ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EFFECTS OF PRE-TREATMENTS ON QUALITY CHARACTERISTICS AND OIL YIELDS OF SESAME SEEDS

M.Sc. THESIS

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

SUSAM TOHUMUNA UYGULANAN ÖN İŞLEMLERİN KALİTE ÖZELLİKLERİ VE YAĞ VERİMİNE ETKİSİ

YÜKSEK LİSANS TEZİ

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HAZİRAN 2015

Gülşah KARATAŞ, a **M.Sc.** student of ITU **Graduate School of Food Engineering** student 506121511**,** successfully defended the **thesis** entitled "**Effects of Pretreatments on Quality Characteristics and Oil Yields in Sesame Seeds**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

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Date of Submission : 04 May 2015
Date of Defense : 02 June 2015

To my beloved family,

FOREWORD

I wish to express my gratitude to my supervisor Assoc. Prof. Dr. Neşe ŞAHİN YEŞİLÇUBUK for her encouragement and invaluable suggestions throughout this study. I am grateful for her support, guidance and motivation.

I would like to thank also to my co-advisor, Assist. Prof. Dr. Halil Mecit ÖZTOP for his enlightening suggestions throughout study.

I would like to thank to Prof. Dr. Selma TÜRKAY for supplying sesame seeds and for her help throughout the study.

I would like to thank to Res. Assist. Ayşe SAYGÜN fo her support.

I would like to express special thank to my fathers Salih KUŞCUOĞLU and Turan KARATAŞ, my mothers Şehnaz KUŞCUOĞLU and Hanife KARATAŞ, also to my brothers Vefa and Berat KARATAŞ.

Finally, I would like to dedicate this study to my dear husband Safa KARATAŞ. I want to thank to him because of his endless support, love, patience, and help.

May 2015

Gülşah KARATAŞ
Food Engineer

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ABBREVIATIONS

AOX **:** Antioxidant Capacity
AP **:** Amplitude
CPMG **:** Carr-Purcell-Meiboom-Gill
EtOH **:** Ethanol
FFA **:** Free Fatty Acids
G **:** Grinded
HPLMWT **:** High Power Level Microwave Treatment
LPLMWT **:** Low Power Level Microwave Treatment
MC **:** Moisture Content
MPLMWT **:** Medium Power Level Microwave Treatment
MWT **:** Microwave Prereatment
NG **:** Non-grinded
NMR **:** Nuclear Magnetic Resonance
PV **:** Peroxide Value
RSS **:** Raw Sesame Seeds
TPC **:** Total Phenolic Content
UAET **:** Ultrasound Assisted Ethanolic Treatment

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EFFECT OF PRETREATMENTS ON QUALITY CHARACTERISTICS AND OIL YIELDS IN SESAME SEEDS

SUMMARY

In the last 30 years, vegetable oil especially the pressed oil consumption increased because of effects on human health. They have high amount of beneficial compounds such as antioxidants, essential oils, minerals, and vitamins. However, in order to produce the amount of consumers' demand, industry has been applying refining for years. This situation causes decrease in bioactive compounds present in vegetable oils. Nowadays, popular oilseed production method is pressing without refining process. These oils are generally defined as "cold-pressed oils, virgin oils or unrefined oils". Indeed, there is a misundersting about these terms between consumers. Virgin oil does not mean cold-pressed oil, and vice versa. Cold-pressed oils are vegetable oils obtained without altering the nature of the oil, by mechanical procedures such as expelling or pressing. They may have been purified by washing with water, settling, filtering and centrifuging only. Therefore, they maintain their beneficial compounds.

Heat treatments are used to increase high oil yield in industrial applications. Roasting and microwave treatments are the most popular methods applied as pre-treatments. On the other hand, there becomes a risk in loosing beneficial compounds present in the seeds. Therefore, it is needed to solve the problems in both heat treatments. Ultrasonic treatments have emerged in the last few years that are used to increase oil yield with GRAS solvents. In this method, solvent behaves like heat to disrupt cell walls of seeds and so oil is produced.

Research studies were performed for increasing oil yield and quality of vegetable oils such as soybean, sunflower, olive oil, and rapeseed. Apart from these seeds, there are many types of other seeds that have high oil and high bioactive content such as hazelnuts and sesame seeds.

Sesame seeds have magical beneficial compounds but unfortunately World doesn't perfectly know about them yet. They have high amount of oil, protein, antioxidants, phenolic compounds, minerals and etc. Sesame seeds themselves, oil, cake, and hulls have separately these magical compounds. There is lack of information about how sesame oil can be obtained in high yield without loosing quality. Therefore, in this thesis, Turkish type sesame seeds were treated by different pretreatments to have high oil yield and quality characteristics.

In the experimental studies, three treatments were chosen which were conventional treatment (roasting), microwave treatment (MWT), and ultrasonic assisted ethanolic (UAE) treatment. Each treatment was applied before hydraulic pressing and obtained press oil and sesame cake were analysed for various parameters.

In the experimental studies, firstly, the quality characteristics of sesame seeds were determined before pretreatments and pressing. Moisture content, refractive index, ash content, oil content, protein content, fatty acid composition, free fatty acid content, peroxide value, and oxidation stabilities were analysed and compared for control samples and treatments.

In the next steps, sesame seeds were roasted, treated with microwave, and treated with ultrasound. For each treatment, oil yield and quality characteristics were determined. In experiments, following effects were searched: for roasting; duration, temperature, and starting moisture content, for microwave treatment; energy power level and duration, for ultrasonic treatment; alcohol-water concentration, solid/liquid content, duration, and amplitude.

Findings that are obtained from this experiment can be summarized as follows:

According to the results, moisture content was decreased from 5.1±0.03% to 2.2±0.05% by 165 °C roasting and 0.9±0.002% by 220 °C roasting. By applying microwave treatment with different depth and power level, moisture content was decreased by 1.5-3.5%. High power level at 1 cm depth provided the best result in 1.2% moisture content. Ultrasonic treatments didn't have effect on moisture content as much as heat treatments. But moisture content was decreased by 1.0-1.5%.

Refractive index for non-treated and treated samples didn't change in a great deal. Therefore, ultrasonic effect wasn't studied.

Free fatty acid (FFA) content increased from 2.5±0.26% to maximum 6.3±0.1% in sesame cake oil and 15.7±1.21% in press oil by roasting, 11.6±0.55% in sesame cake oil and 6.7±0.26% in press oil by microwave treatment, 15.8±0.52% in sesame cake oil and 8.0±0.32% in press oil by ultrasonic treatment. When the results were compared, it was clearly seen that treatments didn't decrease FFA content. When treatments were compared with each other, high level microwave in non-grinded samples and 210°C roasting in non-grinded samples can be acceptable for having low FFA content.

Oil content of sesame seeds were determined by Soxhlet extraction. According to the results, oil content increased from 48.7±3.18% to maximum 56.6±3.55% by 210 °C roasting in grinded seeds, 63.3±3.12% by medium power level of microwave at 1 cm depth, and 62.5±2.20% by solid/liquid:1/10 ultrasonic treatment. High oil content was obtained at by medium power level of microwave treatment and by solid/liquid:1/10 ultrasonic treatment.

Peroxide value (PV) increased from 3.4±0.27 meq/kg oil to 10.0±0.10 meq/kg oil after ultrasonic treatment during 20 days of storage. After 20 days of storage, PV of raw sesame seeds decreased from 9.2±0.59 meq/kg oil to 7.7±0.56 meq/kg oil after 165°C roasting, 4.6±0.54 meq/kg oil after high level microwave treatment. For 30 days of torage, results were similar to that of 20 days storage. Again high level microwave and 165°C roasting gave us low PV meaning that we can obtain longer shelflife for sesame oil.

Maximum total phenolic content (TPC) of sesame seeds, sesame oil, and sesame cake were found as 63.7±3.00, 108.9±5.47, and 185.3±10.14 mg gallic acid/mL for 210°C roasted samples, high level microwave treated samples, respectively. Ultrasonic treatment couldn't be effective for obtaining high amount of TPC. In contrast, AOX results showed that ultrasonic treatment was effective as heat

treatments. However, three power level microwave treatments were the most effective for obtaining high antioxidant activity.

In NMR analysis, T2 (relaxation time) Carr-Purcell-Meiboom-Gill (CPMG) experiments were conducted for oils which were obtained in MWT, UAET, and roasting treatments. For T2-CPMG experiments, there was no significant difference found between the T2 values and relative areas of each compartment for MWT and roasting treatments. This result was expected, as exchange times are very slow in the absence of gradients. For UAET, that is a homogenization technique, the number of peaks decreased to three after the treatments. T2 values of the peaks were not different from the microwave and high temperature ones. At 90% amplitude for the 96% EtOH samples, sonication time was doubled and resulted a decrease in the T2 values. This showed that ethanol interacted with oil more at higher sonication times.

Oxidation stability was determined by Rancimat method. According to the results, induction time was longer in 210 ℃ roasting and high MWT when it was compared to non-treated one. Ultrasound treatment was not effective as roasting and MWT. Induction time was recorded as 14.9±1.56 h for non-treated sesame oil, 14.5±0.55 h for 210℃ roasted sesame oil, 13.53±1.85 h for high MWT, 11.85±0.73 h for medium MWT, and 11.55±1.10 h for 90% amplitude UAET. Looking at the TPC and TEAC results, oxidation stability went through in the same order. Therefore, higher oxidation stability values of sesame oil could be attributed to higher antioxidants (lignans) together with tocopherol..

The first aim of this study was to find oil yield after treatments. Oil yield was found in both grinded and non-grinded sesame seeds. Oil yield was calculated bu applying mass balance by taking into consideration of press oil and sesame cake oil. In grinded sesame seeds, oil yield increased from 38.8% to 56.0%, 68.8%, 70.0%, and 63.8% by roastings, medium level at 1 cm depth, high level at 1 cm depth, and ultrasonic treatment with 96% ethanol concentration, respectively.

As it was concluded that each treatment had effects on oil yield and quality characteristics of sesame oil. But it is clearly seen that microwave treatment and roasting gave the best results. For ultrasonic treatment, ethanol concentration, time, amplitude, and solid/liquid were important and showed different results to compare in itself. However, when it was compared with heat treatments, more study is needed. In industrial scale, medium/high level of microwave or roasting can be used to have high oil yield with high functional properties and oil quality for sesame seeds.

SUSAM TOHUMUNA UYGULANAN ÖN İŞLEMLERİN KALİTE ÖZELLİKLERİ VE YAĞ VERİMİNE ETKİSİ

ÖZET

Son 30 yıldır bitkisel yağların insan sağlığına olan pozitif etkilerinden dolayı, tüketicilerin bu yağlara olan talebi artmıştır. Bitkisel yağlar yüksek miktarda yararlı bileşenler içermektedir; bunlara örnek olarak antioksidanlar, esansiyel yağlar, mineraller ve vitaminler verilebilir. Fakat tüketici talebinin karşılanması için endüstriyel üretimlerde rafinasyon uygulamalarına sık sık karşılaşılmaktadır. Bu durum da bitkisel yağların biyoaktif bileşenlerinin zarar görmesine neden olmaktadır.

Günümüzde popüler üretim metodu rafinasyon yapmadan veya yüksek sıcaklık kullanmadan bitkisel yağ elde etmektir. Bu üretim tekniği ile elde edilen yağlar genellikle "soğuk pres yağı, rafine edilmemiş yağ veya virjin yağ" olarak tanımlanmaktadır. Aslında bu konuda tüketiciler arasında bir yanlış anlama söz konusu olmuştur. Çünkü virjin yağlar, soğuk pres yağı anlamına gelmez ya da aynı şekilde soğuk pres yağı demek virjin yağ demek değildir. Genel anlamda, soğuk pres yağları yağın doğasını değiştirmeden elde edilen, sadece mekanik yollarla (presleme gibi) işlenen bitkisel yağları tanımlar. Bu yağlar sadece suyla, filtrelemeyle ya da santrifüjleme ile saflaştırılabilir. Bu yüzden de yararlı bileşenlerini korumuş olurlar. Endüstriyel ölçekli üretimlerde yüksek verim ile yağ elde etmek için genellikle ısı uygulaması yapılır. Kavurma ve mikrodalga uygulaması buna örnek olarak gösterilebilir. Diğer yandan, sıcaklık uygulandığı için tohumdaki yararlı bileşenleri kaybetme riski doğmaktadır. Bu yüzden, iki uygulamada da problemi çözmek gerekmektedir. Ultrasonik uygulama son birkaç yılda öne çıkan ve GRAS özellikteki çözücüleri kullanarak yüksek kalitede ve verimlilikte yağ eldesinde kullanılan önemli bir metottur. Çözücü tohumun hücre duvarlarına zarar verme etkisi ile ısı gibi davranır ve bu şekilde yağ ekstrakte edilir.

Soya yağı, ayçiçek yağı ve zeytinyağı gibi bitkisel yağlarda yüksek verim elde etmek için çeşitli çalışmalar yapılmıştır. Bu yağların dışında Türkiye'de de büyük öneme, yüksek yağ verimliliğine ve yüksek biyoaktif bileşenlere sahip olan fındık ve susam yağının da çalışılması gerekmektedir.

Susam mucizevi yararlı bileşenlere sahiptir, ne yazık ki Dünya bunu henüz çok fazla bilmemektedir. Susam yüksek miktarlarda yağ, protein, mineral, ve fenolik bileşenlere vb. sahiptir. Susam tohumunun sahip olduğu bu bileşenler kadar, elde edilen susam yağı, susam küspesi ve kabukları da bir o kadar bu bileşenlerce yüksek içeriğe sahiptir. Literatürde hiçbir yararlı bileşeni kaybetmeden susam yağında yüksek verimlilik elde etmek için çok fazla çalışma yapılmamıştır. Bu yüzden tez çalışmasında Türk tipi susam tohumu kullanılarak yüksek verim ve kalitede susam yağı elde edilmesi amaçlanmıştır.

Deneysel çalışmalarda, konvansiyonel uygulama (kavurma), mikrodalga uygulaması ve ultrasonik destekli alkollü uygulama seçilmiştir. Her bir susam tohumu numunelerine bu işlemler uygulanmış ve hidrolik pres ile preslenerek yağ ve küspe elde edilmiştir.

İlk olarak ham susam tohumunda ön işlem ve pres yapılmadan önce kalite parametreleri belirlenmiştir. Nem miktarı, refraktif indeks, kül miktarı, protein miktarı, serbest yağ asidi içeriği, peroksit sayısı, ve oksidasyon stabilitesi, analizleri susam tohumları için yapılmıştır.

Diğer kısımlarda, susam tohumu kavurma, mikrodalga ile ön işlem ve ultrasonik destekli alkollü ön işleme maruz bırakılmıştır. Her bir uygulama için kalite parametreleri ve yağ verimliliği belirlenmiştir. Deneylerde şu etkiler incelenmiştir: kavurma için süre, sıcaklık, ve başlangıç nem içerikleri; mikrodalga uygulaması için ön işlem süresinin etkisi ve mikrodalga gücü; ultrasonik destekli alkollü ön işlem için ise alkolün su içeriği, tohum/alkol oranı, ön işlem süresi ve ultrasonik enerji gücü.

Deneyler sonucunda elde edilen sonuçlar aşağıdaki gibi özetlenmiştir:

Sonuçlara göre nem içeriği 165°C kavurma ile; %5.1±0.03'dan %2.20±0.05'e, 210°C kavurma ile; %0.9±0.00'e düşürülmüştür. Farklı derinliklerde ve mikrodalga gücünde uygulanmış örneklerde ise nem içeriği %1.5-3.5 arasında azaltılmıştır. 1 cm derinlikteki yüksek enerjili mikrodalga uygulaması %1.2±0.25 ile en iyi sonucu vermiştir. Ultrasonik uygulama bu işlemler kadar etkili olmasa da %1-1.5 arasında nem içeriğinde bir azalmaya sebep olmuştur.

Refraktif indeks değerlerinde uygulamaların hiçbirinde önemli ölçüde değişiklik görülmemiştir.

Serbest yağ asitleri (SYA) içeriği en fazla kavurma ile; küspedeki yağda %2.5±0.26'dan %6.3±0.01'e ve pres yağında %15.7±1.21'e, mikrodalga uygulaması ile; küspedeki yağda %11.6±0.55'e ve pres yağında %6.7±0.26'a, ultrasonik uygulama ile de; küspedeki yağda %15.8±0.52'e ve pres yağında %8.0±0.32'e yükselmiştir. Sonuçlar karşılaştırıldığında, SYA'nın ön işlemlerle azalmadığı gözlemlenmiştir. Uygulamaları birbirleri ile karşılaştıracak olursak, öğütülmemiş tohumda uygulanan yüksek güçlü mikrodalga uygulaması ve öğütülmemiş tohumda 210°C'deki kavurma belirli oranda düşük SYA içeriği elde etmek için kullanılabilir.

Susam tohumlarının yağ miktarları Soxhelet ekstraksiyonu ile belirlenmiştir. Yağ miktarı en fazla 210°C kavurma ile %48.7±3.19'dan %56.6±3.55'e, mikrodalga uygulamada 1 cm derinlikte orta derecedeki güçte %63.3±3.12'e, katı/sıvı:1/10 ultrasonik uygulamada ise %62.5±2.20'e yükselmiştir.

Peroksit değeri, 3.41±0.272 meq/kg yağ'dan 10.0±0.10 meq/kg yağ'a yükselmiştir. Diğer uygulamalar için 20 ve 30 gün boyunca yağlar karanlıkta depo edilmiş ve peroksit değerindeki değişimler bulunmuştur. 20 gün muhafaza edilen ham susam yağı peroksit değeri 9.2±0.59 meq/kg yağ'dan 165°C kavurma ile 7.7±0.56'e, yüksek derecedeki güçlü mikrodalga uygulaması ile de 4.6±0.54'e düşürülmüştür. 30 günün sonunda elde edilen verilen 20 günün sonunda elde edilen veriler ile benzerlik göstermiştir. Yüksek güç kaynaklı mikrodalga uygulaması ve kavurma sonucunda elde edilen yağın peroksit sayısı daha düşük bulunmuştur, bu durum ürünün oksidasyonunun daha düşük olduğunu göstermektedir. Susam tohumu, susam yağı ve küspede elde edilen en yüksek toplam fenolik madde miktarları sırasıyla şu şekildedir: 210°C kavurma için 63.7±3.00, yüksek güç kaynaklı mikrodalga

uygulaması için 108.9±5.47 ve 185.3±10.14 mg gallik asit/mL'dir. Ultrasonik uygulama ise toplam fenolik madde miktarının artmasında etkili olmamıştır. Bu durumun aksine, toplam antioksidan aktivitesi ısıl ön işlem uygulamalarının gösterdiği etki göstermiştir. Fakat en etkili uygulama her üç güç uygulaması ile birlikte mikrodalga uygulaması olmuştur. Mikrodalgalar tohumun yüzeyinde ve içinde yayılarak fazla miktarda antioksidan maddenin ekstrakte edilmesini sağlamıştır.

NMR analizinde susam yağları için T2 Carr-Purcell-Meiboom-Gill (CPMG) deneyleri düzenlenmiş olup, her 3 uygulama için sonuç alınmıştır. Orta güçteki mikrodalga ve kavurma uygulamaları için, T2 ve her bir bölüm için bağlı alanlarda herhangi önemli bir farklılık gözlenmemiştir. Bu beklenildiği gibi bir durumdur. Ultrasonik uygulama sonunda tepe noktalarının sayısı azalmıştır. Ancak tepe noktalarındaki T2 değerleri kavurma ve mikrodalga uygulamalarından farklı bulunmamıştır %90 genlik ve %96 etanolle uygulanan deneylerde, sonikasyon süresi ikiye katlandığı için T2 değerlerinde düşüş gözlenmiştir. Bu sonuç etanolün yüksek sonikasyon sürelerinde daha fazla yağ ile etkileşimde olduğunu göstermiştir.

Oksidasyon stabilitesi Rancimat metoduyla belirlenmiştir. Elde edilen sonuçlara göre, 210°C'de kavurma ve yüksek güç kaynaklı mikrodalga uygulanmış yağların yüksek indüksiyon zamanına sahip olmuştur. Ultrasonik uygulama bu uygulamalar kadar etkili olmamıştır. İndüksiyon zamanı sırasıyla; işlem görmemiş susam yağı için 14.9±1.56 sa., 210°C kavurma için 14.5±0.55 sa., yüksek güç kaynaklı mikrodalga uygulaması için 13.53±1.85 sa., orta güç kaynaklı mikrodalga uygulaması için 11.8±0.73 sa. ve %90 genlikteki ultrasonik uygulama için 11.5±1.10 sa. olarak kaydedilmiştir. Toplam fenolik madde ve toplam antioksidan aktivitesi ile oksidasyon stabilite analizi sonuçlarının paralellik göstermiştir Bundan dolayı yüksek oksidasyon stabilitesine sahip susam yağı yüksek miktarda antioksidan ve tokoferol içeriğine katkıda bulunmuştur.

Bu çalışmanın amacı öncelikle uygulamalardan sonraki yağ verimini tespit etmektir. Yağ verimi hem öğütülen hem de öğütülmemiş susam tohumlarında incelenmiştir. Kütle denkliği yardımıyla pres yağı ve küspedeki yağ miktarları kullanılarak yağ verimi hesaplanmıştır. Öğütülmüş susam tohumlarında yağ verimi sırasıyla %38.8'den %56.0'a (kavurmalar), %68.8'e (orta güçteki mikrodalga uygulaması), %70.0'a (yüksek güçteki mikrodalga uygulaması) ve %63.8'e (%96 etanollü ultrasonik uygulama) yükselmiştir.

Sonuç olarak, herbir uygulama kendi içinde yağ verimi ve kalite parametreleri bakımından etkilere sahip olmuştur. Mesela ultrasonik uygulama için etanol konsantrasyonu, süre, enerji gücü ve katı/sıvı oranı kendi içerisinde farklı sonuçlar vermiştir. Fakat açıkça görülmektedir ki kavurma ve mikrodalga uygulaması hem verim hem de diğer özellikler açısından en iyi sonuçları vermiştir. Endüstriyel ölçekte orta/yüksek güçteki mikrodalga uygulaması veya kavurma uygulanarak yüksek verimde ve fonsiyonel özellikte kalitede ürünler elde edilebilir.

1. INTRODUCTION AND PURPOSE

In recent years, consumer demand has showed an alteration from refined edible and salad oils to unrefined natural oils produced by only mechanical processes. The reason of tendency is the great deal of studies on positive side of vegetable oils, and many studies about negative health effects of oils generating destructive components during refining and frying. These findings spread through people as breaking news. Nowadays, consumers prefer their foodstuffs not only according to the taste and odour, but also to their positive components. There are lack of companies producing natural press oils. Also we can see these products on the special corner of the markets.

The most important disadvantage of press oils is low oil yield, thus higher cost. In recent years, in order to increase oil yield, some pretreatments are applied before pressing. The most common technique used is undoubtly roasting. Generally, hazelnut, walnut, pistachio, and sesame are roasted to increase oil yield. Classical roasting and microwave roasting are the most preferable techniques. They affect not only oil yield, but also the quality of oil by means mechanisms. The latest technique is exposing the product to ultrasonic treatment with ethanol.

By considering the requests, low cost and natural oil production are important as well as the quality of oils. These techniques mentioned above should respond in positive ways.

Sesame (Sesamum indicum L.) is cultivated in several countries such as India, Sudan, China and Burma which are considered as the major producers and consumed in all over the world. Sesame is an important cash crop for small and marginal farmers in several developing countries. It is cultivated for its seeds which contain 38–65 % oil of very high quality and 18–25 % protein. The great diversity of sesame types, their wide environmental adaptation and considerable range of seed oil content. Sesame oil has a mild, pleasant taste. An important characteristic of sesame oil is its resistance to oxidative deterioration. Sesame oil from roasted sesame seeds has a distinctive flavor and a long shelf life. By considering these advantages, sesame seeds have been chosen as the raw material.

There are studies about quality changes of sesame oils on microwave and convententional roasting. However, there is not any study on ultrasonic pretreatments and comparative pretreatments for three methods.

The aim of this study was to find the quality and yield differences between pretreatments. For this purpose, conventional and microwave roasting, and ultrasonic assisted ethanolic pretreatments were applied to Turkish type raw sesame seeds. After that, these pretreated seeds were pressed to go through quality characteristic properties mentioned in methods section. These methods and pretreatments were compared to find the best application to have been able to get high sesame oil yield and quality.

2. LITERATURE REVIEW

2.1 History of Sesame

Sesame seed and its oil are known for their excellence over foodstuffs. It has been used for thousands of years in all over the world with its unlimited products. Cultivated sesame species, *Sesamum indicum* L., is believed to have originated in Africa and spreaded to Egypt, India, the Middle East, China, and other countries. Figure 2.1 shows world sesame cultivation plants [1].

