ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSITUTE OF TECHNOLOGY

DEPARTMENT OF CHEMICAL ENGINEERING

Extraction, characterization and optimization of castor oil from Castor seeds for production of synthetic detergent

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A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, Department of Chemical Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in Chemical Engineering under Process Engineering stream

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Acronyms and Notations

FFA	Free fatty acid
S.V	Saponification value
I.V	Iodine vale
A.V	Acid value
Sp.gr	Specific gravity
FDA	Food Drug Administration
NFPA	National Fire Protection Association
EN	European Normalization
EC	European Community
EEC	European Economic Community
ISO	International Organization for standardization
MBAS	Methylene Blue Active Substance
LABS	Linear Alkyl Benzene Sal phonate
ANOVA	Analysis of Variance
ABCD	Interaction of the amount of castor oil, sodium hydroxide, sodium silicate and sodium sulphate
V/V	Volume per Volume
V/W	Volume per weight
F	Amount of Feed for extraction
L	Amount of solvent for extraction
M	Mixed point of leaching
Xsolv	Mole fraction of solvent
Mt	Total mass amount
X_A	Mole fraction of liquid
M_A	Amount mass of substance 'A'
M_B	Amount mass of substance 'B'

X_{Mt}	Mole fraction of the total mass
FCI	Fixed Capital Investment
TPC	Total Product Cost
DF	Discount Factor
Df	Degree of Freedom
MOR	Minimum Rate of Return
NPV	Net present value
PV	Present value

Abstract

Non-biodegradability process and non-solubility of mineral oil soap and synthetic detergent products cause to pollute fresh tap water. To overcome this problem replacing of the raw material of mineral oil by vegetable oil is the possible solution. Therefore; the objective of this study was extraction and optimization of castor oil from Castor seed for production of synthetic detergent. The extraction was carried out using soxhlet extraction units. In the soxhlet extraction a n-hexane was chosen to determine the effect of time and particle size on yield of the extraction oil.

For the soxhlet extraction, the minimum oil yield has been determined as 24.7% after the extraction time of 2hours with particle size of 4mm and maximum oil yield 49.34% was found at the extraction time of 6hours in a particle size ranges from 2.55mm. Therefore, increasing extraction time and decreasing particle size will increase the amount of oil extracted. The research also revealed some properties of castor oil in terms of values obtained by the determination of saponification value of 172.4oil as proportional to the standard saponification of value of 177oil and the acid value (AV) of 11.22 maximum than the standard acid value of 10. Other parameters used to determine the quality of castor oil include specific gravity and pH tests. For the agitated mixing, the best quality (1.8cm of height foamability, 8.52 minimum pH value and good cleansing power) of silk fabric detergent was obtained. Therefore, increasing surfactants and decreasing caustic soda and vice versa adjusted the alkalinity of the detergent. And also increasing sodium silicate with sodium sulphate increases the cleansing power and foamability height of the produced detergent respectively.

This paper work concludes that castor oil is good solvent for the production of synthetic detergent. However, as this paper use of only four ingredients is not enough for good quality of silk fabric detergents. Hence using other ingredients like optical brightness and enzymes was recommended for more good quality of synthetic detergents.

1. INTRODUCTION

1.1.Background

The washing industry, usually known as soap industry, has roots over 2000 years, a soap factory having been found in the Pomp excavation. However, among the many chemical process industries, none has experienced such a fundamental change in a raw material as have the washing industry. Soap itself was never actually "discovered", but instead gradually evolved from crude mixture of alkaline and fatty acid.

Scientifically, the term detergent covers both soap and synthetic detergent, or "syndets" but it is widely used to indicate synthetic cleaning compounds as distinguished from soap. Detergent differs from soap in their action in hard water. Although soaps are excellent cleaners, they do have disadvantages. As salts of weak acids, they are converted by mineral acids in free fatty acids. These fatty acids are less soluble than the sodium or potassium salts and form precipitate or soap scum.

Because of these, soaps are ineffective in acidic water. Also soaps form insoluble salts in hard water such as water containing magnesium, calcium or iron. The insoluble salts from bath rub rings, leave film that reduce hair luster, and gray/roughen textiles after repeated washings. Synthetic detergents, however, may be soluble in both acid and alkaline solutions and do not form insoluble precipitate in hard water **[1]**.

Many of the activities of man, starting from the primitive techniques to today's high technological industrial activities have in small or large ways impacted on man and his environment while the various products developed are highly desirable for the enhancement of the citizenry's well being and sustenance of the nations' economy. The impacts precipitated may be catastrophic if allowed to build up and uncontrolled. Industrial revolution and evolution have been targeted principally at satisfying immediate changing demands rather than tailored towards a structured, wholesome and guided global program that will satisfy not only temporary human needs but are environmentally safe. The result of this is an increasing ecological degradation that has severely polluted water, land and air **[2]**.

The detergent and soap making industries are no exceptions to the above trends for while they provide us with cleansing agents, their processing and by-products are also a cause of public concern. For instance, detergents, unlike soaps, have proved very effective cleansing agents in hard and cool water whereas soap is often ineffective under such conditions.

It was observed, however that many of these detergents were neither soluble nor biodegradable, that is they were so stable that when they flow into the soil in laundry sewage water, they remain unchanged resisting conversion into less complex and more soluble substances. They thus, create suds and foams in fresh tap water, naturally occurring ground and surface waters.

To correct these odds require that environment issues be considered at the initial stages of conceptualization and development of synthetic detergents and other products as well. This will not only reduce pollution to the barest minimum but also save costs of treating these products. A deep knowledge and good manipulation of the process chemistry with a view to eliminating wastes is the most viable means of achieving this objective.

Above 75 percent of detergents used in the early 1960s were for the most part made with alkyl benzene, made from propylene tetramer coupled to benzene, Tetra propylene is a very highly branched alkyl molecule. Research into the bacteria decomposition of alkyl based detergents showed that branched molecules are indigestible to the bacteria that must decompose the detergents when they reach the ground. To be biodegradable, a detergent should be based on straight chain alkyl molecule; example of straight chain is ricinoleic acid obtained from the castor bean.

This research work is aimed at studying the replacement made to the biodegradable detergents. Production of environmentally friendly synthetic detergents (soft detergents) from castor oil has the dual advantages of using locally sourced raw materials that can be grown and generating wastes that are appetizing to micro organisms (bacteria).

1.2.Problem statement

Production of detergents in the world was developed due to both a displacement of fatty soaps, and due to the increase of the total consumption of detergents. The most widely used are detergents in a powdered form, in particular those for domestic use. During the last decade, the release of liquid detergents increased significantly, mainly for industrial applications. This is due to the fact that during the use and storage of detergents in liquid form their drying is excluded, liquid compositions do not give up dust, they are easily dispensed, can be quickly and easily mixed with water. In addition, liquid detergents can be conveniently transported in rail tank cars, tank trucks and drums.

Currently, synthetic detergents are used for washing textiles, cleaning household items, vehicles and equipment. In addition, in the industry they facilitate technological processes in the bleaching and dyeing of fabrics, furs and skins. And also many of mineral detergents were neither soluble nor biodegradable, that is they were so stable that when they flow into the soil in laundry sewage water, and they remain unchanged, resisting conversion into less complex and more soluble substances. They create suds and foams in fresh tap water, naturally occurring ground and surface waters. To correct these odds require that environment issues be considered at the initial stages of conceptualization and development of synthetic detergents well and the vegetable oil component of detergent has more advantage on the reducing of fungal infections, sunburn and inflamed skin. Due to all this purposes, vegetable (castor oil) detergent is better than the other mineral detergents.

1.3.Objectives

1.3.1. General objectives

The general objective of this research is to develop the process of extraction and optimization of castor oil from Castor seeds for production of synthetic detergent.

1.3.2. Specific objectives

- ✓ To characterize castor oil.
- ✓ To characterize silk fabric synthetic detergent production from castor oil.
- ✓ To study the effects of operating conditions and ingredients type on the quantity and quality of the silk fabric synthetic detergent.
- ✓ Cost analysis of silk fabric synthetic detergent production from castor oil using phosphate free additives.

1.4.Significance of the study

This paper is aimed at the replacement of mineral detergent which makes precipitate in hard water with synthetic detergent from the castor oil. By doing so the first beneficial will be farmers who are going to prepare a farm of this plant. This is because they will be raw material suppliers for the industries that are engaged in the production of castor based synthetic detergent.

For the country like Ethiopia in which 85% of its people follow agriculture based way of life, such type of project is going to upgrade the society economic status. This type of product will minimize using mineral based detergents by replacing them with biodegradable and renewable synthetic detergent which has better important for textile, fabrics and toilet washes. The relevance of the production and use of synthetic detergents, which have the following advantages:

1. Production of synthetic detergents is based on a cheap raw material base the products of processing of petroleum and gas. The calculations show that the cost of production of synthetic detergents is not more than 65-70% of the cost of production of the 47% common soap. Implementation of a broad program for the production of detergents allows freeing up a large amount of a dietary fat.

2. Synthetic detergents do not interact with the salts of hard water or the reaction yields products, which are easily removed from the fabric. Many synthetic detergents equally well clean in soft and hard water, and some even in seawater.

2. Literature review

2.1.Introduction

The first detergent to be utilized by man was soap, an innovation traditionally attributed to ancient Egyptian culture. However, when the word detergent is used today, it is assumed to refer to the synthetic detergents (tenside, syndets or surfactants), which have assumed increasing chemical and economic importance in the post-world war periods. The first synthetic detergents were developed by the Germans during the First World War period.

In the late nineteen-twenties and early thirties long-chained sulphonate-alcohols were sold as neutralized sodium salts. This metamorphosed to the long-chain alkyl aryl sulphonates sodium salts with benzene as the aromatic nucleus. The alkyl portion was from the kerosene fraction produced from petroleum industries. In the United Kingdom, Teepol a secondary Olefin sulphate from petrochemical sources was produced and still being produced in England and Western Europe to this day. The worldwide manufacture of synthetic detergents has increased from the 1949 level of 30,000 tons to an estimated 1.5 to 2 million tons per year **[3]**.

Cleaning agents traditionally include synthetic detergents and soap, as well as materials to supplement their action: bleaches, conditioners, washing salts, restorers of color, soaking materials, and stain removers. The main purpose of detergents is the cleaning of objects, surfaces, fabrics and articles made of textile and non-woven fabrics from pollutions of different nature. There are different types of feed stocks that are used for the production of synthetic detergent. These include linseed oil, palm seed oil, castor seed oil, sunflower seed oil, jatropha seed oil and animal fats. Oilseed plants are used for the production of synthetic detergent through the process called saponification reaction which is a process by which any ester converted to an alcohol and salt by alkaline hydrolysis process in the presence of other additives chemicals. Oils that are extracted from plants have been used in this world since the ancient times and already used in many cultures. As an example the castor plant has been known to man for ages. Castor beans have been found in ancient Egyptian tombs dating back to 4000 B.C and during that time, the castor oil was used thousands of years ago in the wick lamps for lighting. In Ethiopia the castor plant found in Easter and Western Oromiya,

Amahara, Arba Minch, Harar, Gambella and Tigray with different varieties (i.e. in color; red brown, and white).

2.1.1 Castor oil (Ricinus Oil)

Ricinus communis Linn is a tall glabrous and glaucous annual sometimes shrubby or almost small tree, 2-4 m high; found through India, mostly growing wild on waste land and also cultivated for its oil seeds **[4]**. The Ricinus communis Linn is described on figure 2.1a below.

2.1.2 Castor bean flowers and fruits

Flowers occur most of the year in the dense terminal clusters (inflorescences), with female flowers just above the male flowers. This species is clearly monoecious, with separate male and female flowers on the same individual. There are no petals and each female flower consists of a little spiny ovary (which develops into the fruit or seed capsule) and a bright red structure with feathery branches (stigma lobes) that receives pollen from male flowers. Physically figure 2.1b describes the flowers and fruits of the castor bean.

2.1.3 Castor seeds

The shiny seeds of castor plants are a little larger than pinto beans and have very beautiful and intricate designs. At one end a small, spongy structure called the caruncle, which aids in the absorption of water when the seeds are planted. They are unquestionably among the most deadly seeds on earth, and it is their irresistible appearance that makes them so dangerous **[5]**. Figure 2.1c below shows the structure of shiny seeds of castor plants.

(a)

(b)

(c)

Figure.2.1 Castor plant cultivation phase (*Source: http://en.wikipedia.org/wiki/Castor and laboratory image*)

2.1.4) Phytochemistry of castor seed

Per 100g, the leaves are reported to contain on a zero-moisture basis, 2670mg calcium, and 460mg phosphorous. The leaves contain isoquercetin 2-5 dihydroxy benzoic acid and epicatechin. They also contain rutin, hyperoside, quercetin, chlorogenic acid, neochlorogenic acid and gallic acid.

The seed contains 5.1-6% moisture, 12-16% protein, 45-50.6% oil, and 2-2.2% ash. Seeds are high in phosphorus, 90% in the phytic form. Seed coat contained 62% lipids and higher amounts of phosphatides and non-saponifiable matter than seed kernel. Roots, stems and leaves contain several amino acids. Flowers gave apingenin, chlorogenin, rutin, coumarin and hyperoside. Castor oil is consists principally of ricinoleic acid with only small amounts of dihydroxystearic, linoleic, oleic, and stearic acids **[5]**.

2.2) Chemistry of castor oil

Plants oils are typically composed of triglyceride molecules (technically called esters) composed of a 3-carbon alcohol (glycerol) plus three 18-carbon (or 16-carbon) fatty acids. Unlike the saturated fatty acids of animal fats which are solid at room temperature, plant fatty acids are typically unsaturated and liquid at room temperature, with one or more double bonds between the carbon atoms (mono-unsaturated and polyunsaturated).

Relative to other vegetable oils, castor oil has different physical and chemical properties which vary with the method of extraction the oil. The castor oil that obtain from the cold pressing has low acid value with low iodine value and has slightly higher saponification value compared to the solvent-extracted oil, and the oil is lighter in color **[3]**. CasChem supplies a variety of castor oil grades whose uses are dictated by acid value, moisture level, color and purity. Castor oil also known as ricinus oil is a triglyceride of fatty acids which occurs in the seed of the castor plant. The ricinoleic acid comprises over 84% of the total fatty acid composition. Other fatty acids present were linoleic (7.3%), oleic (5.5%), palmitic (1.3%), stearic (1.2%) and linolenic (0.5%). For the purpose of this study free fatty acid, iodine value, acid value and saponification value matter were reviewed.

2.2.1) Free Fatty Acid

High concentrations of free fatty acids are undesirable in crude oils because they result in large losses of the neutral oil during refining. In crude fat, free fatty acids estimate the amount of oil that will be lost during refining steps designed to remove fatty acids **[6]**.

High levels of free fatty acids especially linolenic acids are undesirable in finished oils because they can cause off favours and shorten the shelf life of oils. The quantity of free fatty acid in oil is an indicator of its overall quality. They may be formed through hydrolysis or in the advanced stages of oxidation. An excessive amount of free fatty acids lowers the smoke point of oil and will cause 'popping' of the oil during cooking. High quality oils are low in free fatty acids.

2.2.2) Iodine Value

Iodine value is a measure of the unsaturation of fats and oils, and is expressed in terms of the number of centigrams of iodine absorbed per grams of the sample (% iodine absorbed) during oxidation, which consumes the double bonds resulting in a reduction in iodine. It is an indicator for double bindings in the molecular structure, which influences the long term stability properties of the oil (important for storage). Oils having high iodine number are polyunsaturated indicating the degree of unsaturation and are desired by oil processors, while a lower iodine number is indicative of lower quality. The determination of the iodine value is important in the classification of fats and oils. The classification is as follows:

a) Drying fats and oils: oils with an iodine value of 130-200,
b) Semi drying fats and oils: oils with an iodine value of 100-130, and
c) Non-drying fats and oils: oils with an iodine value lower than 100.

Castor oil is generally classified among non-drying fats and oils.

2.2.3) Acid Value

Acid value is the number of milligrams of potassium hydroxide necessary to neutralize the free acids in one gram of oil sample. The samples that contain virtually no free acids other than fatty acids, the acid value may be directly converted by means of a suitable factor to

percent free fatty acids. Where vegetable oils are used as lubrication products, the acid value can affect the properties of the lubrication oil, if larger quantities reach the oil sump.

2.2.4) Saponification Value

Saponification is the chemical reaction in which an ester is heated with an alkali (especially the alkaline hydrolysis of a fat or oil to make soap). Saponification value is however, the amount of alkali necessary to saponify a definite quantity of oil sample. It is a measure of the average molecular weight (or chain length) of all the fatty acids present. As most mass of a fat is in the three fatty acids, it allows for comparison of the average fatty acid chain length. The smaller the saponification value, the longer the average fatty acid chain **[6]**.

Table 2.1: Physio-chemical characteristics of castor oil in different situation

Properties	Cold-pressed oil	Solvent extraction oil	Dehydrated oil
Specific gravity	0.961-0.963	0.957-0.963	0.962-0.937
Acid value	3	10	6
Iodine value	80-88	82-89	125-145
Saponification value	179-185	177-182	185-188

Source: Ogunniyi, (2006)

2.3) Different types of detergent/soap making oils

Fats and oils are esters of different fatty acids and glycerol. Fats and oils are divided into three classes, fixed oils, mineral oils and essential oils. Fixed oils form the main raw materials for soap making as they decompose into fatty acids and glycerol when strongly heated, and can be easily saponified by alkali. Fixed oils, which include both animal and vegetable fats and oils, are classified as follows.

- Nut oils
- Hard Fats
- Soft Oils
- Castor Oils

Castor Oil: - The oil is obtained from extracting or expressing the seed of a plant which has the botanical name Ricinuscommunis. The oil is not only a naturally-occurring resource; it is inexpensive and environmentally friendly. Castor oil is viscous, light yellow, non-volatile and non-drying oil with a bland taste and is sometimes used as a purgative. Relative to other

given vegetable oils, it has a good shelf life and it does not turn rancid unless subjected to excessive heat. Hence this paper focused on this oil for production of synthetic detergents.

2.4) Uses of castor oil

Although the castor oil is not edible oil, it is more versatile than other vegetable oils as the castor oil is widely used as a starting material for many industrial chemical products because of its unique structure. The castor oil is one of those vegetable oils that have found usage in many chemical industries. It is the raw material for many chemical products and also as the additives in drugs. The usage of castor oil can be divided into industrial, soaps and detergent, food, medicine and also biodiesel and biofuel industries **[7]**.

2.4.1) Castor oil in soap and detergents

Castor oil should be used at low percentages to avoid overly soft soaps. Also often used in balms, soaps, shampoos, hair oils, and other thick emulsions for the skin and hair. Castor oil-based synthetic detergent is hastened; since microbiological breakdown is simplified.

2.5) Detergency

2.5.1) Definition of Detergents

Synthetic detergents: - are multi-component compositions and they may be liquid, paste-like and powdery. They comprise surface active agents (surfactants) and other organic and inorganic substances which increase the efficiency of the surfactants. First detergents were soaps, derived from naturally occurring substances. However, fatty soaps have some drawbacks. Their detergent effect is manifested only in an alkaline medium; with calcium and magnesium salts, contained in hard water, they form insoluble salts, which deposit on the fabrics and contaminate them. Alkali compounds, contained in the soap, weaken the strength of wool and silk fabrics, and fabrics made of polyester fibers, especially at elevated temperatures, and may also discolour fabrics.

2.5.2) Development of the detergent industry

The first synthetic detergents were created in Germany during the First World War, due to a large deficit of dietary fat, and after the war the synthetic detergents industry flourished in the United States, Japan and some European countries. In different countries, synthetic detergents were produced from various raw materials. For example, in the United States sodium oleyl taurate began to be actively used, Germany aliphatic sulfates (sulfates of fatty alcohols), in

the United Kingdom - a secondary olefin sulfate, derived from petrochemical sources, which is released in England in large quantities **[8]**.

Thus, synthetic detergents finally were established on the market. So, in the years 1940-1972 the demand for synthetic detergents in the United States increased 1000-fold to 4.5 million tons per year. Production of detergents in the world was developed due to both a displacement of fatty soaps, and due to the increase of the total consumption of detergents. Currently, the world production of synthetic detergents amounts to tens of millions of tons per year. However, most of them (70%) are consumed only by residents of the most developed countries, constituting about 20% of the population.

The most widely used are detergents in a powdered form, in particular those for domestic use. During the last decade, the release of liquid detergents increased significantly, mainly for industrial applications. This is due to the fact that during the use and storage of detergents in liquid form their drying is excluded, liquid compositions do not give up dust, they are easily dispensed, can be quickly and easily mixed with water. A range of **cleaning agents** includes cleaners for dishwashing, cleaners for bathrooms, toilets, glass, household and specialty cleaners.

2.5.3) Use of additives in Detergent industry

Synthetic detergents are formulated from six groups of substances:

Surfactants: - Are organic chemicals, obtained through complex chemical reactions, from oil or fat raw materials. They have wetting, emulsifying and dispersing properties, enabling the removal of dirt ("soil") from fabrics and keeping the soil suspended in the washing water. Detergents usually contain several types of surfactants such as soaps (anionic), alkylbenzene sulphonate (anionic), ethoxylated fatty alcohols (non-ionic). The mixture is carefully balanced to control foaming and provide the appropriate washing efficiency (for the required washing temperatures, types of fabric and water hardness); at a price the consumer is willing to pay.

Builders: - Builders are key detergent components which remove the calcium and magnesium ions presents in hard water and in soils, thus lowering the concentration of surfactants necessary to perform the detersive action. Sodium silicate and sodium sulphate are alkali builders commonly used in detergent making.

Bleaching agents: - Bleaching agents eliminate stubborn stains and ensure hygiene by killing bacteria through a chemical oxidation performed by a per-oxygen generator, usually sodium perborate. The latter is usually active only above 60°C and so, for lower washing temperatures, an activator is added: e.g. tetra acetyl ethylene diamine (TAED).

Enzymes: - In particular, proteases, lipases and amylases. Catalyse the degradation of some stains and thus facilitate their elimination.

The main components of synthetic detergents are represented by anionic (about 70% of the total use of surfactants), cationic, amphoteric or ampholytic (developed recently, so far very expensive and not widely used) and nonionic **surfactants**. Modern detergents use surfactants which have a degree of biodegradation of at least 90%. The number of surfactants of various types in synthetic detergents reaches 35% by weight (Table 2.2).

Table.2.2.The composition of synthetic detergents, %

Material	**For cotton with whitening**	**For synthetic fabrics**	**For wool and silk fabrics**	**For soaking and pre-washing**
Surfactant	20-18	25	30-35	15
Sodium tripolyphosphate	35-40	50	5	40
Sodium perborate	10-20	-	-	-
Sodium silicate	5-7	5	1-5	-
Soda	15-20	-	15-20	-
Sodium carbonate	10	10	-	-
Sodium sulfate	Up to 10	Up to 8	Up to 8	Up to 25
Perfumes	0.1-0.3	0.1-0.3	0.1-0.3	0.1-0.3
Water	Up to 8	Up to 8	Up to 5	Up to 8

Source: www.InfoMine

Virtually all powder detergents contain mineral salts, of which **phosphates** are most widely used: sodium tripolyphosphate, trisodium phosphate, tetrapotassium pyrophosphate, and others, capable of forming complexes with polyvalent cations. Liquid formulations preferably use trisodium phosphate, chlorinated sodium tripolyphosphate and trisodium phosphate, in enzyme-containing detergents small amounts of Ca or Mg salts are used.

