QUANTITATIVE ANALYSIS OF OIL LOSS DURING THE EDIBLE OIL REFINERY PROCESS

BY

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DECLARATION

The analysis described in this thesis was carried out by my self at the main laboratory of Unilever Ceylon Limited, under the supervision of Mr.H.I.S.C. Gunasekara, laboratory manager, Unilever Ceylon Limited and Dr. Nirmali Wickramaratne, Head, Department of Physical Sciences, during the industrial training period from 11th November 2003 to 12th February 2004.

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TEACHERS

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ABSTRACT

Unilever Ceylon Limited is one of major manufacturing companies in Sri Lanka and its major products are detergents, foods and personal products. The total annual production is approximately 81000 tons of which 70 % is from detergents, 22 % from foods and 8 % from personal products.

Edible oil refining is one of the major processes in food production. The activity in the refinery, which is entirely batch based, includes neutralization, deodorization, intereterification and bleaching.

In order to maintain the efficiency and to minimize the oil loss during the refinery process, regular monitoring was important.

Therefore free fatty acid content in original oil blend, total fatty matter in the soap stock and neutral oil in soap stock were monitored for different batches of Astra oil blends during December to 31st of January. Free fatty acid content in the oil blend and Total fatty matter in the soap stock was determined using Unilever Method of Analysis and the neutral oil content in the soap stock was determined using A.O.C.S. Official method (G 5-40).

According to the results mean value of the TFM (%) is 4.99 ± 1.33 and the standard deviation is 2.31 ±1.02. The distribution of TFM (%) is positively skewed.
Kurtosis of the distribution shows that the peakness of the distribution is higher than the normal and equal number of observations lie below and above the mean. The TFM (%) of the soap stock varied irregularly during the two months and a strong quadratic relationship between the TFM (%) and the FFA (%).

The (%) neutral oil content is 0.32±0.13 and the standard deviation of the distribution is 0.20 ± 0.09. The distribution is positively skewed. Kurtosis shows that the distribution is flatter than the normal. Most of the (%) neutral oil values exist below and around the mean value.
The results of (%) neutral oil content has been fluctuated irregularly during the two months of analysis but at a very low level.

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CHAPTER 01 - INTRODUCTION

1.1.Unilever Ceylon Limited

Unilever Ceylon Limited has been in existence since 1939 and the manufacturing sites are at Grandpass, Bandaragoda, Agarapathana and Sapugaskanda (Lindel).

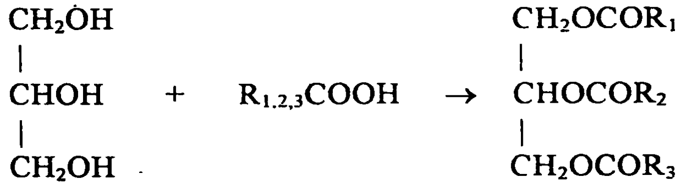
The Grandpass site, which is located in a predominately commercial area in Colombo, caters essentially to domestic household and the industrial markets in the traditional Unilever core – businesses of detergents, personal products and foods. Gradual expansion over the years with increasingly complex needs has resulted in fragmented development, rationalised to a greater extent to manage the present volume.

The total annual out put of the grandpass site is approximately 81,000 tons, of which, 70 % is from detergents, 22 % from foods and 8 % from personal products. The major food product is Astra margarine and raw oils for margarine industry are imported from Malaysia.

1.2.Oils and Fats

Oils and fats are triglycerides of fatty acids. Most of the physical and chemical parameters of oils and fats are determined by the nature of the side chain of the fatty acid and the unsaturation of the carbon chain.

Therefore each and every crude oil has a characteristic melting point and slip point due to their different side chains and differences in the number of multiple bonds.



$$\begin{array}{lclcl} CH_2OH & & & & CH_2OCOR_1 \\ | & & & & | \\ CHOH & + & R_{1,2,3}COOH & \rightarrow & CHOCOR_2 \\ | & & & & | \\ CH_2OH & & & & CH_2OCOR_3 \end{array}$$

Formation of triglycerides

1.3.Oils and Fats used in Margarine Industry

In margarine industry palm kernel oil, palm oil and palm stearine are used as the major raw materials. They are mixed together according to a predetermined ratio and is called the blend. The purpose of making the blend is to maintain the melting point and the slip point at a certain level as required by the Unilliver Standards.

1.3.1.Palm Kernel Oil

Palm kernel oil is extracted from the fruit pulp of the oil palm (*Elaeis guineensis*). Palm kernel oil is a pale yellow colour liquid. Once set, it has the appearance of an almost pure white or slightly yellow fat. Its nutty taste and smell is typical Palm kernel oil(Karleskind et al, 1996). The main physical and chemical characteristics such as physical properties, **Fatty Acid and triglyseride Composition** are summarized in tables 1.1, 1.2, and 1.3 respectively.

Table 1.1 Main physical and chemical characteristics of palm kernel oil

D40	0.899 – 0.913
V50 (c.p.)	17 – 20
Melting point ©	23 –30
Iodine value	16 –23
Saponification value	242 – 254

Source: Oil and fat manual (Volume 1)

Table 1.2 Fatty Acid Composition of palm kernel oil

Nature	**% of Fatty Acids**
C6 : 0	< 0.8
C8 : 0	2 - 5
C10 : 0	3 - 5
C12 : 0	44 - 51
C14 : 0	15 - 17
C15 : 0	-
C16 : 0	7 - 10
C16 : 1	< 0.1
C17 : 0	-
C18 : 0	2 - 3
C18 : 1	12 - 18
C18 : 2	1 - 4
C18 : 3	< 0.7
C20 : 0	< 0.3
C20 : 1	< 0.5
C22 : 0	

Source: Oil and fat manual (Volume 1)

Table 1.3 Triglyceride composition of Palm kernel oil

Nature	% of total TG	Nature	% of total TG
C28	< 2	C42	8 - 10
C30	1 - 3	C44	5 - 10
C32	5 - 8	C46	4 - 7
C34	7 - 10	C48	5 - 8
C36	19 - 24	C50	1 - 4
C38	15 - 18	C52	1 - 4
C40	9 - 11		

Source: Oil and fat manual (Volume 1)

1.3.2.Palm Oil

Palm oil is extracted from the mesocarp of fruits produced by the Elaeis guineensis Jacq oil palm(Karleskind et al, 1996). The main physical and chemical characteristics such as physical properties, Fatty Acid and triglyceride Composition are summarized in tables 1.4, 1.5, and 1.6 respectively.

