



UNIVERSITI PUTRA MALAYSIA

UTILISATION OF USED COOKING OIL FOR SOAP MAKING

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ABSTRACT

Today, plant cooking oil is one in all the foremost vital components in food production business likewise as food preparation reception. As a consequence, great deal of waste cooking oil was created particularly in developing countries. With decreasing renewable energy offer and increasing of waste, it is main interest to utilize the waste cooking oil by changing it into usable and helpful product that is soap. Somehow, the source of the waste oil may be varies and the quality of oil can be decreases within the consumption itself. To investigate the quality of the oil, all the important parameters values are determined and the averages were taken into consideration. The parameters are color purity, viscosity, peroxide value (PV), iodine value (IV), acid value (AV), free fatty acid (FFA) and saponification value (SAP). Thirty different oils were collected and selected. Laboratory analyses were conducted on the used palm cooking oil samples collected from different sources of kitchen cooking. The result showed that the mean saponification value (SAP) of oils are 100% did not meet the Asian and Pacific Coconut Community (UN Economic and Social Commission for Asia and the Pacific) (APCC) standards since 142.0 is the standard value while range between 20.0 and 52.0 are the obtained value, however, 25% were within the stipulated limits recommended by Codex Alimentarius Commission (Codex) the governmental community standard. The mean iodine value (IV), acid value (AV), free fatty acid (FFA) and peroxide value (PV) of the oils constituting 75% fell within the APCC while 25% did not. For the mean of iodine value obtained from the experiment is between 7.0 to 36.0 while the peroxide are lies in the range of 4.0 to 16.0. Then, for the acid value calculated from the test carried out are 1.8 to 6.2 where as the free fatty acid value are estimated half of the acid value based on the theoretical approaches. The results imply that in general, the quality of used palm cooking oil in terms of the parameters considered fell short of both the Codex and APCC standards. Therefore, further improved processes are required to enhance the quality of oils produced to meet the required standards and to produce safe soap product that are able to be used as a detergent for daily life.

ABSTRAK

Hari ini, minyak masak adalah salah satu komponen penting dalam perniagaan pengeluaran makanan dan juga sebagai penyediaan makanan. Akibatnya, banyak minyak masak sisa dicipta terutamanya di negara-negara membangun. Dengan penurunan tenaga boleh diperbaharui dan peningkatan sisa, minat utama untuk menggunakan minyak masak sisa dengan mengubahnya menjadi produk berguna dan bermanfaat yang sabun. Entah bagaimana, sumber minyak sisa mungkin berbeza-beza dan kualiti minyak dapat berkurang dalam penggunaannya sendiri. Untuk mengkaji kualiti minyak, semua nilai parameter penting ditentukan dan purata diambil kira. Parameter-parameter ini adalah ketulenan warna, kelikatan, nilai peroksida (PV), nilai iodin (IV), nilai asid (AV), asid lemak bebas (FFA) dan nilai saponifikasi (SAP). Tiga puluh minyak yang berbeza dikumpulkan dan dipilih. Analisis makmal telah dijalankan ke atas sampel minyak goreng sawit yang digunakan dari pelbagai sumber memasak dapur. Keputusan menunjukkan bahawa nilai saponifikasi min (SAP) minyak adalah 100% tidak memenuhi piawaian Masyarakat Kelapa Pasifik Asia dan Pasifik (Suruhanjaya Ekonomi dan Sosial PBB untuk Asia dan Pasifik) (APCC) sejak 142.0 adalah nilai piawai manakala jarak antara 20.0 dan 52.0 adalah nilai yang diperolehi, tetapi 25% berada dalam had yang ditetapkan oleh Suruhanjaya Codex Alimentarius (Codex) standard komuniti kerajaan. Nilai iodin (IV), nilai asid (AV), asid lemak bebas (FFA) dan nilai peroksida (PV) minyak yang merangkumi 75% jatuh dalam APCC manakala 25% tidak. Untuk nilai purata iodin yang diperolehi daripada eksperimen ialah antara 7.0 hingga 36.0 manakala peroksida terletak dalam lingkungan 4.0 hingga 16.0. Kemudian, bagi nilai asid yang dikira dari ujian yang dijalankan adalah 1.8 hingga 6.2 di mana nilai asid lemak bebas dianggap separuh daripada nilai asid berdasarkan pendekatan teori. Hasilnya membayangkan bahawa secara umum, kualiti minyak goreng sawit yang digunakan dari segi parameter yang dianggap kurang dari kedua-dua piawaian Codex dan APCC. Oleh itu, proses lebih baik diperlukan untuk meningkatkan kualiti minyak yang dihasilkan untuk memenuhi piawaian yang diperlukan dan menghasilkan produk sabun yang selamat yang boleh digunakan sebagai detergen untuk kehidupan seharian.

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CHAPTER 1

INTRODUCTION

1.1 Background

Fats and oils are naturally occurring esters used as energy-storing compounds by plants and animals. They are derived from propane 1,2,3-triol, $\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$ (commonly known as glycerol or glycerine). This molecule has the capacity to combine with one, two or three molecules of carboxylic acid. In practice, most fats are triesters derived from propane 1,2,3,-triol and a variety of long-chain carboxylic acids, sometimes called fatty acids.

Oils are fats that are liquid at room temperature, like the vegetable oils used in cooking. Oils come from many different plants and from fish. Oils are not a food group, but they provide essential nutrients. Therefore, oils are included in United States Department of Agriculture (USDA) food patterns. Some commonly eaten oils include: canola oil, corn oil, cottonseed oil, olive oil, safflower oil, soybean oil, and sunflower oil. Some oils are used mainly as flavorings, such as walnut oil and sesame oil. A number of foods are naturally high in oils, like nuts, olives, some fish, and avocados. Foods that are mainly oil include mayonnaise, certain salad dressings, and soft (tub or squeeze) margarine with no trans fats. Most oils are high in monounsaturated or polyunsaturated fats, and low in saturated fats.

Oils from plant sources (vegetable and nut oils) do not contain any cholesterol. In fact, no plant foods contain cholesterol. A few plant oils, however, including coconut oil, palm oil, and palm kernel oil, are high in saturated fats and for nutritional purposes should be considered to be solid fats. Solid fats are fats that are solid at room temperature, like butter and shortening. Solid fats come from many animal foods and can be made from vegetable oils through a process called hydrogenation. Some common fats are: butter, milk fat, beef fat (tallow, suet), chicken fat, pork fat (lard), stick margarine, shortening, and partially hydrogenated oil.

All fats and oils are a mixture of saturated fatty acids and unsaturated fatty acids. Unsaturated fatty acids include monounsaturated and polyunsaturated fats. Oils are fats that are liquid at room temperature, like the vegetable oils used in cooking. Oils come from many different plants and from fish. Oils contain more monounsaturated and polyunsaturated fats. Solid fats are fats that are solid at room temperature, like beef fat, butter, and shortening. Solid fats mainly come from animal foods and can also be made from vegetable oils through a process called hydrogenation. Solid fats contain more saturated fats and or trans fats than oils. Saturated fats and trans fats tend to raise “bad” or Low-density lipoprotein (LDL) cholesterol levels in the blood, which in turn increases the risk for heart disease. To lower risk for heart disease, cut back on foods containing saturated fats and trans fats.

Oils and fats are important parts of human diet and more than 90 percent of the world production from vegetable, animal and marine sources are used as food or as an ingredient in food products. Oils and fats are a rich source of dietary energy and contain more than twice the caloric value of the equivalent amount of sugar.

Their functional and textural characteristics contribute to the flavor and palatability of natural and prepared foods. They contain certain fatty acids which play an important role in nutrition and are also carriers of fat-soluble vitamins. Standards for 24 vegetable oils are prescribed in Section 2.2 of Food Safety and Standards (Food Product Standards and Food Additives) Regulations, 2011.

Deep-fat frying is one of the most common processes in the preparation and manufacture of foods. The aim of deep-fat frying is to seal the food by immersing it in hot oil so that all the flavors and juices are retained within the crispy crust. The quality of the products cooked using this method depends not only on the frying conditions, such as the temperature of the heated oil, frying time, food weight, and frying oil volume, but also on the types of oil and the kinds of foods used (Varela, 1994). During deep-fat frying, the fat is continuously being exposed to elevated temperatures (150-180°C) in the presence of the substrates air and water. A complex series of reactions such as hydrolysis, oxidation, polymerization, isomerization, and cyclization takes place during the deep-fat frying. These reactions result in the formation of volatile and nonvolatile compounds affecting the sensory, functional, and nutritional qualities of the frying oil.

In general, deep-fat frying decreases the content of unsaturated fatty acids in frying fat and oil. Researchers (Tynek et al, 2001; Cuesta et al, 1991) have found a relative loss of the C18:2 fatty acid and a decrease in the iodine value of oil after heating due to more intensive thermo-oxidative transformations that occur compared to heated oil containing food. The decrease in the iodine value can be attributed to the destruction of double bonds by oxidation, scission, and polymerization. According to previous studies (Orthofer et al, 1996; Tyagi and Vasishtha, 1996;

Choe and Min, 2007), the heat treatment causes the oxidative rancidity resulting in an increase in the free fatty acids. This is why heated and unheated fats and oils should be monitored by means of analysis, e.g., the free fatty acid content (FAC) and iodine value (IV) indicating the degradation of the fatty acid (FAs). Usually many oils can be used for frying, e.g., palm oil, corn oil, cotton oil, soya oil, canola oil, sesame oil, and sunflower oil (Valenzuela et al, 2003). Several different oils are usually blended to get a healthy oil mixture. Therefore, the formulation should be low in its content of linoleic and linolenic acids, whereas it should contain a high level of natural antioxidants to be stable in the heating process.

Cooking oil of plant and animal origin or synthetic fat is used in frying, baking, and other types of cooking. It is also used in food preparation and flavoring not involving heat, such as salad dressings and bread dips, also termed edible oil. Cooking oils are liquid, although some oils that contain a high amount of saturated fat, such as coconut oil, palm oil and palm kernel oil, are solid at room temperature. Cooking oils are derived from animal fat, as butter, lard and other types, or plant oils from the olive, maize, sunflower and many other species. Different types of cooking oil include: olive oil, soybean oil, palm oil, canola oil (rapeseed oil), corn oil, pumpkin seed oil, sunflower oil, safflower oil, peanut oil, grape seed oil, sesame oil, rice bran oil and other vegetable oils, as well as animal-based oils like butter and lard. Oil can be flavored with aromatic foodstuffs such as herbs, chilies or garlic. Different oils such as palm oil are known to support the growth of fungi and bacteria especially when it contains moisture. Under unfavorable conditions lipolytic enzymes of oils are active and produce free fatty acid (FFA) content of less than 2%. Different microorganisms such as *Aspergillus niger* and *Mucor* sp. survive in oil by producing the lipase (Adams and Moss, 1999).

The ability of fungi to produce spores makes them survive in anaerobic conditions of the oil because their spores are resistant to heat. The fungi *Aspergillus flavus* is important because of its ability to produce aflatoxin, which sometimes induce toxic syndromes especially cancer. The presence of bacteria such as *Enterobacter* has also been found and pathogenic *Bacillus* sp. microorganisms which can cause food poisoning, bacteremia and endocarditis (Okechalu et al, 2011).

In the present study, physical and chemical parameters were used as an indicator for assessment of quality of thermally oxidized oil samples. The most common change in the oil or fat during use is the darkening. Food compounds (as carbohydrates, phosphates, sulfur compounds, and trace metals) react with the oil or their breakdown products, which contributes to the formation of color. Vegetable oils are a popular cooking medium in many parts of the world. Despite problems related with the intake of excessive calories and health concerns regarding the ingestion of trans-fatty acids, the flavor and texture of fried food continue to be greatly appreciated.

1.2 Used Cooking Oil From Palm Oil

Plant cooking oil is extraction product that can get from plants normally in vegetables, flowers, fruits and also from palm and coconut tree. Malaysia is one of the countries that produce and process their own oil for use of domestic, industry and processing. Natural oil and gases that are gained from the bottom of the sea like the one that is in Terengganu state are normally processed to become petroleum or fuel for automobile transportation. In this case study, we are about to study only plant oil that is specified in the palm oil that is used for cooking oil at home and processing industry.

Palm oil is an oil that comes from palm tree fruit. It is normally reddish in color, due to the high amount of carotenoids. It is sometimes boiled and strained, leaving an ivory to tan color in the oil. Palm kernel oil is different in that it is more solid and has higher amounts of wax. Coconut oil, also related, comes from the coconut palm, not the oil palm. With fats and oils, the object might be to “clear” incoming lots or test a frying oil to determine whether it is still acceptable for frying, i.e., whether it will produce good food. They might also be (and are) used for regulatory screening and could even be used to assure product safety. For example, it is possible that the use of degraded oil could adversely affect heat transfer. If a product being cooked needed to reach a certain temperature to assure that salmonellae or other pathogens were killed, the use of badly abused oil could be a potential safety hazard (Stier,2004).

Lipids in edible oils are susceptible to photo-oxidation and auto-oxidation during processing and storage, which is a major problem for the oil industry (Choe and Min, 2006). Oxidation may cause undesirable flavors and taste, decomposing the

nutritional quality, and leading to production of toxic compounds. Oxidation of oils may be influenced by different factors such as the degree of unsaturation, heat, light, oil processing, antioxidants and transition metals. Another important issue is the reusing of fried oils. This practice is not only restricted to roadside food stalls, and reputable food outlets in large cities also use this technique to lower their costs. The repeated heating of cooking oil result in oil that is more prone to lipid peroxidation (Jaarin et al, 2011).

Furthermore repeated frying of oils darken the oil at different rates, and the oil is discarded only when the oil becomes foamy or smelly (Azman et al, 2012). The waste edible oil is usually collected from the oil drainage of hotels and restaurants. The oil obtained after heat dehydration, slag-removing, neutralization and precipitation is called "hogwash oil," which is non-edible oil with brown color, special smell, and many harmful ingredients. In recent years, some people have illegally used hogwash oil directly or mixed it with cooking oil to fry food, therefore causing great damage in public health. To recycle hogwash oil will not only avoid a waste of valuable resource, but also potentially avoid secondary pollution.

Palm oil is chosen because it is one of Nature's richest sources of Vitamin E to cotrienols and pro-Vitamin A carotenoids. It is cholesterol-free. Studies have shown that palm olein (liquid portion of palm oil) and olive oil have similar beneficial effects on plasma cholesterol levels. Additionally, animal and cell-culture studies have found that palm tocotrienols inhibit the growth of certain types of cancer. Stable at high temperatures, palm olein is the ideal choice for household and industrial frying as it is less prone to oxidation. Palm oil is also odorless and neutral in flavor, thus preserving the natural taste of food. Unlike other vegetable oils, palm

oil is naturally semi-solid at room temperature; it does not require hydrogenation and is, therefore, free of trans fats. Palm oil is one of the 17 edible oils cited by the Food and Agriculture Organisation (FAO) / World Health Organisation (WHO) Food Standard under the CODEX Alimentarius Commission Programme (Codex).

Palm oil, like olive oil, is a fruit oil. It is the only vegetable oil that contains an equal proportion of unsaturated and saturated fatty acids. It is particularly rich in saturated palmitic acid (44%), and monounsaturated oleic acid (40%). Palm oil is also naturally very stable because of its low content of polyunsaturated fatty acids (10%), in addition to its Vitamin E content. With a balanced composition (50% saturated and 50% unsaturated), palm oil is perfect for cooking, even frying, as it is very heat-resistant. It doesn't break down or mutate when used for frying. It is also naturally trans-fat free and cholesterol free. A truly accurate article would have established palm oil as one of the best alternatives to corn or sunflower oil for cooking. Palm oil's excellent heat resistance and balanced composition make it one of the healthier options available (Pelouze,2015).

Palm oil is a common cooking ingredients and originate in western Africa, it has spread to most part of the tropical and subtropical zones of the, but particularly to Malaysia and Indonesia (Brien, 2009). During the frying process, oil will experience degradation reactions caused by heat, air, and water, resulting in oxidation, hydrolysis and polymerization. Degradation reaction products contained in this oil will reduce the quality of the oil and cause adverse effects for humans (Bhattacharya et al. 2008). Recycling used cooking oil using adsorbents, such as silica gel, magnesium oxide, aluminium hydroxide gel and activated clay, has been studied (Lin and Reynolds, 1998; Miyagi and Nakajima, 2003) for improving the quality

parameter of used cooking oil. The indicators of poor oil quality include elevated Free Fatty Acids (FFA), change of color, low smoke point, low iodine value, total polar material, peroxide value, high foaming properties and increased viscosity (Kheang et al. 2006).

Some of the most environmentally friendly biodiesel feedstocks are used cooking oil and waste grease. According to the EPA's Renewable Fuel Standards Program Regulatory Impact Analysis, released in February 2010, biodiesel produced from waste grease results in an 86% reduction in greenhouse gases, compared to petrodiesel. There are two general categories of waste oil and grease. The cleanest and easiest to work with is used cooking oil, also called waste vegetable oil or used fryer oil. This is edible oil that has been used multiple times in a deep-fat fryer. The second type is called "trap grease". Restaurants are required to install grease traps in their drains to prevent fats and oils that go down the drain from entering sewer pipes. The grease in these traps can be collected to make biodiesel. Making of soap by using the waste cooking palm oil based because the oil has high percentage of free fatty acids. Despite the lower glycerin levels, palm oil soap making is still appealing because of the nice creamy/stable lather it produces and the hardness it adds to the soap. Palm oil is a shelf stable semi-solid oil that provides a good source of steric acid, one of those oils that helps contribute to the hardness of a bar of soap.

1.3 Soap Making From Waste Cooking Oil

The main challenge to biodiesel production from used oils and greases is the high percentage of free fatty acids (FFA) in the feedstock. Fats and oils are composed of triglycerides – three fatty acid molecules attached to a glycerol molecule. In used oils and greases, some of the triglycerides have broken down so that the fatty acids are separated from the glycerol molecule. These are called free fatty acids. These free fatty acids tend to react with the alkali catalyst in biodiesel production to form soap instead of biodiesel. This reduces the level of free catalyst and thus reduces the speed of the transesterification reaction. Soap formation tends to inhibit the separation of the ester from the glycerin and slow down the reaction. In addition, because the soap must be removed and discarded, more soap formation means less biodiesel.

Frying at high temperatures easily oxidizes cooking oil and this is harmful to health. It is important to use a stable cooking oil as at least three changes can happen to the oil at high frying temperature of 140°C or more because of those cases which are the fatty acids of the oil split up to form 'breakdown' products, attacks by air and moisture form oxidised products and non-volatiles (called polar materials) are formed and accumulated in the frying medium. The oil oxidizes and forms polymers that cause the kitchen walls to be sticky. Additionally, the non-volatiles spoil the quality and taste of the fried food and pose health risks in the long term.

A stable cooking oil such as palm olein prevents the above from occurring; thus the undesirable effects of high-temperature frying. Palm olein is stable and its use for frying will not lead to excessive smoking, spattering, and foaming. It leaves less gummy residue in the pan after cooking. It has a balanced fatty acid composition

(it has a moderate amount of linoleic acid and a small amount of linolenic acid – the two polyunsaturated fatty acids that may be polymerized easily) and a high content of Vitamin E, which is a natural antioxidant. In order to compete with palm olein as a stable frying oil, many other vegetable oils have to be partially hydrogenated. However, this process is not desirable as it leads to the formation of harmful trans fats in the oils.

