Evaluation of Physicochemical Characteristics of Locally Produced and Commonly Imported Edible Oils in Addis Ababa, Ethiopia

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This is to certify that the thesis prepared by Abebaw Andargie, entitled: *Evaluation of physicochemical characteristics of locally produced and commonly imported edible oils* and submitted in partial fulfilments of the requirements for the Degree of Master of Science (Medical Biochemistry) complies with the regulations of the university and meets the accepted standards with respect to originality quality.

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Operational Definitions

Merkato market: The largest market area in Addis Ababa, Ethiopia.

Sholagebya: Large market area in the north area of Addis Ababa city.

Adisugebya: Large market area in the east area of Addis Ababa city.

Mesalemya: Market area in the south east area of Addis Ababa city.

Locally produced edible oils: Edible oil produced by local oil millers and processers.

Commonly imported edible oils: Edible oils that are commonly imported to the country for the purpose of cooking.

Physicochemical characteristics: Physical and chemical aspects of edible oils used to assess the quality of edible oils.

Acronyms

AAU	Addis Ababa University
AV	Acid value
ATP	Adenosine triphosphate
CB POL	Chief Brand palm oil
CHD	Coronary Heart Disease
CSO	Cotton seed oil
ESA	Ethiopian Standards Agency
ETC	Electron transport chain
FAO	Food and agriculture organization
FFA	Free fatty acids
GTP	Growth and transformation plan
HDL	High density lipoprotein
IIM	Insoluble impurities
IV	Iodine value
LDL	Low density lipoprotein
LCPUFA	Long chain polyunsaturated fatty
LSO	Line seed oil
MUFA	Monounsaturated fatty acids
NSO	Niger seed oil
PV	Peroxide value
PUFA	Polyunsaturated fatty acids

RB POL	Reinna brand palm oil
RV	Relative viscosity
RI	Rifractive index
SBO	Soybean oil
SFO	Sunflower oil
SG	Specific gravity
SV	Saponification value
SFA	Saturated fatty acids
TFA	Tran fatty acids
UAE	United Arab Emirates
UN	United nation
USA	United States of America
WHO	World health organization

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Abstract

***Background**: Fats and oils are a heterogeneous group of predominantly hydrophobic compounds. Although many plant parts may yield oil in commercial practice, oil is extracted primarily from seeds mainly using solvent extraction. Edible oils sold in Addis Ababa are mainly imported from Asian countries while others are locally produced. The quality of edible oil is a measure of identity and edibility and it is determined by analysis of physicochemical characteristics of edible oils following standard procedures.*

***Aims of the study:** The aim of this study is to assess the physicochemical characteristics of commonly imported and locally produced edible oils.*

***Methods and materials:** A total of 16 samples (12 locally produced and 4 commonly imported edible oil samples) were collected randomly in local markets. All samples were taken immediately to the laboratory and stored at room temperature until analyses were completed. The physicochemical properties, physical parameters like refractive index (RI), specific gravity (SG) and relative viscosity (RV) and chemical parameters like iodine value (IV), peroxide value (PV), saponification value (SV), acid value (AV), Free fatty acid contents (FFAs) and insoluble impurities (IIM) were assessed using standard procedures.*

***Results:** Most of the physical characteristics of imported edible oils are within the recommended values. Palm oils have significantly the lowest mean IV of all. Mean IV of Chief Brand palm oil is below the WHO recommended value while mean IV of Reinna Brand palm, rape seed and niger seed oils are higher than the recommended value. The mean SV of line seed, niger seed and cotton seed oils are higher than the recommended values. The mean PV of rape seed oil is higher than ESA (Ethiopian Standard Agency) recommended values. The mean AV of locally produced edible oils are higher than the ESA recommended values except cotton seed oil while mean AV of imported edible oils fall in the recommended value. The mean IIM values of locally produced oils exceed more than ten times than the Ethiopian standards recommended value while the imported oils of mean IIM values are very close to the maximum recommended value.*

***Conclusion:** Commonly imported edible oils have relatively better physicochemical characteristics than locally produced edible oils.*

Keywords: locally produced edible oils, commonly imported edible oils, physicochemical characteristics.

1. Introduction

1.1 Fats and Oils

Human beings from time immemorial have been using plants for a multitude of purposes. Oils have always been an integral part of human foods, being essential for health. Industrially, they play an important role in the development of different areas of chemical products, pharmaceutical, cosmetics, paints and most importantly, food (Atef, 2010).

Fats and oils are a heterogeneous group of predominantly hydrophobic compounds. The distinction between fats and oils does not have a chemical basis (Janet, 2006). Those fats/oils that remain liquid at normal (ambient) temperature are generally taken as oil and those that remain solid, fats. Generally fatty acids are energy particles which supply hydrogen atoms to the Electron Transport Chain (ETC) for the production of Adenosine triphosphate (ATP) molecules. The most common source of fatty acids is triglyceride in which three fatty acid molecules remain connected to a glycerol molecule, as its synthesis is described in Fig. 1.1.

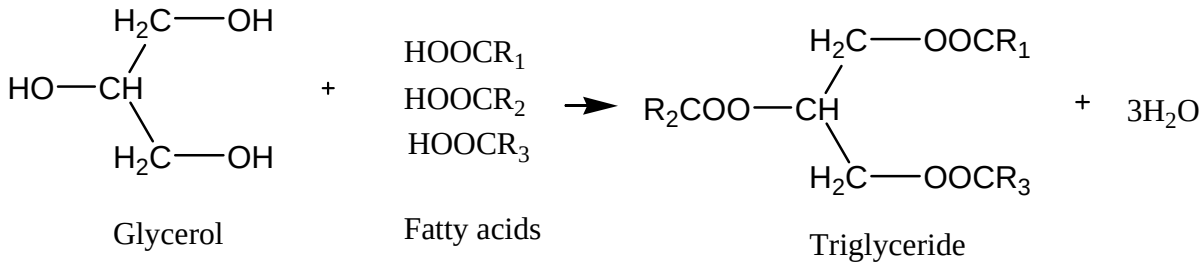

Fig. 1.1 *Diagrammatic representation of triglyceride synthesis by esterification of glycerol with fatty acids.*

Triglycerides are the basic structural units of cooking oils. In each fatty acid molecule, carbon atoms are arranged like beads of a chain**.** Hydrogen atoms occupy the free valency spaces of the tetravalent carbon atoms. The carboxyl group is called the carboxyl terminal of the fatty acid. The other end with three hydrogen atoms is known as the methyl end. If all the free valencies of the carbon chain are occupied by hydrogen atoms, the fatty acid is said to be saturated fatty acid. Palmitic acid is a common saturated fatty acid. If hydrogen atoms are deficient, the free electrons will be shared by adjacent carbon atoms forming double bonds between them. Such fatty acids possessing double bonds belong to the category of unsaturated fatty acids (USFAs). Examples include oleic acid, linolenic acid etc.

USFAs can be converted to saturated fatty acids (SFAs) by addition of hydrogen atoms under high pressure and temperature, an industrial process called hydrogenation (Gardner, 1995). As the content of hydrogen atoms is higher in saturated fatty acids they will deliver more hydrogen atoms to the ETC, for energy production. Hence replacing SFA with USFA is likely to improve glucose oxidation, which would definitely benefit the diabetic population. Fatty acids are not only energy sources but have many important functions in the body. They serve as constituents of cell membranes and as precursors of some biologically active compounds like eicosanoids, endocannabinoids, neural factors etc (Hibbeln et al., 2006). Eicosanoides include prostaglandins, prostacyclines and thromboxanes and lipoxins which regulate inflammation and associated processes. Endocannabinoides and neural factors like isofurans, neurofurans, isoprostanes etc are believed to be important in regulating mood and behavior (Nemet, 2006). All fatty acids required for the synthesis of these physiologically important compounds belong to the polyunsaturated fatty acids (PUFAs) group.

Depending on the positions of the double bonds present fatty acids are grouped as ω-3 or ω-6 fatty acids. Important ω-3 fatty acids are alpha lenolenic acid, stearidonic acid, eicosatetraenoic acid, eicosapentaenoic acid, docosapentaenoic acid, docosahexaenoic acid and nisinic acid. ω-6 fatty acids of physiological significance include linoleic acid, gamma lenolenic acid, eicosadienoic acid, arachidonic acid, docosadienoic acid, adrenic acid, docosapentaenoic acid, calendic acid etc. Eicosapentaenoic and docosahexaenoic acids are two important ω-3 fatty acids capable of decreasing the risk of coronary artery disease (Bucher et al., 2002).

1.2 Role of Trans Fatty Acids in Health

Fat containing Trans Fatty Acids (TFA) are referred to as Trans fat. TFA are USFAs, which differ from naturally occurring fatty acids in the spatial arrangement of some hydrogen atoms. In cis form the fatty acid is called oleic acid where as the Trans form is referred to as elaidic acid. Straightening and twisting of the oleic acid chain at its double bond as may occur in repeated heating can result in the formation of elaidic acid. Normally TFA are the products of hydrogenation. Such fat may contain partially hydrogenated TFA also, which are believed to have harmful effects in the body. As Ghafoorunissa described, TFA raised Low density lipoproteins (LDL) and reduced High density lipoproteins (HDL) cholesterol, increased ratio of total cholesterol: HDL cholesterol, a powerful predictor of Coronary heart disease (CHD) risk.

The adverse effects on serum LDL and HDL explain just part of CHD risk (Ghafoorunissa, 2008).

TFA also increase other intermediate risk end points of cardiovascular disease, namely, increase in serum triglycerides, lipoprotein, serum markers of chronic inflammation and endothelial dysfunction and decrease in particle size of LDL.

TFA were also positively associated with increased risk of diabetes. Recent studies show that insulin resistance initiates in adipocytes and affects insulin sensitivity in skeletal muscle and liver. Dietary fatty acids modify insulin sensitivity through their incorporation into structural lipids in skeletal muscle and adipose tissue that affects fluidity and responses of insulin receptors (Lovejoy, 2002). Furthermore, TFA may compromise early infant growth and development especially by inhibiting biosynthesis of long chain polyunsaturated fatty acids (Mozaffarian, 2006). The American Heart Association recommends limiting the TFA content of food to the least possible level (less than 1% of the total fat) so as to protect the heart.

1.3 Extraction of Edible vegetable oils

Although many plant parts may yield oil in commercial practice, oil is extracted primarily from seeds (Janet, 2006). Oils extracted from plants have been used since ancient times and in many cultures. For instance, in a 4,000 year-old "kitchen" unearthed in Indiana's Charlestown State Park, archaeologist Bob McCullough found evidence that natives used large slabs of rock to crush hickory nuts, and then boiled them in water to extract the oil (Paul, 2010). Most commercial oils are extracted at heat above 400°F and very few of them are bottled, stored and shipped with attention to light, heat and air exposure. In addition to being exposed to high temperatures, many commercial oils are extracted using chemical solvents, such as hexane. These oils are often bleached and deodorized to hide the fact that they have been made rancid in the extraction process (Paul, 2010).

The modern way of processing vegetable oil is by chemical extraction, using solvent extracts, which produces higher yields of required products and is quick and less expensive. The most common solvent is petroleum derived hexane. Another way of processing vegetable oil is physical extraction method, which does not use solvent. It is made by the traditional way using different types of mechanical extraction (Ascherio et al., 1994). This method is typically used to produce the more traditional oils and it is preferred by most healthy food consumer in the United States of America (USA) and Europe. Oil seed presses are commonly used in developing countries, among people for whom other extraction methods would be prohibitive expensive. The amount of oil extracted by using these methods varies widely.