The use of effective substitutes for phosphates in synthetic detergents is very important in connection with the pollution of water bodies with nutrients. The number of complexing agents in synthetic detergents reaches 40% by weight. Synthetic detergents by 15-20% consist of **soda ash**, which is a water softener, and used for the grease removal and as a cleaning agent. Proportions of the remaining components do not exceed 10% by weight.

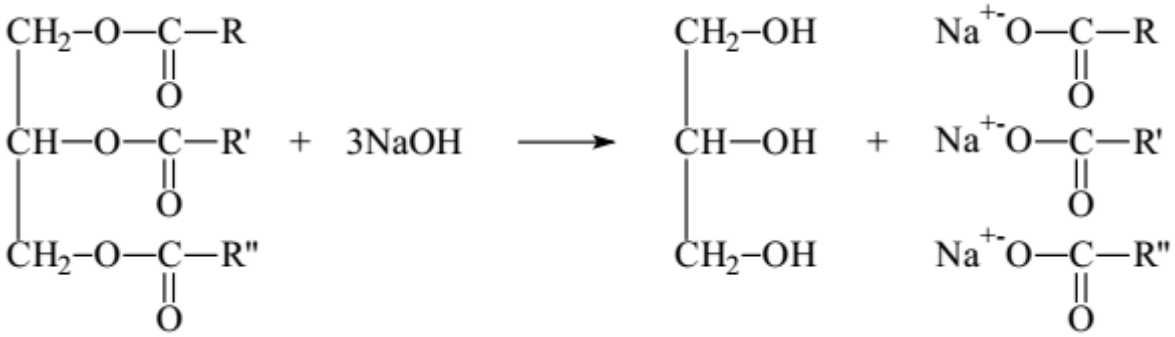
Thus, the basic components of synthetic detergents are surfactants, water softeners, chemical and optical brighteners, foam stabilizers and perfumes.

2.5.4) Chemistry of Detergents/soaps

Detergents use a synthetic surfactant in place of the metal fatty acid salts used in soaps. They are made both in powder and liquid form. Most detergents have soap in their mixture of ingredients, but it usually functions more as a foam depressant than as a surfactant.

Detergents are the product of the reaction between a fat/oil and sodium hydroxide:

Fat/oil +3NaOH → glycerine + 3 soap/detergents



Triglyceride Caustic soda Glycerine Metal soap/detergent

2.5.5) Classification of synthetic detergents

Synthetic detergents are classified by the aggregate state (consistency), the composition and method of application **[9]**.

i) By the aggregate state (consistency)

The worldwide production of powdered agents exceeds 80% of the total release of synthetic detergents. Those are the most concentrated agents. They are suitable for administration to the supporting components and for packaging. By the composition they are usually a mixture

of anion-active (for washing and soaking of articles of cotton and linen), nonionic (for synthetic fabrics) surfactants and auxiliary components. However, powdered synthetic detergents are often potent allergens, and traditional surfactants used in them, have the ability to accumulate.

ii) ***Solid (lump)***

Cleaners work well for washing in conditions of scarce water resources, recreation, travel, tourism and everyday life, as they allow an efficient processing of washed items. Washing by hand a small amount of product in a small volume of cleaning solution is still relevant, despite the rapid increase in production of washing machines and improving their designs. For hand washing exceptionally effective are synthetic detergents in a lump form. Solid detergents can be released as tablets. Such agents are convenient and easily dosed; there is no allergic reaction to them.

iii) L***iquid*** **detergents**

Its production uses less energy and it is simpler, because they do not require drying. Liquid detergents do not cause allergic reactions, and more economical in dosing. The fact that their production is not sufficiently developed; can be explained only by the lack of an effective cleaning action for all kinds of fabrics, because they do not contain chemical bleaches, alkali metal salts and enzymes. Therefore exhibit detergency only in soft water and mainly for wool and silk.

iv) ***Paste-like***

Compositions contain up to 40% of water. Their composition can include almost all supplements, except unstable chemical bleaches.

v) ***By composition***:

There are synthetic detergents without peroxide compounds and biological additives, with peroxide compounds and biological additives, for wool, fine fabrics and baby clothes, for colored fabrics (the name of such agents include the designation "Color"), and their use requires special temperature conditions.

vi) ***By purpose***

There are five groups of detergents. Agents for the washing of articles made of cotton and linen fabrics contain up to 25% of surfactants, up to 20% of alkaline electrolytes, up to 35% of polyphosphates, alkylolamides, carboxymethyl cellulose, and sometimes bleach. These agents should not be used for washing wool products as a high alkalinity (pH 10-11.5) destroys the protein substance keratin, from which fibers of wool fabrics are composed. Detergents for the washing of articles of wool, silk and synthetic fabrics do not contain sodium perborate and create a softer environment (pH of 8.0-9.5).

vii) ***Universality of synthetic detergents***

The presence of alkaline salts in such compositions (pH - 9-10) has no negative effect on products from the protein and synthetic fibers, as at 30-40°C the activity of the alkaline substance is low. Products made of cotton and linen fabrics are washed using universal detergents at a higher temperature (60-80°C). Approximately 45% of all synthetic detergents for the household use are universal detergents, the same amount is represented by agents for cotton and linen fabrics, and only 10% of output is accounted for by detergents, used for the washing of articles from wool, silk and chemical fibers.

viii) By the method of application

The following detergents are distinguished: with high (non-specified) foaming (for hand washing and washing machines of the agitator type) and with reduced foaming (for washing in automatic and semi-automatic washing machines). Among agents, enhancing the action of detergents, we note bleaches, conditioners; anti-static agents. 90% of the total release of **bleaches** is accounted for chlorinated bleaches due to their low cost and versatility. Modern bleaches have lower concentrations of active chlorine, may be used at lower temperatures and with a short time of bleaching.

ix) Softeners (conditioners):

Making the fabric soft and velvety, are represented by liquids. The most in demand in the market are multi-functional means, which in addition to softening and providing a pleasant smell, contribute to improving the sliding of an iron, reduce creasing when washing, facilitate the smoothing of fabrics with iron, contribute to the color retention, protect against stains, help keep the shape of the product, and increase the absorbability of fabrics.

x) Antistatic agents:

These are used to reduce the static-charge accumulation on fabrics of synthetic fibers. They contain surfactants, which form a thin film on the fabric, retaining water, thus improving the electrical conductivity and decreasing the static characteristic of fibres.

The **stiffeners** make the fabric denser; provide hardness, attractive appearance, and a better ability to launder. Figure 2.2.Below shows the general classification synthetic detergent

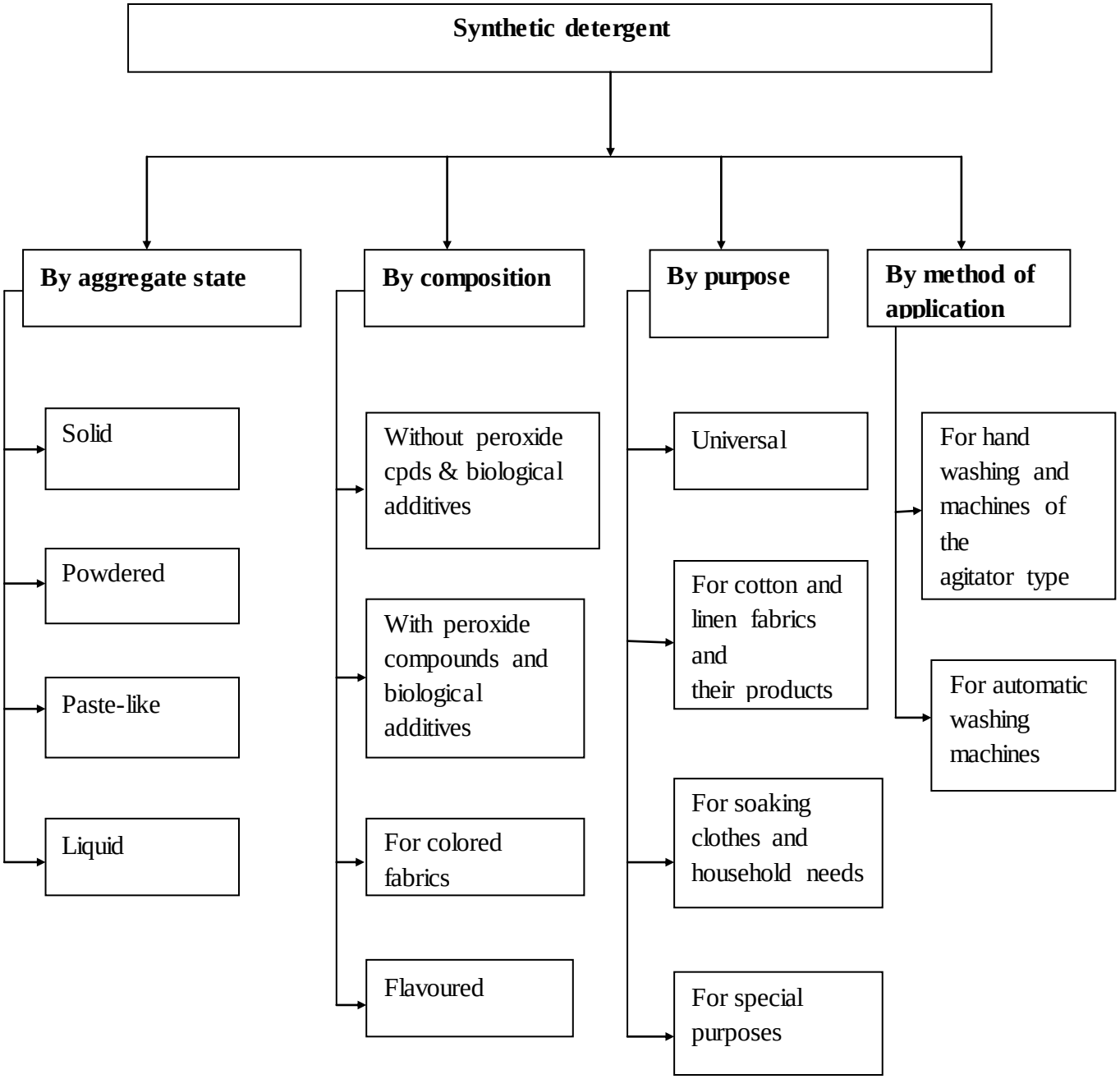


Figure .2.2 Classifications of synthetic detergents (*Source: "InfoMine" based on the review of the technical literature*)

2.5.6) Detergent Foamability

Foams are usually formed in systematic hexagonal texture as a result of gas dispersion through a continuous surfactant solution**.** It is thermodynamically unstable and they are stabilized by surfactants to prevent bubble coalescence. Foams are generally described in terms of their foamability defined as the capacity of the surfactants to form foam irrespective of the special foam properties, and foam stability describing the variations of foam height or volume with time, immediately after foam generation **[10]**.

Foaming studies are often performed according to the Ross-Miles, ASTM D 1173-63, in which a surfactant solution is poured onto an identical surfactant solution, after which the height of the foam produced is measured (often during some minutes). The initial foam height is a measure of foamability and the decay of the foam with time is a measure of foam stability. Another common method is the Bikermann method in which a stream of air is bubbled through a surfactant solution at increasing speed until the rate of foam breakdown is equal to the rate of foam production **[11]**. The importance of the described effects for finding the optimum surfactant system in detergents is shown in Figure 2.3.below.

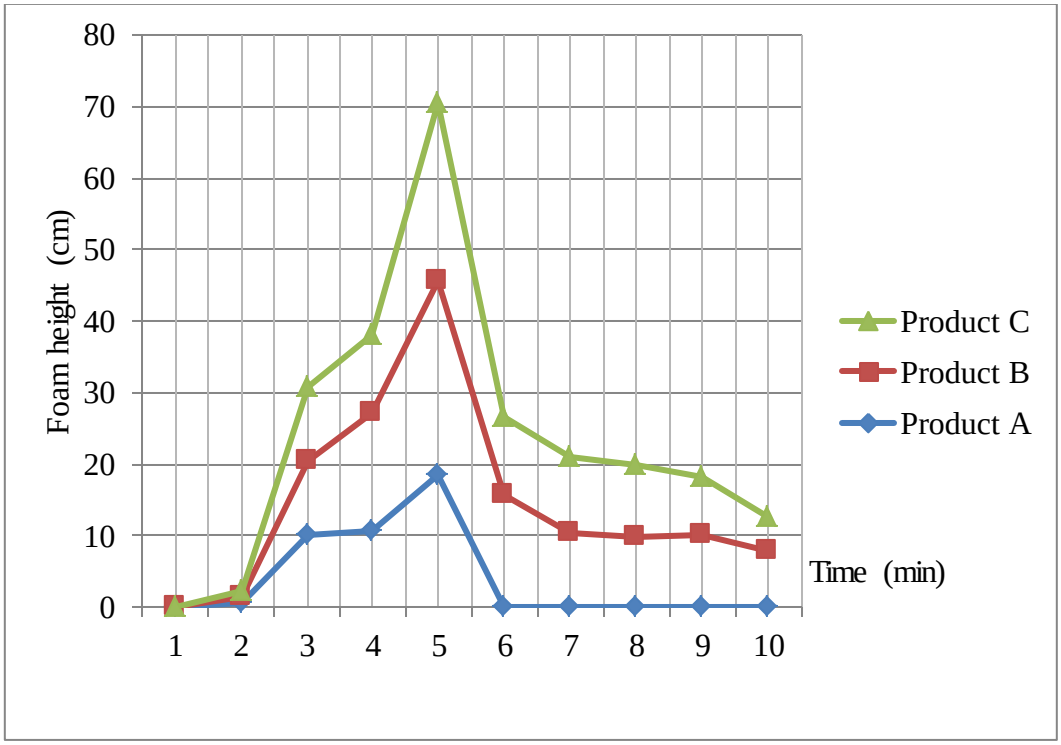


Figure 2.3 Build-up and breakdown of the foam of different high-foaming light-duty detergents in presence of an oily soil (Source :*(**[12]***)

2.6) Biodegradation and its law

Biodegradation is biochemical decomposition of organic compounds to simple compounds, mediated by living organisms such as bacteria, protozoa, actinomycetes, fungi and algae. The mechanism of that process is very complex and involves numerous chemical and biological reactions. In the natural environment, biodegradability is the common characteristics of the matter of vegetal and animal origin, enabling the matter and energy turnover in the nature. However, no material, even a natural one, can undergo biodegradation unless the environmental conditions are accessible for active microorganisms **[13]**. The course and rate of biodegradation processes depend on many factors, including environmental ones (temperature, humidity, pH), availability and type of the microorganisms involved, as well as the properties and chemical structure of the material undergoing decomposition.

Biodegradability tests are widely used in the following areas:

- Development of new technologies for manufacturing environmentally friendly products, such as: packaging, synthetic detergents and textiles
- Development of new and improvement of existing techniques of wastewater treatment and disposal of waste

A number of methods of testing biodegradability depending on the type of the test substance have been developed. For example, the rules, requirements and test methods for environmentally friendly (i.e. vegetable) oils and lubricants are relatively comprehensive. For example; Benzene is regarded as recalcitrant under strictly anaerobic conditions. The majority of the published studies show that benzene is not an aerobically biodegraded **[14]**.

2.6.1) Legislation of Biodegradability

The development of legislation specifically for surfactants was focused primarily on the detergent industry. In direct response to the concern over surfactants and foam on rivers, European legislation was developed in the early 1970s **[15]**, was intended to be a framework directive to address biodegradability in the four major surfactant groups, anionic, non-ionic, cationic and amphoteric. The enforcement of the legislation was intended to rest with the Member States which had the responsibility to determine compliance with the directives from analysis of formulated products. The extraction process, in practice, provided additional technical complications to establishing non-compliance with the subsequent legislation.

One of the intended 'daughter directives' was published on the same date: directive 73/405/EEC **[16]**, provided the required test methodology for anionic surfactant primary biodegradability based on reduction of MBAS and set a test level of 80% or greater for the use of these surfactants indetergents. The second 'daughter' directive, 82/242/EEC, was published in the early 1980s and covered non-ionic surfactants based on reduction of BiAS **[17]**.

The perceived weakness in the current legislation for surfactants in detergents is that it does not cover all types of surfactants and it only considers primary rather than ultimate biodegradability. It is estimated that 50% of surfactants in use fall outside the scope of the current legislation. However, based on information collected from surfactant and detergent manufacturers prior to the detergents regulation publication, less than 100,000 tonnes or 3 % of all the surfactants currently used in this sector within the EC are unlikely to meet the 'ready biodegradable' threshold.

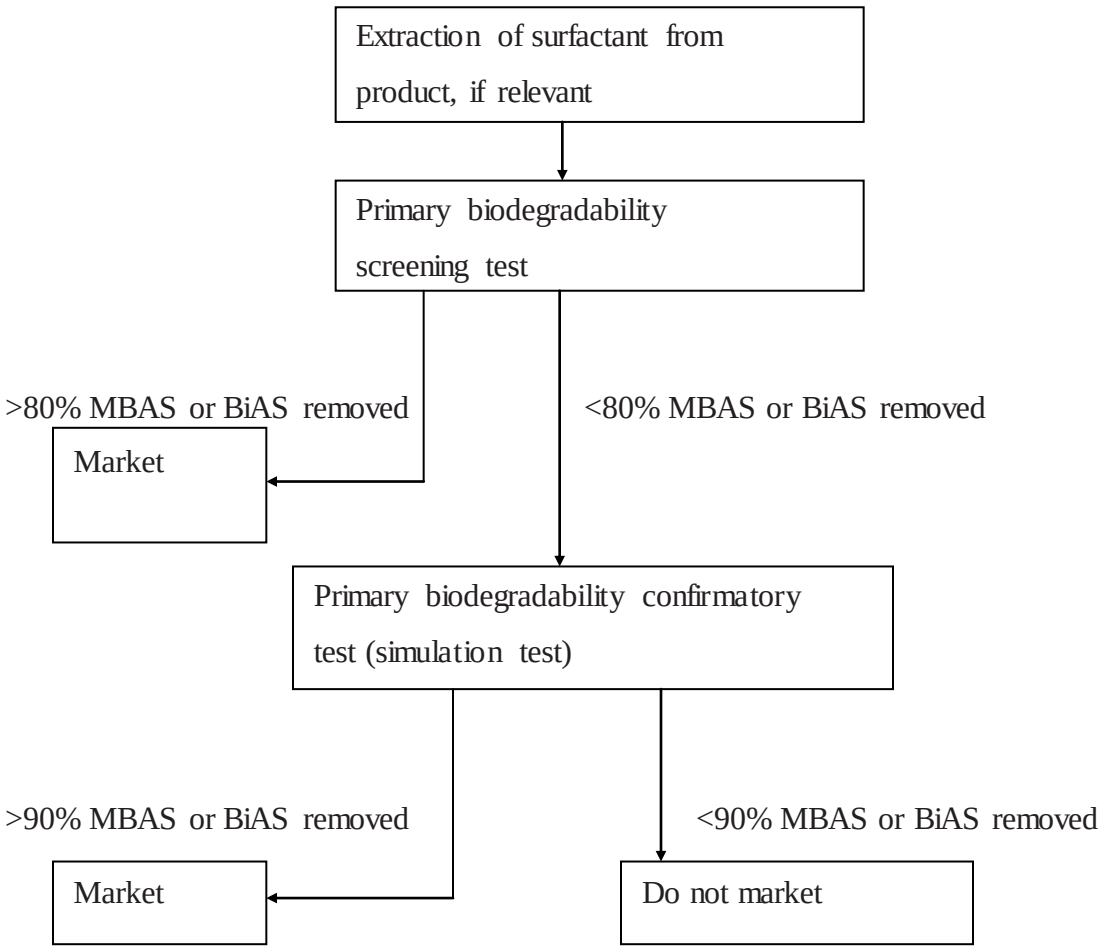


Figure 2.4 Testing frameworks for surfactants in washing, rinsing and cleaning products prior to the Detergents Regulation (Source: *Routledge, E.J and Sumpter, J.P. (1996) Oestrogenic activity of surfactants and some of their degradation products, Toxicol. Chem., 15(3), 241–8)*

2.6.2) Detergents Regulation

The Detergents Regulation (648/2004/EC) **[18]** was published in March 2004 and is intended to come in to effect in Member States on 8 October 2005. This legislation will replace all the existing detergent specific legislation and elevate the formal surfactant biodegradability criteria for placing detergents on the market.

International testing standards (EN ISO 17025) **[19]** or good laboratory practice (GLP) is now specified for biodegradability testing although existing data will be accepted if they provide a comparable level of scientific quality. The existing voluntary labeling of detergents now forms part of this Regulation and this has been expanded to list any preservative used in the product and the presence of allergenic perfume ingredients (as defined by the Scientific Committee on Cosmetics and Non Food Products) in excess of 0.01%. The bigger challenge for both authorities and manufacturers is to address surfactant biodegradability within the context of sustainable activity.

2.7) Phosphate - containing detergents

Phosphorus (P) is one of the major nutrients needed to sustain all forms of life and cannot be substituted. Similar to fossil fuels, phosphorus (P) is a non-renewable resource and its availability for future generations is becoming obscure. Moreover, with increase in population growth, change towards meat-rich diets and growing demands for food production will further push an increasing demand for phosphate in the near future **[20]**. Globally, 148 million tonnes of phosphate rock is mined every year and approximately 90% is used for food production primarily for the production of agricultural fertilizers (82%) and a smaller fraction for animal feed additions (7%) and food additives (1 –2%). The remaining 9% goes to industrial uses such as detergents and metal treatment and other industrial applications.

2.8) Phosphate free detergents

After 30 years of research no adequate substitute for **Sodium tripolyphosphate (**STPP) has been found: that is, a single substance which can take its place in a detergent formula without requiring other undesirable additions to the formula and without decreasing, below an acceptable level, the level of cleanliness and hygiene achieved. Phosphate-containing one, using several new chemicals along with a different balance of existing ones, with a series of changes being necessary to resolve the succession of problems which arise when STPP is not

used **[5]**. Phosphate-free formulations as a general rule contain some or all of the following chemicals:

- ✓ **Zeolite A** as a principal builder, this is an artificial, insoluble compound based on aluminum and silicate
- ✓ **PCAs (polycarboxylates)** , non-biodegradable long chain petrochemical molecules, used to reduce deposition of calcium and magnesium salts which result from the poor ion removal properties of zeolite A
- ✓ **Reinforced surfactant system:** higher total surfactant load and/or modified proportions of different surfactants
    - ➢ increased enzyme content
    - ➢ Perborate activators added or levels increased to improve bleaching.

No other single chemical offers all, or even most, of these different properties, so that P-free detergents systematically contain a number of "new" chemicals as well as necessitating a complete change and reinforcement of other elements of the formulation.