1.4 Saponification Mechanism

Saponification is a process by which triglycerides are reacted with sodium or potassium hydroxide (lye) to produce glycerol and a fatty acid salt, called 'soap'. The triglycerides are most often animal fats or vegetable oils. When sodium hydroxide is used, a hard soap is produced. Using potassium hydroxide results in a soft soap. Lipids that contain fatty acid ester linkages can undergo hydrolysis. This reaction is catalyzed by a strong acid or base. Saponification is the alkaline hydrolysis of the fatty acid esters. The mechanism of saponification is:

1. Nucleophilic attack by the hydroxide
2. Leaving group removal
3. Deprotonation

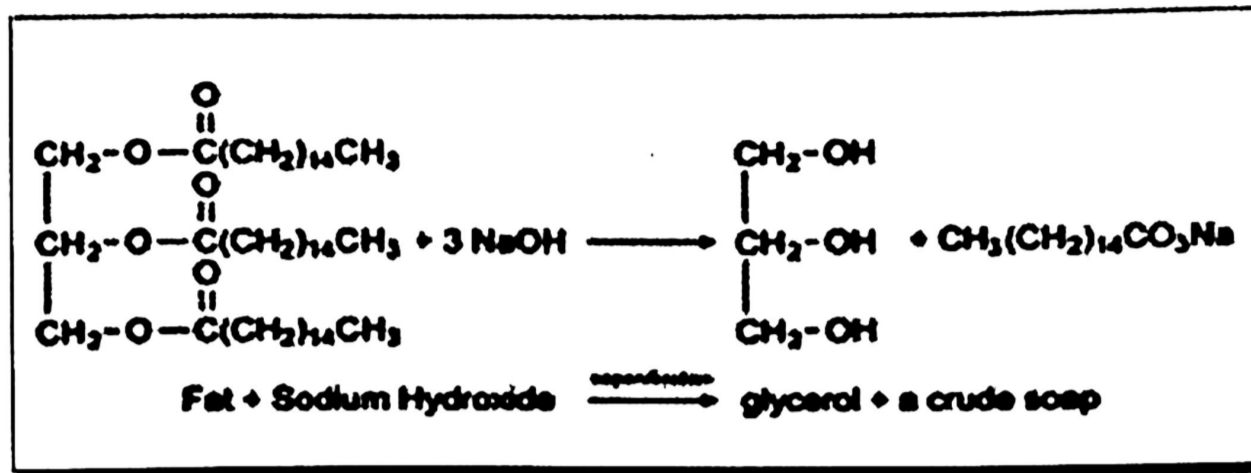
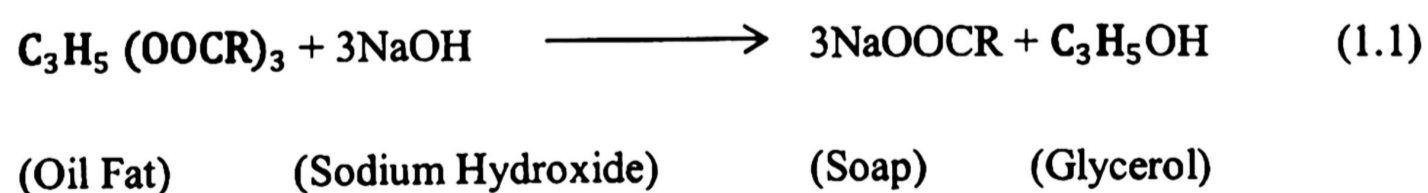


Figure 1.1 Saponification mechanism process (Brien, 2009)

While most often the one-step triglyceride reaction with lye is considered, there is also a two-step saponification reaction. In the two-step reaction, steam hydrolysis of the triglyceride yields carboxylic acid (rather than its salt) and glycerol. In the second step of the process, alkali neutralizes the fatty acid to produce soap. The two-step process is slower, but the advantage of the process is that it allows for purification of the fatty acids and thus a higher quality soap.

Lubricating grease is produced by dispersing thickening agents in mineral or synthetic oil. Several thickening agents exist but soap-base is the most popular. Several soap bases like sodium, lithium, calcium, aluminum etc. are used in lubricating grease production. Soap comprises of the metallic salts of long chain monocarboxylic acids. Generally, soap making is based on alkaline hydrolysis of fat and oil in a reaction known as saponification, according to the equations below



To produce Sodium Soap Grease, it is fibrous in structure and is resistant to moderately high temperature but not to water. In applications where high temperatures, dynamic stress, or centrifugal effects are significant, sodium-base greases are more efficient than calcium-base greases. However, they are emulsified by water.

Saponification may result in both desirable and undesirable effects. Wet chemical fire extinguishers use saponification to convert burning oils and fats into non-combustible soap. The chemical reaction further inhibits the fire because it is endothermic, absorbing heat from the surroundings and lowering the temperature of the flames.

While sodium hydroxide hard soap and potassium hydroxide soft soap are used for everyday cleaning, there are soaps made using other metal hydroxides. Lithium soaps are used as lubricating greases. There are also "complex soaps" consisting of a mixture of metallic soaps. An example is a lithium and calcium soap.

1.5 Problem Statement

Cooking oil is one of the ingredients that people in industrial and home living using almost every day to preparing their food. The usage of cooking is considered as crucial thing especially to the food that needs a deep frying method of cooking. Other than using it for deep-frying cooking, oil are usually being used to produce a food that can need the oil to mix with the food to change their shape, taste, texture and etc. Unfortunately, the left over cooking oil that is no longer to be used in cooking and being throw away as a waste product. People normally throwing out the used cooking oil in the sink at their home kitchen that flowing in the water piping system, but it is actually may cause blockage inside the pipe and will seriously lead to pipe bursting. Rather than that, it also can pollute the water sources as the waste of cooking oil are already used by mixed with other chemicals or dangerous food materials. Hence, there are some people smartly turning the waste cooking oil into home-made soap but the oil quality in making soap is not properly controlled and determined scientifically. In our urbanization era, researchers are about to come out with a new product that are environment friendly and only use a low cost of production so that low class of people are able to buy the soap affordably. Practically, there are problems like long period of reaction time of saponification, incomplete saponification or no saponification at all during the production process. Other than that, the shelf life made soap cannot be scientifically figured out. Because of this case, an issue that related to the lack of confidence to use the soap product made from the recycle method comes out. Rather than that, the relationship between fatty acid content inside of each oil sample between their particular acid value, iodine, peroxide and saponification value also need be study and proved to accomplish the study of effect on the made soap from the used cooking oil.

1.6 Research Objectives

There are three main objectives of this project study which are :

1. To measure the quality of used cooking oil.
2. To use the oils for saponification process to home-made soap.
3. To investigate the effect of the determined values for the oil samples with the characteristic of soap produced.

1.7 Scope Of Study

This study topic will be focused on the utilization of used cooking oil from palm oil that is normally in frying cooking method industrially and even domestically. In this project, the utilization of oil is focusing on producing soap through saponification process done in the lab. In order to do the saponification process, the quality of used cooking oil must firstly determine in terms of its viscosity, free fatty acid value, acid value, iodine value, peroxide value and lastly saponification value. The determination of these values is obtained from the titration experiment using some chemicals such as sodium hydroxide, sodium thiosulphate solution, Wij's solution, phenolphthalein indicator solution and some more. The mixture will be heated up to certain temperature for each procedure until the solution turns to the desired condition to show its active reaction. While after doing the saponification process, there are some parameters that are controlled such as output weight, pH value, smell odour and color parameter based on spectrophotometer light ray.

CHAPTER 2

LITERATURE REVIEW

The general information on the input used oil characteristics and mechanism that are happened during the reaction process. Besides, the basic concept for the oil quality analysis methodology are also being reviewed to give the affirmation on the steps selected. Finally, the studies between the determined values for the oil quality determination with the saponification mechanism using the used oil samples are being reviewed in this part.

2.1 Waste Frying Oil

In industrial frying, quality staff may monitor one or more chemical indices or markers during the frying operation in an effort to maintain optimum product quality. These values are usually determined during the product development process and generally include sensory testing. Shelf life can only be determined by testing. There are programs that allow estimations of shelf life, but the test panel is the true arbiter. Product characteristics are defined upfront by marketing, but Research and Development (R&D) must determine the processing parameters that allow the production of foods that meet those standards (Stier,2014). He had proved in his article which is 'There is a direct relationship between the quality of the food being produced and the oil in which it is being fried. As oil degrades, the quality of the food being cooked in this oil changes.

Cooking oil that has been used for cooking foods have become very murky, dark colored and has the smell terrible. Cooking oil that has been used for frying will experience color change, turbidity, and odor, which means reduce of quality (Brien, 2009). There are numerous vegetable oils derived from various plants such as soybean, cottonseed, peanuts, sunflower, palm, palm kernel, coconut seed, castor seed and rapeseed oil. These oils can be further classified as edible and non- edible; edible oils are mostly used in cooking. Over the years, vegetable oils have been used in various methods of cooking. They are used in deep -frying, baking food processing etc. Deep frying involves submerging the food in hot, liquid fat at a high temperature of 1500C-1900C . It is primarily a dehydration process, which means that water and water-soluble substances are extracted from the product being deep fried and transferred to the cooking fat.

In this method of cooking, water, oxygen and heat are the main factors, which determine the kinetics of oxidation and polymerization processes. As deep fat frying is normally carried out at high temperatures (between 1500C and 1900C) and in the presence of air and moisture, these frying oils and fats will undergo physical and chemical deterioration which will affect their frying performance and the storage stability of the fried products. During deep-frying, the fat and oil decompose forming volatile, non-volatile, monomeric and polymeric, oxidised or non-oxidised compounds . These products are formed as a result of oxidation of unsaturated fatty acids. The intensity of these reactions depends on duration, method of heat treatment, frying medium and type of product . Foods commonly prepared by deep frying in Kenya include fish, chicken, French fries, mandazi and sausages. After deep frying, many people are tempted to keep the oil to be reused for long periods of time. This causes adverse effects on flavour, stability, colour and texture of fried product and

may be harmful to human health. There is convincing evidence that replacing dietary saturated fats with polyunsaturated fats (PUFA) decreases risk of cardiovascular diseases. Therefore, PUFA rich foods such as vegetable oils, fatty fish, and marine omega-3 supplements are recommended. However, PUFA are easily oxidizable when heated and there is concern about possible negative health effects from intake of oxidized lipids. Little is known about the degree of lipid oxidation in such products (Chebet et al, 2016).

These scientists claimed that frying oils are monitored by measuring properties such as: acid value, peroxide value, anisidine value, conjugated diene, total polar materials (TPM), and polymeric triglycerides (PTG). The oil should be replaced when these parameters are above specification. It has been recommended that TPM should not exceed 24% and PTG should not exceed 12%. In most European countries, frying oil should be discarded when TPM and PTG together exceed 24–27% (Gertz, 2006). It would be better if these standards could be made more uniform. These measurements require laboratory procedures and a number of simple instrumental methods suitable for use in a food-processing factory have also been examined. It must be remembered that oxidative deterioration starting during food processing can continue during storage even at -5 to $+10$ °C.

The level of polar compounds is determined through elution of non-polar material from a silica column using toluene and polymeric triacylglycerols are measured by high-performance liquid chromatography (HPLC) of the frying oil in tetrahydrofuran solution using a refractive index detector. These procedures require a laboratory and other simpler robust procedures that can be used in the kitchen have been developed. Stier (2004) has reviewed tests available to monitor deep-frying fats

and oils. The pH drops towards acid values approaching the isoelectric point of myofibrillar proteins that tend to coagulate and some water is released (Toldrá, 2007). As a consequence of changes occurring during frying triacylglycerols containing octanoic and other short chain acids are produced. These can be identified and measured by gas chromatography (GC) after methanolysis and it is suggested that this becomes the basis of a method of detecting the onset of rancidity at an early stage (Bruhl et al, 2008; Velaso et al, 2004). The pH of the solution in the flask varies with added sodium hydroxide (NaOH). The pH changes quite slowly at the start of the mixing, and almost all the increase in pH takes place in the immediate vicinity of the endpoint. The pH change during this titration is caused by the proton-transfer reaction (Cao et al, 2008).

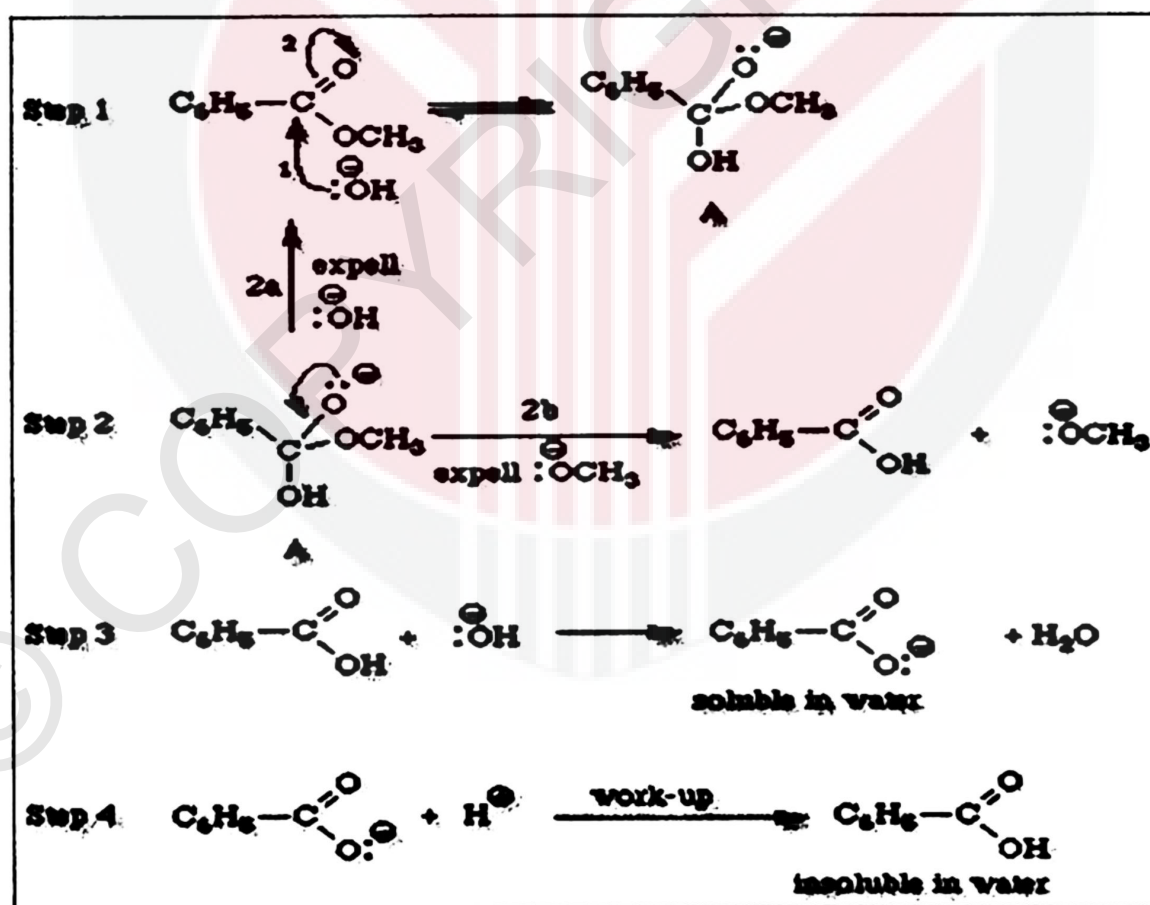


Figure 2.1 : The mechanism of how pH of oil are changed during saponification (Cao et al,2008).

2.2 Free Fatty Acid Value

Stier summarized the different tests used for fats and oils in a recent textbook. The most common chemical test conducted by fryer operators is for free fatty acids. This is due to tradition and because it is an easy test to perform. Unfortunately, many have not taken the time to establish whether there is a real relationship between oil and food quality. Free fatty acid values that are used as endpoint indicators vary with the product being produced. Snack food manufacturers are more conservative than those producing breaded products or french fries. The value of some of these analyses with frying fats is debatable, and care must be taken in both their use and in the analysis of the results.

Mater (2015) concluded in his paper that the FFAs can prevent the production process by deactivation of the catalyst, soap formation (the reason is that the alkaline catalysts react with the free fatty acids to form soap during the transesterification reaction) and also the separation between the glycerol and biodiesel. A two-step process is developed to convert the high FFAs content in the acids oils into esters. Therefore, a pretreatment step of waste frying oil is necessary to remove free fatty acids before proceeding with the alkali transesterification step. In naturally occurring fats each molecule is derived from two or three different fatty acids. Table 2.1 gives some common fatty acids: fifty or so are found in nature, the vast majority having an even number of carbon atoms in their molecule (Hill and Holman, 1979).

Table 2.1: Some Common Fatty Acids (Hill and Holman, 1979).

Structure	Systematic name	Common name	Occurrence
$\text{CH}_2(\text{CH}_2)_{16}\text{COOH}$	Octadecanoic acid	Stearic acid	Mainly in animal fats
$\text{CH}_2(\text{CH}_2)_{10}\text{COOH}$	Dodecanoic acid	Lauric acid	Coconut oil, palmkernoloic
$\text{CH}_2(\text{CH}_2)_{14}\text{COOH}$	Hexadecanoic acid	Palmitic acid	Most fats especially palm oil
$\text{CH}_2(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Octadec-9-enoic acid	Oleic acid	Most fats especially olive ore

(Journal of Food and Drug Analysis, 2013) had claimed that palm olein mainly consists of saturated fatty acids and monounsaturated fatty acids, and thus more stable. The polar compounds were derived from oxidation and the thermal reaction of oil during frying. Due to the high free fatty acids content in waste frying oil (16.415%), the transesterification reaction of this oil can risk the soap formation in the presence of potassium hydroxide. To avoid the saponification reaction, the pretreatment of this oil by the esterification reaction with sulfuric acid in the presence of methanol was required to reduce the free fatty acids (FFA) to the limit necessary to achieve the transesterification reaction (Mater,2015).

The physicochemical properties of used waste frying oils vary from those of refined and crude oils. During frying, the chemical composition of the vegetable oils change, as well as the physical and organoleptic properties. This is due to degradation of free fatty acids (monounsaturated and polyunsaturated).

At high temperatures the free fatty acids are very sensitive, they undergo chemical transformations such as:- oxidation reaction, polymerization and hydrolysis. Heat and water accelerate the hydrolysis of triglycerides and enhance the content of FFA in the oil. In addition, the viscosity of the oil increases due to the formation of dimeric and polymeric acids and glycerides in used frying oils (Ridha and Snoussi, 2015).

2.3 Oil Clarity

Oil viscosity is typically measured and defined in two ways, either based on its absolute viscosity or its kinematic viscosity. The absolute viscosity of oil is its resistance to flow and shear due to internal friction and it is measured with SI units of Pa·s. In contrast, the kinematic viscosity of oil is its resistance to flow and shear due to gravity and it is measured with SI units of m²/s. The kinematic viscosity of oil can be obtained by dividing the oil absolute viscosity with its corresponding density. It has been well established that temperature has a strong influence on the viscosity of fluids with viscosity generally decreasing with increase in temperature. The Arrhenius model is commonly used to describe the relationship of the temperature dependence on vegetable oil viscosity (Diamante and Lan, 2014).

Oil clarity is another “quick test” used. Some operators feel that as oils become darker and less clear, it is no longer fit for use. An oil clarity test, called the visibility tester, is used by Kentucky Fried Chicken (KFC). KFC stores use a stainless steel rod attached to a shiny silver disk or plate. The rod has a scale showing three indented marks that are used to judge shortening quality. The shiny disk is

lowered into the oil with the depth of insertion monitored on the rod. A penlight is held next to the rod, turned on, and the disk is observed. If the disk is invisible at or above a certain depth the oil is discarded . The unit basically measures oil color or clarity (Stier, 2014).

He then continue with to explain about an instrument that was designed to measure viscosity of used frying oils based on the formation of “polymerized and oxidized matter” or POM. The inventors selected viscosity as the parameter to measure because they felt that the formation of degradation products during frying would result in an increase in this particular index. These researchers determined that oil in excess of 15% POM was unfit for human consumption.

It is worth noting that increases in polymers result in the increase in the viscosity of the oil, thus suggesting that the determination of viscosity can be considered as a suitable rapid test for monitoring oil quality. Many other standard methods that have been used to monitor changes in the frying medium include conjugated dienes, measuring absorbance at 232 and 268 nm using ultraviolet UV absorption spectrophotometer. As the frying time increases the dienes level plateau, probably the rate of formation of dienes and their conversion into polymers reach equilibrium. Fatty acid analysis and C18:2/C16:0 ratio is determined by capillary column gas–liquid chromatography (Kochhar, 2016).

Kochhar then continued to explain that there are actually much attention has been given to the polar compounds or materials (determined by IUPAC standard method 2.507). Total polar materials (TPM) include free fatty acids, mono- and diacylglycerols, monomers, dimers, polymers, oxidized fatty acids, soaps, browning reaction products, and so on. TPM can increase from less than a 5% level in freshly

refined frying oils to greater than 25% during a food-service frying operation. As most of the earlier methods are somewhat time-consuming, so a number of commercially available quick tests have become available to monitor oil quality during frying operations. Moreover, quality control in the production of fried food also demands a simple test that uses no chemicals, is easy to use and cost-effective, and correlates to official methods such as total polar material (TPM).

