ADDIS ABABA UNIVERSITY

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Fatliquor Product Development from *Vernonia galamensis* Seed Oil via Modified Sulphitation Process

By

Senait Gebeyehu Nadew

DECEMBER, 2014

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By: Senait Gebeyehu Nadew

Advisor: Ato Gizachew Shiferaw (Assistant Professor)

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Approved by the Examining Board:

Chairman Department's Graduate Committee	Signature	Date
Ato Gizachew Shiferaw Advisor	Signature	Date
Ato Teshome Worku Internal Examiner	Signature	Date
Ato Lelissa Daba External Examiner	Signature	Date

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Acronyms

A	Total alkalinity
AOAC	Association of Official Analytical Chemists
ANOVA	Analysis of Variance
AR	Analytical Reagent grade
AV	Acid Value
BASF	Baden Anilline and Soda Factory
BDU	Bahir Dar University
BTPP	benzyl-tri-phenyl phosphonium chloride
CCD	Central Composite Design
CI	Capital Investment
D	Total sulphur as sulphite
EV	Ester Value
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FT-IR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
HPLC	High Performance Liquid Chromatograph
IS	Indian Standards
ISO	International Standards Organization
IUP	International Union of Leather Chemists Physical Testing Methods
LIDI	Leather Industry Development Institute
PTC	Phase Transfer Catalysis
R	Response variable
RSM	Response Surface Methodology
SG	Specific Gravity
SV	Saponification Value
TEBA	tri-ethyl-benzyl ammonium chloride

Abstract

Fatliquor is one of the most important chemical used in leather processing industry. It is currently imported with foreign currency. This research showed the potential of locally available raw material *vernonia galamensis* seed oil for production of sulphited fatliquor, which will potentially substitute the imported vegetable oil sulphited fatliquor.

4.5 liter purified Vernonia oil was obtained from 22 kg Vernonia seed. FAME is prepared from vernonia oil with 85% yield. The sulphited fatliquor was synthesized using vernonia oil, FAME and concentrated sodium bisulphite solution. The process involves preparation of seed, extraction and purification of oil, preparation of FAME and 40% by weight sodium bisulphite solution, oxidation of mixture of vernonia oil and FAME, sulphitation of the mixture with sodium bisulphite, washing excess sodium bisulphite and finally drying the sulphited fatliquor.

Design-Expert 7.0.0 three-level-three-factor face-centered CCD was applied for experimental design and statistical analysis of results. A total of 20 experiments were conducted at conditions of reaction temperature 60, 65 and 70^0C, amount of sodium bisulphite solution 20, 30 and 40% and 10, 12.5 and 15 h reaction time. From the analysis of experimental results the interaction effects were studied and the optimal sulphitation reaction process conditions, which will maximize the degree of sulphitation, were found to be 70^0C reaction temperature, 30% amount of sodium bisulphite and 12.5 h reaction time which gave 3.36% degree of sulphitation.

The physicochemical characterization of the synthesized fatliquor and the visual and physical properties test on the fatliquored leather met the IS 14488 and BASF specification respectively.

From the preliminary feasibility study for 2750 kg/day capacity Sulphited fatliquor production plant, Birr 40.95 million TCI is required. The unit product cost was estimated 28.85 Birr. The project was financially feasible with 51.6% RORI, Birr 66.16 million NPV, 2 years and 4 months payback period, 2.6 profitability index and 42% IRR.

1. Introduction

1.1 Background

Leather making is a very complex course including lots of physical and chemical changes. On one hand, the useless parts were removed from raw hide to get pure collagen fiber and opened up the structure of collagen fiber. On the other hand, tanning agent was introduced to strengthen the stability of collagen fiber and other necessary materials were added to make leather usable, such as fatliquor, retanning agent and finishing agent. Moreover different mechanical actions were needed in the course of those changes [1].

Fatliquor is a largest amount of leather-chemistry material in leather industry and has extremely important impact on the performance of leather [2, 3]. It can penetrate to the collagen fibers, making the leather lubricant and plastic. The fatliquor can make the molecular chain segment easily move, give the leather softness, water proof, moisture and flexibility [4]. Since all Ethiopian leather factories apply chrome tanning, they use anionic type of fatliquor.

Vernonia (*Vernonia galamensis*) is a potentially novel industrial oilseed crop. It plays a great role in oleochemical industries and as alternative cash crop. It is one of the only few plants that contain naturally occurring epoxydized oils in its seeds known as vernonia oil. The best quality of vernonia oil is that all of the epoxy acid is present as trivernolin, which is rich in epoxy fatty acids and has low viscosity [5, 6]. The trivernolin can be converted into vernolic acid (72 – 80% of the seed oil) [7]. Vernolic acid group serves as a key starting material for the synthesis of different important chemicals [8].

Vernolic acid is a useful raw material for the manufacture of adhesives, varnishes, paints and coatings [9]. Also degradable lubricants, lubricant additives, epoxy resins, plastic formulations for PVC, insecticides, insect repellants and reactive monomers in polymer synthesis [10, 11]. Vernonia oil has also been used as a source of hydroxyl alkoxy fatty esters and for the synthesis of epoxy secondary amides [12]. Currently vernonia product on the market includes Vernola Super gloss, a car-care product used on tires, leather and rubber bumpers [13, 14].

1.2 Statement of the Problem

Currently Ethiopia has 32 leather industries which produce different leather products with total production capacity of 2,382,600 Hide and 38,533,800 Skin per year. The data collected from 26 leather industries, with 76.73% utilized capacity, show that on average 7,514,793 kg fatliquor is used annually which costs around Birr 405,798,822 [15].

Most of the chemicals used for tannery production are imported with foreign currency. And even if fatliquor production is a simple technology currently almost all the tannery factories of our country are dependent on imported fatliquor which is known to be very expensive and the increment in the exchange rate of dollar escalates the loss of foreign currency reserve.

On the other hand *vernonia galamensis,* which is originated in Ethiopia and can grow in all over the country, is a potentially novel industrial oilseed crop. It is a tropical, indeterminate annual plant. It requires a well-drained soil and can grow under low rainfall (up to 200 mm) and is most suitable for dry land farming. What makes interesting about the seed oil is that the oil (35 – 42% of the seed) contains as the major fatty acid vernolic acid (72 – 80%) of the oil [16, 17]. The vernolic fatty acid has unique characteristics for formulation of different products through different processes and has low viscosity.

Therefore, the rationale of this research work is to exploit the potential of *vernonia galamensis* seed oil for sulphited fatliquor production through modified sulphitation process which will potentially compete with the imported vegetable oil based sulphited fatliquor product.

1.3 Objective of the Research

1.3.1 General Objective

The main objective of this research is to study the effect of the independent variables and their interactions in the production of sulphited fatliquor using locally available raw material, *Vernonia galamensis* seed oil, via modified sulphitation process.

1.3.2 Specific Objectives

The specific objectives are:-

- Preparation, extraction and purification of Vernonia oil.
- Characterization of the physicochemical properties (Moisture content, specific gravity, Acid value, Saponification value and Iodine value) of vernonia oil.
- Investigation of the effect and interaction of the three important sulphitation reaction parameters namely reaction temperature, amount of sodium bisulphite and reaction time on the degree of sulphitation using Design-Expert Software 7.0.0 for three-level-three-factor face-centered central composite design (CCD).
- Determination of the optimal operating parameters and generate the model equation for the three independent variables which will maximize the degree of sulphitation.
- Characterization of physicochemical properties (pH of emulsion, Total active ingredient, Unsaponifiable matter, Total alkalinity, Total sulphur as sulphite and Total ash content) of sulphited fatliquor.
- Test the fatliquoring effect of synthesized sulphited fatliquor on leather at Leather Industry Development Institute (LIDI).
- Preliminary feasibility study for sulphited fatliquor production plant from *Vernonia galamensis* seed.

1.4 Significance of the Study

The significance of this research can be seen from different perspectives.

- Provide a means to exploit and manage local resources.
- Provide a new potential industrial oilseed crop, *vernonia galamensis* seed oil, for production of sulphited fatliquor.
- Provide an economically feasible option to produce sulphited fatliquor locally, which will play a major role to substitute the imported sulphited fatliquor that saves foreign currency and create job opportunity.
- Serve as a starting material for further research studies on the application of *vernonia galamensis* oil for other potential purpose.

1.5 Scope of the Study

The thesis work generally covers vernonia oil extraction, vernonia oil refining, vernonia oil characterization, fatty acid methyl ester (FAME) preparation and synthesis of sulphited fatliquor through modified sulphitation process, characterization of produced fatliquor, actual test of synthesized fatliquor on leather. Extraction, refining, characterization of vernonia oil, preparation of FAME and characterization of the produced fatliquor were done using a standard procedures and test methods.

2. Literature Review

2.1 Introduction

The literature review of this research covers the available raw materials for fatliquor production, fatliquor production technologies, parameters that affect fatliquor production, physicochemical properties and specifications of sulphited fatliquor and finally fatliquoring process.

Almost all oils and fats are ester of glycerol and long-chain fatty acids. The five fatty acids namely palmitic, stearic, oleic, linoleic and linolenic are the main fatty acids in oils and fats. The first two fatty acids are saturated and the rest three are unsaturated. The selection of oils and fats for fatliquoring thus depends upon the type and composition of fatty acids [18].

Fatliquor is a term generally used to represent an emulsifiable oil and fatliquoring operation is done by treating the leather with an oil-in-water emulsion of the fatliquor [18]. There are different technologies for production of anionic fatliquor which mostly used in chrome tanning. Saponification using strong alkali, sulphation using sulphuric acid, sulphur trioxide or chlorosulfonic acid and sulphitation using a strong solution of sodium bisulphite are the available technologies for anionic fatliquor production. Also modified sulphitation process can be applied for sulphited fatliquor production. It can be produced using mixture of oil and FAME and concentrated sodium bisulphite solution similar to sulphitation process.

Sulphited oil compared to saponified oil and sulphated oil exhibit some advantageous property. It gives higher emulsion stability to acids, hard water and metal ions, gives deeper lubrication, avoid charring or darkening and no pH adjustment required. Parameters affecting production of modified sulphited fatliquor includes reaction temperature, concentration of sodium bisulphite, amount of sodium bisulphite, reaction time, mixing rate and FAME to oil ratio. Indian standard methods and specifications are available for characterization of sulphited fatliquor and IUP standard method and specification is available for fatliquored leather characterization.

2.2 Raw materials for Fatliquor Production

Fats, oils and waxes are the primary raw material source for fatliquor production. In addition to the method of application and emulsion formation characteristics of fats, oils and waxes, the ultimate lubrication properties and the physical characteristics of the resulting fatliquor and fatliquored leather depend upon the type of raw material used [19].

Fats and oils used in leather manufacture fall into three broad classifications triglycerides, fatty esters and mineral oils. The most important fats and oils are the triglycerides of fatty esters. This includes fish, plant and animal oils. They are similar in that they are esters of glycerin and are different in that they are made up of different fatty acids. They may be characterized by their analysis of such factors as free acid content, iodine value, saponification value etc. [18].

Waxes differ from oils and fats in that they are esters with high monohydric fatty alcohols. Sperm oil is an exception and it can be considered as a mixture of oil and wax. They are not greasy to touch and do not contain glycerol combined with fatty acid. The plant waxes are obtained from the outer surfaces of leaves, fruits, flowers or stems of plants [18, 19].

Fatty acids present in oils and fats may be saturated or unsaturated. The presence of unsaturated oils is responsible for fluidity in oil. Fats contain less unsaturated acids than in oils. Vernonia oil extracted from vernonia plant seed contains unsaturated vernolic acid. Typical fatty acid composition of the most widely traded commodity oils are shown in Appendix A.

If the oil contains high portions of unsaturated linolenic acid, they are of drying type of oils like linseed oil and are not useful as lubricants. Semi-drying oils such as soy bean and cotton seed oil and non-drying oils which include olive and castor oil are the preferable raw material for synthesis of fatliquor. Characteristic average values of the main fatty substances are shown in Appendix A.

2.2.1 Vernonia Seed Oil

Vernonia is a new potential industrial oilseed crop. The extracted oil is used for many applications. The company Ver-Tech International identified over seventy potential uses of vernonia oil [20]. In this literature review description of the vernonia plant, its distribution, extraction, potential application and chemistry of vernonia oil is covered.

2.2.1.1 Description and Distribution of Vernonia Plant

The genus vernonia (*vernonia galamensis*) or ironweed is one of the largest groups in the family of Asteraceae (sunflower family) [21]. It comprises of more than a thousand species which vary from annual herbs and shrubs to perennial trees [22]. Robert E. Perdue first identified vernonia near the old city of Harar in Eastern Ethiopia in December 1964 [23]. A typical *vernonia galamensis* seed is shown below in Figure (2.1).

Figure 2.1: *Vernonia galamensis* seed

Vernonia is essentially a tropical, indeterminate annual plant and requires a well-drained soil. It has the ability to grow under low rainfall, marginal conditions and is most suitable for dry land farming [24, 25, 26].

Vernonia is limited in distribution and is endemic primarily to Eastern Africa. This plant grows in a wild form in Ethiopia, Eritrea, Malawi, Tanzania and Kenya. The greatest diversity of vernonia is found in east Africa while a single variety found in West Africa. It has been found to grow in areas with less than 600 mm rainfall, at an elevation ranging from 700 to 2400 m above sea level and thrives in sandy soils [24, 27].

Vernonia grows in many parts of Ethiopia, especially around the city of Harar, with an average seed yield of 2000 to 2500 kg per hectare. It is reported that the Ethiopian strains of vernonia have the highest oil content up to 41.9% with up to 80% vernolic acid content [28]. In other review seed yield up to 4000 kg per hectare, equivalent to 1625 kg per hectare of oil with an oil content of 40% using unimproved local materials were obtained, which seem to be higher than those found elsewhere [5, 6].

Traditionally, farmers considered it to be an indigenous weed, so they tended to eradicate it in order to free their land for other crops. But due to the increased awareness of the importance of vernonia, however, it is now considered as a potential crop for inclusion in the agricultural system of the country [29].

2.2.1.2 Extraction of Oil

Extraction of vernonia oil can be done using different methods. Mechanical pressing and Solvent extraction using different solvents can be applied according to the desired output.

The oil extracted from vernonia seeds by solvent extraction yield of up to 42% has been reported [9, 20, 28]. In other review by Mills *et al.* it was found that Soxhlet extraction yielded somewhat more oil (38%) than cold extraction with hexane at room temperature (35%). The oil obtained at room temperature contained less free fatty acids [30]. Mechanical pressing method can also be applied for vernonia oil extraction. The cake formed after oil extraction is high (43.75%) in crude protein and is suitable for animal feed [31].

2.2.1.3 Chemistry of Vernonia Oil

The seed of *vernonia galamensis* contains vernonia oil which contains as the major fatty acid vernolic acid (72 – 80%), a naturally occurring epoxidized fatty acid. Vernonia oil also contains 12 – 14% linoleic acid, 4 – 6% oleic acid, 2 – 3% palmitic acid and 2 – 3% stearic acid [16, 17]. Depending on the fatty acid type and composition, Vernonia oil shows the physical and chemical properties presented in Table (2.1).

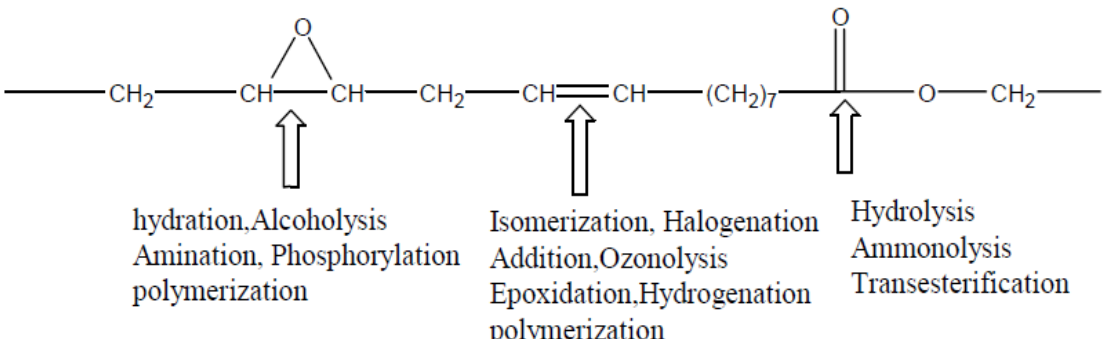
Table 2.1: Physical and chemical properties of Vernonia oil

Property of Vernonia Oil	Value
Iodine value, g I_2/100 g oil	104 – 108
Saponification value, mg KOH/g oil	165 – 210
Unsaponifiable, wt%	1.0 – 8.0
Refractive Index at 25^0C	1.4740 – 1.4860

(Source: Manuel des crops gras, AFCEG, Paris, 1992)

The iodine value measures the degree of unsaturation. Iodine value of vernonia oil makes the oil a non-drying type. This makes the oil suitable for synthesis of fatliquor. Higher Saponification value means, oils of smaller molecules and so their penetrating powers into the leather is high, gives softness to leather [18].

Vernolic acid (cis-12, 13-epoxycis-9-octadecenoic or 18:1 epoxy), is primarily present in the oil as the triglyceride trivernolin. The unique and special structure of epoxy acid within the triglyceride enables a wide variety of reaction characteristics of the ester group, the double bond, and the epoxy group as shown in scheme (2.1) [27].



Scheme 2.1: A wide variety of reaction characteristics of epoxy acid within the triglyceride

2.2.1.4 Application of Vernonia Oil

The development of industrial crop for semiarid zones is important in both developing and developed countries. Many plants suitable for arid and semiarid zones are regarded as having high potential for industrial crop. Vernonia is an oil seed crop which can be a candidate crop for arid and semiarid zones in both developing and developed countries [27].

Vernolic acid which is derived from vernonia oil is a useful raw material for the manufacture of adhesives, varnishes, paints and coatings. Using vernolic acid for paints and coating helps to avoid photochemical pollution [9]. Also degradable lubricants and lubricant additives, epoxy resins, plastic formulations of polyvinyl chloride, adhesives, insecticides and insect repellants and reactive monomers in polymer synthesis [10, 11].

Other applications of the products that developed from vernonia oil are for the construction of polyurethane foams, for the synthesis of interpenetrating polymer networks, as pH stabilizers, waxes, glues, emulsifiers and rust suppression, and in organic formulation of carriers for slow-release pesticides and herbicides. Vernonia oil has also been used as a source of hydroxyl alkoxy fatty esters and for the synthesis of epoxy secondary amides [27]. Current vernonia product on the market includes Vernola Super Gloss, a car-care product used on tires, Vinyls, flash boards, leather, and rubber bumpers [13, 14].

2.2.2 Sodium Bisulphite

Sodium bisulphite (sodium hydrogen sulphite) is a chemical compound with the chemical formula $NaHSO_3$. This salt of bisulphite can be prepared by bubbling sulfur dioxide in a solution of sodium carbonate in water as shown in the reaction scheme (2.2) below.

$$SO_2 + Na_2CO_3 \text{ (aqueous)} \longrightarrow 2\ NaHSO_3 + 2\ CO_2 \text{ (in water)}$$

Scheme 2.2: Reaction of sodium carbonate with sulphur dioxide to produce sodium bisulphite and carbon dioxide

The physical and chemical properties of both sodium bisulphite anhydrous and 40% sodium hydroxide solution are shown in Table (2.2) below.

