Wolkite University

COLLEGE OF ENGINEERING AND TECHNOLOGY
DEPARTMENT OF CHEMICAL ENGINEERING

A FINAL YEAR THESIS SUBMITTED TO DEPARTMENT OF CHEMICAL ENGINEERING IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

PRODUCTION OF LAUNDRY SOAP FROM LEATHER SOLID WASTE

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DECLARATION

We declare that, this thesis project is entitled with “Production of laundry soap from leather solid waste” for the BSc. Degree at Wolkite University, hereby submitted is our work and have not previously been submitted as complete experiment in this university. And that all resources of materials used in this thesis have been properly acknowledged.

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LIST OF ABBREVIATION

AV:	Acid value
BFD:	Block flow diagram
BOD:	Biological oxygen demand
DC:	Direct cost
DPC:	Direct production cost
FCI:	Fixed capital investment
FC:	Fixed cost
FFAV:	Free fatty acid value
IC:	Indirect cost
INS:	Iodine number of soap
LSW:	Leather solid waste
PEC:	Purchased equipment cost
PLC:	Private limited company
ROI:	Return on investment
SAP:	Saponification value
SFE:	Supercritical fluid extraction
TCI:	Total capital investment
TDS:	Total dissolved solid
TFC:	Total fixed cost
TPC:	Total production cost
TS:	Total solids
WCI:	Working capital investment

ABSTRACT

This final year project aims at production of soap from solid leather waste. The fleshing solid waste resulting from the pertaining process in tannery industry have higher amount of fat content. Those fats if properly extracted can be used in different aspects. In this project extraction of fat from this waste was performed at (65-70^{0}C) temperature by employing Soxhlet extraction. The effect of extraction was carried out by varying the solvent used and making other conditions constant (i.e. PH, temperature and time). The best extraction solvent among the compared solvents, Hexane and Petroleum ether for the specified fat source were selected. Due to extraction capacity having a higher yield, process safety, volatility and stability parameters the solvent Hexane was preferred. The fat was then characterized by different parameter resulting at PH of 6, acid value 0.53%, free fatty acid 0.2% with 0.1382mg/g of fat saponification value of animal fat. The effect of sample variation was also performed by differentiating their moisture content.

The dry sample fat yield was greater than that of the moist. But fragrance during saponification reaction and it darkened the final laundry soap. Beside this additional cause for the fragrance as analyzed was the deficiency of water in sodium hydroxide solution. The technical and economic feasibility of the work for laundry soap production was performed. Results from the feasibility study indicated that the proposed work was feasible with return on investment (ROI) 22% and the payback period of the project is estimated to be 2.7 years.

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CHAPTER ONE: INTRODUCTION

1.1 Background

Soap is a salt of a compound, known as a fatty acid. A soap molecule has a long hydrocarbon chain with a carboxylic acid group on one end, which has ionic bond with metal ion, usually sodium or potassium. The hydrocarbon end is non-polar which is highly soluble in non-polar substances and the ionic end is soluble in water. They are prepared by the saponification process, which is, reacting the oil which contains triglycerides with caustic soda (NaOH) to give the soap. Throughout history people were known to have taken bath in herb waters and other additions to the bathing medium thought to be beneficial. Soaps are mainly used as surfactants for washing, bathing, and cleaning, but they are also used in textile spinning. (www.ijmer.com)

Soaps can be produced from vegetable oils, animal fats, cooking oil, and etc. Through various chemical processes. The most common method in production of soap is semi boiling others include full boiling and cold process. Animal fats are common source of soap making; these fats can be obtained from animal meat, animal hides or skins.

Tannery solid wastes like skin trimmings, keratin wastes, fleshing wastes, chrome shaving wastes and buffing wastes generated in the industries contribute mainly potential fat content that can be converted to laundry soap. (Kanagaraj *et al.,* 2006). The availability of this resource in Ethiopia is very promising to study the feasibility of the fat extracted from tannery solid waste used as laundry soap.

In this present study, Animal fleshing - a proteinaceous solid waste obtained from untanned hides/skins has been focused, as this contributes about 56-60% of the wastes generated from pre-tanning operations in tanneries. Instead of disposing them, it would be better to recycle them and reuse them as a raw material for another industry. The solid wastes were characterized for pH, moisture content, volatile organic compound, total nitrogen content, and sodium content using standard solid waste analysis methods (H. Ozgunay et al., 2007).

1.2 Statement of problem

The sustainability of the leather industry crucially depends on how well it manages the liquid and solid wastes. Fleshing from animal hides/skins is one such waste that is high in solid waste content. Solid waste products are potent pollutants in water and are also highly odorous when they are decomposing in their solid form. Leather processing generates a heavily contaminated liquid waste, considered to extremely hazardous due to the abundant presence of heavy metals.

These skin/hides fleshing wastes from tanneries contain significant quantity of protein and fat content and are currently being wasted in to dumping sites or in open areas, consequently creating the fleshing waste disposal a major environmental problem in Ethiopia. For instance the tannery industries have been draining its toxic waste water in to the river for about many years during the tanning process. As new reports and several studies indicate the rivers that found near to the tannery industries are the most polluted rivers in the country as the same time, it is also a water source of many inhabitants thus the communities living near river continue to suffer from health problem like skin blisters, diarrhea, gastroenteritis urinary tract infections and liver diseases, animals too have suffer loss of hair and sometimes crippled and even die, and also farming done by using water from the river produces food crops containing high levels of toxic compounds further exacerbating the problem. In addition the people have been problem of soap market in country by the reason of shortage of soap industry there for soap distribution of soap for all country side is the problem.

Therefore, this project helps to produce laundry soap from these locally available and environment polluting tannery solid waste. In addition to this, the industry will enhance its public image and also reduce the influence of the environmental regulating agency on the tanning sector.

1.3 Objectives

1.3.1 General objective

The main aim of the project was to produce laundry soap from leather solid wastes.

1.3.2 Specific Objectives

- To extract fat from leather solid wastes.
- Characterization of fat from solid waste.
- Selection of best solvent.
- To produce laundry soap from fat obtained from solid waste.
- Characterization the produced laundry soap.
- To calculate material and energy balance.

1.4. Significance of the project

This research was aim to justify the best alternative use of leather solid waste as a raw material for the production of laundry soap instead of disposes at environment because this waste is environmental pollutant. The production of laundry soap from these locally available and environment polluting tannery solid waste was used as one of the best scientific method of waste treatment from tannery industries and also it was used to balance soap market and distribute for all society.

CHAPTER TWO: LITERATURE REVIEW

2.1 Overview of soap

Soaps are the sodium salts or potassium salts of stearic acids or any other fatty acids. They are prepared by the saponification process, which is, reacting the oil which contain triglycerides with caustic soda (NaOH) to give the soap.

In other words, it is a substance, that when dissolved in water removed dirt from dirty materials. Scientifically, a typical soap contains 80% mixed oils and 20% coconut oil with about > 0.2% free alkali. A formula for soap consisting of water, alkali and oil was written on a Babylonian clay tablet around 2200 BC.

Soap is integral to our society today, and we find it hard to imagine a time when people were kept sweet-smelling by the action of perfume rather than soap. However, the current widespread use of soap is only a very recent occurrence, despite the fact that it has been made for more than 2500 years. The first recorded manufacture of soap was in 600BC, when Pliny the Elder described its manufacture by the Phoenicians from goats tallow and ash, and it was known among the British Celts and throughout the Roman Empire. However, these people used their soap medicinally, and it was not until the second century AD that it was used for cleaning, and not until the nineteenth century that it began to be commonly used in the Western world (Soap and detergent. (2016)).

Recent market analysis by Euro monitor (2000) shows that in 1999 soaps and detergents together represented around 12.4 % of consumer expenditure on household goods in industrialized countries and between 2.6 % to 5 % in the developing world. For the developed economies this reflects the growing maturity of the market and intense price competition in the market place. The report however suggests that there is much greater scope for marketers to induce consumers in the emerging markets to raise consumption levels. The same analysis showed that bar and liquid soaps accounted for around 40% of the personal wash sector and around 7% of the total personal care market worldwide in 1999.

The market for soap is also growing much faster developing countries than in developed countries.

Wide and growing income differentials exist in developing countries and each segment of the population consumes the products it can afford while aspiring to a better product at a future date. This, together with the sheer increase in population, has been the driving engine for the soap industry.

The world market for soaps and detergents was worth US$ 88 billion in 2000 Asia, Western Europe and North America account for about 87% of total industrial soap Consumption.

Global soap and detergent consumption has grown by 29% in the five years to 2000. The primary engines (drivers) of this sales growth were Western Europe (+31%), Asia (+59%) and Latin America and the Caribbean (+41%). During the same period, The mature North America market expanded by just 14%, while the impact of Economic recession has severely curtailed sales in Australasia and the Pacific Rim During the last couple of years. The Middle East and African regions are believed to have expanded sales by some 72% and 65% respectively during the period, form a Low base (Global market for soap)

2.1.1 Soap in Ethiopia

There are various industries of soap in Ethiopia. These are Akay consultancy and industry PLC, Star soap and detergents, Rape soap and detergent, Palm Ethiopia PLC, Gullele soap factory and so on. The demand for laundry soap is associated with urbanization, since the consumption of laundry soap is associated with urban population, the demand for the product is assumed to grow by 4% corresponding to the annual growth rate of the urban population.

Table 1 Soap demand in Ethiopia

SUPPLY OF LAUNDRY SOAP IN TONS PER YEAR	**Local**	**Imported**	**Total**
1997	14,342	22,404	36,746
1998	10,874	14,302	25,176
1999	26,146	20,438	46,585
2000	17,194	18,043	35,237
2001	14,766	25,738	40,505
2002	19,249	27,290	46,539
2003	11,632	22,808	34,440
2004	14,975	16,443	31,419
2005	16,825	24,634	41,459
2006	N.A.	23,496	-

Source: *CSA Annual Survey Manufacturing Industries Customs Authority*

In general the demand for soaps is related to the growth in income. Therefore the estimation of the demand gap left out by the domestic suppliers, is made based on 8.7% annual gross domestic product growth rate achieved in 2005.

Table 2 Demand projected for laundry soap

PROJECTED DEMAND OF LAUNDRY SOAP (YEAR)	**Tons**
2008	24,608
2009	26,748
2010	29,075
2011	31,605
2012	34,355
2013	37,344
2014	40,592
2015	44,124
2016	47,963

Source: *CSA Annual Survey Manufacturing Industries Customs Authority*

2.2 The Chemistry of Soap

Soaps are water-soluble sodium or potassium salts of fatty acids. Soap contains a positive ion, usually sodium and potassium, and a negative ion usually the anions of long hydrocarbon chained carboxylic acids obtained by the hydrolysis of animal or vegetable fats. The hydrocarbon chains length may vary from 10-30 carbons (mostly12-18).