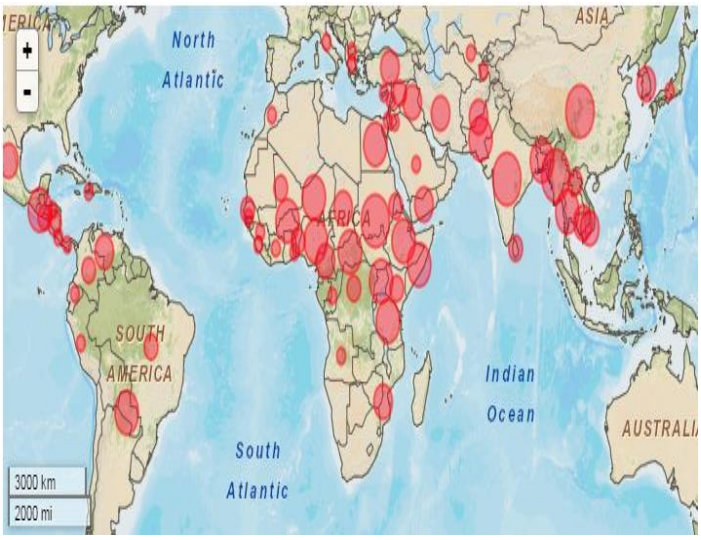

Figure 2.1: World sesame production **[1]**

There are many stories about how sesame first came out and used. In a historic book called the "Thebes Medicinal Papyrus", found in Egypt, sesame was referred as the potential source of medicinal effect and energy. Hippocrates in Greece also noted its high nutritional value. In the time of Assyrians, it was believed that Gods created the world by drinking sesame wine. Ancient Greek soldiers carried sesame seeds as energy source [2]. In traditional Indian medicine, "Ayurveda", sesame oil has been used as the massage oil for human body since 700–1100 BC. [3]. The most familiar magic words, "Open, sesame!" from the Arabian Night stories, have been still used in all over the world. In these stories, it is believed that opening of sesame capsule and scattering seeds show the sesame's magic power.

The widespread usage of sesame lies in its high oil content, nutritious protein, roasted flavor, and other magic properties. It is also considered as a food beneficial

to health in some countries such as Japan, China, and India. Many scientific studies have been conducted to investigate the health-promoting effects of sesame [4]. Although such high values placed on sesame seed and oil, there have been few scientific studies to reveal their functions.

2.2 Botany and Cultivation of Sesame

The genus Sesamum, belonging to the Pedaliacea family, is the biggest of sesame's 16 genera and has 36 species most of which are wild and has not been well studied over the years because of its complexity and lack of taxanomy information. The name "sesame" comes from the Arabic word "semsin".

Sesame is an annual plant that can reach a height of 2 m, generally found in 100-120 cm height under high moisture conditions. It is adapted to the tropics and subtropics, but is more common in the equator, mostly north of it. It is indeterminate, producing leaves, flower buds, flowers, and capsules continuously, as the season progresses and if growing conditions permit. Some varieties have many branches, some of them have few branches, and others are unbranched. The growth period for sesame usually ranges from 3 to 4 months but flowering begins as early as 30−40 days after sowing. Blooming continues until maturity, and the seeds scatter suddenly from the capsule. The Arabic (magic word) "open sesame" is said to have originated from the movement of the opening of the sesame capsules. The seeds vary considerably in color, size, and texture of the seed coat. The color changes from white through brown, gold, gray, violet, and black [5].

In most of the sesame-growing areas the plants are harvested by the traditional methods. They are firstly cut, collected, and stacked together to dry. When the bundles dry, the capsules are opened. Then the bundles are mixed and inverted over a smooth surface and shaken in order to be sure that all the seeds are released from capsules (Figure 2.2) [5]. The seeds are collected, dried and if necessary they are cleaned, stored, and marketed. It is important that crop should be dry before harvesting. It is recommended that the seed should be stored at moisture of 6% or less.

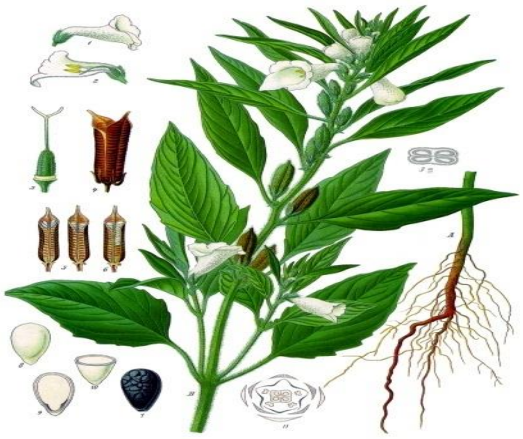

Figure 2.2: *Sesamum indicum* plant **[5]**

Seed yields range from 5730 to 7935 kg/ha depending on the varieties obtained by cultivation techniques. Table 2.1 summarizes the area harvested, yields, and the production of sesame seeds at 5-year intervals in the major producing countries and regions for the period of 2003 to 2013 according to FAOSTAT records [1]. In 2003, the leading countries in area harvested were India (26.5%), Sudan (23.45%), Myanmar (20%), and China (11%), with more than 80% of the total area. In 2008, the leading countries in area harvested were India (26.5%), Sudan (22%), Myanmar (21%), and China (7%), with more than 76% of the total area. In 2013, the leading countries in area harvested were Sudan (26.5%), India (22%), Myanmar (19%), and Tanzania (8%), with more than 76% of the total area. As can be seen from the values, the top countries are generally constant. The highest percentage for production in 2003 were India (27%), China (21%), Myanmar (18%), Sudan (11%), and Uganda (4%). The highest percentage for production in 2008 were Myanmar (25%), India (19%), China (18%), Sudan (11%), and Uganda (4%). The highest percentage for production in 2013 were Myanmar (22%), India (16%), China (14%), Sudan (14%), and Uganda (4%). It is obvious that the flag of harvested area and production is in the hand of Myanmar, India, China, Sudan and Tanzania. However, when it comes to yield, the average for 3 years, was 12.877 kg/ha in Egypt, while it was 3852.66 kg/ha in India. If the area and yield are compared, the improvement in sesame production is lower than expected. Improved varieties, better cultivation techniques, and the introduction of machine harvesting are required if the production of sesame is to be increased [2].

Table 2.1: Area harvested, yields, production of sesame seeds between 2003-2013

Countries	Area Harvested, 1000 ha			Yield, kg/ha			Production, 1000 mt		
	2003	2008	2013	2003	2008	2013	2003	2008	2013
Brazil	24000	10000	10000	6250	7000	7000	15000	7000	7000
China	**687000**	**471600**	**448000**	8632	12432	13125	593000	**586293**	**588000**
Egypt	30234	28211	30000	12225	13074	13333	36961	36882	40000
Ethiopia	91527	185912	282950	6774	10046	6613	62000	186772	187121
India	**1700300**	**1809100**	**1860000**	4600	3539	3419	**782100**	**640300**	**636000**
Mexico	55600	48398	63642	5576	6126	6524	31000	29651	41522
Myanmar	**1267000**	**1431000**	**1590000**	3955	5870	5597	**501090**	**840000**	**890000**
Nigeria	167000	317080	340000	4790	3835	4853	80000	121610	165000
Pakistan	59719	90639	84000	4132	4523	4167	24673	40997	35000
Somalia	63000	58586	70000	4762	9228	10000	30000	54064	70000
Sudan	**1500000**	**1489080**	**2157540**	2167	2350	2605	325000	350000	562000
Thailand	63504	65614	70000	6375	6750	7429	40484	44290	52000
Turkey	44000	28589	24807	5000	7114	6231	22000	20338	15457
Uganda	240000	286000	290000	5000	6049	6207	120000	173000	180000
Total	*6401829*	*6811775*	*8337417*	*1230334*	*140642*	*167686*	*2875280*	*3383617*	*4171800*
Average	*304849*	*324370*	*397019*	*5730*	*6697*	*7985*	*136918*	*161124*	*198657*

2.3 Use of Sesame As Food

Sesame (*Sesamum indicum L.*) is one of the most important oilseed crops worldwide and also plays an important role in human nutrition. There are many reasons why people use sesame seed. The oil content of sesame seed is quite high (about 50%), and is also very stable against oxidative deterioration. Furthermore, it has high nutritional value since the protein content is about 20%. The good flavor generated by roasting sesame seeds is also a highly desirable characteristic. This product has been used as an essential constituent in different recipes [7]. Sesame seed itself or products/by products can be used for different purposes. Table 2.2 shows different usages of sesame as a food ingredient.

Sesame seed is used in several ways around the world. In East Asia, people usually like the roasted flavor, so in China, Korea, Japan, and other Asian countries, roasted sesame seed is generally used as a topping or decorating for many baked foods such as breads, biscuits, and crackers. In China, roasted seed may be ground into a paste-like product. Sesame oil is consumed as a hardened oil in margarine, and also used for cooking oil. In the Near East and North Africa including Turkey, sesame paste is generally used. For example, the paste is used for the base in “Tahina” and “Halva” [5].

Tahina is sesame paste and named in different regions such as tehineh, tahini, benne, simsim, gingelly and tehina. It is produced by using sesame seeds and seeds are dehulled, roasted and ground into paste form. Tahina is used in preparation of some local foods such as Hommus Tahina, salads and mixed with honey and molasses called “Pekmez”. It is also the main ingredient of Halva. Tahina has high nutritive value, which is rich in lipids (57-65 %), proteins (23-27 %), carbohydrates (6.4-9.%), niacin (4.5 mg/100 g), thiamin (1.08 mg/100 g) and some minerals such as calcium (100 mg/100g), phosphorus (807-840 mg/100 mg), and iron (9 mg/100g)[8]. It helps digestive systems to work more quickly, high oil content supplies energy [9].

Table 2.2: Different uses of sesame as food [5,14]

Type of sesame forms	Products	How it is used
Seeds	Confectionery	sesame seed mixed with honey or syrup and roasted into a sesame candy.
Seeds	Cookies	sesame seeds poured in honey and caramelized by sugar.
Seeds	Crackers and Biscuits	sesame seed is baked
Dehulled seeds	Bakery	used in outer surfaces of breads and hamburgers, also used as an ingredient in breads
Roasted seeds	Oil blends	roasted seeds are mixed with other oils to have strong flavour
Oil	Margarine	sesame oil and other seed oils are mixed to produce margarines
Oil	Cooking oil	used like other oils in frying
Oil	Salad oil	salad oil generally used in Asia
Oil	Body creams and soaps	generally for intramuscular injections and to cure pustules
Dehulled and roastes seeds	Sesame paste	known as Tahini and used in humus, blended with pekmez and other sweet foods
Sesame paste	Halva	produced by blending tahini, sugar and other ingredients
Sesame cake	Animal feed	Press cake rich in protein and antioxidants

2.4 Seed Composition and Quality

Sesame seed is a good energy source. It is rich in fat, protein, carbohydrates, fiber and some minerals. The composition varies according to the type of sesame seed, processing conditions and cultivation areas. Average composition of whole and dried sesame seeds are presented in Table 2.3:

Table 2.3: Average composition of whole and dried sesame seeds[10]

Nutrient (proximates)	Value per 100 g
Water	4.69 g
Energy	573 kcal
Protein	17.73 g
Total lipid (fat)	49.67 g
Ash	4.45 g
Carbohydrate	23.45 g
Fiber	11.8 g
Sugars, total	0.30 g

2.4.1 Oil content

The average oil content was found to be 55% in white-seed strains and 47.8% in black-seed cultivars, while the content can vary depending on the species and cultivation conditions [11]. Figure 2.3 represents different sesame oil varieties [12].

Figure 2.3: Different sesame oil varieties[12]

Ashri (1998) reviewed findings of oil contents in China, India, Israel, South Korea, U.S.A., and Venezuela. These studies included hundreds of different sesame seed

types. The average oil percentages varied from 47.0% to 53.1% in Venezuela and in China. Israil type sesame had 34% oil because of seed immaturity due to environmental factors [13]. It was reported that the oil content of Turkish variety sesame seeds changed between 52 to 61% [14]. The fatty acid composition of sesame oil is desirable with about 80-85% of unsaturated acids and only 15-20 % of saturated ones. Elleuch et al.(2007), Sheheta et al. (2000) studied the quality characteristics of raw sesame seeds, Tunisia sesame, Egyptan sesame and non-defined sesames, respectively. Fatty acid composition is shown in Table 2.4: [10, 15, 16].

Table 2.4: Fatty acid composition(%) of raw sesame seeds [10, 15, 16].

Fatty acids	Elleuch et al. (2007)	Shehata et al. (2000)	USDA (2015)
Palmitic acid, 16:(0)	11.18	8.02	4.44
Stearic 18:(0)	6.40	5.38	2.09
Oleic 18:(1)	44.06	38.81	18.521
Linoleic 18:(2)	35.56	45.66	21.37
Linolenic 18:(3)	0.50	0.30	0.38

It is certainly clear that fatty acid composition changes with the seed type and growing conditions. Fatty acids of the oil consist mainly of oleic and linoleic acids, with small amounts of palmitic and stearic acids but with only trace amounts of linolenic acid. Linoleic and linolenic acids are considered to be essential fatty acids for humans. According to recent studies on prostaglandins which are a group of physiologically active, lipid compounds have diverse hormone-like effects in animals and which are synthesized in the cell from the essential fatty acids. Linolenic and linoleic fatty acids have independent roles in the synthesis of prostaglandins, and the ratio of linolenic to linoleins fatty acids in the composition of fatty acids is important [5].

2.4.2 Protein and carbohydrate content

Sesame seeds are also a potential source of proteins. It has nearly 30% protein in the meal composition. This meal can be used as a protein source in the food industry. Sesame proteins contain two major storage protein; 11S globulin and 2S albumin. Total of the 11S globulin and 2S albumin is 95% of the protein. The remained part of the protein is 7S globulin [17].

Sesame proteins are also rich in amino acid composition. The amino acid compositions of sesame and soybean are shown in Table 2.5 for comparison [10, 17].

Glutamic acid and arginine together with sulfur-containing amino acids like methionine and cysteine are high in sesame. Most plant proteins are low in total sulfur-containing amino acid such as soy protein (1.68 g/16 g of N) [18], wheat flour (3.8 g/16 g of N), barley grain (4.0 g/16 g of N), rice milled (3.7 g/16 g of N) [19], and maize corn flour (3.5 g/16 g of N). Sesame is unique in having high total sulfur-containing amino acid content. Thus, the amino acid composition of sesame protein can be used as a supplementing diet base on cereal and legumes.

Table 2.5: Amino acid composition of sesame **[10, 17]**

Amino Acid	***Sesame (mg / g protein)***	***Soybean (mg / g protein)***	***USDA reference for sesame (value / g)***	***USDA reference for soybean (value / g)***
Isoleucine	42	51	0.763	1.971
Leucine	75	82	1.358	3.309
Lysine	31	68	0.569	2.706
Methionine	36	16	0.586	0.547
Cystine	25	17	0.358	0.655
Phenylalanine	51	58	0.940	2.122
Tyrosine	39	37	0.743	1.539
Threonine	39	41	0.736	1.766
Valine	54	52	0.990	2.029
Arginine	140	81	2.630	3.153
Alanine	51	46	0.927	1.915
Aspartic acid	91	120	1.646	5.112
Glutamic acid	200	190	3.955	7.874
Glycine	55	46	1.215	1.880
Proline	42	57	0.810	2.379

The carbohydrate content in sesame seed is about 18–20 %. The presence of low amounts of glucose and fructose is seen on sesame, but no starch is present. Most carbohydrates seem to be present as dietary fibers.

2.4.3 Vitamins and minerals

Sesame seed contains a significant amount of the B group vitamines. Table 2.6 shows the average mineral and vitamin contents of sesame seeds [10].

Table 2.6: Average mineral and vitamin contents of sesame seeds **[10]**

Minerals	Value per 100 g	Vitamins	Value per 100 g
Calcium, Ca	975 mg	Thiamin	0.791 mg
Iron, Fe	14.55 mg	Riboflavin	0.247 mg
Magnesium, Mg	351 mg	Niacin	4.515 mg
Phosphorus, P	629 mg	Choline	25.6 mg
Potassium, K	468 mg	Vitamin E (alpha-tocopherol)	0.25 mg
Sodium, Na	11 mg		
Zinc, Zn	7.75 mg		
Copper, Cu	4.082 mg		

Among the vitamins in sesame seed, the presence of vitamin E is very interesting because of the effectiveness of sesame seed as a health food. Vitamin E is found as eight structural forms that include four tocopherols (α-, β-, γ-, δ- tocopherols).

α -Tocopherol is the only form of vitamin E in vitamin supplements whereas γ -tocopherol is the predominant form of vitamin E. γ -Tocopherol has many beneficial properties. The most important one is the effect on human cancer cells. Also, it has the advantage of prevention of aging [20]. Sesame seed is also rich in various mineral constituents. As shown in Table 2.6, calcium and phosphorous, which are often deficient in modern diets, are found in high concentrations [10].

2.4.4 Lignans

The lignan antioxidants are unique for sesame and are present in the oil. The lignans such as sesamin (2,6-bis-(3,4-methylenedioxy phenyl)-cis-3,7-dioxa-bicyclo (3.3.0)-octane) and sesamolin (2-(3,4-methylenedioxy phenoxy)- 6-(3,4-methylenedioxy phenyl)-cis-3,7-dioxabicyclo (3.3.0)-octane) and their derivatives (sesamol,

sesaminol) prevent the oxidation of the oil and provide long shelf-life and stability to the oil [21]. Figure 2.4 shows the basic structure of lignans. Sesame lignans are considered as the most important and characteristic components of sesame seed in view of their various functional activities. The lignans are digested by the microflora found in the intestine of the humans.

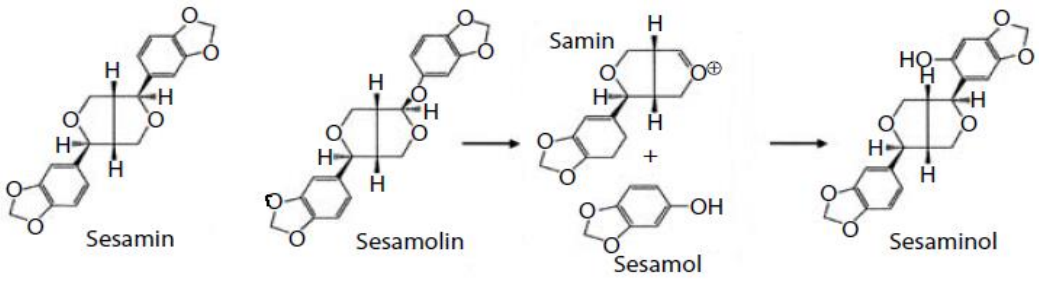

Figure 2.4: Structure of sesame lignans **[5]**

When sesame seeds are roasted at 200 ^{0}C for 60 min, phenolic compounds and sesamolin could be degraded to sesamol. Infrared roasting of sesame seeds at 200 ^{0}C for 30 min provides degradation of sesamolin to sesamol [22]. In sesame oil, the content of sesamol increased under heating conditions while the content of sesamolin decreased and the sesamin content slightly changed. Sesamolin also degraded when the oil was heated at 200 ^{0}C for 20 min. [23].

2.4.4.1 Sesamin, sesamolin and sesaminol

Sesamin has a typical lignan structure of the β-β′ (8-8′)-linked product of two alcohol radicals as shown in Figure 2.4. Sesame seed contains sesamin usually about 0.4% in sesame oil. It is highly hydrophobic and can be obtained as a crystalline product from sesame oil. The biosynthesis and activities of sesamin were extensively studied. Bhunia et al. (2015) has reported that sesamin possesses an anti-oxidative property, cholesterol and lipid lowering activity. Furthermore its protective activity against liver damage and anti-hypersensitive activity was also mentioned [24].

Sesamolin has a unique structure involving one acetal oxygen bridge in a sesamin-type structure as shown in Figure 2.4 and seems to be characteristic lignan of sesame seed [25].

Namiki (1995) reported that sesaminol was first found as one of the antioxidative component in sesame seed. It was isolated as the major antioxidative factor from the refined sesame oil [17]. Table 2.7 shows the minor constituents found in sesame oil [25].

Table 2.7: Minor constituents of sesame oil **[26]**

Compound	Content (mg/kg oil)
Lignans	
Sesamin	6490
Sesamolin	1830
Polyphenol	23.06
Sesamol	8.11
Tocopherol	
γ - Tocopherol	358.0-663.5
α - Tocopherol	3.10-6.86
δ - Tocopherol	7.84-13.02
Phytosterol	5100-7600
Sitosterol	2687-4132
Campesterol	706.8-1001

2.4.4.2 Synergistic effect of sesame lignans with tocopherol

In order to determine whether sesame lignans are related to synergistic effect of sesame seed with tocopherol, a study has been conducted using sesaminol and sesamin. The addition of either of these sesame lignans reduced the level of lipid peroxide in liver and increased the levels of α -tocopherol in plasma and liver, and in these effects, sesaminol was more effective than sesamin [26]. When a variety of sesame seeds containing higher sesamin and sesamolin contents were used, levels of γ-tocopherol increased greatly in the livers and brains of rats and also significantly in kidneys [27].

2.4.5 Flavour and taste

Since sesame is used widely in food as a whole seed or as a paste, its flavor and taste are gaining attention. The characteristic flavor of roasted and unroasted sesame seeds is a very important factor in the deliciousness of various sesame foods. For the roasted sesame flavour, many chemical studies have been done and more than 400 components have been isolated and identified. They have been classified as pyrazines, pyridines, pyrroles, furans, thiophens, thiazoles, carbonyl compounds, and

others. Among them, alkylpyrazines are the main components and provide the representative deep-roasted flavor, whereas thiazoles and thiophenes are assumed to contribute to the characteristic roasted sesame flavor [5]. Off-flavor is a critical quality defect of roasted sesame oil, which affects the preference of consumers. Sesame oil industry has worked to solve the off-flavor problems for a long time. Oxidation is one of the reactions which produce off-flavors in the oil. Although sesame oil is resistant to oxidation, serious problems can be seen in the production of off-flavor compounds.

Undesirable off-flavor compounds and nutritional loss from the oxidation of oil decrease the quality and value of oils. The oxidation of oil is affected by some factors such as temperature, light, fatty acid composition, antioxidants, and prooxidants. When sesame seeds are roasted at high temperature like 250˚C, free fatty acids are produced by hydrolysis of mono-di-, and triacylglycerols in the seeds and these free fatty acids can accelerate the oil oxidation [28]. Since there is no refining in the manufacturing of roasted sesame oil, free fatty acids remain in the oil and off-flavour production can increase. Roasted sesame oil also naturally contains useful antioxidants such as tocopherols and lignans, which can decrease off-flavor compound formation [5].

2.5 Sesame Allergy

Food allergy becomes very important because of its effect on health. It can cause very serious autoimmune illnesses. Adverse immune responses to foods or food ingredients affect nearly 1-3% of adults and 4-6% of children [30]. The main food allergens are mostly proteins or glycoproteins with molecular masses of 10–60 kDa. Food allergy is delegated of Type-I (immediate type) allergies which are interposed by Immunoglobulin E (IgE) antibodies [29, 30].

Sesame food allergy in children is increasing, especially in the developing countries of Europe [31]. Compared with other allergies to animal foods such as egg and milk, plant food allergies are lower. The incidence rate of allergy to peanuts is highest, followed by sesame seed [32].

Food Allergen Labeling and Consumer Protection Act of 2004 (FALCPA) food alergen awareness program defined for eight common foods that cause serious allergic reactions: milk, eggs, peanuts, tree nuts such as almonds, walnuts, and

pecans, fish, shellfish such as crab, lobster, and shrimp, soy and wheat [33]. Nowadays sesame seed is one of these food items that is to appear on food labels in European Union. Sesame seed is also mandatory labeled in Australia, Canada, Hong Kong, United Kingdom and, United States for its allergen effect on public health [34, 35].

Alergenicity of sesame can occur in many different ways. Paths to influence of allergic reactions into patients that involved clinical trials about sesame allergenity are shown in Table 2.8. Urticaria, angiodema, atopic dermatitis is the most widely encountered complaints about sesame allergenity [36, 37].

In many researches, 2S albumin (β-globulin) family was found as the major allergens in sesame seeds. Despite 2S albumin is a member of globular proteins rich in methionine and cycteine, not all 2S albumin isoforms in sesame are sulfur-rich. After 2S albumin, 11S globulin (α-globulin) is also suggested as most widely sesame seed allergen [17, 29]. In several studies, it had been thought that IgE-binding epitopes had an important place to diagnoses and treatment as mentioned before. These studies were indicated that genetically engineered allergens with decreased IgE-binding capacity can retain their activity back [38]. Most of researches indicate that strategy of avoidance is the best way for treatment of allergenity like sesame seed [29, 39].

2.1 Sesame Production in Turkey

Sesame seed has a great importance in Turkish culture as well. Two of its common usage areas are tahini and tahini halva production. In addition to that, sesame used on the surface of makes Turkish bagel (simit) famous worldwide. Unfortunately, in recent years sesame production in Turkey has diminished seriously. While the production was nearly 35.000 tonnes in 1998, it has dropped to 16.000 tons in 2012. Figure 2.5 shows the decreasing pattern for sesame production in Turkey [1]:

Table 2.8: The proportion of patients that involved in clinical trials about sesame allergenity and the shape of occurance of allergic reactions **[36,37]**

Sypmtoms	Beyer et al., 2002[a] %	Pastorello et al., 2001[b] %
Urticaria	40	40
Angiodema	60	-
Diarrhea	-	-
AD* (Egzama)	20	40
Anaphylaxis	-	10
GI**	40	10
Rhinits	5	-
Asthma	5	10
Mouth and throat itchiness	10	30

Results are expressed as percentage.