2.4 Soap Making Process

Oil is fatty acid esters formed by reacting fatty acids with glycerol. The hydrolysis of esters under alkali condition is called saponification. Saponification reaction is not reversible. Excess alkali could help completely hydrolyze the oil to glycerol and fatty acid salt. The saponification of glycerol ester could produce glycerol and detergent such as sodium, potassium soap, etc. Therefore, the saponification of waste edible oil could be directly to produce soap and washing powder (Deng, 2009).

Although at present, palm oil and palm kernel oil for local soap production (as a source of fat and oil) are readily available, nearly all the alkali for soap making is imported (Onyegbado et al 2002). Edewor (1984) estimated an annual availability of over 30,000 tonnes of potassium hydroxide KOH derivable from cocoa-pod waste alone, in the country, which more than meet the importation requirements of KOH and NaOH of 26,000 tonnes in 1985 but the knowledge gap in developing the formulation for using this type of alkali has hampered the technical, economic and social benefits derivable from their use.

Onifade (1994) asserted that the dumping of cocoa-pod wastes in concentrated heaps on the farms (the usual practice in Nigeria) was adverse to soil fertility and that hogs and other livestock could not completely remove the total wastes available, as fodder. According to (Idika and Maduakor, 2013), several agricultural wastes are littered all over the environment and accumulation of these wastes pose a serious health hazard. Apart from being an eyesore, even their proper disposal is a waste of resources which are a potential source of raw materials needed in soap making. Therefore, such agricultural wastes could be converted to potash and used for soap making and consequently, lubricating grease production.

Consistency depends on different factors such as the nature and quality of the metallic soap content, percentage of free fatty acids, percentage of alkaline substances used in the saponification process, speed of cooling, temperature of 17 dispersion, method of manufacture, temperature during storage, action to which it has been subjected to use, and water content. In general, soap content is the most important factor. Grease with a high percentage of soap has a high consistency. The consistency of greases during operation is modified by time of use and by the degree of mixing and stirring. Any grease or plastic materials having a consistency that depends on the shearing actions to which they have been previously subjected are customarily referred to as thixotropic (Nolan, 2004).

With rapid economic development, resource shortage and environmental pollution have increasingly become a bottleneck in ongoing social development. "Cyclic economy," a new type of economic development, became an important model in building a resource-conserving and environment-friendly society. In accordance with the concept of cyclic economy, changing "waste" into renewable

resources not only repairs the impact caused by the disposal of waste but also provides a supplement of resources, thus it can help to alleviate the pressure on resources shortage (Deng, 2009).

He then further stated that because of the fact that the waste edible oil is not soluble in alkali solution and the saponification is an interface reaction, any factor that influences the two-phase interaction and dispersion of oil water would affect the speed and saponification degree. These factors include the complexity of the compositions of waste edible oil, its response in the process of degeneration, its dispersion in aqueous solution, the breakdown of soap film, and the collision of molecules between waste edible oil and alkali. And these factors are closely related to the reaction time, temperature, the amount and the concentration of alkali.

2.5 Acid Value of Oil

The acid value (AV) is a common parameter in the specification of fats and oils. It is defined as the weight of KOH in mg needed to neutralize the organic acids present in 1g of fat and it is a measure of the free fatty acids (FFA) present in the fat or oil. An increment in the amount of FFA in a sample of oil or fat indicates hydrolysis of triglycerides (Structure on the left). Such reaction occurs by the action of lipase enzyme and it is an indicator of inadequate processing and storage conditions (i.e., high temperature and relative humidity, tissue damage). The source of the enzyme can be the tissue from which the oil or fat was extracted or it can be a contaminant from other cells including microorganisms. Besides FFA, hydrolysis of triglycerides produces glycerol. FFA are a source of flavors and aromas (Kardash, 2005).

He further explained that on one side, there are short chain FFA which tend to be water soluble and volatile with characteristic smell. On the other side, we have long chain saturated and unsaturated fatty acids. The later are more prone to oxidation in their free form and their breakdown products (aldehydes, ketones, alcohols, and organic acids) provide characteristic flavors and aromas. In most cases these flavors and aromas are considered a defect in oils, fats, and foods that contain them. However, there are instances where hydrolysis of triglycerides and oxidation of FFA are key in the development of desirable flavor and aroma in foods (Cao et. al, 2008).

The AOAC method to determine AV in fats and oils is based on a titration in ethanol using phenolphthalein as indicator. Disadvantages of this and similar methods are the use of organic solvents (volume and toxicity), the need for heating the reaction media, incomplete solubility of the oil/fat, the need to pre-neutralize the solvents, use of large amounts of sample, and the possibility of error to detect the color change of the indicator when analyzing colored samples. There are some non-titration methods designed to overcome these disadvantages. However, in spite its drawbacks, the titration method is still the most used due to the fact that it does not require expensive equipment. A titration is a volumetric technique in which a solution of one reactant (the titrant) is added to a solution of a second reactant (the analyte) until the equivalence point is reached. The equivalence point is the point at which the titrant has been added in exactly the right quantity to react stoichiometrically with the analyte. When an acid is titrated with a base, there is typically a sudden change in the pH of the solution at the equivalence point. If a few drops of indicator solution have been added, this sharp increase in pH causes an abrupt change in color, which is called the endpoint of the indicator. The actual

magnitude of the jump in pH, and the pH range which it covers depend on the strength of both the acid and the base involved, and so the choice of indicator can vary from one titration to another. To learn how to choose an appropriate indicator, we need to study in some detail the variation of pH during a titration (Cao et. al, 2008).

Free fatty acid or acid value determination is used in quality monitoring of frying operation. But since they both are volatilized and are converted to other decomposition products, they do not correlate well with fried-food quality. Nevertheless, it should be reported here that the free fatty acid content of oil has a strong effect on its smoke point, and oil absorption of fried food is affected by the smoke point of frying fat. A significant negative correlation between oil absorption by doughnuts and smoke point has been reported (Orthofer et al, 1996). Moreover, the presence of FFAs in the frying oil has been shown to catalyze further hydrolysis of triacylglycerols, and promote oil oxidation perhaps by increasing the solubility of oxygen. The catalytic effect of the carboxyl groups is probably due to the formation of free radicals via homolytic decomposition of hydroperoxides (Miyashita and Takagi, 1986). High correlation ($R^2 > 0.91$) between free fatty acids and total polar material (TPM) has been reported for a system with the same oil and food (Fristch, 1981). However, the determined acid value of given used frying oil is nearly meaningless, because there is no direct relationship between the quality of a used oil and free acidity.

Anisidine value (AnV) quantifies the secondary oxidation products, mainly α - and β -unsaturated aldehydes. AnV determination (using AOCS method Cd 18-90 or IUPAC method 2.505) is a good indicator for the frying oil quality in use. But it is

somewhat difficult to conduct, so it is mostly used as a research method. There are, however, some snack manufacturers who have employed Near Infrared Spectroscopy (NIR) to monitor changes in anisidine value during frying operations. Polymers are the largest class of degradation products in a frying oil heated at elevated temperature. The polymers include dimers, trimers, tetramers, and so on, and are formed through oxidative and thermal reactions. Usually, an official method, such as AOAC method 993.25, AOCS method Cd 22–91, or IUPAC method 2.508, is used to determine the polymer content. The measurement of polymers is an excellent marker of oil degradation, but this is not routinely applicable in oil quality monitoring, due to the long time involved in the analysis. Also, a skilled technician is needed to operate the equipment, high pressure liquid chromatography (HPLC), used in the official methods. Polymers content is used as a regulatory index (for determining end of fry-life or oil discard point) in certain European countries e.g., limit of 25% in Belgium and 24% in Germany (Orthoefer et al, 1996).

2.6 Iodine Value of Oil

The iodine value (or iodine adsorption value or iodine number or iodine index) in chemistry is the mass of iodine in grams that is consumed by 100 grams of a chemical substance. Iodine numbers are often used to determine the amount of unsaturation in fatty acids. This unsaturation is in the form of double bonds, which react with iodine compounds. The higher the iodine number, the more C=C bonds are present in the fat. It can be seen from the table that coconut oil is very saturated, which means it is good for making soap. On the other hand, linseed oil is highly unsaturated, which makes it a drying oil, well suited for making oil paints. The

iodine value is a measure of the degree of the unsaturation of an oil. Technically it is the value of the amount of iodine, measured in grams, absorbed by 100 ml of a given oil. Although the iodine value may sound uninteresting, it has some very important health implications. All fats and oils are composed of fat molecules known as fatty acids. The molecules can be classified into three categories depending on their degree of saturation. There are saturated fatty acids, monounsaturated fatty acids, and polyunsaturated fatty acids (Fristch, 1981).

He claimed that no oil in nature is composed entirely of any one of these three. All dietary oils contain a mixture. Soybean oil, for example, is referred to as a polyunsaturated oil because that is the predominant fatty acid. It also contains 24 percent monounsaturated fatty acids and 15 percent saturated fatty acids. Coconut oil is also a mixture. It contains 92 percent saturated fatty acids, 6 percent monounsaturated fatty acids, and 2 percent polyunsaturated fatty acids.

The terms saturated, monounsaturated, and polyunsaturated refer the degree of hydrogen saturation. A saturated fatty acid contains all the hydrogen atoms it possibly can. In other words, it is fully saturated with hydrogen. A monounsaturated fatty acid contains all but one pair of hydrogen atoms it can hold. A polyunsaturated fatty acid is lacking two or more pairs of hydrogen atoms. The iodine value is a measure of the amount of unsaturated fatty acids in the oil. A fatty acid that is missing any hydrogen atoms is classified as being unsaturated. This includes all monounsaturated and polyunsaturated fatty acids (Hill and Holman, 1979).

Although the iodine value is used primarily in industry, it is of value to us because it gives an indication of the oil's stability and health properties. Coconut oil has an iodine value of 10. This indicates that it contains a high amount of saturated

fatty acids and a very small amount of unsaturated fatty acids. The higher the iodine value, the greater amount of unsaturation. As noted above, coconut oil is 92 percent saturated and 8 percent unsaturated. Soybean oil, in contrast, has an iodine value of 130. It contains only 15 percent saturated fatty acids with 85 percent unsaturated fatty acids, thus the reason for its high iodine value. The higher the iodine value, the less stable the oil and the more vulnerable it is to oxidation and free radical production. High iodine value oils are prone to oxidation and polymerization. During heating, such as when used in cooking, oils with a high iodine value readily oxidize and polymerize. Polymerization is an irreversible process which causes the fatty acids to become hard, insoluble, plastic-like solids (Cao et al, 2008).

Because of their tendency to harden when oxidized, polyunsaturated vegetables have been used extensively as bases for paints and varnishes. When we use polyunsaturated vegetable oils in cooking sometimes the oil spills onto the outside of the pan. If the outside of the pan is not thoroughly cleaned, over time you will notice a buildup of a very hard, amber colored, varnish-like substance on the bottom of your fry pans. This is polymerized vegetable oil. The oil you used in cooking has literally turned into varnish. It takes a scouring pad and a lot of elbow grease to scrub it off the pan. When high iodine value oils are heated, you are creating polymerized fatty acids in your food. The higher the temperature or the longer the exposure to heat, the greater the degree of polymerization. These products of oxidation have been shown to be associated with numerous health problems, including cancer and atherosclerosis (hardening of the arteries). Coconut oil has the lowest iodine value of any dietary oil. Therefore, it is very resistant to oxidation and polymerization. It makes a very safe cooking oil (Kardash, 2005).

2.7 Peroxide Value of Oil

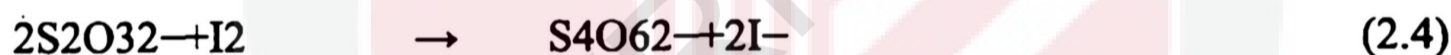
Peroxide value (PV) states the milliequivalents of peroxide oxygen combined in a kilogram of oil and able, under testing, to liberate iodine from potassium iodide; the iodine is next estimated using a standard sodium–thiosulfate solution (Methods of Analysis of Oils and Fats, 1958; Official and Tentative Methods of the American Oil Chemists' Society). Some tests, such as the Lea value, refer to the millimols of peroxide oxygen present, and the result will therefore be numerically one-half that expressed as milliequivalent of O₂. The size of the result is an indication of how well-represented in the present oil the first stage of oxidation still is. Oxidation may not have gone very much further; in any case, the amount of off flavor able to develop depends on the fatty-acid groups in which the peroxide is present (AOCS(iv) Sherwin, 1966). Peroxide value determination is a standard test for fresh oils, but it has limited value for frying oil quality in use since peroxides (not being stable) decompose at elevated frying temperatures (Kochhar, 2016). Peroxide value is measure of oxidation or rancidity and the color darker is also effect from oxidation. The peroxide value (PV) determines the concentration of hydroperoxide, the primary oxidation products. The principle involves peroxides liberating iodine from potassium iodide, i.e.



The amount of ROOH is then determined by measuring the amount of iodine formed, which is done by titration with sodium thiosulfate and using a starch indicator:



The amount of peroxides is calculated back by the amount of sodium thiosulfate ($\text{Na}_2\text{S}_4\text{O}_6$) consumed. It is expressed as peroxide value (PV) in units of milli-equivalents (meq) peroxide per 1 kg of fat extracted from the food. A general rule is that PV should not be above 10–20 meq/kg fat to avoid rancidity flavor (Connell, 1975). The peroxide value (PV) is a very important characteristic of lipid quality. The assessment of hydroperoxides provides an estimate of the overall oxidation status for lipids and lipid-containing foods especially in the primary phase of oxidation, generally known as the induction period. In the official AOCS methods (1997), method Cd 8b-90, hydroperoxides are reacted with iodide ions to form iodine and the PV is determined by titration of the liberated iodine with thiosulphate using starch as an indicator:



PV is usually expressed as the milliequivalents of peroxides per kilogram of lipids but can also be divided by 2 and expressed as millimoles of active oxygen per kilogram lipids (SI units).

The extent of lipid oxidation can also be determined by other titrations leading to the estimation of the acid value (AOCS method Ca 5a-40), the epoxide or oxirane value (AOCS method Cd 9–57), and the iodine value (AOCS method Cd 1d-92). The amount of free fatty acids, also formed during lipid oxidation as a result of secondary oxidation of unsaturated aldehydes and other degradation products of hydroperoxides, can be assessed by titration against sodium or potassium hydroxide, using phenolphthalein as an indicator, and expressed as the acid value (AV). Epoxy

derivatives (oxiranes), which are formed by reaction of hydroperoxide groups with reactive double bonds, react with excess acids to open the epoxy ring and form hydroxyl derivatives. The excess acid can be determined by titration against alkali and the epoxide value can be calculated and expressed as mmol epoxide groups per kg of lipids. Finally, the degree of unsaturation of lipids can be assessed as the iodine value (IV), which will be useful when studying oxidation of a substrate. Lipids are reacted with a halogenation agent, e.g. iodine trichloride (ICl_3) or iodine monobromide (IBr), and the unreacted halogen is converted by reaction with a potassium bromide solution into free iodine, which is titrated with a sodium thiosulfate. In general, the volumetric methods suffer from some problems related to the large amount of lipids required and the compromised efficacy of the reaction of lipid oxidation products with the different reagents and the sensitivity of these reactions to temperature, pH, solvents, oxygen, and other coexisting chemicals. In addition, the carbonyl value provides an estimate of the aldehydes and ketones that are formed as secondary oxidation products during lipid oxidation. The carbonyl groups react with hydroxylamine hydrochloride to liberate hydrochloric acid in equivalent amounts, which are assessed by titration with potassium hydroxide using bromophenol blue or bromocresol green as an indicator (Bhalerao et al, 1961).

The determination of the peroxide value is the traditional and most used parameter for measuring the primary products of oxidative degradation. From this value, the propagation step of the free radical chain mechanism and the accumulation of hydroperoxides can be followed. However, it is not possible to use the peroxide value alone to judge the quality of edible oils, because hydroperoxides decompose during storage. This decomposition can take place faster than the formation of new hydroperoxides, depending on certain storage conditions such as temperature, light

or metal traces. Although the oil has already been damaged by oxidation, and higher levels of degradation products have already formed, the speed of hydroperoxide decomposition can result in falsely low levels of these compounds. In this instance, the peroxide value tells us nothing about the real quality of the product. In order to avoid misinterpreting peroxide values, it is necessary to know the history of the sample. However, the peroxide value is a suitable parameter for measuring the deterioration of quality over time. After the induction period, during which the peroxide value increases slowly, a steep increase indicates that the oil has gone bad.

In general, the aim of oil production should be to produce oils with peroxide values as low as possible, without the formation of secondary reaction products. A higher peroxide value at the beginning of the storage period has a negative effect on the storage stability of the oil. For refined oils, producers should aim for a peroxide value below 1, better 0.5 meq O₂/kg oil, while the peroxide value for virgin oils can be higher, up to 3 meq O₂/kg oil. In most cases, the methods for determining peroxide concentration in fats and oils use the reactivity of the bound oxygen with other compounds, like potassium iodide or Fe²⁺, and the resulting reduction of the hydroperoxides. These methods are known as static methods, because they describe the state of the oil at the present time.

The standard method for determining the peroxide value is based on the method originally described by Lea (1931) and Wheeler (1932) which uses the iodometric titration of delivered iodine by standard sodium thiosulfate solution to a starch endpoint after the reaction of potassium iodide with bound oxygen from hydroperoxides. The amount of delivered iodine is proportional to the concentration

of peroxides in the oil. Different scientific organizations such as the German Society for Fat Science (DGF method C-VI 6a) (DGF, 2008) or American Oil Chemists' Society (AOCS method Cd 8-53) (AOCS, 1992) standardized this method.

The method is empirical and strongly depends upon the design of the experiment and the behaviour of the technician because the oils are susceptible to oxygen from the air, light or absorption of iodine by unsaturated fatty acids (Robards et al, 1988). Therefore, to obtain comparable and reliable results it is strongly recommended that the conditions of the method are very precisely maintained. To improve the sensitivity of the method, it is possible to identify the starch-endpoint colorimetrically, or to determine the liberated iodine electrochemical.

According to this method, the peroxide value gives the concentration of peroxides in mmol/kg oil, or it measures the amount of oxygen bound in the unsaturated fatty acid molecules in meq O₂/kg oil. A correlation between the peroxide value and sensory evaluation is not given (Acker et al, 1969), which makes it difficult to assess a product as unfit for human consumption from the peroxide value alone. In some countries, limits for the peroxide value are defined, e.g. Germany with 10 meq O₂/kg oil for virgin oils and 5 meq O₂/kg for refined fats and oils. A limit for virgin olive oil is also defined in the regulation (EWG) 2568/91 (Anon, 1991) as 20 meq O₂/kg oil.

Auto-oxidation, where peroxide is the main product that gives rise to objectionable flavor in food products, proceeds through the free radical chain reaction, where it attacks on the double bond at room temperatures. Photo-oxidation is a much faster reaction that involves attack at double bond (Lawson et al, 1997).

Rancidity of food items can be the result of auto and photo-oxidation, which are natural oxidation and chemical degradation processes of edible oils, where fatty acid esters of oils are converted into FFA giving a smell observed in many vegetable oils (Anwar et al, 2003). Indicators of poor oil quality include elevated FFA, low smoke point, change of color, low iodine value, peroxide value, total polar material, high foaming properties and increased viscosity (Kheang et al, 2006). The double bonds found in fats and oils play an essential role in autoxidation.

Oils with a higher degree of unsaturation are highly susceptible to autoxidation. The best test for autoxidation (oxidative rancidity) is determination of the peroxide value (PV). Peroxides are intermediated in the autoxidation reaction. In contrast it is not always useful in quality control, especially in the absence of sensory evaluation and other tests. As soon as the food, feed or product is manufactured it begins to go through a variety of chemical and physical changes. Oxidation of lipids is one more common and often undesirable chemical change that may influence flavor aroma nutritional quality and in some cases even the fineness of the product. The tertiary oxidation products; dimers and polymers are formed as a result of polymerization of secondary oxidation products. These products cause darkening of the oil color, formation of foam on the oil surface and an increase in viscosity of the oil. Autoxidation is a free radical reaction involving oxygen that leads to deterioration of fats and oils which form off -odors and off- flavors. PV value is useful to assess the extent to which spoilage has taken place. Autoxidation can be inhibited or retarded by some methods such as vacuum packing, modified atmosphere packing and refrigeration/freezing. Addition of natural antioxidants and precursors of plant origin into the frying oils is the best way of enhancing oxidative and flavor stability (Lawson et al, 1997).