Each fat or oil is made up of a distinctive mixture of several different triglycerides. In a triglyceride molecule, three fatty acid molecules are attached to one molecule of glycerin. There are many types of triglyceride each type consist of its own particular combination of fatty acids. The fatty acids are the components of fats and oils that are used in making soap is a function of acids and fatty acids are functions of fats and oil. Soaps are made from fats and oils or their fatty acids, by treating them chemically with a strong alkali.

An alkali is a soluble salt of an alkali metal like sodium or potassium, originally, the alkalis used in soap making where obtained from the ashes of plants, but they are now made commercially. The common alkalis used in soap making are sodium hydroxide (NaOH), also called caustic soda' and potassium hydroxide (KOH) (Kuye and Okorie, 2002).

All soaps and detergents contain a surfactant as their active ingredient. This is an ionic species consisting of a long, linear, non-polar 'tail' with a cationic or anionic 'head' and a counter ion. The tail is water insoluble and the head is water soluble. A difference in solubility which has two important implications. Firstly, this makes the surfactant molecule a wetting agent. The tails migrate to align themselves with the solid water interface, lowering the surface tension at that point so that it penetrates the fabric better. Secondly, it allows the oily dirt particles to form an emulsion with the water: the tails of many surfactant molecules surround an oily dirt particle, forming a micelle with a drop of oil in the center and the ionic heads of the surfactant molecules pointing outwards and hence keeping the micelle in the polar solution. In conclusion, the basic reaction in soap making is between a neutral fat and an alkali.

2.3 Types of soap

There are different kinds of soap, depending upon the usage..

Bathing bars: The bathing bar shall be a product containing acceptable surface active agents which could be used for bathing purposes. The price of bathing bars were determined according to the total fatty matter contained in them and more importantly the type of fatty matter used.

Baby soap: Baby soaps are not much different from ordinary soaps, but they are comparatively of high purity. Baby's skin is soft and sensitive. Hence the oil used for making baby soap should be clean and bleached. No pigments are allowed in baby soap and fragrance materials added should be bare minimum.

Medicinal soap: As per many advertisements medicinal soaps are supposed to contain deodorants antiseptics and some medicines that cure skin diseases. They say that medicinal soaps are cleansing agents well as antiseptics. Here soap is treated as a carrier of medicines that is it serves the purpose an ointment or oil.

Kitchen soap: They are further categorized into two: Cleanser and detergents; Cleansers are often made with mild abrasives and they are formulated to eliminate heavy oil or solid particles and hard to remove stains and detergents are made to remove tough grease and release the solid dirt particle in the foam created by the detergent.

Laundry soap: Laundry soap is formulated to eliminate grease, solid particles and organic compounds from clothes. They can be found in liquid, powder and gel forms.

Glycerin soap: Glycerin is normally produced during the process of soap production. Soap which includes glycerin in them tends to make your skin feel moister.

Liquid soap: Liquid soaps are actually very difficult to produce and many of the commercial liquid soaps are just in fact detergents. (www.Soap history.net)

2.4 Laundry soap

Laundry soap is a cleansing agent or detergent, made from animal and vegetable fats, oil and greases, chemically the sodium salt of a fatty acid, formed by the interaction of fats and oil with alkali.

2.4.1 Source of laundry soap

The ingredients in laundry soaps are sodium hydroxide, perfume, additives (color) fat /oil. Laundry soaps are made from different fats; those are animal and vegetable fat. Animal fat is the major source of fat. Fats and oil as well as their blends are used in the manufacturing of soaps. These fats are of vegetable or animal origin (www.soap-making-resource.com/fattyacids).

Table 3 source of fat

Vegetable fat	Animal Fats
Coconut Castor	Tallow
Palm Neem	Lard
Cottonseed Sunflower	Fish Oils
Rice Bran Soya bean	
Palm kernel Rapeseed	

Source: *Chemical Business*, February 2000 Mowrah Karanja

2.4.2 Types of fatty acids

There are two groups of fatty acids: the saturated and the unsaturated.

Saturated fatty acids: contain no double bonds in their chemical structure, and are therefore

"Saturated" with hydrogen atoms. Because of their chemical structure, they have a solid consistency at room temperature.

They are stiff molecules which tend to increase the melting point of oils. Saturated fatty acids themselves are solids at room temperature. As they increase in size from lauric to stearic, the melting point of the oil increases. Saturated fatty acids in soap have good cleaning properties and support foam. The longer chains also tend to harden soap.

Unsaturated fatty acids are typically liquid at room temperature and differ from saturated fats in that their chemical structure contains one or more double bonds. They tend to have good cleaning power, but lather poorly.

Fats and oils are made up mainly of a variety of fatty acids. The main conditioning fatty acids are oleic (1 unsaturated bonds), linoleic (2 unsaturated bonds) and linoleic (3 unsaturated bonds). The more unsaturated bonds, the better the conditioning and the more easily it is absorbed by the skin, but the softer the oil is in soap, the more prone to oxidation. The basic molecule of oils and fats is triglyceride, which is classified as being of animal or vegetable origin. The presence of unsaturation in molecules vegetable origin of fatty acid tend to lower the melting point and to cause them to be in the liquid state at room temperature. While animal fats, being relatively more saturated, are solid or semisolid, at the same temperature. The fat and oils most commonly used in soap preparation are lard and tallow from animal sources, coconut, palm and olive oils from vegetable source. Vegetable fats are relatively unsaturated and liquid under the ordinary condition. The fatty acids in soap making are lauric acid, myristic acid, palmitic acid, stearic acid oleic. They are obtained from mutton, tallow, beef tallow (animal fats), palm oil, and palm kernel oil. In the composition of fatty acid in laundry soap Lauric acid is saturated fatty acids whose single bond helps in soap hardening. It also has good cleansing agent and supports foaming. The percentage of plamitoleic acid is between 0.00-2.20 percent. This acid is unsaturated. It makes soap to be mild, have good cleaning power but foams poorly. It was seen that palmitic acid can be saturated and unsaturated fatty acids, the C16 and C16:1 respectively. Stearic acid i.e. the C18 has three members the oleic acid C18:1, the linoleic acid C18:2 and the linoleic acid C18:3. The stearic itself is a saturated fatty acid while the other three are unsaturated fatty acids. They help increase mildness in soap.

The fat and oils most commonly used in soap preparation are lard and tallow from animal sources, coconut, palm and olive oils from vegetable source. The fatty acids in soap making are lauric acid, myristic acid, palmitic acid, stearic acid oleic. They are obtained from mutton, tallow, beef tallow (animal fats), palm oil, and palm kernel oil. The animal fat can also be obtained from leather waste.

The higher amount of fat found in fleshing solid waste may be evaluated in different fields such as the chemical industry, soap production, biodiesel production, and the production of fat liquors. But first, solid wastes should be characterized so that they can be reused (Theorstensen, 1969).

2.5 Extraction of fat from leather solid waste

2.5.1 Overview of leather industry

Leather is one of the most widely traded commodities in the world. The leather and leather products industry plays a prominent role in the world’s economy, with an estimated global trade value of approximately US$100 billion per year.

Historically, the tanning industry was characterized by small or medium-size family businesses. The leather industry has an important role for countries economy in the light of its large scale of potential for employment, growth and exports. Turkish leather industry has taken a prominent place of the world leather trade with its high export productivity for the manufacture of leather products to move to where labor is cheapest, Trade in hides and skins, and semi-processed, tanned leather goods is lucrative business. This is particularly the case for some developing countries where the dynamism of the sector has led to a move up the value-added chain and strong market positions. As a result, developing countries hold a 45% share of world trade in leather manufactures.

2.5.2. Leather manufacturing (Tanning process)

The chemicals traditionally used for tanning have been derived from plants, whereas the most common nowadays is a combination of chrome salts (chrome tanning) and readily usable vegetable extracts (vegetable tanning) (Buljan 1994). While chrome tanned shoe leather is the most widely produced leather.

In most cases raw hides produced at slaughterhouses are preserved by pickling and drying for transport to tanneries and further treatment. In the very few cases that hides are instantly tanned there is no need for preservation. During the tanning process at least ±300 kg chemicals (lime, salt etc.) is added per ton of hides.

1. Pertaining (Beam house operations)

- **Soaking:** The preserved raw hides regain their normal water contents. Dirt, manure, blood, preservatives (sodium chloride, bactericides) etc. are removed.

- **Fleshing and trimming:** Extraneous tissue is removed. Unhairing is done by chemical dissolution of the hair and epidermis with an alkaline medium of sulfide and lime. When after skinning at the slaughterhouse, the hide appears to contain excessive meat, fleshing usually precedes unhairing and liming.
- **Bating :** The unhaired, fleshed and alkaline hides are neutralized (deliming) with acid ammonium salts and treated with enzymes, similar to those found in the digestive system, to remove hair remnants and to degrade proteins. During this process hair roots and pigments are removed. The hides become somewhat softer by this enzyme treatment.
- **Pickling:** Pickling increases the acidity of the hide to a pH of 3, enabling chromium tannins to enter the hide. Salts are added to prevent the hide from swelling. For preservation purposes, 0.03 - 2 weight percent of fungicides and bactericides are applied.

2. Tanning

There are two possible processes:

- **Chrome tanning:** After pickling, when the pH is low, chromium salts (Cr^{3+}) are added. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature. The chromium-tanned hide contains about 2-3 dry weight percent of Cr^{3+}. Wet blue, i.e. the raw hide after the chrome-tanning process, has about 40 percent of dry matter.
- **Vegetable tanning:** Vegetable tanning is usually accomplished in a series of vats (first the rocker-section vats in which the liquor is agitated and second the lay-away vats without agitation) with increasing concentrations of tanning liquor. Vegetable tannins are polyphenolic compounds of two types: hydrolysable tannins (i.e. chestnut and myrobalan) which are derivatives of pyrogallols and condensed tannins (i.e. hemlock and wattle) which are derivatives from catechol. Vegetable tanning probably results from hydrogen bonding of the tanning phenolic groups to the peptide bonds of the protein chains. In some cases as

much as 50% by weight of tannin is incorporated into the hide (Ockermann and Hansen, 1988).

- **Finishing:** Wet blue Chromium tanned hides are often re tanned - during which process the desirable properties of more than one tanning agent are combined - and treated with dye and fat to obtain the proper filling, smoothness and color. Before actual drying is allowed to take place, the surplus water is removed to make the hides suitable for splitting and shaving. Splitting and shaving is done to obtain the desired thickness of the leather.