*AD: Atopic dermatisis

**GI: Gastrointestinal Symptoms

a: Study actualized with 20 people that had age range between 2-28.

b: Study actualized with 10 people that had age range between 4-36

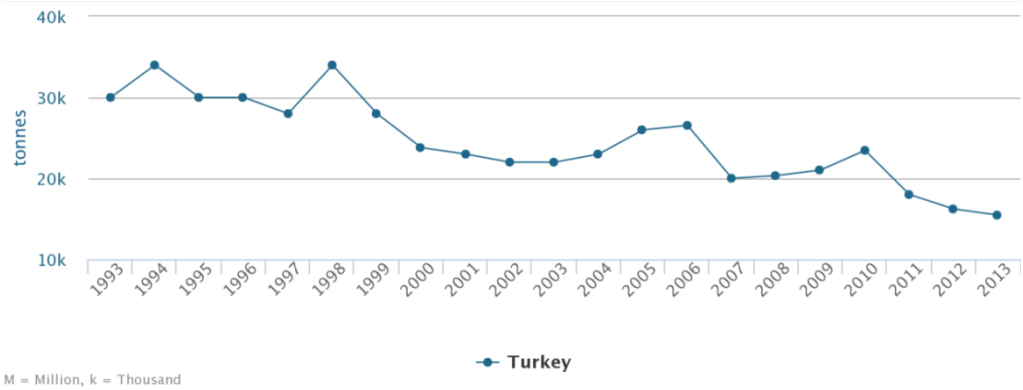

Figure 2.5: Production of sesame seed in 1993-2013 of Turkey**[1]**

The color of sesame seeds are mostly yellow and brown, just only less than 10% is black. Trace amount of sesame seeds is white grown in Aegean region. In Turkey, Mediterranean region and Aegean have higher plantation area than North and internal zones. In 2012, Aegean region has 52% of total sesame cultivation area in Turkey which corresponds to 15.000 ha area [40].The second area is Mediterranean region having 33.8% ratio. Marmara region and internal regions have lower

cultivation area. Antalya, Adana, Osmaniye, Edirne, İzmir ve Kütahya are the most known sesame producer cities. Table 2.9 shows the sesame oil producer countries in the world. Although Japan has not planted area, it has 45.500 tonnes of sesame oil production. Turkey is eighth among with 30.120 tonnes of sesame oil production [40].

Table 2.9: World sesame oil production **[40]**

Order	Countries	Production (tonnes)
1	China	230.600
2	Myanmar	249.000
3	Tanzania	194.670
4	India	82.100
5	Sudan	56.000
6	Japan	45.500
7	Mozambique	37.500
8	Turkey	30.120

2.2 Sesame Oil Technology, Pressing, and Extraction of Oil

Oil production from different sources is important to provide oil for the use as food or in cosmetics and raw material for the production of chemical products. The main important point is the separation of the oil from the seed with appropriate methods. But only looking at the oil production for high quality oil is not enough, harvesting, pretreatment of the harvested material, and the storage conditions until processing should be considered. Another important point in oil production is whether the seed is extracted by pressing or solvent extraction.

The aim of the extraction method is to optimize the oil yield with maintaning of the oil quality. In this connection, not only the removal of contaminants or substances affecting the sensory quality or storage stability of the oil are important. In extraction process, mechanical and chemical methods are applied. Nowadays, the use of more environmentally friendly methods for the oil processing has been considered. These methods increases the oil yield without using solvent extraction by the use of enzymes or improves the refining process. Before extraction, some pretreatment parameters are important. Handling, cleaning and drying methods are to be

considered. Cleaning from foreign materials can be seen as an unnecessary or simple step, but in fact it is the key point of all process. Since foreign matter, such as stems, broken seeds, stones and foreign seeds, often contains higher amounts of moisture, chlorophyll, fibers, minerals and free fatty acids or a higher population of microorganisms, to ensure that high-quality oil and meal are obtained, all these matters should be eliminated. In addition, the moisture content of the raw material is important, because depending on the form of the seed material, up to 40% of the volume of stored seeds consists of hollows, in which an appropriate relative humidity is adjusted, depending on the amount of seed moisture. This humidity sets roasting or exraction process of seeds [51]. Since sesame seeds consist of significant amounts of hulls, which contain major parts of fiber, the removal of the hulls is recommended. Advantages of dehulling of the seeds before processing gives higher quality oil with regard to the sensory characteristics, and a lower temperature can be applied during pressing. Dehulling starts with the purification of the raw material to remove impurities such as foreign seeds, broken seeds, and dirt. The content of seed moisture is necessary to ensure an appropriate elasticity. At high-moisture contents, the elasticity of the seeds is too high for the dehulling process, thus raw material should be dried [51].

Pressing for the production of oil has been known for several hundred years and only after World War II this process was replaced by solvent extraction. Today, more than 98% of the oil production worldwide is carried out by solvent extraction, but for special oils, such as extra virgin olive oil or virgin rapeseed oil, sesame oil, or oils produced in rural areas, pressing is indispensable. The aim of the pressing process is to separate the oily phase from the solid phase of the seed material. Solvent extraction seems to be more advantageous than pressing, but the consumer demands virgin oils since they are healthier which makes price higher. A special phenomenon can be observed for cold-pressed edible oils from roasted seeds such as nut oils or pumpkin seed oil, which show a higher oxidative stability than corresponding virgin oils from unroasted seeds [41]. Prior et al. (1991) found a higher oxidative stability of canola press oil after heat treatment of the seeds, which decreased with subsequent refining [42].

During the roasting process, seed material is treated by heat between 180 and 220°C resulting in a better availability and extractability of bioactive compounds as well as the formation of new antioxidants.For example, generation of sesamol from the degradation of sesamolin during roasting of sesame seeds Lee et al. (2009) occurs which improve the stability of the resulting oil [43].

2.3 Virgin and cold-press oils

Codex Alimentarius (CA) Standard for Named Vegetable Oil, defines "virgin oils" as "obtained, without altering the nature of the oil, by mechanical procedures, e.g. expelling or pressing, and the application of heat only. They may have been purified by washing with water, settling, filtering and centrifuging only [44]. On the other hand, CA Standard for Named Vegetable Oil defines "cold pressed oils" as "obtained, without altering the oil, by mechanical procedures only, e.g. expelling or pressing, without the application of heat. They may have been purified by washing with water, settling, filtering and centrifuging only."

According to the German Guideline (GG), virgin and cold-pressed oils are identical to each other. If a careful, gentle mechanical extraction of the raw material without application of heat was carried out, it can be named as "cold-press oil". Heat application is allowed during preparation of the raw material and/or of the oil after the pressing process.

German Society of Fat Science indicates virgin oils that there are no heat treatment in the raw form. Only pressing of untreated raw material is expected. For cold press oil in extraction process, heat is not applied, only roasted seeds can be processed. Therefore, roasted sesame seed oil can be named as cold press sesame oil or natural oil. Cold-press oils from roasted seed material present a special aspect, because such heat treatment results in a better oxidative stability of the oil that can be explained by better extractability of antioxidants during pressing [48].

2.4 Hydraulic pressing and sesame oil

Being informed about positive contribution to human health thanks to fatty acids and bioactive compounds of vegetable oils day by day, the consumer demand on the natural and extra natural oils is has been increasing. In fact, natural oil has 8000 years history in the world. The development of appropriate production techniques providing that oil yield increased by solvent extraction 120 years ago and purification of oil after refining processes led unnatural oil producing companies to be pulled out of the markets. 15-20 years ago, new interests in the olive oil and other natural oils began to occur. One of the most important reason of these interests is the tendency towards to less processed foods in order to be healthy. It is known that natural oils protect their natural structure while refined oils loss their almost all of the beneficial compounds. Another reason is the curiosity of consumers to the natural oils because of their taste and odour [45].

Producers have handled that advantageous choice in order to earn more. In conclusion, olive oil, sunflower oil, grape seed oil, flax seed oil and sesame oil have started to take part on the markets. The common properties of these oils are the high price in wide range. While one of the reasons in high prices is type of seed oil, the other one is the production technique such as pressing and thus the oil yield becomes lower [46].

According to Codex Alimentarius, cold press oils are vegetable oils that no heat treatment is applied in order not to deteriorate the natural structure and only mechanical treatments are applied. These oil types are only washed, waited, purified and centrifuged [47].

The main difference between natural and cold press oils is the heat treatment that can be applied <50ºC in virgin oils. Pressing technique used in the production of natural oils protect tocopherols, sterols and phenolic compounds.

Oilseed materials for extraction can be divided into low-oil containing materials (18−22%) or high-oil containing materials (>22%)[48]. Sesame seeds can definitely be classified as high-oil vegetable material. Conventional vegetable oil extraction is carried out by pressing or solvent extraction. Solvent extraction is the most efficient and widespread method, but it has some industrial disadvantages such as safety

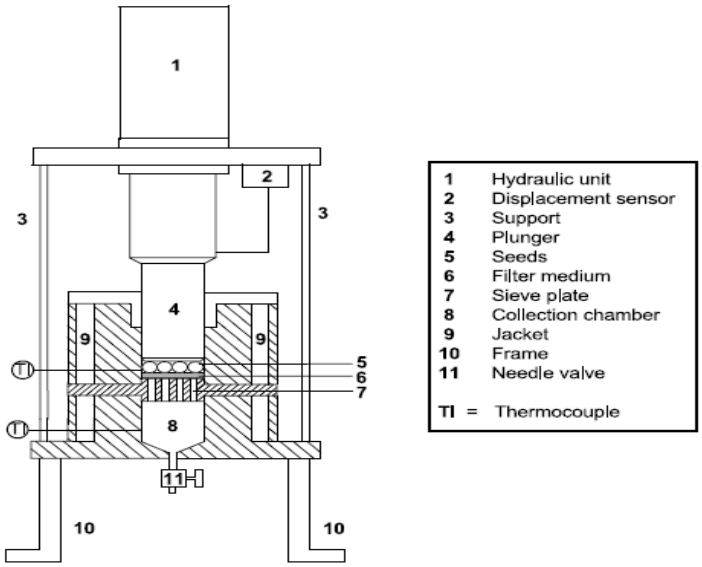

Figure 2.6: Schematic representation of hydraulic press[50]

problems due to usage of flammable solvents, high operation costs and poor quality products because of high processing temperatures. Especially for high oil containing seeds, this quality reduction is unacceptable [49]. On the other hand, mechanical pressing is less harmful and intensive than the solvent extraction method [50].

Mechanical pressing has the advantage of safety and simplicity in whole process and is more efficient. Also, pressed materials have better natural properties, end products are free of chemicals such as free fatty acids, trans fatty acids and oxidative products [51]. Pressing can be defined as a compression step to take out a liquid from a porous matrix. Hydraulic presses are used for pressing cocoa in order to extract the cocoa butter, in olive oil production, and in sesame oil production. The pressures are very high as follows: 100 MPa for cocoa 40 MPa for olive oil [52] and 20 MPa for sesame oil [54]. In Figure 2.6, typical schematic representation of the hydraulic presses is shown [50].

In a typical experiment, seeds are placed in the presschamber, then the piston is lowered on top of the seeds. The seeds are allowed to equilibrate to the pressure for at least 10 min without applying pressure on the seeds. After this, the piston is lowered again and again until whole oil part is extracted from seed (my laboratory experience)

After all these, extraction by just pressing the seeds stays inefficient. During pressing of oilseeds it should be effectively pressed. Some methods have been found to

improve the oil extraction efficiency of mechanical presses. Conventional heat treatment is the most appropriate method for optimum oil extraction. In production of oil by pressing, in order to increase the yield of oil, generally heat (roasting or conditioning) is used in pre-treatment stage. In recent years, together with traditional heat treatment like roasting, microwave roasting, ultrasound asissted alcoholic extraction and enzymatic pre-treatments attract attention. Aim of these operations is to provide easy extraction of oil. Pre-treatments are essential because it completes the breaking down of oil cells, lowers the viscosity, coagulates the proteins, and adjusts the moisture content at an optimum level for pressing. Pretreatments also provide enzymatic inactivations [51].

2.5 Pretreatments Applied On Sesame Seeds

2.10.1 Conventional method: Roasting

Roasting is the most important step in coffee, nut especially hazelnut and peanut and sesame seed processing. It causes apparent physical, chemical, structural and sensorial changes. Roasting process in sesame provides more flavour, desired color and texture changes. Roasting process is used in different forms because of broad usage of sesame seed. For example, sesame paste (tahini) is produced by milling of roasted sesame. Additionally, sesame oil is prepared from roasted sesame seeds which has significant flavour and extented shelf-life. Since roasting affects the product quality, control of roasting process is important.

Color is one of the process control parameter during roasting, because the brown pigments in sesame seed increase during browning and caramelization reactions. It was reported that non-enzymatic browning and phospholipids degradation were responsible for color formation in sesame oil. Additionally, texture is another important control parameter during roasting [55]. Sesame oil from roasted sesame seeds has characteristic odour and taste. It has higher oxidative stability than other vegetable oils [55]. Yen (1990) reported that sesame oils roasted between 180°C and 220°C have no differences in characteristics, such as acid value, saponification value and refractive index [56]. On the other hand, it was found that the volatile components of sesame oil at different roasting temperatures (160, 180, 200, and 220°C) and roasting times (10, 20 and 30 min). It can be concluded that, volatiles increased with the increasing roasting temperature and time [57].

The seeds are often roasted to enhance the flavor of the oil, but sometimes this process can reduce the antioxidant content of seed oil. Seed roasting is determined as a critical step in the processing of sesame seed oil. It was stated that roasting at 150–180ºC had no effect in the oxidative properties of oil, and tocopherol and sesamolin contents were not affected at temperature of roasting around 180ºC. In another study, oil quality of sesame seed, temperature and roasting time were investigated. Oxidative properties didn't change in significant amounts between 160ºC and 250ºC. It was stated that high-quality product could be obtained by roasting sesame seeds for 25 min at 160ºC or 180ºC, for 15 min at 200ºC, or for 5 min at 220ºC. Taking into consideration of antioxidant content, lipid stability and sensorial properties, roasting at 180ºC for 25 min produced the most acceptable oil [59].

In a study about sterols, the total sterol content has been found approximately as 5400 mg/kg for white sesame seeds and 5000 mg/kg for dark sesame seeds, with campesterol including 12% of the sterols, β-sitosterol including 22% of the sterols and Δ^5-avenasterol including 12% of the sterols in white sesame seeds, and 11%, 30% and 11% of the sterols in dark sesame seeds [59]. The high level of Δ^5-avenasterol has been defined as the indicative of antioxidant behaviour for sesame seed oil [60].

Mohamed and Awatif (1998) used the unsaponifiable fraction of sesame oil as a natural antioxidant. The Δ^5 and Δ^7 avenasterols including 12% and 0.6% of the unsaponifiables in non-roasted white sesame seeds, and 14% and 0.8% of the unsaponifiables in roasted white sesame seeds, respectively. Similar levels were found for dark sesame seeds. The tocopherol and lignan contents of the unsaponifiable fraction were higher in the white sesame seeds than in the dark ones, but they decreased significantly during roasting. But in contrast, the sesamol content increased during roasting, to 16 mg/kg for white sesame seeds and 12 mg/kg for dark sesame seeds [59].

In another study by Elleuch et al. (2007), white sesame seed was used in order to detect the quality characteristics in nonroasted and roasted state for halva production. Raw sesame seed (RS1) showed higher moisture content (16.20 %) than roasted sesame seed (RS2) as 2.98%.

The polyphenols content of RS2 (598 mg/100 g) was found to be higher than polyphenol content of RS1 (260 mg/100 g). The raw sesame seed contained 52.24% of oil, while roasted one contained 32.84% of oil. That is the proof that oil was localised in hulls. Also oil yield was studied by using Soxhlet extraction as hot extraction and cold extraction. Hot extracted where roasted sesame was extracted showed higher oil yield than cold extracted where sesame was unroasted. The difference in the yield at each extraction was explained due to the effect of heat on oil extraction [15]. In a study, it was explained that both oil yield and process costs depended on seed preparation and pre-treatments (roasting) before pressing. Also, in the case of the size of sesame seeds, oil yields were increased by reducing their sizes. According to study, size of seed, pre-treatment temperature of the seed and moisture content were the control mechanisms to achieve best results and get higher oil yield. It was stated that seed cleaning is another supporter factor for increasing oil quality and oil yield. Pressing efficiency could increase with efficient removal of foreign material [52].

Willems et al (2008) studied experimental determination and modeling of yield and pressing rates in oilseeds. Experiments were performed for sesame, linseed, rapeseed, and jatropha at different temperatures of 40, 80, 100˚C, respectively. At the end, it was found that, temperature only had a significant influence around 100^0C. According to the study, increasing temperature from 40˚C to 80˚C didn't affect oil yield. Around 100˚C, protein and oil globules coagulate which increase the yield [49].

The effects of sesame seed pre-treatments including roasting, steaming, and roasting with steaming in Sudan and Egypt sesame seeds were investigated. Raw sesame seed and roasting with steaming showed higher oxidative stability [61]. In a summary, traditional roasting changes typical color, texture, aroma, chemical composition, nutritional value, and shelf-life. During roasting fatty acids, peptides, amino acids, vitamin E, and lignans reveal alternations. Enzymes are inactivated, microorganisms, toxins, and allergens are removed. According to the studies mentioned above, roasting has positive effect on oil yield.

2.10.2 Microwave pretreatment

Microwave heating is shown as an alternative pretreatment method to traditional pretreatment due to low processing time, energy saving property, providing high quality and high nutritional value products [62].

There are differences in the mechanisms of microwave heating and traditional heating. In traditional thermal processing, energy is transferred to the material by convection, conduction, and radiation from the surfaces of the material, while microwave energy is delivered directly to materials with the electromagnetic field. Because microwaves can penetrate materials and store energy, uniform heating is achieved. As microwaves can transfer energy through the whole volume of the material, processing time is reduced and overall quality is enhanced. Microwaves are energy-containing electromagnetic waves whose position is in the electromagnetic spectrum. Figure 2.7 shows electromagnetic spectrum identified by their frequencies, energy, and wavelength [63].

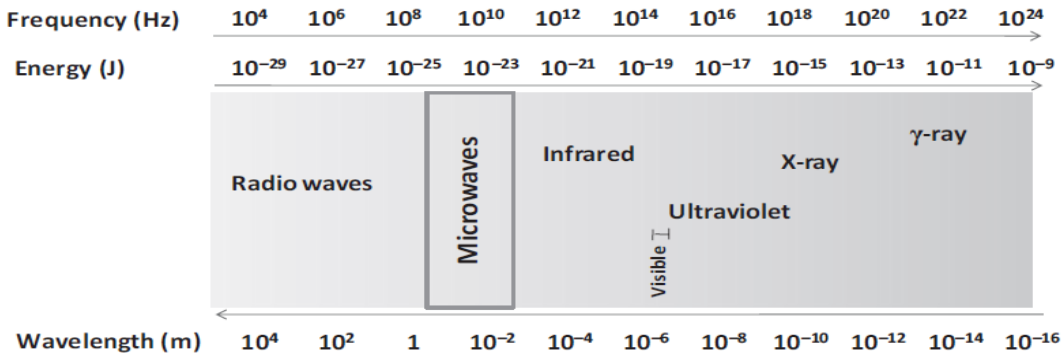

Figure 2.7: The representation of electromagnetic spectrum[63]

Table 2.10 shows two microwave heating frequencies allowed for use in the United States for industrial heating.

Table 2.10: Microwave frequencies approved by Federal Communications Commission (FCC) [65]

Frequency (MHz)	Wavelength (ʎ) (cm)	Uses
2450	12.2	Microwave ovens Industrial heating
915	33.0	Industrial heating

Microwave equipment consists of three components. These are source, transmission lines, and applicator. The microwave source generates the electromagnetic radiation, and the transmission lines deliver the electromagnetic energy from the source to the applicator. In the applicator, the energy is absorbed or reflected by the material [63]. Energy is transferred to materials by interaction of the electromagnetic fields at the molecular level, and the dielectric properties determine the effect of the electromagnetic field on the material [65].

Materials show different responses to convert electromagnetic energy into heat. Therefore, it is important to know the dielectric characteristics of the material for better microwave heating. The capacity of each material to absorb microwave energy is directly related to the degree of penetration of microwaves in the material. When absorption occurs, the conversion of electromagnetic energy into heat depends on the relation between the dielectric loss factor (ε″) and the dielectric constant (ε′).This relation is known as the dissipation factor (tan δ) **(2.1)**:

$$\tan\delta = \varepsilon''/\varepsilon' \qquad \textbf{(2.1)}$$

If the dissipation capacity is higher for a sample, microwave will less penetrate into the same sample. Therefore, the ratio ε″/ε′ defines the capability of each material to convert electromagnetic energy into heat [63]. Water in foods is responsible for dielectric heating. Because of its dipolar nature, water molecules get together with the high frequencies, then heat is generated from collisions with the near particles. Also, mineral ions migrate under the influence of the electric field, and generate heat [66].

Heat generation in food is also dependent on the frequencies applied. When lower microwave frequencies are present, then higher penetration exist. Consequently a more uniform and faster heating are obtained [67].

The major food components: water, carbohydrates, lipids, protein and minerals interact differently with microwaves. During microwave treatment, like in other heating treatments, different chemical changes occur that affect oil quality and safety. Some components are destroyed while other potentially hazards are formed. The main classical degradation patterns observed in the triacylglycerols include hydrolysis, oxidation, and thermal polymerization. The chemical nature of the fatty acids within the triacylglycerols, particularly their unsaturation degree, will

determine its susceptibility towards oxidation and polymerization, while the presence of water will enforce hydrolysis. Other minor components, such as vitamins and some sterols, can be regarded as protective factors, against oxidation and polymerization, respectively. The temperature achieved during food heating and the heating period will further determine the extent of the degradation effects, while comparing with other conventional heating technologies [66]. Among the different and new available methods, microwave pretreatment of seeds is a simple and desirable technique for production of high quality oil with high nutritional properties. Microwave pretreatment provides high availability of desirable phytosterols and tocopherols in the extracted oil or pressed oil. Instead of traditional thermal treatment, microwave treatment of seeds receives attention. When it is compared with traditional methods, microwave pretreatment for oil extraction has many advantages such as: improvement of extracted oil yield and quality, direct extraction capability, lower energy consumption, faster processing time [48, 68]. The most important characteristic of microwave heating is volumetric heating that is whole part of seed is applied [69].

Microwave pretreatment prevents stress reactions in oil seeds. By using microwave pretreatment in oil seeds, a higher extraction yield can be obtained due to cell membrane rupture. In addition to that, generated permanent poress provide oils to move through the permeable cell walls [48]. According to Azadmard-Damirchi et al. (2010), microwave pretreatment can increase the yield of extracted oil.

They also found that microwave treatment time could also increase the yield of extracted oil [69]. Similarly, Uquiche et al. (2008) have found that microwave pretreatments of hazelnuts could increase oil yield [48].

Cheng et al. (2011) investigated microwave pretreatment coupled with solvent extraction for the production of crude palm oil. The results showed that the oil yield of palm fruits by microwave heat treatment was higher than that of conventional heat about an average of 20%. Fatty acid composition of the crude palm oil showed an incrase in lauric acid (C12:0) as microwave exposure time increased. Palm oil after microwave treatment also exhibited desirable and very low free fatty acid (FFA) (0.26%) and moisture content (0.05%). In addition, vitamin E and carotene contents were recorded at highest levels after 2 min microwave treatment [70].

In the study of Azadmard et al. (2010), rapeseed was treated with microwaveand possibility of increasing yield of extracted oil, oxidative stability and nutritional content were investigated. Microwave pretreatment was applied for 2 min and 4 min and oil was then extracted by using press. In order to compare the results, oil was also extracted from untreated rapeseed by solvent extraction and press. Results showed that solvent-extracted oil had the highest phytosterol content. Microwave pretreatment of rapeseed increased the yield of extracted oil by 10%, phytosterols by 15%, and tocopherols by 55%. Oil extracted from untreated rapeseed by press had oxidative stability about 1 hour, while microwave pretreatment increased oxidative stability to 8 hours. It was advised that treating rapeseed with microwave gives a good yield of oil, with a high amount of nutritional content, and can produce oil with a longer shelf life [69].

In another study by Yoshida et al. (2005), peanut seeds were roasted in microwave for 6, 12, 20 and 30 min at a frequency of 2450 MHz. The fatty acid distributions of triacylglycerols (TAGs) and phospholipids (PLs) were studied. Before microwave roasting, free fatty acids and PLs were in low amount, but when treatment was applied, a significant increase occured [71]. Microwave heating (950W, 9 min) on grapeseed oil extractability and quality was compared with traditional heating (50ºC, 2h, fluid bed dryer). Both of the methods provided increased oil viscosity, whereas microwave heated oil was higher than traditionally heated oil [66].

Microwave heating influenced the color of seed and olive oils. When seed oils (soybean, peanut, sunflower and mixture of soybean/peanut oils) were heated by microwave from 2 to 18 min (120 to 227ºC) their color changed gradually from yellow-brown to light brown.

An increase in viscosity and density values was observed when vegetable oils were heated for both traditional (180ºC, 120 min) and microwave heating (500W, 120 min) of olive oil, sunflower oil, and high oleic sunflower oil. Viscosity increase in different vegetable oils subjected microwave and traditional treatment is shown in Figure 2.8 [66].