2.8 Saponification Value of Oil

The saponification value gives an indication of the nature of the fatty acids constituent of fat and thus, depends on the average molecular weight of the fatty acids constituent of fat. The greater the molecular weight (the longer the carbon chain), the smaller the number of fatty acids is liberated per gram of fat hydrolyzed and therefore, the smaller the saponification number and vice versa.

Saponification value (or "saponification number"/"Koettstorfer number", also referred to as "sap" for short) represents the number of milligrams of potassium hydroxide required to saponify 1g of fat under the conditions specified. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. As most of the mass of a fat/tri-ester is in the 3 fatty acids, the saponification value allows for comparison of the average fatty acid chain length. The long chain fatty acids found in fats have a low saponification value because they have a relatively fewer number of carboxylic functional groups per unit mass of the fat as compared to short chain fatty acids. If more moles of base are required to saponify N grams of fat then there are more moles of the fat and the chain lengths are relatively small, given the following relation:

$$\text{Number of moles} = \text{mass of oil} / \text{average molecular mass} \quad (2.5)$$

The calculated molar mass is not applicable to fats and oils containing high amounts of unsaponifiable material, free fatty acids (>0.1%), or mono- and diacylglycerols (>0.1%). Handmade soap makers who aim for bar soap use NaOH (sodium hydroxide, lye). Because saponification values are listed in KOH (potassium hydroxide) the value must be converted from potassium to sodium to make bar soap,

potassium soaps make a paste, gel or liquid soap. To convert KOH values to NaOH values, divide the KOH values by the ratio of the molecular weights of KOH and NaOH (1.403) (Schumann and Siekmann, 2005).

Unsaponifiables are components of an oily (oil, fat, wax) mixture that fail to form soaps when treated with sodium hydroxide (lye) or potassium hydroxide. Since saponifiable components of the original oil mixture do form soaps, the result of a soap making procedure is a mixture of soaps and other, frequently oily, materials. Unsaponifiable constituents are an important consideration when selecting oil mixtures for the manufacture of soaps. Unsaponifiables can be beneficial to a soap formula because they may have properties such as moisturization, conditioning, vitamins, texture, etc. On the other hand, if the proportion of unsaponifiables is too high, or the specific unsaponifiables present do not provide significant benefits, a defective or inferior soap product can result (Gunstone et al, 2016).

Table 2.2 Saponification table plus the characteristics of oils in soap (Soap Making Resource LLC, 2008)

Oil Or Fat (Acid)	Sap	Hard/Soft	Cleansing	Fluffy Lather	Stable Lather	Skin Care
avocado oil	133.7	soft	fair	yes	no	amazing
coconut oil	191.1	hard	great	yes	no	fair
castor oil	128.6	soft	fair	yes	yes	great
olive oil	135.3	soft	good	no	no	great
palm oil	142	hard	great	no	yes	fair
peanut oil	137	soft	fair	no	yes	great
soybean oil	135.9	soft	good	no	yes	fair
sweet almond oil	137.3	soft	good	no	yes	amazing

CHAPTER 3

METHODOLOGY

These experiments were planned and conducted to measure the quality of used palm cooking oil which had been collected from domestic application. The methodology to doing these experiments comprise of all steps to determine the input quality analysis, saponification process and lastly checking for the produced soap quality. About 30 samples of used cooking palm oil are collected and tested, to figure out the color range, viscosity, acid, free fatty acid, iodine, peroxide and lastly saponification value. Then, after the hard soap produced from the saponification process, the characteristic of the soaps are tested after being dried after 1 week and above.

3.1 Project Flowchart

The flowchart that shown in Figure 3.1 shows the planning of this study that are conducted within two semester of during final year study 2017/2018 session. The problem statement are determined to lead for the choosing of the methodology step in order to do the research study and to solve the problem. The scope of study related to the project are recognized to gain some important information and listing all the procedure required to get the project in successful way. Some literature reviews on published papers are done to get addition views on how to get the project in desired ways. Then after all the materials and equipment involved are readily prepared, the project procedures can successfully carried out. Data collection and analysis are also done after doing the step involved. Next, the data obtained are interpreted to make the conclusion and lastly are ready for presentation and thesis writing.

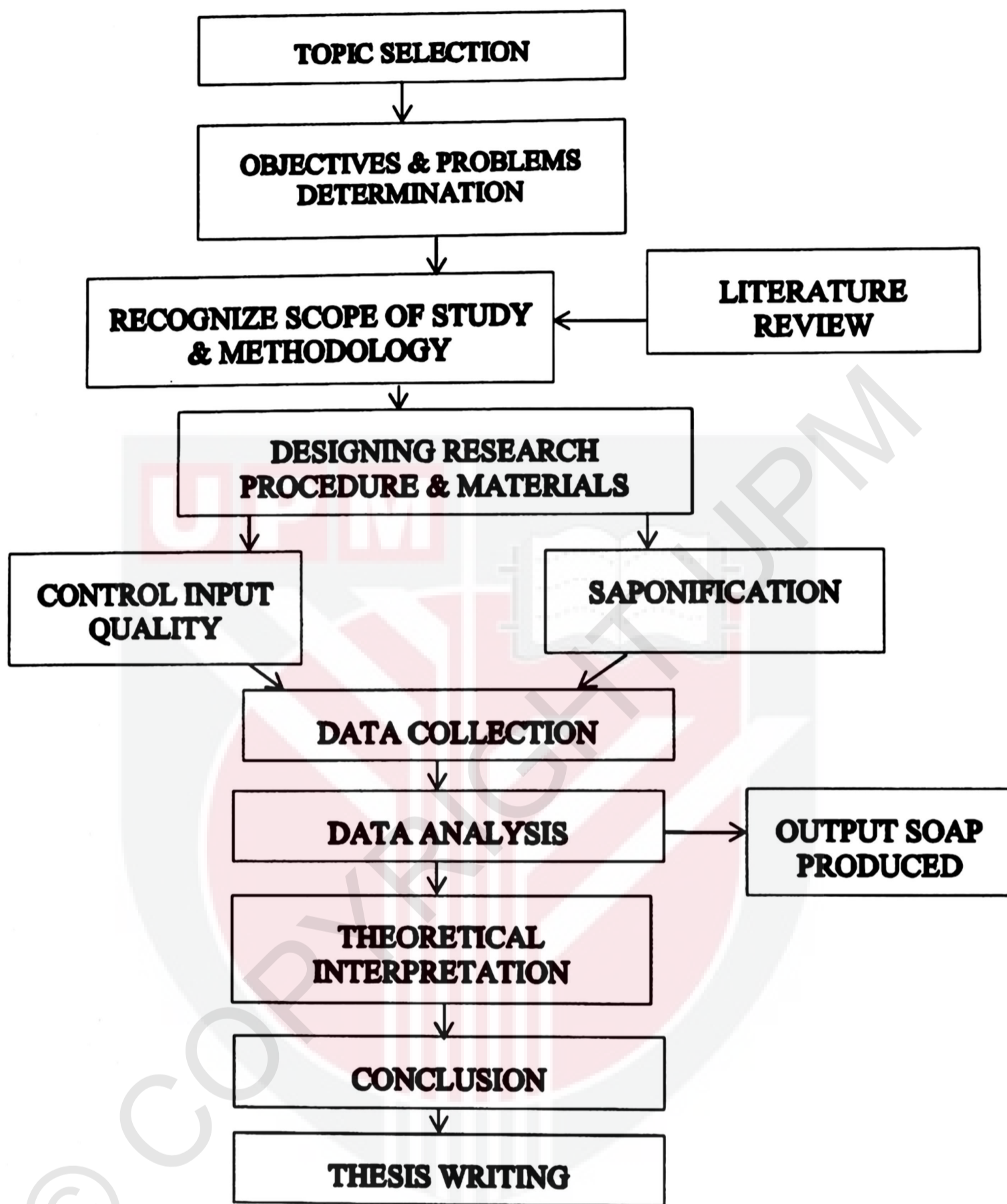


Figure 3.1 Flow chart of project planning

3.2 Introduction to process

There are a number of simple physical tests used by the food service industry and in industrial frying. Most of these very simple tests were designed for and are used in restaurant operations. They have been developed to meet the criteria noted earlier; they are simple and inexpensive. They are used to “measure” foam, oil color and oil clarity.

The selected for lab friendly experiment test that will be used in this experiment is titration and heating. Basically, it is really important to check the quality value of oil before saponification process. It is because a relationship exists between the free fatty acid value of oil with iodine value and saponification value in terms of acid value, it shows the rancidity level of the oil as well as the purpose of determining the product's shelf life. And, the peroxide value is to show the oxidation level stored in the oil sample used. As for saponification process, the reaction between palm oil and sodium hydroxide solution is exothermic in nature because heat is liberated during the reaction. The white suspension formed is made up of soap and glycerol. The process of formation of soap is called saponification. Test using red and blue litmus papers shows that soap suspension is basic in nature and not acidic in nature. The process of precipitation of soap from the suspension is called salting out. Last but not least, study the final product produced by the experiment.

During frying process, oil is continuously or repeatedly subjected to high temperatures in the presence of air and moisture. Three essential degradation reactions occurs under these conditions are:- Hydrolysis causing from the moisture content of fried food. This reaction produces free fatty acids (FFA), mono- and diglycerides. Oxidation causing from the contact with oxygen. Reaction products are

oxidized monomeric, dimeric and oligomeric triglycerides and volatile materials such as aldehydes and ketones. - Polymerization causing from these two reactions, and high temperatures. This reaction produces dimeric and polymeric triglycerides with ring structure [11-13]. Because of these degradation reactions mentioned above, a number of physical and chemical changes occur in frying oils including increase in viscosity, density, FFA content, total polar material (TPM), polymerized triglycerides, and decrease in smoke point, the number of double bonds, etc. If the frying process is continued, these materials will undergo further degradation and finally the oil will not be appropriate for frying. The frying oil has to be discarded. Since all degradation products are of polar character, TPM content of frying oil is a good indicator of its degradation level. Thus, in many countries, TPM content of frying oil has been legally accepted as the limit value to decide discard it or not. For example, in Turkey, TPM content of frying oil must not exceed the top level of 25%. In addition to TPM, as the oil deteriorates, some changes in its physical and chemical properties occur. For instance, during frying, oil's double bonds are ruptured and so its fatty acid composition changes, FFA level and saturation degree increase. The change in the fatty acid composition influences some oil properties such as iodine value, viscosity, density, heating content. Thus, these properties can also be used to monitor the quality of the frying oil (Huseyin et al, 2011).

3.3 List of Material and Equipment Used

The materials and chemicals used are as follows:- 30 samples of used cooking oil, ninety-five percent ethyl alcohol or rectified spirit neutral to phenolphthalein indicator, phenolphthalein indicator solution, standard aqueous sodium hydroxide solution 1.0 N, distilled water, cyclohexane, potassium iodide (free from potassium iodate) - 10% solution prepared fresh, starch solution indicator that are prepared by weighing 5 g of starch is mixed with 0.01 g of the mercuric iodide with 30 ml of cold water and slowly poured it with stirring into one liter of boiling water, boiled for three minutes, allowed to cool and decant off the supernatant clear liquid, Wij's iodine monochloride solution, sodium thiosulphate solution 0.1N concentration, acetic acid - chloroform solvent mixture (3: 2) that are prepared by mixing 3 volumes of glacial acetic acid with 2 volumes of chloroform, alcoholic sodium hydroxide solution, standard hydrochloric acid approximately 1.0N – 0.95N and lastly fragrance detergent.

Meanwhile, the equipments used are as follows:- viscometer with spindle type LV02, general electric spectrophotometer having an effective slit width of 10 millimicrons and using absorption cells of 10.0 and 50.0 mm sample lengths, 40 ml test tube, 250 ml test tube, 1000 ml test tube, 250 ml conical flask, 100 ml measuring cylinder, stirrer, hot plate, burette, 2 ml syringe, 500 ml erlenmeyer flask, 1 m long air condenser, or reflux condenser (65 cm minimum in length) to fit the flask, hot water bath or electric hot plate fitted with a thermostat, filter paper, weighing balance and last but not least spatula.

3.4 Input Analysis (Before The Saponification)

Preparation of Test Sample

Liquid Oils:- All samples were collected from home kitchen. Clear sediment free liquid are used directly after inverting container several times. If the liquid sample contains sediment release all sediment from walls of the container and distributes uniformly throughout the oil for determination of moisture. For determinations in which results might be affected by the possible presence of water. The oils are filtered to obtain a clear filtrate. The oil sample is left to be neutrally at room temperature.



Figure 3.2 Preparation of oil sample

3.4.1 Viscosity Measurement

The Brookfield Dial Reading Viscometer measures fluid viscosity at given shear rates. Viscosity is a measure of a fluid's resistance to flow. The Dial Viscometer rotates a sensing element in a fluid and measures the torque necessary to overcome the viscous resistance to the induced movement. This is accomplished by driving the immersed element, which is called a spindle, through a beryllium copper

spring. The degree to which the spring is wound, indicated by the red pointer, is proportional to the viscosity of the fluid. The Viscometer is able to measure over a number of ranges since, for a given spring deflection, the actual viscosity is proportional to the spindle speed and is related to the spindle's size and shape. For a material of given viscosity, the resistance will be greater as the spindle size and/or rotational speed increase. The minimum viscosity range is obtained by using the largest spindle at the highest speed; the maximum range by using the smallest spindle at the slowest speed. It using the principle where consistency in greases is analogous to viscosity in oils, the corresponding coefficient being defined in the same way as that of viscosity. For the apparatus needed to do the test are beaker 100mL and oil sample meanwhile it only using the Brookfield Viscometer with the selected spindle that are suitable for oil type liquid which is LV02 spindle type. As for the procedure is by setting the LV02# type of spindle is and the viscometer is set about 200 rpm to check its viscosity. Then the start button is pressed to start the rotational speed and take reading after the reading is stable with higher efficiency percentage.



Figure 3.3 Viscometer

3.4.2 Determination of Acid Value

The acid value is defined as the number of milligrams of potassium hydroxide required to neutralize the free fatty acids present in one gram of fat. It is a relative measure of rancidity as free fatty acids are normally formed during decomposition of oil glycerides. The value is also expressed as percent of free fatty acids calculated as oleic acid. The acid value is determined by directly titrating the oil/fat in an alcoholic medium against standard potassium hydroxide/sodium hydroxide solution. The value is a measure of the number of fatty acids which have been liberated by hydrolysis from the glycerides due to the action of moisture, temperature, and lipolytic enzyme lipase.

Firstly, the oil is mixed or melted fat thoroughly before weighing. The mass of the test sample shall be taken based on the color and expected acid value. For this test, about 10g of oil are weighed to be used. An appropriate amount of the cooled oil sample is weighed accurately in a 250 ml conical flask and 100 ml of freshly neutralized hot ethyl alcohol and about one ml of phenolphthalein indicator solution are added. The mixture is boiled for about five minutes and titrate while hot against standard alkali solution shaking vigorously during the titration.

$$\text{Calculation: Acid value} = 39.997 \times V \times N / W \quad (3.1)$$

Where, 39.97 = molecular weight of sodium hydroxide, V = Volume in ml of standard sodium hydroxide used, N = Normality of the Sodium hydroxide solution; and W = Weight in g of the sample

Table 3.1 Table of acid value (AOCS method, 1992)

Expected Acid Value	Mass of Test portion	Accuracy of weighing of test portion
<1	20 g	0.05 g
1 to 4	10 g	0.02 g
4 to 15	2.5 g	0.01 g
15 to 75	0.5 g	0.001 g
>75	0.1 g	0.0002 g

3.4.3 Calculating free fatty acid (FFA) value

Free fatty acid analysis indicates efficiency of alkali refining and deodorization. Less than 0.05% FFA is the industry standard for finished oil. Free fatty acid may be easily determined by titration with an acid or base indicator. Newly developed indicator test strips are also used for FFA analysis. The acidity is frequently expressed as free fatty acid. For oryzanol (oil extracted from the hard outer brown layer of rice after chaff (rice husk) has its own acidity and contributes to the measured FFA content when present in the oil. FFA content determined by using phenolphthalein as the indicator needs to be corrected. The formula for calculating real FFA content is shown below.

$$\text{Free fatty acids as palmitic acid} = \frac{25.6 \text{ VN}}{w} \text{ percent by weight} \quad (3.2)$$

$$\text{Acid value} = \text{Percent fatty acid} \times 1.99 \quad (3.3)$$

$$\text{It gives:- Free fatty acids (FFA)} = \text{Acid Value} / 1.99 \quad (3.4)$$



Figure 3.4 Acid value and Free Fatty Acid determination

3.4.4 Determination of Iodine Value

This particular analysis is an example of iodometry. A solution of iodine is yellow/brown in color. When this is added to a solution to be tested, however, any chemical group (usually in this test C=C double bonds) that react with iodine effectively reduce the strength, or magnitude of the colour (by taking iodine out of solution). Thus the amount of iodine required to make a solution retain the characteristic yellow/brown colour can effectively be used to determine the amount of iodine sensitive groups present in the solution. The chemical reaction associated with this method of analysis involves formation of the diiodo alkane (R and R' symbolize alkyl or other organic groups): The precursor alkene (RCH=CHR') is colourless and so is the organoiodine product (RCHI-CHIR').

In a typical procedure, the fatty acid is treated with an excess of the Hanuš or Wijs solution, which are, respectively, solutions of iodine monobromide (IBr) and iodine monochloride (ICl) in glacial acetic acid. Unreacted iodine monobromide (or monochloride) is then allowed to react with potassium iodide, converting it to iodine, whose concentration can be determined by titration with sodium thiosulfate.

The iodine value of an oil is the number of grams of iodine absorbed by 100g of the oil when determined by using Wijs solution. The oil sample taken in cyclohexane is treated with a known excess of Wijs solution. The excess of iodine monochloride is treated with potassium iodide and the liberated iodine estimated by titration with sodium thiosulfate solution. The iodine value is a measure of the amount of unsaturation (number of double bonds) in a fat.

An appropriate quantity of the dry oil is weighed accurately as indicated in the Table 3.2 below, about 1g of oil is weighed into a 500 ml conical flask with glass stopper, to which 15 ml of cyclohexane have been added. The content is swirled and mixed well. The weight of the sample shall be such that there is an excess of 50 to 60 percent of Wij's solution over that actually needed. 25 ml of Wij's solution is pipette and the glass stopper is replaced after wetting with potassium iodine solution. Swirled for proper mixing and keep the flasks in dark for half an hour for non-drying and semi-drying oils and one hour for drying oils in the room temperature. And also blank is carried out simultaneously.

Then the chemicals are removed from dark region. 20 ml of potassium iodide solution is added, followed by 150 ml of recently boiled and cooled water, rinsing in the stopper also. Liberated iodine is titrated with standardized 0.1N sodium thiosulphate solution, using starch as an indicator at the end until the blue color formed disappears after thorough shaking with the stopper on.

$$\text{Calculation: Iodine value} = 12.69 (B - S) N / W \quad (3.5)$$

Where, 12.69 = Reichert value, 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.