2.5.3 Leather Wastes

The leather industry commonly uses hides and skins as raw materials, which are the byproducts of meat and meat products industry. Although the leather industry is environmentally important as a user of the by-product of the meat industry, it is perceived as a consumer of resources and a producer of pollutants that are liquid, solid and gaseous in nature it products highly quantity of fat-originated solid and liquid wastes while processing hides and skins. These wastes cause environmental problems and must be utilized.(Ertan Alptekin, Mustafa Canakci, 2011) .

2.5.3.1 Liquid and Gaseous Waste

Tannery effluents are ranked as the highest pollutants among all industrial wastes. The Tanning process involves an important consumption of water and generates a complex pollution consisting of a mixture of organic and inorganic substances that rather difficult to treat. The capacity of world leather process is 15 million tons of hides and skins per year.

The waste water discharge from world tanneries is about 600 million m3 per year. On average 45 -50 m3 of wastewater is discharged from tanning industry per ton of raw hide processed. The main discharge of waste water originates from wet processing stages in the beam house, the tanning process, and the post-tanning operations. It has been revealed that beam house processes and tanning processes contribute 80–90% of the total pollution load that includes biological oxygen demand (BOD), chemical oxygen demand (COD), total solids (TS), total dissolved solids (TDS), chromium

(Cr), sulfides (S2−), sludge, etc.). Compared to emissions to water, air emissions occur generally in relatively small quantities.

Traditionally tanneries have been associated with odor rather than any other air emissions,

Although the emissions of organic solvents are a major problem. Whether a tannery has the following air emissions depends on the type of processes employed. Air emissions from Tannery are particulate, organic solvents, hydrogen sulfide, ammonia and odor.

Ammonia can be formed in de-liming processes and the dyeing process. Good housekeeping Practices, such as effective washing and process control, can minimize these emissions.

Extraction fans above processing vessels or improved process control can also minimize odors. May arise from degradation of organic matter or from chemical substances that are also toxic. Odors can arise from storing hides and skins, from beam house operations (sulfides, ammonium), from ammonia releases in dyeing, from VOC released in finishing processes and from the waste water treatment.(Wintana Kessahun, AAIT).

2.5.3.2 Solid waste emission

According to the data received from the studies of several researchers, approximately 200 kg of leather is manufactured from 1 tone of wet-salted hide. This amount constitutes about 20% of rawhide weight. More than 600 kg of solid waste is generated during the transformation of rawhide into leather. That is to say, solid wastes containing protein and fat that constitute more than 60% of rawhide weight are disposed to the environment by leather factories without turning them to good use. In world leather industry, the data from FAO reveals that approximately 8.5 million tons of solid waste is generated during the production of 11 million tons of rawhide processed in the world. Annually, all leather industries put together use 2.3 million pieces of hides and 44.3 million pieces of skins as an input for processing at full capacity operations.

The main sources of solid wastes are from trimming, fleshing, splitting and shaving processes. A further potential source of solid waste is the sludge from the effluent treatment plant. The solid waste generation from tannery process in the world is estimated at 6 million tons per year. At an average 80% of solid waste is generated from tanning industry per ton of raw hide processed. Solid wastes generated by the leather industry in these stages of processes may be classified as follows:

i. wastes from untanned hides/skins (trimmings, fleshing wastes)
ii. Wastes from tanned leather (shaving wastes, buffing dust)
iii. Wastes from dyed and finished leather (trimmings from leather)

Data obtained from research reveals that 80% of solid wastes are generated during pre-tanning processes, while 20% of the wastes are caused by post-tanning processes. Due to the bad smell they produce during their putrefaction and their harmful chemical content, untanned hide/skin wastes have negative effects on the soil and/or water resources of the environment where they are discharged, in other words on the local plant flora and animal fauna.

The chemical composition of solid wastes generated from beam house operations (flashings, Trimmings, splits) depends mainly on a kind and quality of the raw material, treatment type and process conditions. The main components are proteins and fat, up to 10.5% (w/w) for both groups. Water content is high, moisture amounts up to 60%. These wastes contain small amounts of mineral substances, 2-6% (w/w). Chromium compounds are not present in the Material.

From Different researchers, it has been observed that pre-fleshing and lime fleshing wastes from the processes before degreasing include higher amounts of fat compared to other waste sources (40-70%). The fat obtained from lime fleshing waste is generally regarded to be of low quality due to its dirty color and bad smell resulting from sulfide contact. Pre-fleshing process is carried out so as to remove flesh and to promote the penetration of the chemicals for better leather products. The fat content of the leather industry wastes is remarkable. However, these wastes are not evaluated effectively and there is almost no application method to recover these wastes. According to Aquim (2004), the quantities of solid waste generated in pre-fleshing operations are 6 kg of subcutaneous tissue per 26 kg of salted hide. Gutiérres and Osório (2004) reported the following salted hide characterization: 43.51% of water, 13.74% of ash, 4.08% of fats and 40.55% of collagen substance. The fat content is high due to the subcutaneous tissue. Also, according to Wist and Schmidt (1992), the fatty matter composition varies according to the type of animal, feeding and climate, and basically consists of: glycerides (50%), phosphatides (20%), fatty esters (10%), fatty acids (10%) and stearin (1%). (Zulfikar Abajihad, November 2011)

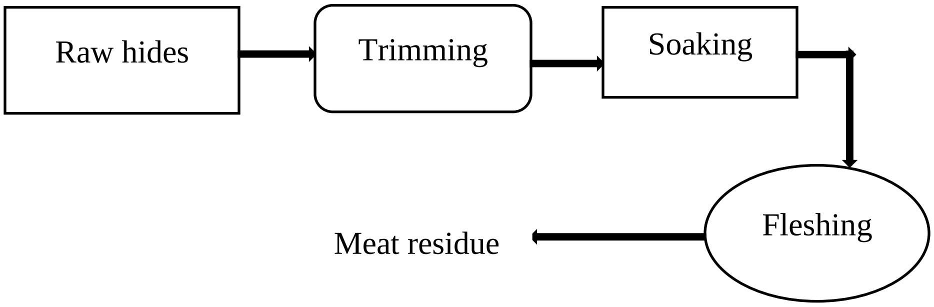


Figure 1 solid waste emission from leather processing

2.5.3.3 Environmental Impacts of Tannery Solid Waste

Raw and green flashings, limed flashings, splits (splitting waste) and trimmings putrefy easily and give rise to noxious smells. In many tanneries, it is the foul odor which emanate from some of these putrescible solid wastes which accounts for much of the smell traditionally associated with tannery wastes. Some of the bio-degradable tannery solid wastes are sources of pathogenic bacteria and volatile organic compounds emission Vegetable and chrome tanned shavings and splits do not easily decompose. If they are not utilized, problems of disposal are encountered. Primary and secondary sludge obtained during the treatment of tannery wastes are also putrescible. Some of tannery solid waste contains chromium metal which is the most widely used in tanning industries as chromium salt and it causes carcinogenic effect when it enters human body through food chain. The standard safe limit for chromium metal in the soil is 150ppm.

2.5.3.4 Attempts for Treatment of solid waste

The tanning process usually includes such operation steps as: pre-tanning, tanning and post tanning. In these steps, large amounts of leather solid wastes (LSWs) and wastewater are produced. It was reported that about 1000 kg of wet salted hides would yield only 200 kg of finished leather (ca. 20% of raw hides); while it would generate more than 600 kg of solid wastes and byproducts (beyond 60% of the raw hides) (Cabeza et al., 1998; Chen et al., 2008).

The conversion of raw skin/ hides into the finished leather needs the use of about 100 chemicals to remove unwanted components, which will also generate various LSWs or wastewater (Bodalo et al., 2007; Chen et al., 2008; Pans wad et al., 2001). Thus, pollution to the environment inevitably will occur. As a result, the contamination caused by leather making severely threatens the environment and the health of human beings. How to treat these pollutants attracts much attention. Consequently, developing new strategies to treat leather wastes is urgent. Presently, there are two dominating material streams and systems for leather waste treatments: wastewater and solid waste.

2.5.4 Liquid waste treatment

A. Physical-chemical treatment (primary)

The objective here is the removal of settle able organic and inorganic solids by sedimentation, and the removal of materials that will float (scum) by skimming. Approximately 25-50% of the incoming biochemical oxygen demand (BOD5), 50-70% of total suspended solids (SS), and 65% of the oil and grease are removed during primary treatment.

Effluent is passed through oil and grease trap for the removal of floating and insoluble oil and grease particles. Oil and grease trap is a baffled wall channel where wastewater is subjected to up and down flow for the removal of floating particles at the top surface. Separated oil and grease layer is collected from the top layer by manual skimming operation through collecting troughs and drain pipe. From oil and grease trap effluent is collected in equalization tank. Equalization tank is provided to ensure the complete mixing of varying quality and quantity.

B. Biological treatment (secondary)

In most cases, secondary treatment follows primary treatment, its goal being the removal of biodegradable dissolved and colloidal organic matter using aerobic biological treatment processes. Aerobic biological treatment is carried out in the presence of oxygen by aerobic micro-organisms (principally bacteria) that metabolize the organic matter in the wastewater, thereby producing more micro-organisms and inorganic end products (principally CO2, NH3, and H2O). Biological treatment is achieved by providing activated sludge process. In this treatment soluble BOD is stabilized by oxidation of organic matter by microorganisms. Nutrient and food is supplied to microorganisms for enhancing their growth. Bottom sludge from secondary clarifier is re circulated back in the aeration tank. Excess biomass is transferred into bio sludge tank. Clear overflow from secondary clarifier is transferred to the tertiary treatment.

C. Advanced (tertiary) treatment

Tertiary or advanced wastewater treatment is employed to reduce residual COD load and/or when specific wastewater constituents are not removed by previous treatment stages. Tertiary treatment consists of chemical oxidation, pressure sand filter and activated carbon filter. Suspended solids get removed in pressure sand filter and activated carbon filter provides treatment for removal of color and COD so that final treated wastewater meets the discharge norms. Backwashing of both the filters is done daily for cleaning of filter beds. The backwashed water is diverted back into wastewater collection sump for further treatment.

2.5.5 Different fat extraction method and solvent selection

2.5.5.1 Fat extraction method

Extraction is the withdrawing of active agents or a waste substance from a solid or liquid mixture with a liquid solvent. The solvent is not partial miscible with the solid or liquid. By intensive contact the active agent transfer from the solid or liquid mixture (raffinate) into the solvent (extract). After mixing the two phases are separated which happens either by gravity or centrifugal forces. For recovery of the solvent and to get the active agent in pure form a further separation process is necessary (rectification or re-extraction).

Depending on the phases following types of extraction exist:

- Solid- liquid extraction.
- Liquid- liquid extraction.
- Gas- liquid extraction is called absorption.