As can be seen from Figure 2.8, the viscosity of microwave heated VOO has the highest value compared to OO, SO, and HOSO have. The viscosity difference between microwave heated and traditional heated oils are clearly seen.

Chiavaro et al. (2010) studied on the oxidative stability of peanut oil, high oleic sunflower oil and canola oil with increasing microwave heating times. Microwave heating during 15 minutes at 720 W caused an induction time reduction of nearly 26% and 23% comparing with initial values, respectively in peanut and canola oils [73].

Several works with vegetable oils investigated the effect of microwave treatment in fatty acid fraction. It was reported that a higher nutritional quality loss occurred with microwave heating when compared to conventional heating (electric oven) studied on three vegetable oils (virgin olive oil, peanut and sunflower oils). Saturated fatty acids did not show significant changes after heating. On the other hand, both unsaturated and polyunsaturated fatty acids were significantly decreased. The ratio between linoleic and stearic acids in corn and soybean oils continuously decreased during microwave heating exposure at different power settings.

The effect of microwave heating in the sterols fraction of vegetable oils is not extensively studied. By studying extra virgin olive oil, olive oil, sunflower oil and high oleic sunflower oil, significant differences were not observed after microwave heating in all the samples. Sterol compounds were mentioned as resistant to degradation through microwave radiation. It was showed that tocopherols gradually decreased with microwave heating time.

When microwave heating was compared with conventional heating, higher degradation rates were observed in the conventional heating, it was reported that losses became after 10 minutes of microwave heating (500W) which was equivalent to 10h (180ºC) under conventional oven heating. When exposed to 120 minutes of microwave heating, virgin olive oil and olive oil reported losses around 96 and 85%, respectively, in their total polyphenols content. Under conventional heating, only a 10% reduction was observed in the virgin olive oil, compared with a 64% reduction in olive oil [66].

Dostolava et al. (2005) tested the oxidative stabilities of pork lard, sunflower, rapeseed, peanut and high-oleic peanut oils under microwave heating conditions. Vegetable oils and lard were heated in a microwave oven for 40 min between 25°C and 200°C. The peroxide value, the contents of conjugated dienoic and trienoic acids, and polymers. Sunflower oil was found the least stable oil because of low content of

γ-tocopherol. Rapeseed oil was more stable because of high γ-tocopherol level. Conventional treated peanut oil was relatively stable [74].

Conventionally roasted and microwave heated cumin seed samples were compared; the optimum condition in the conventional roasting was found as 125 °C for 10 min and in the microwave treatment, the best condition was found as 730 W for 10 min. Under these conditions, the yields of the volatile oils were similar in both cases [80].
There are limited studies on microwave treated sesame seeds. Some researchers used microwave heating (500 W, 2350 MHz) as a sesame roasting method. All of the α -tocopherol in the seeds was lost after 8 min of microwave heating, and all of the α-tocopherol was lost after 16 min, whereas only 6.5% and 20% reductions in α-tocopherol levels were found after 20 min and 30 min of heating, respectively. The original contents of sesamin, sesamolin and sesamol were 6824 mg/kg, 5642 mg/kg and 54 mg/kg, respectively. The sesamin and sesamolin concentrations decreased by 20% after 30 min of microwave heating. Lipids in general were not significantly affected by microwave heating for up to 30 min, by which time the seeds had a burnt and bitter taste. It was also noted a significant reduction in the antioxidant levels of sesame seeds processed using microwave heating. Under appropriate conditions, microwave energy has similar effects on oil quality as the oven-roasting process [58].

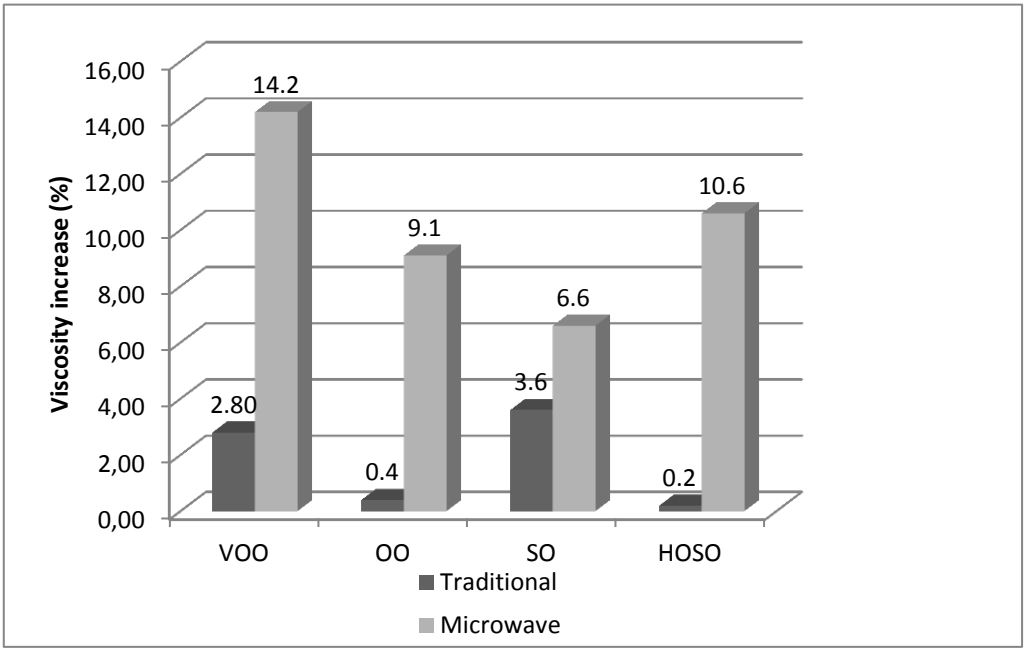

Figure 2.8: Viscosity increase(%) in different vegetable oils subjected to microwave heating and conventional heating(VOO-Extra virgin olive oil; OO-Olive oil; SO-Sunflower oil; HOSO-High oleic sunflower oil)

2.10.3 Ultrasound assisted ethanolic pretreatment

Ultrasound is defined as sound waves with frequencies above the sounds that human hears (>16 kHz). Basic definition for ultrasound refers to pressure waves with a frequency of 20 kHz or more [80]. Generally, ultrasound equipment uses frequencies from 20 kHz to 10 MHz. Figure 2.9 shows different frequency ranges of ultrasound [79].

There are two types of applications of ultrasound in the food industry: high and low intensity. High-intensity ultrasound utilizes high power levels (>1 W cm^{-2}) and low frequencies (<0.1 MHz). There has been a growing interest in the use of high-intensity ultrasound as a preservation method [81].

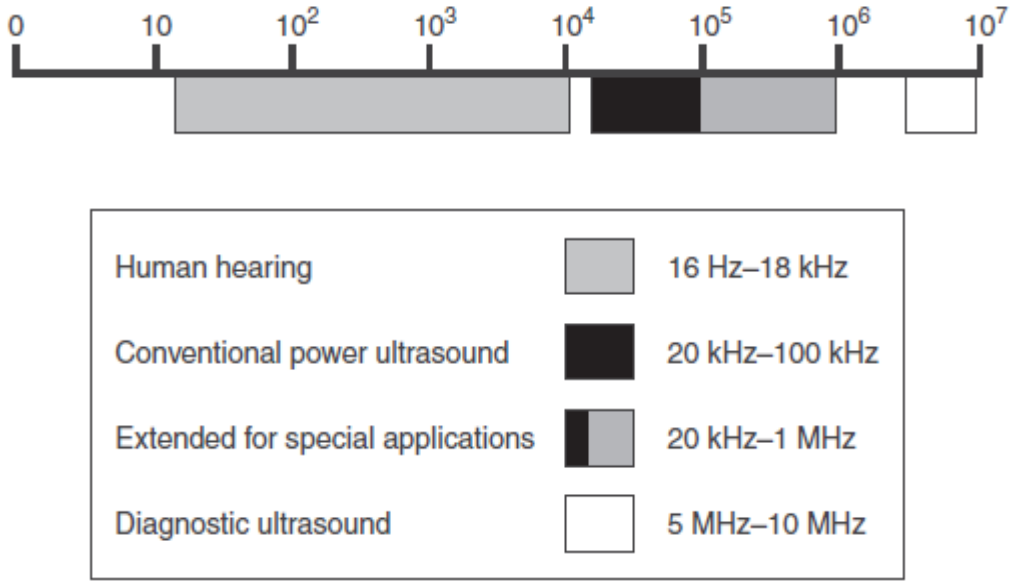

Figure 2.9: Frequency ranges of ultrasound[80]

Low-intensity ultrasound is used to provide information about the physical properties of food materials. Power levels are lower than the power levels of high-intensity applications (<0.1 W cm^{-2}) and the frequencies are higher (0.1–100 MHz). Low-intensity ultrasound provides information about physicochemical properties, while high-intensity ultrasound is used to change physical or chemical properties of foods [81, 82].

Power ultrasound shows its effects by acoustic cavitation. Ultrasound is transmitted with waves which compress and strech molecular structure of the medium. During each streching phase which is called “rarefaction”, negatice pressure is produced,

intermolecular forces are broken, then cavities in other words microbubbles are formed. When many cycles of cavities are formed, there becomes a collapse and large amounts of energy are released. That phenomenon increases temperatures to thousands of Kelvin and pressures to hundreds of atmospheres. In fact, there are two situations in collapsing of bubbles: (i) bubbles behave like a reactor which provides high pressure and temperature and (ii) bubbles produce shock waves which create shear forces [83].

Since the temperature and pressure are very high inside the bubbles, the violent shock wave and high-speed jet are generated which enhance the penetration of the solvent into the cell tissues and accelerate the intracellular product release into the solvent by disrupting the cell walls. Moreover, the violent shock wave and high-speed jet cause the molecules to mix better that enhance the mass transfer rate [84].

The main applications of ultrasound in food processes are related to heat or mass transfer operations. Most of the ultrasonic applications in literature are found in liquid–liquid and liquid–solid systems due to the fact that ultrasonic waves are transmitted in liquids. Ultrasonic field from another type of energy is required for the application of ultrasound. The transducers are the devices that are used to convert energy, which is coming from a power generator, to mechanical energy which causes ultrasonic vibrations. There are two types of transducer: magnetostrictive and piezoelectric. Magnetostrictive transducer is made of metallic alloys. It has advantage of reaching high levels of acoustic power about 150 W/cm^2. It is very stable and reliable. However, it has lower efficiency below 50% than piezoelectric transducers which has power at about 95%. Piezoelectric transducers are used relatively much more than the other. The transducers are attached to the vibrating system which transmits the vibration from the transducer to the medium. In liquid applications, the most commonly used systems are baths and probe-type systems. Figure 2.10 represents the general probe system [80]. In the probe systems, ultrasound is directly applied by a vibrating horn. Type and geometry of probes can vary depending on the aim of usage [85]. In applications with probe systems, the distance between the sound material and sample is an important parameter due to the attenuation of the ultrasonic field with the distance. The level of acoustic intensity and the type of material could influence the magnitude of the ultrasound effects in the transport process. In this case, it is important to consider that the treated sample

can affect the transmitted acoustic field. When level of applied ultrasonic intensity is higher, more ultrasound is observed to affect mass transport [80].

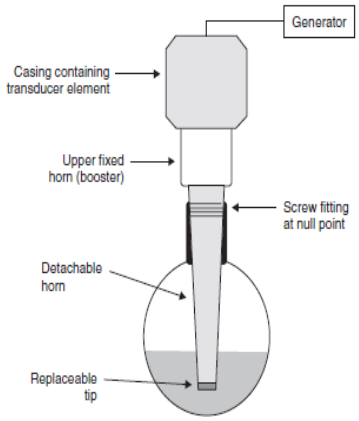

Figure 2.10: Representation of general changeable probe system[80]

Applications of power ultrasound have been studied in microbial and enzyme inactivation, separation, emulsification, heat and mass transfer enhancement, cutting, crystallization, and extraction in foods and plants.

Ultrasound is believed to improve the extraction of proteins and oils from plant seeds, such as soybeans (e.g., flour or defatted soybeans) or other oil seeds. In this case, the destruction of the cell walls facilitates the pressing (cold or hot) and then reduces the amount of press cake [86]. Therefore, ultrasound may reduce the dependence on a solvent and enable the use of alternative solvents which may provide more economic, environmental, and health and safety benefits [87].

The application of ultrasonic extraction in food processing is interesting, because it provides an increase in both the extraction yield and rate. It causes a reduction in the extraction time. It is possible to apply ultrasonic extraction to enhance the aqueous extraction and also in some areas where organic solvents can be replaced with generally-recognized-as-safe (GRAS) solvents, which may provide economical, environmental, as well as health and safety benefits [87]. Classical oil extraction technologies are based on the use of solvent to remove lipophilic compounds from plant. The choice of a suitable solvent influences efficiency of extraction [90]. The most widely used solvent is hexane in the world. Ultrasound extraction has been recognized for application in the edible oil industry to improve efficiency of extraction and reduce extraction time.

Jime´nez et al. (2007) studied the effect of high-power ultrasound on olive paste to extract olive oil. Direct sonication by an ultrasound probe (105 W/cm^2 and 24 kHz) and indirect sonication with an ultrasound water bath (150 W and 25 kHz) were applied, and their effects were compared with traditional thermal treatment. Better extractability was obtained with direct sonication for high-moisture olives (>50%), whereas indirect sonication gave greater extractability for low-moisture olive fruits (<50%). Oils from sonicated pastes showed lower bitterness and higher levels of tocopherols, chlorophylls, and carotenoids [85].

In a study by Liu et al. 2011, with the increased use of ultrasonic treatment, the oil extraction rate was increased. When the ultrasonic power went to 500W, the oil extraction rate reached 95.11%. This is explained with the increased caviatation with increasing ultrasonic power. However, when the ultrasonic power was more than 500 W, the oil extraction rate was slightly reduced. This might be due to the high power and the obvious instantaneous thermal effect, caused the high local temperature, lead to protein denaturation. The watermelon seed oil extraction rate was increased with ultrasonic time, and became stable after ultrasound application for 20 sec. [84].

In a study by Yuting et al. (2013), ultrasound assisted ethanolic extraction (UAE) was found to be the most effective in extracting pomegranate seed oil. In this study, the final oil yield by UAE reached 25.11%, significantly higher than that of solvent extraction (20.50%) [87].

The study by Zhang et al. (2008) made a comprehensive research on ultrasound assisted pre-treatment of oils. Flaxseed oil was extracted by means of ultrasound pre-treatment. At normal conditions, flaxseed oil is extracted from flaxseed by press and solvent extraction. Pressing and solvent extraction resulted with lower yields and had more energy consumption. Also the use of organic solvent is not desirable. Additionally, flaxseed oil cannot stand at high temperatures and can degrade easily. Because of these, ultrasound-assisted extraction was used [80].

The effect of ultrasonic power on the yield of flaxseed oil was found. The yield of flaxseed oil increased almost linearly with increasing ultrasonic power. When the power was increased from 20 to 50 W (1.5 folds increases), the yield of flaxseed oil was increased from 66.7% to 84.9% (18.2% increases). As the larger amplitude of

ultrasonic wave was applied on liquid medium, more bubbles were created and collapsed. Similar results were obtained in a study of ultrasound-assisted extraction of oil from soybean and tannin from myrobalan nut. Based on the results, the maximum ultrasonic power of 50 W was chosen as the output power. Figure 2.11 shows the effect of experimental duration for extraction on the yield of flaxseed oil. It can obviously be seen that the yield of flaxseed oil increases with the extraction time in solvent extraction and ultrasounassisted extraction methods. The probable reason were the disruption of the cell walls by ultrasonic waves which increases the surface area for extracting more oil.

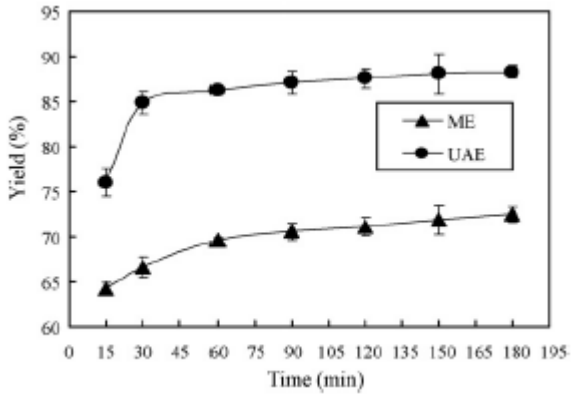

Figure 2.11: The effect of ultrasonic extraction time on the yield of flaxseed oil [80]

In the UAE, the yield of flaxseed oil decreased with the increase in temperature. The yield of flaxseed oil was about 83% at 30 ^{0}C and decreased to 77% at 50 ^{0}C. The results showed that there were no remarkable differences in the oil profiles extracted by both methods. This indicates that the compositions of flaxseed oil are hardly affected by the application of ultrasound [80].

In a study by Shah et al. (2005), and Sharma and Gupta (2006), the benefit of using ultrasonic pretreatment before extracting oil from the seeds of *Jatropha curcas* L., almond, and apricot seeds by aqueous enzymatic oil extraction was investigated [88, 89]. Ultrasound pretreatment of the almond and apricot seeds before oil extraction and enzymatic oil extraction provided higher yield and reduction in extraction time. Therefore, ultrasonic pretreatment may reduce oil extraction time and may improve extracted oil in the production process [89].

Although there are many studies about ultrasound assisted extraction or pre-treatment, there is lack of information about sesame oil treatment. Since oil content is

extremely high when it is compared with other oilseeds, it can be advantageous to investigate on sesame seeds.

2.6 Oxidation Stability of Edible Oils

Oxidation in fats and oils is a detrimental process. It deteriorates the sensory quality and nutritive value of a product, and oxidation products also present health hazards. Oil oxidation is affected by several internal and external factors such as fatty acid composition, content and activity of antioxidants, irradiation, temperature, oxygen pressure, surface area in contact with oxygen, and water activity. Thus oxidative stability of oils during storage may depend on the oil source and manufacturing process [16].

The oxidative stability is defined as the resistance to oxidation. Resistance to oxidation is explained as the period of time to reach critical point of oxidation. It is an important indication for oil quality and shelf life. In oxidation process, off-flavour compounds are formed which cause oils to be unacceptable to consumers. Oxidation of oil also destroys essential fatty acids, and produces toxic compunds. The complex process of oxidation has different mechanisms, which depends on types of oxygen. Two types of oxygen react with edible oils. One is called atmospheric triplet oxygen and the other is singlet oxygen.

Important oxidation mechanisms in edible oils are autoxidation photosensitized oxidation. Autoxidation is a free radical chain reaction, where atmospheric triplet oxygen, $^3O_2$, reacts with a lipid radical. Triplet oxygen is a radical compound with two unpaired orbitals in the molecules. Photosensitized oxidation in edible oils occurs in the presence of light, sensitizers, and atmospheric oxygen, where singlet oxygen is produced [90].

Free radicals (R•, ROO•, etc.) have one or more unpaired electrons, that includes hydrogen atoms, transitions metals, the oxygen molecule. Autoxidation is the oxidative deterioration of unsaturated fatty acids consisting of a free radical mechanism. The intermediates are radicals (R•, odd electron species). Autoxidation reactions involve an initiation step and a propagation step, which continues until the operation of one or more termination steps.

(I) Initiation Step

$$RH \rightarrow R^{\bullet} + H^{\bullet}$$

or

$$X^{\bullet} + RH \rightarrow R^{\bullet} + XH$$

(II) Propagation Step

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet}$$

(III) Termination Step

$$R^{\bullet} + R^{\bullet} \rightarrow R - R$$

$$R^{\bullet} + ROO^{\bullet} \rightarrow ROOR$$

$$ROO^{\bullet} + ROO^{\bullet} \rightarrow ROOR + O_{27}$$

The hydrogen atom in the FA in edible oil is removed, and lipid alkyl radicals are produced in the initiation step. Heat, metal catalysts, and UV and visible light can accelerate free radical formation of FA. Autoxidation of linoleic and linolenic acids produces only conjugated products. The lipid alkyl radical reacts with diradical atmospheric $^{3}O_2$ and forms the lipid peroxy radical.

The primary oxidation products, lipid hydroperoxides, are stable at room temperature and in the absence of metals. However, in the presence of metals or at high temperature they are decomposed to alkoxy radicals and then form aldehydes, ketones, acids, esters, alcohols, and short chain hydrocarbons [91].

Duration for secondary product formation from the primary oxidation product, hydroperoxide, can be different for different oils. Secondary oxidation products are formed after hydroperoxide formation in olive and rapeseed oils. In the case of sunflower and safflower oils, secondary oxidation products are formed when there is an appreciable concentration of hydroperoxides. Most decomposition products of hydroperoxides are responsible for the off-flavor development in the oxidized edible oil [92].

2.11.1 Factors affecting the oxidation of edible oil

2.11.1.1 Fatty acid composition of oils

Oils that contain high percentages of polyunsaturated fatty acids oxidize more quickly than oils containing low percentages of unsaturated fatty acids. Soybean and sunflower oils stored in dark had shorter induction period than coconut and palm kernel oils [93]. The autoxidation rate depends on the rate of alkyl radical formation in the lipid, and the formation rate of FA alkyl radical depends mainly on the types of FA [93].

2.11.1.2 Pretreatments

Oil-processing method affects the oxidative stability of the oil. Roasting of safflower and sesame seeds before oil extraction improves the oxidative stability of the oils. The oxidative stability increases as the roasting temperature of the seeds increases as well [94, 95].

2.11.1.3 Storage, temperature, and light

Autoxidation of oils and the decomposition of hydroperoxides increase as the storage temperature increases [94, 95]. The concentration of the hydroperoxides increases until the advanced stages of oxidation.

2.11.1.4 Oxygen

The oxidation of oil can take place when oil, oxygen, and catalysts are in contact. Both concentration and type of oxygen affect the oxidation of oils. The effect of oxygen concentration on the oxidation of oil increased at high temperature and in the presence of light and metals.

2.11.1.5 Minor compounds

Edible oil consists of mainly triacylglicerols, but it also contains minor components such as free fatty acids, diacylglycerols, metals, phospholipids, peroxides, chlorophylls, carotenoids, phenolic compounds, and tocopherols. Some of them accelerate oil oxidation. Crude oil contains metals such as iron or copper, but the refining process reduces their concentrations. Edible oils manufactured without refining, e.g., extra virgin olive oil and sesame oil, contain relatively high amounts of

metals. Table 2.11 shows copper and iron contents in edible oils. Metals increase the rate of oil oxidation due to the reduction of activation energy. Metals also accelerate autoxidation of oil by decomposing hydroperoxide [93].

Table 2.11: Copper and iron contents in edible oils[93]

Oil	Metal content	
	Copper (ppb)	Iron(ppm)
Cold press sesame oil	16	1.16
Crude soybean oil	13.2	2.80
Virgin olive oil	9.8	0.73
Sunflower oil	5.2	0.26
Refined olive oil	15	0.08

Tocopherols are the most important antioxidants in edible oils. Tocopherol contents of sesame oils range between 404 and 540 ppm, depending on the cultivars [59]. Tocopherols compete with unsaturated oils for lipid peroxy radicals.

α-tocopherol showed the highest prooxidant activity than γ- and δ-tocopherol in soybean oil. On the other hand, prevention of tocopherol oxidation and removal of oxidized tocopherols during oil processing are strongly recommended to improve the oxidative stability of the oil [96].

Although sesame oil contains high amounts of unsaturated fatty acids, oxidative stability of the oil is good because of the presence of lignan compounds as well as tocopherols. Sesame oil also contains phytosterols such as campesterol, stigmasterol, beta- sitosterol, and 4, 5-avenasterol, with -betasitosterol as the predominant compound. Sitosterol behaves partly as a prooxidant by increasing the solubilization of oxygen [60]. Autoxidation rate of sesame oils at 60°C was detected lower than those of corn oil, safflower oil, and a mixture of soybean and rapeseed oils [97, 98]. Roasted sesame oil had greater oxidative stability than unroasted sesame oil.

2.11.2 Determination of secondary oxidation products

2.11.2.1 p-Anisidine value test

The oxidation in oils can be determined by the measurement of the formation of carbonyl compounds. The para-anisidine test determines the amount of aldehydes in vegetable and animal fats. Aldehydes in oil react with the para-anisidine reagent under acidic conditions to give yellowish products [16]. TOTOX value has been used as an oxidative indicator, combining peroxide (POV) and *p*-anisidine values (PAV) as follows:

$$\text{TOTOX value} = 2\,(\text{POV}) + \text{PAV}$$

2.11.2.2 Measurement of induction time of oxidation (Rancimat, Swift test)

Although it is scientifically accepted that oxidation generally develops in the initial stages, after a certain period of time, oxidation rate starts increasing due to the fact that more unstable hydroperoxides are produced and are more easily broken down. Induction time is an important parameter for the quality of the lipid, dependening on many factors, such as type of oil, fatty acid composition, and presence of catalysts such as metals and light.