Table 2.2: Physical and chemical property of sodium bisulphite (solid and 40% solution)

Property	Value
Sodium bisulphite	
Melting point, ^0C	150
Density, g/ml	1.48
Water solubility, g/L	300
Sodium bisulphite solution 40%	
pH	5.2
Specific gravity	1.33
Freezing point, ^0C	6
Boiling point, ^0C	104
Vapour pressure, mmHg at 20^0C	32
Iron, ppm	≤ 3
SO_2 content, wt%	24.2 – 25.0
NaOH Anhydrous, wt%	15.0 – 16.0
Appearance	Clear to yellow liquid, with a slightly sulfurous odour

(Source: Reference [32], [33] and [34])

In organic chemistry sodium bisulphite has several uses. It forms a bisulphite adduct with aldehyde groups and with certain cyclic ketones to a sulfonic acid [35]. It can also be used for production of sulphited fatliquor. The other main use of sodium bisulphite is as a mild reducing agent in organic synthesis in particular in purification procedures. It can efficiently remove traces or excess amounts of chlorine, bromine, iodine, hypochlorite salts, osmate esters, chromium trioxide and potassium permanganate [36].

Another use of sodium bisulphite is as a decoloration agent in purification procedures because it can reduce strongly coloured oxidizing agents, conjugated alkenes and carbonyl compounds. Industrially sodium bisulfite is a common reducing agent in the chemical industries [36].

2.3 Fatliquor Production Technologies

Oil and water are immiscible as the interfacial tension is high. In order to lower the surface tension, some surface active material (emulsifier) is necessary. Further affinity of oil to water depends not only on the interfacial tension but also on the balance of polar (hydrophilic) and nonpolar (hydrophobic) groups present in the oil. The polar groups in oil are OH, COOH, - SO_3H and Cl; and nonpolar groups are CH_3, C_2H_5 etc. The process of saponification, sulphation, sulphitation and treatment with suitable emulsifying agents introduces polar groups into the oil. When the polar groups are more, oil becomes water miscible and form stable emulsion [1].

The three principal types of fatliquoring systems are anionic (negatively charged), cationic (positively charged) and nonionic. Since all Ethiopian leather factories apply chrome tanning they use anionic type of fatliquor. This includes soaps, sulphated oils, sulphonated oils and sulphited oils which uses different production technologies.

In this research, fatliquor will be produced by sulphiting the oil using concentrated sodium bisulphite solution. So, sulphited fatliquor production and modified sulphitation production technology is discussed in detail.

2.3.1 Saponification Process

When oil is heated with alkali like caustic soda or caustic potash the fatty acids of the oils are separated from glycerin or long chain alcohol and salts of those fatty acids finally result. These salts are called soaps. Groups like –COOR where R is monovalent metal, are strongly soluble into water and ionize as follows:

$$(\text{Hydrocarbon chain}) - COONa \longrightarrow (\text{Hydrocarbon chain}) - COO^- + Na^+$$

Scheme 2.3: Soap formed when oil react with alkali

The negatively charged carboxyl groups of soap electrically react with the positively charged protein and the insoluble hydrocarbon chain of the soap projects out of the protein molecules into air. These projected insoluble hydrocarbon chains make the leather waterproof and bind the neutral oil molecules by its strong love for the latters [18].

The oil droplets in an oil-in-water emulsion formed by using soap as an emulsifying agent are generally coarse and also break very quickly with acid. Such emulsion, therefore, cannot penetrate deep into leather and cannot give the same degree of softness as sulphated oils [37].

2.3.2 Sulphation Process

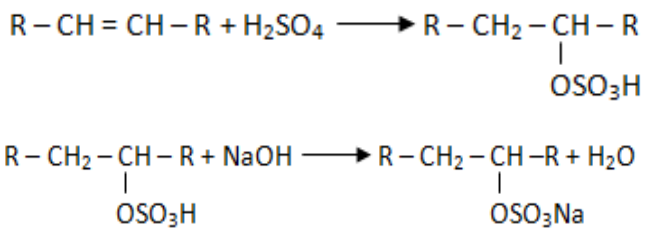
Leather, particularly chrome tanned leather, is acidic and has a pH of about 5 to 5.5 at the same time of fatliquoring after neutralization. At this pH, soap emulsions are too near the precipitation point for proper control. Although soaps are used in some fatliquoring, greater stability at low pH is desired for most application. This is done by sulphation or sulphitation of the oils [38].

Sulphated oils are very commonly used because they give good, fine oil dispersions and are less sensitive to acid than soap fatliquors [19]. Furthermore, as the pH is decreased, since they are

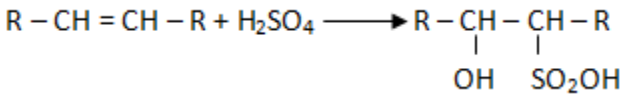
stronger acids, the emulsion is stable in pH ranges as low as pH 3, depending upon the nature of the oil and extent of sulphation [38].

They are made by treating fish, animal or vegetable oils with sulphuric acid at carefully controlled temperature maintained below 35^0C. The main purpose is to introduce polar (hydrophilic) groups so that the oils can be emulsified with water. These unsaturated oils react with sulphuric acid to form C – O – S bonds where by the carbon of the oil is attached to a sulphated group (-OSO_3H) [39].

The reaction between unsaturated oil (since saturated oils are less chemically active and therefore difficult to sulphate) and sulphuric acid is exothermic and therefore acid is added very slowly with constant stirring to avoid any rise of temperature.



Scheme 2.4: Reaction between oil and sulphuric acid to give sulphated oil (Main reaction)



Scheme 2.5: Reaction of oil and sulphuric acid results sulphonated oil (Side reaction)

The techniques of manufacturing fatliquoring oils are as varied as the material used. The following general rule is applying. The refined oil is received in large quantities for a temporary storage, then chilled and further filtered [38].

The sulphation is done by the addition of 10 – 20% strong sulfuric acid. The resultant product is washed with strong salt water to remove any surplus sulphuric acid, the salt being necessary to prevent the sulphated oil emulsifying with water at this stage. Then strong NaOH solution is added to give the sodium salt of the sulphated oil and to neutralize these traces of acid [19].

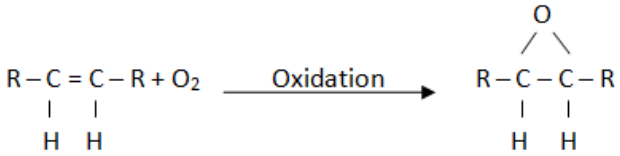
The oil may then be blended with other oils. The product is shipped in wooden barrels or lined steel containers. Tank cars may be used in shipping some fatliquor oils [38].

In addition to Sulfuric acid, SO_3 from stabilized liquid SO_3, SO_3 from sulfur burning and subsequent conversion of the SO_2 formed, SO_3 from boiling concentrated oleum and chlorosulfonic acid can be used as a sulphating agent for sulphated oil production [40].

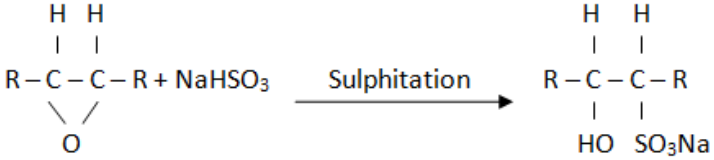
2.3.3 Sulphitation Process

Another method of obtaining emulsifying properties is to sulphite the oil. In this process the oil is well mixed with a strong solution of sodium bisulphite ($NaHSO_3$) while the mixture is thoroughly aerated by blowing compressed air [18, 39].

Sulphited oil is prepared by subjecting the oil to oxidative sulphitation using 20 – 40% by weight strong solution of sodium bisulphite from 60 – 80^0C for a period of until a complete water emulsifiable product is obtained usually for about 10 to 15 hours. Finally brine wash is followed to remove excess sodium bisulfite [41].



Scheme 2.6: Oxidation reaction of unsaturated oil to form epoxide oil



Scheme 2.7: Sulphitation reaction of oxidized oil and sodium bisulphite to give sulphited fatliquor

The emulsions produced with sulphited oil are stable in the presence of salts and hard water. Unlike the sulphated oils and soaps, they are also stable in the presence of strong acid and chrome liquors. They gives deeper lubrication and therefore they are favored for suede, where a greasy surface is undesirable, and for gloving and soft leathers, where good lubrication is essential [18, 39].

Another advantage of sulphited oil is no pH adjustment is required and due to the use of sodium bisulphite rather than sulphuric acid, sulphur trioxide or sulphours acid no charring or darkening occurred [41].

The greater stability of sulphited oils is a result of the carbon sulphur linkage in these oils. The hydrophilic group in sulphited oils is a sulphonate ion which gives a stronger bond with the carbon atom than does the oxygen atom (strong ionization). So in strong acid and/or salt solutions the –C–S– bond will be much more stable than the –C–O– bond in sulphated oils [39].

The softening power and handle of the different oils in fact has not been investigated in detail and as such their selection for using alone or in blends is based on the trial, experience and price. The normally conceded order from the point of softening is olive–Neat's-foot–Soya Castor in decreasing order of softening and increasing the dry feel (castor gives least softening and maximum dry feel) [18].

2.3.4 Modified Sulphitation Process

Sulphited oils used as oiling agents for leather and skins are produced by oxidation of oils with oxygen containing gas mixtures, for example air and simultaneous or subsequent sulphitation with alkali hydrogen sulphite. However, since the oxidizability of oils and fats decreases with decreasing iodine number, relatively highly unsaturated fats and oils, i.e. those having iodine numbers above about 100 and preferably above about 130 are normally used [42].

Sulphitable oils having an iodine number below 100, for example sperm oil, are subjected to oxidizing sulphitation, the oxidation velocity of the fats decreases drastically and products difficult to emulsify in water and having poor emulsion stability are obtained [43].

In order to be able to use these sulphitation products for oiling leather and skins, they have to be mixed with emulsifiers or with water emulsifiable oils or fats which are capable of co-emulsifying the difficultly emulsifiable sulphitation products. The sulphited fats according to the invention by Hans-Herbert Friese *et al.* (1986) are distinguished by high water emulsifiability with excellent emulsion stability. They are therefore particularly suitable for fatliquoring [43].

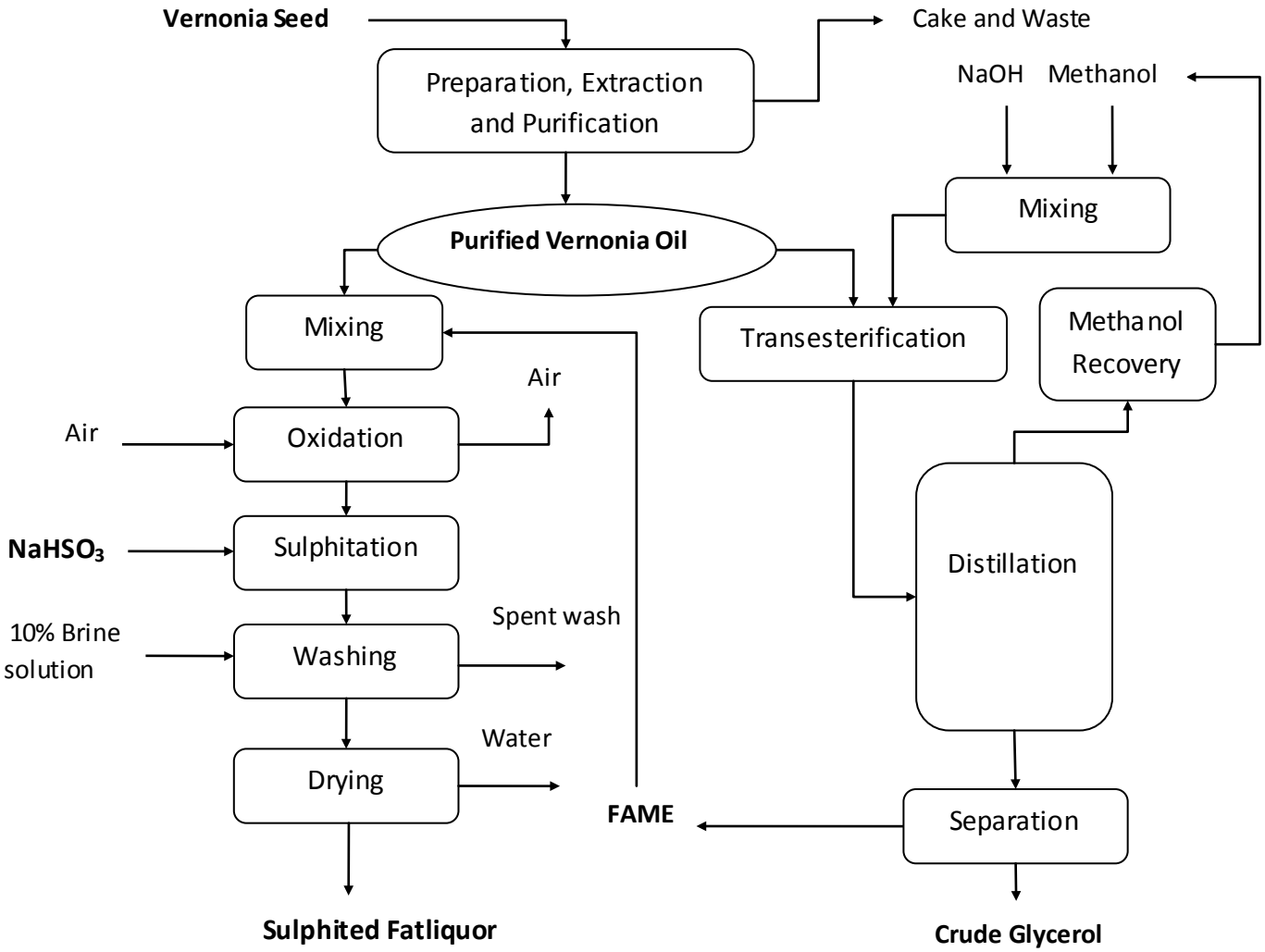


Figure 2.2: Schematic diagram for modified sulphited fatliquor production

Production of fatliquor using modified sulphitation process follows the same principles as sulphitation process. The only difference arises in modified sulphitation process some amount of FAME is added to make the oil easily oxidizable. The schematic diagram of modified sulphited fatliquor production from vernonia oil is shown in Figure (2.2).

2.4 Parameters Affecting Modified Sulphited Fatliquor Production

There are different parameters which affects modified sulphitation reaction. The main factors which highly affect includes reaction temperature, amount and concentration sodium bisulphite, reaction time, mixing speed, oil to FAME weight ratio and purity of reactants.

2.4.1 Reaction Temperature

Sulphitation reaction is an endothermic reaction. It is favored with increasing temperature for completion of the reaction. Also the kinetic theory says that motion and velocity of molecules are directly proportional to Kelvin temperature. As a result the kinetic energy and molecule velocity increases with increasing temperature which results rise in reaction rate.

Jones T. J. *et al.* (1978) proposed that an increase in reaction temperature reduces the viscosity of oil and increases the mobility of the sodium bisulphite liquor. But higher temperature greater than 80^0C may cause overheating of oil which results oxidation and polymerization of oil.

2.4.2 Amount and Concentration of Sodium Bisulphite

Reaction rates can be increased if the concentration of reactants is raised. An increase in concentration produces more collisions, which results raise in reaction rate. As stated in works by H. A. Gold Smith *et al.* (1948) and El-Shahat H. *et al.* (2011), the amount of sodium bisulphite used ranges from 20 to 40% based on oil weight and the concentration is usually 40% (the maximum concentration) for the synthesis of sulphited fatliquor.

2.4.3 Reaction Time

At low temperature the viscosity of vernonia oil increases considerably which results lower reaction rate and correspondingly higher reaction time for completion of the reaction. In addition sulphitation reaction is a complex type of reaction which involves breaking and forming of bonds so it generally takes longer reaction time.

A study by El-Shahat H. *et al.* (2011) showed that production of sulphited fatliquor from Jojoba oil in presence of phase transfer catalyst (PTC) namely benzyl tri-phenyl phosphonium chloride (BTPP) and tri-ethyl benzyl ammonium chloride (TEBA) requires 5 h reaction time to get higher degree of sulphitation. In absence of catalyst the sulphitation reaction gets maximum degree of sulphitation between 10 to 15 h reaction time [41, 44].

2.4.4 Mixing Speed

A very efficient stirring device is necessary in sulphitation process to ensure uniformity of sulphitation process which is necessary to give stronger ionization. The uniformity depends on consistency of oil oxidation and degree of mixing with the sodium bisulphite solution. Some manufacturers use high speed specially designed mixers which entrap air in the oil instead of using a blower to give uniform oxidation and mixing for sulphited oil production [38].

2.4.5 Oil to FAME Weight Ratio

To use low iodine value oils such as vernonia oil for fatliquoring it has to be mixed with emulsifiers or with water emulsifiable oils or fats which are capable of co-emulsifying the difficulty emulsifiable sulphitation products. Oils and fats form readily water emulsifiable sulphitation products with excellent emulsion stability. They are mixed before oxidation and/or sulphitation step with fatty acid esters having iodine numbers of from 60 to 100 in a ratio by weight of oil or fat to ester of from 9:1 to 1:4 [43].

For the synthesis of sulphited fatliquor from vernonia oil the minimum ratio of oil to FAME is 70:30 from the trial works. The reason for choosing the minimum ratio is desired emulsion stability was formed using this ratio and from economic point of view for production of FAME.

2.4.6 Purity of Reactants

Impurities present in vegetable oil also affect the sulphitation reaction significantly. Also hydrolysis of glycerides resulting in free fatty acids may liberate eventually on the dried leather as spues which results poor quality of fatliquored leather.

Another trouble due to rancidity of the oil is that free fatty acid form compounds with chromium, alum or zirconium salts used in tanning, which may make the leather water repellent and difficult to wet back uniformly for dyeing and finishing purposes. So rancid oils and fats, especially if they contain hard fatty acids, should be avoided and the leather should be kept dry and free from mould. As a result purification of crude oil is necessary for production of desired quality sulphited fatliquor and fatliquored leather [19].

2.5 Properties and Specification of Sulphited Fatliquor

Indian standard IS 14488 (1986) was adapted for sulphited oil specifications with the recommended test method as described and shown in Table (2.4) below [45].

2.5.1 Physical Conditions

The material shall be pourable at temperature ≤ 27 ± 2^0C. Appearance of any graininess or a slight physical separation like a liquid and semi-solid portion appearing especially in winter season or long storage shall not be considered as defect as long as the two portions individually or together form ready emulsions in water.

2.5.2 Emulsion Characteristics

The emulsion shall satisfy the following requirements:

- The fatliquor shall form stable emulsion in hot water (55 – 65^0C) when diluted in 1:10 ratio;
- The water emulsion containing 3 to 4 percent total fatty material shall remain stable for at least 40 minutes at room temperature without creaming or separation;
- The sulphited fatliquor shall be capable of being readily washed out with water without leaving any oily feeling to hand; and
- 10 percent emulsion shall remain stable for 40 minutes when mixed with 5 percent solutions of sodium chloride, calcium chloride and magnesium sulphate and 5 percent basic chromium sulphate solution in separate containers without creaming and oil separation.