Table 3.2: Iodine value estimation (AOCS method, 1992)

Expected Iodine Value	Weight of oil to be taken for estimation (g)	
	Maximum	Minimum
5	6.3460	5.0770
10	3.1730	2.5384
50	0.6612	0.5288
100	0.3173	0.2538
150	0.2125	0.1700
200	0.1586	0.1269

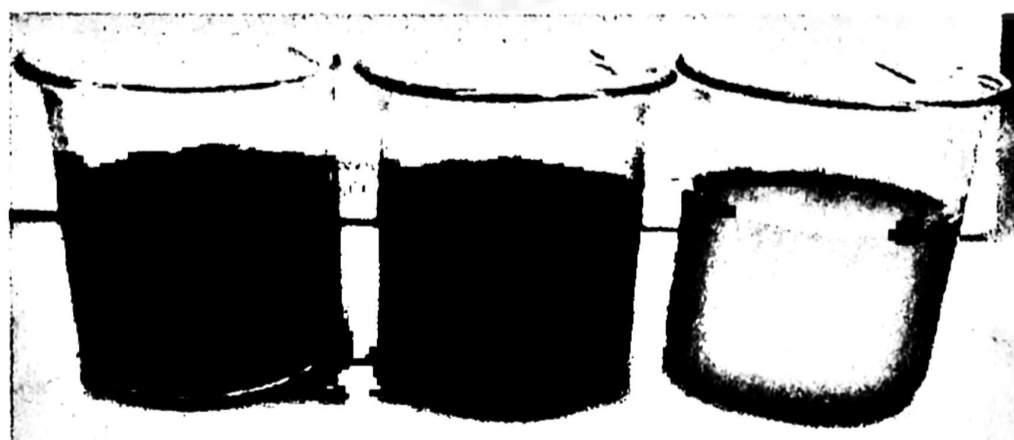


Figure 3.5 Iodine value preparation test

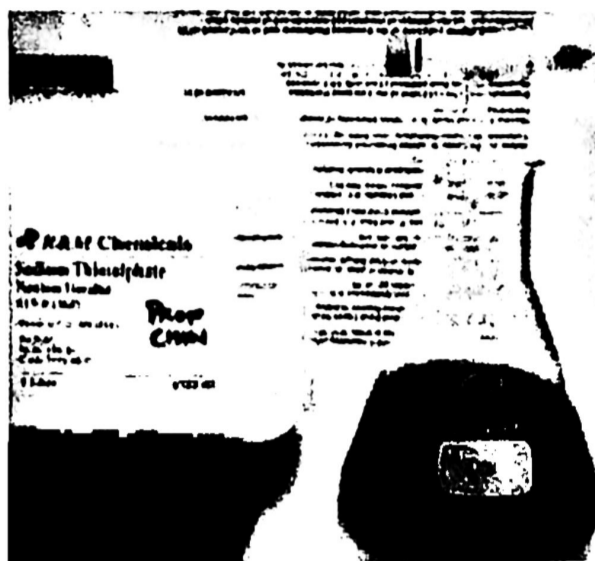


Figure 3.6 Iodine value determination by titration

3.4.5 Determination of Peroxide value

Peroxide value (PV) is primarily an indication of oil oxidation (hydroperoxide formation). Fully refined oil, after deodorization, has a PV of zero. Peroxide value steadily increases post deodorization. Peroxide value is determined by reacting the oil with iodine followed by titration with sodium thiosulfate. Oil from a refinery should be less than 1.0 PV. This is an indication of the extent of oxidation suffered by an oil.

5 g sample is weighed into a 250 ml stoppered conical flask. 30 ml acetic acid chloroform solvent mixture (18 ml of acetic acid and 12 ml of chloroform solvent mixture) is added and swirled to dissolve. 0.5 ml saturated potassium iodide solution is added with a mohr pipette. The mixture then lets 's stand for 1min in dark with occasional shaking, then about 30 ml of water is added. The liberated iodine is slowly titrated with 0.1 N sodium thiosulphate solution, with vigorous shaking until yellow color is almost gone. Using addition about 0.5 ml starch solution as an indicator and the titration is continued shaking vigorously to release all 2 from CHCl₃ layer until blue color disappears. Fresh oils usually have peroxide values well below 10 meq/kg. A rancid taste often begins to be noticeable when the peroxide

value is above 20 meq/kg. (between 20 – 40 meq / kg). In interpreting such figures, however, it is necessary to take into account the particular oil or fat.

Calculation: Peroxide value expressed as milli equivalent of peroxide oxygen per kg sample (meq/kg):

$$\text{Peroxide value} = \text{Titre} \times N \times 100 / (\text{Weight of the sample}) \quad (3.6)$$

Where, Titre = ml of Sodium Thiosulphate used (blank corrected), N = Normality of sodium thiosulphate solution.



Figure 3.7 Peroxide value preparation test

3.4.6 Determination of Saponification Value

The saponification value is the number of mg of sodium hydroxide required to saponify 1 gram of oil. The oil sample is saponified by refluxing with a known excess of alcoholic sodium hydroxide solution. The alkali required for saponification is determined by titration of the excess sodium hydroxide with standard hydrochloric acid. The saponification value is an index of the mean molecular weight of the fatty acids of glycerides comprising a fat. Lower the saponification value, larger the molecular weight of fatty acids in the glycerides and vice-versa.

The sample is melted if it is not already liquid and filter through a filter paper to remove any impurities and the last traces of moisture. Make sure that the sample is completely dry. The sample is mixed thoroughly and weighed about 2.0 g of dry sample into a 250 ml Erlenmeyer flask. 25 ml of the alcoholic sodium hydroxide solution is pipetted into the flask. A blank determination is conducted along with the sample. The sample flasks are connected and the blank flask with air condensers kept on the water bath, boiled gently but steadily until saponification is complete, as indicated by the absence of any oily matter and appearance of the clear solution. Clarity may be achieved within one hour of boiling. After the flask and condenser have cooled somewhat wash down the inside of the condenser with 1 ml of distilled water. The excess sodium hydroxide with 0.95N hydrochloric acid is titrated using 1.0 ml phenolphthalein indicator.

$$\text{Calculation: Saponification Value} = 39.97 (B-S) \times N / W \quad (3.7)$$

Where, B = Volume in ml of standard hydrochloric acid required for the blank, S = Volume in ml of standard hydrochloric acid required for the sample, N = Normality of the standard hydrochloric acid and, W = Weight in gm of the oil/fat taken for the test.

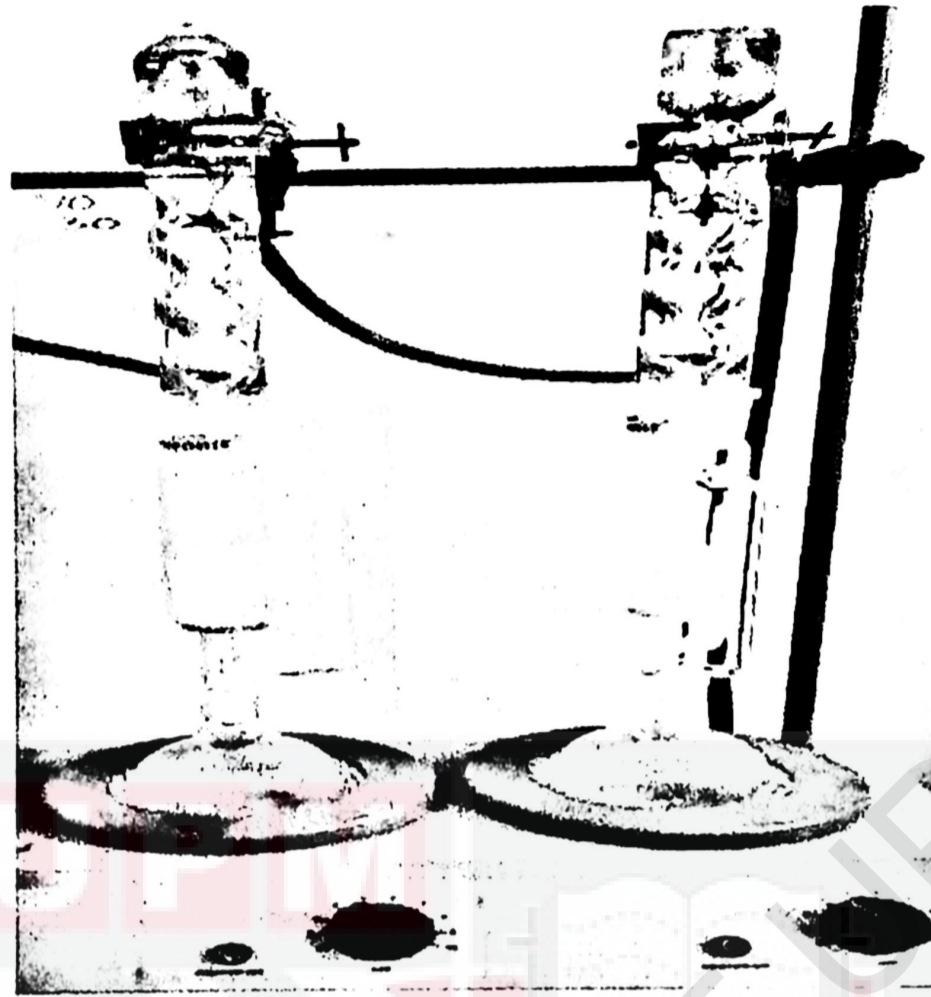


Figure 3.8 Reflux condenser used for determining of saponification value

3.4.7 Determination of color purity using spectrophotometer

The color of an oil depends on its source and degree of processing. Carotenoid and chlorophyll pigments are responsible for color. Chlorophylls may also be a prooxidant that limits the useful life of an oil. Color is removed by bleaching. Final oil color is determined by a color comparison technique, such as the Lovibond system. In this system, color is expressed as red and yellow components. For example, the color of fully refined soybean oil may be 0.8 R, 8.0 Y (0.8 red, 8.0 yellow). Chlorophyll may be determined separately by spectrophotometry.

Absorption at any specific wave length, is the value it is desired to measure, expression of the results in terms of tri-stimulus values. It is a quantities of colored substances in oils to select any single wave length at which the transmittance will be an exact function of the color, total transmission, or the visual transmission of the oil.

It is necessary or desirable to express the color in terms of a single value, the Y of the tri-stimulus values may be used as it is a direct measure of the transparency in terms of visibility function

Oils were clarified, if cloudy, by filtration through filter paper. Fifty millimeter cells were used except in the case of very dark oils. The comparison cell may be filled with water or carbon tetrachloride with practically identical results, but a pure, colorless sample of carbon tetrachloride is preferable because its refractive index is so close to those of most oils.

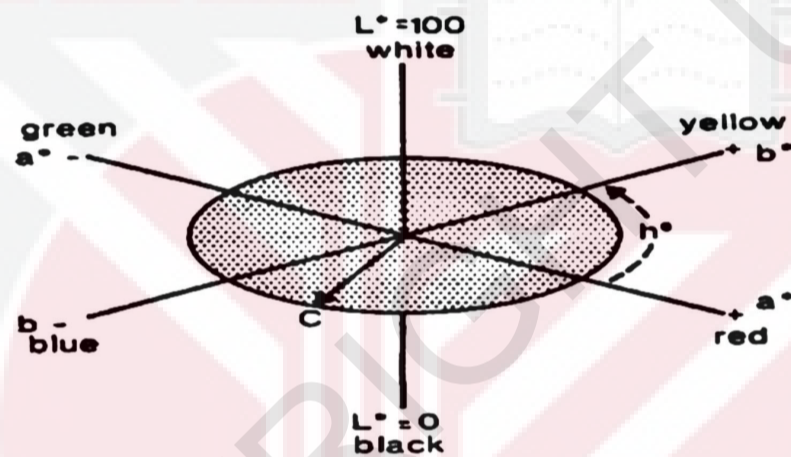


Figure 3.9 Color characteristics (Weatherall and DCoombs, 1992)



Figure 3.10 Oil color testing

3.5 Saponification process

Saponification is the hydrolysis of fats or oils under basic conditions to afford glycerol and the salt of the corresponding fatty acid. In saponification, a water molecule is removed from a fatty acid or an ester. Sodium stearate, sodium oleate or sodium palmitate is formed. It is precipitated from the solution by addition of NaCl. The addition makes the sodium salt of fatty acid partially insoluble in water and the product then separates out of the solution the remaining solution has glycerol and sodium chloride.

There are two kinds of saponifications which are homogeneous saponification and heterogeneous saponification. In homogeneous saponification, the waste edible oil is first dissolved in an appropriate solvent (such as ethanol) to form a homogeneous solution, then the reaction takes place in the medium of alkali catalyst in water bath, and brine is added in the last step to precipitate out soap. While in heterogeneous saponification, the waste edible oil is directly hydrolyzed in the medium of alkali catalyst in water bath, and brine is also added in the last step to precipitate out soap. The main purpose of this study is to complete saponification in one-step method. Using homogeneous saponification, separation and recycle of the solvent are very difficult; using heterogeneous saponification, the reaction time is long due to the reaction starts from the molecules surface of waste edible oil, but its advantages are that the saponification product can be obtained directly and the isolation and drying of soap are relatively easy. In my project, heterogeneous saponification in water bath was chosen to conduct the reaction since the method are quite easy and time saving moreover the equipment prepared in the lab are also limited.

3.5.1 Saponification process – soap process making

Materials required are as follows:- used palm cooking oil, sodium hydroxide solution, measuring cylinders, glass beaker (250 ml), glass rod, hot plate, spatula, knife, filter paper and pH meter.

100 mL is measured of oil in a 250 ml glass beaker. 20 g is measured of 0.99% sodium hydroxide NaOH pallet in another measuring cylinder and it was added to the beaker containing oil. 40 ml of water is added into 20 g of 0.99% NaOH pallet. Vigorously stir the mixture using a glass rod. When touched the beaker from outside. It is observed that the beaker is warm. Placed the beaker on an electric hot plate. The beaker is heated until 100°C till the mixture become a whitish paste. Removed the beaker from the plate and allowed it to cool. A red litmus paper is dipped in the suspension formed. When dipped in the suspension, the red litmus paper changes its color to blue. A filter funnel is taken out and a filter paper is placed in it and fixed in a stand. Placed a beaker below the funnel. The contents of the beaker are poured into the funnel over a glass rod and filtered the contents of the beaker. After filtration, soap is left behind on the filter paper. The soap is transferred to another filter paper using a spatula and dried it by pressing with another filter paper. Then, it was cut into the desired shape with a knife.

3.6 Output analysis (after saponification)

For the output analysis of the product produced, some measurements are conducted to determine the soap formation parameter. These types of qualitative and quantitative data will be taken as to study the effect of input analysis on the soap product formed which are:-

3.6.1. Measurement of the quantity of hard soap output

The quantity of final product produced are weighed. Whole product quantity obtained after the saponification completed are weighed. After the soap are fully dried up to four days, then the soap are solid enough to be taken to weigh it. The equipment used is electronic weighing balance.

3.6.2. pH determination (pH meter)

The pH meter is used to determine the pH of the soap. Even though the saponification mechanism is a neutralization reaction, since the alkali amount are kept constant, the pH value of each soap produced from different oil samples are different as well. Since the soap produced are in solid shape, to prepare the sample, a 2g of hard soap are cut and weighed. The 2g soap then are dissolved in warm water to turn it into a solution or liquid soap. Then the pH can be determined when the probe is dipped inside the dissolved liquid soap.



Figure 3.11 The pH meter that are used to check the pH value

3.6.3. Soap Scent (sensory)

This test was carried out to identify the presence of any unpleasant or rancid odours associated with each soap. Samples of each soap (20 g) were placed into separate test tubes which were then closed and allowed to rest for 5 hours. Ten subjects were asked to smell the soaps and grade their odours.

These factors are influenced by partial oxidation. Oxidation can produce off flavor and odor in an oil. Flavor analysis in the refinery is commonly performed by a laboratory analyst on a pass/fail basis. Formal taste analyses may be conducted by trained panelists. Descriptors of a satisfactory oil flavor are “nutty,” “bland,” or “buttery.” Unsatisfactory descriptors of oil flavor are “rancid,” “burnt,” “painty,” or “fishy.” The smell of the soap is physically tested and by smell sensory. Any weird smell are detected and recorded.

3.6.4. Colour formed (using spectrophotometer)

Spectrophotometry is used to measure the color properties change in the soap. The equipment is about to measure how much a chemical substance absorbs light by measuring the intensity of light as a beam of light passes through soap product. The basic principle for the equipment is that each compound absorbs or transmits light over a certain range of wavelength. The solid soap sample are prepared by cutting it into rectangle shape that give out smooth surface area. About 5cm x 4cm x 3 cm of soap sample are required to be cut to accommodate the light ray hole area. Then the reading will be appear on computer software by L*, a* and b* values.



Figure 3.12 Soap color determination using Spectrometer

Chapter 4

RESULTS AND DISCUSSION

The experiments that are conducted for the project would show the results in terms of output hard soap produced by the saponification mechanism and also the quantitative values for acid, free fatty acid, iodine, peroxide and saponification value. Other than that are the values determined from the pH, viscosity and color measurement from the useful equipment. All of the data are being tabulated and discussed. The quantitative values hard soap analysis are also being shown and discussed in this part to clarify the value as well.

4.1 Used Cooking Oil Analysis

4.1.1 Viscosity & pH value of oil

Based on data Table 4.1 below, it shows that each of 30 oil samples used has different viscosity after being tested with rheometer under 200 rpm speed. Based on the viscometer reading that are shown on the Figure 4.1, all of the waste cooking oils studied were found to be Newtonian fluids. Oil sample no 4 was the most viscous (167.5 cP with 67.0% efficiency) while oil sample no 1 was the least viscous (110.0 cP with 45.0% efficiency) among the oils tested. The higher shear range used did not significantly affect the absolute viscosities of the used cooking oils at the different efficiencies. The viscosity reading shows a highest reading for the oil solution that are more viscous and has high speed of flow of the oil compared to the oil sample that are less viscous and has low speed of flow of the oil. As we know that there is no relationship between the viscosity and density of a fluid. While viscosity is the thickness or thinness of a fluid, density refers to the space between its particles.

However, both properties are affected by temperature and time when the oil are exposed to the heat when cooking. When a fluid is heated, its particles move far apart, and it also becomes less viscous. A liquid that is dense does not necessarily have to be viscous, and the opposite is also true. Since the oil viscosities are tested in normal room temperature, so the temperature does not bring effect or changes to the original state of flow for each oil sample.

But somehow since these samples are taken from the same sources of vegetable oil which from palm cooking oil, according to Choi et al. (2014) viscosity of new palm oil ranges approximately between 32 to 36 cP when it taken under standard room temperature. Since our reading for all samples are all above 100 cP , so it is proved that there are viscosity effect on the oil after used for heating treatment during cooking for several times. The changes of viscosity may vary caused by different application of oil during deep frying or use repeatable for more than two times. From the physical view of the samples, we also can figure out which sample has the highest viscosity and which one has the least reading. Below is the table that shows the viscosity and pH values for all oil samples tested.