Table 1.4 Characteristics and Chemical composition of palm oil

D40	0.895 - 0.900
V50 (c.p.)	25 - 31
Melting point(c)	27 - 45
Iodine value - palm	51 - 54
Iodine value - Oleine	56 - 61
Iodine value - Stearing	22 - 49

Source: Oil and fat manual (Volume 1)

Table 1.5 Fatty Acid Composition

Nature	% Total FA		
	Palm	Oleine	Stearine
C12 : 0	< 0.2	,0.2	<0.2
C14 : 0	1-2	1	1-2
C16 : 0	43-46	39-41	46-69
C16 : 1	<0.3	<0.2	<0.2
C17 : 0	-	-	-
C18 : 0	4-6	4-5	4-6
C18 : 1	37-41	43-44	20-38
C18 : 2	9-12	10-12	4-10
C18 : 3	<0.4	<0.4	<0.2
C20 : 0	<0.4	<0.4	<0.3
C20 : 1			
C22 : 0			

Source: Oil and fat manual (Volume 1)

Table 1.6 Triglyceride composition (GC)

Nature	Total Triglycerides		
	Palm	Oleine	Stearine
C46	<1	-	1-4
C48	4-11	1-4	12-55
C50	40-45	37-45	33-49
C52	38-43	43-51	5-37
C54	6-11	7-12	0-9

Source: Oil and fat manual (Volume 1)

1.4.Impurities in Crude Oils

The crude edible oils and fats contain impurities such as free fatty acids, sterols, tocopherols and coloured compounds like carotenoids.

Free fatty acids will generate free radicals, which are the major cause of rancidity. In oil blend of margarine major free fatty acid that found is palmitic.

$CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}COOH$

Palmitic acid

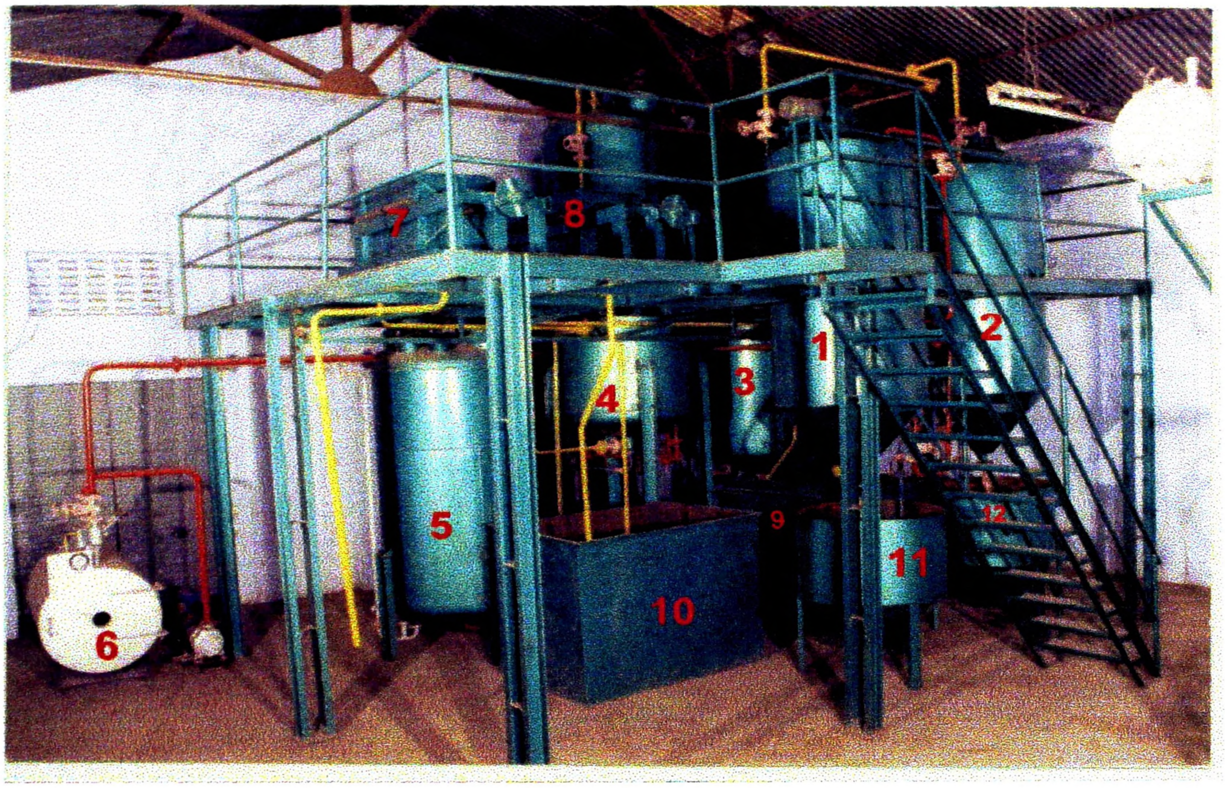
1.5.Edible Oils and Fats Refinery

The main objective of the edible fat and oil refining is the removal of the free fatty acid content and to maintain the level of FFA less than 0.04 % (Formo et al, 1979). The activity in refinery, which is entirely batch based, includes, neutralisation, deodorisation and modification of oil through interesterification. Bleaching is also carried out, as a step during the process of neutralisation.

Most commonly used practical method in refinery process is, treatment of the oil with an alkali. This method is capable of removing free fatty acids completely, by converting in to oil insoluble soap. The above process is called neutralization.

1.5.1.Edible oil refinery Plant

EDIBLE OIL REFINERY 5 TONNES PER DAY



1. Neutralizer
2. Neutralizer
3. Bleacher
4. Deodourizer
5. Cooler
6. Thermic Fluid Boiler
7. Filter Press
8. Filter Press
9. Raw Oil Tank
10. Bleached Oil Tank
11. Soap Pan
12. Soap Pan

Steam generator and vacuum pump are on the back side and so can not be seen.
Berometric Condensor and catchalls with 40ft. tower not shown.

Figure 1 Edible oil refinery unit

1.5.2.Neutralisation

Most important and generally practiced method of refining is the treatment of oil with an alkali. Neutralization effects an almost complete removal of free fatty acids, which are converted into oil insoluble soaps. Other acidic substances that exist in oil and impurities combine with the alkali and are been removed from the oil by adsorption on the soap formed during the operation.

The alkali most commonly employed for Neutralisation is caustic soda. Caustic soda has the disadvantage of saponifing a small proportion of neutral oil in addition to react with free fatty acids. This process is referred to as parasitic saponification; for this reason, in order to minimize the parasitic saponification other alkalie, such as sodium carbonate, have been tried and yet non of the other alkali have been accepted to any extent of caustic soda.

$$RCOOH + NaOH \rightarrow RCOO^{-}Na^{+}$$

Formation of Soap

1.5.2.1.Selection of NaOH

The selection of the proper amount and strength of NaOH for Neutralisation is highly important in the case of any oil or fat that is to be refined with caustic soda.