2.5.3 Odor

The product shall be free from rancid or putrefactive odor of the oils.

2.5.4 Chemical Requirements

Sulphited oil fatliquors, besides meeting the other characteristics mentioned above, shall also meet the chemical requirements mentioned in Table (2.3).

The pH of 10% fatliquor emulsion should be between 6.5 and 7.5 of sulphited fatliquors used for leathers lubrication. The stability of emulsion and penetration of the fatliquor into the leather depends on pH value of emulsion and leather to be fatliquored. The leather is neutralized using sodium bicarbonate and a neutralized fatliquor emulsion is required to introduce desired properties into the leather.

Table 2.3: Chemical properties requirement

SL.NO.	Characteristic	Requirement	Recommended Test Method
I	pH of emulsion (1:10 dilution in water)	6.5 – 7.5	IS14488, CLAUSE 4.4,ANNEX A-2
Ii	Total active ingredient, percent by mass	≥ 60	IS14488, CLAUSE 4.4,ANNEX A-3
Iii	Unsaponifiable matter, percent by mass	≤ 15	IS14488, CLAUSE 4.4,ANNEX A-4
Iv	Total alkalinity in mg equivalent per 10 g	≤ 5	IS14488, CLAUSE 4.4,ANNEX A-5
V	Total sulphur as sulphites (SO_3) as, percent by mass	≥ 1.8	IS14488, CLAUSE 4.4,ANNEX A-6
Vi	Total Ash, percent by mass	≤ 4.5	IS14488, CLAUSE 4.4,ANNEX A-7 and ANNEX A-8
Vii	PCP content, mg/kg	≤ 5	IS14488, CLAUSE 4.4,ANNEX A-9

(Source: IS 14488 (1986))

Total active ingredient in sulphited fatliquor gives the desired characteristics to the fatliquor. High amount of total active ingredient means high amount of oil is available for lubrication of the leather. The hydrophilic part makes this oil to bond with the protein to gain a stable effect. The oil part gives the leather softness, pliability, and stretch; the ability to take up or resist water, smoothness and oiliness of the grain.

Unsaponifiables are components of an oily mixture that fail to form soaps when blended with sodium hydroxide. As an indication of the characteristics of fatliquor, however, the figure is rather meaningless, since, apart from the possibility of a mixture of oils being present, the oils and their fatty acids will have undergone some modification during processing [46].

Total alkalinity is the name given to the quantitative capacity of an aqueous solution to neutralize an acid. Measuring total alkalinity is important in determining the fatliquor ability to neutralize acidic media in fatliquoring process.

The reaction depth and degree of conversion were determined by the amount of SO_3 fixed (degree of sulphitation). The stability of the resulting emulsions also evaluated according to the content of SO_3 in the sulphited oil [47]. Also as stated by El-Shahat H. *et al.* (2011) in the synthesis of fatliquor it should be noted that SO_3 content of the resulting constituents is of great importance, so that the degree of conversion was estimated mostly as SO_3 content. The sulphited fatliquor synthesized from Jojoba oil, 3.2% SO_3 content was obtained using 20% by weight of oil feed of $NaHSO_3$ (40% solution) and a reaction period of 5 h.

The ash content is a measure of the total amount of minerals present within the fatliquor. Determination of the ash content is important for determination of fatliquor quality. It is often important to know the mineral content of fatliquor during fatliquoring process because this also affects the physicochemical properties of fatliquored leather.

2.6 Fatliquoring

In the leather industry, hides and skins proceed via various chemical and mechanical operations to produce high quality finished leather. When chrome tanned leather dries out it becomes bony, hard and thus it will be rendered unsuitable for use in most purposes. Besides, its colour turns darker and becomes less appealing [3]. To avoid this problem and to produce soft leathers, fatliquoring is added as a step after the tanning process [48].

Fatliquoring, a post-tanning operation, involves incorporating fat, grease or oils into the skin of the leather before the leather is dried. Fatliquor improves the physical characteristics of leather such as tensile strength, wetting properties, water proofness and permeability to water vapor and air [49]. The fatliquor also keeps the fibers apart during drying and reduces frictional forces

within the fibre weaves thus allowing the fibers to move laterally over each other [2, 3]. A BASF company presents a quality requirement (IUP specification) for the main type of leather as shown in Table (2.4) [50].

Table 2.4: Quality requirement for the main type of leather (General data)

Property	Shoe upper leather	Sole leather	Lining leather
Sulphate ash, %	≤ 2	≤ 2	≤ 2
Chromium content, %	> 2.5	-	< 2.5
Fatty substance, %	3 – 8	< 3.5	5 – 11
Tensile strength, N/mm^2	≥ 20	> 25	≥ 20
Elongation at break, %	> 40	< 30	< 100
Split tear force, N/mm	> 40	-	> 40
Stitch tear strength, N	> 80	> 130	> 40

To allow a small amount of oil to be spread uniformly over a very large surface of the leather fibers it is necessary to dilute the oil. Although this could be done with a solvent such as benzene, it is cheaper, safer and more convenient to use the method of emulsification [39].

For an emulsion with water, the oil is dispersed in microscopically small droplets, having a milky, white appearance. It is important that the oil drops remain in emulsion until they penetrate the leather otherwise a greasy/oily surface might be obtained. The addition of surfactant to the oil helps to increase the tendency for oil and water to mix (to emulsify) [39].

3. Materials and Methods

3.1 Materials

The major raw materials used during the experimental work ware vernonia seed, sodium bisulphite, sodium hydroxide, methanol and sodium chloride. Vernonia seed was acquired from Adet Agricultural Research Center, West Gojjam. All the other chemicals were analytical reagent grade and bought from different chemical stores in Addis Ababa.

3.2 Equipments

The equipments used during the experimentations includes mechanical pressing machine, a glass reactor equipped with a mechanical stirrer, water bath, condenser, crusher, separating funnel, vacuum pump, shaker, balance, oven, magnetic stirrer, Bunsen burner, Muffle furnace, different size conical and Erlenmeyer flasks, beakers, measuring cylinders, burette, testing drum and tensile machine.

The experimental work was started in March and end in August a total six months was spent for the laboratory works. Extraction of vernonia oil using mechanical press oil extractor was done at Bahir Dar University (BDU). Vernonia oil refining, preparation of FAME, synthesis of sulphited fatliquor and characterization of the refined oil and synthesized fatliquor were done at School of Chemical and Bio Engineering Laboratory, AAiT and the actual test of the synthesized fatliquor on leather was conducted in collaboration with Leather Industry Development Institute (LIDI). The overall structure of the experimental works is shown in Figure (3.1).

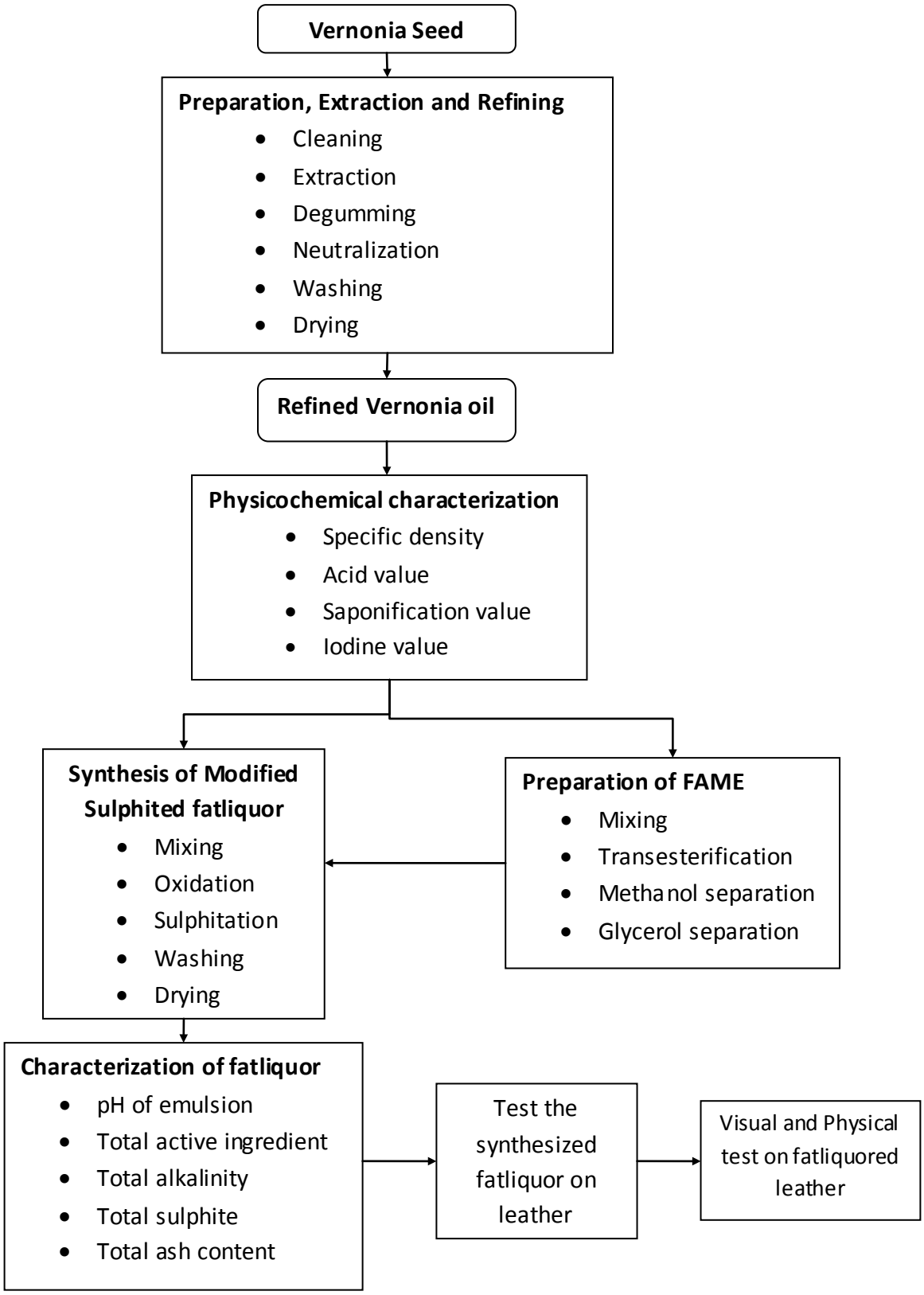


Figure 3.1: Frame work of the experiment

3.3 Experimental Method

3.3.1 Preparation of Vernonia Seed

Vernonia seeds were first cleaned from dirt, dust, sand, small stones and washed manually. Then the prepared Vernonia seeds were sun dried for one day. The clean seeds were weighted and 2 kg vernonia seeds were further dried in an oven at 90^0C for an hour for lipase deactivation. Then crushed using a crushing mill with particle size of 1.0 – 2.0 mm for solvent extraction analysis and the rest were used for mechanical extraction of the oil.

3.3.2 Extraction of Vernonia Oil

Mechanical extraction method was applied for vernonia oil extraction. The pressing machine was cleaned and the speed was adjusted to the desired level. Then the prepared and sun dried seeds were feed continuously in to the screw pressing machine. The crude vernonia oil was collected at the bottom and the cake was removed. A typical screw pressing machine pressing vernonia seeds is shown in Figure (3.2) below.

Figure 3.2: Screw press extractor

For soxhlet extraction 80 g of grinded vernonia seed (packed in a filter paper) and 240 ml hexane solvent was placed in the soxhelt extraction unit. Then the solvent and crushed mixture was heated at constant temperature of 70^0C for 3 h to extract the oil. After extraction the solid suspension from the supernatant solution was separated using centrifuge at 5000 rpm for 20 minutes. Finally the solvent and oil was separated using distillation and the solvent was recovered using condenser. The oil was collected for yield analysis.

Figure 3.3: Crude Vernonia oil extracted using mechanical and solvent extraction method

The yield of oil extracted will be calculated using equation (3.1) given below

$$\text{Yield of oil} = \left(\frac{\text{mass of oil}}{\text{initial mass of seed}}\right) \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3.1)$$

3.3.3 Purification of Crude Vernonia Oil

3.3.3.1 Settling

The crude oil extracted using mechanical pressing machine was separated from solid suspensions and impurities by using centrifuge at speed of 5000 rpm for 20 minutes.

3.3.3.2 Degumming

Degumming was done to avoid the interference of phosphatides, gums and other complex compounds during sulphitation reaction and to avoid rancidity (increase in free fatty acid) of oil during storage.

Distilled water 3 wt% of oil at 70^0C was mixed with the oil. Then the mixture was stirred at speed of 200 rpm for 1 h heated at 70^0C. Finally the mixture was separated using centrifuge at 3500 rpm for 30 minutes.

3.3.3.3 Neutralization

The free fatty acid content of the crud vernonia oil was estimated using acid value and amount of sodium hydroxide needed to neutralize free fatty acid is calculated as shown in Appendix D.

Neutralization was done by heating the oil at 70^0C. Calculated amount of NaOH was added to the oil and stirred at 200 rpm. Then sodium chloride (about 10% of the weight of the oil) was added to help settle out the soap formed. The mixture was stirred for 1 hour. After an hour mixing, the mixture was transferred into a separating funnel and allowed to stand for one hour then the soap formed was separated from the oil. Hot water was added again and again to the oil solution until the soap remaining in solution was removed. The neutralized oil then was drawn off into a beaker. Finally, trace water was removed in an oven drying at a temperature of 105^0C for 6 hours.

3.3.4 Characterization of Vernonia Oil

The vernonia seed moisture content and the specific gravity, acid value, saponification value and iodine value of purified Vernonia oil was determined for the physicochemical property.

3.3.4.1 Determination of Moisture Content

First the empty dish was weighed. Then accurately weigh about 4 g of Vernonia seeds into an empty dish. The sample was dried in an oven at 105^{0}C for 7 h, weighing each 2 h till constant weight is obtained and finally the weight was taken and compared with the initially recorded weight. The percentage weight in the seed was calculated using the formula:

$$\text{Moisture content} = \frac{(w_1 - w_2)}{w_2} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.2)$$

Where w_1 is original weight of the sample before drying and
w_2 is weight of the sample after drying.

3.3.4.2 Determination of Specific Gravity

After the sample was filled into graduated cylinder (50 ml) and its temperature was recorded. Hydrometer was used to measure the specific gravity of the oil at 20^{0}C specified. Hence, the density of the oil is determined using the specific gravity as:

$$SG_{oil} = \frac{\rho_{oil}}{\rho_{water}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.3)$$

Where SG_{oil} is specific gravity of oil,
ρ_{oil} is density of oil in g/ml and
ρ_{water} is density of water at 20^{0}C in g/ml.

3.3.4.3 Determination of Acid Value

To determine the Acid value, first Standard alcoholic KOH solution (0.1N) was prepared by dissolving KOH (pellet) with ethanol. The solution was filtered and stored in brown bottle for

five days. Furthermore, a mixture of 95% ethanol and diethyl ether in a ratio of 1:1 by v/v was prepared by mixing 25 ml diethyl ether and 25 ml of ethanol. Then a weighed quantity of oil (w = 2.5 g) sample was dissolved in 25 ml of 1:1 mixture of ethanol and diethyl ether. The solution was titrated with 0.1N ethanolic KOH solution in presence of 5 drops of phenolphthalein as indicator until the end point (colorless to pink) is recognized. Finally volume of 0.1N ethanolic KOH for sample titration was noted. The total acidity in mg KOH/gm was calculated using the following equation:

$$\text{Acid value} = \frac{56.1 \times V \times N}{w} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.4)$$

Where V is the volume expressed in milliliter of 0.1N solution of ethanolic KOH,

N is concentration of ethanolic KOH and

w is weight in gram of the test portion.

3.3.4.4 Determination of Saponification Value

The Saponification value determination was conducted by dissolving oil in an ethanolic KOH solution. This solution is then heated for half an hour so that the oil completely dissolves in the ethanolic KOH solution.

A weighted amount of oil (W = 2 g) was added to 25 ml of 0.5N ethanolic potassium hydroxide solution and the reflux condenser was attached to the flask. Then the mixture was heated, and as soon as the ethanol boils, the flask was occasionally shaken using magnetic stirrer until the oil was completely dissolved, and the solution was boiled for half an hour. After the oil was completely dissolved, 5 drops of phenolphthalein indicator was added and the hot soap solution obtained was slowly titrated with 0.5N hydrochloric acid (and volume V_a was recorded). Similarly a blank determination was carried out upon the same quantity of

potassium hydroxide solution at the same time and under the same conditions (and volume V_b was recorded). The final result was calculated using equation:

$$\text{Saponification value} = \frac{56.1 \times N \times (v_b - v_a)}{W} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.5)$$

Where W is weight of oil taken in gram,

N is normality of HCL solution,

V_a is volume of HCL solution used in the test in milliliter and

V_b is volume of HCL solution used in blank in milliliter.

3.3.4.5 Determination of Iodine Value

The iodine value of oil is the number of grams of iodine absorbed by 100 g of the oil, when determined by using Wiji's solution. For this research Wiji's method was applied to determine the iodine value of oil.

A standard Wiji's solution was prepared by dissolving 9 g of iodine trichloride (AR) in 300 ml carbon tetrachloride (AR) and 700 ml glacial acetic acid (AR). Allow the solution to stand for three days before use.

To determine the iodine number, first the oil was dissolved in 5ml tetra chloride (AR) in a ground in glass stopper conical flask and 25 ml standardized Wiji's solution was added. Then the stopper was replaced at once and the flask was allowed to stand for 30 minutes at 20^0C in the dark. When the reaction was completed, 15 ml 10% KI solution and 50 ml water was added. Finally the free iodine was titrated with 0.1N sodium thiosulphate until the color is pale yellow. A few drops of starch solution were added and the titration was continued until the blue color is discharged. The volume of 0.1N thiosulphate was recorded. Similarly a blank determination

was done for the same length of time and at the same temperature. The result was calculated using equation:

$$\text{Iodine value} = \frac{1.269\ (\mathrm{a}-\mathrm{b})}{\mathrm{w}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.6)$$

Where w is the weight of oil used in the test,

a is the ml of 0.1N thiosulphate required for the blank determination and

b is the ml of 0.1N thiosulphate required for the titration.

3.3.5 Experimental Design for Fatliquor Production

In this work the sulphited fatliquor was prepared using purified vernonia oil, FAME and concentrated sodium bisulphite solution. Experimental data analysis was done using Design-Expert 7.0.0 software.

The experimental design selected for this study was three-level-three-factor face-centered central composite design (CCD) and the response variable measured was the degree of sulphitation. In addition analysis of physicochemical properties of sulphited fatliquor was done at School of Chemical and Bio Engineering laboratory, AAiT and its fatliquoring effect on leather was carried out at LIDI.

The three independent variables studied for the modified sulphitation process were reaction temperature, amount of sodium bisulphite and reaction time. The independent variables interaction effect was analyzed to obtain maximum degree of sulphitation. In addition to achieve maximum degree of sulphitation rotational speed was set at 250 rpm, the concentration of sodium bisulphite set to its maximum concentration (40 wt%) and the ratio of oil to FAME was fixed to the minimum amount of FAME requirement (70:30 weight ratio).