Soxhlet extraction was employed for removal of essential oil from solid waste. These two samples were added with known quantity of hexane which was then soxhleted for 5 hour. When extracting lipids or fats from a material, both the methods as well as the solvents chosen to perform a complete extraction are important. If these two elements are not taken in to consideration, the extraction may not be complete, or the extract may contain a large quantity of undesired impurities

- Conventional Soxhlet extraction

Principles and mechanisms Classical techniques for the solvent extraction of nutraceuticals from plant matrices are based on the choice of solvent coupled with the use of heat and/or agitation.

In a conventional Soxhlet system plant material is placed in a thimble-holder, and filled with condensed fresh solvent from a distillation flask. When the liquid reaches the overflow level, a siphon aspirates the solution of the thimble-holder and unloads it back into the distillation flask, carrying extracted solutes into the bulk liquid. In the solvent flask, solute is separated from the solvent using distillation. Solute is left in the flask and fresh solvent passes back into the plant solid bed. The operation is repeated until complete extraction is achieved.

- Supercritical fluid extraction (SFE) method:

SFE is the process of separating one component (the extract ant) from another (the matrix) using supercritical fluids as the extracting solvent. Extraction is usually from a solid matrix, but can also be from liquids. Carbon dioxide (CO_2) is the most used supercritical fluid, sometimes modified by co-solvents such as ethanol or methanol.

Extraction conditions for supercritical CO_2 are above the critical temperature of 31°C and critical pressure of 74 bars. Addition of modifiers may slightly alter this. SFE produces very high purity oil but the operating and investment costs are very high.

- Solvent Extraction method

Solvent Extraction is a process which involves extracting oil from oil-bearing materials by treating it with a low boiling solvent as opposed to extracting the oils by mechanical pressing methods (such as expellers, hydraulic presses, etc.) The solvent extraction method recovers almost all the oils and leaves behind only 0.5% to 0.7% residual oil in the raw material.

In the case of mechanical pressing the residual oil left in the oil cake may be anywhere from 6% to14%. The solvent extraction method can be applied directly to any low oil content raw materials. It can also be used to extract pre-pressed oil cakes obtained from high oil content materials. Because of the high percentage of recovered oil, solvent extraction has become the most popular method of extraction of oils and fats. The process solvent extraction is basically a process of diffusion of a solvent into oil-bearing cells of the raw material resulting in a solution of the oil in solvent. Various solvents can be used for extraction. However, after extensive research and consideration of various factors, such as commercial economics, edibility of the various products obtained from extraction, physical properties of the solvent especially its low boiling point etc. food grade n-hexane is considered to be the best and it is exclusively used for the purpose. In a nutshell, the extraction process consists of treating the raw material with hexane and recovering the oil by distillation of the resulting solution of oil in gasoline called miscella. Evaporation and condensation from the distillation of micelle recovers the gasoline absorbed in the material. The n-hexane thus recovered is reused for extraction. The low boiling point of hexane (67°C / 152°F) and the high solubility of oils and fats in it are the properties exploited in the solvent extraction process. Generally solvent extraction method has several advantages like high oil yield and less turbid oil than mechanical extraction and relative low operating cost compared with supercritical fluid extraction.

2.5.5.2 Solvent selection

A suitable extracting solvent should be selected for the extraction of targeted nutraceuticals using the Soxhlet extraction method. Different solvents will yield different extracts and extract compositions (Zarnowski& Suzuki, 2004). The most widely-used solvent to extract oils from leather solid waste is hexane. Hexane has a fairly narrow boiling point range of approximately 63–69 8C and it is excellent oil solvent in terms of oil solubility and ease of recovery. However, n-hexane, the main component of commercial hexane, is listed as No. 1 on the list of 189 hazardous air pollutants by the US Environmental Protection Agency (Mamidipally& Liu, 2004).

- ✓ **Solvent types**: Hexane and petroleum ether

Petroleum ether defined as low boiling point, flammable hydrocarbon mixture that is produced from is refined from petroleum as the intermediate distillate between the lighter naphtha and the heavier kerosene It has specific gravity of between 0.6and 0.8 depending on its composition. Petroleum ether also a number of medical and laboratory uses. So it can be used as a tool for making plant based extracts. The solvent in the other hand is dangerous and a fire hazard than hexane. Petroleum ether are extremely volatile, have very low flash points and present in significant fire hazard.

Hexane is the most excellent use of hexane is its function as a solvent. It have reduced risk of flammability, less toxic and give higher oil yields than petroleum ether. It is used as a cleaning solvent and as an industrial degreaser.

2.6 Methods in the production of soap

Various attempts have been made to produce soap. Three conventional methods of soap making are generally used:

1. **Full boiling:** The process consists of 4 stages: Saponification of the oil with alkali, graining out of the soap/Boiling on strength and Filling. The process is started by

putting the melted oil into the boiling tank and running a weak caustic soda solution into the oil. The mixture is then slowly boiled to start the saponification. In graining out of the soap is to separate the waste lye which is a mixture of glycerin produced during the soap boiling process and excess caustic soda solution from the soap. The graining is complete when the soap is practically free from foam and floats as clean soap on the lye.

2. **Cold processed:**

This process involves the treatment of fat or oil with a definite amount of alkali and no separation of waste lye. The process involves stirring into the milled fat in a tank, half of its weight of caustic soda solution of at the temperature of 24°C for coconut and 38°C to 49°C for the blend. The pushing of the caustic solution into the oil must be done not only slowly and continuously.

When the solution is being run into the oil, the mixture must be stirred in only one direction.

When all the caustic soda solution had been run into the oil and the mixture stirred for 30 to 45 minutes, chemical reaction takes place with lot of generation of heat, finally resulting in the saponification of the oil. The content of the tank looks thin, but after some few hours it becomes a solid mass.

3. **Semi -Boiling process:** For this process in which the fat is first of all melted, followed by treatment with a weak 9-10% caustic soda solution followed by boiling of the mixture. The quantity of caustic soda required for the saponification of the oil is 14-15% of the weight of the oil. This weight of caustic soda is dissolved in ten times its weight of water to obtain a 9% solution. When the caustic solution is added into oil, then saponification starts when an emulsion is formed as the soap is stirred. More caustic solution is then added in to prevent the thickening of mass. After sufficient solution is added bit by bit to complete the saponification and the boiling of the mass continues until the soap was clear. During the boiling process moderate heat was maintained and each addition of caustic soda solution must be allowed to react with the oil before the next addition is made. A hurried addition in the initial stages of the process may retard the saponification, or at the final stages of the saponification

may result in the drying of the soap, while judicious addition will keep the mass in a form of smooth homogeneous emulsion. If the soap shows any signs of separation and graining, further water is added to bring the mass to a homogeneous state. If opaque ends appear and vanish, the soap is more oily and requires more caustic, while if the soap is graining, or turbid and white, it indicates a high level of presence of un reacted caustic, and requires more oil.

Among the above three processes the semi boiling processes is chosen because it is suitable for the production to produce laundry and all other types of soft and liquid soaps. The process does not permit the removal of waste alkali which contains the glycerin produced in the soap making process, and hence the glycerin, which tends to decrease the hardening property of the soap and improves the cosmetic property, is retained in the finished soap. This method has some advantage over the other two since large quantities of good soap can be produced within a short time. The use of this method also allows a high percentage of fillers to be added in soaps, thus it increases the soap bulk.

2.7 Production of soap

1. Saponification: A mixture of tallow (animal fat) and coconut oil is mixed with sodium hydroxide and Heated. The soap produced is the salt of a long chain carboxylic acid. In saponification, formation of salt by reaction of the base with a long chain fatty acid yields.

[6] Fat + 3NaOH Glycerin + 3Soap

Splitting of oils and fats by hydrolysis, or under basic conditions (saponification), yields fatty acids, with glycerin (glycerol) as a byproduct.

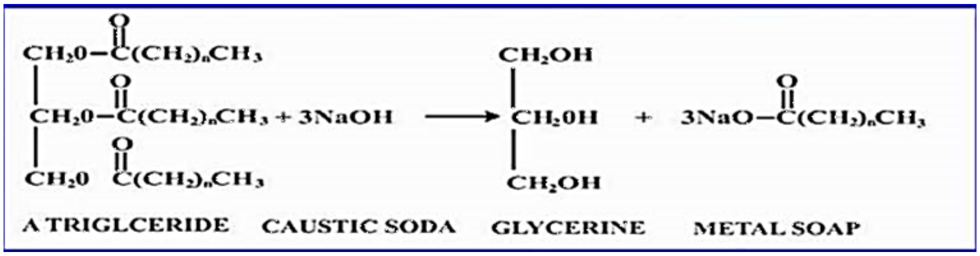


Figure 2 saponification reaction

2. Soap washing:

The soap still contains most of its glycerin at this stage, and this is removed with fresh lye in a washing column. The column has rings fixed on its inside surface. The soap solution is added near the bottom of the column and the lye near the top. As the lye flows down the Column through the center, a series of rotating disks keeps the soap / lye mixture agitated between the rings. This creates enough turbulence to ensure good mixing between the two Solutions.

3. Moulding and cutting

In this step, melted soap is poured into shaped-mould for it to “set” and harden in.

Sometimes, the soap is “broken out” of the mould and “split” down to required sizes with a wire. The soaps are cut using cutting machine which can be made locally into different designs and size.

4. Stamping

This is the use of special stamp (either electric or manual) and trade marks on the products (soap products). Wooden or plastic, handmade stamp and stamp box or manual stamping machine are used. (Abba, 2008).

5. Drying

Soap is normally obtained as having moisture content. Drying is required to reduce this water content of the soap to a carefully defined and controlled level, especially for toilet soap bars. Soap at control moisture content will generally produce, after, subsequent processing, a bar of the required appearance. This cannot be achieved until the soap has been aired for hours or up to about 1 month in the case of dry hard soap that takes longer to use up. 6. Packaging

This is the use of special materials to package products to the market. The products are finally packed in cartons. Wrapping the soaps into nice paper or clean polythene will add greatly to its sales value. The cost associated with packaging material is an important factor in the cost of production. The cost packaging could be high for consumer products. Therefore, it is always important for a soap producer to estimate his packaging cost in order to represent his operating expenses which have great impact on the selling prize and profit or gain.

2.8 Qualities of laundry soap

Hardness - This refers to the hardness of the soap bar. Higher is harder. A range of 29 to 54 is satisfactory. A low Iodine value also contributes to hardness.

Cleansing - This refers to the soap's ability to grab on tools. A soap molecule is a chain of carbon atoms. One end of the chain attracts water, the other end attracts oil.

Condition - Conditioning refers to the soap’s emollient content. A soap’s emollients are left on the skin. They help the skin retain moisture. They sooth the skin and keep it soft.

Bubbly lather - This refers to the soap’s ability to lather up and get bubbly.