It might be supposed that the NaOH to be used could be quite simply determined on the basis of the free fatty acid content of the oil blend. Therefore the percentage of the FFA in the oil blend is first determined and according to the following chart (Table 1.7) as predetermined and calculated, the sodium hydroxide is added to the oil bled in the reactors.

Table 1.7 Determination of the amount of NaOH

(Only for palm oil, palm kernel oil and palm stearine)

For 10 Tons of oil		
FFA (%)	**4 N NaOH** (IN LITRES)	**Water** (IN LITRES)
0.01	1	40
0.02	2	80
0.03	3	120
0.04	4	160
0.05	5	200
0.06	6	240
0.07	7	280
0.08	8	320
0.09	9	360
0.10	10	390
0.11	11	430
0.12	12	470
0.13	13	510
0.14	14	550
0.15	15	590
0.16	16	630
0.17	17	670
0.18	18	710
0.19	19	750
0.20	20	780

1.5.2.2.Effect of Neutralisation treatment on specific Impurities

Alkali refining of an oil with caustic soda readily reduces the free fatty acid content to 0.01-0.03 %. With a weaker alkali, such as Sodium Carbonate, it is difficult to get the free fatty acid below about 0.1 %.

Alkali refining effects essentially complete removal of phosphatides from oils. In fact it has been stated that the phosphorous content of refined oil is an acceptable criterion of the overall efficiency of refining and that it should not exceed about 0.5 ppm. This corresponds to about 0.0015% phosphatides(Formo et al, 1979).

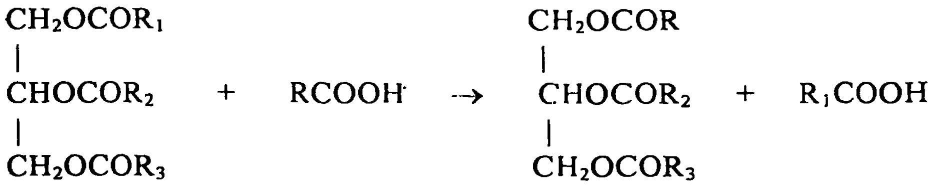
1.5.3.Addition of Soda Ash (Sodium Carbonate)

Main purpose of adding Sodium Carbonate is to absorb the moisture content in the oil.
2.5 kg of soda ash is added for each 10 Tons of oil blend under temperature of 110° c and boiled under a vacuum over $25'$ Hg.
All the unsaponified free fatty acids during the neutralisation process will be saponified under the above condition.

1.5.4. Interesterification

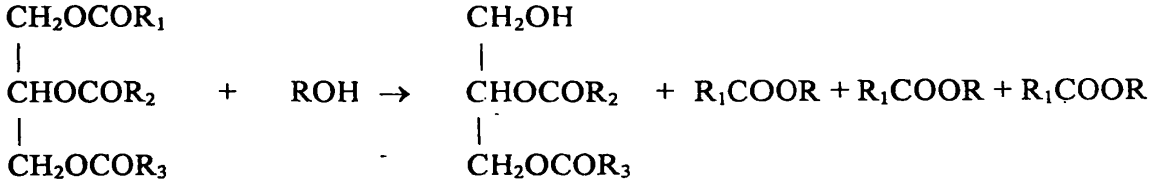
The term **interesterification** refers to reactions in which a fat or other material composed of fatty acid esters is caused to react with fatty acids, alcohols, or other esters with the interchange of fatty acid groups to produce a new ester. Thus, the reaction of an ester with an acid is called acidolysis, the reaction of an ester with an alcohol is called is called alcoholysis and the reaction of one ester with another is termed ester interchange or transesterification(Karleskind et al, 1996).

Acidolysis



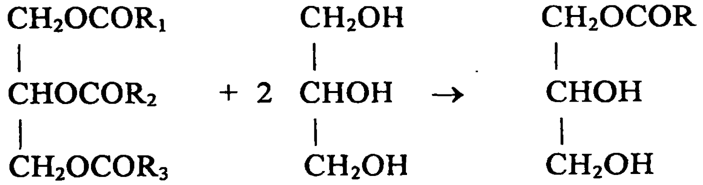
$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array} + RCOOH \rightarrow \begin{array}{l} CH_2OCOR \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array} + R_1COOH$$

Alcoholysis



$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array} + ROH \rightarrow \begin{array}{l} CH_2OH \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array} + R_1COOR + R_1COOR + R_1COOR$$

Transesterification



$$\begin{array}{l} CH_2OCOR_1 \\ | \\ CHOCOR_2 \\ | \\ CH_2OCOR_3 \end{array} + 2\ \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array} \rightarrow \begin{array}{l} CH_2OCOR \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

($R = R_1$, R_2 or R_3)

Main purpose of interesterification process is to reduce the slip point below the body temperature by modifying the structure of the triglyceride (27° C).

1.5.5.Draining

At this step oil blend is washed with 2000 litres of water in order to remove the soap that is formed at the neutralisation process and the interesterification process and other water soluble impurities like gums. The water wash is drained out and collected at the **soap stock** tank. Purified oil blend is subjected to deodorization process.

1.5.5.1.Soapstock

The soap stock from alkali refining is a source of valuable fatty acids. Normally it is acidulated to produce free fatty acids. These are used as a high-energy ingredient in feeds or for chemicals. Soap produced during the neutralization process used to make hard soaps.

The value of soap stock is determined by its total (combined or free) fatty acid content, and this varies considerably according to the method of refining.

Soap stock from batch refining seldom falls below 40 % in total fatty acids and runs as high as 50 %. The product from continuous caustic soda refining is usually between 35 and 40 % in total fatty acids(Formo et al, 1979).

1.5.6. Deodorization

The characteristic odour of an oil or fat is mainly due to the aldehydes and ketones. These are capable of causing rancidity by generating free radicals. To eliminate aldehydes and ketones oil is heated at a temperature of 100^0 c, dried under vacuum of $25'$ Hg, as they are less heat stable.

1.5.7.Bleaching

Standard method of bleaching is by adsorption or treatment of the oil with bleaching earth or carbon.

The various chemical methods are applied in bleaching the edible fats and oils and all those methods depend on oxidation of the pigments to colourless or lightly coloured materials. Most of the refining methods enumerated accomplish considerable reduction of oil. The carotenoids are not all together stable to heat and are converted to colourless compounds by hydrogenation(Formo et al, 1979).

1.5.8. Filtration

Refined oil is filtered through the filter press and collected at the Refined Oil Tank (ROT).

1.6.Introduction to the Analysis

Due to the continuous stirring in the neutraliser small amount of neutral oil could be mixed with the soap that formed during the neutralisation process. When the soap is drained out small amount of oil could be transferred to the soap stock.