2.9) Extraction of Oils

2.9.1) Principles of oil extractions

Commercially, there are three methods used for the production of castor oils: batch hydraulic pressing, continuous mechanical pressing and solvent extraction. Each of these technologies will be detailed below. The first step of the process, common to all technologies, is the preparation of raw material. And scaling, cleaning, dehulling (or decorticating), cracking, drying, conditioning (or cooking), and flaking respectively are discussed below.

i) Scaling: Initially the oilseeds are weighed and sent to the cleaning step.

ii) Cleaning

A good quality oilseed has around 2% of impurities when it comes from the field. These foreign materials are removed when the oilseeds reach the storage unit and also before starting the extraction of oil. Some examples of foreign materials are a combination of weed seeds, sticks, pods, dust, soil, sand, stones, and tramp metal. Tramp metal is considered hazardous to storage facilities and also for the oil processing operations, so it is the first impurity to be removed, using a magnetic force that pulls these metals from the mass of grain. Sticks and pods are larger and lighter than the oilseeds and can easily be removed by airflow equipment.

iii) Drying

Due to the high oil content in its composition, oilseeds must have a low moisture content in order to prevent deterioration during storage and also to ensure that downstream unit operations are efficient. This operation is conducted in a dryer.

The main goal of size reduction operation is to increase surface area to facilitate oil removal from the seed inside. This operation must be conducted at proper moisture content. If the moisture level is too low, the seeds are "conditioned" with water or steam to raise the moisture to about 11%. A solvent extraction operation is going to have a higher yield if the flakes are about 2.03 to 4.3 mm. Thinner flakes tend to disintegrate during the solvent extraction process and reduce the miscella percolation rate **[21]**.

iv) Cracking

Cracking mill is the equipment used to crack oilseeds. This equipment consists of two sets of cylindrical corrugated rolls in series, operating at differential speeds to assist in breaking the oleaginous materials apart.

v) Dehulling

Another unit operation is dehulling because some oilseeds present outer seed coat known as hull, rich in fiber and poor in oil and protein. The removal of these hulls will produce a better cake with high protein content by weight. Another problem observed with hulled seeds is that the hull will reduce the total yield of oil by absorbing and retaining oil in the cake.

vi) Flaking

The equipment that performed flaking operation is named flaking mill. Two large diameter rolls in parallel, turning in opposing direction at approximately 250 to 300 rpm, and forced together by hydraulic cylinders. As the oilseeds are pulled through, they are stretched and flattened, forming flakes, in the range of 0.3 to 0.4 mm thick and 8 to 18 mm in diameter.

The flowchart below may be altered depending on raw material to be processed.

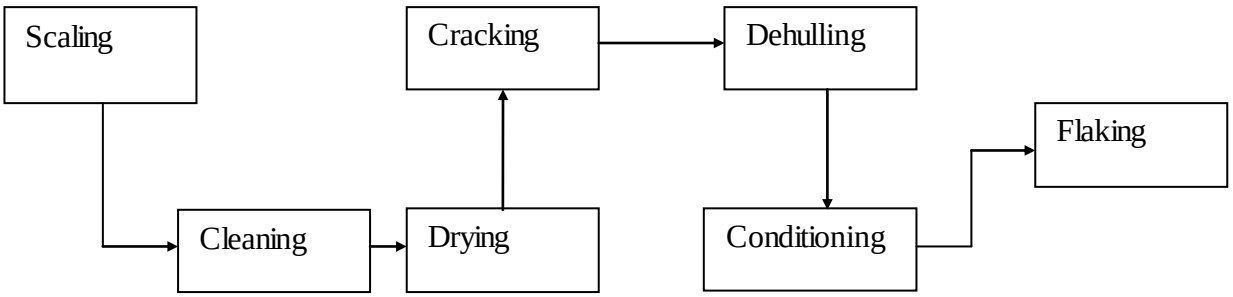


Figure.2.5. Unit operations for raw materials preparation (adapted from Anderson, 2005).

2.10) Methods of seed oil extraction

Quality of oil depends on the type of extraction. Manufacturing of castor oil includes the collection of raw materials for the extraction and selection of extraction method.

2.10.1) Batch hydraulic pressing

In the late nineteenth century, oilseeds were processed in manual presses, where layers of grains were placed into the equipment, separated by filter cloths, filter press plates and force was applied via hydraulic cylinder. When the oil has stopped flowing, the workers opened the machine, removed the mass of crushed grain and put more fresh material. At the beginning of the twentieth century the vegetable oil industry worked basically with the hydraulic presses but even making use of a hydraulic cylinder, work with this type of equipment was considered labor intensive. With the emergence of the continuous screw- press, the only application that still requires the hydraulic press is the one that requires gentle handling, such as processing and production of cocoa butter **[22]**.

In a typical hydraulic pressing there are three stages as can be identified in Figure 2.6given below. The application of compressive load causes the seeds to force the air out of the macro pores. This process continues until a critical point that occurs when the seeds respond to pressure through their points of contact. When the first drop of oil leaks out of the mass, it begins the second stage (dynamic stage), where the air is displaced by the liquid and an air/fluid mixture is extracted. The oil flow increases rapidly to its maximum, which is when the second stage ends. The last stage (final stage) begins when the maximum instantaneous flow rate, i.e. the volume is completely filled with fluid, is reached. Z_1, Z_2 and Z_3 indicate the height of grain layer inside the extractor; P_T is the applied force by the extractor, t_0 is the initial time, taken when the oil starts flowing and T is final time, indicating that the process ends.

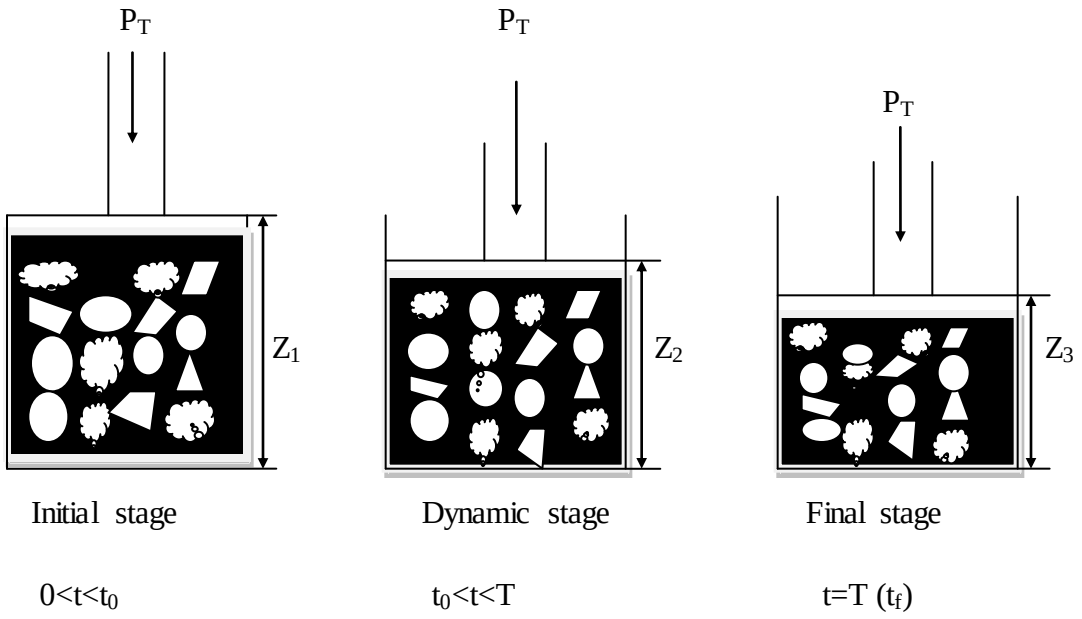


Figure.2.6. Stages of hydraulic expressions (Mrema and McNulty, 1985 in Owolarafe et al., 2008).

2.10.2) Continuous mechanical pressing (screw press)

Among the physical processes for the extraction of castor oils, the continuous mechanical pressing emerges as the best technology to serve small farmers. That´s because this type of equipment associates both small scale and low cost when compared to the other methods cited. Another important advantage is the possibility of using cake resulting from the pressing as fertilizer or animal feed, since it is free of toxic solvents. The operating principle of this equipment consists a helical screw which moves the material, compressing it, and at the same time, eliminating the oil and producing the cake. Optimization of the continuous mechanical pressing consist of defining the optimum parameters, such as temperature and moisture content of grain, or adjustments on the press, in order to reach optimum yields of oil, using a minimum value of pressure applied by the press.

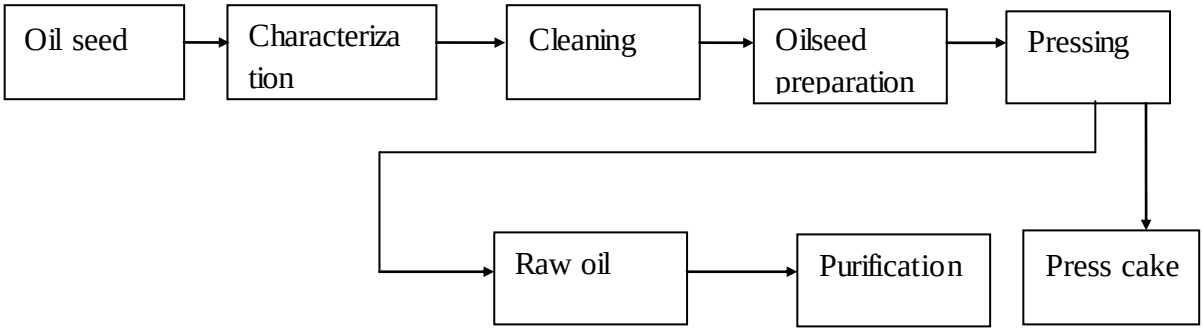


Fig.2.7. Screw press scheme (adapted from Jariene et al., 2008).

2.10.3) Supercritical CO_2 extraction

Although solvent extraction is efficient and has high oil yield, the problems presented by this technique have made scientists to research for new routes. One technique that has been used is the supercritical-fluid (SCF) extraction. A fluid is considered supercritical when it presents diffusivity similar to gas and density comparable to liquids.

In the 1980's the use of supercritical CO_2 for the extraction of oilseeds such as soybean, cottonseed, corn germ, rapeseed, and sunflower. The oils obtained were shown to have similar quality compared with hexane extracts; they also had lighter color and lower iron and phospholipids content, resulting in a lower refining loss and reduction of subsequent refining steps. Despite the many advantages of $SCCO_2$ extraction and also the high volume of research carried out, commercial-scale $SCCO_2$ extraction of oilseeds was not readily accepted. The process based on $SCCO_2$ extraction is simpler than conventional hexane extraction in terms of eliminating the need for hexane evaporators and meal desolventizer, but $SCCO_2$ process has some disadvantages such as high equipment costs and the inability to achieve continuous processing of high volumes of oilseeds under SCF conditions. Those two reasons are considered major impediments to commercialization of the $SCCO_2$ process.

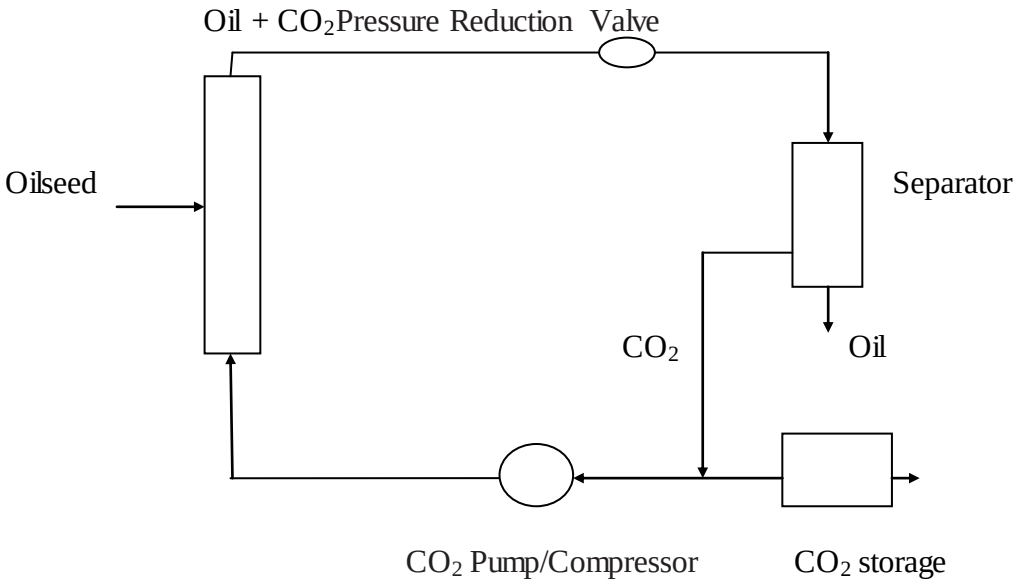


Figure.2.8. Flow diagram of a supercritical carbon dioxide extraction system (*Source: Virendra P. S. and Diwaker Pandey extraction of oil 2006-07*)

2.10.4) Solvent extraction

Extraction with solvents is the most effective method for the recovery of oil (almost 98%), rather than the previous method. When performed at low temperature, the solvent extraction has another advantage over screw-pressing: better quality of oil produced. This is because during expelling a sudden heating of the oil can occur, changing some parameters of its quality. It is expected that residual oil in the meal to be less than 1 percent after commercial solvent extraction. The process known as pre-press is designed to prepare the high oil content raw material to the solvent extraction. Mechanical pressing reduces the oil by half to two thirds of its original level facilitating solvent extraction by reducing the amount of oil to be extracted, the size of extractor equipment and also the volume of solvent used.

The choice of solvent type is based on solubility of oil in the selected solvent, cost and safety. Light paraffinic petroleum fractions, pentane (boiling point 88-97°F), hexane (boiling point 146-156°F), heptanes (boiling point 194-210°F) and octane (boiling point 419-507°F) can be used for oil extraction. Currently hexane is widely used for commodity vegetable oil extraction. Hence; this paper is focused on castor oil extraction using hexane for production of synthetic detergent.

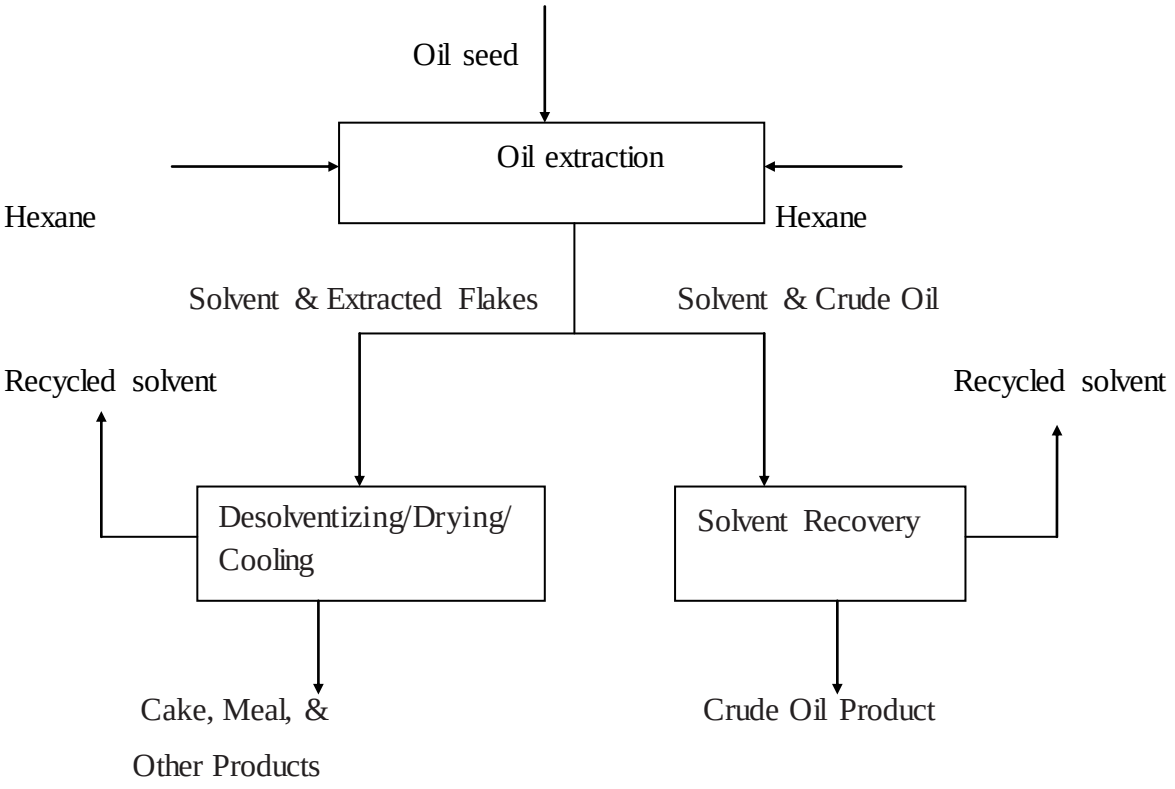


Figure.2.9. Simplified flow diagram of a hexane extraction process (*Source: http://www.aromathyme.com/essentialoils.html*)

2.11) Factors influencing the rate of castor oil extraction

The factors which affect the growing plants thus leading to variations in oil yield and composition, includes moisture contents, samples particle size, reaction time, solvent to sample ratio.

The parameters are discussed in this paper as follows;

2.11.1) The Role and effect of Moisture in Oil Extraction

Oil and water can each wet the solid components of oilseeds, though the two differ in affinity for the hydrophilic surfaces of particles. Water has a higher affinity and wets the surface of particles at a faster rate than oil due to its polarity and absorption ability. Research has proven that particles are selectively wetted by liquids with lower surface tension at the interface; hence water will tend to displace oil from the surface of particles. At a certain moisture content all the surface of the particles will be saturated by water and the oil will flow freely from the molecular forces. Thus, moisture increases the flow of oil through the pores of the press cake, hence reducing the amount of oil entrained in the cake and increasing the oil yield mostly in mechanical expression. High moisture content stops oil flow possibly because the structures of the finely milled particles have been altered (high aggregation).

2.11.2) The effects of temperature in oil extraction

Temperature is increased for oilseeds after pre-treatments such as cracking, dehulling, and milling by heating, roasting and steaming of oilseeds prior to extraction and is termed thermal treatment of oilseeds. Better extraction is achieved by heating, which reduces the oil viscosity and releases oil from intact cells, and also reduces moisture in the cells. Temperature plays an active role in the seed treatment for mechanical extraction and ensures an effective solvent process by heating the solvent which hastens the extraction process. At the right temperature and moisture content, the individual oil droplets unite to form a continuous phase and flow out maximizing oil yield.

2.11.3) Effect of reaction times

Oil yield obtained (expressed in percent) was extraction time dependent. In general, the oil yield increased with increase in extraction time.

2.11.4) Effect of Solvent to solid ratio

Solvent to solid ratio is another important parameter that affects oil extraction efficiency and recovery. The volume of the solvent should not be more than an optimized volume because the cost of the solvent recovery could be too high, thereby increasing the total operational cost.

2.11.5) Effect of particle size

Particle size plays a great role on the yield of castor seed oil. Smaller particle size gives high yield while samples with large particle size deliver low yield. That means less oil is extracted from the larger particles compared to the small size of the particles. The reason is that larger particles with smaller contact surface area, have more resistant to solvent entrance and oil diffusion towards the solvent. Therefore, less amount of oil will be transferred from inside the larger particles to the surrounding solution in comparison with the smaller ones. Thus, an increase in particle size will decrease the oil yield

2.12) Properties of hexane

n-Hexane is a very volatile aliphatic hydrocarbon. It is a constituent in the paraffin fraction of crude oil and natural gas and is also used as an industrial chemical and laboratory reagent. Laboratory grade n hexane contains approximately 99% n-hexane. "Hexane" or "hexanes" is a commercial and industrial product consisting of a mixture of hydrocarbons with six carbon atoms and includes n-hexane and its isomers 2-methylpentane and 3-methylpentane as well as small amounts of other hydrocarbons **[23]**.

Laboratory and industrial solvents such as "hexane" and petroleum ether contain n-hexane from <0.1% to as much as 33%. Many commercial grades of n-hexane contain appreciable amounts of other hydrocarbons in addition to n-hexane (for instance, toluene or such solvents as acetone or methyl ethyl ketones). Various types of commercial grades of n-hexane are available, and the constituents besides n-hexane are usually an intentional part of the process for preparing these commercial mixtures.

2.12.1) Physical and chemical properties of hexane

The National Fire Protection Association (NFPA) has assigned n-hexane a health hazard identification code of 1 (slight) and flammability code of 3 (serious) (NFPA 1994). n-Hexane is flammable and may be ignited by heat, sparks, and flames. n-Hexane can react vigorously

with oxidizing materials such as liquid chlorine, concentrated oxygen, and sodium hypochlorite. Information regarding the physical and chemical properties of hexane is located in Table 2.3 below.

Table.2.3. Physical and chemical properties of n-hexane

Properties	**Information**
Molecular weight	86.18
Physical state	Liquid
Melting point	-95^0C
Boiling point	69^0C
Density	0.6603 at 20^0C
Solubility in water	Insoluble
Organic solvents	Miscible with alcohol, ether
Flash point	-22^0C
Flammability limits at 25^0C	1.1-7.5%

Source; www.wikipedia physical and chemical properties of n-hexane

2.13) Leaching (mass transfer) of solvent extraction

Leaching is a liquid-solid operation. The two phases are in intimate contact, the solute(s) can diffuse from the solid to the liquid phase, which causes a separation of the components originally in the solid. A special leaching process, when an undesirable component is removed from a solid with water, is called washing. Leaching is widely used in the biological and food processing industries, such as the separation of sugar from sugar beets with hot water, the extraction of oils from peanuts, soybeans, sunflower seeds, cotton seeds, and castor beans.

2.13.a) Preparation of Solids for Leaching

This depends on the proportion of the soluble constituent present, its distribution throughout the original solid, the nature of the solid, and the original particle size. If the soluble material is surrounded by a matrix of insoluble matter, the solvent must diffuse inside to contact and dissolve the soluble material and then diffuse out. Biological materials are cellular in structure and the soluble constituents are inside the cells. Because the cell walls provide

another resistance to diffusion, the rate of leaching may be slow. In this case the biological materials are cut into thin wedge-shaped slices to reduce the diffusion distance of solvent.

2.13.b) Rates of Leaching

Generally there are five rate steps in the leaching process:

1) The solvent is transferred from the bulk solution to the surface of the solid.
2) The solvent penetrates or diffuses into the solid (intraparticle diffusion).
3) The solute dissolves from the solid into the solvent.
4) The solute diffuses through the mixture to the surface of the solid (intraparticle diffusion).
5) The solute is transferred to the bulk solution.

Step 1 is usually fast. The controlling rate process is generally the intraparticle diffusion or the dissolving step.

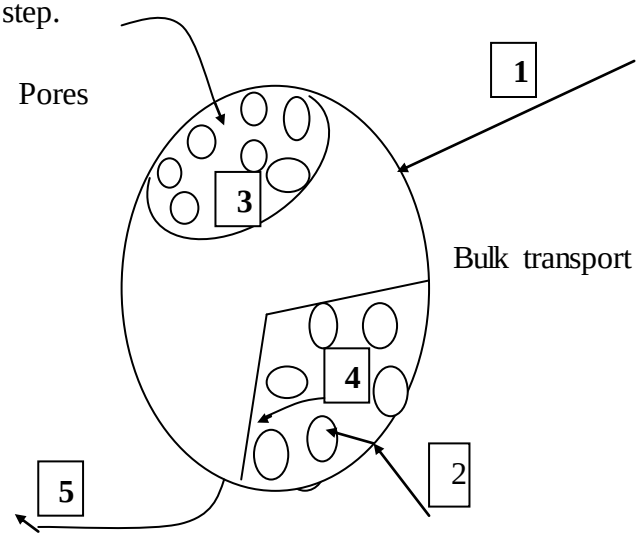


Figure.2.10. General Description of rate transfer in leaching

2.14) Principles of solid-liquid extraction (Leaching)

The principle for the solid-extraction is the soluble compounds of a solid matter, existing of an inert matrix and the active agent, are extracted by a solvent. The extract can be included in the extraction matter in solid or liquid form. It can be included in the cells like oil in oil seeds or as fine dispersion on the solid matter like caffeine in coffee.