INS - A measure of the physical qualities of the soap based on the SAP and iodine value. If the value is not in "Essentially Soap", it is estimated by subtracting the Iodine Value from the KOH. It is used to predict the physical characteristics of the soap bar. (www.soapcalc .net)

CHAPTER THREE: MATERIALS AND METHODS

Chemicals used

KOH, phenophtaline, ethanol: were used for leather waste characterization.

Hexane: was used as a solvent for fat extraction.

Petroleum ether: was used as a solvent for fat extraction.

Distilled water: was used as production solvent to make solution of NaOH.

Perfume: was used as remove the odor of fat

NaOH: was used as production of soap.

Leather solid waste: was used as a main raw material for soap production.

From this chemicals and raw materials NaOH and leather solid waste were used as the main raw material for production of laundry soap.

Equipment used

Electric oven: was used to dry leather solid waste.

Different size flask: was used to measure samples.

Refrigerator: was used to keep samples from lose of moisture and was kept it as a fresh sample.

Soxhlet apparatus: was used to extract fat from leather solid waste

Condenser: was used for cooling purpose.

Burette: was used for adding chemicals

Magnetic stirrer: was used for mixing purpose

Beaker: was used to store samples

3.1 Raw material preparation

The major raw material for the production of laundry soap is fat from solid leather waste. The raw materials were collected from locally wasted leathers.

Figure 3 Sample solid leather waste from fleshing

The procedure for production of fat from solid leather waste in laboratory scale is as follows:-

These leather wastes were collected by fleshing from locally wasted leather. It was taken mainly from the pre tanning processes of leather because at that stage most of fat and protein content are removed from the animal skin by the mechanical process called fleshing. Fleshing was done by using knife. Two waste samples were prepared. The first sample (sample 1) was subjected to dry in an electric oven at 90^0C for 24hrs then grinded mechanically. And the second (sample 2) was simply allowed to stay in the refrigerator after it was cut in to pieces (Warra, A.A, 31 January 2013).

Figure 4 Dried Raw material sample

In a conventional Soxhlet system the samples prepared were placed in a thimble-holder, and filled with condensed fresh solvent from a distillation flask. When the liquid reaches the overflow level, a siphon aspirates the solution of the thimble-holder and uploads it back into the distillation flask, carrying extracted solutes into the bulk liquid. In the solvent flask, solute is separated from the solvent using distillation. Solute is left in the flask and fresh solvent passes back into the plant solid bed. The operation is repeated until complete extraction is achieved. The figure below shows that a Soxhlet apparatus:

Figure 5 Soxhlet apparatus

3.1.1 Fat Extraction in distillation unit

The solvent fat mixture formed as a result of Soxhlet method was then subjected to roller distillation unit. Then oil was recovered as a bottom product and the solvent at the top product.

Figure 6 separation of fat from solvent by distillation

3.2 Laundry soap preparation

The preparation of laundry soap was by using Semi -Boiling process: For this process in which the fat was first of all melted, followed by treatment with a weak 9-10% caustic soda solution followed by boiling of the mixture.

Steps in Laundry Soap

- ✓ 25g of fat was measured
- ✓ To prepare a solution of caustic soda Weigh the lye or caustic soda proportional to

Amount of caustic soda =saponification value*measured value of fat

=0.1382mg/g*25000mg=3.45g

Amount of solution = 3.45/0.3= 11.51g

Amount of water = 11.51-3.45=8.06g

- ✓ The solution was then mixed and added slowly to the fat, then it was stirring continuously for about 30-45 minutes until it attains the condensed milk-like consistency.

Figure 7 saponification process

- ✓ Pour the homogenous viscous soap mixture into the molder, allow to set at room temperature for 24 hours or until soap solidifies. other shaping material were used as a molder instead of molder since lack of molder in laboratory.
- ✓ And then cut the soap into bars of suitable sizes.
- ✓ Allow to age from 7 to 10 days to complete the saponification reaction **(**Bradshaw ,G.B. ,and W.C.Meuly-1942).

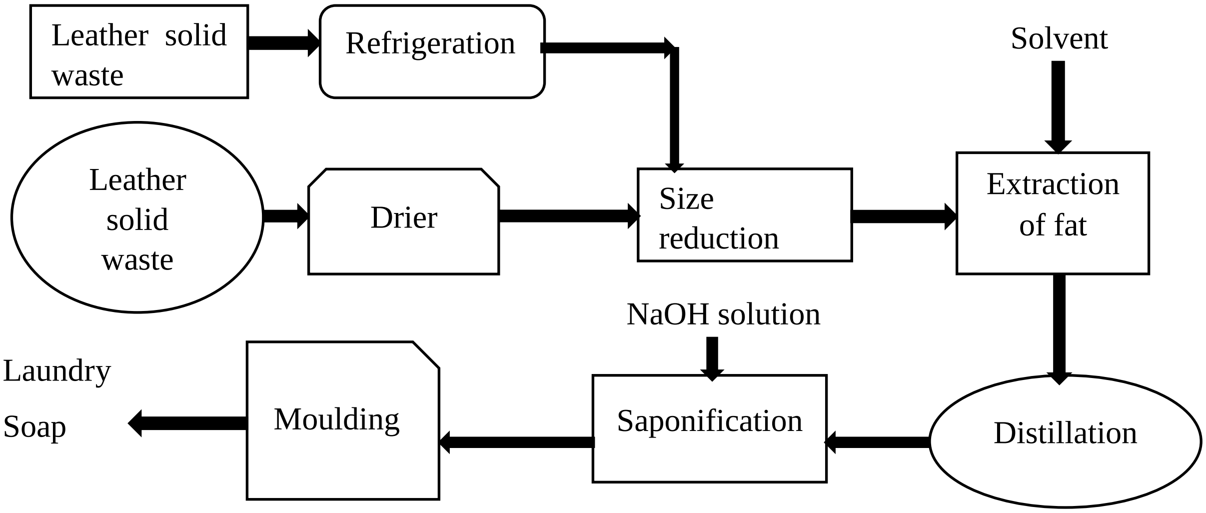


Figure 8 BFD of laundry Soap production

Figure 9 laundry soap

3.3 Product analysis

Determination of the yield

25g of the sample was placed in the thimble and about 100ml of n-hexane was poured into the round bottom flask. The apparatus was heated at 70°C and allowed for 5 hrs. for extraction process. At the end, the cake was dried in the oven at 100°C until the constant weight (W2) is attained and weighed to get (W2). The percentage of oil extracted was determined as:

$$\text{Fat yield (\%)} = \frac{\text{Fat extracted}}{\text{Solid leather waste}} * 100$$

Moisture Content

An empty crucible dish was dried in an oven, and weighed. A sample was measured before it enters an oven. It was transferred to and placed in a hot air oven set at 90°C for 24 hr. Thereafter the petri dish was removed, and the sample was cooled and weighed.

Moisture %= $(W_1 - W_2/W_1)*100$

Where, w1 = weight in gram before drying, w2= weight in gram after drying.

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. The pH electrode was standardized with buffer solution and the electrode immersed into the sample and the pH value was read and recorded.

Determination of Acid Value (Acid Number)

The acid value (AV) is the number that expresses, in milligrams the quantity of potassium hydroxide required to neutralize the free acids present in 1g of the substance.

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 color was observed and the volume of 0.1M KOH (V0) was noted. The Acid value was calculated as:

Acid Value (AV) = $V * C * MKOH/ 2 * 100\%$

Saponification Number

The saponification value is the number of mg of potassium hydroxide required to neutralize the free acids and to soaponify the esters in 1 g of the substance.

Determination of free acid value

Determination of the free fatty acid has its own laboratory apparatus. But in our lab there is no free fatty acid analyzer therefore the free acid value was calculated using the following formula.

Free fatty acid value = $Acid\ Value\ /2$

NOTE: All the above analyses were performed on the oil extracted using n-hexane as a solvent except the percent yield.

CHAPTER FOUR: RESULTS AND DISCUSSION

4.1 The effect dry and moist sample in the laundry soap

The fat yield from the dried sample was greater than that of the moist sample. In the moist sample extraction time was long due to the moisture content where as in the first sample extraction was fast and easy. The defect of the first sample was its dryness degree and time it stays in the oven affects the soap quality resulting in color change when compared to the normal and fragrance occur it undergo saponification.

4.2 The effects of solvent parameters, residence time and Temperature on fat yield

The extractions were performed using different solvent under varying extraction time :(3 - 5hr) & temperature (65-70 °C)

Table 4 yield of fat on solvent variation

Run no	Temp(°C)	PH	Residence time	Hexane(ml)	Sample before(g)	Sample after(g)	Fat yield(ml)
1	65	6.66	4	100	25	15.2	9.7
2	68	6.66	4	100	25	14.1	10.8
3	70	6.66	3	100	25	14.7	10.1
4	70	6.66	4	100	25	11.5	13.35
5	70	6.66	5	100	25	10.57	14.24

Run no	Temp(°C)	PH	Residence time	Petroleum ether(ml)	Sample before(g)	Sample after(g)	Fat yield (ml)
1	70	6.66	3	100	25	16.5	8.34
2	70	6.66	4	100	25	13.5	11.41
3	70	6.66	5	100	25	12.7	12.12

4.2.1 Effect of solvent type on fat yield

The extractions were performed by using two solvents, such as hexane and petroleum ether under varying temperature, and residence time. As observed from experiment to compare their extraction capacity at the same temperature and residence time hexane was the best solvent. It was gave high yield at short time than that of petroleum ether.