Table 4.1 Viscosity and pH reading on 30 oil samples

Sample number	viscosity(rpm)/efficiency(%)	average of oil pH
1	110.0/45.0	4.02 ± 0.01
2	165.8/66.3	3.94 ± 0.01
3	163.0/65.2	3.87 ± 0.01
4	167.5/67.0	3.82 ± 0.01
5	129.8/64.9	3.80 ± 0.02
6	128.0/64.0	3.86 ± 0.02
7	164.0/82.0	3.88 ± 0.01
8	153.0/76.8	3.86 ± 0.02
9	148.0/74.0	3.94 ± 0.01
10	131.2/65.6	3.96 ± 0.01
11	133.2/66.6	3.97 ± 0.01
12	137.6/68.9	3.98 ± 0.01
13	123.0/61.5	4.02 ± 0.01
14	126.6/63.4	4.06 ± 0.02
15	131.0/65.5	4.07 ± 0.01
16	126.6/63.3	4.09 ± 0.02
17	133.8/66.9	4.13 ± 0.01
18	130.0/65.0	4.12 ± 0.01
19	129.6/64.8	4.14 ± 0.01
20	124.2/62.1	4.14 ± 0.01
21	127.2/63.6	4.16 ± 0.01
22	123.8/61.9	4.13 ± 0.01
23	130.6/65.3	4.12 ± 0.01
24	146.0/72.4	4.13 ± 0.01
25	125.0/62.5	4.18 ± 0.01
26	128.2/66.3	4.14 ± 0.01
27	126.5/65.8	4.11 ± 0.01
28	130.6/69.3	4.07 ± 0.01
29	129.6/63.1	3.97 ± 0.01
30	124.5/62.9	4.07 ± 0.01

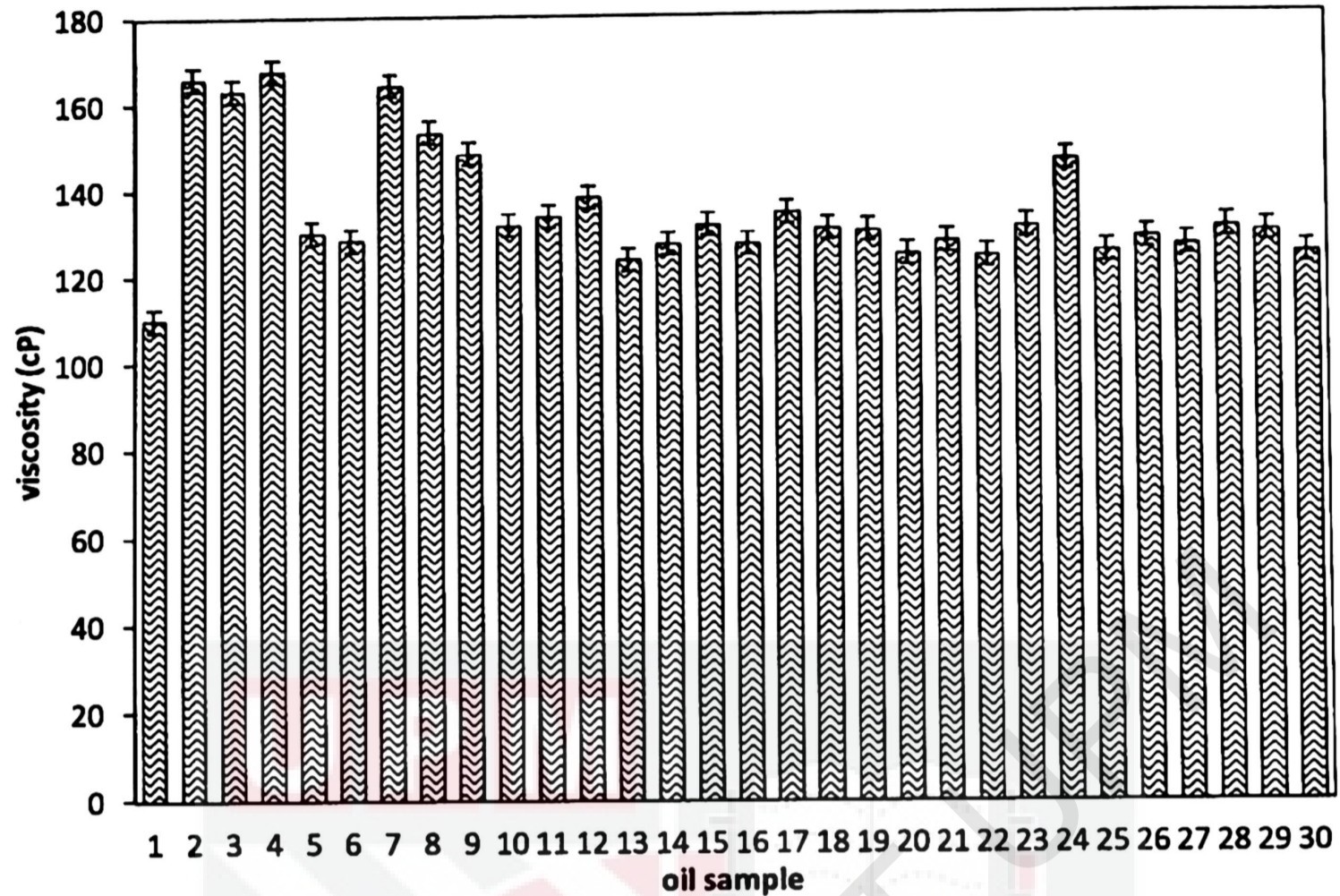


Figure 4.1 Average viscosity reading on 30 oil samples

Meanwhile for the pH value of the oils are determined to show the initial condition of pH state for each oil before being neutralized when doing the saponification process with the mixing of alkali compounds. Basically all oil especially used cooking oil are acidic cause it has the fatty acid value contained in each oil, but the values can be varies and different. From the Figure 4.2, the pH values of the used cooking oil samples are lies between 3.8 until 4.2. The values are categories in acidic phase where the values are in medium state of acidic solution.

Oil sample no 5 shows the most acidic properties when it turn to give 3.8 of it pH value while oil sample no 25 is the least acidic oil since the pH shown is 4.18. Since the amount of bases that are used to react with the oil saponification are kept constant, the pH value of the soap produced may also be varies because it is affected by its initial pH value of oil itself.

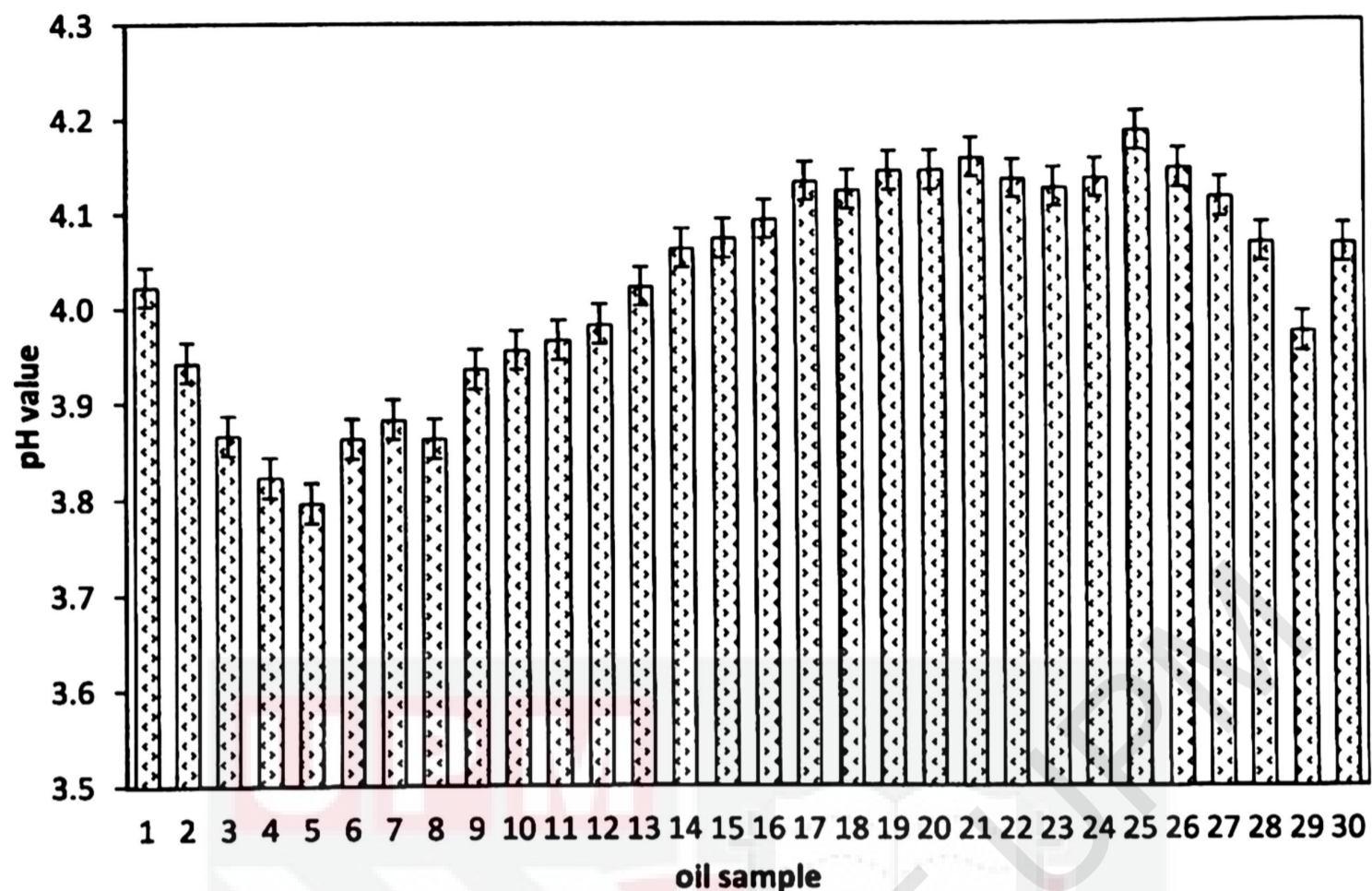


Figure 4.2 Average of pH values for 30 oil samples tested

4.1.2 Colour Characteristics Effect

Based on the result tabulated in Table 4.2, the colour characteristic of the oil samples are shown. Using a spectrophotometer as a color detector equipment, shows the results in term of L^* , a^* and b^* reading. The reading is actually describing the skin colors for the 81 European subjects in terms of the CIELAB color parameters L^* , hue angle a^* , and chroma b^* are shown. The CIELAB parameters for any individual measure skin color as it would have been visually perceived. The skin of the lower forearm has characteristics determined by both hereditary skin color and environmentally induced melanotic pigmentation. The ventral forearm, however, is relatively infrequently exposed to ultraviolet radiation and provided a readily accessible site to place over the viewing port of the spectrophotometer. The distribution of CIELAB parameters for the 81 subjects represents objectively the ventral forearm skin-color phenotype of the group. The range of each color space

parameter within the group provides a numeral specification of the distribution of the corresponding color attribute as it would have been visually perceived. . The L * values ranged from 28.03 to 25.58 for the oil samples tested. It represented a difference in this color attribute that would have been just visually apparent for two colors that were otherwise similar with respect to hue angle and chroma. The apparent asymmetry of the distribution within the group was confirmed by a goodness of fit test that showed that the hypothesis that the L * values were normally distributed about a mean of 26.672 could be rejected at the 95% level of confidence. This meant that there were a few individuals of oils whose the color was much lighter than would be expected from a normally distributed range of L * values. The hue angles (a*) ranged from -2.0 to 3.2. A goodness of fit test applied to the distribution of hue angle values showed that the hypothesis that it was normal about a mean of 0.8393 could not be rejected at the 95% level of confidence. A difference in hue angle was noted between some subjects as the only color attribute that distinguished them because they were otherwise similar with respect to L * and C. The chroma (b*) values ranged from 5.35 to 1.39. A goodness of fit test of the hypothesis that the values were normally distribute about a mean of 3.287 could not be rejected at the 95% level 0 confidence. Below is the results shown from spectrophotometer reading.

Table 4.2 Color measurements reading from spectrophotometer

oil	sample color		
	L*	a*	b*
1	27.88	0.91	5.35
2	25.91	3.20	3.22
3	27.47	2.56	5.02
4	27.90	1.08	5.02
5	26.94	0.10	3.37
6	27.20	0.15	4.27
7	25.88	-2.00	1.39
8	28.03	0.21	5.12
9	26.73	-1.95	2.49
10	26.58	-0.29	2.87
11	26.74	-0.52	3.14
12	26.94	1.11	4.85
13	25.74	1.57	2.26
14	25.85	2.15	2.53
15	25.74	2.17	2.50
16	25.96	0.93	2.66
17	25.76	2.14	3.02
18	25.67	2.24	2.25
19	26.43	0.78	3.40
20	25.66	1.84	2.32
21	26.45	1.92	3.80
22	27.03	0.02	3.69
23	26.37	1.06	2.86
24	26.97	0.42	3.31
25	26.41	0.67	2.64
26	27.94	2.00	4.50
27	26.45	-0.96	1.69
28	27.01	1.32	2.59
29	26.88	-1.32	3.48
30	27.64	1.67	2.99

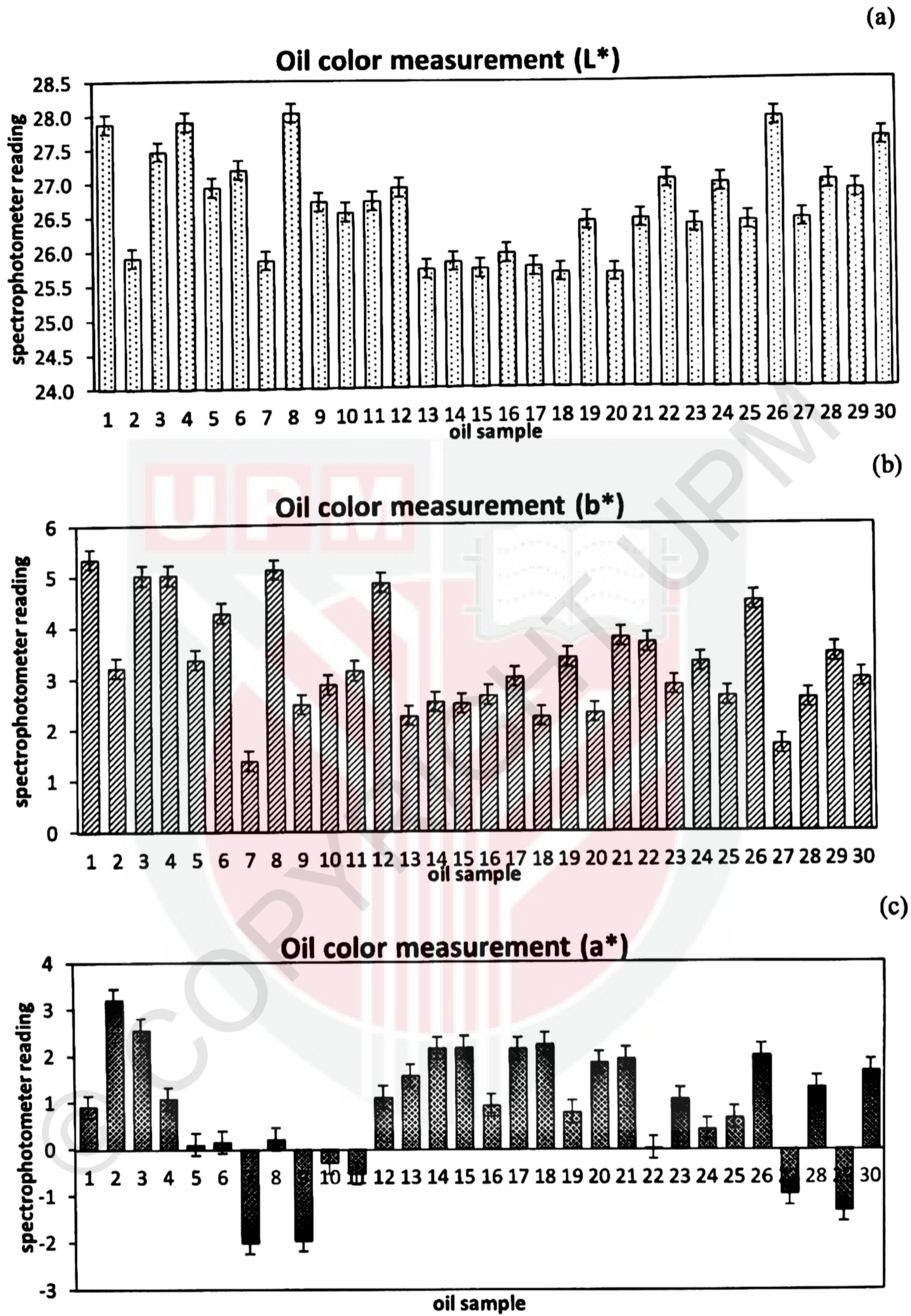


Figure 4.3 The characteristic of oil color that results from spectrophotometer where (a) black to white range, (b) blue to yellow range and (c) green to red range

4.1.3 Acid Value and Free Fatty Acid Analysis

The obtained results for the acid (AV) and free fatty acid (FFA) values are shown on the Table 4.3 as well. From the results, we can tabulate a graph to show a trends of average acid and FFA value after the testing had done on each oil samples.

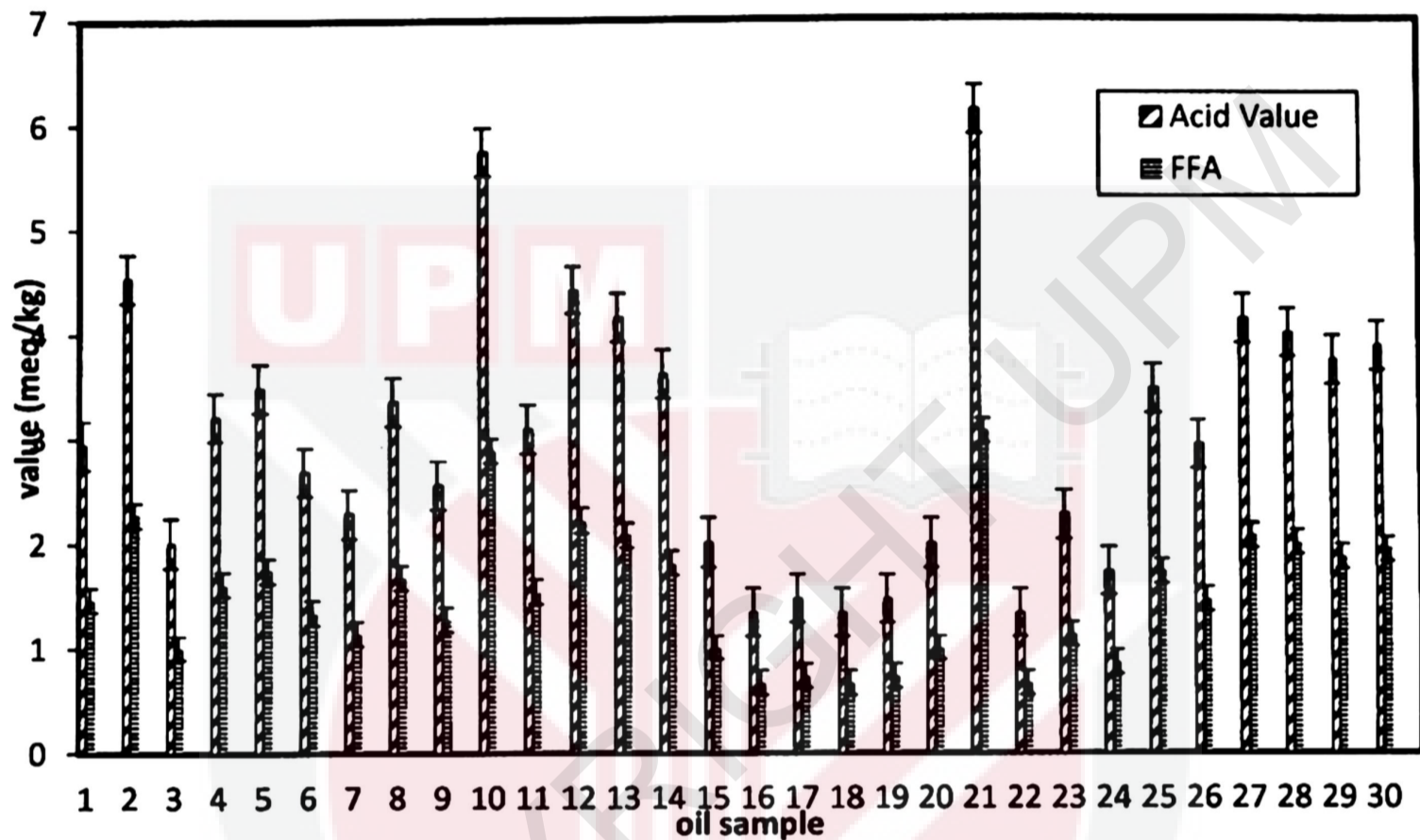


Figure 4.4 The average of acid value and free fatty acid value obtained

The FFAs of the oils extracted from used cooking oil samples are shown in Table 4.3. For all 30 fresh frying oils, the most predominant free fatty acids (FFAs) are oil sample no 21 and 10. The determination of free fatty acid values from titration experiment give out the value for oil sample no 21 about 3.066 since the acid value obtained is double of its FFA's value. The oil sample no 18 and 16 had the smallest amount of FFA and acid value which is 1.3 for acid number and 0.67 for their FFA number which is the smallest number.

This small number of free fatty acid proves that this type of oil are safe to be used and derived into another product compared to the other which contain higher content of fatty acid. High content of free fatty acids in palm oil affect the quality of palm oil and leads to various health and environmental issues. The maximum free fatty acids content set by the Palm Oil Refiners Association of Malaysia in crude palm oil is 5% and $< 0.1\%$ in refined bleached deodorized oil. The decrease of FFA's in oil sample 18 and 16 could be explained by the oxidation of unsaturated fatty acid (USFA), which changes to primary and secondary oxidation products during the frying process. In frying medium, the other highest reduction was in oil sample no 22 since it also get the same free fatty acid number as the sample of 16 and 18. Regarding the changes of FFA's and acid number in the used oils that are already used in the deep-fat frying process, the changes are quite varies depends on what the consumer tend to use as their food materials. In the Table 4.3, it shows the reading of titration for determining the acid value and free fatty acid (FFA) respectively.