A total solid-liquid extraction process includes the preparation of the extraction material, separation and recovery of the solvent from extract and separation and recovery of solvent from extraction residual.

2.15) Manufacturing of synthetic detergent from castor oil process

Cleaning products come in three principal forms: bars, powders and liquids. The first step in manufacturing all three forms is the selection of raw materials. Raw materials are chosen according to many criteria, including their human and environmental safety, cost, compatibility with other ingredients, and the form and performance characteristics of the finished product. While actual production processes may vary from manufacturer to manufacturer, there are steps which are common to all products of a similar form. Detergents use a synthetic surfactant in place of the metal fatty acid salts used in soaps. Most detergents have soap in their mixture of ingredients, but it usually functions more as a foam depressant than as a surfactant.

Both batch and continuous blending processes are used to manufacture liquid and gel cleaning products. In a typical continuous process, dry and liquid ingredients are added and blended to a uniform mixture using inline or static mixers. Recently, more concentrated liquid products have been introduced. One method of producing these products uses new high-energy mixing processes in combination with stabilizing agents.

2.15.a) Detergent premix manufacture

This is usually made first as a premix. This step simply consists of neutralizing surfactants (castor oil) with either caustic soda (NaOH) or potassium hydroxide.

2.15.b) Ingredient mixing/Chemical reaction

The castor oil and alkaline solution mixture is then charged into a closed reaction vessel and the ingredients (sodium silicate, sodium sulphate and perfumes) are added at the reaction temperature of 110^0C. Sodium silicate addition is used to eases removal of dirt and prevents deposition of dirt particles. Addition of sodium sulphate is to induce the foaming ability of the detergent. And also fragrance (perfumes) is added to improve the aromatic properties of the detergent and finally the physical and chemical character of the detergent is analyzed. Figure 2.11 below shows process follow diagram of liquid detergent production the castor oil.

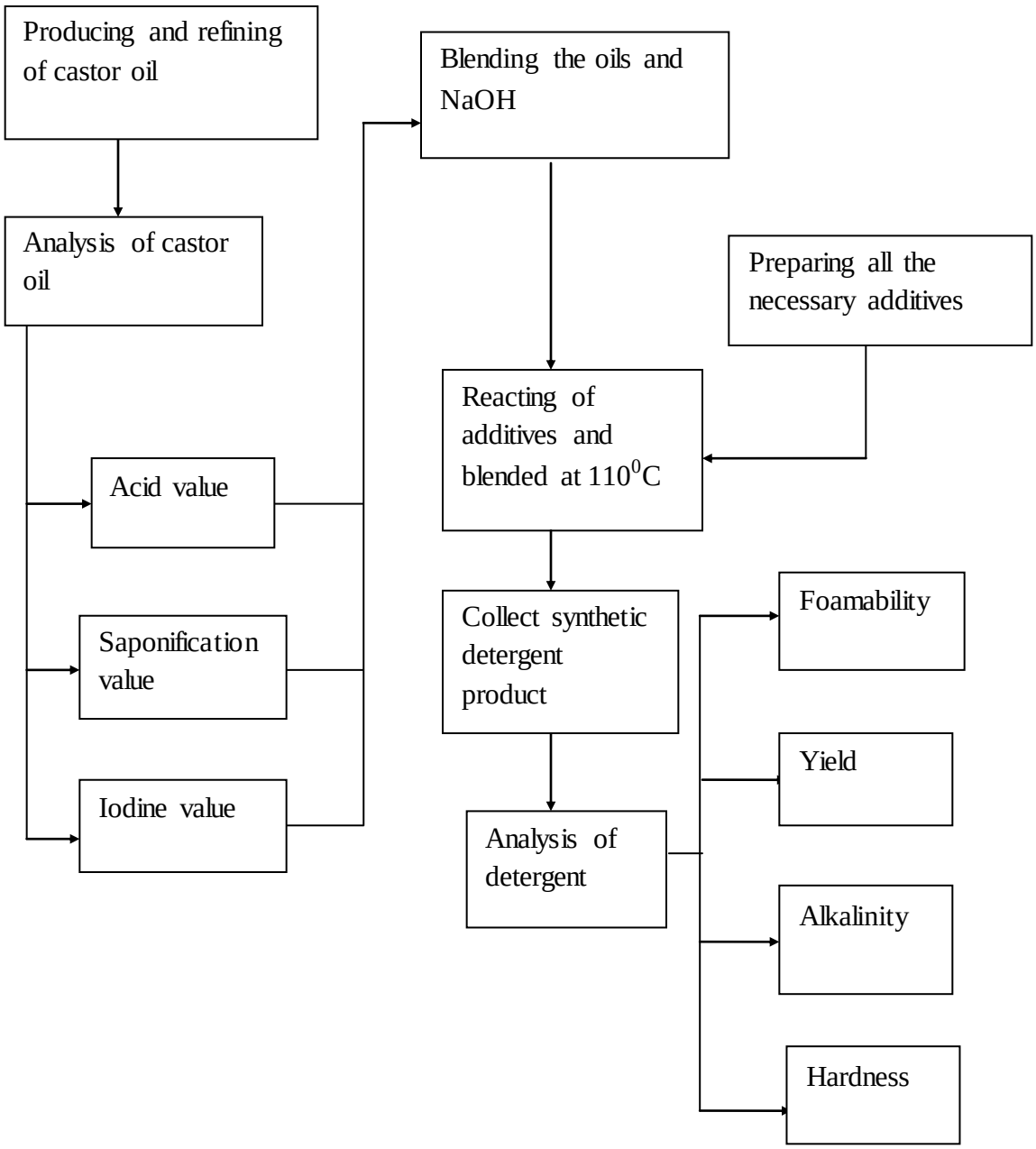


Figure.2.11. Process flow diagram of silk fabric synthetic detergent production from castor oil (*Source: Debesh Mishra, on detergent production, 109ch0476*)

3. METHODOLOGY

3.1 Extraction of castor oil from castor seed

Castor seed was obtained from Oromiya region of Horro Guduru zone. Impurities like stones, dusts and metals were removed by hand. The flesh off the seed easily and leaving the rinsed shell to dry for seven hours before extraction.

3.1.1. Main materials needed

1Kg (1000 gm.) of castor seeds

3000 ml round- bottom flask

Distillation head

Thermometer and viscometer

Heating mantle

Power supply

Two 5000 mL rounded bottom flask

Mortar and pestle

Analytical/electronic mass balance

Oven dryer

Water bath and soxhlet

Viscometer

PH meter

Separating funnel

3.1.2. Main chemicals needed

8.5 L of hexane

Distilled water

3.2 Methods

3.2.1) Experimental works for castor oil extraction

Experimental works were done in Chemical Engineering Department Research Laboratory class rooms and the raw materials collected from the farmer at Oromiya region of Horro Guduru zone.

3.2.2) Determination of moisture content of the seeds

25g, 30g, and 35g of the cleaned sample seed was weighed and dried in an oven at 130°C and the weight was measured every 2hrs. The procedure was repeated until a constant weight was obtained. The percentage moisture in the castor bean was calculated using the following:

$$\text{Moisture \%} = \frac{W1-W2}{W2} * 100 \quad (3.1)$$

Where: W_1 = Original weight of the sample before drying; W_2 = Weight of the sample after drying

3.2.3) Size reduction and sieve analysis of the seeds

The moisture was removed by placing the sample in an oven at 130°C for 6hours. The dried castor seed bean was crushed in mortar and pestle. The sample was sieved using with set of sieves sizes arranged in descending order 2.55mm, 3.5mm, 4mm, 4.5mm and 5mmto obtain particular sizes of 2.55mm, 3.5mm and 4mm. This is because to investigate the effect of particles size on yield and quantity of oil.

3.2.4) Pre-treatment of castor seeds

The castor beans undergo various processing in the course of its preparation for extraction. The unit operations involved are:

- ✓ ***Clearing:*** The castor beans had some foreign materials and dirt which was separated by hand picking.
- ✓ ***Drying:*** The cleaned beans were sun dried in the open, until the casing splits and sheds the seeds. The beans were further dried in the oven at 130°Cfor 6hrs to a constant weight in order to reduce its moisture content, which was initially at about 5 to 7%.

- ✓ ***Winnowing:*** The separation of the shell from the nibs (cotyledon) was carried out using tray to blow away the cover in order to achieve very high yield.
- ✓ ***Grinding (size reduction):*** Mortar and pestle were used to crush the beans into a paste (cake) in order to weaken or rupture the cell walls to release castor fat for extraction.

3.2.5) Solvent extraction

Experimental work was conducted using soxhlet equipment by solvent extraction process. The solvent that is applied in this extraction is n-hexane. The result from soxhlet extraction like extraction time was used as the starting parameter.

3.2.5a) Operation of Soxhlet extraction

Normal hexane was poured into round bottom flask and 35g of the sample was placed in the thimble and was inserted in the centre of the extractor. The Soxhlet was heated to 69.9^0C using water bath. This was allowed to continue for two, four and six hours. The experiment was repeated by placing the same amount of the sample into the thimble again by varying particle sizes (2.55mm, 3.5mm and 4mm) and at constant volume of solvent (315mL). The weight of oil extracted was determined for each run hours. At the end of the extraction, the resulting mixture *(miscella*) containing the oil was heated to recover solvent from the oil. Schematic description and pictorial setup of the Soxhlet apparatus was described in the figure of 0.4A Appendix A.

3.2.5b) Determination of the yield of castor seed oil extracted

35g (W_1) of the sample was placed in the thimble and 315mL of normal hexane were poured into the round bottom flask for each run repeatedly. The apparatus was heated at 69.9°C and allowed for 2hrs, 4hrs and 6hrs continuous extraction using Soxhlet apparatus. The experiment was repeated for 2.55mm, 3.5mm and 4mm respectively for each run.

$$\% \text{ oil yield} = \frac{W1-W2}{W1} * 100 \quad (3.2)$$

Where: W_1=Sample weight before extraction and W_2= sample weight after extraction and dried in the oven.

3.3 Refining of castor oil

Oil refining comprises various processes of clarification of oils to rid them of impurities and free fatty acids, and any unwanted odour, and the bleaching of the oil to remove objectionable colour. There are some common methods of oil refining:

3.3.1) Alkali Refining

Irrespective of the process used in the extraction of oils, the crude oil may contain certain amounts of objectionable impurities which may consist of pulp, and other components of the oil seeds or nuts in suspension. The presence of free fatty acids, water and other impurities are chiefly responsible for the rancidity of oils, thus making saponification of the oil very difficult. One of the common methods used in the refining of oils is by the use of weak caustic solution, referred to as alkali refining. During the process, the free fatty acids in the oil react with the weak caustic soda solution to form soap stock which also absorbs some colour, odour and impurities from the oil, thus rendering the oil clean.

3.3.2) Boiling of the oils

A simple method of clarifying oil involves boiling the oil in half its volume of water for 2-4 hours depending on the amount of the oil volume. Some scenting materials like lemon grass, orange peels, etc, are added to the boiling oil. During the boiling process the steam from the oil-water mixture takes along with it some of the undesirable odour of the oil while the scenting materials give some scent (deodorize) to the oil. After the boiling, the fire is put out and the mixture allowed cooling. The clean clarified oil which floats on the top of the water is then siphoned from the separator funnel while the water with the settled impurities from the oil is drained off from the bottom of the separator funnel. In this paper the extracted oil is refined by this method using orange peel.

3.4 Characterization of refined castor oil

Relative to other vegetable oils, castor oil has different physical and chemical properties which vary with the method of extraction the oil.

3.4.1) Materials and chemicals needed

Viscometer, PH meter, NaOH, KOH, HCL, Carbon tetra chloride, Potassium iodide and Sodium thiosulphate

3.4.2) Methods

Some of the physical and chemical characteristics are determined as follows:

3.4.2i) Determination of Specific Gravity

The density of the oil was determined by using density bottle. A clean and dry bottle of 25ml capacity was weighed (W_0) and then the bottle was filled with the oil, stopper inserted and reweighed to give (W_1). The oil was substituted with water after washing and drying the bottle and weighed to give (W_2). The expression for specific gravity (Sp.gr) is:

$$\text{Sp.gr} = \frac{W1-W0}{W2-W0} = \frac{Mass of the substance}{Mass of an equal volume of water} \quad (3.3)$$

3.4.2ii) Determination of viscosity of the oil

35mL of oil was poured into a test tube and a viscometer was used to measure the viscosity at a temperature of 20^0C. Its picture analysis is described under appendix 0.1B

3.4.2iii) Determination of pH Value

2g of the sample was poured into a clean dry 25ml beaker and 13ml of hot distilled water was added to the sample in the beaker and stirred slowly. It was then cooled in a cold-water bath to 25°C. The pH electrode was standardized with buffer solution and the electrode immersed into the sample and the pH value was read and recorded.

3.4.2iv) Determination of saponification value

2g of the oil was placed in a conical flask to which 25ml of ethanoic potassium hydroxide (0.1M) was added and the mixture allowed boiling gently for about 60 mins with shaking at regular intervals of 5mins.

Few drops of phenophthalin indicator, as specified by International Standards Organization (ISO 3657, 1988) was added to the warm solution and then titrated with 0.5M HCl. The end point was reached when the pink colour of the indicator just disappeared. The same procedure was followed for the blank. The saponification value (sv) is given by:

$$\text{SV} = 56.1 * \frac{N\,(VO-Vi)}{m} \quad (3.4)$$

Where: V_O = volume of HCl solution used for the blank test, V_I = volume of HCl solution for the determination, N = actual molarity of HCl used, and m = mass of sample

3.4.2v) Determination of Acid Value

25ml of Toluene and 25ml of ethanol was mixed in a 250ml beaker. The resulting mixture was added to 2g of oil in a 250ml conical flask and few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1M KOH to the end point with consistent shaking for which a dark pink colour was observed and the volume of 0.1M KOH (V0) was noted. The Acid value was calculated as:

$$\text{Acid value (AV)} = 56.11 * \frac{\text{V x C}}{\text{m}} \quad (3.5)$$

Where V =Volume of potassium hydroxide (ml), C=Concentration of potassium hydroxide, 56.11 =Molecular weight of potassium hydroxide, M= sample weight

3.4.2vi) Determination of Iodine value

The method specified by ISO 3961 (1989) was used. 0.4gm of the sample was weighed into a conical flask and 20ml of carbon tetra chloride was added to dissolve the oil. Then 25ml of Dam's reagent was added to the flask using a safety pipette in fume chamber. Stopper was then inserted and the content of the flask was vigorously swirled. The flask was then placed in the dark for 2 hours and 30 minutes. At the end of this period, 20ml of 10% aqueous potassium iodide and 125ml of water were added using a measuring cylinder. The content was titrated with 0.1M sodium-thiosulphate solutions until the yellow colour almost disappeared. Few drops of 1% starch indicator was added and the titration continued by adding thiosulphate drop wise until blue coloration disappeared after vigorous shaking. The same procedure was used for blank test and other samples. The iodine value (I.V) is given by the expression:

$$\text{Iodine value (IV)} = 12.69 * \frac{C(V1-V2)}{M} \quad (3.6)$$

Where: C = Concentration of sodium thiosulphate used; V_1 = Volume of sodium thiosulphate used for blank; V_2 = Volume of sodium thiosulphate used for determination, M = Mass of the sample.

3.5 Production of Silk fabric Detergent

Detergents are synthetic products that facilitate the formation of foam, the emulsification of one liquid in another or the wetting down of a solid surface by a liquid. They have replaced bars of laundry soap and now represent 90 %of worldwide consumption of hygiene products.

3.5.1a) Materials

500ml of beaker

Agitator reactor

1.5liter of castor oil

250ml of product holder

3.5.1b) Chemicals

1.12L of 0.1N caustic soda

320mL of distilled water

192mL of sodium silicate

425.6 g of Sodium sulfate

20mL of fragrance/perfume

3.5.2) Methods

3.5.3) Experimental works for phosphate free liquid detergent

Experimental works were done in Chemical Engineering Department Research Laboratory class rooms.

3.5.4) Procedure of phosphate free liquid detergent production

The amount of detergents produced is depending on the costumer and specific application of the detergents produced. It is not common from one producer to other producers. But every produced detergent has their; own standard quality and all additives components. In this paper from the all types of liquid detergents it is focused on silk fabric liquid detergent.

The following procedure is required to obtain 100mlsilk fabric of liquid synthetic detergent from castor oil is as follows;

- ⇨ 30milliliter of the castor oil was measured into a plastic container that has the mixer on the top.

- ⇨ 4gm of NaOH was weighed and a 500ml amount of distilled water was added to it for preparing a 0.2 N NaOH solution and 15mL of its solution is mixed.

The caustic soda was stirred well using a stirring rod until it blends with the oil. The caustic soda was poured very gradually into it and stirred gently in one direction to enhance thorough mixing of the solution.

All the following ingredients were added and reacted at 110^0Ctemperature

- ⇨ 2.66g of Sodium sulphate and 1mLof Sodium silicate is added to the solution in the given proportion.
- ⇨ 0.3ml of fragrance/perfumes was added to improve the aromatic properties of the detergent and finally the physical and chemical character of the detergent was analyzed.

Note: All the above procedures are repeated for each (35mL of castor oil, 15mL NaOH, 21.28gm of Na_2SO_4, 5mL of Na_2SiO_3) on the run required and also some amount of heat/ethanol is required to facilitate the reaction of those ingredients.

3.5.5) Characterization of fabric liquid detergent

3.5.5a) Materials: 100mL of measuring cylinder, pH meter, three test tubes, five numbers of filter paper, ruler and clock.

3.5.5b) Chemicals: $CaCl_3$, $MgCl_2$, $FeCl_3$ and distilled water.

3.6) Methods

Synthetic detergent has different quality standard from one producer to other producer depending on the surfactant and additives used for the production. In this paper the characterization is focused on the water hardness, alkalinity foamability and cleansing power.

3.6.1) Saponification test

To check whether the saponification is completed or no, "ribbon test" was performed. In this test a small sample of the detergent from the beaker was taken. When a little quantity of the detergent is pressed between the thumb and forefinger, the detergent should come out in the form of firm shiny ribbons with slight opaque ends and be clear when held against the light. If the opaque ends appear and vanish, the detergent is oily and requires more caustic, while if the detergent is grainy, or turbid and somewhat white, it indicates a high level of unreacted caustic, and requires some oil.

3.6.2) Alkalinity test

5mL of the detergent solution was added to a beaker or test tube. Using a pH meter the alkalinity of the detergent solution is determined. The electrode of the pH meter is dipped inside the detergent solution. The pH value of the solution is recorded. This is carried out for all the cases.

3.6.3) Cleansing power checking

A drop of used brake oil was placed on two separate thin strips of filter paper. It is made sure that the strips of filter paper will fit in the test tubes.

- ✓ One filter paper with oil spot is placed in the tube containing detergent and water.
- ✓ A second strip is placed in the tube containing only water. Each one is shaken well and made sure that the filter paper is immersed in the solution.
- ✓ After 2 min the filter paper was removed and rinsed with tap water.
- ✓ The paper strips were thrown in the trash can. The cleaning power of water versus detergent was compared. This reaction was carried out for all the run samples prepared.

3.6.4) Foamability test on detergent produced

About 5mL of the castor oil based detergent was added to a 500ml measuring cylinder containing 100ml of distilled water. The mixture was shaken vigorously so as to generate foams. After shaken for about 2mins, the cylinder was allowed to stand for about 10mins. The height of the foam in the solution was measured and recorded. This reaction was carried out for all the run samples prepared.

3.6.5) Hardness of produced detergent in hard water

The sodium and potassium salts of most carboxylic acids are water soluble. However, the calcium, magnesium, and iron salts are not. Thus when detergents are placed in hard water that contains such ions, are insoluble, curdy solid forms. Most of us have seen these results in the form of a bathtub ring or detergent scum floating in bath or wash water.

- ❖ Place 5 mL of detergent solution in each of three test tubes.

- Add 2 mL of 1% calcium chloride ($CaCl_2$) one detergent-containing tube. Repeat this process, using 1% magnesium chloride ($MgCl_2$), and 1% iron (III) chloride, $FeCl_3$, solutions.
- Mix the contents by stoppering and inverting each tube several times. (Do NOT shake vigorously.)
- Note: whether or not a precipitate forms and how much of a precipitate is formed.

3.7) Design of experiment

Data analysis has performed by DESIGN EXPERT software using general factorial design method. For soxhlet extraction we had two factors, time with three levels (2hr, 4hr and 6hr) and particle size with three levels (2.55mm, 3.5mm & 4mm) while in fabric synthetic detergent the factors to be studied are basic ingredients of on synthetic detergents (surfactants/castor oil, NaOH, Na_2SiO_3, Na_2SO_4) with levels two by taking temperature (110^0C), water (5mL) and perfume (1mL) as constant factor. This design of the experiment helps us to differentiate the significance of the main and the interaction factors. It also used to develop the mathematical model that will describe the effects of the main and interaction factors on the response.

4 RESULT AND DISCUSSION

4.1) Extraction of castor oil from castor seed result

I) Determination of Moisture Contents in castor seed

30Kg of the castor seed was collected on December, 2016 from Western Oromiya Horro Guduru Zone and by taking 100, 150, 200, 250 and 300 grams of castor seed, the moisture content of the sample was obtained (Table4.1) using equation 3.1, after drying the seed in the oven at 130^0C for the varying of the hour.

Table 4.1.Moisture content of castor seed at different time of drying

	Drying time(hour) at 130^0C and its moisture content							**% average moisture content**
Sample weight in grams	**0**	**2**	**% moisture**	**4**	**% moisture**	**6**	**% moisture**	
	100	94.248	6.103	93.1199	7.388	93.1	7.41	6.967
	150	142.45	5.3	140.24	6.9595	140.245	6.9557	6.41
	200	190.76	4.844	186.605	7.178	186.55	7.21	6.411
	250	238.45	4.84378	233.26	7.1765	233.188	7.2096	6.40996
	300	286.14	4.84	279.912	7.1765	279.83	7.21	6.4088

The moisture content of the castor seed of sample with 100, 150,200, 250 and 300gms was 6.967, 6.41, 6.411, 6.40996 and 6.4088%, respectively. Thus, the average moisture content of the three samples will be 6.52%.

4.2.Castor oil optimization and present yield of soxhlet extractor (%w/w)

In this experiment 30Kg of castor seed were first decorticated using knife and hands making 28.56Kg of the flaked pure beans ready for extraction. Means from 1gm of castor seed 0.066gm of flake was removed.

The yield can be calculated using equation 3.2 and shown in table4.2.