Table 5 Solvent Comparison

	Hexane	**Petroleum ether**
Solvent extraction capacity	Excellent	Fair
Process safety	Less hazardous	Hazardous
Solvent volatility and stability	Less volatile and stable as compared	Highly volatile, unstable
Economic consideration	Cheap	Expensive

4.2.2 Effect of temperature on fat yield

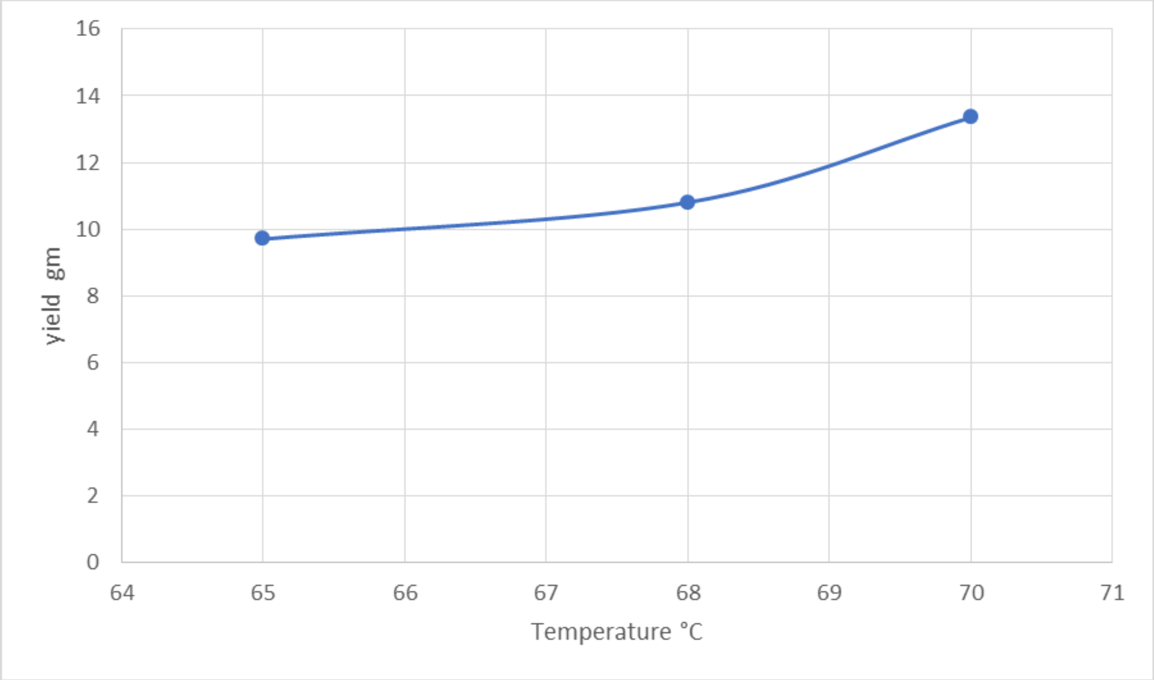


Figure 10 effect of temperature on fat yield

As it was observed on experiment before temperature is the major factor on extraction of fat from leather solid waste. When the temperature increases the amount of yield increase and when temperature decrease the amount of yield decrease at the constant of other factors. The experiments were done by varying a temperature at 65°C, 68°C, and 70°C. From these temperature variations the higher yield was observed at 70 °C and the lower yield was observed at 65°C. Therefore adjusting temperature at 70 °C is better for extraction of fat. Figure 9 shows the extraction yield was directly related to extraction temperature i.e. the yield increased as extraction temperature increased. According to this study the maximum fat yield is obtained at 70°C.

4.2.3 Effect of residence time on fat yields

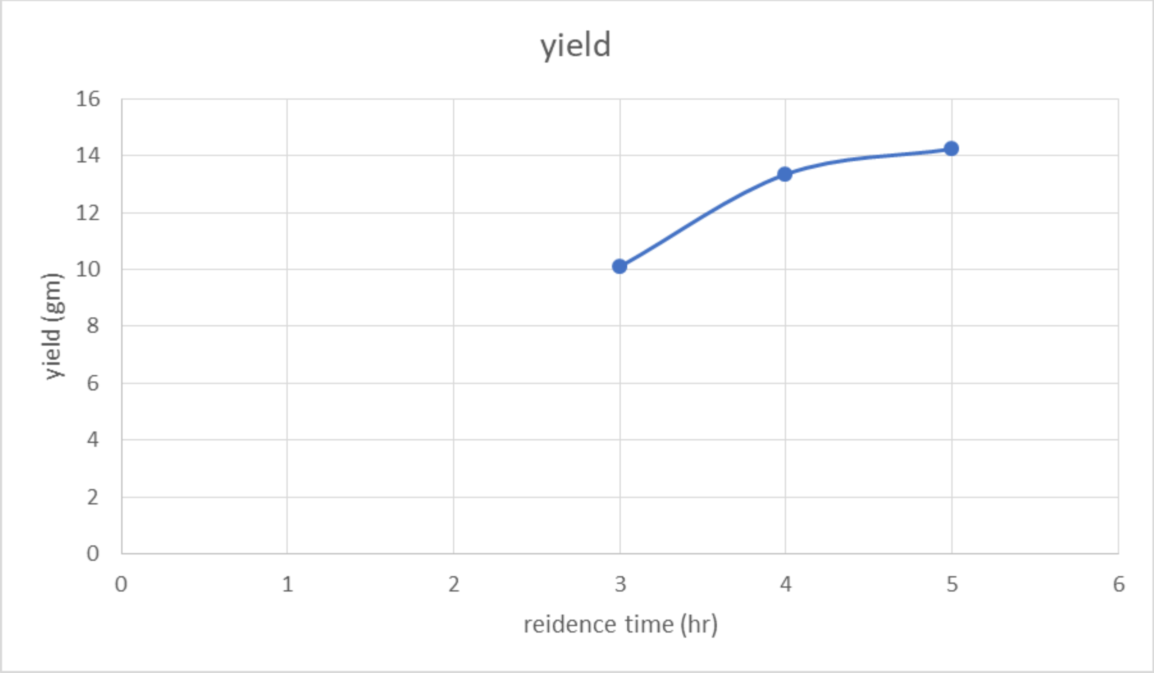


Figure 11 effect of residence time on fat yield

The residence time was also another effect on the extraction of fat from leather solid waste. It is directly proportion with in fat yield, when the residence time increase the amount of fat yield increase and when the residence time decrease the amount of fat yield decrease. The above experiments were done by varying residence time from 3 hours to 5 hour at one time interval (3, 4, and 5hours) at a constant of other factors.

From these time intervals the higher yield was extracted at 5 hr. and the lower yield was extracted at 3hr. Figure 10 shows the extraction of yield was directly related to extraction i.e. the yield increased as extraction time increased. According to this study the maximum fat yield was obtained at 5 hr.

4.3 Leather Solid Waste Characterization

- **Moisture content**

Moisture content = (A – B)/A *100%

Wet solid leather waste (A) = 1kg =1000g

Dry solid leather waste (B) = 380g

Moisture content = (A-B)/A*100%

((1000-380)/1000) *100 = 62%

- **PH**

The pH of the fleshing before hydrolysis was 6.8 and stored at 4 ºC in refrigerator.

4.4 Fat yield and its characterizations

1. Fat yield

From experiment 5 values were calculated as:

The extracted fat yield from solid leather waste is given by the following equation:

$$\text{Fat yield (\%)} = \frac{\text{Fat extracted (g)}}{\text{Solid leather waste}} * 100$$

(14.24/25) *100 = 56.96%

2. Color

This was done by visual observation which has light yellow color.

3. PH

The PH of fat yield was determined by using PH meter. The PH meter was adjusted by buffer solution, and then the PH meter was immersed into sample, and the PH reading was 6.

4. Acid value

Saponification value of fat = 0.1382mg/g of fat

Acid Value (AV) = V*C*56.11/ 2* 100%

V= volume of added KOH for titration= 3.7ml=0.0037liter

C= concentration of KOH=0.1mol/liter *M*=mass of sample= 2g

Molecular weight of KOH=56.11g/mol

Black volume = 1.8ml

Sample volume = 3.7ml

V = 3.7ml – 1.8 = 1.9ml V = 0.0019 AV = 0.53%

5. Free fatty acid value

FFAV= AV/2 = 0.26%

4.5 Characterizations of laundry soap

1. Fatty acid distribution laundry soap

Table 6 Results on fatty acid distribution of laundry soap

Fat	Type	Laurie	Palmitic	Stearic	Oleic
Animal	Laundry	1.81	45.47	5.29	36.20

Source: From chemistry of laundry soap

Table 7 Structure of Acids Commonly Found in Soap

Acid	**Structure**
Palmitic acid	$CH_3(CH_2)_{14}COOH$
Stearic acid	$CH_3(CH_2)_{16}COOH$
Oleic acid	$CH_3(CH_2)_7CH=CH(CH_2)_7COOH$
Lauric acid	$CH_3(CH_2)_{10}COOH$
Myristic acid	$CH_3(CH_2)_{12}COOH$

PH

The PH of the laundry soap was determined by using PH meter. The PH meter was adjusted by buffer solution, and then the PH meter was immersed into sample, and the PH reading was 9.8.

CHAPTER FIVE: MATERIAL AND ENERGY BALANCE

5.1. Material Balance

Note: All material balances had performed based on the experimental work in the laboratory. Balance on drying moisture content of the fleshing from solid waste is 62% of fresh dry solid waste.

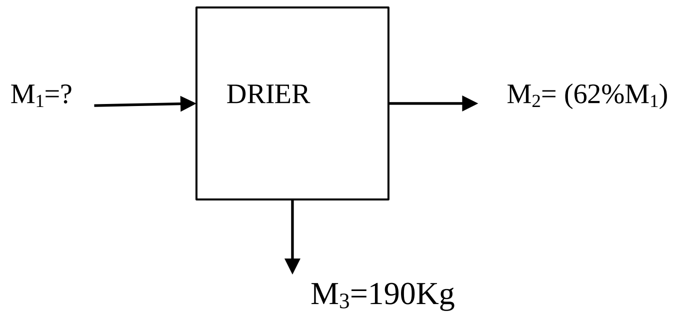
The laboratory experiment to manufacture laundry soap was based on 1kg of leather solid waste. For industrial level the amount of leather solid waste rises to about 500kg per day. From this figure, that the scale up factor is about 500 x. - Design capacity: 500kg/day of solid leather waste 300 operating days/year

- Final product: laundry soap

Total Material Balance

Accumulation=Output + Consumption – Input – Generation

Balance on drier



$M_3=0.38kg$

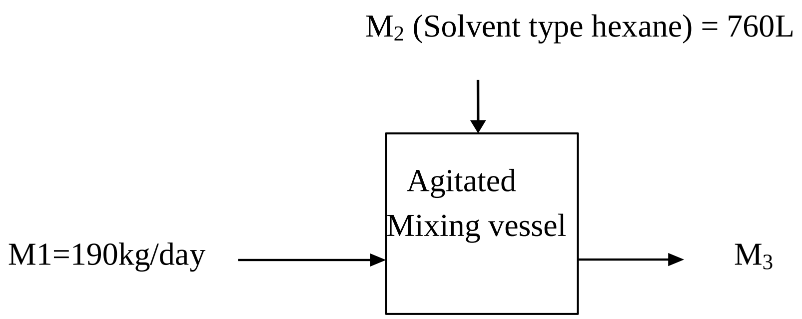
$M_1+M_2=M_3$

$M_1=(62\%M_1)+0.38kg$

$M_1(1-0.62)=0.38kg*500$

$M_1=500kg=500kg/day$

Balance on agitated vessel extraction



Density of Hexane (ρ) =655kg/m^3 @ 25oC

(https://macro.isu.edu/howto/solvent/hexane.htm)

Volume of Hexane =760L

Mass of Hexane (m_2) = density of Hexane (ρ)*volume of Hexane

m_2 =655kg/m^3*(760L*1m^3/1000L)

m_2= 497.8kg/day

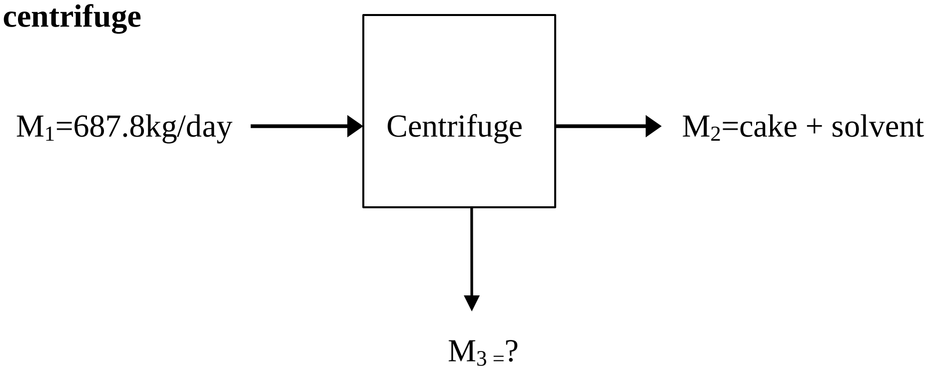
M1=0.38kg*500 = 190kg/day

$M_1+M_2= M_3$

$190+497.8=M_3$

687.8kg/day =M_3= (wt. of solvent, oil and cake)

Balance on centrifuge



$M_1=M_2+M_3$, $M_3=M_1-M_2$

From the laboratory experiment 5 by using hexane solvent, for 25gm of dry solid waste, 10.57gm of cake was wasted.