Table 4.3 Measurements reading for acid value and FFA determination

Sample number	Acid value	FFA value
1	2.93 ± 1.00	1.47 ± 1.00
2	4.53 ± 1.10	2.27 ± 1.10
3	2.00 ± 0.40	1.00 ± 0.40
4	3.20 ± 0.80	1.60 ± 0.80
5	3.47 ± 0.60	1.73 ± 0.60
6	2.67 ± 0.50	1.33 ± 0.50
7	2.27 ± 1.00	1.13 ± 1.00
8	3.33 ± 1.10	1.67 ± 1.10
9	2.53 ± 0.40	1.27 ± 0.40
10	5.73 ± 0.70	2.87 ± 0.70
11	3.07 ± 0.30	1.53 ± 0.30
12	4.40 ± 0.40	2.20 ± 0.40
13	4.13 ± 0.70	2.07 ± 0.70
14	3.60 ± 0.40	1.80 ± 0.40
15	2.00 ± 0.40	1.00 ± 0.40
16	1.33 ± 0.30	0.67 ± 0.30
17	1.47 ± 0.30	0.73 ± 0.30
18	1.33 ± 0.70	0.67 ± 0.70
19	1.47 ± 0.20	0.73 ± 0.20
20	2.00 ± 0.40	1.00 ± 0.40
21	6.13 ± 0.40	3.07 ± 0.40
22	1.33 ± 0.30	0.67 ± 0.30
23	2.27 ± 0.20	1.13 ± 0.20
24	1.73 ± 0.40	0.87 ± 0.40
25	3.47 ± 0.60	1.73 ± 0.60
26	2.93 ± 0.70	1.47 ± 0.70
27	4.13 ± 0.60	2.07 ± 0.60
28	4.00 ± 0.50	2.00 ± 0.50
29	3.73 ± 0.60	1.87 ± 0.60
30	3.87 ± 0.80	1.93 ± 0.80

4.1.4 Effect On The Saponification Value

The result in Table 4.4 shows that the mean SAP values of oil from all the different sources produced at different used time constituting 100% fell off from standard saponification number for palm oil and thus did not meet the standard number, however, the mean saponification value of oil was significantly lower than that of oils freshly from all the other processing. The low saponification values recorded in comparison with the APCC and Codex Alimentarius 2005 might be due to high level of impurities as indicated by that high saponification values recorded is suggested has low level of impurities. In this experiment, it is obtained that there are 30 different values of saponification number for use cooking oils that are get from different kind of sources.

There are at least a different between majority of the readings with the mean which is 33.37 with the saponification number that lies between 50.32 until 20.23 respectively. There are huge different between the readings due to technical errors and human errors during taking the reading of titration and reaction. This might due to addition of too much phenolphthalein into the sample solution. Secondly, the readings are not taken immediately after the solution turned colorless. Oil fat is made out of a majority of short chained fatty acids, hence it should have high number of saponification value. Theoretically triglycerides containing long fatty acids will have a lower saponification number than triglycerides with shorter fatty acids. Somehow, this type of fatty acid fats like palm oil fat will have high saponification value. This means that, palm oil have the shorter fatty acid chain than other vegetable oils. Due to errors during experiment, the results obtained were quite different from what that are expected. The amount of phenolphthalein dropped into the solution might be too much or too little hence it alters the value of amount of that to be 142.0 or 10%

nearly to this value based on recent study. Below is shows the table of results for saponification value determination.

Table 4.4 Average saponification obtained from titration

Oil sample	average sap value
1	23.18 ± 3.00
2	23.18 ± 3.00
3	20.23 ± 3.00
4	31.08 ± 3.00
5	37.00 ± 1.50
6	48.10 ± 9.00
7	21.21 ± 3.00
8	22.20 ± 5.00
9	37.50 ± 4.00
10	25.40 ± 3.00
11	27.13 ± 3.00
12	37.99 ± 3.00
13	40.70 ± 2.00
14	28.12 ± 3.00
15	46.86 ± 1.00
16	41.44 ± 4.00
17	50.32 ± 3.00
18	27.38 ± 2.00
19	27.38 ± 4.00
20	39.71 ± 2.00
21	39.46 ± 3.00
22	29.10 ± 1.00
23	37.24 ± 2.00
24	34.28 ± 4.00
25	32.31 ± 3.00
26	32.56 ± 4.00
27	43.90 ± 3.00
28	36.01 ± 5.00
29	28.61 ± 2.00
30	31.32 ± 2.00

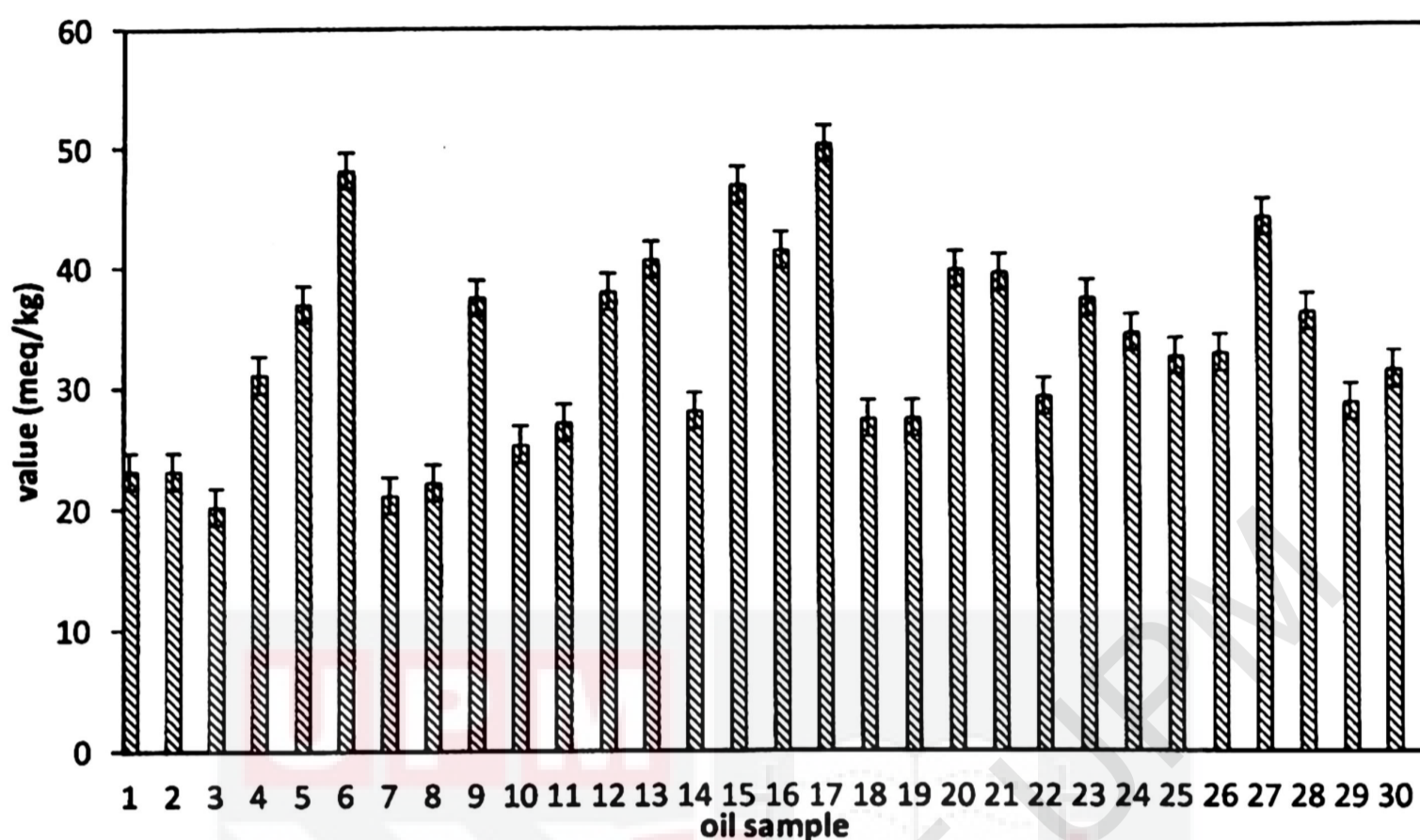


Figure 4.5 The average of saponification number obtained from the titration

4.1.5 Effect On Peroxide Value

From Table 4.5, can be seen that any variations of peroxide value (PV) in treatment of heating that has been done, there is a reduction in PV that differ according the ability of adsorbent to purified based on the time and temperature of heating which given in treatment. The highest percentage reduction of PV in these 30 cooking oil samples are obtained which is 15.67 for oil sample no 3. The maximum standards for PV in the cooking oil released by Codex Stan 210-1999 (Refined, Bleached&Deodorization) Palm Oil is 10-15 milliequivalents of active oxygen/kg oil. Base on this standard, treated used cooking oil cannot reduce the PV to maximum standard value, but have improvement by reduce the PV. It is found that the heating of the oil causes the increase of the index of peroxide at the beginning of cooking to a maximum value and then there is a decrease. Oils that are more unsaturated are oxidized more quickly than less unsaturated oils (Parker et al,

2003). The results showed that the trend of the PV is fluctuated for all samples. In the beginning, the peroxides value of original cooking oils are in same value. This is due to the formation of hydroperoxides of unsaturated fatty acids that were obtained as a result of lipid oxidation. The used vegetable palm cooking oils examined in the this study, showed variations in PV of 30 samples only 1 had a PV below 5 meq/kg. These variations can arise from different factors such as the degree of unsaturation of the fatty acids present in the particular oil, storage, exposure to light, and the content of metals or other compounds that may catalyze the oxidation processes. It was observed that the trends of the peroxide values were unstable because the hydroperoxides of unsaturated fatty acids formed by lipid oxidation are very unstable and break down into a wide variety of volatile flavor compounds as well as nonvolatile products. Therefore, at the beginning the increasing of PV showed that the concentration of hydroperoxides is higher, while the PV decreased when the secondary products are observed. The fluctuated of the peroxide values were due to the rapid decomposition of the peroxides that are formed during primary oxidation to secondary oxidation products. Below is shows the table of results for peroxide value determination.

Table 4.5 Determination of peroxide value for 30 cooking oil samples

Oil sample	ave peroxide value
1	7.47 ± 2.00
2	11.47 ± 3.00
3	15.67 ± 3.00
4	8.00 ± 2.00
5	4.93 ± 2.00
6	10.40 ± 2.00
7	10.53 ± 3.00
8	11.73 ± 5.00
9	7.93 ± 1.00
10	8.53 ± 2.00
11	12.80 ± 2.00
12	8.93 ± 2.00
13	9.27 ± 1.00
14	10.33 ± 2.00
15	9.40 ± 2.00
16	9.60 ± 1.00
17	8.73 ± 1.00
18	12.00 ± 2.00
19	11.73 ± 1.00
20	10.00 ± 2.00
21	11.13 ± 1.00
22	10.80 ± 2.00
23	9.13 ± 1.00
24	12.20 ± 2.00
25	9.47 ± 1.00
26	10.40 ± 2.00
27	11.00 ± 2.00
28	10.47 ± 1.00
29	10.93 ± 1.00
30	11.47 ± 2.00

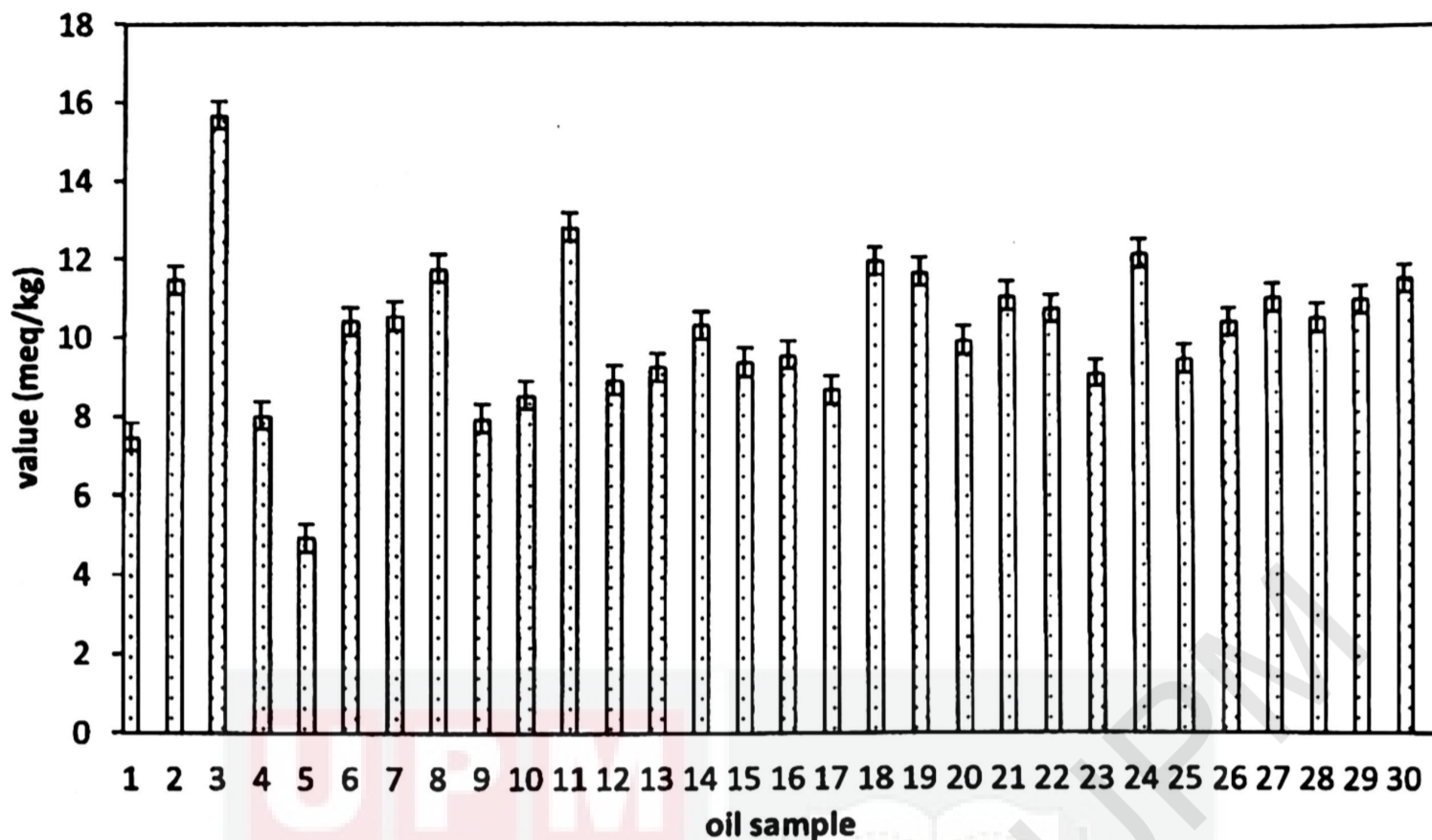


Figure 4.6 Average of peroxide value determined

4.1.6 Effect On Iodine Value

Iodine value is used to measure unsaturation or the average number of double bonds in fats and oils. Decrease in iodine value shows decrease in the number of double bonds and it indicates oxidation of the oil. Iodine value recommended standards are as follows (g of iodine/100g of oil):- Palm 50-55. After frying different types of food, palm cooking oil was found to have relatively lower iodine value which is between 7.0 until 35.5. The iodine values of oils were compared and out of this, it was found that there was decrease in IV in all the oils after frying food. This was in agreement with the finding that there is decreasing trend in iodine value of the oil during deep-fat frying. The decrease in IV with time of frying could be attributed to the changes in fatty acids taking place with duration of frying. The highest decrease in IV was observed in oil sample 15 and 16. A decrease in IV is an indicator of lipid oxidation and is consistent with the decrease in double bonds as oil becomes oxidized. All the oils recorded a decrease in I.V when subjected to different frying

and storage conditions. Iodine value of the oils decreases versus frying time due to consumption of double bonds by oxidation and polymerization. The greater the degree of un-saturation (or high I.V), the more rapid the oil tends to be oxidized, particularly during deep-fat frying. The mean iodine value of oil is 10.1633 which is quite far range from the maximum value of iodine number obtained. The iodine value or iodine number is the generally accepted parameter expressing the degree of unsaturation, the number of carbon-carbon double bonds in fats or oils. Previous study also reported that the higher the amount of unsaturation, the more iodine is absorbed; therefore, the higher the iodine value the greater the degree of unsaturation. Below is shows the table of results for iodine value determination.

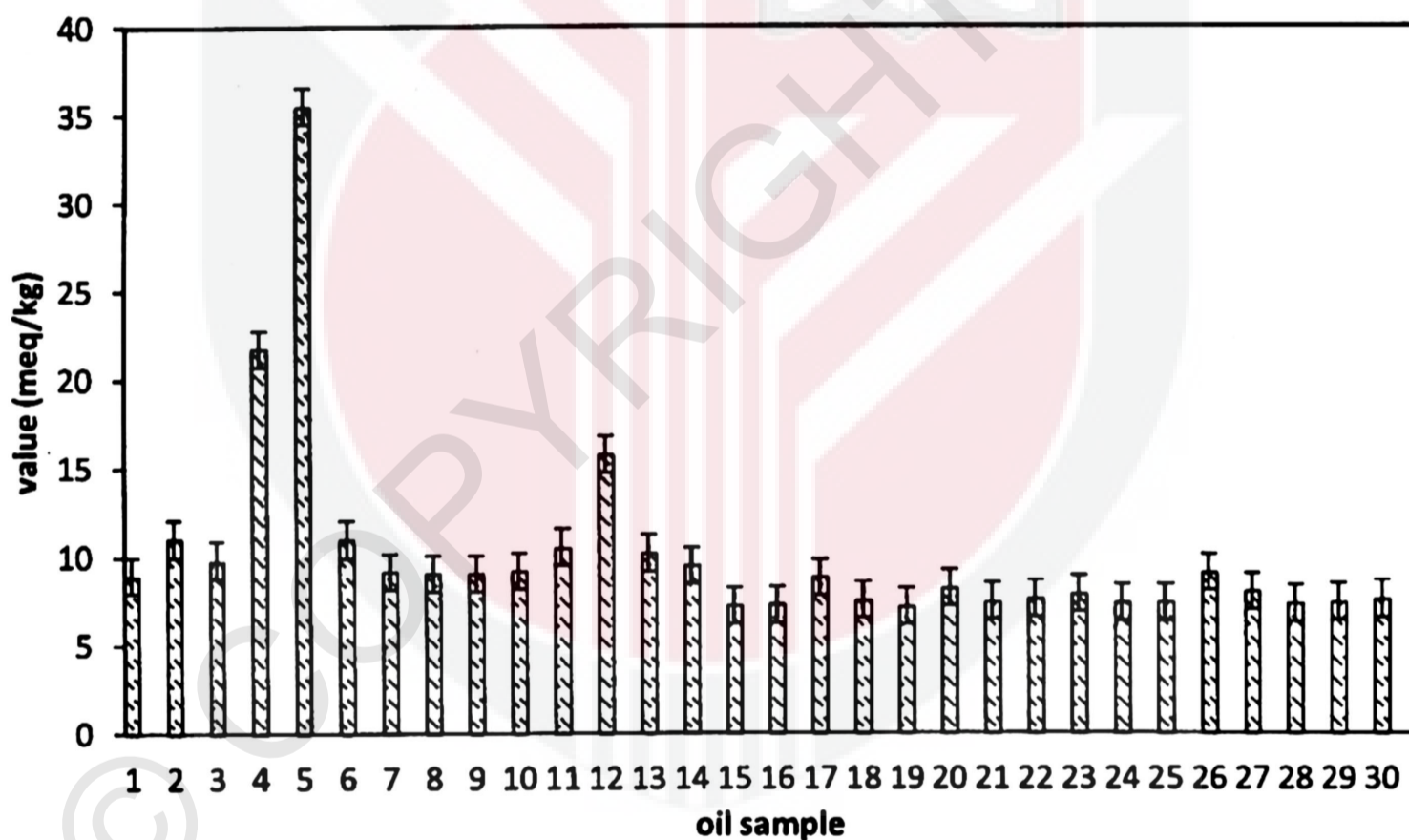


Figure 4.7 Average of iodine value determined

Table 4.6 Determination of iodine value for 30 cooking oil samples

Oil sample	ave. iodine value
1	8.97 ± 1.00
2	11.00 ± 1.00
3	9.81 ± 1.00
4	21.74 ± 14.00
5	35.49 ± 16.00
6	11.00 ± 2.00
7	9.22 ± 2.00
8	9.14 ± 1.00
9	9.14 ± 1.00
10	9.26 ± 1.00
11	10.58 ± 1.00
12	15.82 ± 1.00
13	10.28 ± 1.00
14	9.56 ± 1.00
15	7.28 ± 1.00
16	7.32 ± 1.00
17	8.88 ± 2.00
18	7.57 ± 1.00
19	7.19 ± 2.00
20	8.25 ± 1.00
21	7.49 ± 2.00
22	7.66 ± 1.00
23	7.91 ± 1.00
24	7.40 ± 0.50
25	7.40 ± 2.00
26	9.09 ± 1.00
27	8.04 ± 1.00
28	7.36 ± 1.00
29	7.44 ± 1.00
30	7.61 ± 2.00

4.2 Effect On The Soap Made Product

4.3.1 Color Characteristics

Based on the results tabulated in Table 4.7, there are huge difference of color measurements for the soap product made from the tested used cooking oils compared to the initial reading of measurements for the oil color which are shown previously. This is happened as the effect of saponification mechanism along with the drying process to become a hard soap. Within the drying session, the mix of oil, base, water, detergent are open-dried to the air at ambient condition temperature. From there, oxygen from surrounding will reacts and change the color of soap produced as well. Therefore, the hard soap are seen to be more whitish and yellowish compared to brown or reddish color for used oils. Majority for the reading of characteristics L^* , a^* and b^* are quite high compared to its intial state when the samples are in liquid oil state. When it turns to solid, the color are about double and triple the initial reading parameter. Below shows the color parameter reading of the soap from the spectrophotometer.

