyloglycerols due to different fatty acids composition. When melting profile and enthalpy is changed, oil it may indicate that sample of oil is adulterated. İt is a remarkable result which helps to understand profile of oils. In industry sometimes oils are adulterated by the different oils, low production and high cost of sesame oil makes it valuable oil and prone to adulterations.

Small differences were not observed at first heating entalphies of both samples. Big differences were observed between the ΔH, ΔH1, ΔH2 and total percentage of both samples in terms of palm olein addition.

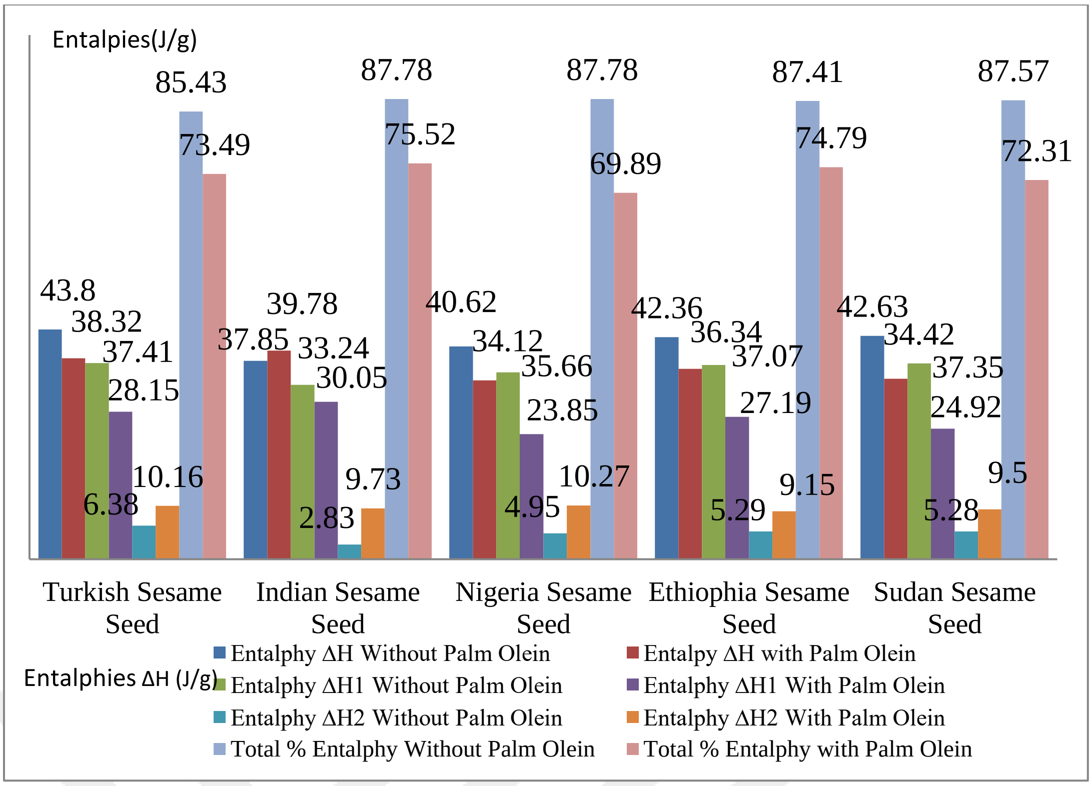


Figure 41. Enthalpies of melting transition from the first heating of pure sesame oil and oil with palm olein

Effect of addition of 20 % of palm olein to sesame oil on first heating enthalpies was shown at figure 41. Each enthalpy type ΔH, ΔH1, ΔH2 and total percentage were compared together with its equivalent.