Thus: 10.57gm= 0.01057kg

25g of sample + 100ml of hexane=?

Density of hexane=0.655g/ml,

Mass of solvent=volume*density,=100ml*0.655g/ml,=65.5g,

mass of sample + mass of hexane =25g+65.5g=90.5g

Mass of cake @ exp.3 = 10.57g

Mass of cake= (687.8kg*10.57g)/90.5g=80.3kg

Assume Mass of Solvent=6.1%of cake

Hence, Mass of solvent =0.061*80.3kg, = 4.89kg

M_2 = Cake + Solvent = 80.3+4.89, = 85.19kg

M_3= 687.8kg-85.19kg

M_3=602.61kg

Balance on distillation unit

Assuming 100% separation on distillation column, since oil and solvent have long different boiling points (Oil=above 300^oC and solvent (hexane) =68^oC), the separation will be possible by simple distillation. The mass balance here is.

Oil balance around the column

From experiment:

From 25g of seed 14.24ml of fat was obtained.

Density of animal fat: 0.87gm/ml

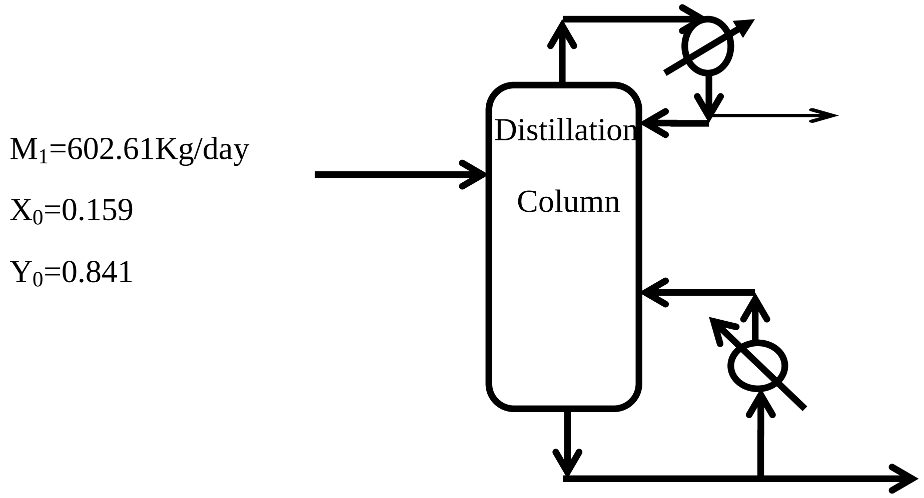
Therefore, the mass fraction of fat is (x_0) =

14.24ml*0.87g/ml / ((14.24ml*0.87g/ml)+mass of solvent,

=12.3888gm/(12.3888gm+65.5gm)

Xo=0.159

Whereas that of Hexane is y_0= 1-0.159= 0.841.



From feed:

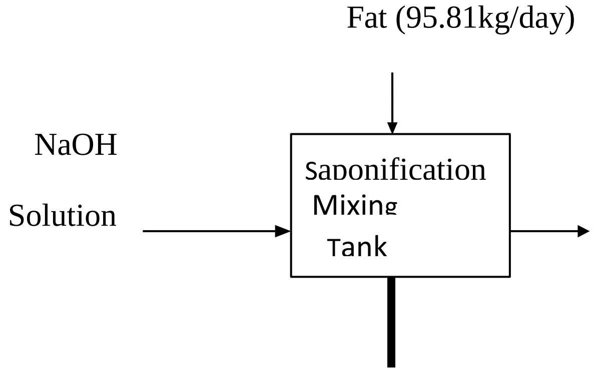
X_0 =0.159 mass fraction of oil in feed and mass fraction of hexane=0.841

Since 100% separation is assumed all fat will separate out as bottom product while the hexane is as top product of the distillation column.

Fat produced = 0.159*602.61kg/day=95.81 kg/day

Hexane recovered = 0.841*602.61kg/day =506.79kg/day

Saponification mass balance



The output from mixing thank is; Glycerin and soap (15% and 85% respectively) = 139.95kg/day

Soap = 0.85*139.95=118.96 kg/day

Glycerin = 0.15*139.95=20.99 kg/day

Fat + NaOH solution=95.81+44.14=139.95kg/day

Table 8 Amount of soap produced

Type	Amount
Fat	95.81 kg/day
Saponification value for Animal fat	$0.1382*10-^{3}$kg/kg of fat
NaOH (0.1382*95.81kg)	13.24kg/day
Solution of water and NaOH(13.24/0.3)	44.14 kg/day
Water (44.14-13.24)	30.9kg/day

5.2. Energy Balance

Energy balance on the dryer

From the literature;

Cpw = 4.18kJ/kg. ^{o}C

Cpf =2.34kJ/kg ^{o}C

Mass flow rate of water ($\dot{m}$w) =12.9 kg/hr

Mass inflow of wet solid waste ($\dot{m}$f) = 20.8kg/hr

Assume inlet and exit temperature to be 30 and 90^{o}C respectively then, the amount of energy required is:

$Q_1 = (\dot{m}wCpw + \dot{m}fCpf)\ \Delta T$

$= (12.9 * 4.18 + 20.8*2.34) * (90 - 30)$

= 6155.64kJ/hr

= 6155.64KJ/3600sec

=1.71KJ/sec

Energy balance on agitator mixer

From material balance

Mass flow rate of fat = 7.9Kg/hr

Mass flow rate of Solvent used=20.74kg/hr

Cp (hexane@25^{0}C)=2.26kJ/kg ^{O}k

Assumptions: Exit temp = 50^{0}C

The energy required in mixer is:

$Q_2 = (\dot{m}f\ Cpf + \dot{m}s\ Cps)\ \Delta T$

$= (7.9*2.34+20.74*2.26) * ((50+273) – (25+273))$

= 1623.6kJ/hr.

Energy balance on centrifuge

From mass balance data

Mass flow rate of sw =28.65kg/hr

Mass flow rate of cake = 3.35kg/hr

Mass flow rate of solvent =0.2kg/hr

Cp (miscilla=cake) = 2.34kJ/kg. ^{0}C

Cp (hexane) =2.26kJ/kg^{0}k

Assumption:

Inlet and exit temperature is 40^o C and 70^0 C respectively

Then total amount of energy required is energy contained in the materials.

Thus the energy required can be calculated as:

$Q_1 = (Cpw\ (\dot{m}c+\dot{m}_{sw}) + \dot{m}s\ Cpf)\ \Delta T$

Q_3= [2.34 (3.35 +28.65) + (0.2) 2.26] (70-40)

=2259.96 kJ / hr.

Energy balance on distillation column

Mass of miscilla =25.1 kg/hr.

Cp (miscilla) = 2.34kJ/kg.^{0} C

Assumptions:

Energy required is equal with the energy contained in the handled materials (Solvent and Oil)

Inlet and exit temperatures are 40^o C and 70^0 C respectively.

Then, heat required for distillation column can be calculated as:

$Q_4 = (\dot{m}fCpw)\ \Delta T$

$Q_4 = 25.1*2.34\ (70-40)$

$=1762$kJ/hr

Energy balance on heater

Mass of fat =3.99kg/hr

Cpf = 2.34kJ/kg^{0}C

Inlet and outlet temperature equals 40^{0}C and 60^{0}C respectively.

$Q_5 = MfCpf\ \Delta T$

$= 3.99*2.34*(60-40)$

$= 186.73$kJ/hr

Energy balance in saponification process

Mass of fat Mf = 95.81kg/hr.

Mass of NaOH=13.24kg/hr.

Mass of water=30.9kg/hr.

Cp of water, NaOH and fat are 4.18, 3.47 and 2.34KJ/kg^{0}C respectively. Inlet and outlet temperature equal to 60^{0}C and 40^{0}C respectively.

$Q = (MfCpf + M_{NaOH}\,Cp_{NaOH} + MwCpw)\ \Delta T$

= (95.81*2.34+13.24* 3.47+30.9*4.18)(20)

= 6104.364kJ/hr

Table 9 Summary of Energy balance

Number	Equipment name	Capacity (kJ/hr)
1	Dryer	6155.64
2	Agitator mixer	1623.6
3	Centrifuge	2259.96
4	Distillation column	1762
5	Saponification Mixing tank	6104.36

CHAPTER SIX: EQUIPMENT SIZING AND COST ESTIMATION

6.1 Equipment Sizing

Sizing and Equipment Listing For the Production of soap The engineer developing a process design must be the responsibility of preparing specific action for individual places of equipment and design data must be developed. Safety factor: is a factor to represent the amount of our design that would be used to account for the changes in the operating performance with time. As a general, safety factor = (10-20) % of capacity of the equipment

The working day per year is 300 days.

Sizing of equipment is depending on the material balance of the plant.

1. Size of hexane storage tank

All tanks are 75% full and take allowance.

Liquid volume = 760L, Tanks considering 80% charge volume, the size is 1000L

2. Storage tanks for dried fleshing waste

Density of Solid to be handled /fleshing waste= 870 kg/m^3 at 25^{0}C

Materials of construction is carbon steel Capacity

$\varrho = m/v, v=m/\varrho = (190Kg)/870kg/m^3=0.218\ m^3$

Required storage volume (Vr)

Vr =V/0.8=0.218*1000L/0.8=272L

3. Sieve/Crusher (SC-1010)

A roller crusher is selected.