The active oxygen method (AOM) involves POV measurements of oil samples after bubbling of air in their interior and heating at 98°C. Rancimat method is an automated type of Swift Test, in which effluent gases after bubbling through the oil are led into a tube containing distilled water. During oxidation reactions various acids (e.g., formic, acetic, and propionic) are formed increasing the conductivity of the solution, which is recorded between two platinum electrodes [98]. Figure 2.12 shows the principle of Rancimat method [99]:

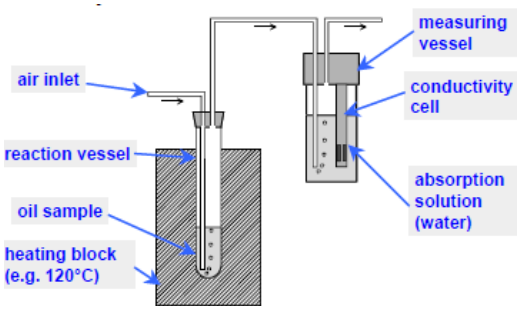

Figure 2.12: Schematic representation of typical Rancimat method

3. MATERIALS AND METHODS

3.1 Materials

Sesame seeds of Turkish variety were kindly provided from Aksu Vital Doğal Ürünler A.Ş, İstanbul. The chemicals and the reagents used in experiments are shown in Table 3.1:

Table 3.12: Chemical used in analysis

Name of Analysis	Chemicals	Brand
Oil content	Hexane	Sigma Aldrich
Protein content	Sulphiric acid	Merck
	Potassium sulphate	Merck
	Copper sulphate	Merck
	Sodium hydroxide	Merck
	Methyl red indicator	Merck
	Boric acid	Merck
	Hydrochloric acid	Merck
Free fatty acid content (FFA)	Ethanol (EtOH)	Sigma Aldrich
	Diethyl ether	Sigma Aldrich
	Phenolphthalein	Merck
	Potassium hydroxide	Merck
Peroxide value (PV)	Chloroform	Sigma Aldrich
	Acetic acid	Sigma Aldrich
	Potassium iodide	Sigma Aldrich
	Starch from potato	Sigma Aldrich
	Sodium thiosulphate	Sigma Aldrich
Total phenol content (TPC)	Hexane	Sigma Aldrich
	Acetone	Sigma Aldrich
	Folin-Ciocalteu	Merck
	Methanol	Sigma Aldrich
	Gallic acid	Sigma Aldrich
Antioxidant activity	Methanol 0.2 N	Sigma Aldrich
	DPPH (2,2-diphenyl-1-picrylhydrazyl) powder	Sigma Aldrich
	Trolox(6-hydroxy-2,5,7,8 tetramethylchroman-2 carboxylic acid)	Sigma Aldrich

3.2 Methods

In this thesis, following analysis and pretreatments were performed to raw sesame seeds, press cake and oils obtained by hdyraulic press after pretreatments:

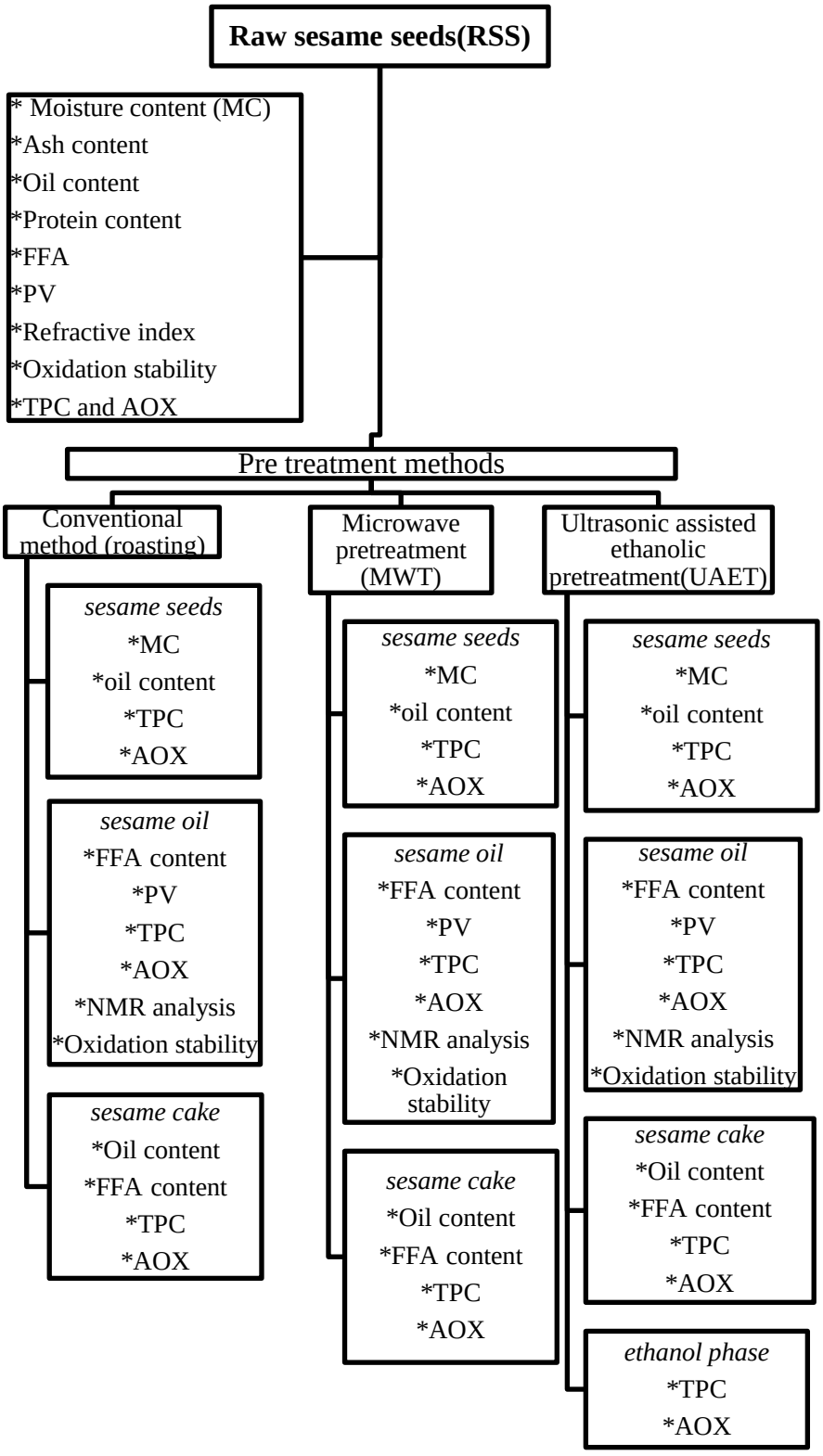

Figure 3.1: Chart of analysis and pretreatments in the thesis

3.2.1 Characterization analysis for sesame seeds

Before starting quality experiments, sesame seeds were cleaned from stones, dust, broken pieces, and other foreign matters. In order to provide cleaned seeds, different scale sieves (150 μm, 300 μm, and 500 μm) were used.

3.2.1.1 Moisture analysis

For raw sesame seeds, microwave treated (MWT) and roasted samples, 10 grams were placed into petri dishes and oven drying method at 105 °C for 4 hours and 130 °C for 3 hours until obtaining constant weight was applied [100]. Analysis were performed triplicate. Average moisture content (M.C.) was calculated in dry basis using the following equation **(3.1)**:

$$M.C.\ (\%) = [(M_1 - M_2) / m] \times 100\ (d.b.) \quad \textbf{(3.1)}$$

M_1 : sample + weight of petri dishes at constant weight (g)

M_2 : dried sample + weight of petri dishes at constant weight (g)

m : weight of sample (g)

For ultrasonic treated samples, moisture analyzer (Radwag, MAC 50, Poland) was used.

Figure 3.2: Moisture analyzer for ultrasonic treated samples

3.2.1.2 Ash content

Ash content was determined by combustion of the sample in porcelain crucibles. Water and other volatile materials were vaporized and organic substances were burned in a muffle furnace beginning from 450 ^{0}C (3 hours) to 550 ^{0}C (3 hours) and ending up at 650 ^{0}C (6 hours). The samples were cooled down in desiccator and samples and crucibles were weighed before and after ashing to determine the content of ash % [101]. Analysis were performed triplicate. Ash content was calculated in dry basis using the following equation **(3.2)**:

$$Ash\ content\ \% = \frac{M_2 - M_1}{\mathrm{m}}\ x\ 100\ \text{(d.b.)} \qquad \textbf{(3.2)}$$

M_1 : weight of empty crucible (g)

M_2 : weight of dried crucible + weight of sample (g)

m : weight of sample (g)

3.2.1.3 Oil content

Oil content of RSS, MWT and roasted samples were determined by automatic Soxhlet extraction (GERHARDT, Soxtherm, Sox 414 model, Germany) and oil content of ultrasonic treated samples were determined by classical soxhlet extraction. For automatic Soxhlet exraction, 3 g of samples were weighed and placed into cartridges. Duration and evaporation temperature were set as 2 h 15 min and 200 ^{0}C, respectively. Hexane was used to extract the oil. After the operation was completed, the extracts were taken to volumetric flask and evaporated using a rotary evaporator at 50 ^{0}C. For classical Soxhlet extraction, firstly volumetric flask was weighed and weight was recorded. 5 g of samples in filter paper were placed into cartridges and weighed. A piece of cotton was put over the cartridge. It was placed to the Soxhlet extractor. Flask was filled with 150 mL of hexane. Flask, extractor, and cooler were connected to each other and placed onto heater. Slow boiling of solvent was provided by adjusting heater degree. After 6 hours of extraction was applied, remained part of solvent was evaporated in 105℃ oven. The samples were weighed and recorded. Oil content was calculated in dry basis using the following equation **(3.3)**:

$$Oil\ content\ \% = \frac{M_1 - M_2}{\mathrm{m}}\ x\ 100\ \text{(d.b.)} \qquad \textbf{(3.3)}$$

M_2 : weight of volumetric flask (g)

M_1 : weight of vol. flask + extracted oil

m : weight of sample (g)

3.2.1.4 Protein Content

Protein content was determined by Kjeldahl method. The method consisted of heating the sample with sulfuric acid, which decomposed the organic substance by oxidation to liberate the reduced nitrogen as ammonium sulphate. In this step, potassium sulphate was added to increase the boiling point of the medium. Chemical decomposition of the sample was completed when the dark-colored sample became colorless. The solution was then distilled with sodium hydroxide, which converted the ammonium salt to ammonia. The end part of the condenser was dipped into boric acid solution. The ammonia was reacted with the acid and the remained part of the acid was titrated with 0.2 N hydrochloride solution in the presence of methyl red indicator. Nitrogen content was calculated in dry basis according to the following equation **(3.4)**:

$$Nitrogen\ \% = \frac{(V)\ ml\ x\ 0.2\ x\ 0.014\ g\ N}{\text{m (g)}}\ x\ 100\ \text{(d.b.)} \qquad \textbf{(3.4)}$$

V: Volume of 0.2 N HCl (mL)

m: Weight of sample (g)

Protein content % = Nitrogen % x 6.25

3.2.1.5 Free fatty acid (FFA) content

Firstly, 10 grams of sesame oil was weighed into 250 mL Erlenmeyer flask. 50 mL, 1/1 (v:v) ethyl alcohol-diethyl ether solution was used to extract oil. Phenolphthalein indicator was dropped. Furthermore, the solution was titrated with 0.1 N potassium hydroxide (KOH) in ethyl alcohol solution. Titration was completed until obtaining permanent pink color. Analysis were performed triplicate and average value was reported. Each used volume of KOH is equivalent to 0.028 g oleic acid [102]. Following equation was used for calculation of FFA content in dry basis **(3.5)**:

$$\text{FFA Content \%} = \frac{\text{V}}{\text{m}} \text{x } 0.028 \text{ x } 100 \quad \text{(d.b.)} \qquad \textbf{(3.2)}$$

V: used volume of 0.1 N KOH in ethyl alcohol in titration (mL)
m: weight of sample (g)

3.2.1.6 Peroxide value (PV)

PV is the measure of active oxygen in one kilogram of oil. AOCS Cd 8-53 acetic acid-chloroform method was used.

2 grams of oil was weighed in erlenmayer flask. 10 mL of chloroform was and then, 15 ml acetic acid and 1 mL potassium iodide indicator were added. The sample was waited in dark for 5 minutes. 75 mL of distilled water and 1 mL of starch were added. Prepared solution was titrated with 0.01 N sodium thiosulphate (Na_2CO_3) solution. Following equation was used for calculation of PV in dry basis **(3.6).**

$$\text{Peroxide value } (\text{meq g}\frac{O_2}{\text{kg}}) = \frac{10 \text{ x V x F}}{\text{m}} \quad \textbf{(3.6)}$$

V = Volume of 0.01 N Na_2CO_3 solution (mL)
F = Adjustment value for 0.01 N Na_2CO_3
m = Weight of sample (g)

3.2.2 Sesame oil production

Grinded (G) and non-grinded (NG) sesame seeds (70-80 grams) were weighed and and oil was obtained by Carver hydraulic press. 20000 lbs pressing force was applied. For the oil yield analysis, pressing operation continued for 3 hours.

At the end of pressing, sesame cake was weighed, oil content, and FFA contents were determined. Weight of input-output sesame cake and sesame oil and yield of oil were calculated by means of mass balance.

Figure 3.3: Hydraulic press used in the experiments

3.2.3 Yield and characterization of press oil

After pressing, sesame seed and press cake were determined. Oil content of the press cake was determined by Soxhlet equipment. Following analysis was performed for the press oil.

3.2.3.1 Determination of oxidation stability

Oxidaton stability was expressed as the oxidation induction period (h), which was measured with the Rancimat 743 (Metrohm AG, Herison, Switzerland) using 3 grams of sesame oil (roasted, microwave treated, and ultrasound treated)(Figure 3.4). Samples were warmed to 111.5℃ with air flow rate of 20 l/h. In the rancimat method, volatile degraded products were measured conductmetrically by using distilled water. The induction period was defined as the necessary time to reach the inflection point of the conductivity curve. Table 3.2 shows the used samples in determination of oxidation stability. Treatments were chosen according to the results of highest oil yield. Analyses were experienced in two replicates.

Table 3.2: Samples used in determination of oxidation stability

Exp. no	Treatments
1	Non-treated sesame oil
2	210℃ roasted sesame oil
3	Medium MWT in 1 cm depth
4	High MWT in 1 cm depth
5	30 min. UAET
6	96% amplitude UAET
7	50% EtOH UAET
8	Solid/liquid:1/10 UAET

Figure 3.4: Rancimat Metrohm 743

3.2.3.2 Refractive index

Refractive index was determined using digital refractometer (HANNA, HI 96801) at 40˚(Figure 3.5) [103].

Figure 3.5: Refractometer used in the experiment

3.2.4 Extraction of phenolic compounds

3.2.4.1 Sesame seeds

For the analyses of total phenolic compunds (TPC) and antioxidant activity (AOX), extraction was performed by the method of Rosa et al. (2011). Oil in grinded seeds were removed with hexane (1:10, w/v). Extraction was repeated three times. Defatted oil (5 g) was mixed with 50 mL of 80 % acetone. Phenolics were extracted at 50 ^{0}C for 30 min. Extracts were centrifugated at 5000 g at room temperature for 2 min. Supernatant was extracted twice at the same conditions and liquid parts were integrated. Solvent was evaporated using a rotary evaporator at 40 ˚C [104].

3.2.4.2 Sesame oil

Phenolics were extracted with methanol:water (80:20, v/v) three times, from an oil-in-hexane (5 g:10 mL) solution with a separatory funnel.

3.2.4.3 Press cake

One gram of sesame cake was extracted with 25 ml methanol for 1 h at 23℃ in a water bath and centrifuged at 10,000 g for 10 min. The residue remaining after methanol extraction at room temperature (23℃) was then extracted with 25 ml methanol for 1 h in a 60℃ water bath and centrifuged (10,000 g, 10 min). The supernatants were filtered through a layer of cheese cloth and stored at 18℃ for further analysis.

3.2.4.4 In ethanol phase

Phenolic compounds passing into ethanol phase during ultrasonic pre-treatment was firstly evaporated by rotary evaporator and kept at -18℃ for future analysis.

3.2.4.5 Determination of phenolic content

TPC was detected with the method of Elleuch et al. (2007). Folin-Cicalteau reagent was used in combined extract [15].

Folin-Cicalteau reagent was diluted (1:10) with distilled water. 0.75 mL reagent was added to 100 μ;L sample. Mixture was waited for 5 min and 0.75 mL of Na_2CO_3 (6 g/L) was added. Mixture was waited again for 90 min in dark. Absorption of the solution at 727 nm was measured. Results were expressed as gallic acid (mg/kg of oil). Calibration curve was prepared by standard gallic acid solutions (0.02-0.14 mg/mL).

3.2.4.6 Antioxidant acitivity by DPPH method

AOX in sesame oil was detected by the method of Chang et al. (2002).

50 mg/mL sample extract was mixed with DPPH in 0.2 N methanol. After vigorously shaking, solution was waited for 30 min.Then, the absorption of the solution at 517 nm was measured using UV-Vis spectrophotometer (PG instruments, T70, England) [106]. Results were expressed as DPPH in dry basis.

Trolox is a water-soluble matter of Vitamin E. In brief, it measures the antioxidant capacity of a sample which is compared to the Trolox standard [107].

3.2.5 Pretreatment methods

3.2.5.1 Conventional method (roasting)

Laboratory scale oven was used for roasting sesame seeds. Sesame seeds were spreaded in dishes uniformly, and put into oven. After roasting, plates were taken to desiccator in order to provide cooling. Roasting was performed at 165℃ and 210℃ for 25 min. and 5 min, respectively [108]. For each roasting conditions, triplicates were used.

3.2.5.2 Microwave pretreatment (MWT)

Sesame seeds were spreaded on glass plates. Household type microwave oven (Arçelik, MD 574s) was used. MW oven has generating power of 1330 watt at 2450 MHz. It operates at a frequency of 2450 MHz, with 1330, 931, 665 and 399 watts of output with 5 different power levels of high, medium high, medium, low, and defrost, respectively. With several trials on sesame seeds in MW, high (HPLMWT), medium (MPLMWT), and low power levels (LPLMWT) were chosen in different durations. Glass dishes were used in oven in order to avoid fast burning. For the first part of the experiment; 180 grams of seeds with a depth of 1 cm, and for the second part of the experiment; 360 grams of seeds with a dept of 2 cm were prepared. For each power levels, 3 replications in two different depths were investigated. After roasting, the seeds were taken to room temperature for cooling. Table 3.3 shows the power levels, amounts, and time relationship used in the experiment:

Table 3.3: The relationship between power levels, amounts of sesame seeds, and roasting time during MWT of sesame seeds

Depth of Sesame Seed	*1 cm*			*2 cm*		
Power of Microwave	Low	Medium	High	Low	Medium	High
Time (min)	10	6	5	10	6	5

3.2.5.3 Ultrasound assisted ethanolic pretreatment (UAET)

UAET was applied in adjustable amplitude device whose brand was Bandelin Sonoplus HD 3100, 20 kHz frequency with an MS 73 probe (Figure 3.5). In the experiments, different weights of ungrinded samples and volumes of ethanol were placed in a glass beaker. Ultrasonic probe was immersed in the middle of beaker that was close to the deep. According to the experiment plan, different amplitudes (AP), weight of samples, volumes of EtOH, and periods were set. After samples were exposed to ultrasonication, ethanol phase was filtered from solute phase. Solute phase was left for one day in order to evaporate residual ethanol in seeds. Experiment plan for UAET is shown in Table 3.4 in order to prevent confusion.

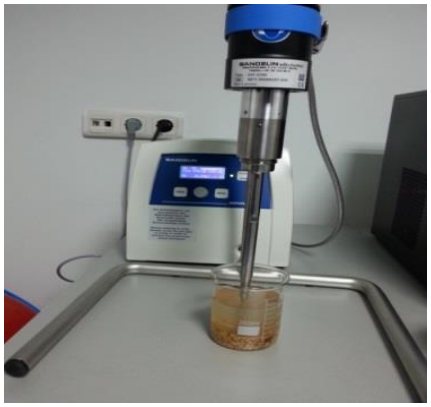

Figure 3.6: Ultrasonic device and probe system used in the experiments

Table 3.4: Experiment plan for UAET

Exp. No	EtOH concentration (%)			Solid/ Liquid ratio		Time (min.)		Amplitude (%)	
	96	75	50	1/5	1/10	15	30	90	75
1	■				■		■	■	
2		■			■		■	■	
3			■		■		■	■	
4	■				■	■		■	
5	■				■		■	■	
6	■			■			■	■	
7	■				■		■	■	
8	■				■		■	■	
9	■				■		■		■

3.2.6 Nuclear magnetic resonance (NMR)

To use NMR relaxometry as a fingerprint for the oil samples obtained with different treatments, experiments were conducted using a 0.5T (22.40 MHz system (SpinCore Inc., Gainesville, FL, U.S.A.). T_2-CPMG (spin-spin relaxation) experiments were conducted using an echo time of 1ms, 600 echoes, 1s repetition delay, 32 scans and 90^o pulse duration of 6μs. The resulting T2 CPMG curve was analyzed through PROPSA software (Magritek Inc., Wellington, New Zealand) for non negative least square analysis to obtain the relaxation spectrum.

3.2.7 Statistical analysis

The results were performed in triplicate and the significance of differences among means were determined at $p < 0.05$ using one way ANOVA followed by Tukey's multiple range test. The IBM SPSS Statistics Program (21^{th} version) was used. Each experiment was evaluated in their own results, and in order to compare the effects of pre-treatments, seperate statistical analyses were used.

4. RESULTS AND DISCUSSION

4.1 Characterization of Sesame Seeds

For quality characteristics of sesame seeds, moisture content, ash content, protein content, oil content, FFA, PV, and refractive index were determined. These are only the mesaured results. Statistical results were given in the next steps. Table 4.1 and Table 4.2 shows the results for characterization analysis of Turkish type sesame seeds.

Table 4.1: Characterization of sesame seeds

Experiments		**Results**
Moisture content (%)		5.1±0.03
Ash content (%)		4.8±0.60
Protein content		19.5±0.09
Oil content (%)		48.7±3.19
FFA (as oleic acid %)		2.5±0.26
PV (meq/kg oil)	0 days	3.4±0.27
	20th day of storage	9.2±0.59
	30th day of storage	14.0±0.97
Refractive Index (at 40℃)		1.490±0.047

All the given values are means of tree determinations ± standard deviation.
All the given values are expressed in dry basis.
Sesame oil samples were stored at 60℃ for PV analysis.

Table 4.2: Characterization analysis for TPC and AOX

Samples	TPC(mg gallic acid(mg)	AOX (mg DPPH/mL)
Sesame seed	11.9±0.96	8.15±0.45
Sesame oil	18.6±1.00	14.5±0.87
Sesame cake	38.0±1.23	42.5±2.00

All given values are means of three determinations ± standard deviation in dry basis.

Results were in accordance with USDA database, except MC which was found 1% lower than the USDA value. Elleuch et al. (2007) found MC of sesame seed as 4.8% [15]. The difference may be because of the type, climate and storage conditions. Ash content was found the same as the values of USDA reports and Elleuch et al. (2007) [15]. Protein contents of various sesame seeds of different origin were found to range between 17.73%-25.77% [10, 15, 26]. Total oil content of sesame seeds varied between 49% -55%. FFA has been found at about 2.5 % as oleic acid, which was lower than literature values. PV and refractive index values were found to be close to literature values.

4.1.1 Conventional method (roasting) and characteristics of treated samples

Roasting was performed at 165 °C and 210 °C for 25 min. and 5 min., respectively. For determination of oil yield, sesame seeds were grinded before treatment. Grinded (G) sesame seeds were analysed for FFA content, oil content and oil yield. Non-grinded (NG) sesame seeds were analysed for MC, refractive index, PV, NMR analysis, TPC, and TEAC for characterization.

In each treatments, hydraulic press was applied to both G and NG seeds separately. MC was calculated before pressing. In all of the analyses, results were expressed as average±standard deviation. Three replicates were used. Weight of samples and calibration curves for TPC and AOX analyses were mentioned in Appendix. Standart calibration curves were prepared by 80% acetone solution for TPC of sesame seeds, 80% methanol solution for TPC of sesame oil, and 50% methanol solution for TPC of sesame cake. Table 4.3 shows the results of analyses for roasted seeds. Oil yield is shown in the further sections in order to compare the differences with other methods.

Table 4.3: Quality characteristics of sesame samples in conventional pretreatment (roasting)

Analysis	Roasting			
	165℃		210℃	
	G	NG	G	NG
MC (%)	-	2.2±0.05[a]	-	0.9±0.002[b]
Oil content (%)	48.3±3.05[a]	33.3±2.32[a]	56.6±3.55[c]	41.6±2.54[b]
FFA content (oleic acid %)	G	NG	G	NG
-Sesame cake oil	15.7±1.21[b]	13.4±0.34[b]	13.0±0.57[b]	11.5±0.15[b]
-Press oil	6.3±0.1[c]	4.6±0.07[c]	4.5±0.08[b]	2.9±0.05[b]
PV (meq/kg oil)	NG		NG	
-20 days storage	7.7±0.56[a]		8.5±0.85[a]	
-30 days storage	11.2±0.24[b]		13.7±0.52[c]	
Refractive index	NG		NG	
	1.475±0.08[a]		1.472±0.07[a]	
TPC (mg gallic acid/mL)	NG		NG	
-Sesame seeds	17.2±0.55[b]		63.7±3.00[a]	
-Sesame oil	22.5±1.79[b]		78.2±1.90[c]	
-Sesame cake	49.7±2.31[a]		151.7±1.98[bc]	
AOX (mg DPPH/mL)	NG		NG	
-Sesame seeds	5.1±0.61[b]		14.6±1.30[a]	
-Sesame oil	15.1±1.20[b]		23.0±1.50[a]	
-Sesame cake	67.0±3.13[b]		96.2±2.59[c]	

All given values are means of three determinations ± standard deviation.
Mean in a row followed by the same letters are not significantly different (P > 0.05).
All given values are expressed in dry basis.
Sesame oil samples were stored at 60℃ for PV analysis.