Soap is the Sodium salts of fatty acids.

$$\mathbf{(R\text{-}COO^{-}\ {}^{+}Na)}$$

By determining the Total fatty matter (TFM) composition of the soap stock we can have an idea about the actual soap composition of the soap stock.

Therefore it is important to determine the oil loss and the soap formed during the neutralization process by analysing the neutral oil content and TFM in the soap stock.

By analysing the TFM %, FFA % and the Neutral oil content we can determine the efficiency of the oil refinery process and also suggest method to minimize any oil loss during the process. Therefore the TFM % and the neutral oil content of the soap that is been drained out at the draining point of the refinery unit was analysed. The FFA% content of the original oil blend was also determined to correlate the oil loss during the process of neutralization.

CHAPTER 02 – MATERIALS AND METHODS

2.1.Determination of the Total Fatty Matter (TFM) of the soap stock and analysis of the % TFM distribution with the batch number

The TFM % of soap samples obtained from the draining point at the oil refinery unit was analysed for 14 batches of refined oil blends.

2.1.1.Total Fatty Matter (TFM)

The total sum of, saponified fatty acids, free fatty acids and the neutral oil in the soap stock is referred to as total fatty matter (TFM). TFM value is used to determine the quality of the soap stock. The TFM value of the soap stock was determined for 14 batches of margarine. The method is applicable to all types of soap stocks and any type of finished or base soaps.

2.1.1.1.Equipment and Reagents Necessary

Apparatus:

Beaker (400 ml), Electronic balance, Separating funnel (500 ml), Flat bottom flask (250ml), Soxhlet flask (500 ml), Condenser and Hot water bath.

Reagents:

4 N Sulphuric Acid, Diethyl Ether, Methyl orange indicator, and Acetone.

2.1.1.2.Preparation of reagents:

Preparation of 4N Sulphuric Acid:

4 N Sulphuric Acid (H_2SO_4) was prepared by diluting 98 % (w/v) H_2SO_4.

2.1.1.3.Sample Collection Method

All samples were collected on batch basis. That is14 soap stock samples for TFM analysis and 15 soap stock samples for neutral oil content analysis were collected randomly from the draining point of different batches of Astra oil blend that were refined during December 2003 to 31st January 2004.

All glassware were cleaned by acid washing to ensure that there are no other contaminants.

2.1.1.4.TFM Analysis

Twenty-five grams of soap was weighed to a well-washed beaker, 100 ml of water was added and boiled. The resulting soap solution was transferred in-to a cleaned 500 ml separating funnel and 25 ml of 4 N Sulphuric was added, mixed and left in a cold-water bath until room temperature was attained.

In-to the cold solution 100 ml of diethyl ether was added and shaken by releasing the pressure from the valve after every 3-4 shakes.

Solution was allowed to settle for 20 minutes. The water phase was drained out to another separating funnel and was once again washed with 50 ml of diethyl ether. The organic phase was separated from the water phase.

Two ether phases were collected to a separating funnel and was washed with 100 ml of water. A drop of Methyl orange was added and once again was washed with water ensuring that there are no more acids residues in the organic phase.

A dried and cooled flat bottom flask (250 ml) was weighed and the ether extract was transferred carefully to the flask. Ether was evaporated on a water bath using a soxhlet condensation (500 ml) unit. Acetone (3 ml) was added to the residue and was again evaporated on a water bath. The evaporated sample was dried in an oven at 100^0 C for 3 hours and total weight of the residue was obtained(UMA).

2.1.2.Determination of the % Free Fatty Acids in the Crude oil

The value total FFA % in the original oil blend is very important in calculating the oil loss during the oil refinery process.

2.1.2.1 Equipments and Reagents Necessary

Apparatus:

Electronic balance, Titration flask, Burette and Hot water bath.

Reagents:

0.1 N NaOH, 80 % Isopropyl alcohol, Phenolphthalein

2.1.2.2.Analysis of % Free Fatty Acids

The sample collection and cleaning of glassware was done as described in the 2.1.1.3. Twenty-five grams of crude oil was weighed and 80 % isopropyl alcohol was added. The mixture was heated at 60^0 C for five minutes. The heated sample was cooled to the room temperature and titrated with 0.1 N NaOH using phenolphthalein as indicator(UMA).

2.2.Determination of the neutral oil content in the soap stock and analysis of the neutral oil (%) distribution

2.2.1.Definition

Neutral oils are the triglycerides of fatty acids. This method allows us to determine the total unsaponified neutral oil (fatty matter) and is applicable to all types of Soap stocks. The neutral oil % will determine the efficiency at the draining point of the refinery process.

2.2.2.Equipment and Reagents Necessary

Apparatus:

Glass - Stoppered cylinder (250 ml), Separatory Funnel (500 ml), Beaker (400 ml) or Soxhlet flask and Flat bottom flask (500 ml)

Regents:

Potassium Hydroxide (14 % by weight), Ethyl alcohol (50% by volume), Ethyl alcohol (10% by volume), Petroleum Ether

2.2.2.1.Preparation of reagents

A solution of 14 % (w/w) Potassium Hydroxide was prepared by dissolving 14 grams of KOH pellets in distilled water until the total weight become100g.

Fifty percent and 10 % Ethyl alcohol (EtOH) was prepared by diluting 95 % EtOH.

2.2.3.Determination of Neutral Oil Content

The soap stock sample was mixed thoroughly and 8 g to 10 g was weighed into an extraction cylinder. A volume of 125 ml of 50% ethyl alcohol, 50 ml of petroleum ether were added and shaken until a homogeneous mixture was obtained.

The resulting mixture was cooled to 20-25^0 C and 10 ml of aqueous KOH 14 % (w/w) was added and agitated gently until thoroughly mixed.

A volume of 25 ml of 50% ethyl alcohol was added to the mixture and agitated gently until thoroughly mixed and allowed to settle until the two layers were completely separated.

Ether / oil layer was siphoned in into a 500 ml separatory funnel. Another four more similar extractions were made on the original solution using 50 ml of petroleum ether for each extraction and all ether fractions were combined in the separator funnel.

Ether extract was washed with 25 ml portions of 10% ethyl alcohol, shaking vigorously each time, until the washings were neutral to phenolphthalein. The neutral ether extract was filtered through the filter paper and the filter paper was washed with the petroleum ether. The ether extraction was transferred in to a weighed flat bottom flask, which has been previously dried and cooled in a desiccator. The ether was evaporated using a water bath and the remainder in the flask was dried in an oven at 105^0 C for 30 minutes.

The total weight of the remainder was measured using an analytical balance.

(A.O.C.S. 1997).

All data received were statistically analysed using Minitab statistical package.