Capacity: 1kg/s=3,600kg/hr

4. Distillation column

Density of fat to be handled /fleshing waste

= 870 kg/m^3 at 25^{0}C and density of hexane=655kg/m^3

, so the average density is 762.5kg/m^3

Materials of construction is carbon steel

Capacity ϱ = m/v, v=m/ϱ

= (602.61Kg)/762.5kg/m^3=0.79 m^3

Required storage volume (Vr)

Vr =V/0.8=0.79*1000L/0.8=987.5L

5. Size of extractor (EX-102)

- If we consider charging volume is 75% the size of extractor
- Volume =mass/density +volume of Hexane
  =190kg/870kg/m^3 +760L*1m^3/1000L

  = 0.218 m^3 + 0.76m^3

  =0.978m^3=978L

V_e= 978L/0.75=1304.5L

6. Pump for Delivering Water

Type	centrifugal
Head	3m
Liquid to be handled washing water	
Density of liquid	1000kg/m^3

Capacity of the pump

V_p = (900Kg)/1000kg/m^3=0.9m^3

7. Size of saponification tank

- If we consider charging volume is 75% the size of tank

Volume =mass/density of fat +volume of NaOH solution
=95.81kg/870kg/m^3 +44.14kg/1330kg/m^3

= 0.11m^3 + 0.033m^3

=0.143m^3=143L

V_s=143 L/0.75=190.6L

Table 10 Equipment sizing and costs

Eq. No.	Equipment Name	Capacity	Material	Q'ty	Unit Price ($, 1)	Amount ($, 2)
DR-1	Dryer	6155.64kJ/hr	C.S.	1	9,700	9,700
SC-101	Roller Crusher	879kJ/hr	1 kg/s	1	8930	9,000
Tk-1	Agitation tank	1623.6kJ/hr	C.S.	1	13,765	13,765
Cf	Centrifuge	2259.96kJ/hr	C.S.	1	18000	18000
DCL-1	Distillation column	1762KJ/hr	C.S.	2	8,305	16610
TK-2	Dried fleshing Waste storage	11.33L/hr	C.S.	1	1700	1700
TK-3	Hexane storage	31.66L/hr	C.S.	1	4400	4400
Tk-4	water storage	1,000L	C.S.	1	18,000	18,000
TK -5	Saponification tank	190.6L	S.S.	1	32,000	32,000
TK-2	Oil storage	7753.1L	C.S.	1	796,027.8	67492
AM200/ SWSP	Extruder	250-400kg/hr 15Kw	C.S		8560	8560
P	Pumps	0.04m^3/hr	Cast iron	4	3300	13200

Source: https://www.matche.com and http://alibaba.com

6.2 Cost estimation

6.2.1 Fixed capital investment

Fixed capital investment values for direct and indirect cost.

Costs of equipment + installation + instrumentation +piping+ electricity+ painting (50 - 60% of FCI)

Purchased equipment cost (PEC) = $212,277

Installation including painting (25-55% of PEC), take 40% of PEC = $84,910.8

Assume that total purchased equipment cost = 40% F.C.I

TPEC = 40%FCI

= $84,910.8

Direct cost (DC)

Instrumentation and control (6-30% of PEC), take 18% of PEC = $38209.86

Piping (10-80% of PEC), take 15% of PEC = $31841.55

530,Electricity (10-40% of PEC), take 25% of PEC = $53069.25

Building, process and auxiliary (40-70% of PEC) , take 50% of PEC = $106138.5

Service facilities (40-100% of PEC), take 40% of PEC = $84,910.8

Land (4-8% of PEC), take 4% of PEC = $8491.08

Direct cost (DC) = summation of all the above cost

= $212,277 + $84,910.8+ $38209.86+ $31841.55+ $53069.25+ $106138.5

+ $84,910.8+ $8491.08 = $619848.84

Indirect cost

Engineering and supervision (5-30% of DC) we take 18% of DC = $111572.79

Construction expense and contractor fee (6-30% of DC) we take 18% of DC = $111572.79

Contingency = 10%of FCI= 0.1*FCI

Indirect cost (IC) = summation of the indirect cost

= $111572.79+ $111572.79+ 0.1*FCI

Fixed capital investment (FCI) = DC + IC = $619848.84+ $111572.79+

$111572.79+ 0.1*FCI

FCI = $842994.4 +0.1FCI

FCI = $842994.4/0.9 = $936660.46

Working capital investment (WCI) = 15% of TCI ………………………… (1)

Total capital investment (TCI) = FCI + WC……….………………………………(2)

From the above two equations:

WC = $165293.02

TCI=FCI+WC=$1101953.48

Total production cost (TPC) estimation fixed cost

- Depreciation = 10% of equipment cost + (2-3%) of building = 0.1*$212277 + $2653.46 = $23881.16
- Local taxes (1-4%FCI) = 2.5% of FCI = $23416.5
- Insurance (0.4-1%FCI) = 0.7% of FCI = $6556.6

Total fixed charge (TFC) = Summation of the above fixed charge

= $23881.16+ $23416.5+ $6556.6 = $53854.28

Total production cost (TPC)

FC = 15% of TPC, TPC = $359028.55

Direct production cost (DPC):

Raw material and inputs: (10-50% of TPC) ,take 10% of TPC = $35902.855

Operating labor (OL): (10-20% of TPC), take 15% of TPC = $8078.14

Direct supervisor and clerical labor: (10-25% of OL), take 18% of operating labor

= $1454.06

Utilities: (10-20% of TPC), take 15% of TPC = $53854.28

Maintenance and repair (M& R):(2-10% of FCI), take 6% of FCI = $56199.62

Operating Supplies: (10-20% of M & R or 0.5-1% of FCI), take 15% of M&R = $8429.9

Laboratory Charges: (10-20% of OL) we take 15% of OL= $7,471.05

Patent and Royalties: (0-6% of TPC) 3% of TPC = $1077.8

Direct product cost (DPC) = the summation of the above production cost

= \$35902.855+ \$8078.14+ \$1454.06+ \$53854.28+ \$56199.62+ \$8429.9+ \$7,471.05 + \$1077.85= \$182160.76

Plant overhead cost (POC): (5-15% of TPC), take 10% of TPC = \$35902.86

1. Manufacturing cost = FC + DPC + POC = \$53854.28+\$182160.76+ \$35902.86

= \$271917.89 6.2.2 General expense

General expense= Administrative costs + distribution and selling costs + research and development costs + Financing (interest)

- Administrative costs (2-6% of TPC), take 4% TPC = 0.04*\$359028.55
- =\$14361.14
- Distribution and selling costs (2-20% of TPC), take 11% of TP=0.11*\$359028.55 =\$39493.14
- Research and Development costs = 5% total product cost=0.05*\$359028.55

=\$17951.42

- Financing(interest) = 5% total capital investment= 0.05*\$1101953.48=\$55097.67

Therefore, general expense

= \$14361.14+\$39493.14+\$17951.42+ \$55097.67= \$126903.37 Working day= 300 day per year

Our product per year is = 85kg/day* 300day/year = 25500/year

Unit sell price = total production cost/annual production=\$359028.55/25500kg/year =\$25/kg

Total selling price is = 25500/year kg/year*\$25/kg = \$637500/year

Annual produced oil=51.45kg/0.85=60.5L*300day/yr.=18158.85L/yr

Annual income is found to be 18158.85L kg/yr.* \$ 9 /kg = \$163,429.4 /yr.
Total income=\$\$637500/yr +\$163,429.4 /yr.=\$800929.4year

6.2.3 Profitability analysis

Gross profit = product sales revenue–total product cost

Gross profit = Sj –Coj= \$800929.4-\$359028.55=\$441900.85/year

Assume: salvage value = 0 and plant service life = 10 year.

Therefore depreciation cost = (fixed cost - salvage value) /service life

Depreciation = v-vs/n

= ($936660.46- 0)/10 =$93666.05/year Gross profit including depreciation Gj =Sj-Coj-dj=$800929.4-$359028.55 - $93666.05/year= $348234.8year

Net profit = gross profit with depreciation (1-Ø), where, Ø= income tax of rate Ethiopia =30% = $348234.8*(1-0.3) = $243764.36/year

Minimum acceptable rate of return (Mar)

Minimum acceptable rate of return (mar) for new capacity with established corporate with low levels of risk=12%

Rate of return (ROI) an initial investment

ROI =net profit/TCI = ($243764.36/$1101953.48)*100%

= 22.12 %

ROI >=M*ar* (12%), 22.12%>12% so the project is feasible

Payback period

(FCI-salvage)/(net profit+ depreciation)

= ($936660.46-0)/$(243764.36+$93666.05)

= 2.7year

(Plant design and Economics for chemical engineers, Vol 4th edition)

CHAPTER SEVEN: CONCLUSION AND RECOMENDATION

7.1 Conclusion

The fat to produce soap uses raw material from the leather solid waste. The higher amount of fat found in fleshing solid waste first, were the fat extracted characterized so that they can be reused as a raw material. From the characterization it was found that PH of 6, fatty acid value 0.53%, free fatty acid value 0.2% and 0.1382mg/g of fat saponification value in animal fat. For the production of laundry soap semi boiling method was selected. This method has some advantage over the other two since large quantities of good soap can be produced within a short time. The use of this method also allows a high percentage of fillers to be added in soaps, thus it increases the soap bulk in addition to that the process does not permit the removal of waste alkali which contains the glycerin produced in the soap making process, and hence the glycerin, which tends to decrease the hardening property of the soap and improves the cosmetic property, is retained in the finished soap. For the extraction of fat two extraction solvent were compared. Those are petroleum ether and hexane solvents. Different parameters are taken to select the effective solvent for the specified fat source. Thus Hexane was preferred due to its best extraction capacity, less hazardous, more stable and economical. The residues from the production have no wastes that are dangerous to the environment and health. The by-product is also biodegradable and we can use it for the production of fertilizer and fibers.

7.2 Recommendations

Further researches have to be done to improve the production of high quality and quantity of soap by further characterizing the fatty acid that are the main composition for laundry soap. Alternative extraction methods of fat such as solid-liquid, supercritical, $CO_{2,}$

Ultrasound Assisted, Microwave-Assisted, Enzyme-Assisted extraction, have to be done Most of the solid wastes including leather solid waste in our country have no or very low conversion to different usable products and as such among the major problems of health especially for cities that found near tannery industries by which most tannery solid waste are sited. Hence, it recommended that government or other investor's to recover this waste product as well as to contribute to the country in reducing the highly rising quantity of wastes. In future the demand of soap and in Ethiopia has increasing demand. Finally, our recommendation forwards to the government and/or non-governmental organization or private investors to give emphasis on treatment of solid leather waste by considering its environment.

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