The crude oil is not considered edible in the most oilseeds. The refinement of crude oils means remove natural color, smell, odor and free fatty acid from crude oil. Final product of refinement is transparent cooking oil. It involves: Chilling plant (remove wax content from crude oil), Neutralizing (remove soap content from crude oil), Bleaching (remove color from crude oil), deodorizing (remove odor at high temperature), Filtration (using wax filter), Cooling and Filtration (using pressure leaf filter) (Murwan et al., 2009).

1.4 Physicochemical quality of edible oils

The quality of vegetable oil is a measure of identity and edibility. This is also related to the method of obtaining the oils from the vegetable source. According to Codex, edible vegetable oils are foodstuffs which are composed primarily of glycerides of fatty acids being obtained only from vegetable sources. They may contain small amounts of other lipids such as phosphatides, of unsaponifiable constituents and of free fatty acids naturally present in the fat or oil (Codex, 2005).

Since edible vegetable oils begin to decompose from the moment they are isolated from their natural living environment, with the production of an unpleasant taste and odor over a period of time to form oils often being referred to as rancid. The unpleasant organoleptic characteristics of the rancid vegetable oils are caused by the presence of free fatty acids and atmospheric oxidation. This process this farther accelerated by the exposure of the vegetable oils to heat, light, moisture, residual natural dyes, pigments and by the presence of transition metals (e.g. copper, nickel and iron) (Kalua et al., 2008). Therefore, a number of parameters have been used to characterize the identity, quality and edibility of vegetable oils for the safety of consumers.

1.4.1 Free fatty acids (FFAs)

For the most part, natural fats and oils are existed in the triglyceride form when freshly extracted from the source. With prolonged storage, however, the triglycerides begin to break down giving rise to FFAs. This hydrolysis is brought about by a variety of agents: presence of moisture in the oil, elevated temperature and, most important of all, lipases enzyme coming from the source or contaminating microorganisms.

Consequently, the neutral oil becomes a mixture of triglycerides, diglycerides, monoglycerides, free fatty acids and glycerol. Some fats/oils are relatively stable but others are notoriously susceptible to hydrolysis.

Whichever the oil, presence of excess free fatty acid are sure indicators to unnatural state of edible oils. The presence of free fatty acid in large excess is undesirable for several reasons; some of them are:

- The oil is no longer the same as the *virgin* oil
- The oil tends to smoke during deep-frying
- The oil is susceptible to rancidity
- The product prepared from such oil turns rancid very soon

Rancid oils markedly lower the esthetic value of edible oils. Such oils also bring about health problems (Shahidi et al., 2002).

1.4.2 Saponification value (SV)

Saponification value of fat or oil is a very valuable test for the determination of adulteration. Since the oil from a given source has a remarkably constant saponification value, any deviation found in the test is an indication to adulteration. When fat is boiled with an excess of alcoholic potassium hydroxide (KOH), the glycerides irreversibly hydrolyze, giving rise to glycerol and fatty soap. The alkali consumed for this titration is a measure of saponification value, and is defined as the number of milligram of KOH needed to saponify one gram of oil or fat. The hydrolysis is limited to glycerides, waxes and phosphatides. Although sterols, hydrocarbons, pigments, etc are lipids, do not react with KOH under the above condition and they contribute to what is known as unsaponifiable matter (Othman and Ngassapa, 2010).

1.4.3 Peroxide value (PV)

Peroxide value is a very sensitive indicator of the early stages of oxidative deterioration of fats and oils. It is an indicator of the level of lipid peroxidation or oxidative degradation. In this process involving unsaturated fatty acids, especially reactive hydrogen atoms from methylene ($-CH_2-$) groups adjacent to double bonds undergo a chain reaction mechanism involving free radicals as intermediates and generating lipid peroxides as end products.

These lipid peroxides later undergo additional chain cleavage at the level of the hydroperoxide group to form secondary oxidation products such as short chain aldehydes and products bearing ketone, epoxy or alcohol groups responsible for the rancid smell and taste of the oil. Peroxide value is used to assess the stability or rancidity of fats by measuring the amount of lipid peroxides and hydroperoxides formed during the initial stages of oxidation.

This help to estimate to which extent spoilage of dietary oil (expressed by the level of rancidity) has advanced. Beside these visible harmful effects on the sensory quality of the oil, peroxidation also makes the oil dangerous for human health, as the free radicals generated by this process are proven to be carcinogenic (Sutapa and Analava, 2009).

1.4.4 Iodine value (IV)

The IV is the number of grams of iodine absorbed per 100 g of oil or fat, when determined using Wij's solution. The test is a measure of unsaturation of a given fat or oil. Since the degree of unsaturation is more or less characteristic to oil source, the test is routinely used for the determination of adulteration by other types of oils. Halogens add across the double bonds of unsaturated fatty acids to form addition compounds. Iodine monochloride (ICl) is allowed to react with the fat in the dark. The amount of iodine consumed is then determined by titrating the iodine released (after adding Potassium Iodide) with standard thiosulfate and comparing with blank in which the fat is omitted.

1.4.5 Refractive index (RI) and Specific gravity (SG)

The RI and SG values of edible vegetable oils are physical measures of adulteration of vegetable oils, since different oils have characteristic density and refractive index. Studies have shown that the contamination of vegetable oils with particulate matters and other chemical adulterants such as KOH brings chemical reaction with fatty acids of vegetable oils with the production of soap i.e. carboxylic acid ester which alter the optical activity of the vegetable oils. This also increases the susceptibility of the vegetable oils to become rancid or spoiled (Williams, 1990). The high specific gravity could be an indication of high molecular weight and unsaturation as the density of an oil increases with increasing molecular weight and unsaturation (Onyeka et al., 2005).

1.4.6 Relative viscosity (RV) and Insoluble impurities (IIM)

Viscosity is the prime quality of edible oil and measure the oil's resistant to flow (the more resistant or thick the oils, the higher its viscosity). As Karmalla reported that viscosity is increase due to presence of insoluble material, oxidation, overheating, and contaminations resulted by air, coolant and water (Karmalla, 1998). For cooking oils the viscosity is also sensitive to the temperature as the high heat disintegrates the structure of the fatty acids in vegetable oils which decreases the viscosity.

Insoluble impurities shall mean the dirt and other foreign matter, expressed as a percentage by mass, which are insoluble in n-hexane or light petroleum under the conditions specified. Such dirt or foreign matter includes mechanical impurities, miniral substances, carbohydrates, nitrogenous substances, various resins, calcium soaps, oxidized fatty acids, lactones, and in part alkali soaps, hydroxy-fatty acids and their glycerides (Othman and Ngassapa, 2010).

1.5 Oil seeds in Ethiopia

The oil seeds sector shows strong growth in Ethiopia, as domestic and world market demands are expected to continue to increase. The sector contributes significantly to the over all growth and development of the country. It supports the livelihoods of many small-scale farmers and businesses involving in trading, transporting and oil crushing as a source of employment and income generation (UNIDO, 2009). Oil seeds are grown on over 3 million holdings (30 % of all holdings) on 800,000 Hectare (8% of total areage) and account 5% of the country's total production of grain products (wijnandas et al., 2009). According to the Central statistical Agency of Ethiopia (CSA), the country produced 0.65 million tonnes of oil seeds, creating employment and a source of income for 3.3 million people (CSA, 2009). The main oil seed crops are sesame, noug (niger seed) and line seed which together account for 86% of the national oil seeds production. According to Ethiopian Investment Agency (EIA), the country's diverse agro-climate provides a natural comparative advantage and ample potential to grow other oil seeds, such as grundnut, sufflower, sunflower, rapeseed, soybean and cotton (EIA, 2009).

As Ethiopian Custom and Revenue Agency reported (ECRA), although Ethiopia is a major producer and exporter of oil seeds, the country imports about three quarter of its domestic edible oil consumption mainly from Asian countries like Malaysia, Indonesia, United Arab Emirates (UAE), Turkey and others (ECRA, 2010). Imports have grown fivefold over the last five years. Palm oil is the major type of imported edible oil. In Addis Ababa there are a number of oil producers (small scale millers and few processers). These producers mainly use cotton seed, niger seed (largely), line seed and rape seed as raw materials to produce the different variety of the oils. The Ethiopia government is aiming to achieve self-sufficiency in edible oil by 2015.

According to the Ethiopian Standard Agency (ESA), all edible oil must be refined, although a number of specific oil seed can be semi-refined. Despite this requirement, many millers are selling crude oil particularly to the low income class (Yared et al., 2011).

Although the locally produced edible oil is available in the market, most consumers prefer to the imported edible oils. This is mainly because of consumers suspect to the quality of locally produced edible oils due to its poor production process, unsafe storing and mixing of different oil seeds during processing.

This dissertation assessed the physicochemical characteristics of such as Reinna Brand palm, Chief Brand palm, soybean and sunflower oils which are commonly imported edible oils and four types of edible oils from locally produced namely cotton seed, niger seed, line seed and rape seed oils. The physicochemical parameters that are very significant and commonly used for determination of edible oils physicochemical characteristics namely; Iodine value (IV), Peroxide value (PV), Acid value (AV), Free fatty acids (FFA), Saponification value (SV), Insoluble impurities (IIM), Refractive index (RI), Specific gravity (SG) and Relative viscosity (RV) are included in this study. The result has been compared to the standard parameters set by the ESA, World Health Organization (WHO) and Food and Agriculture Organization (FAO).

1.6 Literature review

The quality of vegetable oil is a measure of identity and edibility. This is also related to the method of obtaining the oils from the vegetable source (i.e. whether it is virgin oil or cold pressed oil) where both obtained without altering the nature of the oil, by mechanical procedures (e.g. expelling or pressing), and the application of heat only. Storage, handling system, exposure to light and containers used for transportation has a significant effect on the physicochemical quality of edible oils. Many studies have been done for the last many years on the physicochemical quality of edible oils in order to assess the quality of edible oils.

Assessment of the physicochemical quality of palm oil from small holders in Cameron illustrated that PV and FFAs significantly increased as the storage period of the oil increases. PV and FFAs have significantly enhanced by high moisture and impurity levels of the oil at the outset which will make the oil unsuitable for human consumption, as it was demonstrated that oils with low moisture and impurity levels suffered very slight changes on the physicochemical characteristics of the oil (Ngando et al., 2011).

Assessment of edible vegetable oils quality, from both branded and unbranded, in Nigeria showed that all the branded vegetable oils analyzed have good physical and chemical quality of identity with minimal microbial contamination.

The unbranded vegetable oils on the other hand showed increased microbial content (mould and aerobic mesophillic bacteria, although these are within the WHO specified limits) with significantly decreased physical and chemical quality (Chabiri et al., 2009).

The compositional quality of refined edible oils in Sudan showed a significant physicochemical quality variation in most parameters in all refined edible oils included in the study. The RV was increased in all analyzed oils. The study showed that RI of refined sunflower oil was lower than those results obtained by other study (Katheer et al., 2003) but within the range of Sudanese Standard Method of Organization (SSMO).

The IV of refined edible oil of groundnut in the above study lies within the range that reported by SSMO (2006). Whereas, IV of refined edible oil of cottonseed oil was lower than those results of SSMO (2006) while IV of refined edible oil of sunflower was in agreement with those results of one study (Katheer et al., 2003).