Table.4.2. Total %yield of castor oil for soxhlet extractor for constant n-hexane, but different particle size and time

Run	Particle size (mm)	Extraction time (hr.)	Amount of solvent (mL)	Sample weight (gm.)	Cake weight after drying (gm.)	Oil yield (%)
1	2.55	2	315	35	23.26	33.54285714
2	2.55	2	315	35	22.92	34.51428571
3	2.55	2	315	35	23.76	32.11428571
4	3.5	2	315	35	24.73	29.34285714
5	3.5	2	315	35	24	31.42857143
6	3.5	2	315	35	24.21	30.82857143
7	4	2	315	35	25.36	27.54285714
8	4	2	315	35	26.29	24.88571429
9	4	2	315	35	26.36	24.68571429
10	2.55	4	315	35	20.44	41.6
11	2.55	4	315	35	19.37	44.65714286
12	2.55	4	315	35	20.14	42.45714286
13	3.5	4	315	35	25.3	27.71428571
14	3.5	4	315	35	25.29	27.74285714
15	3.5	4	315	35	26.14	25.31428571
16	4	4	315	35	26.02	25.65714286
17	4	4	315	35	25.35	27.57142857
18	4	4	315	35	24.78	29.2
19	2.55	6	315	35	19.478	44.34857143
20	2.55	6	315	35	18.22	47.94285714
21	2.55	6	315	35	17.73	49.34285714
22	3.5	6	315	35	23.3	33.42857143
23	3.5	6	315	35	22.6	35.42857143
24	3.5	6	315	35	21.99	37.17142857
25	4	6	315	35	25.19	28.02857143
26	4	6	315	35	25.26	27.82857143
27	4	6	315	35	25.5	27.14285714

The maximum extraction of castor oil was 49.34% at particle size ranges from 2.5mm for the extraction time of 6rs and the minimum yield obtained was24.7% at maximum particle size and minimum extraction time.

4.2a) Effect of extraction time on percent yield of oil

Percent yield of castor seed oil can be affected by extraction time and particle size. Extraction time plays a great role on the percentage yield of castor seed oil using n-hexane as a solvent. Figure4.1 (a) show that as the contact time increases the oil yield also increases this continues till transfer of oil from the castor bean powder to the solvent attains zero. In other word, when the maximum amount of extractable oil is obtained, the oil yield level remains invariable even by extending the reaction time. So that in the soxhlet extraction the maximum oil yield could be finding at an extraction time of 6 hours and above.

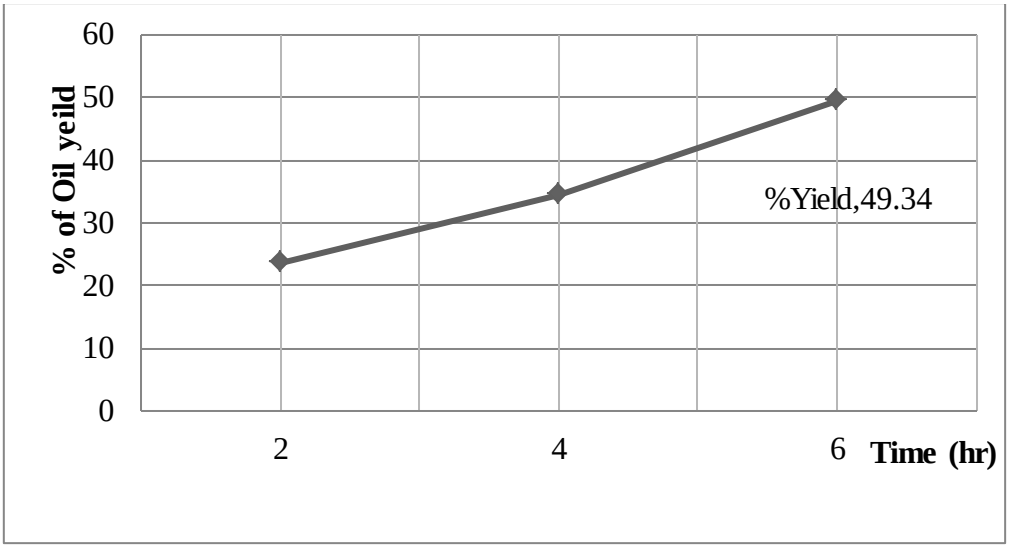


Figure.4.1) The effect of time on castor oil yield

4.2b) Effect of particle size on yield of castor oil

Particle size plays a great role on the yield of castor seed oil. Smaller particle size gives high yield while samples with large particle size deliver low yield. That means less oil is extracted from the larger particles (4 mm) compared to the small size (2.55mm) of the particles. The reason is that larger particles with smaller contact surface area, have more resistant to solvent entrance and oil diffusion towards the solvent. Therefore, less amount of oil will be transferred from inside the larger particles to the surrounding solution in comparison with the smaller ones. Thus, an increase in particle size will decrease the oil yield.Figure4.1 (b) show that as the particle size increases the oil yield decreases.

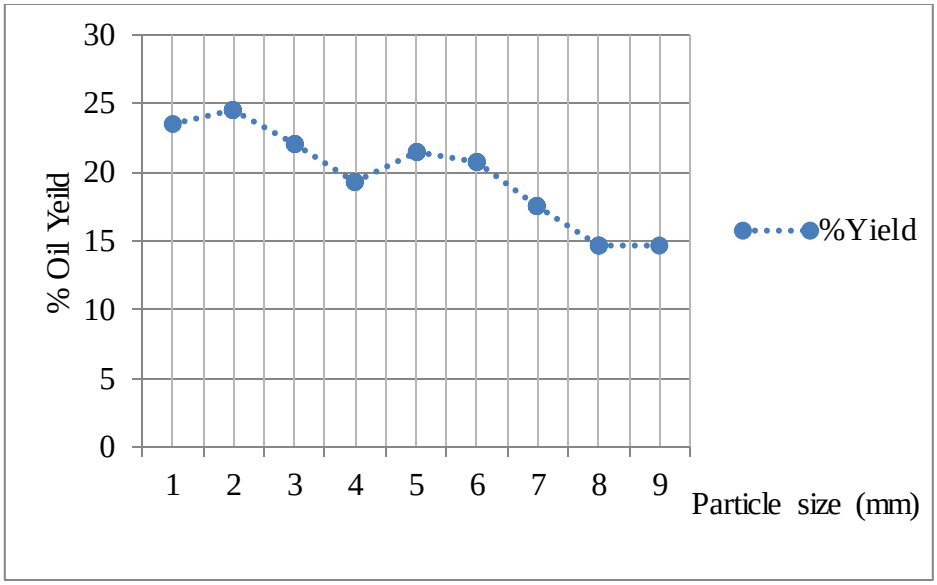


Figure.4.2 The effect of particle size on castor oil yield

4.3) Determination of Physical properties of the castor oil

4.3a) Specific Gravity

Specific gravity of the oil is determined by specific gravity bottle using equation 3.3 described under Chapter three. Figure 0.4A: (a), (b), and(c) given in appendix shows different values of density bottle.

Using equation 3.3

$$\text{Sp.gr} = \frac{W1-W0}{W2-W0}$$

$$\text{Sp.gr} = \frac{77.721-28.2791}{79.7682-28.2791}$$

$$\text{Sp.gr} = 0.96$$

4.3b) Determination of viscosity of castor oil

By taking 35mL of oil and using a viscometer we can get 645mPas of viscosity at 20.4^0C. Figure 0.5A on appendix 'A' shows viscometer with its value.

4.3c) Determination of pH value

Using pH electrode the value of pH 4.45was recorded after immersing the electrode into 2.1mL of the castor oil after the pH electrode was standardize by buffer solution. Figure 0.6A on appendix 'A' indicates pH value of castor oil.

4.3d) Determination of saponification value

Saponification value is calculated through titration using equation 3.4 described under Chapter three. First the blank level changed from pink to colorless at 22.8mL titration volume. The color at which the saponification test changed from pink color to red color was 10.51 mL of titration volume. Titration results for saponification test are illustrated in Table 0.1A and Figure 0.7A on appendix 'A' shows the color change of 2.1mL of castor oil after titration

S. V = $56.1N*\frac{V0-V1}{M}$, where V0 = 22.8mL of volume HCl solution used for blank test

V1= 10.51mL of volume of ethanolic potassium hydroxide

N = 0.5M actual concentration of HCl

M = 2gm calculated using 0.959 specific gravity of oil

Hence, S.V = $56.1*0.5*[\frac{22.8-10.51}{2}]$

= 56.1*0.5*4.67 =172.4

4.3e) Determination of castor oil acid value

Acid value can be calculated using equation 3.5 as follows. For testing acid value, mixture was kept until it changed to pink after 4 mL of titration volume added.

Table 0.2A on appendix 'A' indicates determination of acid value of oil

$$\text{Acid value (AV)} = 56.11 * \frac{\text{V x C}}{\text{m}}$$

Where V =4mL of volume potassium hydroxide

C= 0.1M of potassium hydroxide concentration, 56.11 =Molecular weight of potassium hydroxide and m = 2gm of sample weight/2.1mL of oil

$$A.V = 56.11 * \frac{4x0.1}{2} = 11.22$$

4.3f) Determination of iodine value

Iodine value of the castor oil is calculated using equation 3.6. However, due to absence of carbon tetrachloride and potassium iodide at laboratory and high cost of them from the market, iodine value of castor oil is not calculated in this case.

Generally, the measured and literature value of castor oil physical characteristic was summarized in table 4.3 below.

Table4.3: Experimental Result and literature value of physical property the Extracted castor Oil

Physical property	**Values of the physical property**		**Units**
	Literature value	**Experimental value**	
Color	Light yellow	Light yellow	
Specific gravity	0.957-0.963	0.96	
pH value	-	4.45	pH meter
Acid value	10	11.22	
Saponification value	177-182	172.4	
Viscosity	-	645@20.4^{0}C	mPas
Iodine value	82-89	-	

4.4. Optimizing and quality analysis of detergent from castor oil

In this experiment 1.5L castor oil was prepared through extraction and factors to be studied where basic ingredients of synthetic detergents (surfactants/castor oil, NaOH, Na_2SiO_3, Na_2SO_4) with levels two by taking water and perfume as constant factor.

The response can be measured after mixing of all those ingredients using stirrer at 100mps for 30min agitating hour. The physical characteristics: pH value, foamability and cleaning power of the detergent was determined as the procedure discussed under section of 3.8 above.

Table.4.4. Response of synthetic detergent produced from castor oil at different types of ingredients with constant 1mL value of perfumes

Run	Amount of castor oil (mL)	Amount of NaOH(mL)	Amount of Na_2SiO_3 (mL)	Amount of Na_2SO_4(gm.)	Alkalinity pH	Height of foamability (cm)
1	30	15	1	2.66	9.45	0.76
2	35	15	1	2.66	8.53	0.81
3	30	20	1	2.66	11.64	0.73
4	35	20	1	2.66	11.4	0.88
5	30	15	5	2.66	9.65	0.85
6	35	15	5	2.66	8.84	0.82
7	30	20	5	2.66	11.65	0.88
8	35	20	5	2.66	10.46	0.85
9	30	15	1	21.28	9.43	1.5
10	35	15	1	21.28	8.52	1.75
11	30	20	1	21.28	11.4	1.2
12	35	20	1	21.28	11.2	0.87
13	30	15	5	21.28	9.25	1.62
14	35	15	5	21.28	8.6	1.8
15	30	20	5	21.28	11.26	1.6
16	35	20	5	21.28	11.43	0.98

The maximum height of produced detergent was 1.8cm at high value of sodium sulphate and the best means neither much basic or acidic alkalinity pH of the detergent was 8.52.

4.4a) Effect of surfactants on the production of synthetic detergent

Surfactants offer a unique combination of excellent detergency, rapid wetting, and fast collapsing foam for good rinse ability. Setting reaction time and mixing rate were 30min and 150 rpm, respectively for all the runs. The effect of surfactants at 30 and 35mL on alkalinity of detergent is inversely proportional to caustic soda, 1:5 and 2.66:21.28 amounts of sodium silicate and sodium sulphate respectively. This means as amount of oil increases with constant value of caustic soda, the pH value of detergent is deceases from base to acidic alkalinity and vice versa. Thus, optimum point of alkalinity is 8.52.

4.4b) Effect of sodium sulphate on the production synthetic detergent

Setting reaction time and mixing rate were 30min and 150 rpm, respectively for all the runs. The effect of sodium sulphate at 2.66 and 21.28gm on foamability height of detergent was directly proportional to sodium silicate 1:5. This means as amount of sodium sulphate increases with value of sodium silicate, the foamability height value of detergent was somewhat increases.

4.4c) Effect of sodium silicate on the production synthetic detergent

In the detergent industry sodium silicate provides: Emulsification of organic oils, inhibition of corrosion of metals in processing and washing equipment and dispersion and suspension of particulate matter. Thus from the above table we don't say anything about it. However, it has major role in cleaning power.

4.4d) Effect of sodium hydroxide on the production synthetic detergent

Sodium hydroxide was an alkalinity factor used to convert triglyceride of oil to detergent and glycerol. And also a factor that adjusts the pH value of detergent produced based on the amount of surfactant/oil used in the production of detergent. From the table of 4.8 given above as the amount of caustic soda increases at constant amount of oil, the alkalinity of detergent was increases and vice versa.

4.5) Statistical Analysis on Factors Affecting of synthetic detergent quality

Experimental design was selected for the statistical analysis of the study by selecting General Factorial Design (GFD) and the response measured were the alkalinity, foamability and cleaning power of produced liquid detergent. The four ingredients of detergent production process factors chosen to be studied were: volume of surfactant/castor oil, volume of NaOH, weight of calcium sulphate and volume of sodium silicate. Regression analysis and analysis of variance (ANOVA) was done by using Design Expert 7.0.0 program. The software program was used to generate surface plots, using the fitted equation obtained from the regression analysis, keeping one of the independent variables constant.

Response of the detergent production process was used to develop a mathematical model that correlates the qualities of the detergent produced to the ingredient variables studied. Design Expert software version 7.0.0 was used for the regression analysis of the experimental data and also for evaluation of the statistical significance of the equation developed. The general factorial design results and responses, and the statistical analysis of the ANOVA are given below.

4.5i) Development of Regression Model Equation

The model equation that correlates the response quality of castor oil to synthetic detergent to the process variables in terms of coded factors after excluding the insignificant terms was given below in equation 4.1and 4.2. Final Equation in terms of coded factors:

$$\text{Alkalinity} = 10.17 - 0.3A - 1.14B - 0.027C - 0.033D \quad (4.1)$$

$$\text{Height of foamability} = 1.12 - 0.024A - 0.12B + 0.056C + 0.3D \quad (4.2)$$

A = Volume of castor oil

B = Volume of NaOH

C = Volume of sodium silicate

D = Weight of sodium sulphate

Table 4.5 ANOVA analysis of experimental result

Table 4.5a ANOVA analysis of alkalinity result

Response 1 Alkalinity

Source	**Sum of Squares**	**Df**	**Mean Square**	**F Value**	**P- value Prob>F**
Model	22.07	4	5.52	57.65	< 0.0001
A-Amt of castor oil	1.41	1	1.41	14.73	0.0028
B-Amt of NaOH	20.63	1	20.63	215.57	< 0.0001
C-Amt of Na_2SiO_3	0.012	1	0.012	0.12	0.7348
D-Amt of Na_2SO_4	0.018	1	0.018	0.18	0.6767
Residual	1.05	11	0.096		
Cor Total	23.13	15			

The Model F-value of 57.65 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case volume of castor oil (A) and volume of NaOH (B) are significant model terms on the effects of alkalinity. Values greater than 0.1000 indicate the model terms are not significant.

Table 4.5b ANOVA analysis of height foamability result

Response 2 Foamability height

Source	**Sum of Squares**	**Df**	**Mean Square**	**F Value**	**P- value Prob>F**
Model	1.69	4	0.42	7.67	0.0033
A-Amt of castor oil	9.025E-003	1	9.025E-003	0.16	0.6937
B-Amt of NaOH	0.23	1	0.23	4.17	0.0657
C-Amt of Na_2SiO_3	0.051	1	0.051	0.92	0.3588
D-Amt of Na_2SO_4	1.4	1	1.4	25.44	0.0004
Residual	0.61	11	0.055		
Cor Total	2.3	15			

The Model F-value of 7.67 implies the model is significant. There is only a 0.33% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case amount of sodium sulphate (D) are significant model terms on the foamability height of the produced detergent.

4.5i) Effect of Interaction between Process Variables

The process variables were found to have significant interaction effects on alkalinity. Table4.6 shows the interaction of the four ingredients.

Table 4.6 ANOVA analysis of interaction alkalinity result

Response 1 Alkalinity

Source	**Sum of squares**	**Df**	**Mean squares**	**F- value**	**P-value Prob > F**
Model	23.04	14	1.65	19.24	0.1771
A-Amt of castor oil	1.41	1	1.41	16.48	0.1537
B-Amt of NaOH	20.63	1	20.63	241.18	0.0409
C-Amt of Na_2SiO_3	0.012	1	0.012	0.14	0.7758
D-Amt of Na_2SO_4	0.018	1	0.018	0.21	0.7292
AB	0.21	1	0.21	2.45	0.3621
AC	2.756E-003	1	2.756E-003	0.032	0.8869
AD	0.15	1	0.15	1.8	0.4077
BC	0.098	1	0.098	1.14	0.4790
BD	0.041	1	0.041	0.48	0.6145
CD	0.011	1	0.011	0.12	0.7854
ABC	0.056	1	0.056	0.66	0.5658
ABD	0.095	1	0.095	1.11	0.4841
ACD	0.14	1	0.14	1.58	0.4280
BCD	0.17	1	0.17	1.94	0.3963
Residual	0.086	1	0.086		
Cor Total	23.13	15			

The "Model F-value" of 19.24 implies the model is not significant relative to the noise. There is a 17.71 % chance that a "Model F-value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case NaOH (B) are significant model terms.

Figure 4.3a, 4.3b and 4.4 shows the interaction between castor oil and NaOH, Sodium silicate and Sodium sulphate, castor oil and sodium silicate, NaOH and Sodium sulphate, respectively, on the quality of detergent produced. Generally, an increase in reaction surfactants/castor oil with volume of NaOH is found to increase the alkalinity up to some optimal value in all four cases.

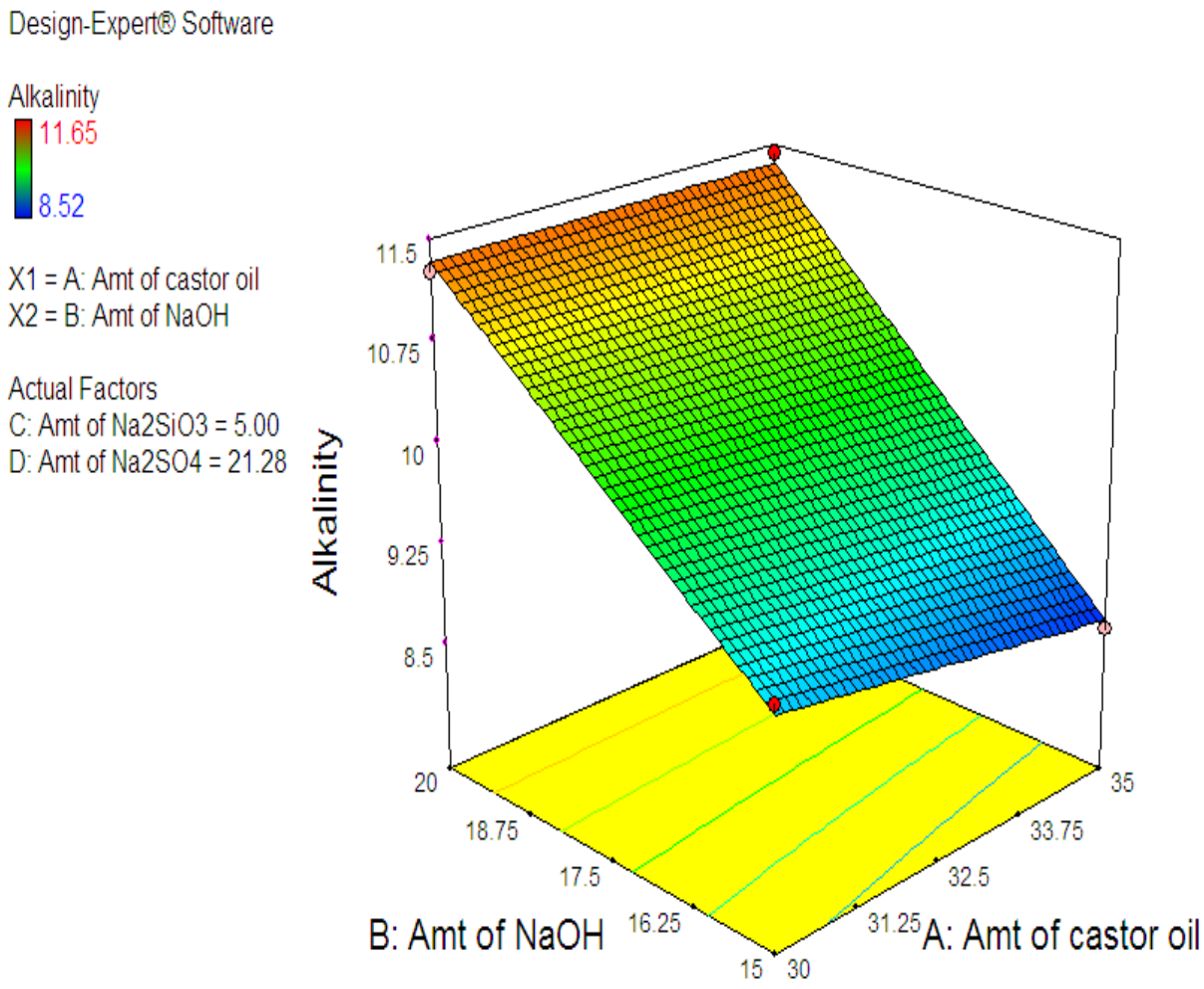


Figure4. 3a: Response surface plot of the interaction effect of castor oil and NaOH versus alkalinity