According to the results, 210℃ had significant effect compared to 165℃ in moisture content (MC) analysis. The results were significantly decreased from 2.20±0.05% to 0.9±0.002%. When the sample was treated with roasting, more flavour and odour compounds were detected. The color was darker than other applications. Generally, in industrial scale, 210-220 °C is used to have longer shelf-life due to lower moisture content.

Oil content had no significant effect between NG and G in 165℃. Grinding in 210℃ increased oil content. The result supported the study of Khan et al. (1983) [51]. It had been stated that when the size of sesame seeds were reduced, oil yield increased.

FFA content in sesame cake oil for roasting in different temperatures had no significant effect, while FFA content in press oil in 210℃ had significant decrease compared to 165℃. The results clearly showed the ineffectiveness of grinding or non-grinding on FFA content.

PV in roasting had no significant effect in 20 days storage. But after 30 days storage, PV showed significant increase for both temperatures. PV is an index of rancidity, thus the high peroxide value in oil reveals that oil has a poor resistance to oxidation during storage. We can say that treatment protects oil from poor resistance to peroxidation. When temperature increased, resistance to peroxidation decreased.

Refractive index showed no significant effect which confirmed the accordance with the other studies.

TPC for sesame seed significantly inreased from 17.2±0.55 to 63.7±3.00 mg gallic acid/mL, TPC for sesame seed significantly increased from 22.5±1.79 to 78.2±1.90 mg gallic acid/mL, and TPC for sesame cake significantly inreased from 49.7±2.31 to 151.7±1.98 mg gallic acid/mL with the change in roasting temperature. When TPC for sesame seeds and sesame oil were compared, there was no change in 165℃ roasting. In contrast, there was significant difference in 210℃. In general aspect, methanol extraction provided higher TPC results. Since methanol has higher polarity than acetone, it provided higher degree of TPC extraction from seed. However, roasting in high temperature resulted in high TPC. High values of TPC are related to the high dietary fibre content. The reason is probably because of the fact that polyphenols are associated with dietary fibre. Shahidi et al. (2006) indicated that cakes and coats of sesame contained higher amounts of polyphenols than the endosperm [107].

AOX showed similar differences as in TPC analysis. The most significant increase was observed in sesame cake after 210℃ roasting.

4.1.2 Microwave pretreatment and characteristics of treated samples

MWs were applied in three different energy levelsat low, medium, and high power levels for 5, 6, and 10 min. 180 grams (1 cm) and 360 grams (2 cm) of sesame seeds were roasted at those conditions.

For oil yield, sesame seeds were also grinded before treatment. G seeds were analysed for FFA content, oil content and oil yield. NG seeds were analysed for MC, refractive index, PV, NMR analysis, TPC, and AOX. Press was applied to both G and NG seeds separately. MC was calculated before pressing as also performed in the same way in roasting. The color of seeds darkened from low level to high level application. For roasted appearance, time was ineffective, while power levels were effective. Table 4.4 shows the results of analyses for microwave treated samples.

According to the results, HPLMWT decreased moisture content significantly from 5.1±0.03% to 1.2±0.25%. There was no effect of depth and grinding in MPLMWT.

Oil content increased from 41.6±1.21 to 63.3±3.12%. Depth and grinding had no significant effect on the results.

When statistical analysis were experienced for grinded and non-grinded states, there was no significant change. Therefore, the effect of grinding on results was ignored.

LPLMWT and MPLMWT had no significant effect on FFA content of sesame cake oil and press oil. But increase in FFA content of press oil was in the lowest amount in HPLMWT. For all the different levels of MWT, FFA contents of sesame cake oil were found to be significantly higher than these of press oil.

PV for 20 days storage increased from 4.6±0.54 to 9.6±0.85, PV for 30 days storage increased from 4.9±0.22 to 10.4±0.72 meq/ kg oil. At that point, power levels behaved like roasting treatment. But, surprisingly the lowest PVs for both storage periods were in HPLMWT. The reason could be explained by short time affect. PV increased gradually with the increasing period of microwave heating or decreasing power level which confirmed the idea of Yoshida and Takagi (1997) [108].

TPC for sesame seed was significantly different in MPLMWT and HPLMWT, which were 36.1±3.58 and 52.6±2.47 mg gallic acid/mL, respectively. TPC for sesame oil didn't vary depending on power levels. TPC for sesame cake increased significantly from 138.0±6.12 to 185.3±10.14 mg gallic acid/mL. When samples were compared in the aspect of TPC, as expected, there was increase from TPC of sesame seeds to sesame cake. The highest TPC results were obtained in HPLMWT. However, it couldn't be understood clearly whether solvent or power level was effective. It is needed that the same solvents should be used in power levels in order to see the difference accurately. It was clear that high level could be applicable for high TPC.

According to the study by Manal Hassan (2013), TPC of Egyptian sesame seeds varied from 33.18 to 57.71 mg tannic acid/100 mg after microwave roasting which was identical to our results [110]. Apart from high dietary fiber content of sesame cake, MWT provided better extraction of phenolic compounds from sesame cake.

The same situation was also valid for AOX results.

Table 4.4: Quality characteristics of sesame samples in microwave pretreatment

Analysis	Microwave pretreatment					
	LPLMWT		MPLMWT		HPLMWT	
	1 cm depth	2 cm depth	1 cm depth	2 cm depth	1 cm depth	2 cm depth
Moisture content (%)	3.7±0.54[a]	3.5±0.50[a]	2.50±0.34[a]	3.0±0.23[a]	1.2±0.25[b]	2.1±0.37[a]
Oil content (%)	46.6±1.98[a]	45.0±2.00[a]	63.3±3.12[c]	53.3±1.27[b]	53.3±1.27[b]	41.6±1.21[b]
FFA content (oleic acid %)						
-Sesame cake oil	10.12±0.54[b]	11.24±0.50[b]	9.46±0.28[b]	9.85±0.41[b]	8.5±0.33[c]	8.9±0.47[c]
-Press oil	4.9±0.12[c]	4.7±0.54[c]	4.2±0.48[c]	4.8±0.13[c]	3.0±0.08[a]	4.0±0.32[b]
PV (meq/kg oil)						
-20 days storage	7.4±0.74[b]	9.6±0.85[b]	6.2±0.58[a]	9.0±0.54[b]	4.6±0.54[c]	7.7±0.26[b]
-30 days storage	8.3±0.62[c]	10.4±0.72[c]	8.0±0.41[a]	8.7±0.32[a]	4.9±0.22[a]	6.6±0.41[b]
Refractive index						
	1.475±0.09[a]	1.482±0.01[a]	1.470±0.07[a]	1.475±0.01[a]	1.468±0.085[a]	1.470±0.074[a]
TPC (mg gallic acid/mL)						
-Sesame seeds	21.9±2.26[a]	-	36.1±3.58[a]	-	52.6±2.47[b]	-
-Sesame oil	30.74±3.45[a]	-	64.6±3.66[a]	-	108.9±5.47[a]	-
-Sesame cake	138.0±6.12[b]	-	146.9±8.10[c]	-	185.3±10.14[c]	-
AOX (mg DPPH/mL)						
-Sesame seeds	8.0±0.98[a]	-	11.2±1.15[a]	-	18.4±1.15[c]	-
-Sesame oil	19.2±2.22[a]	-	29.8±3.10[a]	-	45.0±3.41[b]	-
-Sesame cake	72.5±5.85[c]	-	89.0±2.3[b]	-	105.0±4.8[a]	-

All the given values are means of tree determinations ± standard deviation.
Mean in a row followed by the same letters are not significantly different (P > 0.05).
All the given values are expressed in dry basis.
Sesame oil samples were stored at 60℃ for PV analysis.

4.1.3 UAET and characteristics of treated samples

UAET was applied in 96, 75, and 50% EtOH concentrations (solid/liquid:1/5 constant, 90% AP, at 30 min.) in order to investigate the effects of different alcohol concentrations. Two different durations such as 15 min. and 30 min. (96% EtOH concentration, solid/liquid:1/10 constant, 90% AP) were used in order to investigate the effect of time, 1/5 and 1/10 solid/liquid (96% EtOH concentration, 30 min., 90% AP) were used in order to investigate in order to see the effect of solid/liquid amount, and finally 90 and 75% AP (solid/liquid:1/10 liquid, 30 min., 96% EtOH concentration) were used in order to see the effect of power level.

For calculation of oil yield, sesame seeds were also grinded before treatment. G types were analysed for FFA content, oil content and oil yield. NG types were analysed for MC, refractive index, PV, NMR analysis, TPC, and AOX. Hydraulic press was applied to both G and NG seeds separately. Figure 4.1 showes alcoholic extracts in three EtOH concentrations after removing solid phase. It was aimed to indicate the passage of oil contents to ethanol phase after UAET. Table 4.5 shows the results of analyses for UAET samples.

As can be seen from results, ultrasonic treatment didn't decrease moisture content as other pretreatments did. On the other hand for 15 min. treatment, there was a significant difference in MC, this was because of the ineffectiveness of ultrasonic waves in short time. There was no cavitation and heat generation.

In oil content results, no change was observed in different EtOH concentrations. There was a decrease in 15 min. treatment, the reason is the same with mentioned above. In short time, ultrasonic waves couldn't break the cell walls, as a result, oil content decreased. Whereas EtOH concentration didn't affect oil content, solid/liquid ratio caused significant change. While oil content was 45.0±1.20%, with the increasing EtOH amount, it increased to 62.5±2.20%.

There was no significant difference in FFA content of sesame cake oil with EtOH concentraions, time change, and amplitude change. Similar to oil content results, solid/liquid ratio difference affected FFA content. It decreased from 15.8±0.52% to 7.4±0.23%. Unlike these results, press oil showed significant differences. In EtOH concentrations, FFA content decreased from 6.5±0.02% to 4.5±0.10% which showed that lower alcohol concentration couldn't cause breakage of cell walls. As a result, rancidity was preventedcancelled. There was also significant difference in time parameters. The longer treatment time applied, the

higher FFA content was obtained. The situation was also valid for amplitude parameters. Decrease in FFA content was observed from 9.5±0.06% to 7.4±0.04% when amplitude was lowered.

Solid/liquid ratio didn't affect both FFA content and PV. There was a significant increase in PVs from 5.6±0.05 to 10.0±0.10 meq/kg oil when EtOH concentration was lowered. This was certainly because of the increasing water amount that caused rapid rancidity. 90% amplitude treatment caused a significant increase compared to that of 75% amplitude.

TPC didn't show significant changes in sesame seeds, sesame oil, sesame cake, and ethanol phase in different EtOH concentrations and solid/liquid ratio. The result was unexpected, because higher ethanol should have solved more phenolic compounds. The effective parameters which were time and amplitude caused significant increase. From 15 min. to 30 min. treatment, TPC increased from 1.3±0.04 to 24.0±1.40 mg gallic acid/mL in sesame seeds, from 10.5±0.55 to 50.3±3.00 mg gallic acid/mL in sesame oil, 20.5±1.12 to 75.4±2.20 mg gallic acid/mL in sesame cake, and from 2.8±0.03 to 14.0±0.95 mg gallic acid/mL in ethanol phase. For 75% to 90% amplitude, TPC increased from 24.5±1.20 to 30.3±1.85 mg gallic acid/mL in sesame seeds, from 31.5±0.97 to 50.8±2.66 mg gallic acid/mL in sesame oil, from 72.5±1.51 to 91.3±3.45 mg gallic acid/mL in sesame cake, and from 10.6±0.56 to 16.0±1.20 mg gallic acid/mL in ethanol phase. As can be seen, folding up time to twice, the increase in TPC were 4-5 times, folding up amplitude 1.5 times, the increase in TPC were 1.5 times. The transmission of phenolic compounds in ethanol phase was not high as that of sesame samples. For ultrasonic treatment, minimum 30 min. treatment should be applied in order to have higher phenolic content. When each parameter was compared for each treated samples, it was obviously seen that TPC increased begining from sesame seeds ending up in sesame cake. For example, in 96% EtOH concentration, TPC increased. This result was expected because phenolic contents and antioxidants locate in outer part of seeds. Therefore, alcohol dissolves more compounds in these locations.

The results of AOX were found similar to the results of TPC. This showed that phenolic content and antioxidants had the same properties in sesame samples. To conclude, in ultrasound assisted ethanolic pretreatment, the significative features were time and amplitude in order to have high amount of AOX and TPC.

Figure 4.1 showed the appearance of sesame seeds before and after ultrasound treatment. Ultrasound provided swelling of seeds and color changed from from light to dark.

Table 4.5: Quality characteristics of sesame samples in UAET

Analysis	Ultrasound assisted ethanolic treatments*								
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**
Moisture content (%)	2.6±0.23^{a}	3.2±0.29^{a}	3.9±0.35^{a}	4.5±0.22^{b}	3.1±0.24^{a}	3.5±0.44^{a}	3.0±0.38^{a}	3.4±0.69^{a}	3.9±0.40^{a}
Oil content (%) NG	45.0±1.20^{a}	52.2±1.35^{a}	53.1±3.14^{a}	18.0±0.74^{b}	49.0±1.15^{a}	43.5±0.82^{a}	62.5±2.20^{c}	54.7±1.85^{a}	48.0±0.45^{a}
FFA content (oleic acid, %)	NG								
-sesame cake oil	15.1±0.32^{b}	13.5±1.12^{b}	10.0±0.78^{b}	17.4±0.65^{b}	12.2±0.04^{b}	9.6±0.15^{a}	7.4±0.23^{c}	15.8±0.52^{b}	13.6±0.50^{b}
-press oil	6.5±0.02^{b}	5.9±0.02^{b}	4.5±0.10^{c}	5.0±0.08^{a}	8.0±0.32^{b}	5.3±0.05^{b}	5.1±0.05^{b}	5.5±0.05^{b}	4.5±0.03^{c}
PV (meq/kg oil)	5.6±0.04^{a}	6.3±0.08^{a}	10.0±0.10^{b}	3.5±0.01^{c}	7.9±0.05^{a}	5.0±0.01^{a}	5.0±0.02^{a}	9.5±0.06^{b}	7.4±0.04^{a}
TPC (mg gallic acid/mL)	NG								
-sesame seeds	14.0±0.85^{b}	17.8±1.10^{b}	28.3±2.26^{b}	1.3±0.04^{a}	24.0±1.40^{b}	25.0±0.74^{b}	38.7±0.98^{b}	24.5±1.20^{b}	30.3±1.85^{c}
-sesame oil	25.6±1.14^{a}	48.0±1.75^{a}	64.0±2.52^{a}	10.5±0.55^{c}	50.3±3.00^{b}	30.5±1.93^{b}	54.6±3.04^{b}	31.5±0.97^{a}	50.8±2.66^{c}
-sesame cake	78.2±2.55^{c}	80.5±3.04^{c}	98.9±2.53^{c}	20.5±1.12^{a}	75.4±2.20^{c}	70.5±2.15^{c}	86.3±2.52^{c}	72.5±1.51^{c}	91.3±3.45^{d}
-ethanol phase	9.6±0.42^{b}	12.5±1.00^{b}	16.2±0.97^{b}	2.8±0.03^{a}	14.0±0.95^{b}	9.8±1.12^{b}	15.5±1.23^{b}	10.6±0.56^{b}	16.0±1.20^{b}
AOX (mg DPPH/mL)	NG								
-sesame seeds	7.4±0.63^{a}	12.5±0.52^{a}	20.8±0.90^{a}	2.5±0.02^{c}	15.6±1.05^{a}	10.8±0.93^{a}	20.5±1.30^{a}	14.0±0.80^{a}	17.6±0.78^{a}
-sesame oil	20.7±1.14^{a}	27.8±1.03^{a}	30.5±1.80^{a}	5.6±0.78^{b}	23.5±1.04^{a}	28.3±1.00^{a}	35.4±0.98^{a}	25.8±1.45^{a}	30.6±2.52^{a}
-sesame cake	60.8±2.22^{a}	81.5±3.28^{a}	97.6±2.85^{a}	41.7±1.40^{d}	95.5±2.41^{c}	60.5±1.47^{a}	72.8±1.80^{a}	65.4±1.56^{a}	95.0±2.45^{c}
-ethanol phase	7.0±0.05^{a}	11.5±0.13^{a}	17.5±0.75^{a}	1.8±0.46^{c}	13.5±0.75^{b}	9.6±0.98^{a}	15.4±0.85^{a}	12.5±0.75^{a}	14.3±1.05^{a}

All given values are means of tree determinations ± standard deviation.
Mean in a row followed by the same letters are not significantly different (P > 0.05).
All given values are expressed in dry basis.
Sesame oil samples were stored at 60℃ for PV analysis.

*1: 96% EtOH concentration (solid/liquid:1/10 constant)

*2: 75% EtOH concentration (solid/liquid:1/10 constant)

*3: 50% EtOH concentration (solid/liquid:1/10 constant)

*4: 15 min. treatment (solid/liquid:1/10 constant)

*5: 30 min. treatment (solid/liquid:1/10 constant)

*6: 1/5: solid/liquid (96% EtOH, 30 min.)

*7: 1/10: solid/liquid (96% EtOH, 30 min.)

*8: 90% amplitude (solid/liquid:1/10 constant)

*9: 75% amplitude (solid/liquid:1/10 constant)

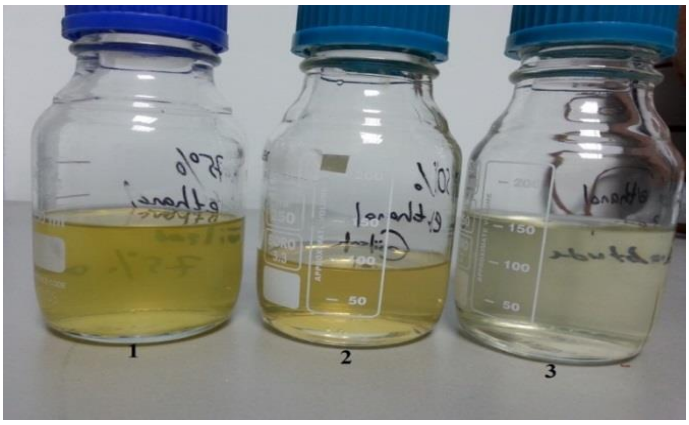

Figure 4.1: Alcohol extracts in ultrasonic treated samples (EtOH extract, 2:75% EtOH extract, 3:50% EtOH extract)

Figure 4.2 showed the appearance of sesame seeds before treatment and after UAET. Ultrasound provided swelling of seeds and color formation from light to dark color.

Figure 4.2: Appearance of sesame seeds before(I) and after(II) UAET

4.1.5 Oil yield for roasting, MWT, and UAET

Oil yield cannot be calculated just from sesame cake and sesame oil content. When the original sesame seeds went through pressing and the amounts were determined, sesame cake already had oil in it. Therefore; it was necessary to extract oil in raw sesame seeds and sesame cake with Soxhlet extraction.

Firstly, total amount of oil in NG RSS and amount of pressed oil were considered for each pre-treatments. Then, oil content and amount of sesame cake was determined by Soxhlet extraction. Finally, oil yield was calculated according to the following equation **(4.1)**:

$$\text{Oil yield} = \text{Total amount of oil} - \text{Oil in the sesame cake} \quad \textbf{(4.1)}$$

Table 4.6 represented oil yields (%) for three pretreatments in G and NG sesame seeds. While grinding had a significant increase in oil yield in HPLMWT in 1 cm, in other treatments, the grinding effect was not significant. The reasons seem to be open to argument. Short time-high power level microwave energy could cause high penetration of waves into the samples so that cell walls broke down fast and at final it gave high oil yield. But this is just assumption. When the results were compared, oil yields of grinded samples were negligible. At that point, treatment factors became prominent. As can be seen from the results, there was a significant increase in oil yield beginning from the oil yield of RSS. Since grinding didn't have significant effect on oil yield, only oil yield of non-grinded seeds were considered.

Oil yield of RSS was increased from 38.5% to 56.7% by 165℃ roasting and to 59.0% by 210℃ roasting, to 47.0% by 1 cm depth LPLMWT, to 71.0% by 1 cm depth MPLMWT, to 70.0% by 1 cm depth HPLMWT, to 63.8% by 50% EtOH UAET. The other parameters caused increase in oil yield. But the most significant effect was observed in these treatments. As it was seen in Table 4.6, oil yield is gradually increasing with pre-treatments. The only decrease was in 15 min. UAET, since time was not enough to start the cavitation and ultrasonic heating to absorb oil from the inner part of seed.

When the effect of treatments were considered, it was necessary to evaluate the results in their own. For roasting treatments, oil yield increased with increasing

temperature. As Willems et al. (2008) reported that increasing roasting temperature provided high oil yield [50]. From the results, MPLMWT and HPLMWT were the best to give high oil yield. Also by using 50% EtOH in 96% AP for 30 min. gave the second highest oil yield.

Table 4.6: Oil yield for roasting, MWT, and UAET

Treatments		**Oil yield (%)**	
		NG	G
Non-treated sesame seeds		38.5[a]	35.4[a]
Conventional treatment	165℃	56.7[b]	48.5[b]
	210℃	59.0[c]	52.0[c]
MWT at 1 cm depth	Low	47.0[a]	39.0[a]
	Medium	71.0[b]	68.8[b]
	High	70.0[d]	47.5[c]
MWT at 2 cm depth	Low	40.0[a]	25.5[a]
	Medium	43.5[b]	52.4[b]
	High	50.5[c]	39.2[c]
UAET	1*	63.8[b]	45.0[b]
	2*	54.5[b]	40.2[b]
	3*	50.0[c]	38.5[c]
	4*	10.5[c]	5.5[a]
	5*	54.5[b]	48.3[b]
	6*	42.5[a]	38.5[a]
	7*	53.2[c]	47.6[c]
	8*	60.8[b]	50.4[b]
	9*	41.6[a]	38.2[a]

1*: 50% EtOH concentration (solid/liquid:1/10 constant)

2*: 75% EtOH concentration (solid/liquid:1/10 constant)

3*: 96% EtOH concentration(solid/liquid:1/10 constant)

4*: 15 min. treatment(solid/liquid:1/10 constant)

5*: 30 min. treatment(solid/liquid:1/10 constant)

6*: 1/5: solid/liquid

7*: 1/10: solid/liquid

8*: 90% AP (solid/liquid:1/10 constant

9*: 75% AP (solid/liquid:1/10 constant)

4.1.5 NMR analysis

An example NMR Relaxation spectrum is given in Figure 4.3. Three type of information is extracted from an NMR Relaxometry spectrum: *number of peaks, T2 values of peaks and relative area of each peak*. Results showed the presence of 4

peaks in all oil samples. These peaks indicate the presence of different proton compartments in the oils. The different peaks are associated with the composition the fatty acids in the samples. T2 CPMG experiments were conducted for oils obtained through microwave and high temperature roasting treatments (high microwave power, medium microwave power, low microwave power levels; 165 ^{o}C and 210 ^{o}C). For T2-CPMG experiments no significant difference was found between the T2 values and relative areas of each compartment. This result was expected, as exchange times are very slow in the absence of gradients. Thus it is difficult to detect the exchange rates in oil samples.

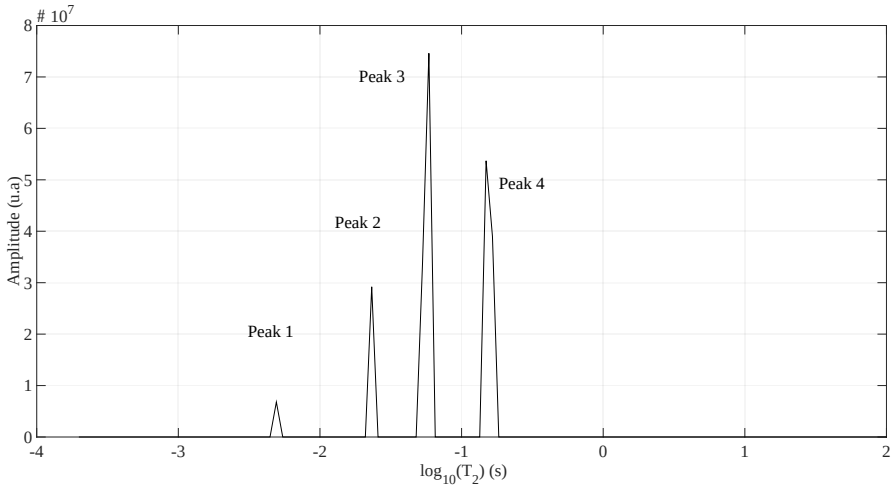

Figure 4.3: A representative relaxation spectrum: for the oils obtained through roasting at 210 ^{o}C

T2-CPMG experiments were also conducted for the samples treated with ultrasound using different ethanol concentrations (50%, 75%, 96%), ultrasonication time (15 min, 30 min) and amplitude (75% and 90%) and solid/liquid ratios (1/5; 1/10).