The AV of refined edible oil of groundnut was higher than those results obtained by SSMO (2006) while the AV of refined edible oil of cottonseed was lower than those results of SSMO (2006). The PV of refined edible oil of sesame, cottonseed, sunflower and corn oils in the above study were lower than those results of Murwan (1994) and within results of SSMO. Whereas, PV of refined edible oil of groundnut and refined edible of olive oil was higher than results of SSMO. Generally, these results were indicated that there was no significant difference in AV among the reined edible oils while significant difference was observed in PV. The above study also assessed the fatty acid profile of six refined edible oils, showed that total amount of saturated fatty acids (Palmitic and Stearic acids). The refined edible oil of cottonseed was high in saturated fatty acids. The refined edible oil of sunflower had less total amount of saturated fatty acids. The total amount of unsaturated fatty acids (Oleic, Linoleic and Linolenic) in groundnut was higher than the other types of refined edible oil samples.

Epidemiological studies have shown a strong positive association between TFA intake and CHD risk. A meta analysis of four prospective cohort studies showed that increase of ~2 % energy TFA was associated with increase in incidence of CHD by 25% and also increase other intermediate risk end points of cardiovascular disease, namely, increase in serum triglycerides, lipoprotein, serum markers of chronic inflammation and endothelial dysfunction and decrease in particle size of LDL (Ghafoorunissa, 2008).

A meta analysis of 12 randomized controlled trials on the effects of isocaloric replacement of SFA or cis MUFA/PUFA with TFA on serum lipids showed that compared with the consumption of equal calories from SFA or cis MUFA/ PUFA, TFA raised LDL cholesterol, reduced HDL cholesterol, increased ratio of total cholesterol:HDL cholesterol, a powerful predictor of CHD risk (Mozaffarian et al., 2006). The adverse effects on serum LDL and HDL explain just part of CHD risk.

Recent studies show that insulin resistance initiates in adipocytes, and affects insulin sensitivity in skeletal muscle and liver. Dietary fatty acids modify insulin sensitivity through their incorporation into structural lipids in skeletal muscle and adipose tissue that affects fluidity and responses of insulin receptors (Odegaard et al., 2006).

TFA can be incorporated in placenta, breast milk, maternal and infant tissues. Studies have shown negative association between TFA and LCPUFA (Long chain polyunsaturated fatty acids) content in cord blood and breast milk lipids. Furthermore, negative associations have been shown between TFA intake and infant early development (birth weight, length, gestational age) (Ghafoorunissa, 2008)

Study on relation of hypertension to the degradation of dietary frying oils showed that the risk of hypertension was positively and independently related to the intake of products resulting from the degradation of vegetable oils during the cooking process in the family household because of production of much polar compounds and inversely related to the concentration of Mono Unsaturated Fatty acids (MUFA) in the serum phospholipids (Federico et al., 2003).

Assessment of physicochemical characteristics of some imported edible vegetable oils and fat marketed in Tanzania showed that before storage, the imported edible vegetable oils physicochemical characteristics largely conformed to international standard of the FAO/WHO specification. The physicochemical properties changed significantly depending on storage time and also with the mode of storage.

As the storage time increased, the quality of oils was deteriorated. The PV of the oils and fat exposed to atmospheric oxygen and light being the highest changing property (Othman and Ngassapa, 2010).

Study on in influence of minor components and additives on fats showed that the micron effects and these minor components have an influence on crystal growth, morphology, heat capacity and polymorphic stability and similarly, the effects on a macroscopic level, such as visual aspects, melting profiles and post hardening have been the subject of research.

Although limited compositional information, especially of additives, hinders appropriate discussions of the relevant mechanisms, some generic guidelines as to what type and strength of effect can be expected have been derived. As a general rule, a more significant influence is observed when the acyl group of the minor component (where present) is similar to those present in the fat itself. Additives may have different effects depending on the fat they are added to, their concentration and the temperature, especially with increasing under cooling which typically reduces the effect of additives (Kevin, 2011).

1.7 Significance of the study

This study evaluates the physicochemical characteristics of the commonly imported and some locally produced edible oils. Evaluating the physicochemical characteristics of edible oils has significant effect as it provides important information to the consumers, producers and sellers such as;

- It allows selecting easily better and safe edible oils from available markets.
- Consumers and retailers will understand the effect of poor handling on the quality of edible oils
- To have effective understanding about locally produced edible oils quality with respect to commonly imported edible oils.
- To contribute important input to the concerned governmental organization about the oils quality available in the market included in this study
- To provide a significant input for edible oil producers (oils included in this study) about the physicochemical quality of edible oils they produce.

2. Hypothesis

- The physicochemical characteristics of commonly consumed edible oils, both from commonly imported and locally produced, are significantly different.
- The physicochemical characteristics of imported edible oils are better than locally produced. Imported edible oils have some preservatives which increases their stability and better processing during production.
- Poor handling system has a significant problem on edible oils physicochemical characteristics. Storage places which are highly expose to sun light, moisture and atmospheric oxygen lead to the easily deterioration of the quality of edible oils.

2.1 Objective

2.1.1 General objective

To evaluate the physicochemical characteristics of selected edible oils from both commonly imported and locally produced oils.

2.1.2 Specific objectives

- To evaluate Physical characteristics like RV, SG and RI of commonly imported and locally produced edible oils.
- To evaluate chemical characteristics like IV, AV, FFAs, SV, IIM and PV of commonly imported and locally produced edible oils.
- To determine the effect of storage places on physicochemical characteristics of selected edible oils.
- To understand if there is basic differences between imported and locally produced edible oils in terms of physicochemical quality.

3. Methods and Materials

3.1 Study design

Laboratory based experimental study was done to evaluate physicochemical characteristics of commonly imported and locally produced edible oils.

3.2 Study area

The study has been conducted in Ethiopian Health and Nutrition Research Institution (EHNRI), Ethiopian Petroleum Enterprise (EPE) and Department of Biochemistry. Addis Ababa City, Ethiopia.

3.3 Source of sample

The edible oils for both commonly imported and locally produced edible oils have been collected from local markets.

3.4 Sampling technique

Samples for commonly imported edible oils and for commonly locally produced edible oils were collected randomly from sellers in the above mentioned local market areas.

3.5 Sample size

A total of 16 edible oils sample for both commonly imported and locally produced edible oils has been collected randomly in the selected market areas. One representative oil sample for each imported edible oils (a total of 4 samples) were collected as packed with plastic bottles. Each brand sample is obtained by well mixing 3 samples with the same production date, expired date and obtained from the same package. Four oil samples for each locally produced, niger seed and line seed oils (a total of 8 samples) were collected. Three oil samples for rape seed and one oil sample for cotton seed oil (a total of 4 samples) were collected. All locally produced oils were collected using sterile plastic bottles with the same procedure and at the same condition except cotton seed oil which was collected as packed. All samples were taken immediately to the laboratory and stored at room temperature until analyses were completed.

2.1 Exclusion criteria

Edible oils having less consumers and with expired production date has been excluded.

2.2 Inclusion criteria

Only edible oils in the selected areas having large consumers and those with similar or nearly similar production date were included in this study.

2.3 Determination of physical parameters

2.3.1 Determination of Refractive Index (RI)

Definition: The ratio of velocity of light in vacuum to the velocity of light in the oil; more generally, it express the ratio between the sine of angle of incidence to the sine of angle of refraction when a ray of light of known wave length (usually 589 nm, the mean of D lines of sodium) passes from air in to the oil. RI varies with temperature and wavelength.

Procedure:

The RI was determined following AOCS Official Method Cd 8-53, 2003. The temperature of refractometer was adjusted to 40°c (50°c was used for palm oils) using circulating hot water. Prisms were cleaned and dried. Few drops of the well mixed sample were placed on the prism. The prisms were closed and allowed standing for 1 min. The instrument and lighting were adjusted to obtain the most distinct reading. Each sample was treated two times and average RI was recorded.

2.3.2 Determination of Relative Viscosity (RV)

Definition: It is prime quality of edible oil and is measure the oil's resistant to flow (the more resistant or thick the oils, the higher its viscosity).

Procedure:

RV was determined following AOCS Official Method Cd 8-53, 200. Carbon dioxide from oil samples was removed by shaking gently at first and then vigorously. Temperature of the sample was kept at 30°c by using SETA KV-8 viscometer water bath. The suspending material in the oil was removed by passing the sample through a filter paper.

The appropriate volume of sample was added to the kinematic viscometer which was held in a water bath at 30°c. The suction was used to draw the sample above the upper mark of kinematic viscometer and then was allowed to fall down.

Then time was started with stopwatch as the sample was passing the upper mark of kinematic viscometer. Finally time was noted when the sample passes the lower mark of U-shaped viscometer. Each measurement was done two times and average time in second was recorded.

Calculation:

$$RV = CT$$

Where, T = time for flow of oil sample

C = Constant of the viscometer

2.3.3 Determination of Specific Gravity (SG)

Definition: It is the ratio of the density (mass of a unit volume) of a substance to the density (mass of the same unit volume) of a reference substance.

Procedure:

SG was determined following AOCS Official Method Cd 8-53, 200. The hydrometer were cleaned and dried. Appropriate amount of the well mixed sample were placed on suitable beaker. The hydrometer, which reads directly the SG, were immersed and allowed standing for 2 minutes. Each measurement was done two times and average SG was carefully recorded.

2.4 Determination of Chemical parameters

2.4.1 Determination of Iodine Value (IV)

Definition: Iodine value of oil is the number of grams of iodine absorbed by 100g of the oil, when determined by using Wij's solution.

Procedure:

IV was determined following AOCS Official Method Cd 8-53, 200. Approximately 0.25 g of the oil was measured into a 500 mL conical flask with glass stopper, to which 25 mL of carbon tetrachloride have been added. The content was mixed well. 25 mL of Wijs solution was pipette and added.

The flask was covered with stopper to prevent loss of halogen by evaporation. The flask was gently swirled and stored in the dark for one hour. 20 mL of the potassium iodide solution and 150 mL of water was added. The flask was shaken and the content was titrated with standardized 0.1N sodium thiosulphate solution, using starch as indicator at the end until the blue color formed was disappeared after through shaking with stopper on. Blank determination has been conducted in the same manner as test sample but without the oil. Measurements were done twice.

Calculation:

IV = (12.69(B – S)N) / W

Where, B = volume in mL of standard sodium thiosulphate solution required for the blank.

S = volume in mL of standard sodium thiosulphate solution required for the sample.

N = normality of the standard sodium thiosulphate solution

W = weight in g of the sample.

2.4.2 Determination of Acid Value (AV) and FFAs content

Definition: the AV is defined as the number of milligrams of potassium hydroxide (KOH) or sodium hydroxide (NaOH) solution required to neutralize the free fatty acid present in one gram of fat. It is a relative measure of rancidity as FFAs are normally formed during decomposition of oil glycerides. The value is mostly expressed as percent of free fatty acids calculated as oleic or palmitic acid.

Procedure:

AV was determined following AOCS Official Method Cd 8-53, 200. After throughly shaking the oil, approximately 5 g of the oil sample was weighted accurately in a 250 mL conical flasks and 150 mL of freshly prepared equal amount of (v/v) diethyl ether and ethanol 95% v/v were added. About one mL of phenolphthalein indicator solution was added. The mixture was boiled for about five minutes and was titrated while hot against standard 0.1N KOH and shaked vigorously during the titration untill the end point. Measurements were done twice.

Calculation:

FFAs as oleic acid percent by weight = 28.2VN / W

AV = percent fatty acid (as oleic) x 1.99

Where V = volune in mL of standard KOH solution

N = normality of the KOH solution

W = weight of the sample in g.

2.4.3 Determination of Peroxide Value (PV)

Definition: The PV is a very sensetive indicator of the early stages of oxidative deterioration of oils. PV therefore provides a means of predicting the risk of the development of flavor rancidity.