Method of differential scanning calorimetry (DSC) was used to analyse second heating temperatures and enthalpies after first and second heating of hexane extracted sesame oil blended with 20 % of palm olein (w/w). Results of second heating are shown at table 14. Temperature of two peaks was detected (Tpeak, T2) and parameter of half width of first peak Tpeak (T1/2). Parameter of first peak (T peak) tempearature and peak half width (T1/2) of palm olein showed slightly differences. Parameter of first peak temperature (Tpeak) and (T2) didn’t show significant differences in pure sample. However significant differences were observed for parameter of half width (T1/2) between mean values of pure sesame oil and sesame oil blended with palm olein. Addition of palm olein to sesame oil changed the melting profile of triacyloglycerols due to different fatty acids composition.

Table 14. Temperature comparison between the second heating of the hexane extracted oil with palm olein and without palm olein

Origin of oils	**Hexane extracted sesame oil without palm olein**	**Hexane extracted sesame oil with %20 palm olein**

	Temperature T peak (▫C)	Peak half width T1/2	Temperature T2	Temperature T peak (▫C)	Peak half width T1/2	Temperature T2
Turkish sesame oil	-19.49 ^{a} ±0.01	3.13 ^{a} ± 0.07	-4.56 ^{a} ±0.12	-20.84 ^{ab} ±0.48	4.47 ^{ab} ±0.24	-6.04 ^{a} ±0.31
Indian sesame oil	-20.94 ^{a} ±1.21	3.24 ^{a} ± 0.55	-5.46 ^{a} ±1.00	-21.75 ^{a} ±0.35	4.55 ^{ab} ±0.21	-6.27 ^{a} ±0.39
Nigerian sesame oil	-19.41 ^{a} ±0.12	2.55 ^{a} ± 0.57	-4.67 ^{a} ±0.13	-19.62 ^{c} ±0.31	4.13 ^{a} ±0.17	-5.06 ^{a} ±0.36
Ethiophian sesame oil	-20.27 ^{a} ±1.40	3.80 ^{a} ± 0.59	-5.40 ^{a} ±1.08	-19.97 ^{c} ±0.50	4.79 ^{ab} ±0.09	-5.74 ^{a} ±1.27
Sudan sesame oil	-20.40 ^{a} ±1.17	3.52 ^{a} ± 0.14	-5.49 ^{a} ±1.18	-19.49^{c}±0.50	5.01 ^{c} ±0	-4.73 ^{a} ±0.29
Total mean value	-20.10 ^{A}±0.95	3.25 ^{A} ±0.55	-5.11 ^{A} ± 0.76	-20.33 ^{A} ±0.95	4.59 ^{B} ±0.33	-5.57 ^{A}±0.78

a,b, - small letters indicate significant differences between values in columns , α=0,05

A, B- big letters indicate significant differences between values in rows , α=0,05