As ultrasound being a homogenization technique, the compartments have merged and the number of peaks decreased to three after the treatments. T2 values of the peaks were not that different from the microwave and high temperature ones. When the effect of ultrasound parameters were investigated, it was found that changing the amplitude from 90% to 75% for the 50% ethanol samples, did not result in change in T2 values butt relative area of the 2nd peak decreased at the lower amplitude. Effect of sonication time was more prominent. At 90% amplitude for the 96% ethanol samples doubling sonication time resulted a decrease in the T2 values. This showed that ethanol interacted with oil more at higher sonication times. Since ethanol has

longer T2 values compared to oil, it is expected to see that as oil integrates with ethanol much longer times, proton exchange between the compartments would accelerate and T2 times would decrease. Increasing the ethanol concentration also resulted in changes in the spectrum. Relative areas of the peaks increased with increasing ethanol concentration.

Table 4.7: T2 (s) values and relative areas of ultrasound treated samples

Treatment Conditions	T2 (s)			Relative Area (%)		
	Peak1	Peak2	Peak3	RA_1	RA_2	RA_3
90% AP-96% EtOH-1/5 (S/L) - 30 min	0.015	0.053	0.15	3.84	52.12	44.79
90% AP-96% EtOH-1/10 S/L-30 min.	0.043	0.089	0.20	22.28	50.42	27.09
90% AP-96% EtOH-1/10 S/L-30 min	0.011	0.053	0.15	3.93	50.03	46.04
90% AP-96% EtOH-1/10 S/L-15 min	0.019	0.072	0.23	7.45	55.59	36.69
90% AP-75% EtOH-1/10 S/L-30 min	0.010	0.065	0.23	3.50	55.83	40.6
90% AP-50% EtOH-1/10 S/L-30 min	0.021	0.065	0.18	8.19	61.55	32.75
75% AP-96% EtOH-1/10 S/L-30 min	0.017	0.065	0.18	6.47	53.65	39.49
75% AP-50% EtOH-1/10 S/L-30 min	0.023	0.065	0.18	7.38	57.43	33.92

4.1.6 Oxidation stability of non-treated and treated sesame oils

Oxidation stability was measured by Rancimat method which gave the result as induction time (h). All of the samples weren't analysed. The treatments which gave the highest oil yields were chosen as mentioned in Table 3.2 and they were analysed for oxidation stability., The results are shown in Table 4.8:

Induction time for non-treated sesame oil was found lower than Elleuch et al. (2007) finding. Induction time for raw sesame oil was found as 14.9±1.56 h while the result

of Elleuch et al. (2007) was 28.23±0.73 h [15]. The reason could be resulted from the type of sesame seed.

When treated samples were compared, the results were partly in accordance with our expectation. 210℃ roasted (14.5±0.55 h), high MWT (13.5±1.85 h), medium MWT (11.8±0.73 h), and 90% amplitude ultrasound treated sesame oil were not found significantly different from non-treated sesame oil which was unexpected. Because normally roasting processes increase the stability of the oils. There was a significant decrease in 50% EtOH UAET and Solid/liquid:1/10 UAET. Looking at the TPC and AOX results, oxidation stability went through in the same order. Therefore, higher oxidation stability of sesame oil could be attributed to higher antioxidants (lignans) together with tocopherol or vise versa. Following Figure 4.4 shows the comparison of oxidation stability with TPC and AOX.

Table 4.8: Induction periods (h) of non-treated and treated samples

Treatments	Induction time (h)
Non-treated sesame oil	14.9±1.56[a]
210℃ roasted sesame oil	14.5±0.55[a]
Medium MWT in 1 cm depth	11.8±0.73[ab]
High MWT in 1 cm depth	13.5±1.85[a]
30 min. UAET	8.7±0.27[b]
90% amplitude UAET	11.5±1.10[ab]
50% EtOH UAET	10.7±0.95[c]
Solid/liquid:1/10 UAET	0.96±0.04[d]

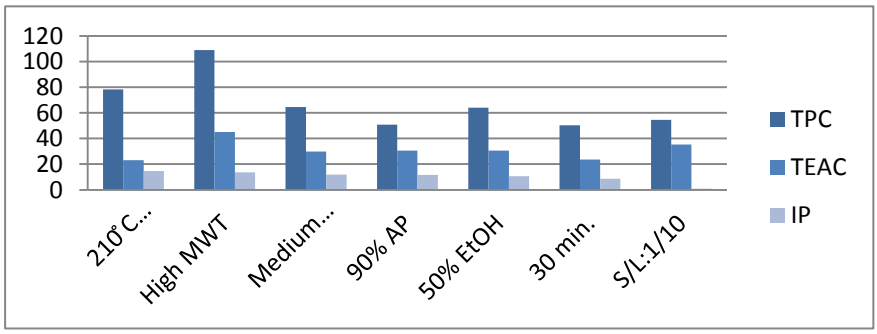

Figure 4.4: Comparison of oxidation stability with TPC and AOX

4.2 Discussions

In order to see the difference and effect of treatments, it was necessary to compare each result with the results of non-treated sesame seeds.

Moisture content was lowered from 5.1±0.03% to 2.20±0.05% by 165℃ roasting, to 0.9±0.002% by 210℃ roasting, to 2.50±0.34% by MPLMWT, 1.2±0.25% by HPLMWT, and to 2.6±0.23% by 96% EtOH conc. UAET. The other parameters were not chosen as comparison matter since their effect was not important as mentioned above. When the results were considered, the most effective treatment was 210℃ roasting and HPLMWT in order to have low moisture content and so high oxidation stability. According to the studies, in order to prolong shelflife of sesame oil, lower moisture content was showed as desired level. At that point, it is important not to have burned sesame seeds or sesame oil. If so, FFA content increases and oxidation stability decreases which are undesirable. It was seen that ultrasound pre-treatment couldn't have an impact on lowering moisture content. The reason was resulted from using high amount of water during treatment. If moisture content increases in some way, peroxide value increases and quality and shelf-life decreases. Therefore, roasting and microwave pre-treatment can be chosen as the best methods.

Oil content of non-treated sesame seeds increased from 48.7±3.19% to 56.6±3.55% by 210℃ roasting, to 63.3±3.12% by MPLMWT, to 53.3±1.27% by HPLMWT, and to 62.5±2.20% by 96% EtOH conc. and solid/liquid:1/10 for 30 min. in 90% amplitude UAET. The remained treatments didn't cause significant difference in oil content. At that point, oil yield should be taken into consideration in order to compare the methods.

In the results of refractive index, there was no significant difference between untreated and treated sesame oils. Therefore, treatments didn't cause a significant modification in the hydrocarbon contents. In literature, there is lack of information about refractive index of sesame oil. According to Hegde (2012), application of two different temperatures (25 and 60 ℃) did not cause any any change in refractive index values. Therefore, refractive index for ultrasound treated samples were not measured since there was no effect [111].

FFA contents for three pre treatments showed significant increase when it was compared to FFA content of raw sesame seeds. Press oils obtained after roasting at

210 ℃ in non-grinded state and high level MW application in 1 cm depth showed negligible increase in FFA content. Besides, FFA content of non-treated sesame oil increased from 2.5±0.26% up to 8.0±0.32% by 30 min. UAET. FFA content came at 15.8±0.52% by 75% amplitude UAET in sesame cake oil. The main reason of FFA increase resulted from presence of high mineral content, high fiber content, high pre-treatment temperatures, and low oxidation stability.

PV of non-treated sesame oil increased from 3.4±0.27 to 14.0±0.97 meq/kg oil after 30 days storage. Sesame oil was waited at 60 ˚C for 30 days, so PV increased spontaneously because of oxidation. When pre-treatments were applied, PV showed decrease after 20 days and 30 days. HPLMWT provided half decrease from 9.2±0.59 to 4.6±0.07 meq/kg oil after 20 days and one fourth decrease from 14.0±0.97 meq/kg oil to 4.9±0.22 meq/kg oil after 30 days. The most significant decrease in PV was observed in MWT. 96% EtOH concentration in solid/liquid:1/5 UAET has also lowered PV . Since antioxidants increased after pre-treatments, PV was lowered in a natural way. Low moisture content also contributed to low PV. In addition to that, roasting and microwave heating caused decrease in PV. It is known that factors such as temperature, moisture, metals, and oxygen affect rate of oxidation. Thermal properties of biological materials are dependent on its moisture content. Reason for highest influence of moisture content may be associated with this fact.

TPC of non-treated sesame seeds increased from 11.9±0.965 to 52.6±2.47 mg gallic acid/mL by HPLMWT, to 63.7±3.00 mg gallic acid/mL by 210 ˚C roasting. 96% EtOH concentration UAET also increased TPC up to 20.8±0.90 mg gallic acid/mL. TPC of non-treated sesame oil increased from 18.6±1.00 to 45.0±3.41 mg gallic acid/mL by HPLMWT, and to 78.2±1.90 mg gallic acid/mL by 210 ˚C roasting. The results of TPC in sesame cake were also similar to these results. There was significant increase in TPC in sesame seeds, sesame oil, and sesame cake after three pre-treatments. Ultrasonic treatment couldn’t be effective for high amount of TPC. It is probable that phenolics could pass to ethanolic phase which required further detailed analysis.

AOX of the samples were listed as an increasing order from unroasted, 165℃, and 210℃ roasted sesame seeds. It’s prospective that roasting increased antioxidant activity. As Lee et al. (2009) pointed out, roasting provides the formation of antioxidant compunds [43]. When it comes to microwave pre-treatment, it is

promising that MW pre-treatment can be useful for gaining high amount of antioxidants in sesame seeds. High power level MW pre-treatment gave the best antioxidant activity. This might be probably due to formation of sesamol from sesamolin [21].

Microwave treatment and 210 ˚C roasting were found to be the most applicable method in order to have low FFA content and PV, high TPC and AOX in sesame seeds.

For oxidation stability, when treated samples were compared, the results were partly in accordance with our expectation. Only 210℃ roasted (14.5±0.55 h) and high MWT (13.5±1.85 h) sesame oil were found to be very close to non-treated sesame oil which was unexpected. Induction times for 210℃ and high MWT were surprisingly found close to induction period of non-treated sesame oil. TPC and TEAC for these treatments were also higher. Therefore, it proved that higher oxidation stability attributed higher antioxidants and lignans. Primary oxidation products were formed in the result of medium MWT and ultrasound treatments.

In NMR analysis, T2 CPMG experiments were conducted for oils which were obtained in MWT, UAET, and roasting treatments. For T2-CPMG experiments, there was no significant difference found between the T2 values and relative areas of each compartment for MWT and roasting treatments. This result was expected, as exchange times are very slow in the absence of gradients. Since ultrasound is a homogenization technique, the number of peaks decreased to three after the treatments. T2 values of the peaks were not that different from the microwave and high temperature ones. At 90% AP for the 96% EtOH samples, sonication time was doubled and resulted a decrease in the T2 values. This showed that ethanol interacted with oil more at higher sonication times.

In the aspect of oil yield, MPLMWT and HPLMWT had give the highest oil content and oil yield after pressing. There was no effect of low MW on oil yield. On the other hand, when it came to medium power level MW in 1 cm depth, oil yield was twice higher than that of raw sesame seed. It was seen that the best treatment was medium power level MW in 1 cm depth. High power level MW in 1 cm and 2 cm, medium power level MW in 2 cm could be applicable for high oil yield. As it was proven, as the depth of samples decreased, oil yields were increased. For ungrinded

seeds, roasting at 165°C and 210°C was not really effective on press oil yield. Similar to non-grinded oil yield results, medium power level MW in 1 cm depth was the preferred treatment. However, high power level MW in 1 cm depth resulted with the highest oil yield. Khan et al. (1983) also reported grinding affect on causing higher oil yields. In ultrasonic pretreatments, by applying 96% ethanol concentration, maximum oil yield was obtained (63.8%). When ethanol concentration was decreased, oil yield also decreased. For grinded seeds, oil yield after 15 min. treatment was 10.5%, while oil yield after 30 min. treatment was 54.5%. When amount of ethanol increased according to seeds, oil yield increased from 42.5% to 53.2% in grinded seeds. Increase in amplitude increased temperature which was believed to be the reason for the increase in oil yield from 41.6% to 60.8% in grinded seeds. Higher amplitudes could form higher cavitation rates.

Following remarks represented the comments about thesis:

- Total phenolic content of treated sesame seeds, sesame oil, and sesame cakes were higher than TPC of non-treated ones. Highest TPC was observed in sesame cakes after three pretreatments. High value of phenolic content is related to high fibre content since phenolic compunds are associated with dietary fibre. Shahidi et al. (2006) stated that the coats of seeds contain higher amounts of phenolic compunds than endosperms [107].
- TPC was measured before and after pre-treatments. It increased significantly with roasting temperature and power level of MWT. According to Jannat et al. (2013), TPC decreased after 220 ˚C for 20 min. since highly oxidative compounds produced. But, below 220 ˚C, TPC increased. In ultrasound treatment, the temperature increased from 20 ˚C to 60 ˚C by cavitation and shear stress. Therefore, increase in TPC is an expected result.
- AOX values similar to TPC, increased by pre-treatments. According to Elleuch et al. (2007), by roasting, antioxidant content increased both for sesame seeds and sesame cake. The main reason was explained as sesamolin was converted to sesamol which was accepted as most effective compound in stabilizing oil. It was also reported that sesamols had a synergistic action with other antioxidants.

5. CONCLUSIONS

By the light of the results, some points can be concluded as followings:

- By applying high level of MW or 210°C roasting, it is probable that due to low moisture content, longer shelf-life for sesame oil could be applicable. Ultrasound assisted alcoholic pretreatments did not have influence on moisture content unlike other treatments.
- Lowest moisture content was observed with the application of 96% ethanol during ultrasound treatment. Parameters considered at the begining of ultrasound treatment didn't cause variations in the results.
- Highest oil contents for each pretreatment were observed as: 56.6% at 210℃ in grinded samples, 63.3% in medium MW level in 1 cm depth in non-grinded samples.
- In the results of refractive index, there was no significant difference between untreated and treated sesame oils.
- PV of treated sesame seeds was decreased by roasting and microwave treatment in both 20 and 30 days storage.
- Three pre treatments caused increase in FFA compared to FFA content of raw sesame seeds.
- Oxidation stability was high in 210°C roasting and high MWT which had also high TPC and AOX.
- In NMR analysis, T2-CPMG experiments for roasting and MWT had no significant difference between the T2 values and relative areas of each compartment. Effect of sonication time was more prominent. Increasing the ethanol concentration also resulted in changes in the spectrum.
- Maximum TPC's in sesame seeds, in sesame oil, and in sesame cake were found as 63.7 and 185.3 mg gallic acid/mL in 210°C roasted samples, high level microwave treated samples, respectively. Ultrasonic treatment couldn't be effective in high amount of TPC.
- In the aspect of oil yield, grinded seeds at 210℃ roasting, MPLMWT, and HPLMWT gave the highest oil content and oil yield after pressing.

Following recommendations can be considered for further researches:

- Sesame oil is a good source of sterols and change in sterol composition should be further investigated after pretreatments.
- Sesame lignans including sesamol and sesamolin should be studied in order to see the high advantageous properties of sesame seeds and in order to increase the usage of sesame oil.
- Fatty acid composition and phenolic compounds should be investigated in order to compare pre-treatments better.
- Sesame cake has high content of antioxidants and phenolic compounds. To recover these beneficial compounds to sesame oil, enzymatic pre-treatments can be used to obtain sesame oils with higher AOX and phenolics.

REFERENCES

[1] **FAOSTAT**, 2014. Sesame seed, http://faostat3.fao.org/browse/Q/QC/E, Date retrieved: 24.11.2014.

[2] **Kahyaoğlu, T.,** 2005. Effect of roasting processed on some properties of sesame and sesame paste: Rheological, color, textural, and moisture adsorption, Phd. Thesis, Gaziantep University, Graduate school of science engineering and technology, Food engineering programme, Gaziantep.

[3] **Weiss, E. A.,** 1983. Oil Seed Crops. *Longman, London, UK.,* pp. 282–340.

[4] **Shyu, Y. S., and Hwang, L.S.,** 2002. Antioxidative activity of crude exctract of lignan glycosides from unroasted Burma black sesame meal. *Food Research International*, 35, 357-365.

[5] **Namiki, M., 1995**. The chemistry and physiological functions of sesame. *Food Review International,* 11**,** 281-329.

[6] **Wikipedia The Free Encyclopedia**, 2015. Sesame, http://en.wikipedia.org/wiki/Sesame/media/File:Sesamum_indicum, Date retrieved: 22.03.2015.

[7] **Xu, J., Chen, S. and Hu, Q.,** 2005. Antioxidant activity of brown pigment and extracts from black sesame Seed (sesamum indicum L.). *Food Chem.*, 91: 79-83.

[8] **Abu-Jdayil, B., Al-Malah,K., Asoud, H.,** 2002. Rheological Characterization of Milled Sesame (tehineh). Food Hydrocolloids, 16: 55-61.

[9] **Lokumcu, F**., 2000. Tahinin Reolojik Karakterizasyonu, Phd Thesis, Istanbul Technical University, Graduate school of science, engineering and technology, Food engineering programme.

[10] **USDA**, 2015. National Nutrient Database for Standard Reference, Release 27.

[11] **Tashiro, T. et al.,** 1990. Oil and minor components of sesame (Sesamum indicum L.) strains. J. Am. Oil Chem. Soc., 67: 506–511.

[12] 800mediagap.com / September_2013_archives

[13] **Ashri, A.,** 1998. Sesame breeding. Plant Breed Rev 16: pp. 179-228.

[14] **Özcan M., and Akgül, A.,** 1994. Physical and chemical properties and fatty acid composition of tahin (sesame paste). Gıda, 19, 411-416. (in Turkish).

[15] **Elleuch, M., Besbes, S., Roiseux, O., Blecker, C., Attia, H.,** 2007. Quality characteristics of sesame seeds andby-products. *Food Chem*., 103, 641-650.

[16] **Gharbia, H., Shehata, A., Shahidi, F.,** 2000. Effect of processing on oxidative stability and lipid classes of sesame oil. *Food research international*, 33, 331-340.

[17] **Tai, S., Lee, T., Tsai, C., Yiu, J., Tzen, T.,** 2001. Expression pattern and deposition of three storage proteins, 11S globulin, 2S albumin, and 7S globulin in maturing sesame seeds. *Plant Physiology and Biochemistry*, 39, 981–992.

[18] **Iwe, M. O., van Zuilichem, D. J., Ngoddy, P. O. and Lammers, W.,** 2001. Amino acid and protein dispersibility index (PDI) of mixtures of extruded soy and sweet potato flours. *LWT - Food Science and Technology*, 34(2), 71-75.

[19] **Peter, R.S.,** 2007. Improving the protein content and composition of cereal grain. *Journal of Cereal Science*, 46(3), 239-250.

[20] **Rangkadilok, N., Pholphana, N., Mahidol, C., Wongyai, W.,** 2010. Variation of sesamin, sesamolin and tocopherols in sesame (Sesamum indicum L.) seeds and oil products in Thailand. *Food Chem*., 122, 724-730.

[21] **Kato, M.J. et al**., 1998. Biosynthesis of antioxidant lignans in Sesamum indicum seeds. *Phytochemistry*, 47: 583–591.

[22] **Gerstenmeyer, E., Reimer, S., Berghover, E., Schwartz, H., Sontag, G.,** 2013. Effect of thermal heating on some lignans in flax seeds, sesame seeds and rye. *Food Chemistry*, 138, 1847- 1855.

[23] **Wu, W.-H.,** 2007. The contents of lignans in commercial sesame oils of Taiwan and their changes during heating. *Food Chemistry*, 104, 341–344.

[24] **Bhunia, K., Chakraborty, A., Kaur, R., Gayatri, T., Bhat, K., Basu, A.,** 2015. Analysis of Fatty Acid and Lignan Composition of Indian Germplasm of Sesame to Evaluate Their Nutritional Merits. *J Am Oil Chem Soc.*, 92, 65.

[25] **Elleuch, M., Bedigian, D., Zitoun, A.,** 2011.Sesame Seeds in Food, Nutrition, and Health. *Nuts and Seeds in Disease Prevention*, Chapter 122, 1029-1036.

[26] **Yamashita, K. et al.,** 1995. Sesame seed and its lignans produce marked enhancement of vitamin E activity in rats fed a low α-tocopherol diet. *Lipids*, 30, 1019 - 1028.

[27] **Ikeda, S., Yasumoto-Shirato, S., and Yamashita, K.**, 2000. Increased vitamin E concentration in rats fed sesame seeds containing a high level of lignans. *Nippon Kasei Gakkaishi*, 51: 1017–1025.

[28] **Edwald Lee and Eunok Choe,** 2012. Changes in oxidation-derived off-flavor compounds of roasted sesame oil during accelerated storage in the dark. *Biocatalysis and Agricultural Biotechnology*, 1, 89-93.

[29] **Zoumpoulakis, P., Sinanoglou, V. J., Batrinou, A., Strati, I. F., Miniadis-Meimaroglou, S., Sflomos, K.,** 2012. A combined methodology to detect c-irradiated white sesame seeds and evaluate the effects on fat content, physicochemical properties and protein allergenicity. *Food Chemistry*, 131, 713–721.

[30] **Wolff, N., Yannai, S., Karin, N., Levy, Y., Reifen, R., Dalal, I., Uri Cogan, F.,** 2004. Identification and characterization of linear B-cell epitopes of β- globulin, a major allergen of sesame seeds. *J. Allergy Clin. Immunol*, 114, 1151-8.

[31] **Gangur V., Kelly C., and Navuluri, L.,** 2005. Sesame allergy: A growing food allergy of global proportions. *Ann Allergy Asthma Immunol*, 95, 4–11.

[32] **Wallowitz, M. L. et al., 2007.** Sesi 6, the sesame 11S globulin, can activate basophils and shows cross-reactivity with walnut in vitro. *Clin. Exp. Allergy*, 37, 929–938.

[33] **FDA Consumer Health Information,** 2009. Food Allergies: Reducing the Risks. (www.fda.gov/ForConsumers/ConsumerUpdates).

[34] **WAO (World Allergy Organization)**, WAO White Book on Allergy, 2011. Chapter 2: The burden of allergic diseases. 27-74. http://www.worldallergy.org/UserFiles/file/WAO-White-Book-on-Allergy_web.pdf

[35] **Holzhauser, T., and Röder, M.,** (2011). Allergens in tree nuts, sesame seeds, mustard, and Celery. *Food Allergens: Analysis Instrumentation and Methods*. Taylor and Francis Group, USA, Chapter 4, 78-121.

[36] **K. Beyer, L. Bardina, G. Grishina, H.A.,** 2002 Sampson. Identification of sesame seed allergens by 2-dimensional proteomics and Edman sequencing: seed storage proteins as common food allergens. *Journal of Allergy and Clinical Immunology*, 110, 154–159.

[37] **Pastorello, E. A. et al.,** 2001. The major allergen of sesame seeds (Sesamum indicum) is a 2S albumin. *Journal of Chromatography B*, 756, 85–93.

[38] **Albrecht, M. et al.,** 2009. Relevance of IgE binding to short peptides for the allergenic activity of food allergens. J Allergy Clin Immunol,124 (2), 328-336.

[39] **Pawankar, R. et al.,** 2008. State of World Allergy Report 2008: Allergy and Chronic Respiratory Diseases. *WAO Journal*, June 2008, Supplement 1.

[40] **TÜİK**, 2013

[41] **Wijesundera C., Ceccato C., Fagan P., Shen Z.,** 2008. Seed roasting improves the oxidative stability of canola (B. napus) and mustard (B. juncea) seed oils. *Eur. J. Lipid Sci. Technol*., 110:360–367.

[42] **Prior E.M., Vadke V.S., Sosulski F.W.,** 1991. Effect of heat treatments on Canola Press Oils. II. Oxidative stability. *J. Am. Oil. Chem. Soc*., 68:407–411.

[43] **Lee SW., Jeung MK., Park MH., Lee SY., Lee J.,** 2009. Effects of roasting conditions of sesame seeds on the oxidative stability of pressed oil during thermal oxidation. *Food Chemisty*, 118, 681–685.

[44] **Food and Agriculture Organization of the United Nations/ World Health Organization, Joint FAO/WHO Food Standards Programme: Codex Alimentarius Commission**, 1993. Codex Alimentarius, Volume 8, Fats, Oils and Related Products, 2nd Edition, Rome Codex Standard for named Vegetable Oils Codex-STAN 210.

[45] **Matthaus, B.,** 2008. Virgin oils – The return of a long known product, *European Journal of Lipid Science and Technology*, 110, 595-596, Weinheim.

[46] **Moreau, R.A. & Kamal-Eldin, A.,** 2009. Introduction, In Gourmet and Health Promoting Specialty Oils, *AOCS Press, USA*, 1-13.

[47] **Matthaus, B., Speener, F.,** 2008. What we know and what we should know about virgin oils-a general introduction, *European Journal of Lipid Science and Technology*, 110,597-601, Weinheim.

[48] **Uquiche, E., Jerez, M., Ortiz, J.,** 2008. Effect of pretreatment with microwaves on mechanical extraction yield and quality of vegetable oil from Chilean hazelnuts, *Innovative Food Science and Emerging Technologies*, 9, 495-500.

[49] **Willems, P., Kuipers, N., De Haan, A.B.,** 2008. Hydraulic pressing of oilseeds: Experimental determination and modeling of yield and pressing rates, *Journal of Food Engineering*, 89, 8–16.