Procedure:

PV was determined following AOCS Official Method Cd 8-53, 200. Approximately 2g of oil sample was measured accurately in 250 mL conical flask. 30 mL of solvent (20 mL acetic acid in 10 mL chloroform solution) was added and swirled to dissolve the sample. 1 mL of KI solution was added and the flask was allowed to stand for one minute with gentle shaking. 30 mL of distilled water and few drops of starch indicator were added. Appearance of blue color on addition of starch indicates presence of free iodine.

The liberated iodine was titrated with 0.1N sodium thiosulphate until the blue color just vanished. Measurements were done twice.

Calculation:

PV ($meqO_2/Kg$) = N x Vx1000/W

Where, N = normality of sodium thiosulphate

V = volume of sodium thiosulphate consumed by sample in mL.

W = weight of sample in g.

2.4.4 Determination of Saponification Value (SV)

Definition: Saponification value shall mean the number of milligrams of potassium hydroxide required for the saponification of one gram of the test portion.

Procedure:

SV was determined following AOCS Official Method Cd 8-53, 200. A test portion of approximately 2g was measured accurately in 250 mL conical flask. Exactly 25 mL of ethanolic potassium hydroxide solution has been added by means of burette. The flask was connected with a condenser and refluxed for one hour. The soap solution was titrated with 0.5 N HCl in the presence of phenolphthalein while it was warm. A blank determination was carried out by refluxing and titrating under the same conditions. Measurements were done twice.

Calculation:

SV = 56.1 (B - S)N / W

Where, N = normality of Hydrochloric acid

B = volume of Hydrochloric acid consumed by Blank in mL.

S = volume of Hydrochloric acid consumed by sample in mL.

W = weight of sample in g.

2.4.5 Determination of Insoluble impurities (IIM)

Definiation: Insoluble impurities shall mean the dirt and other foreign matter, expressed as a percentage by mass, which are insoluble in n-hexane or light petroleum under the conditions specified. Such dirt or foreign matter includes mechanical impurities, miniral substances, carbohydrates, nitrogenous substances, various resins, calcium soaps, oxidized fatty acids, lactones, and in part alkali soaps, hydroxy-fatty acids and their glycerides.

Procedure:

IIM was determined following AOCS Official Method Cd 8-53, 200. Approximately 20g of prepared sample was measured accurately in 250 mL conical flask. The test portion was dissolved by adding 20 mL of n-hexane in to the flask and was shaken. The solution was left for about 30 minutes at 30°c.

Then the solution was filtered through ashless filter paper which was dried previously at 103°c and weighed. The remaining residue on the filter paper was washed with the same solvent. The solvent remaining in it was allowed to evaporate in the open air and the evaporation was completed in the oven at 103°c. The filter paper with its vessel was removed from the oven and cooled in desiccator. The filter paper with its dried sample was measured. Two parallel determinations for each sample were carried out simultaneously to insure that the difference between the two samples was not exceeding 0.05g of insoluble impurities per 100g of sample. Measurements were done twice.

Calculation:

IIM (percent by mass) = (M1 – M2) / Mo)X100

Where, Mo = weight of test portion

M1 = weight of filter paper containig dry residue.

M2 = weight of filter paper

3.10. Data Analysis

Results obtained from each determination are presented as mean ± SE (standard error). Tests for significance in variations were conduct by SPSS version16.0 followed by Student's t-test and Analysis of variance (ANOVA). Variations were considered significant at $p \leq 0.05$.

4. Results

4.1 Recorded physical characteristics before laboratory analysis.

All collected edible oils were analyzed for the presence of visual sediments, appearance of the oils and uncharactherstic odor of the oils in room temperature. Apperance of the oils were analyzed by keeping the samples for 24 hours at room temperatue. The follwing tables (table 4.1 and table 4.2) show the results briefly.

Table 4.1: *Some analyzed charactherstics and important informations of commonly imported edible oils before laboratory analysis.*

Type of oil	**Production Date.**	**Expired Date**	**Sample collection Date**	**Brand name & Imported Area**	**Remark**
SBO	*May 24, 2011*	*May 23, 2013*	*Aug. 8, 2011*	*- Sunny.* *- Imported from A.R.E*	*- Clear appearance* *- Collected as packed plastic bottle* *- SFO and SBO were liquid at room temperature* *- RB POL and CB POL were solid at room temperature.* *- No rancid odor*
SFO	*June 6, 2011*	*June 6, 2013*	*Aug. 8, 2011*	*- hatun* *- Imported from Turkey*	
RB POL	*June, 2011*	*June, 2013*	*Aug. 1, 2011*	*- Reinna.* *- Imported from Malasia*	
CB POL	*June, 2011*	*June, 2013*	*Aug. 1, 2011*	*- Chief* *- Imported from Malaysia*	

SBO = Soybean oil **SFO** = Sunflower oil **RB POL** = Rani Brand Palm oil **CB POL** = Chief Brand Palm oil

Table 4.2: *Some analyzed charactherstics and important informations of locally produced edible oils before laboratory analysis.*

Type of oil	Site of collection	Production Date.	Expired Date	Sample collection Date	Remark
NSO	*Merkato area (Mr)*	*Not known exactly (... june, 2011)*	*Not known exactly (… after 6 months)*	*Aug.6, 2011*	*- Light greenish color at bottom* *- Characteristics odor* *- Has sediments (not clear except Sg oil)* *- Taken from old metal barrel* *- Taken from large plastic container (for Ms and Sg oils)*
	Addisugebia area (Ad)	*Not known exactly (... June, 2011)*	>> >>	*Aug.9, 2011*	
	Mesalemia area (Ms)	*Not known exactly (...May, 2011)*	>> >>	*Aug.11, 2011*	
	Sholagebia area (Sg)	*2011 (the month is not mentioned)*	>> >>	*Aug.8, 2011*	
LSO	*North Merkato area (Mr1)*	*Not known exactly (... May, 2011)*	*Not known exactly (... after 6 months)*	*Aug.6, 2011*	*- Dark color* *- Not characteristics odor* *- Visual sediments (not clear)* *- Taken from old meta barrel*
	East Merkato area (Mr2)	>> >>	>> >>	*Aug.11, 2011*	
	West Merkato area (Mr3)	>> >>	>> >>	*Aug.11, 2011*	
	South Merkato area (Mr4)	>> >>	>> >>		
RSO	*Mr1*	*Not known exactly (... May, 2011)*	*Not known exactly (... after 6 months)*	*Aug.6, 2011*	*- Dark colour* *- Bad odour (rancid)* *- Visual sediments (not clear)* *- Taken from old metal barrel*
	Mr2	>> >>	>> >>	>> >>	
	Mr3	>> >>	>> >>	>> >>	
CSO	*From authorized retailers*	*July 26, 2011*	*July 26, 2013*	*Aug. 25, 2011*	*- Clear appearance* *- Deodorized and bleached* *- No rancid odor*

NSO = Niger seed oil **LSO** = Line seed oil **RSO** = Rape seed oil **CSO** = Cotton seed oil

The following photograph shows samples of edible oils used for laboratory analysis.

Fig. 4.1: *Photograph of edible oils used for laboratory analysis.*

4.2 Results of physical parameters

Results of RI of all analyzed edible oils are briefly explained in (table 4.3) The lowest mean RI values were observed in Reinna and Chief Brand palm oils, 1.461 ± 0.0005 and 1.462 ± .0000, respectively. The values were higher than the ESA and WHO recommended value which is (1.449 - 1.455) for palm oils. The largest mean RI was observed in sunflower and soybean oils with 1.470 ± 0.0005 and 1.470 ± 0.0000 values, respectively. The mean RI value of sunflower was higher than the ESA and WHO value which is (1.467-1.469) but the mean RI value of soybean oil was in the ESA maximum recommended value which is (1.466 - 1.470). line seed and rape seed oils have shown very close mean RI values which were 1.469 ± .0003 and 1.469 ± .0002, respectively.

The mean RI of line seed oil was below the ESA and WHO recommended value which is (1.4715 - 1.4825) while mean RI of rape seed oil was in the maximum recommended value which is (1.465 - 1.469). The mean RI of cotton seed oil was 1.4685 ± .0005, which was more close to the maximum ESA and WHO recommended value (1.458 - 1.466) while mean RI of niger seed oil (1.470 ± .0007) was higher than the ESA and WHO recommended value which is 1.4665 - 1.4695.

Sunflower and soybean oils had the same mean SG value which was 0.9205 ± .0005. The value was within the ESA recommended value which is 0.918 - 0.923. Mean SG values of line seed and niger seed oils were 0.9207 ± .0003 and 0.9200 ± .0010, respectively. The mean SG of line seed oil was within the ESA and WHO recommended value which is 0.912 - 0.933 while mean SG of niger seed oil was below the recommended value which is 0.925 - 0.927. Reinna Brand and Chief Brand palm oils had mean SG values of 0.9110 ± .0000 and 0.9115 ± .0000, respectively and the values were below the ESA and WHO recommended values which is 0.918 - 0.923. The largest mean SG value was observed in cotton seed oil (0.9261 ± .0000) and was in the maximum ESA recommended value which is 0.918 - 0.926. Values of SG are briefly explained in (table 4.3).

Palm oils had the largest RV values of all as shown in (table 4.3). The mean RV values of Reinna Brand and Chief Brand palm oils were 60.07 ± .1200 and 60.01 ± .0600, respectively. Among locally produced edible oils, rape seed oils had the largest RV value which was 55.82 ± .2271. The lowest mean was observed in niger seed oils which was 44.83 ± .3370 while mean RV values of cotton seed and line seed oils were 49.51 ± .0550 and 46.00 ± .2984, respectively. Mean RV values of sunflower and soybean oils were 45.86 ± .0650 and 46.49 ± .1150, respectively.

Table 4.3: *Laboratory analyzed results (mean ± SE) of physical parameters for locally produced and commonly imported edible oils.*

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Oil type	RI (at 40°c)	SG (at 20°c)	Viscosity (mm/s^2)/s (at 30°c)
SFO	*1.470 ±.0005* ***(1.467 - 1.469)***	*0.9205 ±.0005* ***(0.918 - 0.923)***	*45.86 ±.0650*
SBO	*1.470 ± .0000* ***(1.466 - 1.470)***	*0.9205 ± .0005* ***(0.918 - 0.923)***	*46.49 ±.1150*
RB POL	*1.461 ± .0005** ***(1.449 - 1.455)***	*0.9110 ±.0000*	*60.07 ±.1200*
CB POL	*1.462 ± .0000** ***(1.449 - 1.455)***	*0.9115 ±.0000*	*60.01 ±.0600*
NSO	*1.470 ±.0007* ***(1.4665- 1.4695)***	*0.9200 ±.0010* ***(0.925 - 0.927)***	*44.83 ±1.3370*
LSO	*1.469 ± .0003* ***(1.4715 -1.4825)***	*0.9207 ± .0003* ***(0.912 - 0.933)***	*46.00 ±.2984*
RSO	*1.469 ± .0002* ***(1.465 - 1.469)***	*0.9151 ± .0006* ***(0.91 - 0.92)***	*55.82 ±.2271*
CSO	*1.4685 ± .0005* ***(1.458 - 1.466)***	*0.9261 ± .0000* ***(0.918 - 0.926)***	*49.51 ±.0550*

SFO = Sunflower oil **SBO** = Soybean oil **RB POL** = Reinna Brand palm oil **CB POL** = Chief Brand palm oil

NSO = Niger seed oil **LSO** = Line seed oil **RSO** = Rape seed oil **CSO** = Cotton seed oil

SE = Standard Error * = RI value at 50 °c

4.3 Results of chemical parameters

Chief Brand and Reinna Brand palm oils had the lowest mean IV which were 48.96 ± 1.59 and 56.11 ± 2.38, respectively. The mean IV of Chief Brand palm oil was lower than the WHO recommended value which is 50 - 55 for palm oils while mean IV of Reinna Brand palm oil was higher. The mean IV of sunflower and soybean oils were 120.97 ± .07 and 124.04 ± .05, respectively. The mean IV of sunflower was in ESA and WHO recommended value which is 110 - 143 while mean IV of soybean oil was lower than the recommended value which is 129 - 143 as described in (table 4.4)

The mean IV of niger seed, line seed and rape seed oils were 141.32 ± 3.85, 125.10 ± 2.02 and 129.12 ± 2.67, respectively. The mean IV of niger and rape seed oils were higher than the ESA recommended values which are 128 - 134 and 94 - 120, respectively. The mean IV of line seed oil was lower than the ESA recommended value which is 175. The mean IV of cotton seed oil was 114.05 ± .15. The value was within the ESA recommended value which is 99 - 119. Results of IV of all analyzed edible oils are briefly explained in (table 4.4).