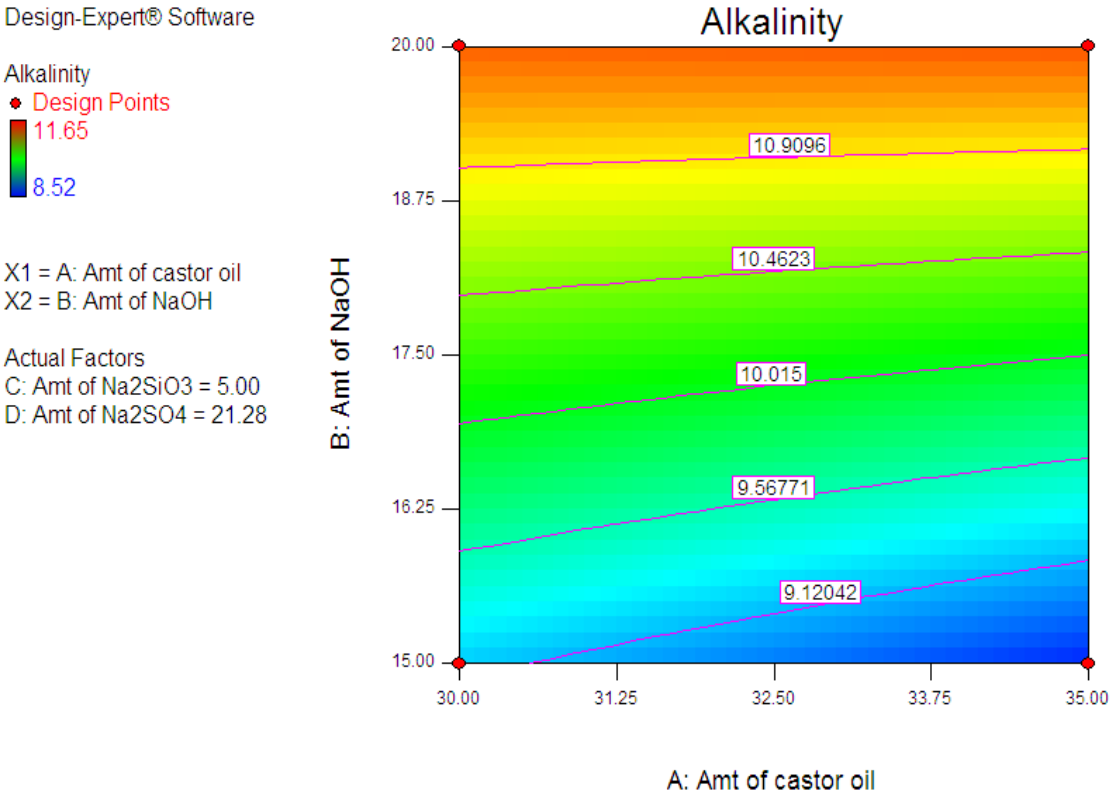


Figure4. 3b: Counter plot of the interaction effect of castor oil and NaOH versus alkalinity

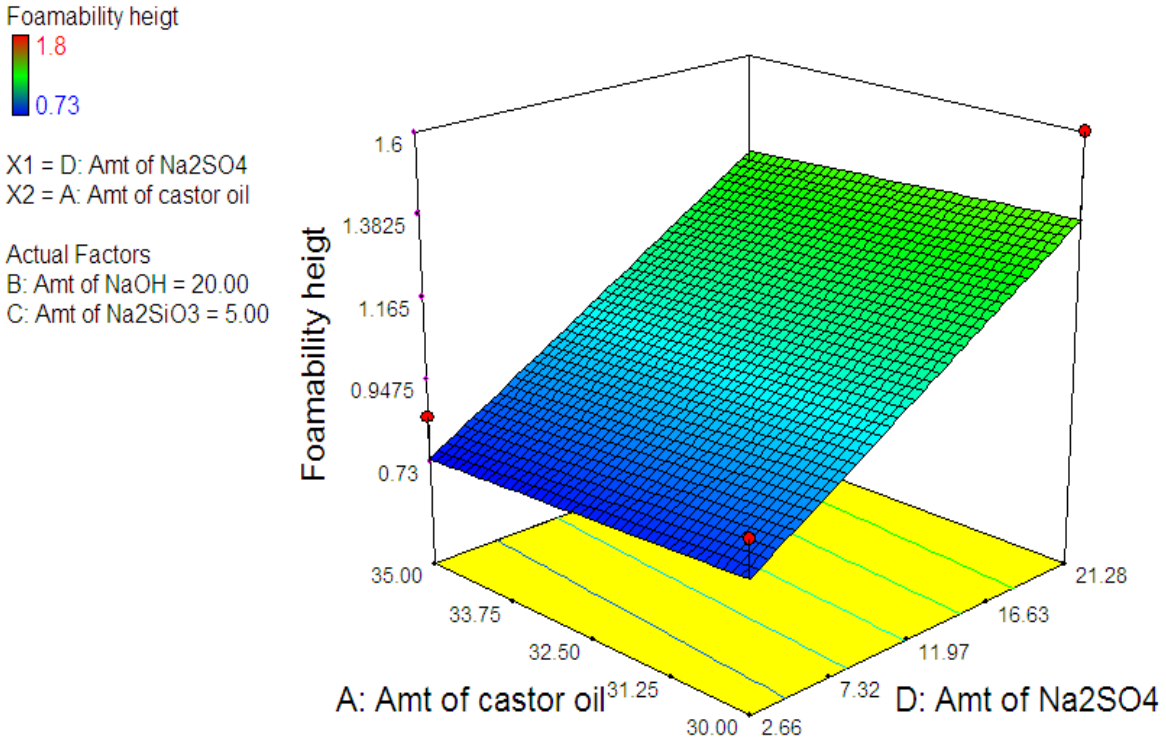


Figure4.4: Response surface plot of the interaction effect of castor oil and Na_2SO_4 versus Height

4.5ii) Optimization of Process Variables

Using the optimization function in Design Expert 7.0.0, it was predicted that at the following conditions; 35mL of castor oil and 15mL of NaOH, an optimum alkalinity of 8.52pH was obtained. And at 35mL of castor oil and 20mL of NaOH, an optimum foamability height was 1.8cm.The ANOVA output shows that the detergent product process alkalinity is highly and significantly affected by the amount of castor oil and the interaction between the amounts of NaOH.

4.6) Analysis of the parameters standardized effect on produced detergent

Analysis methods of parameters standardized effects were depended on procedures given in 3.6c.

Table 4.7.Quality and analysis of synthetic detergent produced

Run	Amt of castor oil (mL)	Amt of NaOH (mL)	Amt of Na_2SiO_3 (mL)	Amt of Na_2SO_4 (gm)	Cleaning power (Good/Not)
1	30	15	1	2.66	Not
2	35	15	1	2.66	Not
3	30	20	1	2.66	Not
4	35	20	1	2.66	Not
5	30	15	5	2.66	Good
6	35	15	5	2.66	Good
7	30	20	5	2.66	Good
8	35	20	5	2.66	Good
9	30	15	1	21.28	Not
10	35	15	1	21.28	Not
11	30	20	1	21.28	Not
12	35	20	1	21.28	Not
13	30	15	5	21.28	Good
14	35	15	5	21.28	Good
15	30	20	5	21.28	Good
16	35	20	5	21.28	Good

4.7) Comparison of properties of produced detergents with two local detergents

When this analysis was done, the run taken was depending on the optimum value of detergent produced.

Alkalinity: - Alkalinity methods of parameters standardized effects were depended on procedures given in 3.6b. This means from table 4.8 the value at which high maximum height and low value of pH was recorded.

Table 4.8 below shows the comparison of alkalinity of produced detergent with local detergent

Run	**Alkalinity (pH) value**		
	Produced detergent	**Local detergent**	
		Shemu liquid detergent	555 liquid detergent
1	8.8	8.54	9.65
2	8.5	9	9.4
3	8.2	9.4	9
Average	**8.5**	**8.98**	**9.35**

Foamability:

Foamability height parameters standardized effects were depended on procedures given in 3.6d.

Table 4.9 below shows the comparison of foamability of produced detergent with local detergent

Run	**Foamability height (cm) value**		
	Produced detergent	**Local detergent**	
		Shemu liquid detergent	555 liquid detergent
1	1.8	8	10
2	1.62	10.5	11
3	1.75	12	10.5
Average	**1.73**	**10.2**	**10.5**

Cleansing power:

Foamability height parameters standardized effects were depended on procedures given in 3.6c.

Table 4.10 below shows the comparison of cleansing power of produced detergent with local detergent

Run	**Cleansing power**		
	Produced detergent	**Local detergent**	
		Shemu liquid detergent	555 liquid detergent
1	Good	Excellent	Excellent

Hardness of detergent in hard water:

Hardness parameters standardized effects were depended on procedures given in 3.6e. However, in this paper due to absence of $FeCl_3$ and $MgCl_2$ chemicals from the market (even in the research laboratory) at that time this part was not considered.

5. ECONOMIC EVALUATION

5.1. Process description and technology selection for detergent production from castor oil

The extracted oil is saponified with sodium hydroxide after the saponification value (S.V) is determined. The mixture of oil, NaOH and other ingredients solution are recommended to stir at 150 rpm for 30min.Then ethanol or some amount of heat is mixed in the mixer with standard agitator to facilitate the reaction.

Castor oil and sodium hydroxide mixture is then charged into a mixer and the ingredients (5%Sodium silicate, 12gmSodium sulphate) are added for 30min saponification reaction at 150 rpm. It is recommended to have 1% of the volume of perfumes.

5.2. Basic Operating Methods

After discussing the basic production process of detergent, the next judgment concerns how the plant will actually be worked. Three basic alternatives: batch, continuous or batch-continuous processes.

5.2a) Batch Operation

One batch of feedstock is done without depending on the next for all processes such as pretreatment, reaction, separation and purification. Batch operations can easily be established and stopped, are good for facilities that do not function for 24 hours a day.

5.2b) Continuous Operation

The process is an unending flow of feed stocks, reactions and purification. These operations are typically of the largest and most efficient ways of integrating energy and mass units. These operations are dependent upon a consistent feedstock, typically single sourced, and are sensitive to process conditions.

5.2c) Batch-Continuous Operation

This operation endeavors to obtain the advantages of both of batch and continuous operations. It is based on mixer that feed the feedstock at once and continuously discharging the product or continuously adding the feedstock and discharging the product at once, a continuous separation and purification process. It used to control the reaction process and

change feed stocks more rapidly than the continuous and batch operations. Table 5.1 compares characteristics of the batch with the continuous operations.

Table5. 1: Comparisons of batch and continuous operations

Characteristics	**Batch process**	**Continuous process**
Typical capital	Less	Greater
Economy of scale	< 10 million gallons per year	> 10 million gallons per year
Feedstock flexibility	Greater flexibility	Less flexibility
Consumption of input	Greater	Less
Product yield	Less	Greater
Typical plant size	Smaller	Larger

(Source: Frazier Barnes & Associates, Memphis, TN)

From the alternatives given in Table 5.1, a continuous process is selected to be well matched with current production capacity for producing liquid detergent from castor oil plant commercially.

5.3) Material balance on major unit operations

Note: All material balances had performed based on the experimental work in the laboratory.

5.3.a) Balance on oven/Drier

Basis: 200kg/hr of fresh castor seed

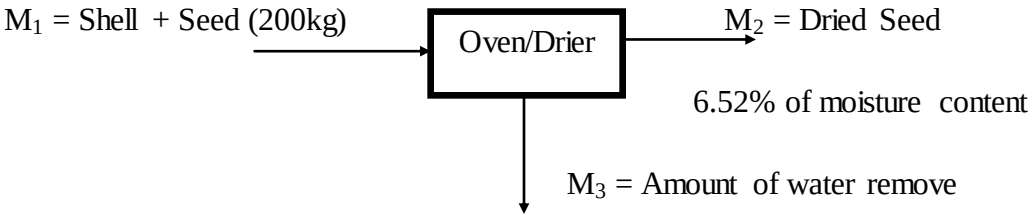
Weight of the flesh from the fresh seed=6.5% of fresh seed

General of Material Balance

$$\text{Accumulation} = \text{Output} + \text{Consumption} - \text{Input} - \text{Generation} \quad (5.1)$$

However there is no reaction, the generation and consumption terms are zero, no accumulation, since Input = output

Taking bases: 200kg/hr



200gm of fresh wet castor seed contains

- ✓ 200 x 0.0652kg water = 13.04kg moisture and
- ✓ 200 – 13.04 = 186.96kg castor dry seed

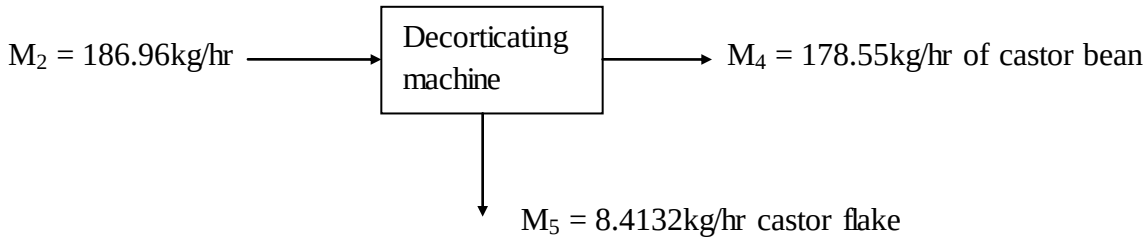
The final product contains 6.52% moisture, the moisture in the product is 13.04/ (6.52-1) = 2.36kg. And so Moisture removed / hr = 13.04 – 2.36 = 10.68kg/hr

5.3.b) Balance on decorticating machine

From laboratory work, wt. Castor flake= 4.5% of Castor seed.

Table 5.2: Average present calculation of castor flake from castor seed

Weight of castor seed (gm)	Weight of castor bean(gm)	Weight of castor flake (gm)	% of castor flake
35	33.32	1.68	0.04
40	38.08	1.92	0.048
45	42.84	2.16	0.048
Average			**0.045**



5.3.c) Balance on size reduction Machine

Here there was 1% of castor bean that less than 2.55mm size was loss, then = 1.7855 kg/hr of castor bean was lost. Then, the amount of raw material left to the extraction vessel with particle size ranges from 2.55-4mm will be M_6 = 176.765kg/hr.

5.3.d) Balance on soxhlet Extraction

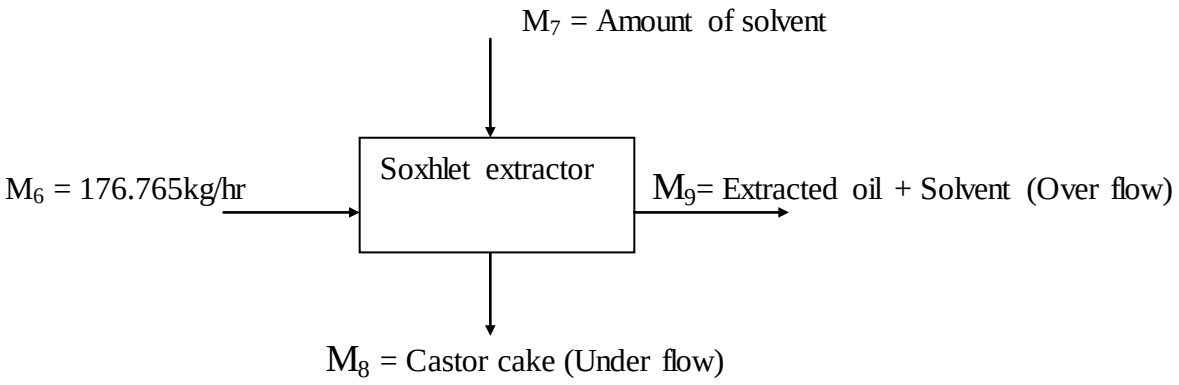
In the laboratory, for 35g of Castor bean, the amount of solvent required should be 9 times. Thus, 315ml of solvent was used, therefore, for 176.765kg/hr of Castor bean 1591.2Lof n-Hexane solvent will be required which is:

Mass of solvent = Density of solvent * Volume of solvent

Density of hexane at 20^0C is 0.66g/mL =0.66kg/L

Therefore: Mass of solvent = 0.66kg/L * 1591.2L/hr = 1050.2kg/hr solvent was required.

Now; from the optimum point of the laboratory castor oil extraction by soxhlet: 35g of the castor bean with an oil content of 49.34 wt% are contacted with 315mL (207.9kg/hr) of fresh hexane. Depending on the equation of (2.2 and 2.3), we can solve the following value.



Total mass balance:

$M_6 + M_7 = Mt$, 176.765 + 207.9 = Mt, Mt = 384.7kg/hr

Balance for castor seed (M_6)

$$M_6 * X_{M6} + M_7 * X_{M7} = Mt * X_{Mt}$$

With the feed concentration X_{M6}= 0.5066 and the suggestion, that no solid particles are included in the overflow, so X_{M7} = 0 follows:

$$176.765*0.5066 + 207.9 * 0 = 384.7 * X_{Mt}$$

$X_A = 0.233$

Balance for solvent (M_7)

$$M_6 * X_{M6} + M_7 * X_{M7} = Mt * X_{Mt}$$

With the feed concentration X_{M6}= 0.4934 and with the knowledge, that pure hexane is used as solvent, X_M = 0, follows:

$$176.765 * 0.4934 + 207.9 * 0 = 384.7 * X_{Mt}$$

X_B = 0.2267

The concentration of compound solvent in the mixing point Mt can be determined by the rule that the sum of the mass percent of each compound in the point Mt has to be 1.

$$XA + XB + Xsolv = 1$$

0.233 + 0.2267 + Xsolv= 1, Xsolv = 0.54

The amount of the leaving flows M_8 and M_9 can be calculated from the mass balance for castor bean

$$Mt * X_A = M_9 * X_{M9} + M_8 * X_{M8}$$

With X_{M9} = 0 (no solid material in the overflow) and X_{M8}= 1-0.54 = 0.46 (underflow)

$$M_8 = \frac{Mt * Xa}{X8} = \frac{384.7 * 0.233}{0.46} = 194.86 \text{kg/hr}$$

From the total mass balance

$$Mt = M_8 + M_9, \; M_9 = Mt - M_8$$

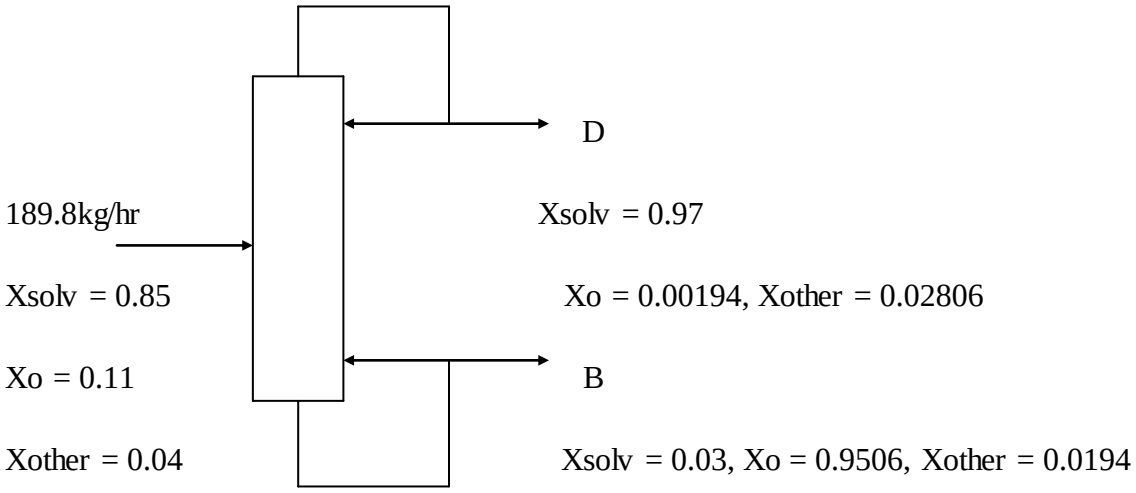
$$= 384.7 - 194.86 = 189.8 \text{kg/hr}$$

The amount of solvent in the oil will be 189.8kg/hr and separated by distillation and the solvent will recycle.

5.3.e) Balance on Distillation Unit

The composition of the vapour in equilibrium with a liquid of given composition is determined experimentally using an equilibrium. However; in this experiment due to absence of time experiment and vapor measuring device, the composition of the feed, the top and bottom product was assumed.

Mole fraction of solvent at feed = 0.85, Mole fraction of top product = 0.97 and Mole fraction of bottom product = 0.03



Oil balance around the column

$$0.11*189.8 = 0.9506*B + 0.00194* D \quad (5.2)$$

Solvent balance

$$0.85*189.8 = 0.03*B + 0.97* D \quad (5.3)$$

From these two equations using simultaneous method calculation the bottom product and the distillate flow rate contains 21.63Kg/hr and 163.2Kg/hr, respectively.

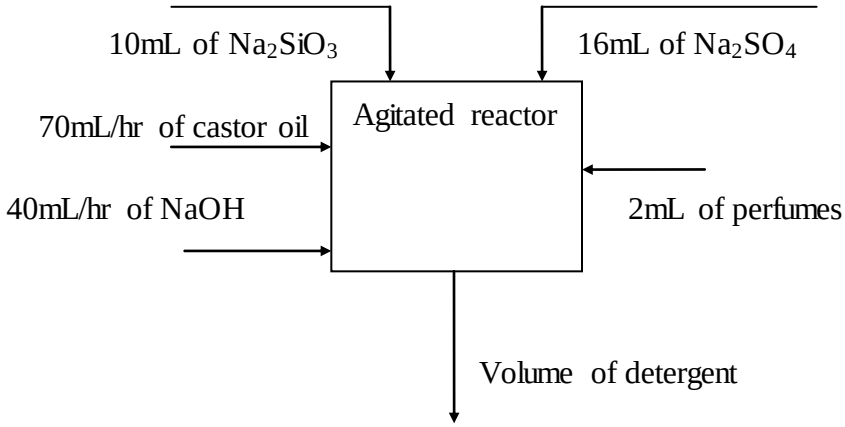
5.3.f) Material balance on agitator reactor for liquid detergent

Basis: 200mL/hr of liquid detergent

The amounts of ingredients for silk fabric liquid detergent production are:

- ✓ Surfactants (castor oil) = 35%
- ✓ Sodium hydroxide (NaOH) = 20%

- ✓ Sodium silicate (Na_2SiO_3) = 5%
- ✓ Sodium sulphate (Na_2SO_4) = 8%
- ✓ Perfumes = 1%



Volume of detergent = 10+ 70 +40 +16+2 = 138mL

Now from 23.82kg/hr of castor oil the liquid detergent produced was calculated as follows:

Density of castor oil = 1.042kg/m^3

Volume of castor oil = 23.82/1.042 = 22.86m^3

Hence; 22.86m^3 of castor oil is used to produce 45.1m^3 of liquid detergent

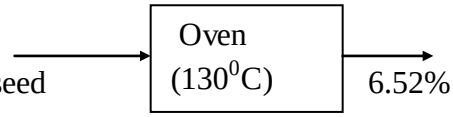
Table5:3 Summary of material balance

Equipment	Input type	Flow rate (kg/hr)	Output type	Flow rate (kg/hr)	Capacity (kg/hr)
Drier	Castor seed	200	✓ Water ✓ Seed	13.04 186.96	200
Decorticating machine	Castor seed	186.96	✓ Flake ✓ Bean	8.4132 178.55	186.96
Size reduction machine	Castor bean	178.55	• Seed • Small seed	176.76 1.7855	178.55
Soxhlet	Castor bean & solvent	384.7	✦ Solvent with oil ✦ Cake	189.8 194.86	384.7
Distillation	Castor oil with solvent	384.7	Distillate Bottom/oil	163.2 21.63	384.7
Neutralizer	Castor oil NaOH	70mL/hr 40mL/hr	Neutralized mixture	110mL/hr	110mL/hr
Agitator reactor	Neutralized mixture Na_2SiO_3 Na_2SO_4 Perfumes	110mL 10mL 16mL 2mL	Liquid detergent	138mL	138mL

5.4) Energy balance

A) Energy balance on the oven/drier

From the laboratory the throughput of the oven is 200kg of wet castor seed per hour, drying it from 65% moisture to 6.52% moisture, the overall thermal efficiency of the oven taking into account the latent heat of evaporation can be estimated as follows.