CHAPTER 03 - RESULTS AND CALCULATIONS

3.1.Results of Total Fatty Matter and Free Fatty Acids

Calculations of the Percentage of Total Fatty Matter

w – Sample weight

w_1 – Weight of the dried flat bottom flask

w_2 – Total weight of the residue and the flat bottom flask

$$\% \text{ TFM} = \frac{(w_2 - w_1)}{w} * 100$$

Calculations for percentage FFA:

Weight of the sample = W
Volume of 0.1 N NaOH required = V
Normality of NaOH = N
Molecular weight of Fatty acid = M

$$\% \text{ FFA} = \frac{V * N * M}{10 * W}$$

The Results obtained for the TFM % and FFA% are tabulated in the table 3.1.

Table 3.1 Results of TFM % and FFA %

Date	Batch	Sample No	FFA (%)	NaOH (litres)	w (g)	w_1 (g)	w_2 (g)	% TFM
01/12/03	1759/60	1	0.12	13	24.90	102.6267	103.1240	1.997
04/12/03	1779/80	2	0.18	20	22.03	102.6279	104.0003	6.229
05/12/03	1787/88	3	0.17	19	25.05	102.6230	104.0232	5.589
10/12/03	1828/29	4	0.18	20	21.54	102.6280	104.0812	6.745
12/12/03	1836/37	5	0.18	20	21.28	102.6342	104.6033	9.253
13/12/03	1853/54	6	0.15	16	25.75	102.8344	103.5702	2.857
16/12/03	1857/58	7	0.16	18	26.60	102.4450	103.8720	3.861
17/12/03	1874/75	8	0.16	18	20.26	102.6249	103.4436	4.040
22/12/03	1915/16	9	0.11	12	28.13	102.6209	103.1240	1.753
05/01/04	1920/21	10	0.18	20	25.83	102.6226	104.5400	7.400
06/01/04	25/26	11	0.18	20	26.14	102.8453	103.9783	4.334
08/01/04	36/37	12	0.14	15	20.50	102.6137	103.0933	2.339
09/01/04	45/46	13	0.18	20	24.81	102.8332	104.3788	6.229
12/01/04	57/58	14	0.18	20	25.51	102.8366	104.6469	7.235

3.1.1. Statistical Interpretation of Percentages of Total Fatty Matter

Results were interpreted using Minitab statistical software. The Descriptive statistics, Skewness, Kurtosis, Regression analysis between FFA % and TFM %, Time series analysis of the distribution were interpreted. To analyse the descriptive statistics, Anderson-Darlin test was used.

3.1.1.1.Descriptive statistics

3.1.1.1.1.Definitions

Mean (x') $= \frac{{}^{N}\sum x}{N}$

Median $= x_a + \frac{(0.50\ N - \text{cumulative } f_a)}{f_m} (x_b - x_a)$

Where x_a is the lower class limit of the median interval

x_b is the upper class limit of the median interval

Cumulative f_a is the number of observations below the median level

f_m is the number of observations below the median interval

Variance $= s^2 = \frac{{}^{N}\sum (x - x')^2}{N}$

Kurtosis

Kurtosis is a term that refers to the " peaked ness " or " flatness " of a frequency polygon.

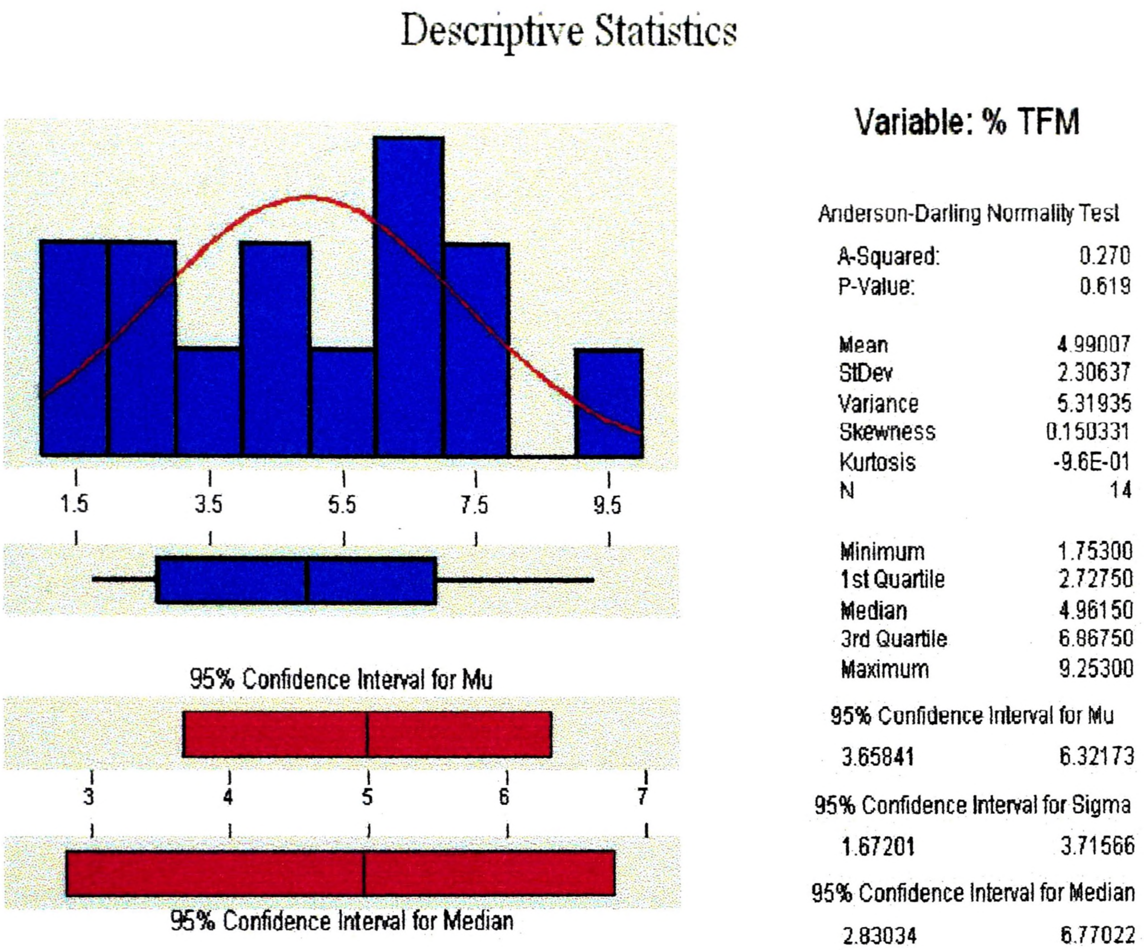
Kurtosis $= \frac{{}^{N}\sum (x - x')^4}{N\ s^4}$

Skew ness $= 3\ \frac{(\text{Mean} - \text{Median})}{s}$

Confidence interval – A confidence interval is a range of values, w1 to w2 that is expected to include the population parameter θ.