Soybean oil had the lowest mean SV which was 105.41 ± 10.48 while cotton seed oil had the largest mean SV which was 209.81 ± .05 as explained in (table 4.4). The mean SV of soybean oil was below the WHO recommended value which is 189 - 195 while mean SV of cotton seed oil was higher than the ESA recommended value which is 189 - 198. The mean SV of Reinna Brand and Chief Brand palm oils were 194.96 ± 3.24 and 192.05 ± 3.70, respectively. Both mean values were in the WHO recommended value which is 190 - 209. The mean SV of sunflower, niger seed, line seed and rape seed oils were 143.48 ± .03, 201.34 ± 5.08, 203.31 ± .4.02 and 138.06 ± 46.63, respectively. Mean SV of sunflower and rape seed oils were below the ESA and WHO recommended values which are 188 - 194 and 168 - 181, respectively while mean SV of niger and line seed oils were higher than the ESA and WHO recommended values which are 188 - 192 and 188 - 195, respectively.

Soybean oil had the lowest mean PV value which was 2.48 ± .00 while rape seed oil had the largest mean value PV which was 12.13 ± 3.01 as shown in (Fig.4.2). Mean PV of rape seed oil was higher than the ESA recommended value which is for all edible oils the PV should be ≤ 10 meqO_2 /Kg of oil and the variation is statistically significant against all analyzed edible oils at $p < 0.05$. The mean PV of Reinna Brand palm, Chief Brand palm, sunflower and cotton seed oils were 3.93 ± .00, 4.02 ±.055, 5.24 ± .25 and 5.72±.12, respectively.

All values were in the recommended value. The mean PV of niger seed and line seed oils were 8.63 ± 2.36 and 7.33 ± 2.26, respectively. Although the mean PV of niger seed and line seed oils were in the recommended value (close to the maximum recommended value), the variation was significantly higher than the PV of commonly imported edible oils at $p < 0.05$.

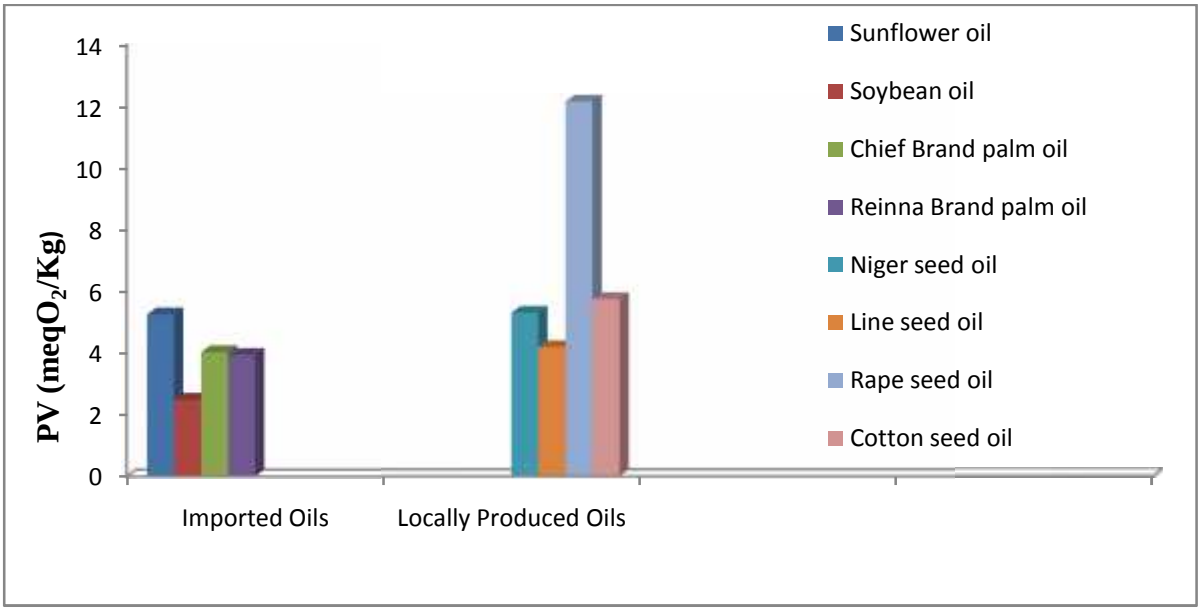

Fig.4.2: *Peroxide Value (PV) of locally produced and commonly imported edible oils.*

AV of the samples indicated that imported edibles oils had lower mean AV than locally produced oils. Sunflower and soybean oils had the lowest mean AV which were 0.225 ± .005 and 0.220 ± .00, respectively while Reinna Brand and Chie Brand palm oils had 0.495 ± .005 and 0.510 ± .030, which were within the ESA recommended value which is for all edible oils AV should be ≤ 0.6 mg NaOH/g of the oil. Among locally produced edible oils mean AV of cotton seed oil, which was 0.230 ± .000, was in recommended value. The mean AV of niger seed, line seed and rape seed oils were 2.198 ± .860, 3.148 ± .560 and 2.123 ± .237, respectively. Those values were significantly higher than commonly imported edible oils at $p < 0.05$ and extremely higher than the ESA recommended value as shown in (Fig. 4.3).

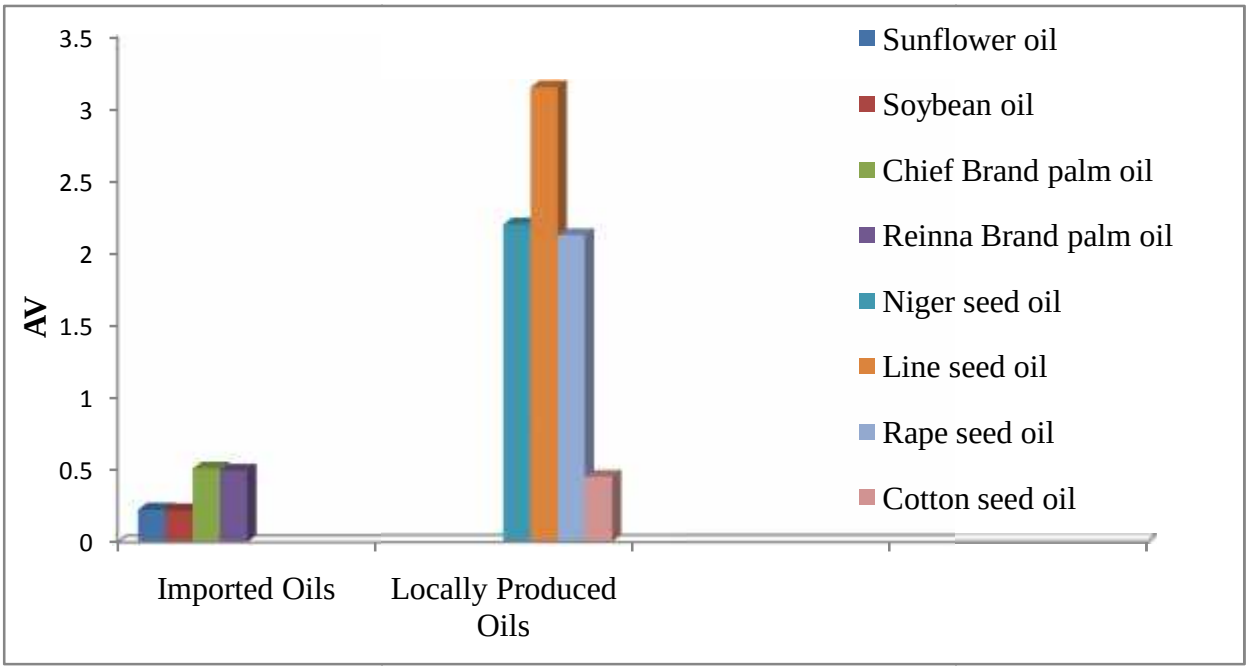

Fig.4.3: *Acid Value (AV) of commonly imported and locally produced edible oils.*

FFAs of the samples indicated that imported edibles oils had lower mean FFAs than locally produced edible oils. Sunflower and soybean oils had the lowest mean FFAs which were 0.114 ± .004 and 0.110 ± .000, respectively while Reinna Brand and Chief Brand palm oils had 0.245 ± .005 and 0.25 ± .010, respectively. As WHO and ESA recommendation as much as possible there should not be FFAs or should not exceed 0.1% and 5% for palm oils. Mean FFAs of sunflower and soybean oils were very close to the maximum recommended value. Among locally produced edible oils cotton seed oil (0.230 ± .000) had relatively low FFAs. The mean FFAs of niger seed, line seed and rape seed oils were 1.103 ± .430, 1.582 ± .280 and 1.065 ± .116, respectively. Those values were significantly higher than commonly imported edible oils at $p < 0.05$ and extremely higher than the ESA recommended values as shown in (Fig. 4.4).

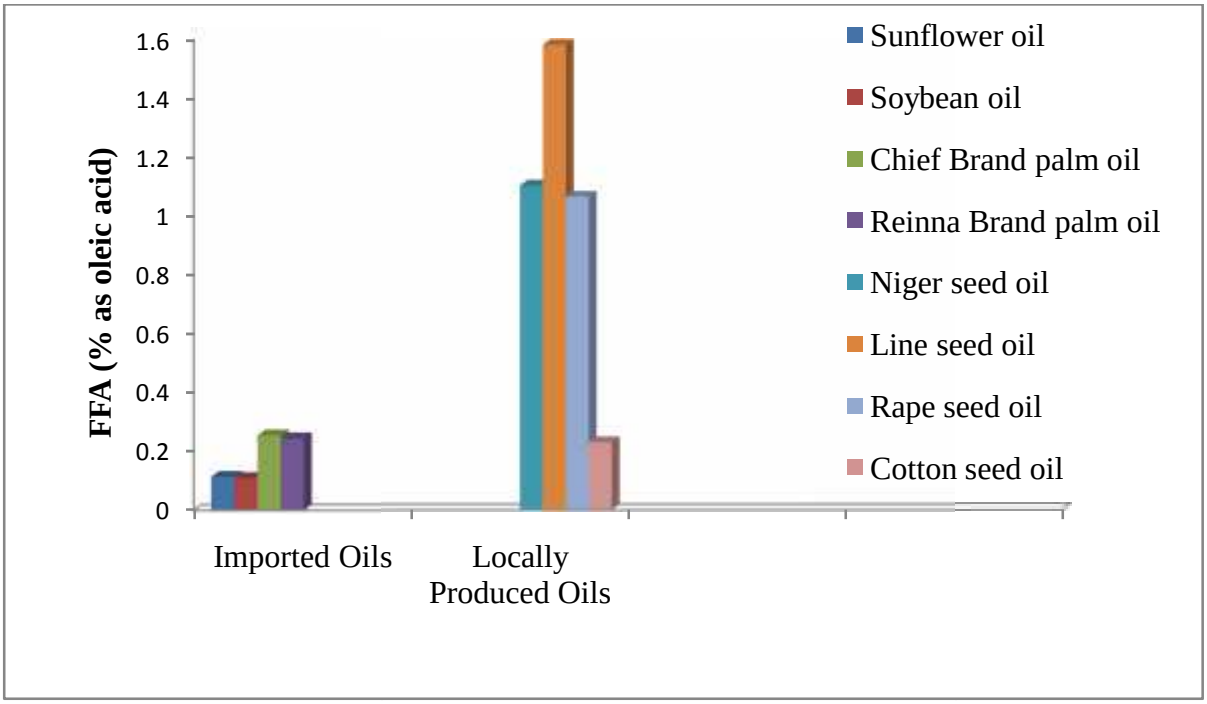

Fig.4.4: *Free Fatty Acids (FFAs) of commonly imported and locally produced edible oils.*