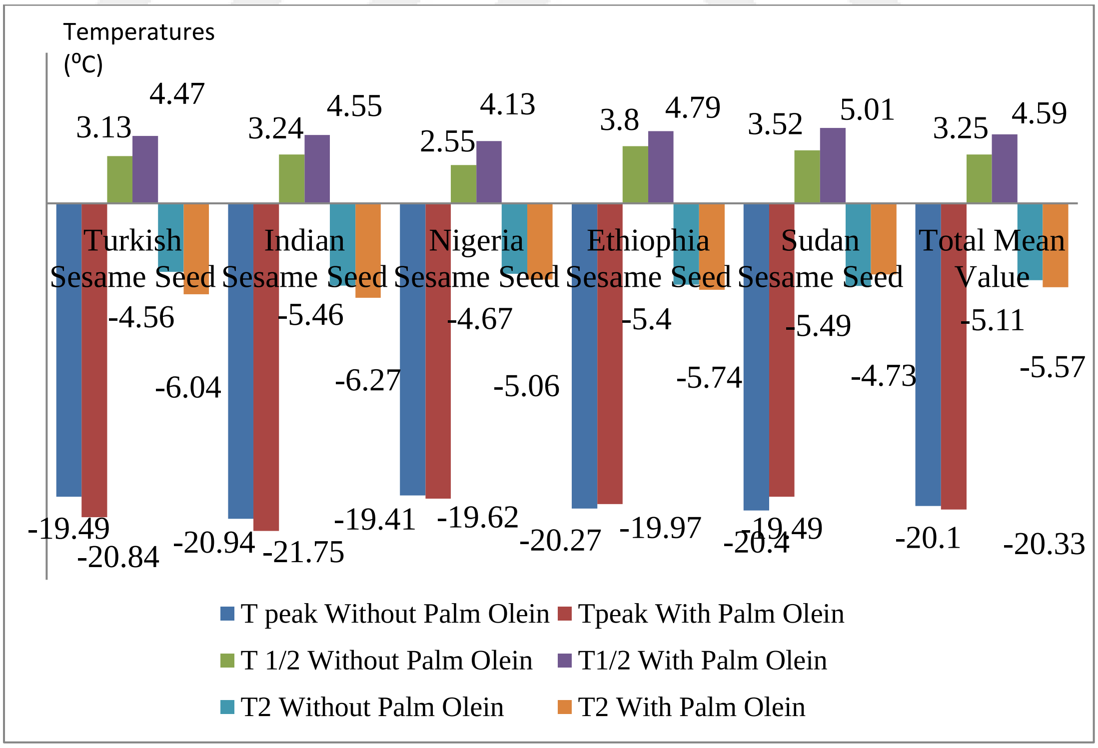


Figure 42. Comparision of temperature between the second heating of the hexane extracted oil with palm olein and without palm olein

Efect of addition of 20 % of palm olein to sesame oil on second heating enthalpies was shown at figure 42 . Each temperature type T, T1/2 and T2 were compared together with its equivalent.

Method of differential scanning calorimetry (DSC) was used to analyse the enthalpies of melting transition during first heating of samples. Results were showed at table 15. Statistical data from enthalpies of the second heating of hexane oils with palm olein and without palm olein were showed at table 15 and demonstrated at fig 43. Each enthalpy type ∆H, ∆H1 and ∆H 2 was compared together with its equivalent

Table 15. Enthalpies of the second heating of pure sesame oil and oil with palm olein

Origin of oils	**Hexane extracted sesame oil without palm Olein**				**Hexane extracted sesame oil with %20 palm olein**			
	Total Enthalpy v∆H [J/g]	**Enthalpy of second peak ∆H1[J/g]**	**Enthalpy of second∆ H2[J/g]**	**percent of second peak %**	**Total Enthalpy ∆H [J/g]**	**Enthalpy of second peak ∆H1[J/g]**	**Enthalpy of second∆ H2[J/g]**	**percent of second peak %**
Turkish sesame oil	43.50^{a} ± 0.27	36.86^{a} ±0.03	6.64^{c} ±0.23	84.72^{a} ±0.45	40.63^{ab} ±0.48	27.22^{bc} ±0.04	13.41^{a} ±0.43	66.99^{a} ±0.68
Indian sesame oil	41.20^{a} ± 3.68	37.59^{a} ±3.93	3.61^{a} ±0.25	91.17^{a} ±1.40	42.65^{a} ±0.93	30.53^{c} ±0.82	12.1^{a} ±0.10	71.58^{b} ±0.37
Nigerian sesame oil	38.87^{a} ± 0.95	33.76^{a} ±1.19	5.10^{ab} ±0.13	86.85^{a} ±0.96	39.54^{ab} ±1.01	26.47^{abc} ±0.81	13.07^{a} ±0.19	66.94^{a} ±0.34
Ethiophian sesame oil	41.70^{a} ± 3.62	36.02^{a} ±4.14	5.68 ^{c} ±0.52	86.27^{a} ±2.44	38.18^{c} ±0.80	25.56^{ab} ±0.97	12.61^{a} ±0.16	66.94^{a} ±1.13
Sudan sesame oil	40.47^{a} ± 2.70	34.91^{a} ±3.37	5.56 ^{c} ±0.67	86.17^{a} ±2.58	34.97^{a} ±2.79	22.56^{a} ±1.97	12.40^{a} ±0.81	64.50^{a} ±0.50
Total mean value	41.15^{A} ±2.53	35.83^{B} ±2.66	5.32^{A} ±1.09	87.03^{B} ±2.65	39.20^{A} ±2.91	26.47^{A} ±2.83	12.72^{B} ±0.58	67.39^{A} ±2.47

a,b, - small letters indicate significant differences between values in columns , α=0,05
A, B- big letters indicate significant differences between values in rows , α=0,05