First Quartile (Q1) $= \frac{N}{4}$ th place of the data set

Third Quartile (Q3) $= \frac{N}{4} * 3$ rd place of the data set



```
Variable: % TFM

Anderson-Darling Normality Test
 A-Squared:              0.270
 P-Value:                0.619

 Mean                  4.99007
 StDev                 2.30637
 Variance              5.31935
 Skewness             0.150331
 Kurtosis             -9.6E-01
 N                          14

 Minimum               1.75300
 1st Quartile          2.72750
 Median                4.96150
 3rd Quartile          6.86750
 Maximum               9.25300
 95% Confidence Interval for Mu
 3.65841               6.32173
95% Confidence Interval for Sigma
 1.67201               3.71566
95% Confidence Interval for Median
 2.83034               6.77022
```

Figure 2 The descriptive statistics for % TFM

According to the descriptive statistics;

Mean value of the TFM (%) = 4.99 ± 1.33 and the standard deviation of the results = 2.31 ±1.02.

The skewness of the distribution = 0.15. Kurtosis of the distribution = – 9.6E-01. Therefore the peakness of the distribution is higher than the normal. That is equal number of observations lie below and above the mean.

3.1.1.2.The time series plot of % TFM

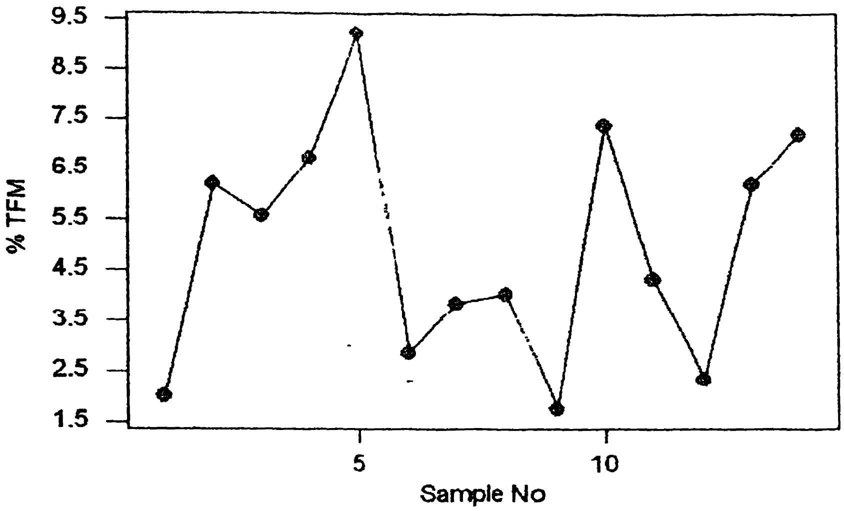


Figure 3. The variation of % TFM is plotted against the batch number

The time series plot (figure 3) shows that the % TFM is fluctuating irregularly with respect to the batch within the range of 1.753 to 9.253.

3.1.1.3.The time series plot of % FFA

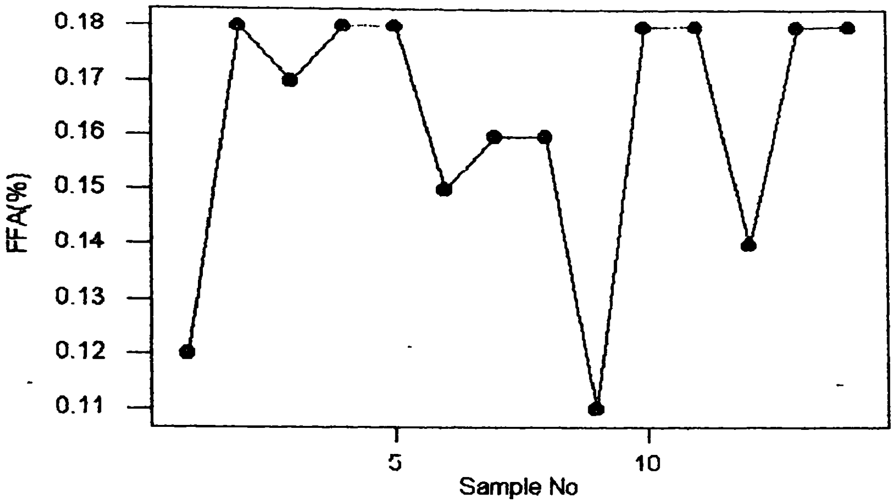


Figure 4 The variation of % FFA plotted against the batch number

The % FFA is fluctuated irregularly in the range of 0.11 to 0.18. Free fatty acid value of seven batches is 0.18.

3.1.1.4.Polynomial Regression Analysis: % TFM versus FFA (%)

The regression equation is

% TFM = 21.4938 - 329.930 FFA (%) + 1379.20 FFA (%)**2

S = 1.10927 R-Sq = 80.4 % R-Sq(adj) = 76.9 %

3.1.1.4.1.Analysis of Variance

Source	DF	SS	MS	F	P
Regression	2	55.6163	27.8082	22.5996	0.000
Error	11	13.5352	1.2305		
Total	13	69.1515			

Hypothesis:

H_0: There is no quadratic relationship between % TFM and % FFA.

H_1: There is a quadratic relationship between % TFM and % FFA.

P = 0.00 < 0.05. Therefore H_0 is rejected and H_1 is accepted.

R-Sq = 80.4 % > 75 %.

There is a strong quadratic relationship between % TFM and % FFA at 95 % confidence level.

3.1.1.4.2.Unusual Observations

Observation	FFA(%)	% TFM	Fit	SE Fit	Residual	St Resid
5	0.180	9.253	6.459	0.423	2.794	2.37R
9	0.110	1.753	0.700	0.828	1.053	1.12 X