Imported edible oils had relatively lower mean IIM than locally produced edible oils. Sunflower and Reinna Brand palm oils with the same mean value of 0.254 ± .002 and Chief Brand palm oil with mean IIM of 0.249 ± .000 and soybean oil with mean IIM of 0.284 ± .000 have shown the lowest mean IIM values. Line seed, niger seed and rape seed oils with mean IIM values of 0.540 ± .014, 0.549 ± .012 and 0.496 ± .028, respectively have shown the largest mean IIM values. Among locally produced edible oils, cotton seed oil had lower mean IIM value than other locally produced edible oils as shown in (Fig. 4.5). The mean IIM values of all locally produced edible oils were significantly higher than commonly imported edible oils ($p < 0.05$) and extremely higher than the ESA recommended value (≤ 0.05%) and FAO/WHO recommended value (≤ 0.01%) for all edible oils.

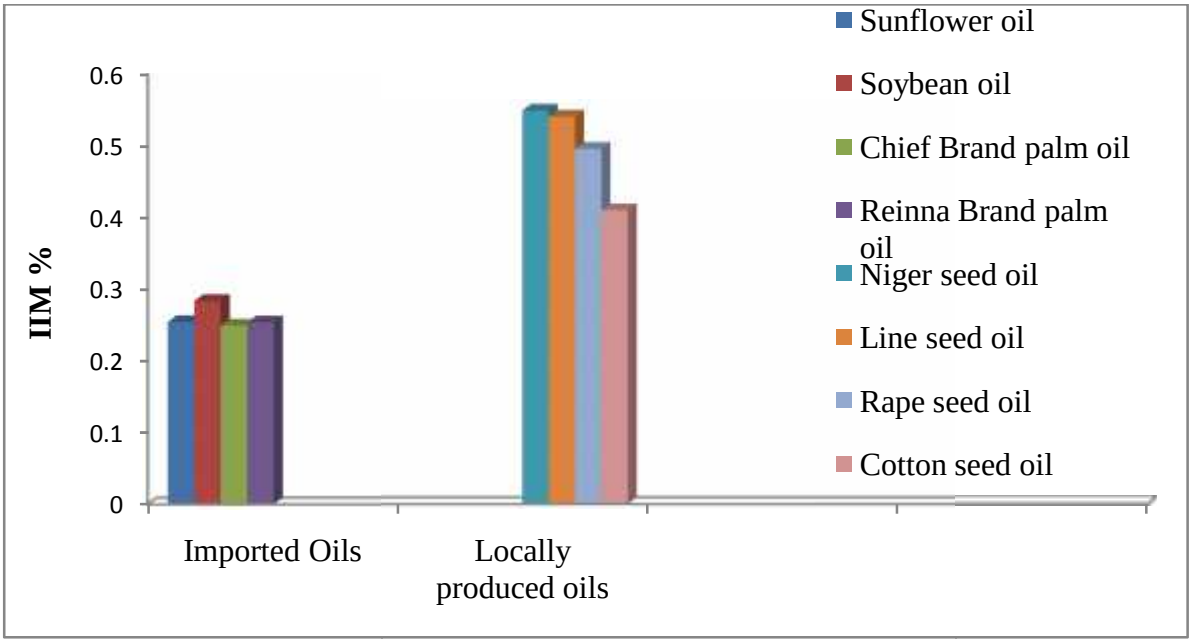

Fig.4.5: *Insoluble Impurities (IIM) of commonly imported and locally produced edible oils.*

The following table (table 4.4) summarizes results of laboratory analyzed chemical parameters of all analyzed edible oils and maximum recommended values set by WHO and ESA. Results are discussed with respect to their standards set by ESA and WHO, although some parameters do not have standards set by ESA or WHO.

Table 4.4: *Analysed chemical parameters and results (mean ± SE) for locally produced and commonly imported edible oils.*

Oil type	**IV (Wij's)**	**SV (mg KOH/g)**	**PV (meq O_2/kg)**	**AV (mg NaOH/g)**	**FFA (as % oleic acid)**	**IIM (% w/w)**
SFO	*120.97 ± .07* ***(110-143)***	*143.48 ±.03* ***(188-194)***	*5.24 ±.25* ***(≤ 10)***	*0.225 ±.005* ***(≤ 0.6)***	*0.114 ±.004* ***(≤ 0.1)***	*0.254±.000* ***(≤ 0.05)***
SBO	*124.0 ±.00* ***(129- 143)***	*105.4 ±10.48* ***(189-195)***	*2.48 ± .00* ***(≤ 10)***	*0.220 ± .000* ***(≤ 0.6)***	*0.11 ± .000* ***(≤ 0.1)***	*0.284 ± .000* ***(≤ 0.05)***
RB POL	*56.11 ±2.3* ***(50 - 55)***	*194.96 ±3.2* ***(190 - 209)***	*3.93 ± .00* ***(≤ 10)***	*0.495 ± .005* ***(≤ 0.6)***	*0.245±005** ***(≤ 5*)***	*0.254 ± .000* ***(≤ 0.05)***
CB POL	*48.9 ±1.59* ***(50 - 55)***	*192.05 ±3.70* ***(190 - 209)***	*4.02 ± .055* ***(≤ 10)***	*0.510 ± .030* ***(≤ 0.6)***	*0.255 ± .010* ***(≤ 5*)***	*0.249 ± .000* ***(≤ 0.05)***
NSO	*141.32 ± 3.8* ***(128- 134)***	*201.34 ±5.08* ***(188 - 192)***	*8.63 ±2.36* ***(≤ 10)***	*2.198 ±.86* ***(≤ 0.6)***	*1.103 ±.430* ***(≤ 0.1)***	*0.549 ±.012* ***(≤ 0.05)***
LSO	*125.10 ± 2.02* ***(175)***	*203.31 ± .4.0* ***(188 - 195)***	*7.33 ±2.26* ***(≤ 10)***	*3.148 ±.560* ***(≤ 0.6)***	*1.582 ± .280* ***(≤ 0.1)***	*0.540 ± .014* ***(≤ 0.05)***
RSO	*129.12 ± 2.67* ***(94 - 120)***	*138.06 ± 46.63* ***(168 -181)***	*12.13 ±3.01* ***(≤ 10)***	*2.123 ±.237* ***(≤ 0.6)***	*1.065 ±.116* ***(≤ 0.1)***	*0.496 ±.028* ***(≤ 0.05)***
CSO	*114.05 ± .15* ***(99 - 119)***	*209.8 ±.05* ***(189 - 198)***	*5.72 ±.12* ***(≤ 10)***	*0.450 ±.000* ***(≤ 0.6)***	*0.230 ±.000* ***(≤ 0.1)***	*0.415 ±.010* ***(≤ 0.05)***

SFO = Sunflower oil **SBO** = Soybean oil **RB POL** = Reinna Brand palm oil **CB POL** = Chief Brand palm oil **NSO** = Niger seed oil **LSO** = Line seed oil **RSO** = Rape seed oil **CSO** = Cotton seed oil * = % as palmitic acid

Note: Values in brackets are maximum recommended values given by WHO and ESA.

5. Discussion

In this study physicochemical characteristics of imported edible oils were found better than locally produced edible oils. Retailers of locally produced edible oils are selling those oils in open market and exposed to sunlight and atmospheric oxygen. Most containers are old metals which may the metal leak to the edible oil. There is no any clear information of locally produced edible oils and it is difficult to know production and expired date. Generally we have observed that individuals participating in retailing and producing of edible oils have less attention and almost no awareness about the edible oils quality. This all leads to deterioration of the oil quality which will expose consumers to different types of diseases as proved in laboratory and discussed below. In contrast imported edible oils were found with better physicochemical characteristics and they are packed in well sealed plastic bottles. Laboratory results of physicochemical characteristics are discussed bellow.

5.1 Physical characteristics

The RI value of edible oils is the physical measures of adulteration of edible oils. It is used in the preliminary identification of the oils since different oils have characteristic RI value (Chabiri et al., 2009). Studies have shown that the contamination of edible oils with particulate matters and other chemical adulterants such as potassium hydroxide brings chemical reaction with fatty acids of vegetable oils with the production of soap i.e. carboxylic acid ester which alter the optical activity of the vegetable oils and increases the susceptibility of the vegetable oils to become rancid or spoiled (William, 1990).

Mean RI of niger seed oil was higher than the ESA and WHO recommended value. Niger seed oils collected from merkato, shoalgebya and mesalemia local markets and the mean RI value of cotton seed, Reinna Brand palm, Chief Brand palm and sunflower oils had higher mean values than WHO/FAO and ESA recommended values while the RI of niger seed oil collected from shoalgebya local market was within the recommended value. Those oils with significantly high mean RI values than the recommended values may be adulterated or mixed with other oils having relatively low optical activities or may be contaminated with particulate matters and other chemical adulterants (Chabiri et al., 2009). The mean RI values of line seed and rape seed oils collected from different local market areas were lower than WHO/FAO and Ethiopian standards recommended values.

Alkaline solutions like potassium hydroxide which brings chemical reaction with fatty acids of vegetable oils with the production of soap i.e. carboxylic acid ester will alter the optical activity of the vegetable oils and increases the susceptibility of the vegetable oils to become rancid or spoiled as proposed by William (1990).

The SG value of edible oils is physical measures of adulteration of edible oils. It is used in the preliminary identification of the oils since different oils have characteristic SG value (Chabiri et al., 2009). This helps to suggest whether the oil is mixed with other oils or not (Othman et al., 2010). Studies have shown that the contamination of edible oils with particulate matters and other chemical adulterants such as potassium hydroxide brings chemical reaction with fatty acids of vegetable oils with the production of soap i.e. carboxylic acid ester which alter the molecular weight of the vegetable oils and increases the susceptibility of the vegetable oils to become rancid or spoiled (William, 1990). High SG also could be an indication of high molecular weight and unsaturation as the density of an oil increases with increasing molecular weight and unsaturation (Onyeka et al., 2005).

The mean SG values of niger seed, Reinna Brand and Chief Brand palm oils were lower than WHO/FAO and ESA recommended values while the mean values of rape seed, line seed, cotton seed and sunflower oils were in the recommended values. Those oils with significantly low mean SG values than the recommended values may be adulterated or mixed with other oils having relatively low molecular weight like cotton seed oils (Chabiri et al., 2009) or there may be any contamination of those oils with particulate matters and other chemical adulterants which alter the molecular weight of the those oils and increases the susceptibility of the vegetable oils to become rancid or spoiled (William, 1990).

As Karmalla (1998) reported that RV is a sensitive parameter to measure the quality of edible oils and increases as a result of insoluble materials, oxidation, overheating, air, water and coolant contaminations or may be decrease as a result of mixing with less viscous edible oils or other solvents. For cooking oils the RV is also sensitive to the temperature (Murwan et al., 2009).