200kg/hr of castor seed (With 93.48% moisture) → Oven (130^0C) → 6.52% of moisture with dried castor seed

200gm of wet castor seed contains

- ✓ 200 x 0.0652kg water = 13.04kg moisture and
- ✓ 200 – 13.04 = 186.96kg castor dry seed

The final product contains 6.52% moisture, the moisture in the product is 13.04/ (6.52-1) = 2.36kg. And so Moisture removed / hr = 13.04 – 2.36 = 10.68kg/hr

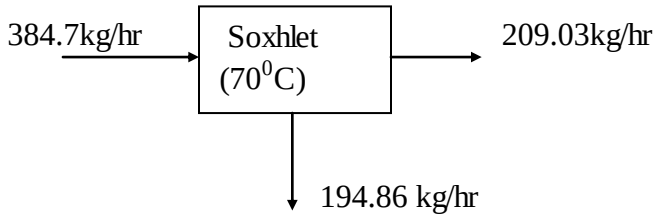
Note: Latent heat varies with temperature. For the most common solvent, water, the latent heat of evaporation is 2501 kJ/kg at 0^0C and 2256 kJ/kg at 100^0C. At ambient temperatures, around 20^0C, a figure of 2400 kJ/kg is a good working approximation. So, for a drying process which requires the evaporation of 1kg/s of water from the solid, an absolute minimum of 2256 kJ/s (2256kW) must be supplied to the process in some way.

Latent heat of evaporation = 2256 kJ/kg

Heat necessary to supply = 10.68 x 2256 = 24094.1 J/hr = $2.409*10^4$kJ/hr

B) Energy balance on the soxhlet

Assuming for extraction of oil from the castor seed bean at 70^0C; taking 2200kJ/kg latent heat of evaporation.



Heat necessary supply to soxhlet = 384.7 * 2200kJ/kg = $84.6*10^4$kJ/hr

C) Energy balance on the distillation

Assumptions and from the laboratory result

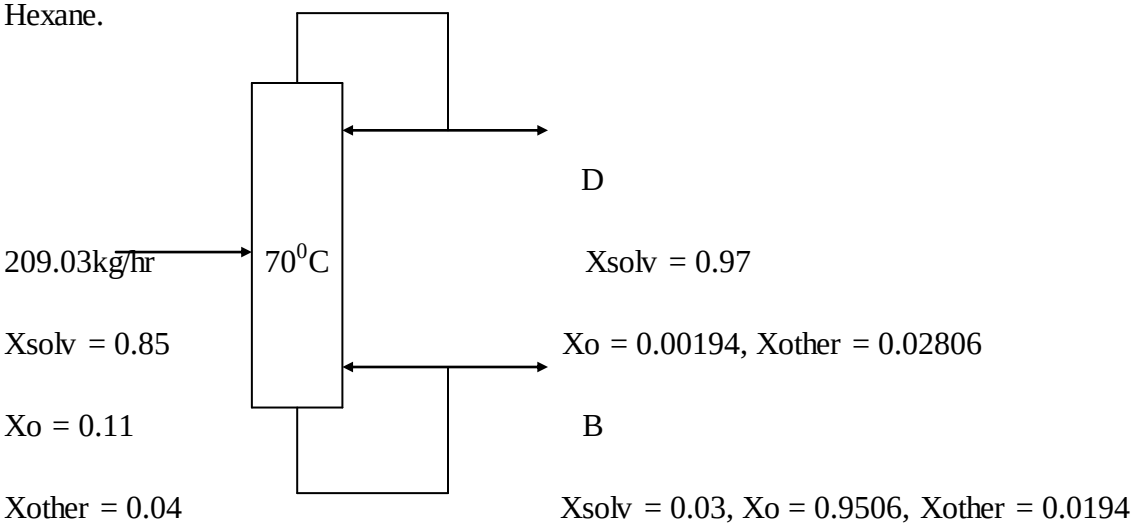
The balance is with no chemical reaction and used to determine the mass of cooling water and steam required for the distillation column operation.

Steam is available at 70^0C and 1 bar.

The rise in cooling water temperature is limited to 25^0C.

Distillation column operates at 1 bar.

From the material balance the distillate contains 97% oil and the bottom contains 3% n-Hexane.



The energy balance can be done on the condenser and Re-boiler.

Inputs: Re-boiler Heat (Q_B) + Feed sensible heat (H_F).

Outputs: Condenser Cooling (Q_C) + top and bottom product sensible heats ($H_D + H_W$).

To minimize heat losses from the system the column and exchangers are properly covered and will be neglected.

In the column the residence time is 6 hours at 70^0C.

Heat capacity data were taken from property tables and chart that is average values.

n-Hexane @ 273K to 1500K, 2.01kJ/kg.K

Castor crude oil: 1.99kJ/kg.K and it is assumed constant in the range;

Basis: 70^0C, residence time for 6 hours in the column

Crude oil/other: 70^0C to 1227^0C, 4.188kJ/kg.K and it is interpolated in the range

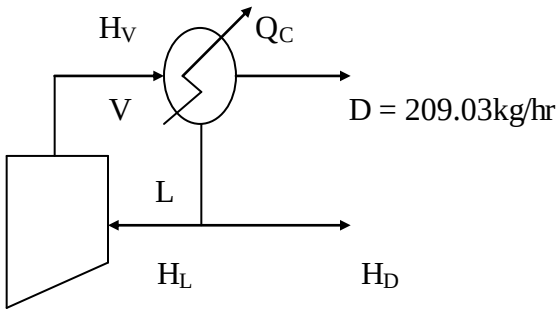
Heat capacities can be taken as additive

Feed, 4% oil = 0.04* 4.188 + 0.85* 2.01 = 1.876kJ/kg.K

Tops, 97 percent n-hexane = 0.97 *2.01 + 0.02806* 4.188 = 2.067kJ/kg.K

Bottoms, 95.06 percent crude oil, 3 percent hexane and 1.94 percent water; Cp = 0.9506*1.99 + 0.0194* 4.188kJ/kg.K + 0.03*2.01= 2.033 kJ/kg.K

Q_C must be determined by taking a balance round the condenser



Where: V=Vapor flow L=Reflux flow H=Enthalpy

Taking the standard average value of the reflux ratio (R) = L/D; No hard and fast rules can be given for the selection of the design reflux ratio, but for many systems the optimum will lie between 1.2 to 1.5 times the minimum reflux ratio. = 1.35

L = D*R = 1.35*209.03kg/day = 282.19kg/day

V = L + D = 282.19 kg/day + 182.1kg/hr * 24hr/day * 18hr/24hr = 3277.8kg/day

From vapour-liquid equilibrium data:

Boiling point of 97 percent hexane/crude oil = 1227^0C

At steady state: Input = output

$H_V = H_D + H_L + Q_C$ Hence; $Q_C = H_V - H_D - H_L$

Assume complete condensation is taking place

Enthalpy of vapor H_V = Latent heat + Sensible heat

Latent heat of hexane at 1227^0C = 2400 kJ/kg

Latent heat of crude oil at 1227^0C=3300 kJ/kg (Assumption)

Taking latent heats as additive H_V = 3277.8 *[(0.03*3300) + (0.97*2400) + (70 - 25) *4.188)] = 8572.95kJ/day.

The enthalpy of the top product and reflux are zero, because they are at the reference temperature. Both are liquid, and the reflux will be at the same temperature as the product. Therefore, $Q_C = H_V$ = 8572.95kJ/day;

Q_B can be determined from a balance over entire system

Input=Output

$Q_B + H_F = Q_C + H_D + H_W$

H_F = 209.05*2.01(1227-70) = 486.16kJ/day

H_W= 23.82 * 24hr/day * 18hr/24hr * 1.99*(1227-70) = 987.189 kJ/day; output temperature of the bottom product is taken to be 1227^0C. Hence,

$Q_B = Q_C + H_W + H_D - H_F$

$Q_B = Q_C + H_W - H_F$

Q_B = 8572.95kJ/day +987.189 kJ/day - 486.16kJ/day

Q_B = 9073.979kJ/day

Q_B is supplied by condensing steam.

Latent heat of steam (From steam table) = 2174 kJ/kg = at 274 kN/m^2

Steam required = $\frac{QB}{Ls} = \frac{9073.979}{2174}$ = 4.174kJ/day

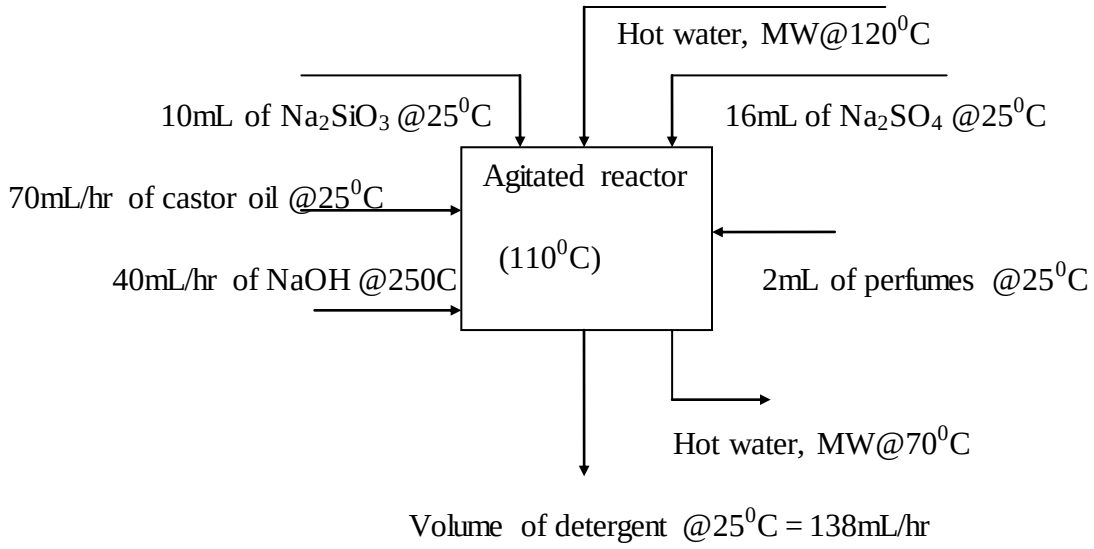
Q_C is removed by cooling water with a temperature rise of 70^0C

Q_C = water flow * 70*4.188

Water flow= 8572.95kJ/day / (70*4.188) = 29.24kg/day

D) Energy balance on the agitator reactor

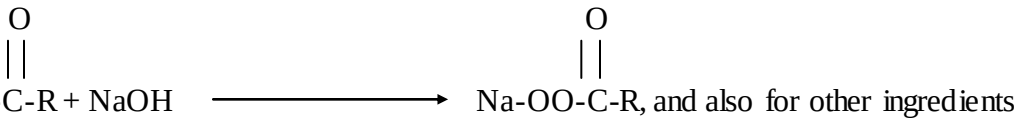
For producing an optimum amount of synthetic detergent the temperature inside the reactor should be maintained at 110^0C. This temperature is assumed to be achieved by supplying hot water at 120^0C and this temperature is assumed to fall to 105^0C so that the temperature inside the reactor is adjusted to the required value after charging the needed ingredients at reference temperature.



Assumption:

The specific heat is constant for a given liquids for small change of temperature. The major component of free fatty acid in the castor oil is Ricinoleic acid.

Where; R = HO-$(CH_2)_5CH_3$-COOH,



$Q_{Na2SiO3} + Q_{Hot\ Water} + Q_{Cleaned\ oil} + Q_{NaOH} + Q_{Na2SiO4} + Q_{Perfumes} = Q_{detergent}$

$M_{Na2SiO3} * Cp_{Na2SiO3} * \Delta T + M_{Hot\ Water} * Cp_{Hot\ Water} * \Delta T + M_{Cleaned\ oil} * Cp_{Cleaned\ oil} * \Delta T + M_{NaOH} * Cp_{NaOH} * \Delta T + M_{Na2SiO4} * Cp_{Na2SiO4} * \Delta T = Q_{detergent} + Q_{Hot\ Water}$

Assuming the heat reaction of all the ingredients is zero except heat reaction of hot water.

$0 + M_{Hot\ Water} + 4.188*(120-70) + 0 + 0 + 0 = M_{detergent} * 1.89*(110-25)$

209.4* $M_{Hot\ Water}$ = 138*160.65, $M_{Hot\ Water}$ = 106mL/hr

5.5) Sizing of main equipment

Storage tanks are sized depended on daily requirement; they can store and the assumption that the plant works for 2 shifts and 6 hour with 10% safety factor for the volume. And for the tanks it should be given 30 days allowance for storage and 80%for design safety.

Amount of castor seed = 1day*18hr/24hr*4800kg/day = 3600kg

Volume of silo = mass/density = 3600/1042kg/m^3 = 3.5m^3 and for the 10% safety factor

Volume of silo = 3.5 + 0.1(3.5) = 3.85m^3/day *30day = 115.5m^3

Amount of hexane = 1day*18hr/24hr*4989.6kg/day = 3742.2kg

Volume of hexane tank = 3742.2kg/660kg/m^3 = 5.67m^3 and for the 10% safety factor;

Volume of tank = 5.67m^3+0.1*5.67m^3=6.237m^3

By the similar approach,

Oven drier size: Tray areas are 0.3–1 m^2 with a depth of material of 10–100 mm, depending on the particle size of the product. Hence taking the average 0.65m^2 size is required.

Decorticating machine size: The crushing rolls, which may vary from a 1cm up to about 1.2 m in diameter, are suitable for effecting a small size reduction. Taking this average: diameter =0.605m

Extraction/leaching storage tank = volume of castor bean + volume of hexane

First amount of castor bean to extraction = 1day*18hr/24hr*295.92kg/day = 221.94kg and

Amount of hexane to extraction = 1day*18hr/24hr*4989.6kg/day = 3742.2kg

Volume of leaching tank = 384.7kg/577kg/m^3 + 3742.2kg/660kg/m^3 = 6.3m^3 and for the 10% safety factor: 6.3 + 0.1*(6.3) = 6.9m^3

Sodium hydroxide amount = 960mL/day * 2130kg/m^3 = 2.05kg/day

Storage tank for sodium hydroxide = 2.05kg/213030m^3 = 0.033m^3 with safety factor

Amount of oil = 1680mL/day * 1042kg/m^3 = 1.751kg/day

Oil storage tank= $1.2m^3$ *30 =$36m^3$

Amount of sodium silicate = 1day*18hr/24hr*921600kg/day = 0.69kg

Sodium silicate storage tank = 0.000288m3/day*30day = $0.1m^3$

Sodium sulphate storage tank = $0.1m^3$

Liquid detergent storage tank = 151.8mL

Agitator mixer tank = $1.1m^3$

Rough sizing of distillation column provides a height of 1.5 m and a diameter of 0.3 m.

5.6) Cost Estimation

5.6.1) Equipment cost

Using rapid capital cost estimation method for cost of each equipment.

1) Cost of oven/drier

A plate drier having surface area $1.858m^2$ costs 9900dollars*20 = 198000br.

Cost relative to capacity is given by using six-tenth rule or by scaling

Cost of equipment A = cost of equipment B (Capacity A/Capacity B) $^{0.6}$, where Equipment's A and B are of the same type.

Therefore Cost of drier = $9900(0.65/1.858)^{0.6}$ = 5271.762dollar*20 = 105435br.

2) Cost of Decorticator

Decorticating machine having diameter of 2.5ft (0.762m) costs 36800dollar, then using six tenth rules, cost of the same machine with 1.2m diameter will be

Cost of 0.605m machine = cost of 0.762m (diameter of 0.605/diameter of $0.762)^{0.6}$

= 36800 $(0.605/0.762)^{0.6}$ = 32042.6 dollars = 640852.5bir

In the similar approach the general table is constructed for other cost of equipment

Note: All construction materials are carbon steel

Table: 5.4. Purchased Equipment Cost estimation

No.	Equipment	Quantity	Size	Standard size of equipment	Unit price of std equipment ($)	New calculated cost ($)	Total cost ($)
	Process equipment						
1	Oven/drier	1	0.65m^2	1.858m^2	4000	2130	2130
2	Decorticating	1	0.605m	0.762m	3000	2612	2612
4	Extractor	1	6.7m^3	0.2m^3	500	1565	1565
5	Distillation	1	0.3m	0.1m diameter	3500	6766	6766
6	Agitator reactor	1	1.1m^3	5hp	800	800	800
	Storage tank						
7	Castor bean	1	115.5m^3	1m^3	200	3456	3456
8	Hexane	1	6.2m^3	0.1m^3	200	2379.4	2379.4
9	Leaching	1	6.9m^3	0.1m^3	200	2492.7	2492.7
10	NaOH	1	0.033m^3	0.1m^3	200	102.8	102.8
11	Na_2SiO_3	1	0.1m^3	0.01m^3	200	796.2	796.2
12	Na_2SO_4	1	≈ 0.1m^3	0.01m^3	200	796.2	796.2
13	Product	1	≈ 0.2m^3	0.01m^3	200	1206	1206
14	Pump	5	-	-	2000	2000	10000
This is generally the cost purchased equipment cost (PEC)					**Total cost in dollar ($)**		**35102.3**
					Total cost in birr(bir)		**702046**

5.6.2) Estimation of Fixed Capital Investment

Fixed capital investment is the capital needed to supply the necessary manufacturing and plant facilities. It is calculated as S.Peters and D. Timmerhaus of cost estimation from table 26 page 210.

Table5. 5: Estimation of Fixed Capital Investment

Categories	**Components**	**Estimation factors**	**Cost in dollar ($)**
Direct cost	Purchased equipment cost (PEC)	PEC	35102.3
	Equipment erection	0.03PEC	1053
	Piping	0.02 PEC	702
	Electrical installation	0.01 PEC	351
	Building	0.02PEC	702
	Instrumentation	0.025 PEC	878
	Total Direct Cost (DC)		**38788**
Indirect cost	Design and Engineering	0.01DC	388
	Contractors fee	0.02DC	776
	Contingency	0.01DC	388
	Total Indirect Cost		**1552**
Fixed Capital Investment	Direct cost + Indirect cost		**40340**
Working Capital (WCI)	0.05FCI		**2017**
Total Capital Investment	FCI + WC		**42357**

5.6.3) Estimation of Total Production Cost

Cost of raw materials

The cost of each raw material per year is estimated by multiplying the raw material required per day by 300 working days per year and 18 working hours per day, and then multiplying by raw material unit price.

Table5. 6: Cost of raw materials

Raw material	**Quantity per annum (kg/year)**	**Unit price ($/kg)**	**Total cost (dollar)**
Castor seed	66582	0.2	13316
NaOH	460.08	32	14722.56
Na_2SiO_3	129.6	32	4147
Na_2SO_4	229.8	32	7353.6
Perfumes	1L	$25/L	25
Hexane	1122.66	28.8	32332.608
Total			**71896.77**

Or; let's assume total product cost = y

Therefore, y = Manufacturing cost + general expenses

But, manufacturing cost is calculated as follows;

Manufacturing cost = Direct production cost + Fixed charges + Plant overhead cost

- ✓ Direct production cost = 60%y
- ✓ Plant overhead cost = 5%y

A) Fixed Charges: (10-20% total product cost)

Depreciation: (depends on life period, salvage value and method of calculation-about 13% of FCI for machinery and equipment and 2-3% for Building Value for Buildings)

Consider depreciation = 10% of FCI for machinery

i.e., Depreciation = 10% ($40340) = $4034

Local Taxes: 1% of FCI =1% ($40340) = $403

Insurances: (0.4-1% of fixed capital investment) Consider the Insurance = 0.4% of fixed capital investment i.e. Insurance = 0.004×$40340 = $161

Thus, Fixed Charges =depreciation +local taxes +insurance

= $4034+ $403+$161= $4598

B) General expenses = Administrative costs + distribution and selling costs + research and development costs

I. Administrative costs = 2%y

II. Research and development costs = 2%y

Now; total product cost(Y) = 0.6Y+0.05Y+0.02Y+0.02Y+fixed charges

Y = 0.6Y+0.05Y+0.02Y+0.02Y+$4598

Y= $14832 = Total Product Cost (TPC), therefore

Total direct product cost (Variable cost) = 0.6 * 14832 = 8899

Plant over head cost = 0.05 * y = 0.05 * 14832 = 742

General expenses = 0.02 * 14832 + 0.02 * 14832 = 593

5.6.4) Profitable analysis

Gross earning/ income and net profit worth calculation (if the product is to selling purpose) the following analysis is required for the feasibility of the project.

Whole sale Selling Price of liquid detergent per liter = $1/L

Total Income = Selling price × Quantity of product manufactured

= $1/L× (20L/batch*6batch/day*300day/year)

=$36000/year

Gross income = Total Income – Total Product Cost = ($36000 - $14832)

= $ 21168

Depreciation (D) = $\frac{\text{FCI}-\text{Salvage value}}{\text{Service life}}$; assuming salvage value =0 and taking 15 service life

$$= \frac{40340-0}{15} = \$2689$$

Net profit = [Gross income - Depreciation] (1-tax rate). Taking tax rate is 34%

= [$21168/year - $2689] (1-0.34)

= $12196

Payback period = $\frac{FCI}{NP+D} = \frac{40340}{12196+2689}$ = 2.7year

So, the payback period of the project is estimated to be 3years

5.6.5) Discounted Cash Flow Return (DCFR)

The discount flow rate of return is the return obtained from an investment in which all investment and cash flows are discounted. It is determined by setting the NPV equation equal to zero and solving for the discount rate that satisfies relation. The discounted rate of return or DCFR of the project and values at individual years, considering the plant capacity starting with 80% capacity at the first year and 90% capacity in the second year and with 100% capacity the remaining project life. Detail manipulation of the first two year is shown below:-

First year

Unit cost of liquid detergent = $1/liter

Annually earning of detergent = $1/L× (20L/batch*6batch/day*300day/year) = $36000/year

Unit cost of castor cake = $0.05/kg

Annually earning of castor cake = 60480kg/yr* $0.05/kg = $3024/yr

Therefore total annual earning = $39024/yr

Now using percent rate of operating time = 80%

Cash inflow = 0.8 * Total annual earning = 0.8 * 39024 = $31219.2/year

Second year

On this the percent rate of operating time = 90%

Cash inflow = 0.9 * Total annual earning

= 0.9 * 39024 = $35122/year

Table5. 7: Projected cash flow of the plant

Year	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Capacity utilization %	-	80	90	100	100	100	100	100
I. Cash inflow (Dollar)	-	**31219.2**	**35122**	**39024**	**39024**	**39024**	**39024**	**39024**
Income(dollar)	-	31219.2	35122	39024	39024	39024	39024	39024
Salvage value(dollar)	-	-	-	-	-	-	-	-
II. Cash outflow(dollar)	42357	**21477**	**25591**	**28435**	**28435**	**28435**	**28435**	**28435**
Total capital Investment (dollar)	42357	-	-	-	-	-	-	-
Raw material (dollar)	30%TCI	8895	11436	12707	12707	12707	12707	12707
Utilities(dollar)	15%TCI	5083	5718	6354	6354	6354	6354	6354
Plant overheads (dollar)	-	594	668	742	742	742	742	742
Depreciation(dollar)	-	3227	3631	4034	4034	4034	4034	4034
Fixed charges(dollar)	-	3678	4138	4598	4598	4598	4598	4598
Discount factor at Interest (12%)	-	**0.947**	**0.8358**	**0.6879**	**0.6574**	**0.5831**	**0.5172**	**0.4588**
Gross Profit(dollar) (I-II)	-42357	9742	9531	10589	10589	10589	10589	10589
Net profit(dollar)	-42357	9742	9531	10589	10589	10589	10589	10589
Present value = DF * Net profit	-	9226	7966	7284	6961	6174	5476	4858

Discount factor: - Is a factor to give present worth for cash flows which occur uniformly over one-year periods after the reference point. This project is new capacity established component; so for the new capacity project the minimum acceptable rate of return (MOR) is 8-12%. Taking this average the value of MOR is 12%. Depending on this MOR, the value discount factor is taken from the table 6 (S. Peters and D. Timmerhaus page 242), Discount factors (F,) with continuous interest to give present worth's for cash flows which occur uniformly over one-year periods after the reference point.

$$\text{Discount factor (DF)} = (1 + \text{MOR})^{-n}$$

For first year; DF = $(1 + 0.12)^{-1} = 0.893$

Present Value (PV) = Net profit *Discount factor

= 9742 * 0.893 = 8699

Such like this the discount factor of the 7-15 years service life was determined.