Three-level-three-factor face-centered CCD was used in the optimization study which requires 20 experiments to be conducted. The twenty experiments were done and the data was statistically analyzed using Design-Expert Software 7.0.0 to obtain a suitable model equation for the degree of sulphitation as a function of the independent variables.

Table (3.1) lists the range and levels of the three independent variables studied. The lower and higher levels are chosen by considering the operating limits of modified sulphitation process conditions.

Table 3.1: Independent variables and levels used in the CCD for the fatliquor production

Variables	Factor coding	Unit	Levels		
			-1	0	+1
Reaction temperature	X_1	^0C	60	65	70
Amount of sodium bisulphite	X_2	wt%	20	30	40
Reaction time	X_3	h	10	12.5	15

Below in Table (3.2) the complete experimental design matrix of CCD for the factorial design was shown. The order in which the runs were made was randomized to minimize systematic errors.

Table 3.2: The complete experimental design matrix

Run	Coded Factors			Actual Factors		
	X_1	X_2	X_3	Temperature (^{0}C)	Amount of Sodium bisulphite (wt%)	Time (h)
1	0	+1	0	65	40	12.5
2	0	0	+1	65	30	15
3	0	-1	0	65	20	12.5
4	+1	-1	-1	70	20	10
5	-1	-1	+1	60	20	15
6	+1	+1	-1	70	40	10
7	+1	-1	+1	70	20	15
8	-1	-1	-1	60	20	10
9	0	0	-1	65	30	10
10	0	0	0	65	30	12.5
11	+1	0	0	70	30	12.5
12	0	0	0	65	30	12.5
13	0	0	0	65	30	12.5
14	0	0	0	65	30	12.5
15	-1	+1	+1	60	40	15
16	0	0	0	65	30	12.5
17	-1	0	0	60	30	12.5
18	+1	+1	+1	70	40	15
19	-1	+1	-1	60	40	10
20	0	0	0	65	30	12.5

3.3.6 Experimental Setup

The oxidation of feed material (mixture of Vernonia oil and fatty acid methyl ester) was done on a water bath equipped with a mechanical stirrer and a vacuum pump outfitted with a control valve to supply air. For sulphitation reaction a 250 ml glass reactor equipped with shaker was used in all experiments. The shaker can be adjusted to the desired temperature and rotational speed. The batch oxidation and sulphitation reaction system was employed for sulphited fatliquor production as shown in the schematic diagram below.

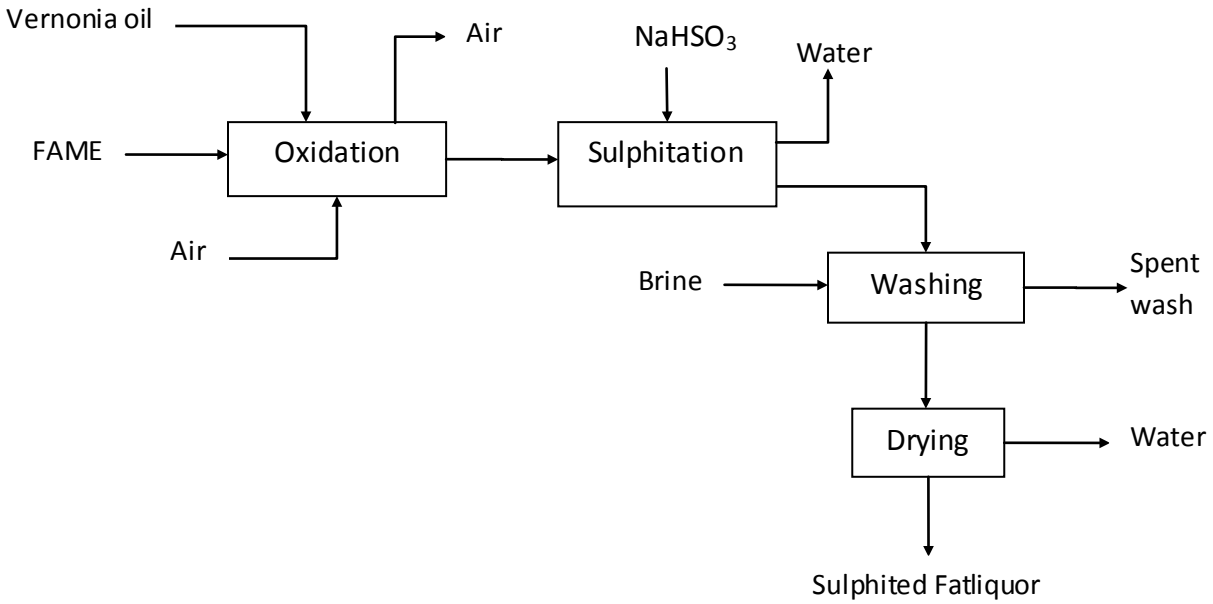


Figure 3.4: Schematic diagram of experimental setups for sulphited fatliquor production

3.3.7 Sulphited Fatliquor Production Procedure

First fatty acid methyl ester was prepared from refined Vernonia oil at specific conditions (from the literature and previous similar works). The parameters were set at speed 500 rpm, 3 h reaction time, 60^0C reaction temperature, 9:1 molar ratio of methanol to oil and 1.125% weight by oil amount of catalyst (NaOH) [51, 52, 53].

Then the refined Vernonia oil was mixed with FAME. The mixture subsequently oxidized by bellowing air at 70^0C for 4 h at 250 rpm to make it suitable for the sulphitation reaction. Subsequently the oxidized mixture was sulphited with concentrated sodium bisulphite solution in a glass reactor equipped with shaker. Finally the sulphited oil was washed twice with 10 wt% sodium chloride at ambient temperature to remove any surplus sodium bisulphite and the fatliquor dried in an oven for 6 h to remove trace water.

3.3.8 Feed Material Requirement

100 g of feed material (70 g purified Vernonia oil and 30 g FAME) was used for each run. Hence, the amount of concentrated sodium bisulphite solution used was calculated based on the amount of feed material as shown below.

The amount of sodium bisulphite solution required when 30% of the weight of feed used was calculated as follows. First the weight of oil was directly measured on balance and the weight of fatty acid methyl ester is estimated from its density.

$$\rho_{FAME} = \frac{m_{FAME}}{V_{FAME}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (3.7)$$

$$\Rightarrow \ V_{FAME} = \frac{m_{FAME}}{\rho_{FAME}} = \frac{30 \text{ g}}{0.84 \text{ g/ml}} = 35.71 \text{ ml}$$

And density of 40% $NaHSO_3$ solution was found to be 1.33 g/ml. For 30% (based on feed weight) of sodium bisulphite solution, feed volume of the solution was calculated as:

$$\rho_{NaHSO_3} = \frac{m_{NaHSO_3}}{V_{NaHSO_3}}$$

$$\Rightarrow \ V_{NaHSO_3} = \frac{m_{NaHSO_3}}{\rho_{NaHSO_3}} = \frac{30 \text{ g}}{1.33 \text{ g/ml}} = 24.39 \text{ ml}$$

For the other experiments similar procedure is followed to calculate the amount of sodium bisulphite solution added.

3.3.9 Yield of Sulphited Fatliquor

From the principle of conservation of mass all the mass in should be out from the reactor since there is only one product out (sulphited fatliquor). The yield is calculated using equation (3.8) given below.

$$\text{Yield, percent} = \frac{\text{Total mass Out}}{\text{Total mass In}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.8)$$

3.3.10 Characterization of Sulphited Fatliquor

For characterization physicochemical properties of the synthesized sulphited fatliquor Indian standard specification and respective method was used. The specification and recommended methods was given in Table (2.3) and they are discussed in detail in the following sections.

3.3.10.1 Determination of pH of water emulsion, IS 14488, CLAUSE 4.4, ANNEX A-2

Ten percent emulsion was prepared by dispersing 10 g of fatliquor in 90 ml water. Then the pH of emulsion was determined by using an electrode pH meter. As the pH of solution of sulphited oil fatliquors varies with the temperature, it should be controlled during the tests, and the test was carried out at 50^{0}C.

3.3.10.2 Determination of Total Active Ingredient, IS 14488, CLAUSE 4.4, ANNEX A-3

About 5 g of the sulphited oil fatliquor was weighed accurately in a 250 ml flask and 25 ml of 50% ethyl alcohol and 25 ml of petroleum ether was added. Then the contents were transferred to a separating funnel. The contents shake vigorously and allowed the layers to separate. The lower alcohol layer was transferred to another separating funnel and it was extracted four

times with petroleum ether. The upper layer was extracted, namely, the petroleum ether layer, with 75% alcohol and the layers was allowed to separate and further extracted with 90% alcohol and absolute alcohol; and the layers was allowed to separate. The petroleum ether layer and alcohol layer was collected in two tarred flasks. The solvents was evaporated, the residues was dried to constant weight in oven; cooled and weighed. Alcohol layer contains the emulsifier and the petroleum ether layer contains the neutral oil. The calculation was done using equations given below.

$$\text{Free oil, in percent (A)} = \frac{F}{W} \times 100 \quad \ldots\ldots (3.9)$$

$$\text{Emulsifier, in percent (B)} = \frac{E}{W} \times 100 \quad \ldots\ldots (3.10)$$

Where F is weight of petroleum ether soluble in g,
E is weight of alcohol soluble in g and
W is weight of the fatliquor sample in g.

$$\text{Total active ingredient, in percent} = A + B \quad \ldots\ldots (3.11)$$

3.3.10.3 Determination of Unsaponifiable Matter, IS 14488, CLAUSE 4.4, ANNEX A-4

The material was completely saponified with alcoholic potassium hydroxide solution and extracted with petroleum ether. The petroleum ether extract is washed with aqueous alcohol and then again with water. The washed ether extract is evaporated and the residue weighed. Unsaponifiable matter is this residue minus the fatty acid present in it, which is determined by titration with sodium hydroxide solution in alcoholic medium.

About 5 g was weighed accurately of the well-mixed sample into the flask. 50 ml of alcoholic potassium hydroxide solution was added. Then the mixture was boiled gently but steadily under a reflux condenser for 1 h or until the Saponification is complete. The condenser was

washed with about 10 ml of ethyl alcohol. The mixture was cooled and transferred to a separating funnel. The transfer was completed by washing the flask first with some ethyl alcohol and then with cold water. Altogether 50 ml of water was added to the separating funnel followed by an addition of 50 ml of petroleum ether.

The stopper was inserted and shakes vigorously for one minute and it was allowed to settle until both the layers are clear. The lower layer was transferred containing the soap solution to another separating funnel, and the ether extraction was repeated at least six times more using 50 ml of petroleum ether for each extraction. When any emulsion was formed, a small quantity of ethyl alcohol was added. All the ether extracts was collected in a separating funnel. The combined extracts were washed in the funnel three times with 25 ml portions of aqueous alcohol shaking vigorously and the alcohol-water layer after each washing was drawing off.

Again the ether layer was washed successively with 20 ml portions of water until the wash-water no longer turned pink on addition of a few drops of phenolphthalein indicator solution. Any of the ether layers was not removed. The ether layer was transferred to a tarred flask and evaporated to dryness on a water-bath under a gentle stream of clean dry air.

To remove the last traces of ether, the flask was placed in an air-oven at 85^0C for about 1 h. To remove the last traces of moisture, a few milliliters of acetone were added and evacuated using a water vacuum pump at about 50^0C for about 15 minutes. Cooled in a desiccator and weighed. The procedure was repeated until constant weight was obtained. After weighing, the residue was taken up in 50 ml of warm neutral ethyl alcohol, containing a few drops of phenolphthalein indicator solution and titrated with standard sodium hydroxide solution.

Weight in g or the fatty acids in the extract (as oleic acid) is calculated using equation (3.12)

$$B = 0.282 \times V \times N \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3.12)$$

Where V is volume in ml of standard sodium hydroxide solution, and

N is normality of standard sodium hydroxide solution.

Unsaponifiable matter is calculated using equation (3.13)

$$\text{Unsaponifiable matter, percent by weight} = \frac{100(A - B)}{W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..\ldots.(3.13)$$

Where A is weight in g of the residue,

B is weight in g of the fatty acids in the extract and

W is weight in g of the material taken for the test.

3.3.10.4 Determination of Total Alkalinity, IS 14488, CLAUSE 4.4, ANNEX A-5

Ten g of the sample was dissolved in 100 ml of water in a conical flask. Then 30 g of sodium chloride, 25 ml of ether and 5 drops of 0.1 percent methyl orange indicator was added and titrated with 0.5N sulphuric acid until the aqueous layer is orange. During the titration stopper the flask and shake the contents frequently. Calculate the total alkalinity as follows:

$$A = \frac{10 \times V \times N}{W} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(3.14)$$

Where A is total alkalinity in milligrams equivalent per 10 g of oil,

V is volume of sulphuric acid in ml,

N is normality of sulphuric acid and

W is weight of the sample in g.

3.3.10.5 Determination of Total Sulphur as Sulphite, IS14488, CLAUSE 4.4, ANNEX A-6

About 2 g of sulphited fatliquor was weighed into a crucible. Then 25 ml 0.1N sodium hydroxide was added. The mixture was evaporated to dryness in a water bath and it was heated in an oven at 100^0C for 1 h. Heat gently over a Bunsen burner until the sample was completely charred. The sample was placed in a muffle furnace at dull red heat for 30 minutes. Allowed to cool and placed in a 400 ml beaker with 200 ml distilled water. Hydrochloric acid was added to make it acidic and boiled. The crucible was removed, it was washed thoroughly with distilled water and washing was returned to the beaker. The boiling was continued by adding 10 ml 10% barium chloride drop using a pipette. Allowed to stand on water bath for 2 h and filtered through a 9 cm filter paper. All the precipitate was transferred to the filter paper and washed it with hot distilled water. The filter paper was transferred to a weighed crucible and ignites gently at first, finally more strongly, until all carbon was completely removed. Allowed to cool, and weighed. Total sulphite expressed as percentage SO_3 is calculated as follows:

$$D = \frac{(w_3 - w_2) \times 80.06}{233.4} \times \frac{100}{w_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3.15)$$

Where W_3 is weight of crucible plus precipitate,

W_2 is weight of crucible and

W_1 is weight of sample taken.

3.3.10.6 Determination of Total Ash, IS 14488, CLAUSE 4.4, ANNEX A-2

About 3 g of sample was weighed in a crucible and heated gently until a charred residue remains. Then the sample was extracted with hot water to remove soluble salts, filtered through a low ash filter paper and washed thoroughly. Then the filter paper and charred residue was burned in a furnace. The dish was allowed to cool and weighed. Calculate the ash content in the following manner:

$$\text{Ash content, percent by weight} = \frac{W_2 - W_0}{W_1 - W_0} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.16)$$

Where W_0 is weight of empty, dry crucible in g,

W_1 is weight of crucible containing the sample before ashing, in g and

W_2 is weight of the crucible containing the residue after ashing in g.

3.4 Application of Sulphited Fatliquor on Leather and Determination of Physicochemical Properties of Fatliquored Leather

3.4.1 Application of Fatliquor on Leather

Two cow hides were used for testing vernonia oil sulphited fatliquor versus Fosfol 36 fatliquor (control test) which is also a vegetable oil sulphited fatliquor.

The wet blue leather pieces were first washed with water for about 10 minutes and water drained off. Then neutralization process was carried out using 2% Tanigan PAK and 1% sodium formate running the drum for 20 minutes. Thereafter, 0.8% sodium bicarbonate was added and the drum was run for further 45 minutes. The leather pieces gave a greenish blue color with bromo cresol green throughout the whole thickness (pH 5.0 – 5.5). The neutralized leather pieces were washed with water. Then, retanning was done first by adding 4% Novatan MAP for 30 minutes. Next 3% Mimosa powder, 2% Retinal LSF 100 and 1% syntan DME at 60^0C for 45 minutes.

Then 8% fatliquor emulsion was added to the testing drum at higher temperature (60^0C). After complete addition of the fatliquor, the drum was run for 45 minutes. Finally 2% formic acid was added for fixation. The leather pieces were washed with water for about 10 minutes, removed from the drum and piled overnight for proper distribution and fixation of the various treatments of chemicals given. Finally sammed set out and left to dry in air through hanging up at room temperature.

For coding the two prepared wet blue leathers were split along the spinal cord and the two right sides were marked for application of the synthesized fatliquor (as LF_1 and DF_2) and the remaining two sides were labeled for the control tests (as CF_1 and CF_2). Next the sides were shaved to 1.6 – 1.8 in thickness and weighted. Two testing drums were also prepared. The weight of wet blue sides and the amount of fatliquor used is shown in Table (3.3) below.

Table 3.3: The weight of wet blue and amount of sulphited fatliquor used

Testing drum	Weight of the shaved wet blue (kg)	Amount of fatliquor used (g)
1 (LF_1, DF_2)	6.5	520
2 (CF_1, CF_2)	7	560

Finally, the dried leather pieces were taken for investigation of visual and physical properties.

3.4.2 Visual Tests

The visual tests including softness, roundness, grain tightness, fullness and overall appearance of the fatliquored crust leather were investigated by professionals. The professionals graded the samples out of ten without knowing which one is the synthesized and which one is the controlled one.

3.4.3 Physical Tests

The sampling of test materials were done according to ISO 2418 (2005), tensile strength and percent elongation tests were done according to ISO 3376 (2002) and the tear load was done according to ISO 3377 (2002) standard testing methods. The tensile strength, percent elongation and tear load were determined.

Fatliquored leather specimen were cut with special steel press knives from the position parallel to the backbone and about 5 cm away from it as specified in the ISO 2418 (2005) standard

methods. Six samples three perpendicular and three parallel from the four cow hides were taken for each tests. Then the samples were coded according to the laboratory design and conditioned for 48 h.

The specimen for measurement of tensile strength and percent elongation has a standard length and width of 50 mm and 10 mm respectively but the thickness varies. The thickness of each specimen is measured at three points along its length. The mean of the three thickness measurement was taken as the thickness of the specimen. Then the cross sectional area of the specimen was calculated by multiplying its width by its thickness. The jaws of tensile machine set 50 mm apart. The specimen was clamped in the jaws. The machine was run until the specimen breaks and the highest load reached was taken as the breaking load.

The tensile strength was calculated using equation (3.18) given below.

$$\text{Tensile strength, N/mm}^2 = \frac{\text{breaking load, N}}{\text{thickness in mm} \times \text{width in mm}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.18)$$

The percent elongation caused by the specified load is calculated as shown in equation (3.19).

$$\text{Elongation at break, in \%} = \frac{\text{mm length at break} - \text{mm initial length}}{\text{mm initial length}} \times 100 \quad \ldots\ldots\ldots\ldots\ldots (3.19)$$

For tearing load calculation a hole (1×10) was punched on the long axis of the leather specimens. The tear load was then calculated from the load required to tear the specimen from a steel rod passing through the hole of the specimen. The tearing load is calculated from the tear specimen as shown below.

$$\text{Tear load, N/mm} = \frac{\text{breaking load, N}}{\text{mean thickness of tear specimen, mm}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3.20)$$

4. Result and Discussion

4.1 Vernonia Seed Preparation, Oil Extraction, Purification and Characterization

4.1.1 Vernonia Seed Preparation

About 24 kg of Vernonia seeds were taken for this research work. First it was cleaned from impurities. From 24 kg Vernonia seeds 324 g waste was removed. Therefore 23.676 kg cleaned Vernonia seeds were gained and 1.35% of the used material was removed as a waste.