RV among niger seed oils, collected from different local market areas have shown significant variation. Niger seed oil collected from shoalgebya had significantly high mean RV value than those collected from merkato, mesalemya and adisugebya local markets ($p < 0.05$). The mean RV value of niger seed oil was significantly lower than mean RV of Reinna Brand and Chief Brand palm oils (with the highest RV value), rape seed and cotton seed oils with $p < 0.05$.

The mean RV values of line seed oil collected from north merkato areas was significantly higher than other line seed oil collected in other local market areas with $p < 0.05$.

There is no significant mean RV value variation among rape seed oils collected in different local market areas. The mean RV value of rape seed oil was significantly higher than all other oils except mean RV value of both palm oils with $p < 0.05$. The mean RV value of cotton seed oil was significantly higher than mean RV value of niger seed oil with $p < 0.05$. Mean RV values of soybean and sunflower oils were significantly lower than mean values of rape seed oil and both palm oils with $p < 0.05$. There is no standard set by WHO/FAO or ESA about the relative viscosity of edible oils.

5.2 Chemical characteristics

Iodine value (IV) is a measure of unsaturation of a given fat or oils. Since the degree of unsaturation is more or less characteristic to oil source, the test is routinely used for the determination of adulteration by other types of oils (Parkins, 1992).Those oils with high IV have high unsaturated fatty acids and they are prone to greater oxidation and less storage stability and those oils with low IV than the recommended values have high saturated fatty acids which also exposes consumers to different types of fatty acid associated diseases specially by increasing serum LDL cholesterol (Kamau, 2008).

Both palm oils had the lowest mean IV of all. Mean IV of sunflower, soybean, niger seed collected from merkato market areas and cotton seed oils were within the recommended value of WHO/FAO standards while mean IV of rape seed and niger seed oils collected from shoalgebya, mesalemya and adisugebya were higher than the recommended value. Those oils with high mean IV than the recommended values are supposed to have high unsaturated fatty acids.

High PUFA is very important in decreasing cholesterol levels, stimulate cholesterol excretion into the intestine and inhibit biosynthesis of cholesterol in the liver. Oils containing high level of PUFA are found to inhibit the activity of hydroxymethylglutaryl-coenzymeA-reductase (HMG-CoA-reductase) which is the regulatory enzyme in cholesterol biosynthesis (Carl et al., 2009; Seddigheh et al., 2009; Ejikeme et al., 2010). However those oils should be kept very carefully and quality should be assured as they are prone to greater oxidation and less storage stability.

The mean IV of Chief Brand palm and line seed oils were lower than the recommended values. As Kamau (2008) suggested, those oils with low IV than the recommended values have high amount of short chain saturated fatty acids. Such fatty acids exposes consumers to different types of fatty acid associated diseases including high LDL cholesterol (Dimberu and Belete, 2011). If saturation is deliberately done in industrial process, the edible oil is likely exposed to contain TFA which are the leading cause in cardiovascular disease (Ghafooruniss, 2008).

SV of edible oil is a very valuable test for the determination of adulteration. Since the oil from a given source has a remarkably constant saponification value any deviation found is an indication to adulteration. An elevated saponification value in edible oils could be attributed to the presence of high FFA content and it also gives a measure of the average length of the fatty acid chain that makes up a fat (Muhammad et al., 2011).

The mean SV of sunflower, soybean and rape seed oils were below the WHO/FAO and ESA recommended values while mean SV of line seed, niger seed and cotton seed oils were higher than the recommended values. Mean SV of Reinna Brand and Chief Brand palm oils were in the WHO/FAO recommended values. Those oils with elevated SV are an indication of adulteration. This also could be due to the presence of high FFA content and there is a positive correlation in this study ($r = 0.254$). As Othman and Ngassapa (2010) suggested edible oils with high SV may have low molecular weight fatty acids and more saponifiable fats. Those edible oils with low SV than the recommended values could be due to the presence of high unsaponifiable maters which are considered as impurities (compounds that do not react with KOH) and/or high molecular weight fatty acids in the edible fatty acids (Muhammad et al., 2011; Othman and Ngassapa, 2010). As Katheer (2003) reported, the variation of SV of edible oils either increase or decrease is largely contributed by mixing of different types of edible oils or the edible oils seed during processing. This is common in our country especially low cost edible oil seeds with high cost edible oil seeds (Yared et al., 2011). This is largely contributed to dilution of edible oils quality which is an adulteration.

PV is used to assess the stability or rancidity. High PV is an indicator of the level of lipid peroxidation or oxidative degradation (Onwuka, 2006). Oils exposed to atmospheric oxygen and light showed a much larger increase peroxide value during storage (Ngando et al., 2011). In this process involving unsaturated fatty acids, especially reactive hydrogen atoms from methylene groups adjacent to double bonds undergo a chain reaction mechanism involving free radicals as intermediates.

Those free radicals will expose to stroke, arteriosclerosis, and ischaemic heart diseases and cancer and generating lipid peroxides as end products (Dimberu and Belete, 2011). These lipid peroxides later undergo additional chain cleavage at the level of the hydroperoxide group to form secondary oxidation products such as short chain aldehydes and products bearing ketone, epoxy or alcohol groups responsible for the rancid smell and taste of the oil. Oxidation may be significantly enhanced by the impurity level and our study shows a positive correlation ($r = 0.201$) although statistically insignificant ($p = 0.41$).

The mean PV of rape seed oil was higher than ESA recommended value. Although PV of the rest edible oils were in the recommended values, locally produced edible oils had significantly higher mean PV than imported edible oils ($p < 0.05$). As Onwuka (2006) suggested, high PV is an indicator of the level of lipid peroxidation or oxidative degradation.

As we have seen in local market areas, locally produced edible oils are retailing with low attention to light and atmospheric oxygen which enhances oxidation of those oils and the edible oils are kept in old and easily scrap metal containers which increases insoluble impurities in the edible oils. As Onwuka and Akaerue (2006) suggested high PV may also enhanced by the presence of insoluble impurities (IIM) especially inorganic metals which activates the enzyme lipase and increases hydrolysis of fatty acids.

FFA content is the most used criterion for determining the quality of edible oils. FFAs are generally present in oils as part of triacylglycerol molecules. The presence of FFAs moieties in edible oils is an indication of the impairment of edible oil quality. AV of the edible oils indicates the extent of FFAs present in the edible oils.

The AV of both palm oils are significantly higher than sunflower and soybean oils ($p < .05$). The mean AV and FFAs of sunflower, soybean, Reinna Brand palm, Chief Brand palm and cotton seed oils fall in WHO and ESA recommended values.

The mean AV and FFAs of niger seed, line seed and rape seed oils are higher than the recommended values. The high FFA is a sure indicator to unnatural state of the edible oils. With prolonged storage, the triglycerides begin to break down giving rise to FFAs and increase the AV (Othman and Ngassapa, 2010). The presence of high AV and FFAs in those edible oils may be brought by a variety of agents: presence of moisture in the oil, elevated temperature and, most important of all, an active lipases coming from the source or contaminating microorganisms and / or activated by inorganic metals (Kalua et al., 2008).

In this study insoluble impurities (IIM) that may contain large amount of inorganic metals and microorganisms have been found to have strong correlation on the AV of edible oils ($r = 0.759$). This may have large contribution in hydrolysis of those oils. Consequently, the neutral oil becomes a mixture of triglycerides, diglycerides, monoglycerides, FFAs and glycerol which make the oil to be easily rancid and loss of its natural characteristics (Ngando et al., 2006).

Oils with high IIM values are highly exposed to dirt and other foreign matter, which are insoluble in n-hexane (Aletor et al., 1990). Such dirt or foreign matter includes mechanical impurities, miniral substances,carbohydrates, nitrogenous substances, various resins, calcium soaps, oxidized fatty acids, lactones, and in part alkali soaps, hydroxy-fatty acids and their glycerides (Rossel, 1999). Those foreign matters significantly enhances oxidation of edible oils (Ngando et al., 2011).

In general the imported oils had lower mean IIM values than locally produced oils. The mean IIM values of locally produced oils exceed more than ten times than the WHO and ESA recommended value while the imported oils of mean IIM values were very close to the maximum recommended value. The high amount of IIM in those edible oils may be due to poor handling and processing which expose the oils to contamination of organic and inorganic substances and, atmospheric oxygen and light. During sample collection, I have seen that especially locally produced edible oils were retailing in old metal container which may the metal leak and poor hygiene of millers during processing. In this study, the level of IIM and degree of peroxidation were positively correlated ($r = 0.201$) although the correlation is statistically insignificant ($p = 0.41$).

6. Conclusion

Commonly imported edible oils have relatively better physicochemical characteristics than locally produced edible oils. The physical parameters, RI and SG of those oils are almost in the recommended values. Both palm oils show very high RV value, may be due to its saturation which makes the oil more viscose. Among locally produced oils, line seed and rape seed oils have significantly low RI value than the recommended value. This may be due to mixing of those oils with other oils or presence of dirt and foreign substances or both. Mean RV of rape seed oil is significantly higher than other locally produced oils. This may be due to presence of insoluble materials, oxidation and contaminations like air, coolant and water.

The chemical characteristics of commonly imported edible oils are significantly better than locally produced oils. The IV of commonly imported oils is almost in the recommended value except Chief Brand palm oil with the lowest IV. This indicates that those oils may contain almost recommended values of unsaturated fatty acids with respect of quality. SV of soybean oil and both palm oils are lower than the recommended values. This may indicate that those oils may contain low FFAs and/ or short chain fatty acids. The PV, AV and FFA are in the recommended values while IIM are slightly higher than the recommended values.

Most locally produced edible oils have chemical characteristics out of the standard values. The IV of niger seed and rape seed oils are higher than the recommended value. This may be due to the presence of high amount of unsaturated fatty acids than recommended values while IV of line seed oil is significantly lower than the recommended value which indicates the oils may contain unsaturated fatty acids less than the recommended values. The SV of niger seed, line seed and cotton seed oils are higher than the recommended value. This may be due to the presence of high FFA and average length of the fatty acid chain that makes up a fat than recommended value while SV of rape seed oil is lower than the recommended value. This may be due to low FFA and average length of the fatty acid chain that makes up a fat. Rape seed oils have higher PV value than the recommended value. This may be due to exposure of those oils to atmospheric oxygen, light and some impurities that may increase peroxidation of the unsaturated fatty acids in the oil. The AV, FFAs and IIM of all locally produced oils (except cotton seed oil with recommended values of AV and FFAs) are higher than the recommended values.

This indicates that those locally produced oils may contain high amount of FFAs, monoglycerides and diglycerides, may be due to the presence of some in organic metals, microorganisms and moisture that activate the enzyme lipase and consequently increase FFAs. Those oils were also with bad smell and not clear appearance during analysis which indicates the oils are rancid.

In general, physicochemical quality of most locally produced edible oils fail to accomplish the minimum requirements set by WHO and ESA for edible oils. This may be due to negligence of local oil producers and vendors in the local markets. Those oils are sold everywhere with less attention to light, container and atmospheric oxygen. Oils of cotton seed produced by 'Addis Mojjo' have relatively physicochemical characteristics very close to the recommended value than other locally produced edible oils. In contrast, most commonly imported edible oils have physicochemical characteristics, which is in the range of recommended value.

7. Limitations

Although this study covers some parameters that are very important to assess quality of edible oils, we couldn't analyze the quantity of some in organic metals that activate the enzyme lipase. Although TFA is an important issue globally, because of its risk to consumers, the study excluded investigation of it. This is mainly due to lack of appropriate instruments.