[50] **Oyinlola, A., Ojo, A., & Adekoya, L. O.,** 2004. Development of a laboratory model screw press for peanut oil expression. *Journal of Food Engineering*, 64, 221−227.

[51] **Khan, L. M., & Hanna, M. A.,** 1983. Expression of oil from oilseed: A review. *Journal of Agricultural Engineering Research*, 28, 495−503.

[52] **Raphaëlle, S., Lanoisellé, J., Vorobiev, E.,** 2013. Mechanical Continuous Oil Expression from Oilseeds: A Review, *Food Bioprocess Technology*, 6, 1–16.

[53] **Venter, M.J., Schouten, N., Hink, R., Kuipers, N.J.M., de Haan, A.B.,** 2007a. Expression of cocoa butter from cocoa nibs. *Separation and Purification Technology*, 55 (2), 256–264.

[54] **Kaya, S., Kahyaoğlu, T.,** 2006. Modeling of moisture, color and texture changes in sesame seeds during the conventional roasting. Journal of Food Engineering, 75, 167-177.

[55] **Lee, S., Jeung, M., Park, M., Lee, Y., Lee, J.,** 2010. Effects of roasting conditions of sesame seeds on the oxidative stability of pressed oil during thermal oxidation, *Food Chemistry*, 118, 681–685.

[56] **Yen, G.C,** 1990. Influence of seed roasting process on the changes in composition and quality of sesame (Sesarnurn indicurn L.) oil. *J. Sci. Food Agric*., 50, 563-570.

[57] **Ryu, S., Kim, S., Xi, J., Ho, C.,** 1999. Influence of Seed Roasting Process on the Changes in Volatile Compounds of the Sesame (Sesamum Indicum L.) Oil, Flavor Chemistry of Ethnic Foods, Chapter 22, 229-232.

[58] **Clifford Hall III**, 2012. Other natural antioxidants – rice bran oil, sesame oil, rosemary extract, flavonoids, *Lipids for Functional Foods and Nutraceuticals*, Chapter 4, 73-112.

[59] **Mohamed, H and Awatif, I.,** 1998. The use of sesame oil unsaponifiable matter as a natural antioxidant. *Food Chem.*, 62, 269–276.

[60] **Gordon, M and Magos, P.,** 1983. The effect of sterols on the oxidation of edible oils. *Food Chem.*, 10, 141–147.

[61] **Ozkoc, S., Sumnu, G., Sahin, S.,** 2014. Recent Developments in Microwave Heating, *Emerging Technologies for Food Processing(Second Edition)*. Chp. 20, 361-383.

[62] **Mello, P., Barin, J., Guarnieri, R.,** 2014. Microwave Heating. *Microwave-Assisted Sample Preparation for Trace Element Analysis*, Chp.2, Pages 59-75.

[63] **Thostenson, E., Chou, T.,** 1999. Microwave processing: fundamentals and applications. *Composites: Applied Science and Manufacturing*, 30, 1055-1071.

[64] **Schiffmann, R.F.,** 2010. Industrial microwave heating of food: principles and three case studies of its commercialization, *Case Studies in Novel Food Processing Technologies*, 17, 407-426.

[65] **Malheiro, R., Casal, S, Ramalhosa, E., Pereira, J.,** 2011. Microwave Heating: a Time Saving Technology or a Way to Induce Vegetable Oils Oxidation? *Advances in Induction and Microwave Heating of Mineral and Organic Materials*, Chapter 26, 597-614.

[66] **Chavan, R.S. & Chavan, S.R.,** 2010. Microwave baking in food industry: a review. *International Journal of Dairy Science*, 5, 113-127.

[67] **Takagi, S., Yoshida, H.,** 1999. Microwave heating influences on fatty acid distribution of triacylglycerols and phospholipids in hypocotyls of soybeans(glycine max L.). *Food Chemistry*, 66, 345–351.

[68] **Mullin J.,** 1995. Microwave processing. In: New Methods of Food Preservation (Gould G W, ed), 112–134. *Blackie Academic and Professional, Bishopbriggs*, Glasgow.

[69] **Azadmard-Damirchi, S., Habibi-Nodeh, F., Hesari, J., Nemati, M., Fathi Achachlouei, B.,** 2010. Effect of pretreatment with microwaves on oxidative stability and nutraceuticals content of oil from rapeseed. *Food Chemistry*, 121, 1211–1215.

[70] **Cheng, S.F., Nor L., M., Chuah, C.H.,** 2011. A microwave pretreatment: A clean and dry method for palm oil production. *Industrial Crops and Products*, 34, 967– 971.

[71] **Yoshida, H., Hirakawa, Y., Tomiyama, Y., Nagamizu, T., Mizushina, Y.,** 2005. Fatty acid distributions of triacylglycerols and phospholipids in peanut seeds (Arachis hypogaea L.) following microwave treatment. *Journal of Food Composition and Analysis*, 18, 3-14.

[72] **Caponio, F.; Pasqualone, A. & Gomes, T.,** 2003. Changes in the fatty acids composition of vegetable oils in model doughs submitted to conventional or microwave heating. *International Journal of Food Science and Technology*, 38, 481- 486.

[73] **Chiavaro, E.; Rodriguez-Estrada, M.T.; Vittadini, E. & Pellegrini, N.,** 2010. Microwave heating of different vegetable oils: Relation between chemical and thermal parameters. *LWT – Food Science and Tecnology*, 43, 1104-1112.

[74] **Dostalava, J., Hanzlik P., Reblova, Z., Pokorny, J.,** 2005. Oxidative Changes of Vegetable Oils during Microwave Heating. *Czech J. Food Sci*., 23, 230-239.

[75] **Behera, S., Nagarajan, S., Rao, M.,** 2004. Microwave heating and conventional roasting of cumin seeds (Cuminum cyminum L.) and effect on chemical composition of volatiles. *Food Chem*., 87, 25-29.

[76] **Butz, P. and Tauscher, B.** 2002. Emerging technologies: Chemical aspects. *Food Research International*, 35(2/3), 279–284.

[77] **Larysa Paniwnyk,** 2014. Chapter 15 - Application of Ultrasound Emerging Technologies for Food Processing (Second Edition), 271-291.

[78] **McClements, D.J.** 1995a. Advances in the application of ultrasound in food analysis and processing. *Trends in Food Science and Technology*, 6, 293–299.

[79] **Mason, T.J., Chemat, F., Ashokkumar, M.,** 2007. Power ultrasonics for food processing (chapter 27) . Ultrasonound Technology, 815-843.

[80] **Zhang, Z., Wang, L., Li, D., Jiao, S., Chena, *D*., Zhi-Huai, M.,** 2008. Ultrasound-assisted extraction of oil from flaxseed. *Separation and Purification Technology*, 62, 192–198.

[81] **Mason, T.J.,** 1998. Power ultrasound in food processing. The way forward. In: Povey, M.J.W., Mason, T.J. (Eds.), *Ultrasound in Food Processing. Chapman & Hall, London*, 105–126.

[82] **Hielscher**, 2010. (http://www.hielscher.com/extraction_01.htm)

[83] **Vilkhu, K., Mawson, R., Simons, L., and Bates, D., 2008.,** Applications and opportunities for ultrasound assisted extraction in the food industry-A review. *Innovative Food Science and Emerging Technologies*, 9: 161–169.

[84] **Li, H., Pordesimo, L., and Weiss, J.**, 2004. High intensity ultrasound-assisted extraction of oil from soybeans. *Food Research International*, 37, 731–738.

[85] **Jime´nez, A., Beltra´n, G., Uceda, M.,** 2007. High-power ultrasound in olive paste pretreatment. Effect on process yield and virgin olive oil characteristics. *Ultrasonics Sonochemistry*, 14 (6), 725-731.

[86] **Shan L., Lianzhou, J., Yang, L.,** 2011. Research of aqueous enzymatic extraction of watermelon seed Oil of ultrasonic pretreatment assisted. *Procedia Engineering*, 15, 4949-4955.

[87] **Yuting, T., Zhenbo, X., Baodong, Z., Martin L.,** 2013. Optimization of ultrasonic-assisted extraction of pomegranate (Punica granatum L.) seed oil. *Ultrasonics Sonochemistry*, 20, 202–208.

[88] **Shah, S., Sharma, A., and Gupta, N.**, 2005. Extraction of oil from *Jatropha curcas* (L.) seed kernels by combination of ultrasonication and aqueous enzymatic oil extraction. *Bioresource Technology*, 96: 121–123.

[89] **Sharma, A. and Gupta, N.,** 2006. Ultrasonic pre-irradiation effect upon aqueous enzymatic oil extraction from almond and apricot seeds. *Ultrasonic Sonochemistry*, 13: 529–534.

[90] **Choe, E., Jiyeun, L., Min, D.,** 2005. Chemistry for Oxidative Stability of Oils, AOCS Press, Chapter 23.

[91] **Kiokias, S., Varzakas, T., Arvanitoyannis, I., Labropoulos, A.,** 2010. Lipid Oxidation and Control of Oxidation Taylor and Francis Group, Chapter 12.

[92] **Guillen, M.D., and Cabo, N.,** 2002. Fourier Transform Infrared Spectra Data Versus Peroxide and Anisidine Values to Determine Oxidative Stability of Edible Oils, *Food Chem*. 77, 503–510.

[93] **Tan, C.P., Che Man, Y., Selamat, J., and Yusoff, M.,** 2002. Comparative Studies of Oxidative Stability of Edible Oils by Differential Scanning Calorimetry and Oxidative Stability Index Methods, *Food Chem*. 76: 385–389.

[94] **Yen, G.C., and S.L. Shyu,** 1989. Oxidative Stability of Sesame Oil Prepared from Sesame Seed with Different Roasting Temperatures, *Food Chem*. 31, 215–224.

[95] **Lee, Y.-C., S.-W. Oh, J. Chang, and I.-H. Kim**, 2004. Chemical Composition and Oxidative Stability of Safflower Oil Prepared from Safflower Seed Roasted with Different Temperatures, *Food Chem*., 84, 1–6.

[96] **Jung, M and Min, D.,** 1992. Effects of oxidized α, γ, β- tocopherols on the oxidative stability of purified soybean oil. *Food Chemistry*, 45, 183-187.

[97] **Fukuda, Y., and Namiki, M.,** 1988. Recent Studies on Sesame Seed and Oil. *Nippon Shokuhin Kogyo Gakkaishi*, 35, 552–560.

[98] **Berthiaume, D., and Tremblay, A.,** 2006. Study of the Rancimat Test Method in Measuring the Oxidation Stability of Biodiesel Ester and Blends. OLEOTEK Inc., 24-34.

[99] **Uwe Loyall**, 2010. Stability Measuring Instruments. Metrohm Ltd., CH-9100.

[100] **Turkish Standards Institue,** 2010. Animal and Vegetable Solid-Liquid Oils– Moisture content and volatility. TS EN ISO 660, Ankara.

[101] **Turkish Standards Institue**, 2001.Spices and other herbs– Total ash content TS 2131 ISO 928, Ankara.

[102] **Turkish Standards Institue,** 2010. Animal and Vegetable Solid-Liquid Oils-Fats Acidity Content Standard. **TS EN ISO 660, Ankara**

[103] **AOAC**, 1990. Official methods of analyses. Association of Official Analytical Chemists: Washington, DC.

[104] **Rosa, L. A.; Parrilla, E. A.; Shahidi, F.,** 2011. Phenolic compounds and antioxidant activity of kernels and shells of Mexican Pecan (Carya illinoinensis). *Journal of Agricultural Food Chemistry*, 59, 152−162.

[105] **Alu'datt, M.H., Alli, I., Ereifej, K., Alhamad, M., Al-Tawaha, A.R., Rababah, T.,** 2010. Optimisation, characterisation and quantification of phenolic compounds in olive cake, *Food Chemistry*,123, 1, 117-122.

[106] **Chang, L., Yen, W., Huang, S., Duh, P.,** 2002. Antioxidant activity of sesame coat, *Food Chemistry*, 78:347-354.

[107] **Shahidi, F., Liyana Pathirana, C., Wall, D.,** 2006. Antioxidant activity of white and black sesame seeds and their hull fractions. *Food Chemistry*, 99, 478-483.

[108] **Yoshida, H and Takagi, S.,** 1997. Effects of roasting temperature and time on the quality characteristics of sesame (Sesamum indicum) oil, *J. Scib. Food. Agr*., 75:19-26.

[109] **Jannat, B., Oveisi, R., Sadeghi, N., Hajimahmoodi, M., Behzad, M., E., Behfar, A.,** 2010. Effects of roasting temperature and time on healthy nutraceuticals of antioxidants and total phenolic content in Iranian sesame seeds (*Sesamum indicum* L.) *Iran. J. Environ. Health. Sci. Eng., 7(1)1, 97-102.*

[110] **Hassan, M.,** 2013. Studies on Egyptian Sesame Seeds (Sesamum indicum L) and its Products. 2. Effect of Roasting Conditions on Peroxide Value, Free Acidity, Iodine Value and Antioxidant Activity of Sesame Seeds (Sesamum indicum L.*). World Journal of Dairy and Food Sciences*, 8(1), 11-17.

[111] **Hegde, D.**, 2012. Sesame(chapter 23). Directorate of Oilseeds Research. Woodhead Publishing, 449-486

APPENDIX A

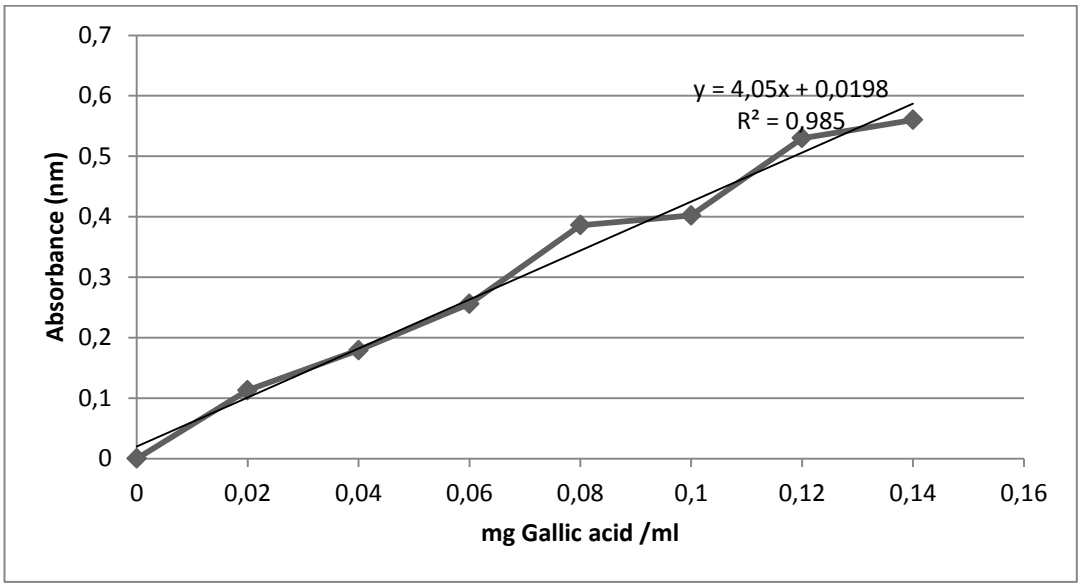

Figure A.1: Standard calibration curve in 80% acetone solution for TPC of sesame seeds

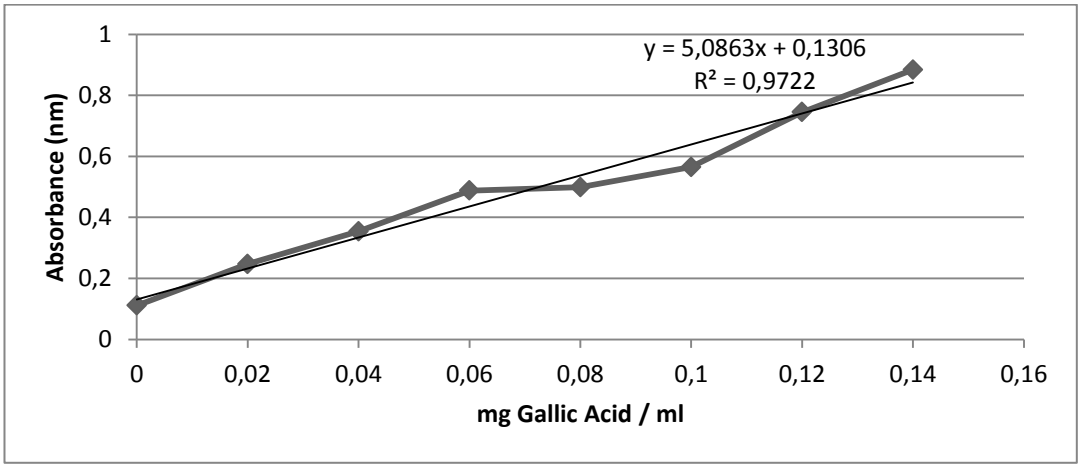

Figure A.2: Standart calibration curve in 80% methanol solution for TPC of sesame oil

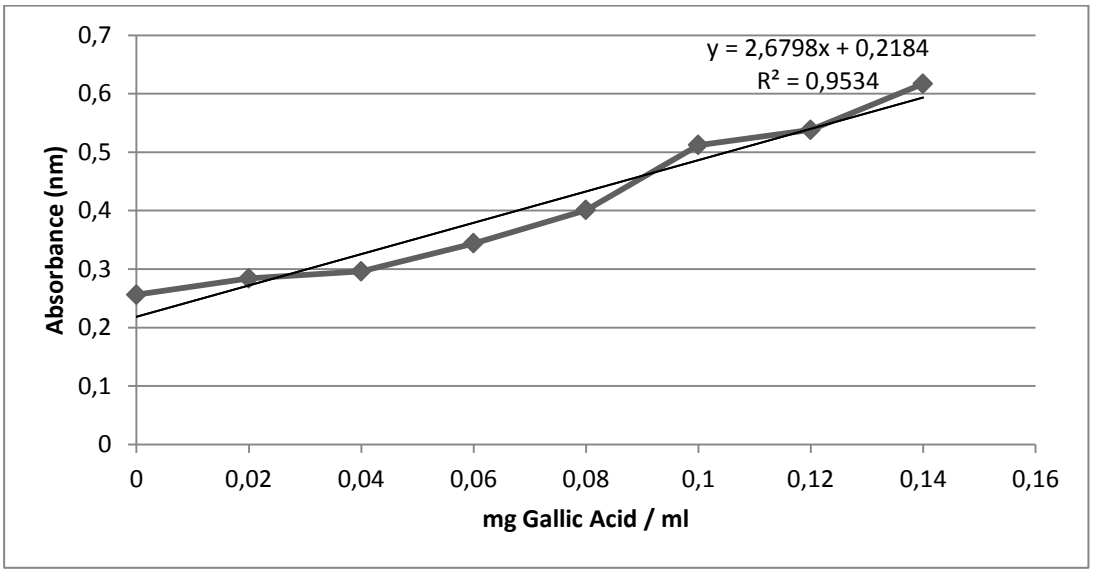

Figure A.3: Standart calibration curve in 80% methanol solution for TPC of sesame cake

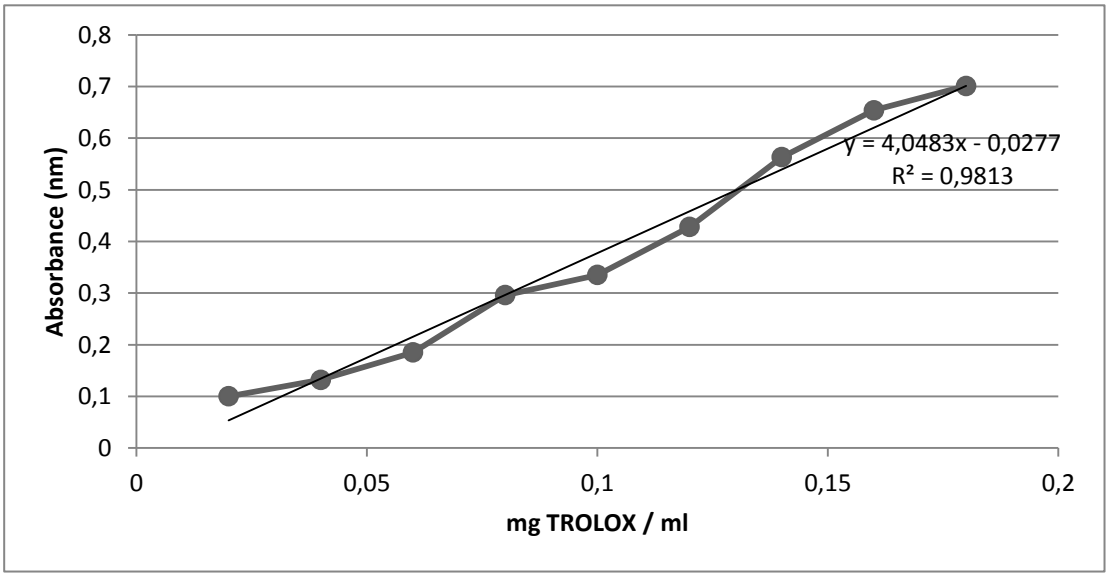

Figure A.4: Standard calibration curve for AOX of DPPH analysis in sesame seeds

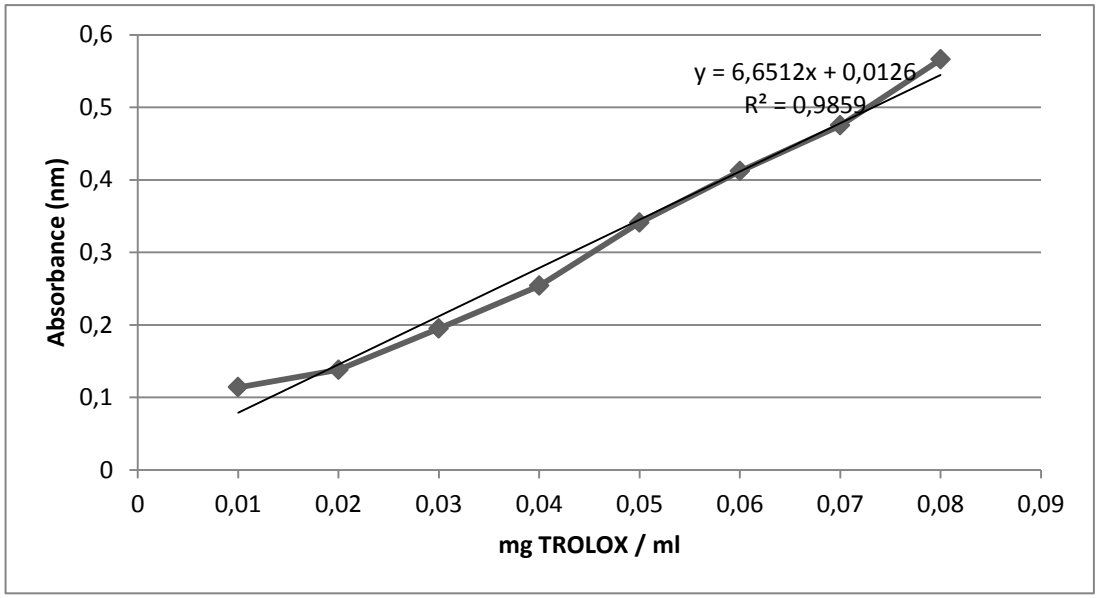

Figure A.5: Standard calibration curve for AOX of DPPH analysis in sesame oil

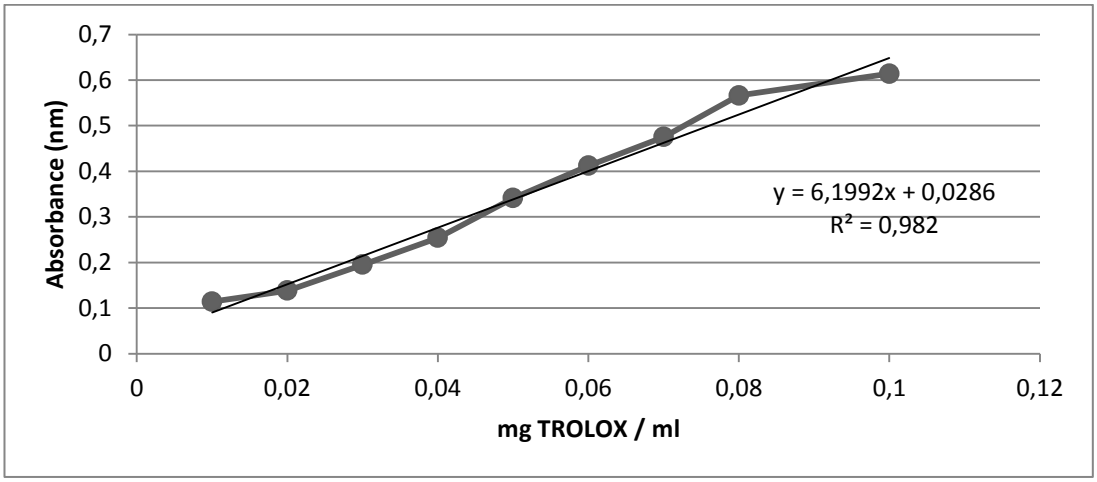

Figure A.6: Standard calibration curve for AOX of DPPH analysis in sesame cake

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