4.1.2 Vernonia Oil Extraction

Mechanical extraction method was used for oil extraction and soxhlet solvent extraction method was applied for yield analysis. From 22 kg vernonia seeds 5.0 liter crude Vernonia oil was extracted using mechanical screw pressing machine. The density of crude oil was found 960 kg/m^3 using hydrometer. Therefore 4.8 kg crude oil was extracted. Yield of oil extraction using mechanical pressing machine is calculated using equation (3.1) as follows.

$$\text{Yield of oil} = \left(\frac{\text{mass of oil}}{\text{initial mass of seed}}\right) \times 100 = \frac{4.8\ \text{kg}}{22\ \text{kg}} \times 100 = 21.82\%$$

Yield of oil using solvent extraction method was calculated similarly and found to be 37%. The percentage yield found in mechanical extraction is lower than that of solvent extraction. But it has an advantage in minimum extraction cost and lower extraction time requirement.

4.1.3 Vernonia Oil Purification

The total amount of crude oil obtained from mechanical extraction was 5.0 liter. From 5.0 liter crude oil 800 g was removed during the purification process. Higher amount of suspended solid (700 g) were removed by centrifuging. About 123 ml distilled water was used for degumming.

After degumming, a total of 24.24 g free fatty acid was neutralized using 3.312 g NaOH and 400 g NaCl. The detail calculation is given in Appendix D.

High amount of solid suspended solid were carried out with the oil during extraction process. This is due to the very nature of Vernonia seeds. The acid value of crude oil was very high which results from high lipase activation of the seeds while extraction. Thus the high amount of free fatty acid should be neutralized in order to avoid rancidity of oil, to make it suitable for further fatliquor processing and to avoid spue formation on fatliquored leather.

4.1.4 Physicochemical Properties of Purified Vernonia Oil

The moisture content of vernonia seeds and density, acid value, Saponification value, ester value and iodine value of Vernonia oil were determined. The A.O.A.C. official methods were followed for characterization. The detail results were discussed below.

4.1.4.1 Determination of Moisture Content

Six samples were taken for analysis. The moisture content of the samples was calculated using equation (3.2). The Vernonia seeds average moisture content was found 5.15%. The moisture content determination of Vernonia seeds conducted laboratory result is given in Table (4.1).

Table 4.1: Moisture content determination for Vernonia seed

Run	Sample weight (g)			Moisture content (wt%)	Average Moisture content (wt%)
	W_1	W_2	$(W_1 - W_2)$		
1	4.015	3.826	0.189	4.9	5.15
2	4.012	3.808	0.204	5.4	
3	4.026	3.785	0.241	6.4	
4	4.014	3.863	0.151	3.9	
5	4.025	3.831	0.194	5.1	
6	4.027	3.826	0.201	5.2	

The moisture content of Vernonia seeds 5.15% is suitable for mechanical extraction with relatively lower lipase activation than the solvent extraction method and without further drying of the seeds.

4.1.4.2 Determination of Density

The specific density of purified oil was measured by using hydrometer and found to be 0.88. The density of oil was then determined using the relation given in equation (3.3) as follows.

$$\rho_{oil} = SG_{oil} \times \rho_{water} = 0.88 \times 1\text{g/ml} = 0.88\ \text{g/ml}$$

Therefore, the density of purified vernonia oil was found to be 0.88 g/ml which it is lower than most of vegetable oils used for fatliquor production.

4.1.4.3 Determination of Acid Value

The titration was done three times to increase the accuracy. The average titration volume was taken for acid value calculation. The laboratory results are presented in Appendix C. The acid value of purified vernonia oil is calculated using equation (3.4).

$$AV = \frac{56.1 \times V \times N}{w} = \frac{56.1 \times 1.52 \times 0.1}{2.5} = 3.41 \text{ mg KOH/g oil}$$

The free fatty acid can be calculated using equation (4.1) given below.

$$FFA = \frac{AV}{2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4.1)$$
$$= \frac{3.41}{2} = 1.705 \text{ mg KOH/g oil}$$

The acid value and corresponding FFA composition of the purified Vernonia oil decreased after neutralization of crude vernonia oil. The lower the acid value of the oil the lower its ability to hydrolyze which will be suitable for synthesis of fatliquor and increase the shelf life.

4.1.4.4 Determination of Saponification Value

The Saponification value of Vernonia oil was determined first by doing the titration three times with the oil and finally a blank test was conducted. The blank test titration was found to be 17 ml. For Saponification value calculation average value was taken. The results found are given in Appendix C. The Saponification value is calculated using equation (3.5).

$$SV = \frac{56.1 \times N \times (v_b - v_a)}{W} = \frac{56.1 \times 0.5 \times (17 - 4.73)}{2} = 172.09 \text{ mgKOH/g oil}$$

The Saponification value of Vernonia oil was found within the range given by Manuel des Crops (1992). Higher Saponification value means oils of smaller molecules and so their penetrating powers into the leather is more, which gives softness to leather when it is used for fatliquoring.

4.1.4.5 Determination of Ester Value

The ester value of Vernonia oil can be estimated using the relation given below.

$$EV = SV - AV \quad (4.2)$$

$$= 172.09 \text{ mg KOH/goil} - 3.41 \text{mg KOH/goil} = 168.68 \text{ mg KOH/g oil}$$

The higher ester value means higher ester content of oil which is also preferable for fatliquor production.

4.1.4.6 Determination of Iodine Value

The weight of oil taken for iodine value calculation was 0.28 g according to the A.O.A.C. official method. The iodine value of the oil was calculated using equation (3.6) as shown below.

$$IV = \frac{1.269\ (a - b)}{w} = \frac{1.269(21 - 1.4)}{0.28} = 88.83\ gI_2/100\ g\ oil$$

The iodine value determined in the experiment deviates from the one given by Manuel des Crops (1992) but the result agrees with the work by Wamalwa, Benson M. (2001).

The iodine number of Vernonia oil determined shows that the oil is a non-drying type of oil and can definitely be applied for fatliquor production. According to Thomas C. T. (1993) higher iodine value (which is not higher than 140) indicates low melting point and good lubricating value for the oil.

The summary of the physicochemical properties of purified Vernonia oil is given in Table (4.2) below.

Table 4.2: Physicochemical properties of purified Vernonia oil

Property	Experimental Result	Unit
Specific Gravity	0.88	-
Density at 20^0C	0.88	g/ml
Acid Value	3.41	mg KOH/g oil
Free Fatty Acid	1.71	mg KOH/g oil
Saponification Value	172.09	mg KOH/g oil
Ester Value	168.68	mg KOH/g oil
Iodine Value	88.83	g I_2/100 g oil

4.2 Analysis of Sulphited Fatliquor Production

The fatty acid methyl ester (FAME) was prepared using purified vernonia oil and 85 percent yield was gained using the specified parameters for synthesis of sulphited fatliquor. And from the trial work done the best combination (minimum FAME required) of oil to FAME was found to be 70:30 weight ratios.

The sulphitation reaction was carried out using a 250 ml capacity glass reactor which was equipped with a shaker. The shaker rotational speed and temperature was adjusted to the desired conditions. The statistical analysis of the sulphited fatliquor synthesis is discussed in the following sections.

4.2.1 Statistical Analysis on Factors Affecting Degree of Sulphitation

The experimental design selected for this study is the Central Composite Design (CCD) and the response variable measured is the degree of sulphitation. Three-level-three-factor CCD apply

the face-centered cubic design. Having three levels instead of five was cited as desirable because it reduced the preparation time and lessened the potential for mistakes in preparing the test serum.

Three-level-three-factor face-centered CCD with a complete 2^K factorial layout, 2K axial (star) points and 6 center points was employed in the optimization study, a total of 20 experiments were conducted, where K is three for three factors (independent variables) used in the analysis. The three sulphitation process variables are reaction temperature, amount of sodium bisulphite and reaction time.

Face-centered CCD is selected according to the region of interest and it is very efficient for fitting a second order model. 2^K factorial layout has been used to fit a first-order model but this model exhibited lack of fit. So the axial (star) runs are added to allow the quadratic terms to be incorporated in to the model.

Design-Expert Software 7.0.0 was used in the least squares regression analysis of variance (ANOVA). The statistical software program is used to generate the model equation, interaction effects of the independent variables and surface plots using the fitted equation obtained from the regression analysis holding one of the independent variable constant. The CCD conditions and their respective responses and the ANOVA are given in Table (4.3) and Table (4.4) respectively.

The actual degree of sulphitation of the sulphited fatliquor produced at different process parameters is determined by using the chemical characterization method of determination of total sulphur as sulphites (IS14488, CLAUSE 4.4, ANNEX A-6). The detail calculations and results are discussed in sections below and in Appendix C.

Table 4.3: Experimental and predicted values

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	Experimental Degree of sulphitation (wt%)	Predicted Degree of sulphitation (wt%)	Residuals
1	65	40	12.5	3.17	3.19	-0.02
2	65	30	15	3.31	3.34	-0.03
3	65	20	12.5	2.58	2.56	0.02
4	70	20	10	2.45	2.46	-0.01
5	60	20	15	1.83	1.84	-0.01
6	70	40	10	3.06	3.04	0.02
7	70	20	15	2.96	2.94	0.02
8	60	20	10	1.81	1.82	-0.01
9	65	30	10	3.30	3.26	0.04
10	65	30	12.5	3.27	3.30	-0.03
11	70	30	12.5	3.36	2.34	0.02
12	65	30	12.5	3.30	3.30	0.00
13	65	30	12.5	3.28	3.30	-0.02
14	65	30	12.5	3.31	3.30	0.01
15	60	40	15	2.48	2.47	0.01
16	65	30	12.5	3.29	3.30	-0.01
17	60	30	12.5	2.65	2.63	0.02
18	70	40	15	3.23	2.22	0.01
19	60	40	10	2.82	2.80	0.02
20	65	30	12.5	3.32	3.30	0.02

4.2.1.1 Development of Regression Model Equation

The model equation that correlates the response (degree of sulphitation) to the sulphitation reaction process variables in terms of actual value after excluding the insignificant terms was given below. The predicted model for percentage of degree of sulphitation in terms of the coded factors is given in equation (4.3).

$$\text{Degree of sulphitation (\%)} = +3.30 + 0.35 * A + 0.31 * B + 0.037 * C - 0.094 * A * B + 0.13 * A * C - 0.087 * B * C - 0.3 * A^2 - 0.43 * B^2 - 0.0045 * C^2 \quad \ldots (4.3)$$

Where A is the reaction temperature,
B is the amount of sodium bisulphite and
C is the reaction time.

4.2.1.2 Model Adequacy Check

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared having a value of 0.9988, 0.9977 and 0.9931 respectively.

The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for the developed correlation is 0.9988. It implies that 99.88% of the total variation in the degree of sulphitation is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure (4.1).

The results in Figure (4.1) demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the three sulphitation reaction process variables to the degree of sulphitation.

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table (4.4). Based on a 95% confidence level, F – value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P – value less than 0.05. It is calculated by model mean square divided by residual mean square. Here the model F – value of 928.48 implies the model is significant. There is only a 0.01% chance that a "Model F – Value" this large could occur due to personal error or disturbance.

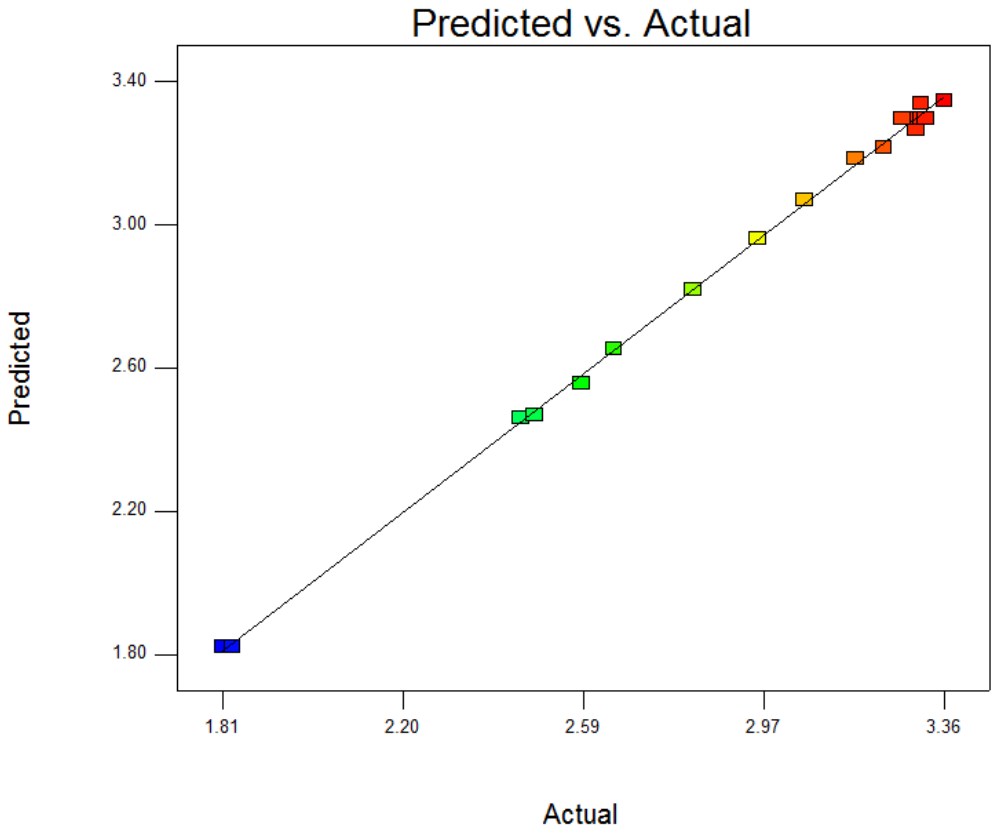


Figure 4.1: Predicted versus actual degree of sulphitation

Table 4.4: ANOVA for the regression model equation and coefficients

Source	Sum of squares	df	Mean square	F – value	P – value Prob > F	Remark
Model	4.54	9	0.50	928.48	< 0.0001	**
A – Reaction Temperature	1.20	1	1.20	2218.22	< 0.0001	**
B – Amount of Sodium bisulphite	0.98	1	0.98	1804.82	< 0.0001	**
C – Reaction Time	0.014	1	0.014	25.22	0.0005	*
AB	0.076	1	0.076	140.10	< 0.0001	*
AC	0.13	1	0.13	230.28	< 0.0001	**
BC	0.061	1	0.061	112.84	< 0.0001	*
A^2	0.24	1	0.24	442.24	< 0.0001	**
B^2	0.5	1	0.5	917.03	< 0.0001	**
C^2	0.00005628	1	0.00005628	0.1	0.7530	
Residual	0.005428	10	0.005428			
Lack of Fit	0.003678	5	0.0007356	2.10	0.2171	not significant
Pure Error	0.00175	5	0.00035			
Cor Total	4.54	19				

Note: * means significant and ** means highly significant

Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, BC, A^2 and B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

This shows that the reaction temperature, amount of sodium bisulphite, reaction time, interaction between reaction temperature and amount of sodium bisulphite, interaction between reaction temperature and reaction time, interaction between amount of sodium bisulphite and reaction time, square of the reaction temperature and square of amount of sodium bisulphite affects the degree of sulphitation significantly.

The "Lack of Fit F – value" of 2.10 implies the Lack of Fit is not significant relative to the pure error. There is a 21.71% chance that a "Lack of Fit F – value" this large could occur due to noise. Non-significant lack of fit is good because we want the model to fit.

4.2.2 Effect of Sulphitation Reaction Process Variables

Based on the analysis of variance, sulphitation reaction was significantly affected by various interactions between the process variables. This result demonstrated that the advantage of using face-centered CCD for experimental data analysis in capturing the interaction between variables that affects the sulphitation reaction. In addition to the interaction effect, significant individual process variables that affect the sulphitation reaction is reaction temperature, A, amount of sodium bisulphite, B, and reaction time, C.

4.2.2.1 Effect of Individual Process Variables

As shown in Figure (4.2) below the degree of sulphitation is significantly affected by reaction temperature. It can be seen from the figure that with increasing reaction temperature the degree of sulphitation generally increases.

The increase in the degree of sulphitation at higher reaction temperature is due to higher rate of reaction. Is it well reported in the literature that the reaction rate of sulphitation reaction is strongly influenced by the reaction temperature. Higher temperature results higher reaction

rate constant which will lead to higher rate of reaction and eventually increases the degree of sulphitation.

As stated by Jones T. J. *et al.* (1978) an increase in reaction temperature reduces the viscosity of oil and increases the mobility of reactant molecules which results higher kinetic energy. Hence, increase in molecule velocity and kinetic energy increases the reaction rate.

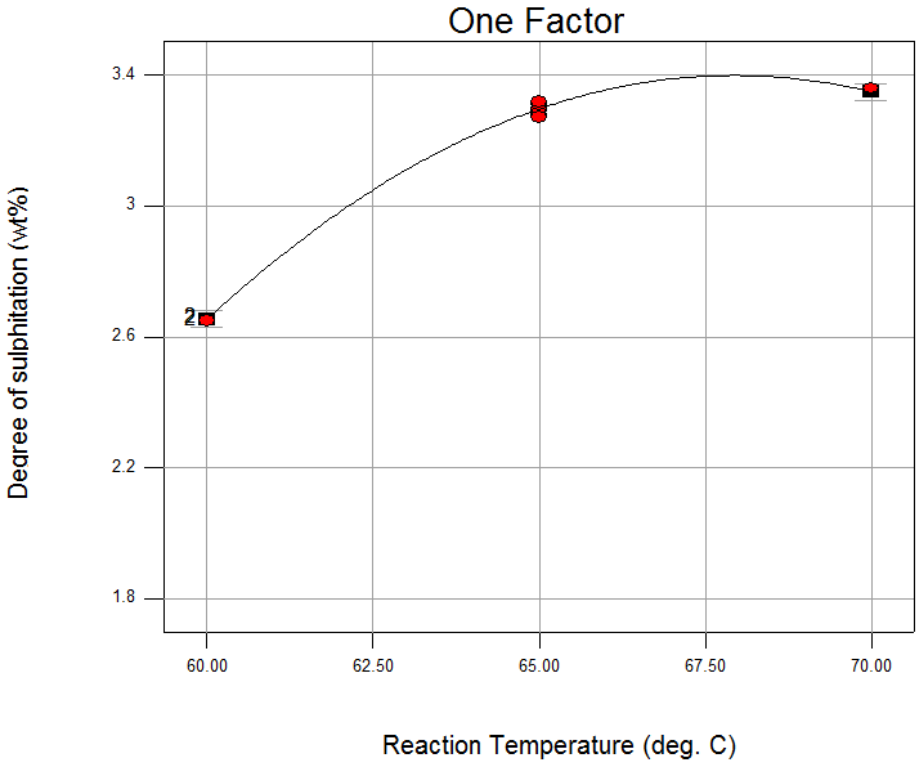


Figure 4.2: Degree of sulphitation versus reaction temperature at amount of sodium bisulphite 30% and 12.5 h reaction time. ^{0}C

The sulphitation reaction consists of a sequence of two consecutive irreversible reactions. First vernonia oil is oxidized by bellowing air to reduce the degree of unsaturation by formation of epoxide ring structures at the double bonds of the vernolic acid. Then the oxidized oil reacted with the concentrated solutions of sodium bisulphite which attaches the sulphonate groups, SO_2ONa, to certain carbon atoms so that sulphonated oils are produced. Both reactions are endothermic reactions which are favored with increasing temperature.