Year	7-8	8-9	9-10	10-11	11-12	12-13	13-14	14-15
DF	0.4069	0.3609	0.3201	0.2839	0.2518	0.2233	0.1981	0.1757
PV	4308	3822	3389	3006	2666	2364	2098	1861

$$\text{NPV} = \sum PV - \text{cash out flow}$$

NPV = 71459 – 42357 = 29102

According to the net present value rule if the value of NPV is positive, the project is acceptable. Hence from the above calculation the project is acceptable.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

Synthetic liquid detergent was produced using surfactants, sodium hydroxide and ingredients (i.e. sodium silicate, sodium sulphate, perfumes) at constant mixing time of 1hours, mixing rate of 150 rpm and at atmospheric pressure. Production of liquid detergent was performed by batch process system. The effects of amount of surfactants, sodium hydroxide, sodium silicate and sodium sulphate on detergent quality were determined. By using Design Expert 7.0.0 soft ware two levels; four factors General Design with full type, when amount of surfactant increases at constant amount of sodium hydroxide, the alkalinity of the detergent will be deceases to the neutrality and vice versa. As the amount of sodium sulphate increases the foamability height of the detergent and good cleansing power was obtained at the high amount of surfactant and sodium silicate.

The interaction effect of the four operating parameters was significantly detected on liquid detergent quality. However; all of these factors had not the interaction effect on the detergent quality. The best alkalinity of detergent was 9.85pH attained at 35mL surfactant and 15mL of NaOH and The maximum height of produced detergent was 1.8cm at high value of sodium sulphate (21.28gm) and sodium silicate (5mL). In contrast, the average high alkalinity was 12.5 at 30mL of surfactant and 20mL of NaOH with low value of sodium silicate.

The physical properties of the produced detergent were determined, with comparing two local liquid detergents. But, the produced liquid detergent from castor oil efficiency was not high enough.

Based on an existing production process and using current best values for ingredients, equipment, and supply costs an economic analysis it is suggested that the production cost of castor oil liquid detergent would be approximately $1/L. Thus, the preliminary economic analysis evaluation suggested that the project is feasible when comparing with the local liquid detergent $1.25/L. Therefore, castor oil can be used as a less expensive supplementary feedstock for detergent production by curing the environment and increasing the agricultural earning.

Recommendations

The oil was extracted using soxhlet extraction method; though, solvent extraction through this method was difficult;

Because to install small scale Castor oil extraction industry, solvent extraction method requires high investment cost due to the requirement of equipment with well designed control system, instrumentation to recover the solvent and the need of high electrical power to separate the solvent from the oil. For this reason, high efficiency of mechanical pressing must be good for the oil extraction.

Liquid detergent was produced using castor oil, NaOH, sodium silicate, sodium sulphate and perfumes. Consequently, using other ingredients like optical brightness and enzymes was recommended for more good quality of synthetic detergents.

REFERENCE

1. Donkor, Peter. Small Scale Soap making, TCC and Intermediate Technology Publications, 1986
2. Regulation on detergents Official Journal of the European Communities L104 (8th April) 1–35, 648/2004/EC (2004)
3. Characterization and extraction of vegetables oil, Ogunniyi, 2006
4. International Journal of research in pharmacology and pharmacotherapeutics (IJRPP)/vol.3/April-June 2014
5. http://server9.webmania.com/users/pfafardea/database/plants.php?Ricinus*communis Accessed on Oct 2010
6. EN ISO 17025 (1999) General requirements for the competence of testing and calibration laboratories. International Organization for Standardization
7. Kirtikar and Basu, Indian medicinal plants. 2nd edition. Vol. III. 1991; 2272-2275
8. International Journal of research in pharmacology and pharmacotherapeutics (IJRPP)/vol.3/April-June 2014
9. Davidsohn AS, Milwidsky BM. Synthetic Detergents (5th Ed.) International Textbook Company Ltd Buckingham Palace Rd London. 1972. Pp. 1 – 150
10. Malysa K, Lunkenheimer K (2008) Foams under dynamic conditions. Current Opinion in Colloid & Interface Science 13: 150-162.
11. Schramm LL, Wassmuth F (1994) Foams: Basic Principles. In: Schram-m LL (ed.) Foams: Fundamentals and Applications in the Petroleum Industry. American Chemical Society Washington, DC, USA.
12. Th.von Rybinski, W. and Schmiedel, P.(1998)Structure and dynamics of surfactant based foams. Progr. Colloid Polym. Sci., 111, 117–26.
13. Routledge E.J and Sumpter, J.P. (1996) Oestrogenic activity of surfactants and some of their degradation products assessed using recombinant yeast screen. Environ. Toxicol Chem., 15(3), 241–8.
14. Okpokwasili GO Nwabuzor CN Primary biodegradation of anionic surfactants in laundry detergents Chemosphere 1988
15. Biodegradability of surfactants in detergents. Official Journal of the European Communities, L347 (17 December 1973), 51–52.

16. Chemistry of Castor Oil and Its Derivatives and Their Applications International Castor Oil Association Technical Bulletin No.2, 1992
17. Biodegradability of non-ionic surfactants. Official Journal of the European Communities, L109 (22 April 1982), 1–17, 82/242/EEC (1982).
18. Regulation on detergents Official Journal of the European Communities L104 (8th April) 1–35, 648/2004/EC (2004).
19. EN ISO 17025 (1999) General requirements for the competence of testing and calibration laboratories. International Organization for Standardization.
20. Smil, V., Phosphorus in the environment: natural flows and human interferences. Annu. Rev. Energ. Environ 2000, 25, 53–88.
21. Solvent extraction characteristics of different size seeds, Wakelyn & Wan, 2006
22. Hydraulic press design and operation, Mrema and McNulty, 1985 in Owolarafe et al., 2008.
23. http:// www.wikipedia physical and chemical properties of n-hexane

APPENDIX

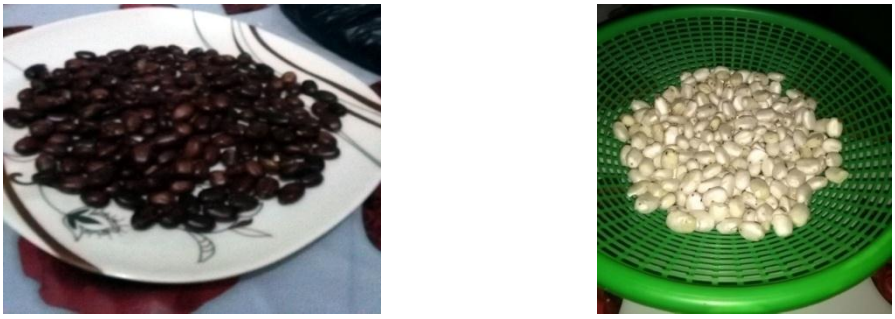
Appendix A. Pre-treatment of castor seeds for oil extraction and apparatus of soxhlet

The castor beans undergo various processing in the course of its preparation for extraction. The unit operations involved are:

- ✓ *Drying:* The beans were further dried in the oven at 130°Cfor 6hrs to a constant weight
  in order to reduce its moisture content, which was initially at about 5 to 7%.

Figure.0.1A. Oven drying apparatus of castor seed

- ✓ *Winnowing:* The separation of the shell from the nibs (cotyledon) was carried out using tray to blow away the cover in order to achieve very high yield.



Before winnowing After winnowing

Figure 0.2A.Separation of shell from the castor bean seed

- ✓ *Grinding (size reduction):* Mortar and pestle were used to crush the beans into a paste (cake) in order to weaken or rupture the cell walls to release castor fat for extraction.

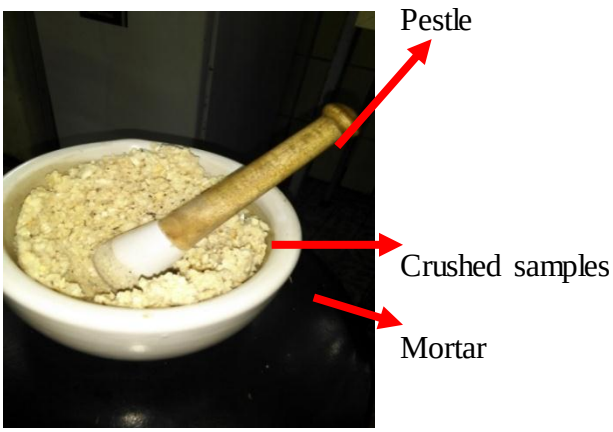
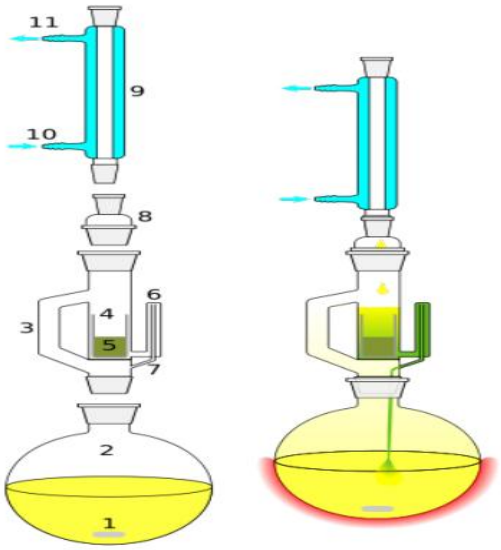


Figure0.3A. Size reduction of the winnowing castor seed (*Source, image during laboratory analysis*)



1: Stirrer bar/anti-bumping granules

2: Still pot (extraction pot) - still pot should not be overfilled and the volume of solvent in the still pot should be 3 to 4 times the volume of the soxhlet chamber.

3: Distillation path, **4:** Soxhlet Thimble, **5:** Extraction solid (residue solid)

6: Siphon arm inlet, **7:** Siphon arm outlet, **8:** Expansion adapter, **9:** Condenser, **10:** Cooling water in, **11:** Cooling water out

Figure 0.4A Schematic description and pictorial setup of the Soxhlet apparatus (***Source: Wikipedia, 2008c and laboratory setup).***

Appendix B. Determination of Physical and Chemical properties of the castor oil

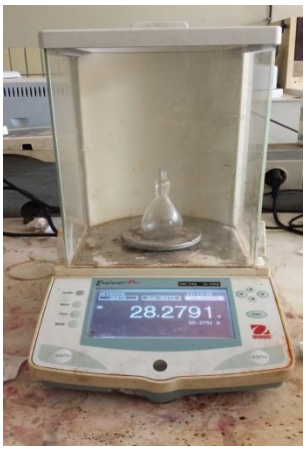


Figure 0.1B (a) Weight of 50mL Empty dry bottle (W_0)

Figure 0.1B (b) Weight of 50mL bottle with water (W_1)

Figure0.1B (c) Weight of 50mL bottle with castor oil (W_2)

Figure 0.1B: (a), (b), and (c) shows different values of density bottles empty, with water and oil measurement value respectively

Figure 0.2B Indicates viscosity value- with viscometer

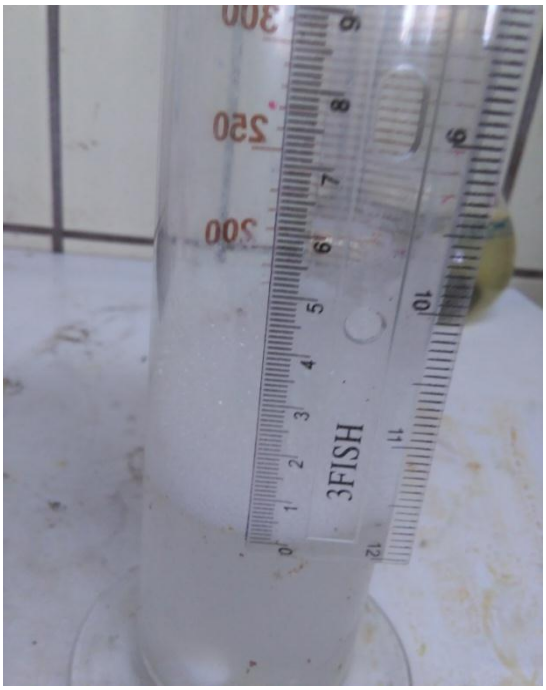
Figure 0.3B Measurement of the- acidity value of castor oil

Appendix C. Figurative description for Physical and Chemical analysis of the synthetic detergent produced

(a) (b) (c)

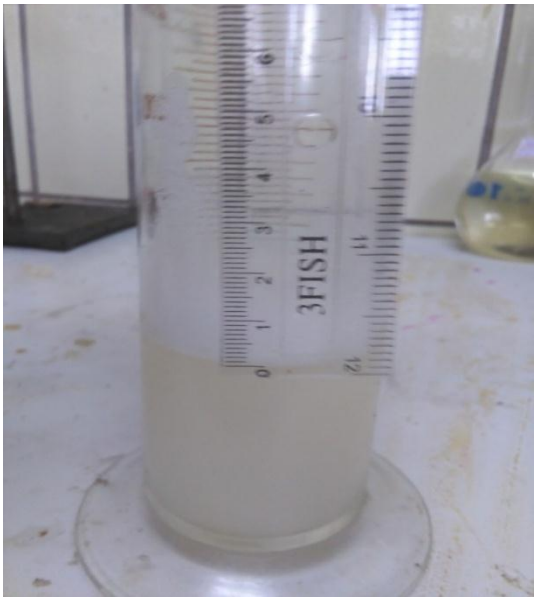
Figure0.1C Color change of 2.1mL of castor oil (a) before addition of phenolphthalein drop, (b) addition of phenolphthalein drop and (c) after addition of 0.5N of HCl for saponification calculation respectively

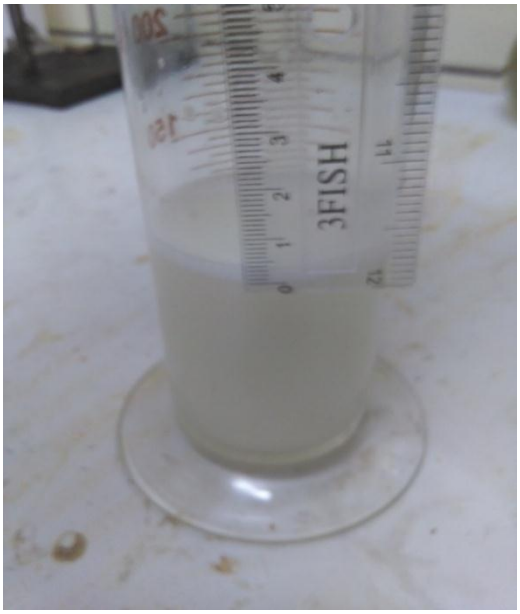
Figure 0.2C Run of Silk fabric liquid detergent produced at the laboratory



(a) (b)

Figure 0.C Foamability height of Shemu liquid detergent before (a) and after (b) shaking of 10min respectively





(a) (b)

Figure 0.4C Foamability height of produced liquid detergent before (a) and after (b) shaking of 10min respectively

Appendix D. Properties of some common fuels and hydrocarbons

Fuel (phase)	Formula	Molar mass, kg/kmol	Density,[1] kg/L	Enthalpy of vaporization,[2] kJ/kg	Specific heat,[1] c_p kJ/kg · K	Higher heating value,[3] kJ/kg	Lower heating value,[3] kJ/kg
Carbon (*s*)	C	12.011	2	—	0.708	32,800	32,800
Hydrogen (*g*)	H_2	2.016	—	—	14.4	141,800	120,000
Carbon monoxide (*g*)	CO	28.013	—	—	1.05	10,100	10,100
Methane (*g*)	CH_4	16.043	—	509	2.20	55,530	50,050
Methanol (ℓ)	CH_4O	32.042	0.790	1168	2.53	22,660	19,920
Acetylene (*g*)	C_2H_2	26.038	—	—	1.69	49,970	48,280
Ethane (*g*)	C_2H_6	30.070	—	172	1.75	51,900	47,520
Ethanol (ℓ)	C_2H_6O	46.069	0.790	919	2.44	29,670	26,810
Propane (ℓ)	C_3H_8	44.097	0.500	335	2.77	50,330	46,340
Butane (ℓ)	C_4H_{10}	58.123	0.579	362	2.42	49,150	45,370
1-Pentene (ℓ)	C_5H_{10}	70.134	0.641	363	2.20	47,760	44,630
Isopentane (ℓ)	C_5H_{12}	72.150	0.626	—	2.32	48,570	44,910
Benzene (ℓ)	C_6H_6	78.114	0.877	433	1.72	41,800	40,100
Hexene (ℓ)	C_6H_{12}	84.161	0.673	392	1.84	47,500	44,400
Hexane (ℓ)	C_6H_{14}	86.177	0.660	366	2.27	48,310	44,740
Toluene (ℓ)	C_7H_8	92.141	0.867	412	1.71	42,400	40,500
Heptane (ℓ)	C_7H_{16}	100.204	0.684	365	2.24	48,100	44,600
Octane (ℓ)	C_8H_{18}	114.231	0.703	363	2.23	47,890	44,430
Decane (ℓ)	$C_{10}H_{22}$	142.285	0.730	361	2.21	47,640	44,240
Gasoline (ℓ)	$C_nH_{1.87n}$	100–110	0.72–0.78	350	2.4	47,300	44,000
Light diesel (ℓ)	$C_nH_{1.8n}$	170	0.78–0.84	270	2.2	46,100	43,200
Heavy diesel (ℓ)	$C_nH_{1.7n}$	200	0.82–0.88	230	1.9	45,500	42,800
Natural gas (*g*)	$C_nH_{3.8n}N_{0.1n}$	18	—	—	2	50,000	45,000

Appendix E, Ideal-gas specific heats of various common gases (*Concluded*), as a function of temperature

$\bar{c}_p = a + bT + cT^2 + dT^3$

(T in K, $\bar{c}_p$ in kJ/kmol · K)

Substance	Formula	a	b	c	d	Temperature range, K	% error Max.	% error Avg.
Nitrogen	N_2	28.90	-0.1571×10^{-2}	0.8081×10^{-5}	-2.873×10^{-9}	273–1800	0.59	0.34
Oxygen	O_2	25.48	1.520×10^{-2}	-0.7155×10^{-5}	1.312×10^{-9}	273–1800	1.19	0.28
Air	—	28.11	0.1967×10^{-2}	0.4802×10^{-5}	-1.966×10^{-9}	273–1800	0.72	0.33
Hydrogen	H_2	29.11	-0.1916×10^{-2}	0.4003×10^{-5}	-0.8704×10^{-9}	273–1800	1.01	0.26
Carbon monoxide	CO	28.16	0.1675×10^{-2}	0.5372×10^{-5}	-2.222×10^{-9}	273–1800	0.89	0.37
Carbon dioxide	CO_2	22.26	5.981×10^{-2}	-3.501×10^{-5}	7.469×10^{-9}	273–1800	0.67	0.22
Water vapor	H_2O	32.24	0.1923×10^{-2}	1.055×10^{-5}	-3.595×10^{-9}	273–1800	0.53	0.24
Nitric oxide	NO	29.34	-0.09395×10^{-2}	0.9747×10^{-5}	-4.187×10^{-9}	273–1500	0.97	0.36
Nitrous oxide	N_2O	24.11	5.8632×10^{-2}	-3.562×10^{-5}	10.58×10^{-9}	273–1500	0.59	0.26
Nitrogen dioxide	NO_2	22.9	5.715×10^{-2}	-3.52×10^{-5}	7.87×10^{-9}	273–1500	0.46	0.18
Ammonia	NH_3	27.568	2.5630×10^{-2}	0.99072×10^{-5}	-6.6909×10^{-9}	273–1500	0.91	0.36
Sulfur	S_2	27.21	2.218×10^{-2}	-1.628×10^{-5}	3.986×10^{-9}	273–1800	0.99	0.38
Sulfur dioxide	SO_2	25.78	5.795×10^{-2}	-3.812×10^{-5}	8.612×10^{-9}	273–1800	0.45	0.24
Sulfur trioxide	SO_3	16.40	14.58×10^{-2}	-11.20×10^{-5}	32.42×10^{-9}	273–1300	0.29	0.13
Acetylene	C_2H_2	21.8	9.2143×10^{-2}	-6.527×10^{-5}	18.21×10^{-9}	273–1500	1.46	0.59
Benzene	C_6H_6	−36.22	48.475×10^{-2}	-31.57×10^{-5}	77.62×10^{-9}	273–1500	0.34	0.20
Methanol	CH_4O	19.0	9.152×10^{-2}	-1.22×10^{-5}	-8.039×10^{-9}	273–1000	0.18	0.08
Ethanol	C_2H_6O	19.9	20.96×10^{-2}	-10.38×10^{-5}	20.05×10^{-9}	273–1500	0.40	0.22
Hydrogen chloride	HCl	30.33	-0.7620×10^{-2}	1.327×10^{-5}	-4.338×10^{-9}	273–1500	0.22	0.08
Methane	CH_4	19.89	5.024×10^{-2}	1.269×10^{-5}	-11.01×10^{-9}	273–1500	1.33	0.57
Ethane	C_2H_6	6.900	17.27×10^{-2}	-6.406×10^{-5}	7.285×10^{-9}	273–1500	0.83	0.28
Propane	C_3H_8	−4.04	30.48×10^{-2}	-15.72×10^{-5}	31.74×10^{-9}	273–1500	0.40	0.12
n-Butane	C_4H_{10}	3.96	37.15×10^{-2}	-18.34×10^{-5}	35.00×10^{-9}	273–1500	0.54	0.24
i-Butane	C_4H_{10}	−7.913	41.60×10^{-2}	-23.01×10^{-5}	49.91×10^{-9}	273–1500	0.25	0.13
n-Pentane	C_5H_{12}	6.774	45.43×10^{-2}	-22.46×10^{-5}	42.29×10^{-9}	273–1500	0.56	0.21
n-Hexane	C_6H_{14}	6.938	55.22×10^{-2}	-28.65×10^{-5}	57.69×10^{-9}	273–1500	0.72	0.20
Ethylene	C_2H_4	3.95	15.64×10^{-2}	-8.344×10^{-5}	17.67×10^{-9}	273–1500	0.54	0.13
Propylene	C_3H_6	3.15	23.83×10^{-2}	-12.18×10^{-5}	24.62×10^{-9}	273–1500	0.73	0.17