8. Recommendation

As the study clearly shows the physicochemical characteristics of locally produced edible oils fail to attain the minimum recommended standards. Although WHO and ESA set standards for edible oils, most edible oils sold in the local markets fail to fulfill the minimum requirements. So the ESA and Ethiopian Health Minister should take the responsibility and aware the local edible oil producers, retailers and consumers about the quality of edible oils and its consequence. So the following measurements are suggested to increase the quality of edible oils.

- ✓ Oil seeds used for production of edible oils should be collected when seeds are well matured.
- ✓ Producers and milers should improve their processing method and hygiene during edible oil production.
- ✓ Producers / and retailers should stop mixing of edible oils or adulterating.
- ✓ Retailers should take care during handling and transporting of the edible oils.
- ✓ As much as possible edible oils should be kept in clean, dry and non-corrosive well sealed bottles.
- ✓ In both locally produced and commonly imported edible oils, there should be clear specification about the saturated, unsaturated and TFA which the oil contains.
- ✓ Consumers also should take care of the edible oils they purchase from local markets and they have to do visual inspection and smell for the presence of rancid smell.

  Finally, it is better to use edible oils with early made long chain unsaturated fatty acids as they are source of essential fatty acids. As much as possible consumers should not use oils sold in the local markets exposed to atmospheric oxygen and light.

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Appendix

Laboratory procedures

1. Determination of physical parameters

1.1 Determination of Refractive Index (RI)

Definition: the ratio of velocity of light in vacuum to the velocity of light in the oil; more generally, it express the ratio between the sine of angle of incidence to the sine of angle of refraction when a ray of light of known wave length (usually 589 nm, the mean of D lines of sodium) passes from air in to the oil. RI varies with temperature and wavelength

Principle: Measurement of the RI of the samples was done by means of a suitable refractometer.

Apparatus: Refractometer

Calibration of the instrument: The instrument were calibrated with the a glass prism of known refractive index by using distilled water which has refractive index of 1.3330 at 20°c and 1.3306 at 40°c, the usual temperature of taking readings.

Procedure:

The temperature of refractometer was adjusted to 40°c (50°c was used for palm oils) using circulating hot water. Prisms were cleaned and dried. Few drops of the well mixed sample were placed on the prism. The prisms were closed and allowed standing for 1 minute. The instrument and lighting were adjust to obtain the most distinct reading possible and determined the RI.

1.2 Determination of Relative Viscosity (RV)

Definition: It is prime quality of edible oil and is measure the oil's resistant to flow (the more resistant or thick the oils, the higher its viscosity).

Principle: Relative viscosity of edible oil will be measured directly by using calibrating U-shaped viscometer under specific temperature.

Apparatus: U- shaped viscometer (kinematic viscometer), water bath and stopwatch.

Procedure:

Carbon dioxide from oil samples was removed by shaking gently at first and then vigorously. Temperature of the sample was kept at 30°c by using SETA KV-8 viscometer water bath. The suspending material in the oil was removed by passing the sample through a filter paper.

The appropriate volume of sample was added to the kinematic viscometer which was held in a water bath at 30°c. The suction was used to draw the sample above the upper mark of kinematic viscometer and then was allowed to fall down.

Then time was started with stopwatch as the sample was passing the upper mark of kinematic viscometer. Finally time was noted when the sample passes the lower mark of U-shaped viscometer. Each measurement was done two times and average time in second was recorded.

Calculation:

Relative Viscosity = CT

Where, T = time for flow of oil sample

C = Constant of the viscometer

1.3 Determination of Specific Gravity (SG)

Definition: It is the ratio of the density (mass of a unit volume) of a substance to the density (mass of the same unit volume) of a reference substance.

Principle: Measurement of the SG of the samples was done by means of a suitable hydrometer.

Apparatus: Hydrometer

Procedure:

The hydrometer were cleaned and dried. Appropriate amount of the well mixed sample were placed on suitable beaker. The hydrometer, which reads directly the specific gravity, were immersed and allowed standing for 2 minutes. Reading were taken and recorded carefully.

2. Determination of Chemical parameters

2.1 Determination of Iodine Value (IV)

Definition: Iodine value of oil is the number of grams of iodine absorbed by 100g of the oil, when determined by using Wij's solution.

Principle: The oil sample taken in carbon-tetrachloride is treated with a known excess of iodine monochloride solution in glacial acetic acid named as Wij's solution. The excess of iodine monochloride is treated with potassium iodide and the liberated iodine is estimated by titration with sodium thiosulphate solution.

Apparatus: 500 mL Erlenmeyer flask, pipettes, titration arrangement and weighing arrangenent

Reagents:

- Concentrated hydrochloric acid (analytical reagent)
- Chloroform solution
- Potassium iodide - 10% solution prepared fresh
- Starch solution
- Wijs solution
- Standard sodium thiosulphate solution - 0.1N

Procedure:

Approximately 0.25 g of the oil was measured into a 500 mL conical flask with glass stopper, to which 25 mL of carbon tetrachloride have been added. The content was mixed well. 25 mL of Wijs solution was pipette and added. The flask was stoppered to prevent loss of halogen by evaporation. The flask was gently swirled and stored in the dark for one hour. 20 mL of the potassium iodide solution and150 mL of water was added. The flask was shaken and the content was titrated with standardised sodium thiosulphate solution, using starch as indicator at the end until the blue colour formed disappears after through shaking with stopper on. Blank determination has been conducted in the same manner as test sample but without oil.

Calculation:

$$IV = (12.69(B – S)N) / W$$

Where, B = volume in mL of standard sodium thiosulphate solution required for the blank.

S = volume in mL of standard sodium thiosulphate solution required for the sample.

N = normality of the standard sodium thiosulphate solution

W = weight in g of the sample.

2.2 Determination of Acid Value and Free Fatty Acids content

Definition: the **acid value** is defined as the number of milligrams of potassium hydroxide / sodium hydroxide solution required to neutralize the FFA present in one gram of fat. It is a relative measure of rancidity as FFAs are normally formed during decomposition of oil glycerides. The value is mostly expressed as percent of FFAs calculated as oleic or palmitic acid acid.

Principle: The acid value and FFAs are determined by directly titrating the oil in an alcoholic medium against standard potassium hydroxide/sodium hydroxide solution.

Apparatus: 250 mL conical flasks, hot plate, titration arrangement and weighing arrangenent

Reagents:

- Ethanol (95 % v/v)
- Diethyl ether
- Phenolphthalein indicator solution
- Sodium hydroxide solution 0.1N.

Procedure:

The oil was mixed thoroughly before weighing. Approximately 5 g of cooled oil sample was weighted accurately in a 250 mL conical flasks and 150 mL of freshly prepared equal amount of diethyl ether and ethanol were added. About one mL of phenolphthalein indicator solution was added.

The mixture was boiled for about five minutes and was titrated while hot against standard alkali solution (sodium hydroxide) and shaked vigorously during the titration untill the end point.

Calculation:

FFAs as oleic acid percent by weight = 28.2VN / W

AV = percent fatty acid (as oleic) x 1.99

Where V = volune in mL of standard potassium hydroxide or sodium hydroxide used

N = normality of the potassium hydroxide solution or sodium hydroxide solution

W = weight in g of the sample

2.3 Determination of Peroxide Value (PV)

Definiation: Peroxide value is a very sensetive indicator of the early stages of oxidative deterioration of oils. PV therefore provides a means of predicting the risk of the development of flavor rancidity.

Principle: When a rancid oil sample is treated with potassium iodide after dissolving in an approprate solvent. Peroxides present in the oil liberate iodine. The test is a volumetric one where iodine formed from KI in the presence of peroxide is determined by titrating with sodium thiosulphate.

Apparatus: 250 mL flask, burette, pipette, weighing arrangement and measuring cylinder

Reagents:

- acetic acid - chloroform solvent
- saturated potassium iodide
- 0.01N sodium thiosulphate
- 0.5% starch indicator.

Procedure:

Approximately 2g of oil sample was measured accurately in 250 mL conical flask. 30 mL of solvent (acetic acid - chloroform mixture) was added and swirled to dissolve the sample. 1 mL of KI solution was added and the flask was allowed to stand for 1 minute with gentle shaking. 30 mL of distilled water and few drops of starch indicator were added. Appearance of blue colour on addition of starch indicates presence of free iodine. The liberated iodine was titrated with 0.01N sodium thiosulphate until the blue colour just vanished.

Calculation:

PV (meq/Kg) = N x Vx1000/ W

Where, N = normality of sodium thiosulphate

V = volume of sodium thiosulphate consumed by sample in mL.

W = weight of sample in gram.

2.4 Determination of Saponification Value (SV)

Definiation: Saponification value shall mean the number of milligrams of potassium hydroxide required for the saponification of one gram of the test portion.

Principle: When the oil is saponified with a slight excess of alcoholic KOH, the reaction results in potassium soaps, glycerol and unreacted KOH. The free KOH can be determined by titrating with 0.5N HCl using phenolphthalein as an indicator

Apparatus: 250 mL flask, burette, pipette, weighing arrangement and measuring cylinder, reflux condenser

Reagents:

- Hydrochloric acid (0.5N)
- Alcholic potassium hydroxide
- Phenolphthalein indicator.

Procedure:

A test portion of approximately 2g was measured accurately in 250 mL conical flask. Exactly 25 mL of ethanolic potassium hydroxide solution has been added by means of burette. The flask was connected with a condenser and refluxed for 1 hour. The soap solution was titrated with 0.5 N HCl in the presence of phenolphthalein while it was warm. A blank determination was carried out by refluxing and titrating under the same conditions.

Calculation:

SV = 56.1 (B – S)N / W

Where, N = normality of Hydrochloric acid

B = volume of Hydrochloric acid consumed by Blank in mL.

S = volume of Hydrochloric acid consumed by sample in mL.

W = weight of sample in gram.

2.5 Determination of Insoluble impurities (IIM)

Definiation: Insoluble impurities shall mean the dirt and other foreign matter, expressed as a percentage by mass, which are insoluble in n-hexane or light petroleum under the conditions specified. Such dirt or foreign matter includes mechanical impurities, miniral substances, carbohydrates, nitrogenous substances, various resins, calcium soaps, oxidized fatty acids, lactones, and in part alkali soaps, hydroxy-fatty acids and their glycerides.

Principle: The oil or fat shall be dissolved with an excess of n-hexane or light petroleum. The solution shall then be filtered and followed by washing the filtering system with the same solvent, drying at 103°c and weighing of the filtering system and dry residue.

Apparatus: Electric oven with temperature regulation, Analytical balance, glass vessel with a wellfitting cover, Conical flask, Desiccator

Reagent:

- N-hexane

Procedure:

Approximately 20g of prepared sample was measured accurately in 250 mL conical flask. The test portion was dissolved by adding 20 mL of n-hexane in to the flask and was shaken. The solution was left for about 30 minutes at 30°c. Then the solution was filtered through an ashless filter paper which was dried previously at 103°c and measured. The remaining residue on the filter paper was washed with the same solvent. The solvent remaining in it was allowed to evaporate in the open air and the evaporation was completed in the oven at 103°c. The filter paper with its vessel was removed from the oven and cooled in desiccator. The filter paper with its dried sample was measured. Two parallel determinations for each sample were carried out simultaneously to insure that the difference between the two samples was not exceeding 0.05g of insoluble impurities per 100g of sample.

Calculation:

IIM (percent by mass) = (M1 – M2) / Mo)X100

Where, Mo = weight of test portion

M1 = weight of filter paper containig dry residue.

M2 = weight of filter paper

This thesis is my original work and has not been presented for a degree in any other university, and that all sources of material used for the thesis have been duly acknowledged.

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