Reaction rates can be increased if the concentration of reactants is raised. An increase in concentration produces more collisions, which results raise in reaction rate. Higher reaction rate increases the degree of sulphitation. Figure (4.3) shows that the effect of amount of sodium bisulphite on the degree of sulphitation. Increasing the amount of sodium bisulphite increases the degree of sulphitation significantly.

The amount of sodium bisulphite is one of the important factors that affect the degree of sulphitation. Stoichiometrically, 30% by weight of concentrated sodium bisulphite (40% concentrated solution) is required for each mole of triglyceride, but in practice, 20 to 50% by weight amount of sodium bisulphite is required in order to drive the reaction to maximum degree of sulphitation. The results obtained in this study are in agreement with this theory, as shown in Figure (4.3), where at higher amount of sodium bisulphite the degree of sulphitation was increased.

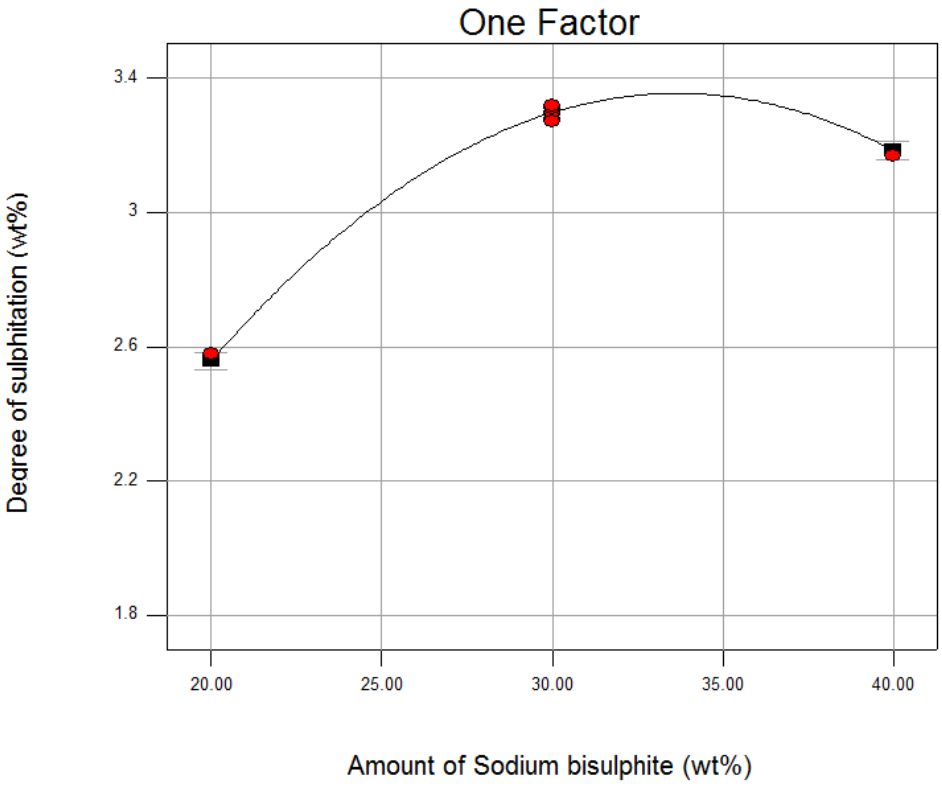


Figure 4.3: Degree of sulphitation versus amount of sodium bisulphite at reaction temperature 75 and 12.5 h reaction time.

Figure (4.4) below illustrates the effect of reaction time on degree of sulphitation. When the reaction time was raised from 10 to 15 h, the sulphitation reaction gets enough time for formation of the sulphonate group which increases the degree of fixation.

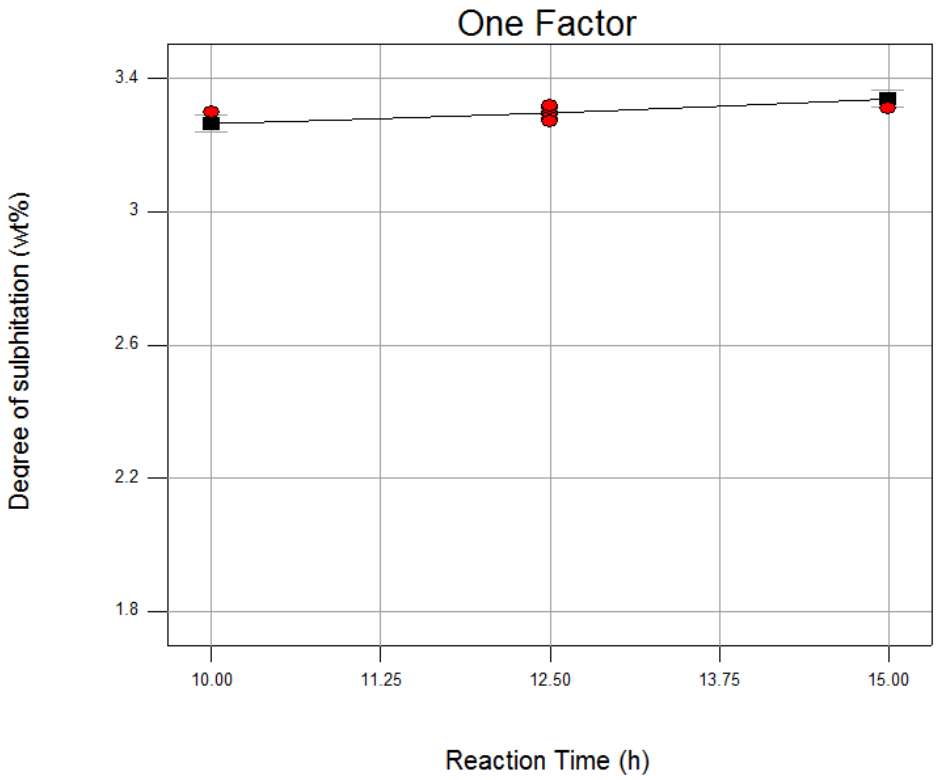


Figure 4.4: Degree of sulphitation versus reaction time at reaction temperature 75 and amount of sodium bisulphite 30%.

As shown from the Figure (4.4) above the effect of one factor which is the reaction time is not highly significant compared to the reaction temperature and amount of sodium bisulphite. This shows that the interaction between the sulphitation reaction processes parameter was significant. This result agrees with the ANOVA output for the regression model equation and coefficient.

4.2.2.2 Effect of Interaction between Process Variables

The most common way to summarize the results of a central composite design experiment is in the form of a response surface plot and via response contours plot.

The process variables were found to have significant interaction effects. Figure (4.5), (4.7) and (4.9) shows the interaction between reaction temperature and amount of sodium bisulphite, reaction temperature and reaction time, and amount of sodium bisulphite and reaction temperature on the degree of sulphitation respectively.

Generally, an increase in reaction temperature is found to increase the degree of sulphitation. This is due to similar explanation given in the previous section.

From the three interaction effects shown in the figures and contours at lower range of reaction temperature, higher amount of sodium bisulphite and higher reaction time, always resulted in the degree of sulphitation higher than when using lower amount of sodium bisulphite and lower reaction time.

On the other hand, at higher range of reaction temperature, totally opposite is observed. Reaction carried out using lower amount of sodium bisulphite and lower reaction time is found to have higher degree of sulphitation as compared to reaction using lower reaction temperature, higher amount of sodium bisulphite and higher reaction time.

The above observations can easily be explained as higher reaction temperature and excess sodium bisulphite will drive the reaction forward and higher reaction period will ensure the sulphitation reaction goes to completion which results in higher degree of sulphitation.

Another notable observation is that at higher range of reaction temperature, the observations showed that using a combination of higher reaction temperature, higher amount of sodium bisulphite and higher reaction time is not beneficial in increasing the degree of sulphitation.

This is because at this process conditions, higher reaction temperature is already sufficient to push the reaction forward.

This phenomena is further supported by the fact that reaction temperature is the most significant process variable that affect the degree of sulphitation as indicated by the highest F – value in the ANOVA as shown in Table (4.4).

The Response Surface Methodology (RSM) was used to optimize the conditions of conversion for vernonia oil sulphited fatliquored and to understand the interaction of the factors affecting the sulphited fatliquor production. Figures (4.5), (4.7) and (4.9) show surface plots between the independent and dependent variable for fixed parameters.

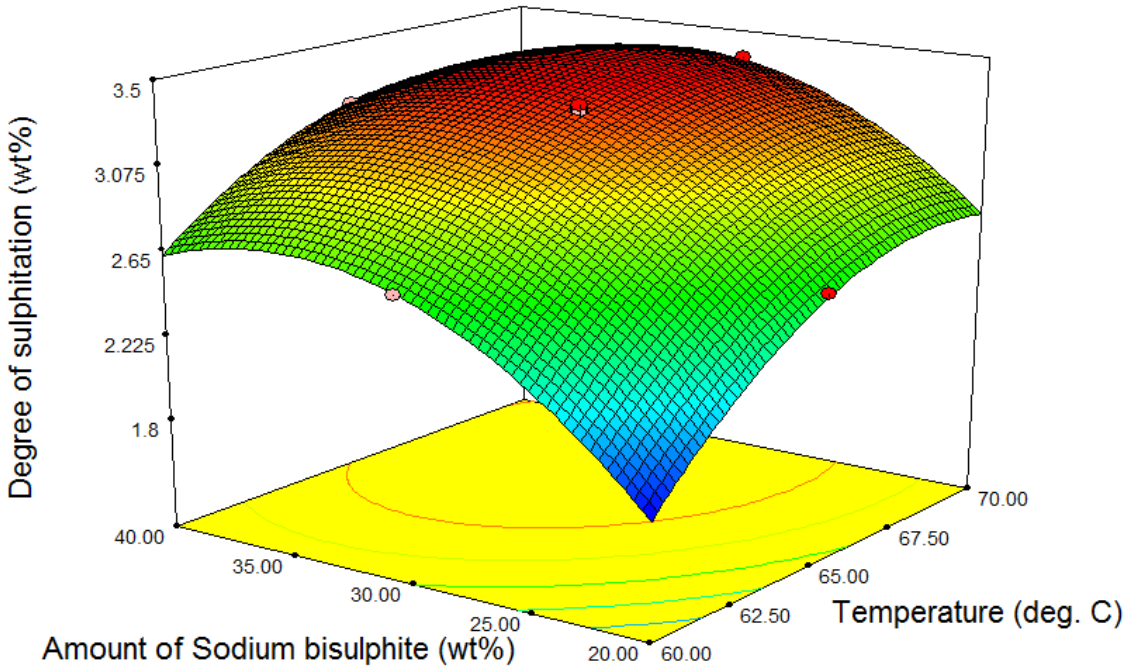


Figure 4.5: Surface plot of the interaction effect of reaction temperature and amount of sodium bisulphite versus degree of sulphitation when the reaction time is 12.5 h.

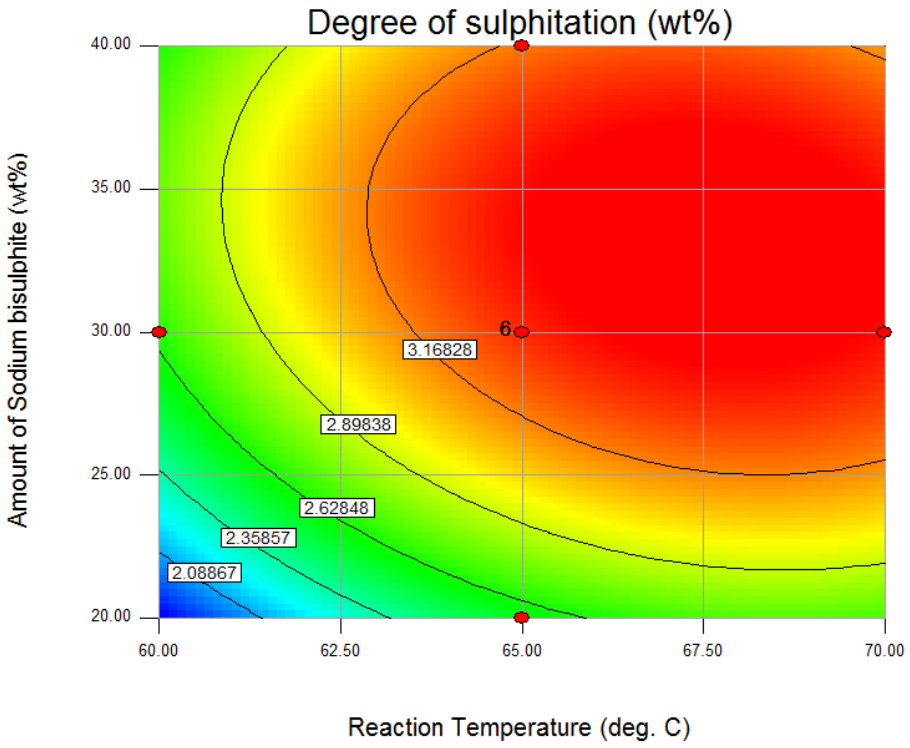


Figure 4.6: Contour plot of the interaction effect of reaction temperature and amount of sodium bisulphite versus degree of sulphitation when the reaction time is 12.5 h.

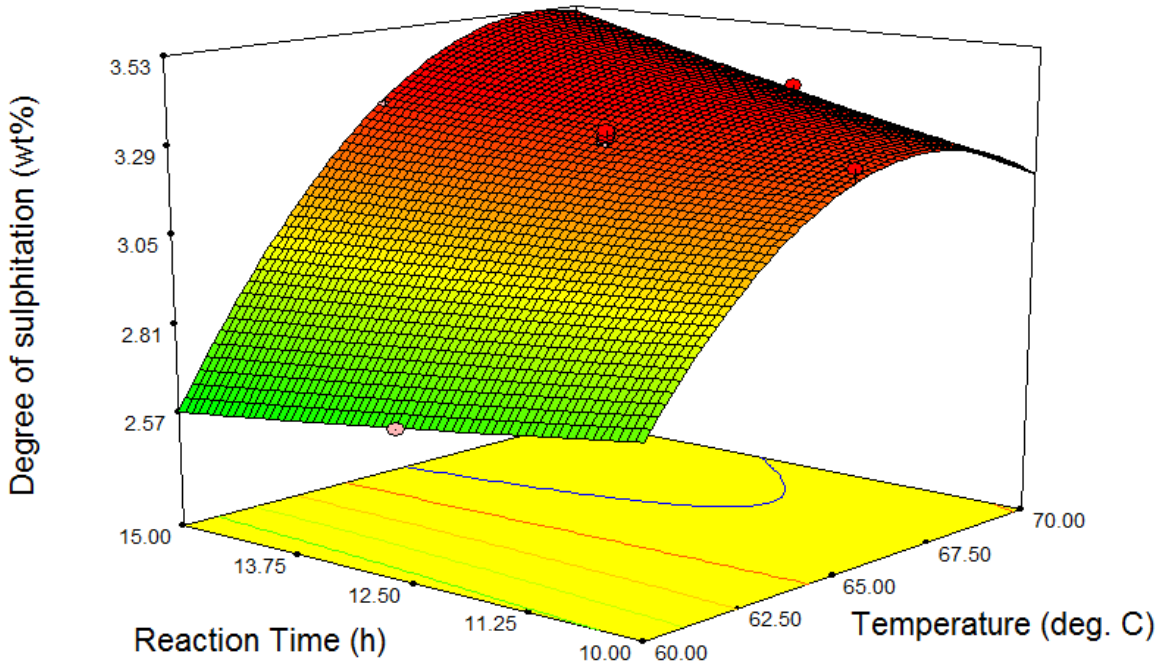


Figure 4.7: Surface plot of the interaction effect of reaction temperature and reaction time versus degree of sulphitation when amount of sodium bisulphite is 30%.

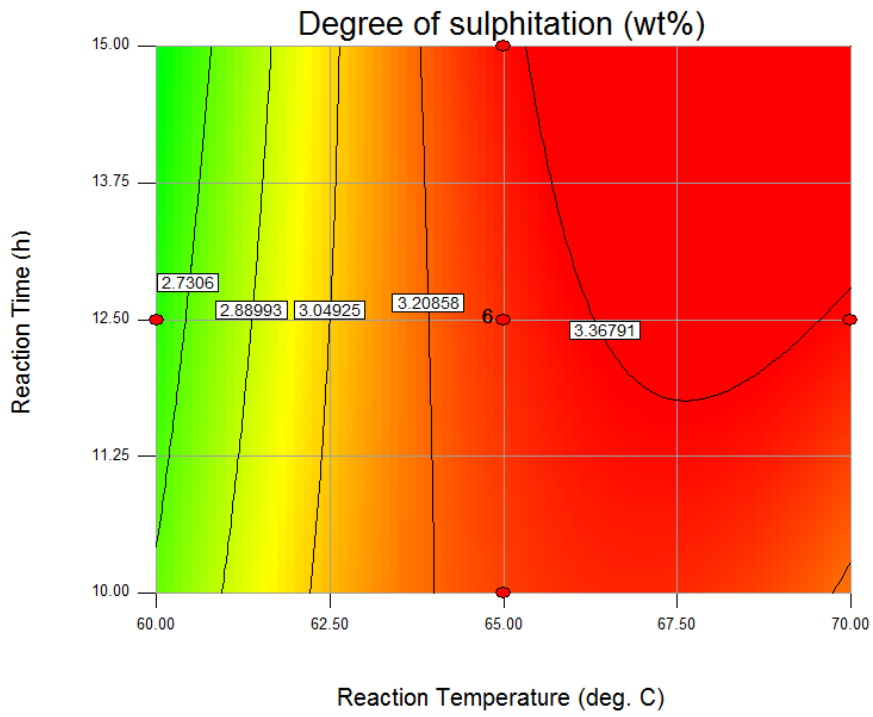


Figure 4.8: Contour plot of the interaction effect of reaction temperature and reaction time versus degree of sulphitation when amount of sodium bisulphite is 30%.