There were significant differences between enhalpies values (∆H, ∆H1) in term of palm olein addition. ∆H2 enthalpy of pure oil also showed significant differences. Comparing mean values of enhalpies in can be seen that (ΔH1, ΔH2) entalphies and % percentage of samples there were significant differences between the pure sesame oil and oil with palm olein what means that addition of palm olein has significant effect on the enthalpies of melting transition, Palm olein addition has changed the melting profile of triacyloglycerols due to different fatty acids composition. When melting profile and enthalpy is changed, oil it may indicate that sample of oil is adulterated. İt is a remarkable result which helps to understand profile of oils. In industry sometimes oils are adulterated by the different oils, low production and high cost of sesame oil makes it valuable oil and prone to adulterations.

Small differences were observed at second heating ΔH, ΔH1 entalphies of palm olein samples. Differences also observed at second heating ΔH2 entalphy of pure oil.

Big differences were observed between the ΔH1, ΔH2 and total percentage of samples in terms of palm olein addition.

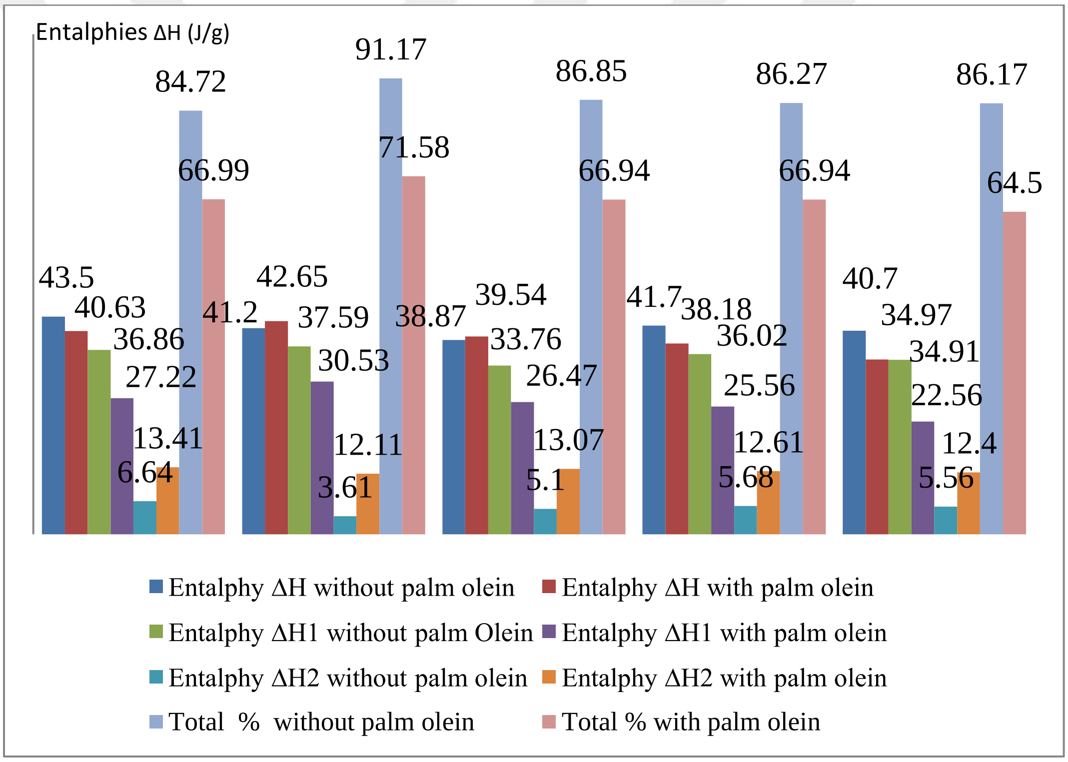


Figure 43. Enthalpy and total percentage comparision between the second heating of oil with palm olein and without palm olein