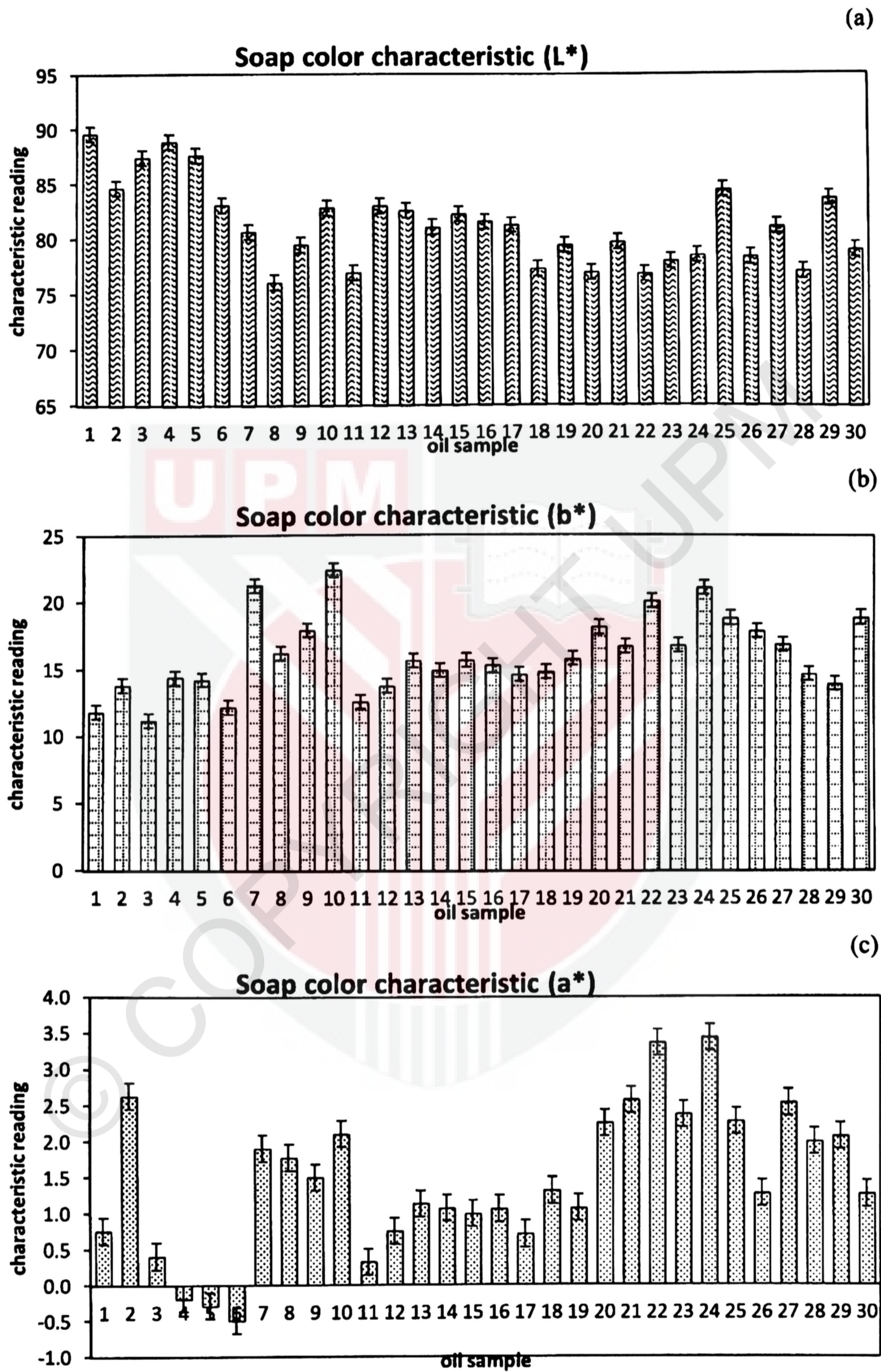


Figure 4.8 Soap color measurements reading from spectrophotometer where (a) black to white range, (b) blue to yellow range and (c) green to red range

Table 4.7 Soap color measurements based on spectrophotometer

Oil sample	Colour purity		
	L*	a*	b*
1	89.57	0.75	11.81
2	84.61	2.63	13.79
3	87.37	0.4	11.15
4	88.82	-0.19	14.36
5	87.56	-0.29	14.18
6	83.03	-0.5	12.14
7	80.62	1.9	21.23
8	76.07	1.77	16.19
9	79.46	1.49	17.89
10	82.8	2.1	22.36
11	76.94	0.32	12.53
12	82.98	0.74	13.73
13	82.58	1.12	15.63
14	81.05	1.06	14.89
15	82.23	0.98	15.66
16	81.54	1.05	15.28
17	81.22	0.7	14.61
18	77.24	1.3	14.82
19	79.38	1.06	15.8
20	76.87	2.24	18.17
21	79.64	2.56	16.74
22	76.75	3.36	20.09
23	77.89	2.36	16.81
24	78.42	3.43	21.1
25	84.38	2.26	18.84
26	78.25	1.26	17.89
27	81.03	2.52	16.89
28	76.98	1.98	14.69
29	83.58	2.05	13.96
30	78.96	1.25	18.91

4.3.2 Effect on pH value

Basically for the saponification mechanism, it reacts acts a neutralization process for any acids. For this project, since the used oils acts as a fatty acids sources, it need to be neutralized by sodium hydroxide as the bases. But since the values of acids are different in each oils tested, the amount of acids that are neutralized during saponification would be different when the amount of bases used are kept constant. From this method, pH values of the soap produced can be obtained and evaluated to see the different effect. However, all of the soaps produced from all sample of used cooking palm oil are in alkali state where the pH values lies between 8.0 until 14.0. Besides the pH, the weight of soap are also recorded to measure if any loss of water or any weight gain due to oxidation exposure when it was dried in the room. And below is the table to shows the soap pH measurements obtained after tested the soap product.

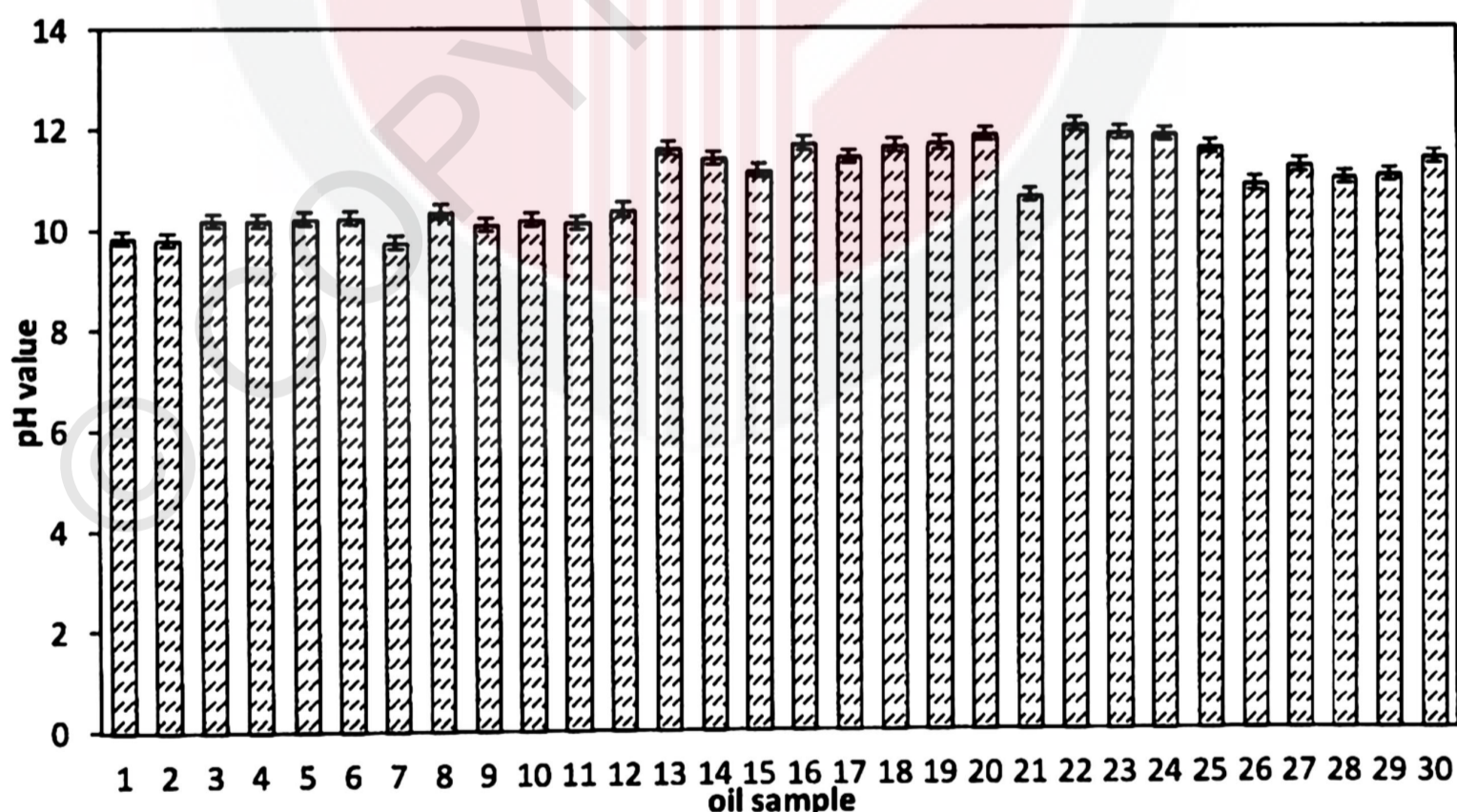


Figure 4.9 Average pH values of the soap produced

Table 4.8 Determination of soap pH for 30 cooking oil samples

Sample	Average soap weight(g)	Average soap pH
1	160.93 ± 2.00	9.83 ± 0.20
2	159.25 ± 2.00	9.81±0.20
3	162.80 ± 2.00	10.2±0.20
4	159.95 ± 2.00	10.19±0.20
5	165.64± 2.00	10.27±0.20
6	163.83± 2.00	10.25±0.20
7	168.39± 2.00	9.78±0.20
8	167.80± 2.00	10.38±0.20
9	165.18± 2.00	10.13±0.20
10	163.50± 2.00	10.22±0.20
11	156.01± 2.00	10.16±0.20
12	162.87± 2.00	10.40±0.20
13	155.33± 2.00	11.61±0.20
14	153.48± 2.00	11.47±0.20
15	156.43± 2.00	11.17±0.20
16	148.57± 2.00	11.7±0.20
17	155.04± 2.00	11.43±0.20
18	154.33± 2.00	11.65±0.20
19	158.37± 2.00	11.7±0.20
20	150.5± 2.00	11.86±0.20
21	151.88± 2.00	10.65±0.20
22	160.95± 2.00	12.06±0.20
23	149.01± 2.00	11.89±0.20
24	153.5± 2.00	11.85±0.20
25	151.35± 2.00	11.6±0.20
26	151.9± 2.00	10.86±0.20
27	152.83± 2.00	11.23±0.20
28	157.38± 2.00	10.97±0.20
29	149.13± 2.00	11.037±0.20
30	162.31± 2.00	11.38±0.20

Chapter 5

CONCLUSIONS AND RECOMMENDATION

In the quest to find an alternative solution for the inappropriate disposal of waste cooking oil in food industries and households this study introduces a sustainable concept of up-cycling waste cooking oil into soap. It has been found that recycling waste cooking oil has a very good potential to make soap rather than disposing it by environmentally unfriendly means. The soap had a slightly fishy odour but gave a neutral odour in the smelling test. The hot process soap resulted into a hard, rough bar and light brown in colour. As for the analysis of the quality of oils before the saponification done, it can be concluded that the oil yield, saponification value, free fatty acid, acid value, peroxide value and iodine value decreases with increase in heating temperature and frequent use. Even though the heating temperature are not specifically recorded in this study, but the frequent use of the oils emphasize the time of the oil expose to high temperature and heating. The higher the iodine value, the less stable the oil and the more vulnerable it is to oxidation and free radical production. High iodine value oils are prone to oxidation and polymerization. The use of waste oil for soap-making can bring a sustainable alternative to prevent the inappropriate disposal of waste cooking oil. Soap-making has great business potential and can easily be set up and run from home. It will not require very much investment capital. Handmade soap making as a business can be well conceptualized for both small and medium-sized entrepreneurs.

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APPENDICES



(Input Analysis Table)

Oil	Sample Color			Viscosity(cP) /Efficiency(%)	Ave. Of Oil pH	Ave. Saponif -Ication Value	Ave. Peroxide Value	Ave. Iodine Value	Ave. Acid Number	Ave. FFA Value
	L*	a*	b*							
1	27.88	0.91	5.35	110.0/ 45.0	4.02	23.18	7.47	8.97	2.93	1.47
2	25.91	3.20	3.22	165.8/ 66.3	3.94	23.18	11.47	10.99	4.53	2.27
3	27.47	2.56	5.02	163.0/ 65.2	3.87	20.23	15.67	9.81	1.99	0.99
4	27.90	1.08	5.02	167.5/ 67.0	3.82	31.08	8.00	21.74	3.19	1.60
5	26.94	0.10	3.37	129.8/ 64.9	3.80	36.99	4.93	35.49	3.47	1.73
6	27.20	0.15	4.27	128.0/ 64.0	3.86	48.10	10.40	10.99	2.67	1.33
7	25.88	-2.00	1.39	164.0/ 82.0	3.88	21.21	10.53	9.22	2.27	1.13
8	28.03	0.21	5.12	153.0/ 76.8	3.86	22.20	11.73	9.14	3.33	1.67
9	26.73	-1.95	2.49	148.0/ 74.0	3.94	37.49	7.93	9.14	2.53	1.27
10	26.58	-0.29	2.87	131.2/ 65.6	3.96	25.41	8.53	9.26	5.73	2.87
11	26.74	-0.52	3.14	133.2/ 66.6	3.97	27.13	12.80	10.58	3.07	1.53
12	26.94	1.11	4.85	137.6/ 68.9	3.98	37.98	8.93	15.82	4.40	2.19
13	25.74	1.57	2.26	123.0/ 61.5	4.02	40.70	9.27	10.28	4.13	2.07
14	25.85	2.15	2.53	126.6/ 63.4	4.06	28.12	10.33	9.56	3.59	1.79
15	25.74	2.17	2.50	131.0/ 65.5	4.07	46.86	9.40	7.28	1.99	0.99
16	25.96	0.93	2.66	126.6/ 63.3	4.09	41.44	9.60	7.32	1.33	0.67

17	25.76	2.14	3.02	133.8/ 66.9	4.13	50.31	8.73	8.88	1.47	0.73
18	25.67	2.24	2.25	130.6/ 65.0	4.12	27.38	12.00	7.57	1.33	0.67
19	26.43	0.78	3.40	129.6/ 64.8	4.14	27.38	11.73	7.19	1.47	0.73
20	25.66	1.84	2.32	124.2/ 62.1	4.14	39.71	10.00	8.25	1.99	0.99
21	26.45	1.92	3.80	127.2/ 63.6	4.16	39.46	11.13	7.49	6.13	3.07
22	27.03	0.02	3.69	123.8/ 61.9	4.13	29.10	10.80	7.66	1.33	0.67
23	26.37	1.06	2.86	130.6/ 65.3	4.12	37.24	9.13	7.91	2.27	1.13
24	26.97	0.42	3.31	146.0/ 72.4	4.13	34.28	12.20	7.40	1.73	0.87
25	26.41	0.67	2.64	125.0/ 62.5	4.18	32.31	9.47	7.40	3.47	1.73
26	27.94	2.00	4.50	128.2/ 66.3	4.14	32.56	10.40	9.09	2.93	1.47
27	26.45	-0.96	1.69	126.5/ 65.8	4.11	43.90	11.00	8.04	4.13	2.07
28	27.01	1.32	2.59	130.6/ 69.3	4.07	36.01	10.47	7.36	3.99	1.99
29	26.88	-1.32	3.48	129.6/ 63.1	3.97	28.61	10.93	7.45	3.73	1.87
30	27.64	1.67	2.99	124.5/ 62.9	4.07	31.32	11.47	7.61	3.87	1.93

(Ouput Analysis Table)

Oil	Soap Weight (g)	Average Soap pH	Odour	Colour Purity		
				L*	a*	b*
1	160.93	9.83	oily & fishy smell	89.57	0.75	11.81
2	159.25	9.81	fishy smell,bit fresh smell	84.61	2.63	13.79
3	162.80	10.20	no smell,bit fishy smell	87.37	0.40	11.15
4	159.95	10.19	fishy smell,bit fresh smell	88.82	-0.19	14.36
5	165.64	10.24	no smell,bit fresh smell	87.56	-0.29	14.18
6	163.83	10.25	no smell,bit sour smell	83.03	-0.50	12.14
7	168.39	9.78	no smell,bit fresh smell	80.62	1.90	21.23
8	167.80	10.38	no smell,oily smell	76.07	1.77	16.19
9	165.18	10.13	no smell,natural smell	79.46	1.49	17.89
10	163.51	10.22	no smell,natural smell	82.8	2.10	22.36
11	156.01	10.16	no smell, detergent&oily smell	76.94	0.32	12.53
12	162.87	10.40	no smell,detergent smell	82.98	0.74	13.73
13	155.33	11.61	fresh smell,bit oily smell	82.58	1.12	15.63
14	153.49	11.42	fresh detergent smell	81.05	1.06	14.89
15	156.43	11.17	no smell,detergent&oily smell	82.23	0.98	15.66
16	148.57	11.70	no smell,oily smell	81.54	1.05	15.28
17	155.04	11.43	detergent&oily smell	81.22	0.70	14.61
18	154.33	11.65	no smell,bit detergent smell	77.24	1.30	14.82
19	158.38	11.70	oily smell	79.38	1.06	15.80
20	150.50	11.86	natural detergent smell	76.87	2.24	18.17
21	151.88	10.65	strong used oil smell	79.64	2.56	16.74
22	160.95	12.06	fresh smell,bit fishy smell	76.75	3.36	20.09

23	149.01	11.89	no smell,bit detergent smell	77.89	2.36	16.81
24	153.50	11.85	fresh smell,bit fishy smell	78.42	3.43	21.1
25	151.35	11.60	natural detergent smell	84.38	2.26	18.84
26	151.90	10.87	no smell,bit oily smell	78.25	1.26	17.89
27	152.83	11.23	no smell,bit fishy smell	81.03	2.52	16.89
28	157.35	10.97	fresh smell,bit oily smell	76.98	1.98	14.69
29	149.13	11.04	fresh detergent smell	83.58	2.05	13.96
30	162.31	11.38	no smell,bit detergent smell	78.96	1.25	18.91