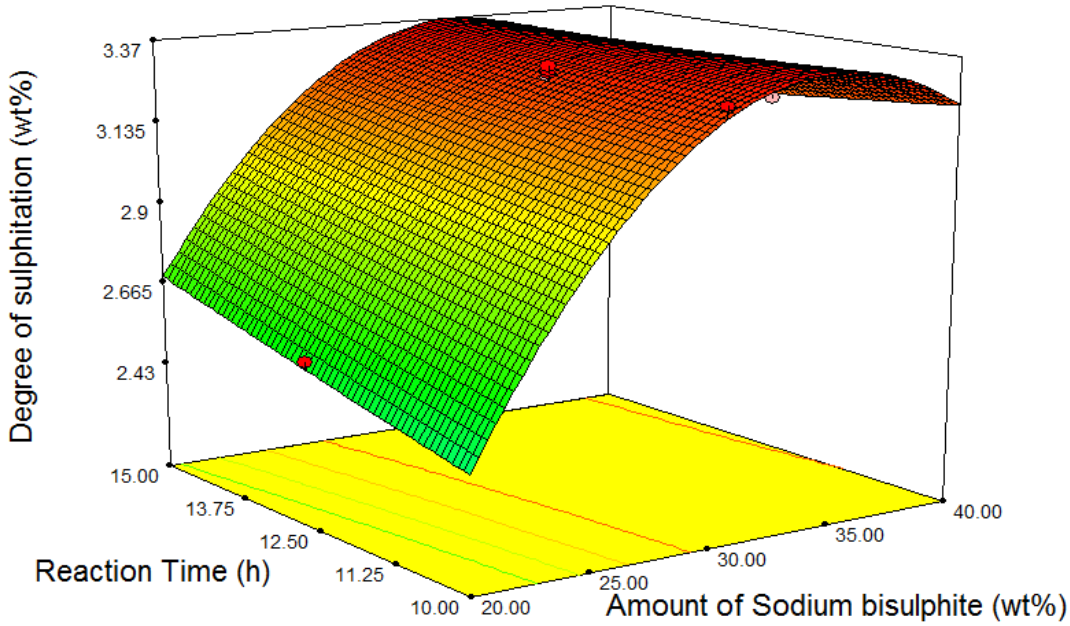


Figure 4.9: Surface plot of the interaction effect of amount of sodium bisulphite and reaction time versus degree of sulphitation when reaction temperature is 70^0C.

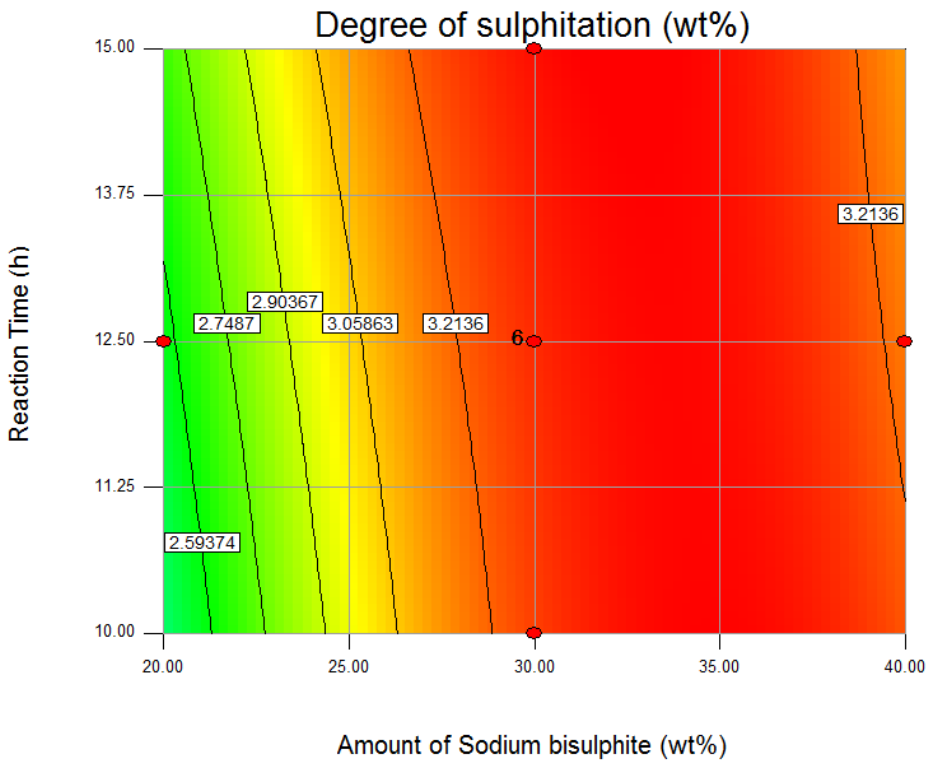


Figure 4.10: Contour plot of interaction effect of amount of sodium bisulphite and reaction time versus degree of sulphitation when reaction temperature is 70^0C.

Figure (4.9) shows the interaction of amount of sodium bisulphite and reaction time on the degree of sulphitation. A relatively lower degree of sulphitation at higher amount of sodium bisulphite could also be due to impurities present in sodium bisulphite like sulphur dioxide and sodium hydroxide which may compete for sodium bisulphite and reduce its availability for sulphitation reaction.

From Figure (4.5), the percent degree of sulphitation increased with increased with increasing reaction temperature at optimal amount of sodium bisulphite. Figure (4.7) shows the percent degree of sulphitation increased with increasing reaction temperature and reaction time. From Figure (4.9), the percent degree of sulphitation gets higher at optimal amount of sodium bisulphite and optimal reaction time.

4.2.2.3 Optimization of Process Variables

The results above have shown that the three sulphitation process variables and the interaction among the variables affect the degree of sulphitation. Therefore, the next step is to optimize the process variables in order to obtain the highest degree of sulphitation using the model regression developed.

Using the optimization function in Design-Expert, it was predicted that at conditions of 70^0C reaction temperature, 30% amount of sodium bisulphite and 12.5 h reaction time, an optimal degree of sulphitation of 3.35% can be obtained. In order to verify this prediction, experiments were conducted and the results were computable with the prediction. It was found that the experimental value of 3.36% degree of sulphitation which is well agreed with the predicted value. Therefore, this study shows that vernonia oil can definitely be used for synthesis of sulphited fatliquor and a higher degree of sulphitation can be obtained from the synthesis of vernonia oil using concentrated sodium bisulphite solution via sulphitation reaction.

4.3 Yield of Sulphited Fatliquor

The yield of sulphitation process does not tell anything about the chemistry and kinetics of the reaction. From the principle of conservation of mass all the mass in should be out since there is only one product out from the reactor (sulphited fatliquor). The yield variation observed in the experimental data analysis arises from the sulphitation reaction, washing and drying process.

Yield of washing the excess sodium bisulphite and drying the trace water is found to be 98% only 2% of the total mass in is removed. High amount of variation arises from the sulphitation reaction conditions. The difference in the reaction temperature, amount of sodium bisulphite and reaction time varies the amount of water in to the system and out of the system which results in yield variation.

Industrially the sulphitation reaction is done simultaneously with the oxidation process. Air is blown at the bottom of the reactor and it should be out of the system to maintain atmospheric pressure. When hot air is out from the reactor it will entrap water vapor which comes with the sodium bisulphite solution and this results minimum amount of water to be left in the product. The laboratory experiments were done by considering this situation.

Table 4.5: Yield of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of Sodium bisulphite (wt%)	Reaction Time (h)	Yield (%)	Degree of sulphitation (wt%)
1	65	40	12.5	81.25	3.17
2	65	30	15	85.07	3.31
3	65	20	12.5	88.89	2.58
4	70	20	10	89.13	2.45
5	60	20	15	88.65	1.83
6	70	40	10	81.49	3.06
7	70	20	15	84.01	2.96
8	60	20	10	93.76	1.81
9	65	30	10	87.63	3.30
10	65	30	12.5	85.21	3.27
11	70	30	12.5	84.75	3.36
12	65	30	12.5	85.44	3.30
13	65	30	12.5	85.68	3.28
14	65	30	12.5	84.61	3.31
15	60	40	15	81.01	2.48
16	65	30	12.5	84.26	3.29
17	60	30	12.5	87.38	2.65
18	70	40	15	76.38	3.23
19	60	40	10	86.12	2.82
20	65	30	12.5	85.21	3.32

Table (4.5) shows that the yield was affected by the sulphitation process parameters. Lower yield is found when increasing the reaction temperature, amount of sodium bisulphite and reaction time. This is due to raising reaction temperature increases the rate of evaporation, increasing the amount of sodium bisulphite increases the amount of water in to the mixture and when it gets longer residence time results higher amount of evaporated water which lowers the yield.

Table (4.5) also shows at higher percent yield the degree of sulphitation is minimum, this is because minimum reaction temperature, small amount of sodium bisulphite and shorter residence time favors lower evaporation rate and minimum degree of sulphitation. On the other hand a higher degree of sulphitation and a percent yield of 85% can be obtained at higher reaction temperature, optimal amount of sodium bisulphite and optimal reaction time.

4.4 Physicochemical Properties of Sulphited Fatliquor

The physicochemical characterization of the synthesized sulphited fatliquor is done based on the Indian standard specifications and recommended methods, IS 14488. The pH value and amount of total sulphur content as sulphite is conducted for all the experiments and amount of total active ingredient, unsaponifiable matter, total alkalinity and total ash content is done for randomly selected ten experiments and compared with the specifications. The results were calculated using equations given in the materials and methods chapter three and the details are given in Appendix C.

4.4.1 Physical Conditions

To allow a small amount of oil to be spread uniformly over a very large surface area of the leather fibers it is necessary to dilute the oil. For fatliquoring process the sulphited fatliquor is applied in the form of emulsion.

The physical condition of sulphited fatliquor produced from Vernonia oil shows that the sulphited fatliquor is pourable at 20^0C, capable of being readily washed out with water without having any oily feeling on hand and does not have any rancid or putrefactive odor.

The 10% emulsion formed using the sulphited fatliquor form a stable emulsion at room temperature. In addition ten percent emulsion formed remains stable for over 40 minutes in the presence of 5% metal salts sodium chloride and calcium chloride mixture.

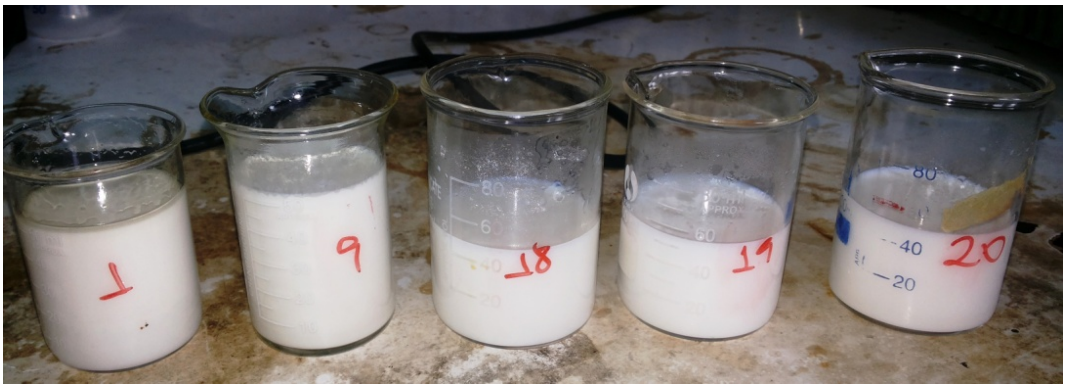


Figure 4.11: Ten percent emulsion formed by sulphited fatliquor

The milky emulsions are indicative of the degree of sulphitation. The combined SO_3 or emulsifier is the fuel which drives the oil droplets into the leather. Anionic emulsifiers ensure a great degree of fixation since they will be attached to the positively charged leather surface.

The emulsions produced by sulphitation of oils are fine which results deep penetration into the leather, making the leather soft and resistant to acid and salt present in normal chrome tanned leathers.

4.4.2 pH of Emulsion

The pH of sulphited fatliquor emulsion is one of the most important properties for determining the property and performance of fatliquor in addition to the method of production and application for fatliquoring.

Table 4.6: pH of 10% emulsion of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	pH Value
1	65	40	12.5	7.78
2	65	30	15	6.86
3	65	20	12.5	7.44
4	70	20	10	6.84
5	60	20	15	6.38
6	70	40	10	6.30
7	70	20	15	6.59
8	60	20	10	7.44
9	65	30	10	6.83
10	65	30	12.5	7.47
11	70	30	12.5	7.11
12	65	30	12.5	7.34
13	65	30	12.5	7.42
14	65	30	12.5	7.39
15	60	40	15	7.61
16	65	30	12.5	7.49
17	60	30	12.5	7.57
18	70	40	15	7.42
19	60	40	10	7.30
20	65	30	12.5	7.34

The pH value of emulsion should be neutral (6 – 8) to be used for fatliquoring. The pH of leather at the time of fatliquoring also plays an important role in the manner in which the oil is fixed and uniformly distributed. The principal result of neutralization of chrome tanned leather before fatliquoring process is reduction of the strong positive charges so that the negative fatliquor emulsion gets absorbed.

The pH of 10% emulsion formed by the sulphited fatliquor was observed to be in the range from 6.30 to 7.58. Experimental results which gives higher degree of sulphitation also gives a pH value within the acceptable range given by IS 14488, CLAUSE 4.4 which is 6.5 to 7.5.

4.4.3 Total Active Ingredient

Total active ingredient is also one of the most important properties of sulphited fatliquor. It shows the amount of fatty matter in sulphited fatliquor that give the desired characteristics to the fatliquor.

Total active ingredient in sulphited fatliquor gives tensile strength, wetting properties, water proofness and permeability to water vapor and air to the fatliquor. High amount of total active ingredient means high amount of oil is available for lubrication of the leather. The hydrophilic part makes this oil to bond with the protein to gain a stable effect.

The total active ingredient of sulphited fatliquor produced was performed and observed to be in the range of percent by weight fatliquor of fatliquor at different sulphitation process parameters. When we compare the experimental results with the IS 14488, CLAUSE 4.4, for sulphited fatliquor minimum percentage of 60% by weight is acceptable. The experimental results for randomly selected ten experiments were shown in Table (4.7) below.

Table 4.7: Total active ingredient of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	Total Active Ingredient (%)
1	65	40	12.5	66.63
3	65	20	12.5	63.03
5	60	20	15	59.03
7	70	20	15	65.43
9	65	30	10	71.63
11	70	30	12.5	66.93
14	65	30	12.5	71.29
16	65	30	12.5	70.78
18	70	40	15	68.63
20	65	30	12.5	70.37

4.4.4 Unsaponifiable Matter

The Unsaponifiable Matter of sulphited fatliquor produced was performed and observed to be in the range of 9.57 to 10.67% by weight fatliquor of fatliquor at different sulphitation process parameters. When we compare the experimental results with the IS 14488, CLAUSE 4.4, for sulphited fatliquor maximum percentage of 15% by weight is acceptable. The selected experimental results for randomly selected ten experiments were shown in Table (4.8) below.

Table 4.8: Unsaponifiable matter of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	Unsaponifiable matter (wt%)
1	65	40	12.5	10.18
3	65	20	12.5	9.63
5	60	20	15	10.67
7	70	20	15	9.51
9	65	30	10	10.63
11	70	30	12.5	10.12
14	65	30	12.5	9.97
16	65	30	12.5	9.98
18	70	40	15	10.58
20	65	30	12.5	9.98

4.4.5 Total Alkalinity

The total alkalinity of sulphited fatliquor produced was performed and observed to be in the range of 1.44 to 3.56 mg per 10 g fatliquor of fatliquor at different sulphitation process parameters. When we compare the experimental results with the IS 14488, CLAUSE 4.4, for sulphited fatliquor maximum amount of 5 mg per 10 g is acceptable. The selected experimental results for randomly selected ten experiments were shown in Table (4.9) below.

Table 4.9: Total alkalinity of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	Total Alkalinity (mg/10 g)
1	65	40	12.5	3.56
3	65	20	12.5	2.55
5	60	20	15	1.44
7	70	20	15	2.12
9	65	30	10	3.35
11	70	30	12.5	3.17
14	65	30	12.5	3.12
16	65	30	12.5	3.16
18	70	40	15	3.50
20	65	30	12.5	3.12

4.4.6 Total Sulphur as Sulphites

The reaction depth was determined by the amount of sulphur trioxide fixed (degree of sulphitation). The stability of the resulting emulsion also evaluated according to the content of SO_3 in the sulphited oil. In addition as stated by El-shaha H. *et al.* (2011) in the synthesis of fatliquor it should be noted that SO_3 content of the resulting constituents is of great significance, so that the degree of conversion was estimated mostly as SO_3 content.

The higher an oil is sulphited (the more polar groups put in), the more soluble it becomes. A study of particle size indicates that the smaller globules are being formed in the sulphited oil emulsion, and this also tends to produce a more soluble and stable emulsion product.

The greater the degree to which the oil is sulphited, the less will be its lubricating effect on the leather surface. This may be due to the consequent reduction in neutral oil (non-polar, unsulphited ester) whilst the greater the sulphitation the greater the emulsion penetration into

the wet leather, reducing the oiliness of the grain and flash surface. This makes the sulphited fatliquor favored for suede, where a greasy surface is undesirable and for gloving and soft leathers, where good lubrication is essential. The experimental results were shown in Table (4.10) below.

Table 4.10: Total sulphur as sulphites (so_3) of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	Degree of sulphitation (wt%)
1	65	40	12.5	3.17
2	65	30	15	3.31
3	65	20	12.5	2.58
4	70	20	10	2.45
5	60	20	15	1.83
6	70	40	10	3.06
7	70	20	15	2.96
8	60	20	10	1.81
9	65	30	10	3.30
10	65	30	12.5	3.27
11	70	30	12.5	3.36
12	65	30	12.5	3.30
13	65	30	12.5	3.28
14	65	30	12.5	3.31
15	60	40	15	2.48
16	65	30	12.5	3.29
17	60	30	12.5	2.65
18	70	40	15	3.23
19	60	40	10	2.82
20	65	30	12.5	3.32

The degree of sulphitation of fatliquor produced was performed and observed to be in the range of 1.81 to 3.36% by weight of fatliquor at different sulphitation process parameters. When we compare the experimental results with the IS 14488, CLAUSE 4.4, for sulphited fatliquor minimum percentage of 1.8% is acceptable.

In addition to the degree of sulphitation pH of emulsion, emulsion stability and total fatty mater plays a great role while selecting sulphited fatliquor. At higher degree of sulphitation the pH value lies within the specification and great emulsion stability was found, but the fatty matter content decreases with increasing degree of sulphitation.

4.4.7 Total Ash

The total ash content of sulphited fatliquor produced was performed and observed to be in the range of 1.97 to 3.69% by weight of fatliquor at different sulphitation process parameters. When we compare the experimental results with the IS 14488, CLAUSE 4.4, for sulphited fatliquor maximum percentage of 4.5% is acceptable. The selected experimental results were shown in Table (4.11) below.

Table 4.11: Total ash content of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	Ash content (wt%)
1	65	40	12.5	2.87
3	65	20	12.5	3.38
5	60	20	15	3.69
7	70	20	15	3.01
9	65	30	10	3.51
11	70	30	12.5	2.98
14	65	30	12.5	3.12
16	65	30	12.5	3.17
18	70	40	15	1.97
20	65	30	12.5	3.04

4.5 Application of Sulphited Fatliquor on Leather and Determination of Physicochemical Properties of Fatliquored Leather

4.5.1 Visual Tests

The sample fatliquored crust leather were evaluated by two professionals and graded out of ten. The sample crust leather is shown in Figure (4.12) and the average results were presented in Table (4.12) below.

Figure 4.12: Fatliquored cow upper crust

Leather especially that used in footwear and leather clothes is in great demand for its unique properties with regard to the comfort to the wearer. Footwear designers and all leather industries always look first at the appearance of the leather. So in addition to the physical tests conducted, the fundamental criteria for the evaluation of a fatty matter and its suitability for leather fatliquoring are mainly shown from the visual properties of the treated leather, including its organoleptic properties like softness, roundness, grain tightness and fullness as shown in Table (4.12).