Effect of addition of 20 % of palm olein to sesame oil on first heating entaphies was shown at figure 43. Each entalphy type ΔH, ΔH1, ΔH2 and total percentage were compared together with its equivalent

6. Thermal analysis of products based on sesame

In this section (DSC) thermodynamic properties of pure sesame oil and sesame based products (halva, tahini) are compared. Results of melting transition from first heating were shown at table 16.

Statistical analyse of first heating on hexane extracted sesame oil with sesame oil products was performed at table 16 and demonstrated at Figure 44. Pure oil values were compared with the hexane extracted oil of the products.

Mean value of pure sesame oil was calculated from values obtained for all analyzed in previous sections sesame oils with various origin (Turkish, Sudan, Nigeria, Etiophia, India). It can be seen that there were no significant differences between mean values of sesame oil and sesam based products in term of temperature and enthalpy values.

This results indicate that analyzed samples of sesame seeds were pure. Oils from this products didnt show differences. This technique was shown that parameters were not different between the pure oil and oils obtained from products.After the extraction, genuine oils were obtained from the seeds. Products of halva and tahini were not adulterated by different oils.

Table 16. Comparision of first heating thermodynamic properties of sesame oil with sesame products

Origin of oils	Hexane extracted oil from sesame products	
	Temperature T peak (▫C)	Enthalpy ΔH (J/g)
TH (Tahini)	-19.72 ^{a} ± 0.21	42.83 ^{a} ± 0.54
CH (Halva)	-20.52 ^{a} ± 0.35	42.55 ^{a} ± 1.14
CHK (Halva with cacao)	-19.59 ^{a} ± 0.22	39.43 ^{a} ±2.54
CHP (Halva with pistachio)	-18.90 ^{a} ± 0.07	39.93 ^{a} ± 0.55
Pure sesame Oil (mean value)	-19.83 ^{a} ±0.82	41.83 ^{a} ±1.95

a,b, - small letters indicate significant differences between values in columns , α=0,05

A, B- big letters indicate significant differences between values in rows , α=0,05

Products didn’t show differences. Highest value of temperature detected in halva sample and lowest was in halva with pistachio. Highest enthalpy detected in also halva sample and lovest was in halva with cacao. Oils from the extraction of sesame seeds were similar to products. Product was not adulterated.