3.1.1.5.Fitted Quadratic plot of % TFM Vs % FFA

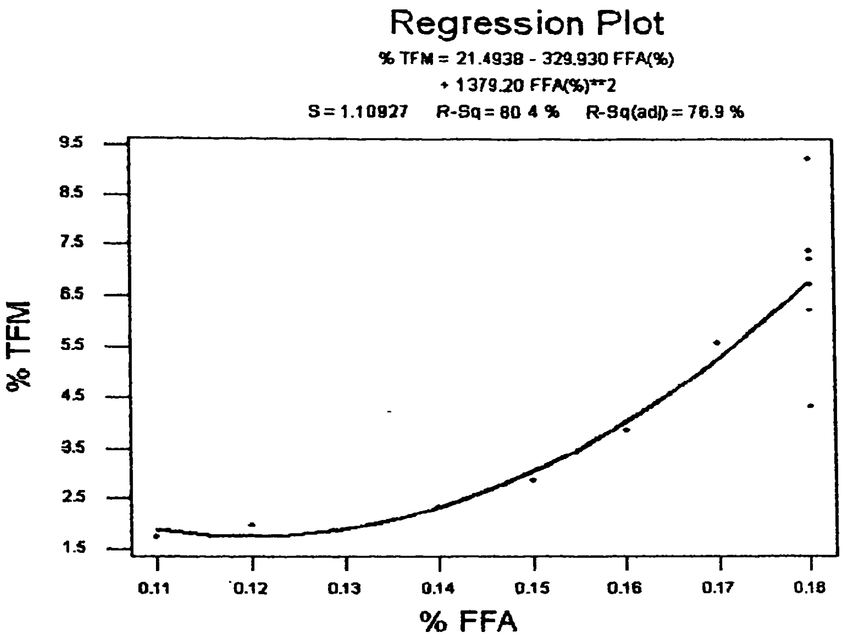


Figure 5 The variation of % TFM with respect to % FFA

R-Sq = 80.4 % > 75 %, that is the quadratic relationship between % TFM and % FFA is strong.

The regression equation is;

% TFM = 21.4938 - 329.930 FFA (%) + 1379.20 FFA (%)**2

3.2. Results of Neutral Oil Content

Calculations

$$\text{Neutral oil percentage} = \frac{(w_2 - w_1)}{w} * 100$$

w – Sample weight

w_1 – Weight of the flat bottom flask

w_2 – Total weight of the remainder and the flat bottom flask

The data obtained for the neural oil content are tabulated in the table 3.2 .

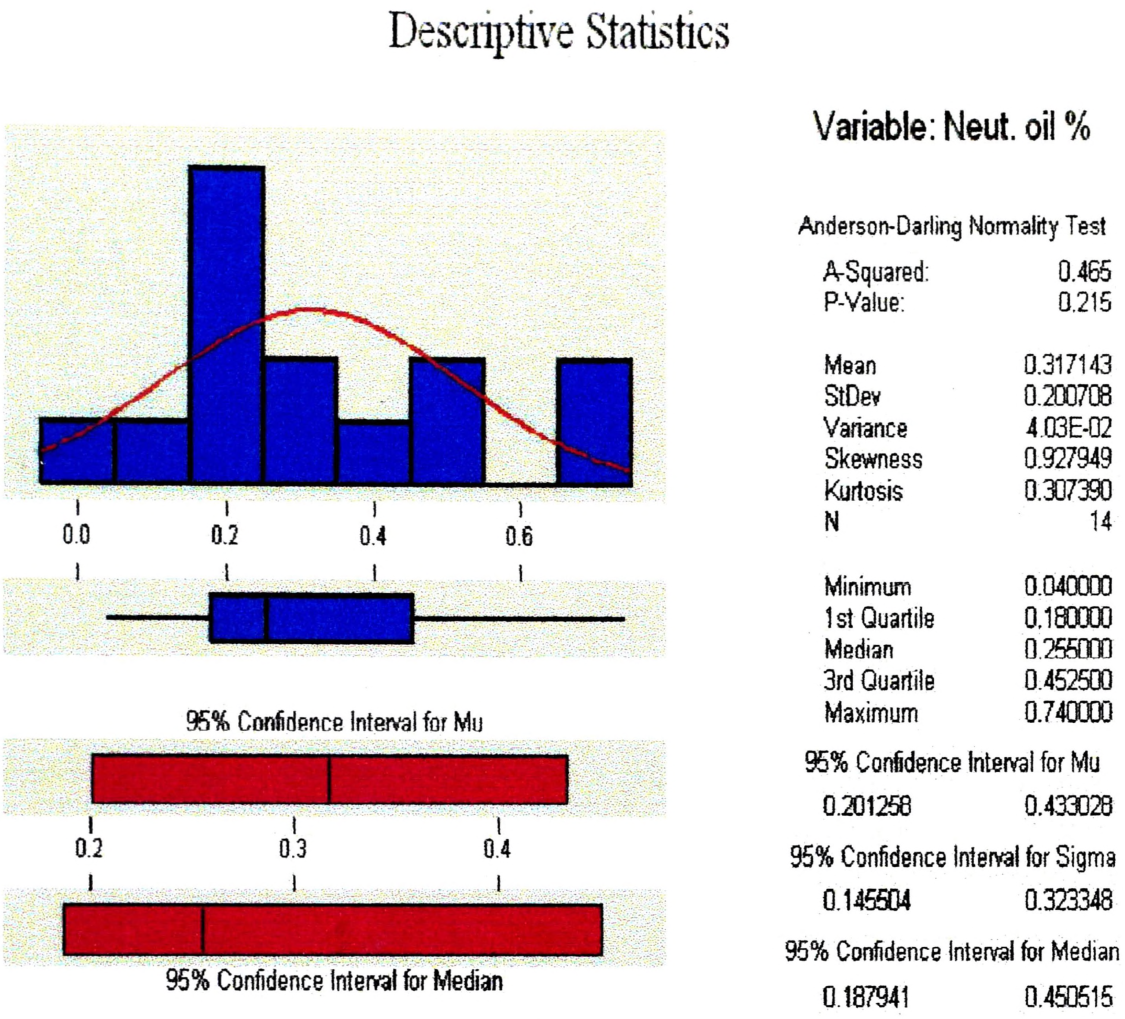
Table 3.2 Results for (%) Neutral oil

Date	Batch	Sample No	w (g)	w_1 (g)	w_2 (g)	Neutral oil (%)
01/12/03	1759/60	1	10.66	143.9150	144.1210	1.93
04/12/03	1779/80	2	10.00	143.9136	143.9880	0.74
05/12/03	1787/88	3	10.36	143.9150	143.9380	0.22
10/12/03	1828/29	4	10.44	143.9100	143.9780	0.66
12/12/03	1836/37	5	10.12	143.9150	143.9620	0.46
13/12/03	1853/54	6	9.57	143.9140	143.9400	0.27
16/12/03	1857/58	7	10.02	143.9152	143.9288	0.13
17/12/03	1874/75	8	10.57	143.9098	143.9260	0.15
22/12/03	1915/16	9	10.03	143.9100	143.9337	0.24
05/01/04	1920/21	10	10.15	143.9130	143.9336	0.20
06/01/04	25/26	11	9.58	143.9050	143.9480	0.45
08/01/04	36/37	12	9.14	143.9148	143.9185	0.04
09/01/04	45/46	13	10.75	143.9135	143.9339	0.19
12/01/04	51/52	14	9.14	143.9036	143.9340	0.33
12/01/04	57/58	15	10.52	143.9020	143.9402	0.36

3.2.1.Statistical Interpretation of the results of Neutral Oil Content:

Results were interpreted using Minitab statistical software. The Descriptive statistics, Skewness, Kurtosis and the time series distribution were tested. To analyse the descriptive statistics, Anderson-Darling test was used.