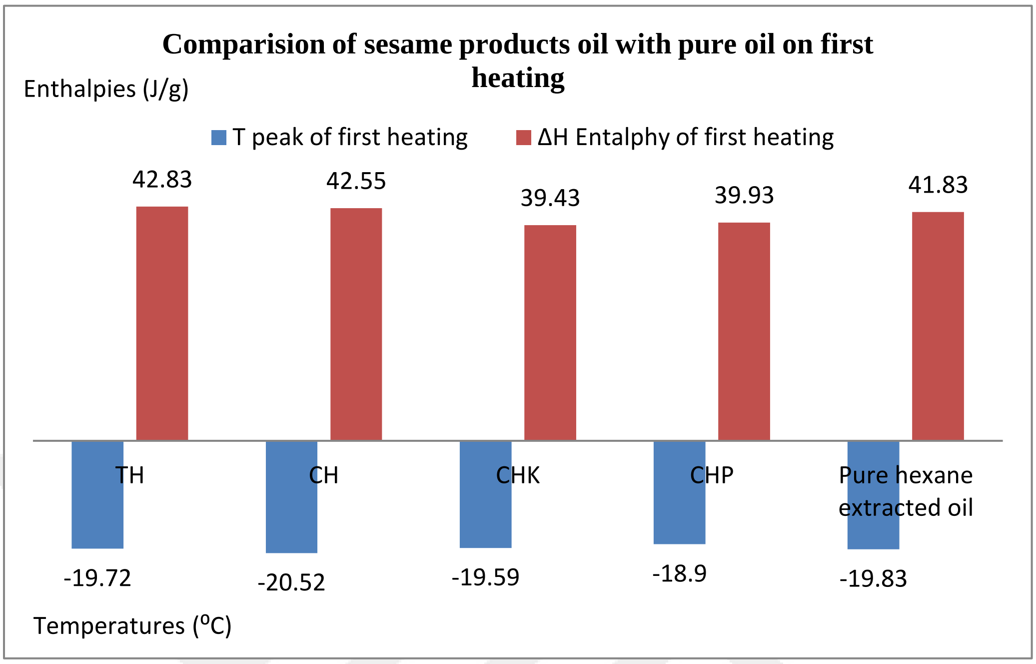


Figure 44. Comparision of first heating of hexane extracted sesame oil with hexane extracted oil of sesame products

Results of thermodynamic properities of sesame oil with sesame products after first heating were shown at figure 44. Temperatures and entalphies of the samples were compared with each other.

Table 17. Comparision of second heating of hexane extracted sesame oil with hexane extracted oil of sesame products

Origin of oils	Hexane extracted oil from sesame products	
	Temperature T peak (°C)	Enthalpy ΔH (J/g)
TH (Tahini)	-19.85 ^{a} ± 0.21	40.03 ^{a} ± 0.45
CH (Halva)	-20.80 ^{a} ± 0.18	43.04 ^{a} ± 1.79
CHK (Halva with cacao)	-19.77 ^{a} ± 0.38	39.63 ^{a} ± 1.93
CHP (Halva with pistachio)	-19.47 ^{a} ± 0.06	41.15 ^{a} ± 0.11
Pure hexan extracted oils (mean value)	-20.02 ^{a} ±0.92	40.91 ^{a} ±2.38

a,b, - small letters indicate significant differences between values in columns , α=0,05
A, B- big letters indicate significant differences between values in rows , α=0,05

Method of differential scanning calorimetry (DSC) was used to analyse for thermal properities of second heating.Comparision between the hexane extracted oil and oils from sesame products was performed and results was shown at table 17. Origin of the sesame didn’t show significant difference on the products composition. That result was not enough to tell if adulteration has performed on sesame products. Products didn’t show differences. Highest value of temperature detected in halva sample and lowest was in halva with pistachio. Highest enthalpy detected in also halva sample and lovest was in halva with cacao. These results indicate that analyzed samples of sesame seeds were pure. Oils from this products didnt show big differences even after second heating. After the extraction, genuine oils were obtained from the seeds. Products was not adulterated.

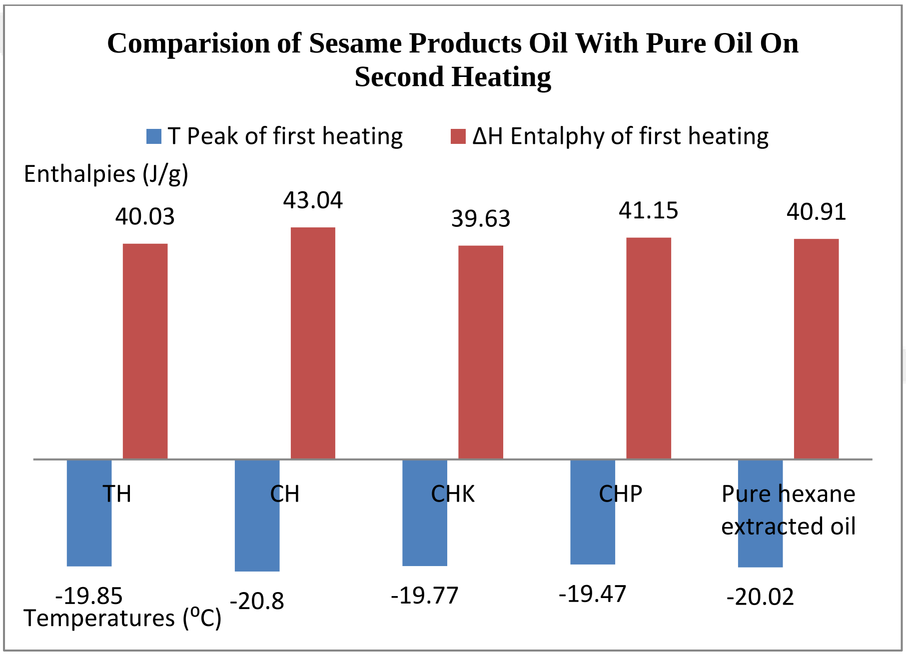


Figure 45. Comparision of second heating of hexane extracted sesame oil with hexane extracted oil of sesame products

Results of thermodynamic properities of sesame oil with sesame products after second heating were shown at figure 45. Temperatures and entalphies of the samples were compared with each other.

7. Discussion and conclusions

DSC method was used to measure changes of thermodynamic properties of samples during phase transition due to changes of chemical composition of sesame oils. This technique provides usefull information about physical changes in analyzed samples these thermodynamic characteristics are sensitive to the general chemical composition of edible oils and fats and thus can be used in qualitative and quantitative analysis for identification of edible oils authenticity. Melting curves are sensitive indicators to identify types of edible oils by this method. One critical limitation of using DSC is the dependence of the thermal transitions on scanning rate.The thermal curve depends on the scanning rate, which makes it difficult, to compare experiments performed at different scan rates Nonetheless, if edible oils give rise to identical for DSC method, this technique promises to offer a sensitive, rapid, and reproducible fingerprint method for quality-control purposes. (Tan and Che Man, 2000)

Based on the obtained results, the following conclusions were formulated:

1. Dry matter content of sesame seeds from different origins didn’t differ significanty.

2. Oil yield from sesame seeds by the hexane extraction method was in the range 50-68 % and by cold pressing 29-41 %.

3. Fatty acid content of seeds was analyzed. Lauric acid was detected only in halva and halva with pistachio samples. Myristic acid was detected only in samples of halva, halva with pistachio, halva with cocoa and Sudan seed oil.

4. Palmitic, stearic, arachidonic, oleic, palmitoleic, gadoleic, linoleic and alpha-linoleic acids were detected in all samples ol oils and products.

5. The fatty acids foun in sesame oil in the highest percentage content were: linoleic (41-44,2 %), oleic (39,9-43,3 %), palmitic (8,6-9,61 %), stearic (4,9-6,1 %).

6. Differential scanning calorimetry was used to analyze thermodynamic properties of sesame seeds from different origin. Results were not differentiated from each other. Seed origin had no influence on thermal properities of sesame oils.

7. Comparision between methods of extraction has shown some differences. Mean values of melting temperature (Tpeak) differed significantly between samples extracted by cold press and by hexane method.

8. Addition of palm olein (20 %) to sesame oil has significantly changed the parameter of peak half width (T1/2) and temperature (T2) and entalphies of second peak (ΔH2) of melting transition curve.

9. Pure oils and oil from sesame products samples were analyzeyde by DSC compared. Results have shown that samples of sesame products didn’t differ from the samples of pure sesame oil and it indicates that sesame products were genuine.

10.Method of differential scanning calorimetry may by used for the detection of adulterations in the sesame products. Thermal properities of the products and sesame seeds are similar but additional palm olein into the seeds significantly affects the temperature and enthalpy values of analyzed samples.

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Appendix – I

TABLES

FIGURES