3.2.1.1.Descriptive Statistics



```
Descriptive Statistics

Variable: Neut. oil %

Anderson-Darling Normality Test
  A-Squared:          0.465
  P-Value:            0.215

  Mean                0.317143
  StDev               0.200708
  Variance            4.03E-02
  Skewness            0.927949
  Kurtosis            0.307390
  N                         14

  Minimum             0.040000
  1st Quartile        0.180000
  Median              0.255000
  3rd Quartile        0.452500
  Maximum             0.740000

95% Confidence Interval for Mu
  0.201258            0.433028
95% Confidence Interval for Sigma
  0.145504            0.323348
95% Confidence Interval for Median
  0.187941            0.450515
```

Figure 6 The descriptive statistics for % Neutral oil

According to the descriptive statistics the mean value of the (%) neutral oil = 0.32±0.13 and the standard deviation of the distribution of (%) neutral oil = 0.20 ± 0.09.

Skewness of the distribution = 0.93, that is the distribution is positively skewed and the Kurtosis of the distribution = 0.31, that is the distribution is flatter than the normal. According to the Skewness and the kurtosis, the number of observations around and below the mean value is high.

3.2.1.2.The time series plot for the (%) neutral oil in the soap stock

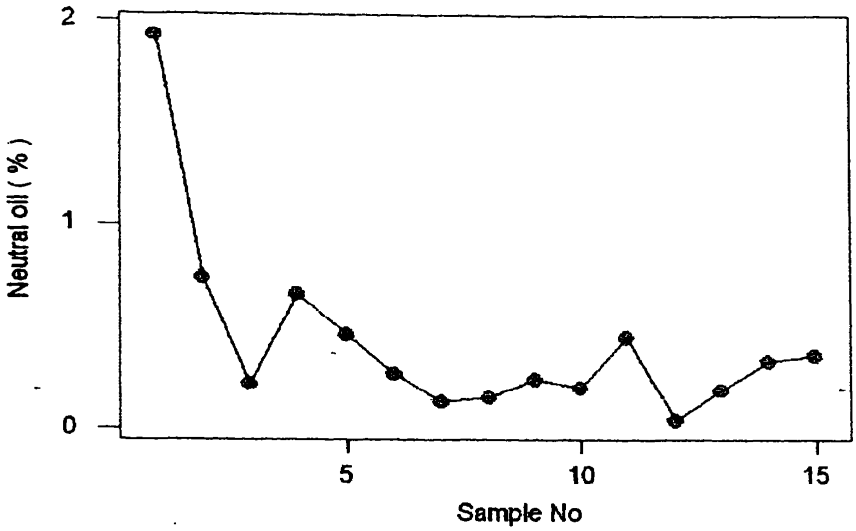


Figure 7 The variation of % TFM with the batch number

The time series plot shows that the neutral oil % is fluctuating irregularly with respect to the batch number within the range of 0.04 to 1.93.

CHAPTER 04 - DISCUSSION

4.1.TFM Analysis

Determining the Oil loss during the neutralization process was a very important factor to determine the efficiency of the process. According to the Analysis of the total Fatty matter, the fatty matter content has fluctuated within the range of 1.75% to 9.25 % (Figure 3). The variation observed could be due to the samples obtained for analysis are from different oil blends. Therefore the variations in the fatty acid composition original oil sample could contribute to this type of variations. The above type of variations could be seen due to the operational factors such as draining and stirring and also due to, crude oil storage conditions and changes in strength of NaOH used for the neutralisation process.

According to the descriptive statistics, Mean value of the TFM (%) was 4.99 ± 1.33 and the standard deviation of the results is 2.31 ±1.02.

The skewness of the distribution was 0.15. That is the distribution of TFM (%) is positively skewed. Kurtosis of the distribution was – 9.6E-01. Therefore the peakness of the distribution is higher than the normal. That is equal number of observations lie below and above the mean.

With the Analysis of the FFA % content of the oil bend also supports the above justification on the fluctuation of the % TFM. The % FFA content also fluctuates within the range of 0.11 % to 0.18 %(Figure 4).

According to the above data when comparing the % FFA and %TFM values the fluctuations lie in the same fashion. This could be an indication the oil loss due to the neutralization process is minimum. This also means that the parasitic saponification during the oil refinery process is minimum.

4.2.Neutral oil content analysis

According to the analysis of the neutral oil content in the soap the content mainly lies within the range of 0.04 % to 0.74 % except in the batch 1759/60 the oil content was 1.93 %. This is due to poor draining procedures followed and the mixing of neutral oil with the soap due to the continuous stirring in the neutraliser.

According to the descriptive statistics the mean value of the (%) neutral oil = 0.32±0.13 and the standard deviation of the distribution of (%) neutral oil = 0.20 ± 0.09.

Skewness of the distribution = 0.93, that is the distribution is positively skewed and the Kurtosis of the distribution = 0.31, that is the distribution is flatter than the normal. According to the Skewness and the kurtosis, the number of observations around and below the mean value is high(Figure 6).

According to the time series plot the (%) neutral oil content has been fluctuated irregularly during the two months of analysis(Figure 7).

It is difficult to determine the actual oil loss since the actual fatty acid composition of the original oil blend and their actual molecular weights are unknown. By performing a GC analysis composition of the original oil blend could be obtained and these results could help in the calculation of actual oil loss. According to the results obtained the oil loss is maintained within a minimum practical possible value 0.317 ± 0.13.

CHAPTER 05 – CONCLUSSION

5.1.TFM Analysis

According to the descriptive statistics; Mean value of the TFM (%) = 4.99 ± 1.33 and the standard deviation is 2.31 ±1.02.The distribution of TFM (%) is positively skewed.
Kurtosis of the distribution shows that the peakness of the distribution is higher than the normal and equal number of observations lie below and above the mean(Figure 2). The TFM (%) of the soap stock varied irregularly during the two months(Figure 3) and a strong quadratic relationship between the TFM (%) and the FFA (%)(Figure 5).

5.2.Neutral oil content analysis

The (%) neutral oil content is 0.32±0.13 and the standard deviation of the distribution is 0.20 ± 0.09. The distribution is positively skewed. Kurtosis shows that the distribution is flatter than the normal. Most of the (%) neutral oil values exist below the mean value(Figure 6).
The results (%) neutral oil content has been fluctuated irregularly during the two months of analysis but at a very low level(Figure 7).

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