It is found from Table (4.12) that the synthesized fatliquor perform better than that of the commercial fatliquor (Fosfol 36). The organoleptic properties are interrelated to one another and one has the counter effect of the other. The synthesized fatliquor has a higher value of

softness and fullness than roundness and grain tightness. The softness has counter effect on the grain tightness.

Generally, the second hide (DF_2 and CF_2) both the synthesized and commercial fatliquor has higher value than that of the corresponding first hide (LF_1 and CF_1). This is due to in addition to the effect of fatliquor the nature and quality of hides used has also an effect on the artistic beauty, appearance and performance of the leather.

Table 4.12: Visual evaluation of synthesized and controlled tests

Tests	Coded factors			
	LF_1	**DF_2**	**CF_1**	**CF_2**
Softness	8	8.5	7	7.5
Roundness	7.25	8.25	6.5	7.25
Grain tightness	7.5	8.25	6.75	8
Fullness	7.5	9	7	7.5
Overall Appearance	8	8	7	7.25

4.5.2 Physical Tests

The mechanical tests include the measurement of the tensile strength, percent elongation and tear load. The mechanical properties have been given the greatest consideration on the evaluation of fatliquored leather, because, it gives an indication of fiber lubricity. The mechanical properties were evaluated according to IUP standard specification of leather.

It is found from Table (4.13) and Figures ((4.13), (4.14) and (4.15)) that the three mechanical properties namely tensile strength, percent elongation and tear load of synthesized sulphited fatliquor gives higher value than that of the commercial fatliquor (Fosfol 36, vegetable oil sulphited fatliquor, pH 6 – 8) commonly used vegetable oil sulphited fatliquor.

The improvement in the mechanical properties of the treated leather is due to good lubrication of the fibers. The sulphited portion of oil (hydrophilic fatty matter) during fatliquoring of chrome tanned leather is chemically bound to the leather fibers, i.e. interacts with active centers in the collagen molecules of leather fibers, while the emulsified portion (hydrophobic portions) is mainly located between the fiber bundles. Because the prepared fatliquor contains hydrophilic and at the same time hydrophobic portions can penetrated into the leather fibers with the prepared fatliquor because of its good penetration power and its emulsion stability.

Table 4.13: Summary of physical tests

Coded factors	Type of tests		
	Tensile strength (N/mm^2)	Percent Elongation (%)	Tear Load (N/mm)
LF_1	27.3	64.5	92.7
DF_2	28.4	74.5	98.2
CF_1	24.4	53.0	65.9
CF_2	23.9	60.3	60.9

The bar graph shown in the figures below is plotted using the average values of synthesized and commercial fatliquor effect given in Table (4.13) above. In all three physical tests the synthesized sulphited fatliquor performs better than that of the commercial one. The results show that the potential of Vernonia oil for substitution of the corresponding imported sulphited fatliquor.

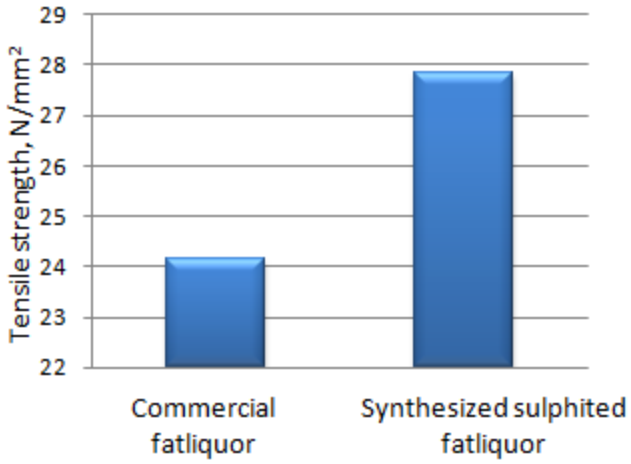


Figure 4.13: Effect of vernonia oil sulphited fatliquor on tensile strength

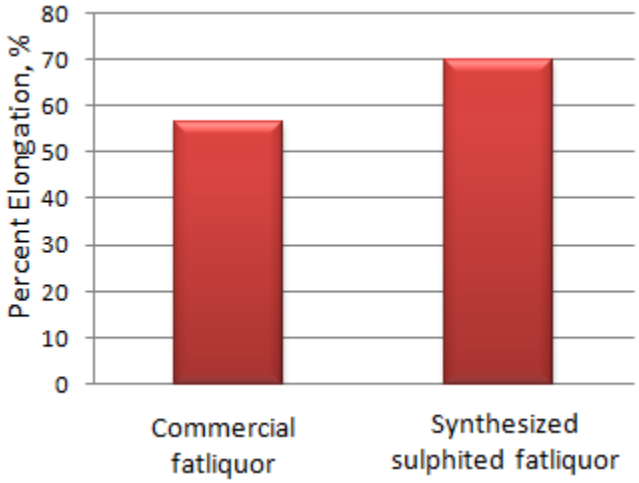


Figure 4.14: Effect of vernonia oil sulphited fatliquor on percent elongation

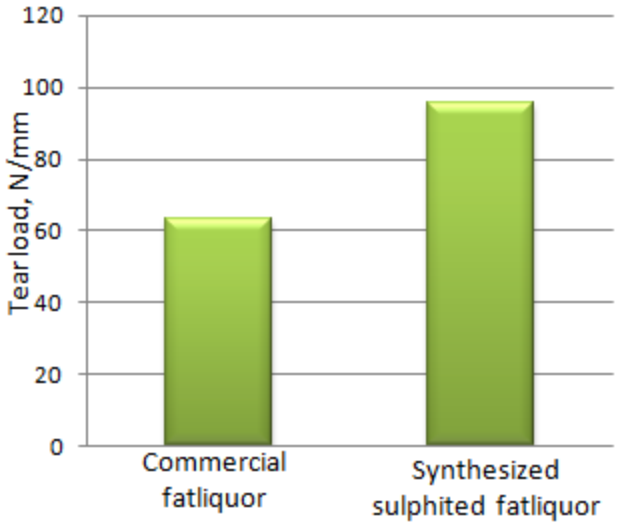


Figure 4.15: Effect of vernonia oil sulphited fatliquor on tear load

In addition to the hydrophilic part of sulphited fatliquor, the hydrophobic part of the sulphited fatliquor is vernonia oil. The result showed that nature and property of vernonia oil also gives the fatliquored leather desired organoleptic and physical properties.

In general, the physical properties which are shown above demonstrates to a far extent the suitability of the prepared sulphited fatliquor from Vernonia oil for fatliquoring of chrome tanned leather, where by all the three tests satisfy the BASF specification for upper cow leather as stated in the literature review.

5. Preliminary Feasibility Study

5.1 Process Description for Sulphited Fatliquor Production

Vernonia oil, FAME and sodium bisulphite were used for the production of sulphited fatliquor via sulphitation reaction. Vernonia seed is prepared and extracted for crude oil production using mechanical pressing machine. The crude oil then purified for FAME and fatliquor production. FAME is prepared from vernonia oil and methanol using sodium hydroxide catalyst at 60^0C reaction temperature, 1:9 Vernonia oil to methanol molar ratio, 1.125 wt% catalyst and 3 h reaction time. Also 40 wt% sodium bisulphite solution is prepared. Once the raw materials are prepared, mixture of Vernonia oil and FAME is mixed in 70:30 weight ratios for oxidation. The oxidation lasts for 4 h. Sodium bisulphite is added in a 250 ml glass reactor containing oxidized oil to shake, for optimal production 70^0C reaction temperature, 30% amount sodium bisulphite solution and 12.5 h residence time is recommended. Then the fatliquor is washed with 10% brine solution which is twice the weight of fatliquor to remove the excess sodium bisulphite. Then the fatliquor is dried for 6 h in an oven to remove the trace moisture.

Basic Operating Methods

Given the choice made for the basic production process of sulphited fatliquor, the next decision concerns how the plant will actually be operated. There are three basic options: batch, continuous or batch-continuous.

Batch Operation – Batch operations are conducted in discreet units. Each batch of feedstock is processed independently of the next for all processes such as preparation, reaction, separation, drying and purification. These type operations can be easily started and stopped and are good for facilities that do not operate 24 hours a day. The product flow can be easily traced and operations are of the batch variety.

Continuous Operations – As the name implies, the process is an on-going flow of feed stocks, preparation, reactions and separations. These type facilities are typically the largest and most

efficient operations. They often can get by with lower inventories and thus less storage space. These processes rely upon a consistent feedstock, typically single sourced, and are sensitive to process changes.

Batch-Continuous – This approach attempts to reap the benefits of both of the above processes as it adapts characteristics of both. In practice it typically consists of batch reactors making independent batches of product followed by a continuous separation and purification process. It garners the efficiencies at the back end of the process while enjoying the ability to control the reaction process and change feed stocks more rapidly than the continuous systems. The following table compares characteristics of the batch with the continuous systems.

Table 5.1: Comparisons of Sulphited fatliquor production technology

Characteristics	Batch	Continuous
Typical capital cost	Less	Greater
Economy of sale	< 500 tons per year	> 500 tons per year
Feedstock flexibility	Greater flexibility	Less flexibility
Consumption of input	Greater	Less
Operating cost per kilogram	Greater	Less
Automation	Less	Greater
Product yield	Less	Greater
Product quality consistency	Less	Greater
Typical plant size	Smaller	Larger

(Source: Ref. [54])

From the alternatives given in Table (5.1), a continuous process is selected to be compatible with the estimated plant capacity for sulphited fatliquor production.

5.2 Material Balance

The capacity of the sulphited fatliquor production plant is taken based on the data taken from 26 leather factories which shows that a total of 9108.84 kg sulphited fatliquor per day is needed based on 4% by weight of shaved wet blue [15].

Assume 300 working days per year, the sulphited fatliquor consumption per year

$$= 9108.84 \text{ kg/day} \times 300 \text{ day/year} = 2732652 \text{ kg/year}$$

For plant cost estimation and cost analysis taking 30% of the market demand

$$= 0.3 \times 2732652 = 819795.6 \text{ kg/year}$$

Therefore, capacity of the sulphited fatliquor production plant = 2750 kg/day

Basis: 1 day

From the literature review and laboratory results, the amount of all the raw material needed and amount of product and byproduct from the plant for the production of sulphited fatliquor is calculated as shown below.

- **Sulphited fatliquor production unit**

The amount of fatliquor feed to the dryer where 2% water is removed

$$= 2750 \times 1.0204 = 2806.122 \text{ kg}$$

The amount of water removed from the dryer

$$= 2806.122 \times 0.02 = 56.122 \text{ kg}$$

The total amount of material feed to the washer where 2% of the feed is removed in the washer

$$= 2806.122 \times 1.02024 = 2863.390 \text{ kg}$$

10% Brine solution used for washing is twice that of the mixture and 2% of the mixture is taking away with the fatliquor.

The amount of Brine solution required

$= 2 \times 2863.390 = 5726.780$ kg

The amount of sodium chloride needed

$= 0.1 \times 5726.780 = 572.678$ kg

The amount of spent wash using material balance

$= (2863.390 + 5726.780) - 2806.122 = 5784.048$ kg

The feed material required where 85% yield of total material feed

$= 2863.390 \times 1.1765 = 3368.694$ kg

To find the amount of Vernonia oil and FAME required for the process

Let x be the oil and FAME feed. The total feed to the reactor will be

$= \mathrm{x} \times 0.3\ \mathrm{x} = 3368.694$ kg

Solving for x give x = 2591.303 kg

The amount of Vernonia oil and FAME feed is 2591.303 kg. From this 70% is Vernonia oil and 30% is sodium bisulphite solution.

Vernonia oil $= 0.70 \times 2591.303 = 1813.912$ kg

FAME $= 0.30 \times 2591.303 = 777.391$ kg

The amount of sodium bisulphite $= 0.30 \times 2591.303 = 777.391$ kg

The amount of sodium bisulphite to prepare 40% solution

$= 0.40 \times 777.391 = 310.956$ kg

The amount of water needed for solution preparation (taking density of water 1000 kg/m^3)

$= 777.391 - 310.956 = 466.435$ kg

From material balance on reactor gives the amount of water removed from the reactor

$= 0.15 \times 3368.690 = 505.304$ kg

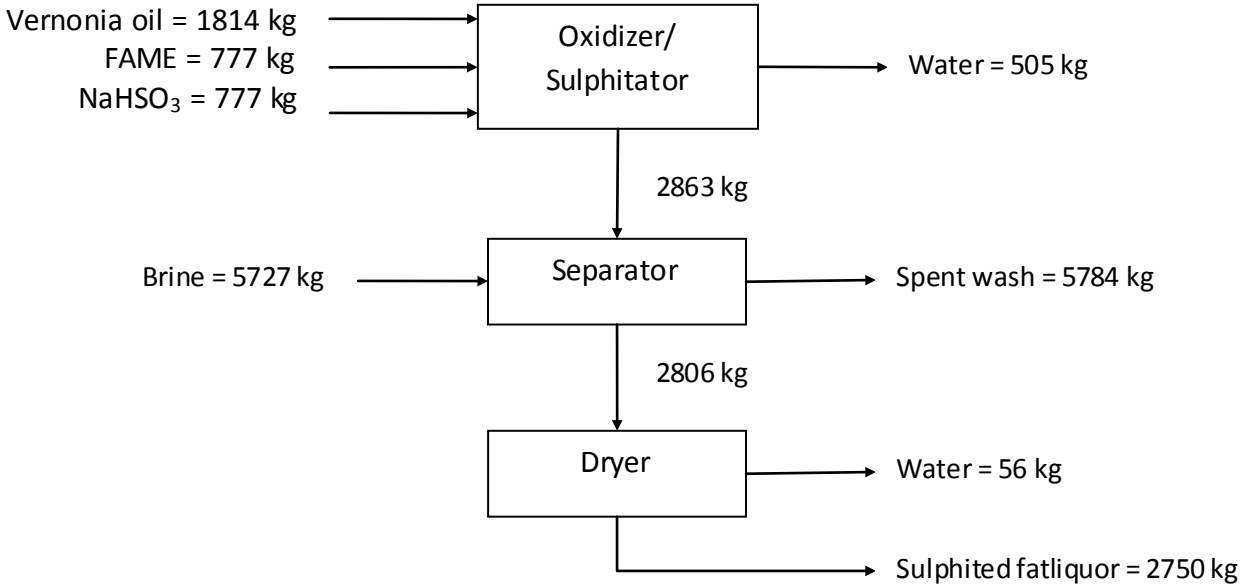


Figure 5.1: Sulphited fatliquor production unit material balance block diagram

- **FAME production plant**

To get 777.391 kg FAME, the amount of Vernonia oil needed for 85% conversion yield.

$= 777.391 \times 1.1765 = 914.578$ kg

Excess methanol is sent to shift the reaction equilibrium in favor of FAME product, Vernonia oil: methanol molar ratio (1:9)

$$= 9 \times \left(\frac{914.578}{926}\right) \times 32.04 = 284.803 \text{ kg}$$

The amount of catalyst needed $= 0.01125 \times 914.578 = 10.289$ kg

From stoichiometry the amount of methanol consumed in the reaction from the ratio 1 kmol

Vernonia oil: 3 kmol methanol

$$= \left(\frac{3 \times 32.04}{926}\right) \times 914.578 = 94.816 \text{ kg}$$

Amount of methanol to be recycled $= 284.803 - 94.816 = 189.987$ kg

Assume 95% methanol recovery on distillation. The amount of methanol sent to the methanol recovery tank

$= 0.95 \times 189.987 = 180.488$ kg

The amount of crude glycerol from material balance

$= 1019.683 - 777.391 = 242.292$ kg

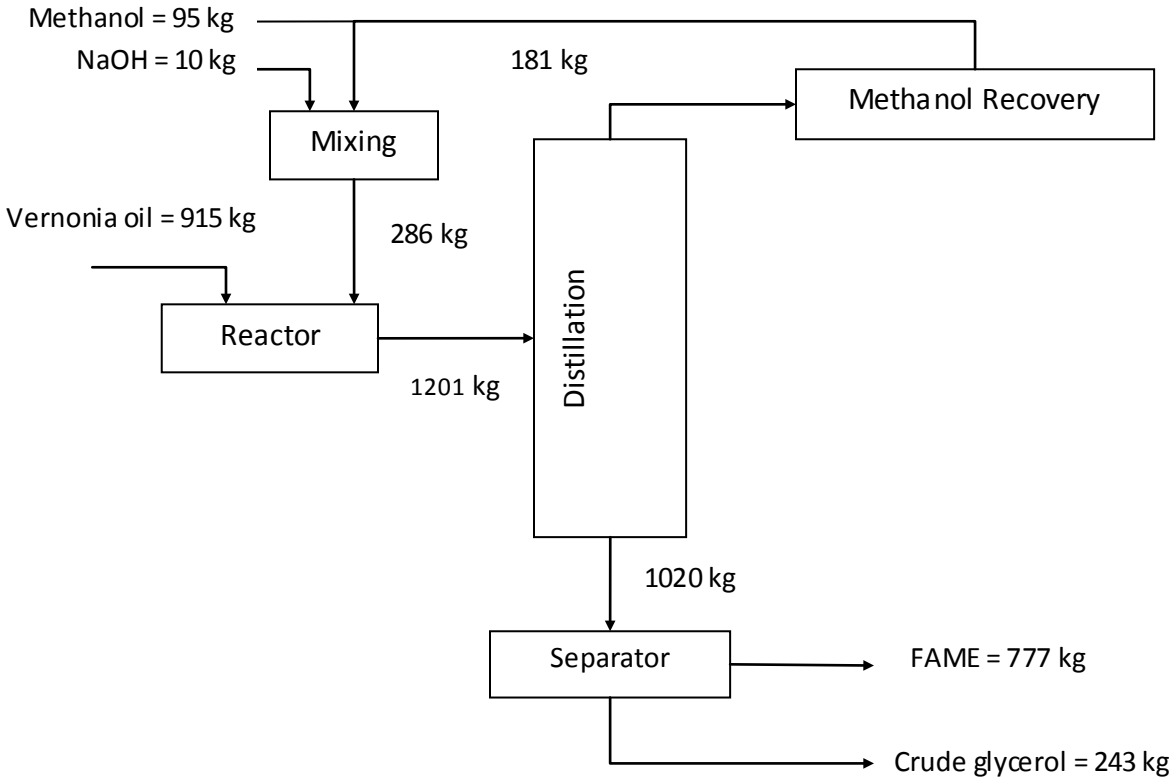


Figure 5.2: FAME production unit material balance block diagram

- **Preparation, Extraction and Purification of Vernonia oil**

The total amount of purified Vernonia oil needed

$= 1813.912 + 914.578 = 2728.490$ kg

The amount of %FFA which is needed to be neutralized is 0.606%. The amount of oil is decreased by 0.606%. The amount of degummed Vernonia oil feed to neutralizer

$= 2728.490 \times 1.0061 = 2745.125$ kg

The amount of sodium hydroxide required to neutralize 0.606% FFA

$$= \frac{\%\ \text{FFA} \times \text{MW}_{\text{NaOH}}}{\text{MW}_{\text{FFA}}} = \frac{0.00606 \times 40}{292.69} = 8.282 \times 10^{-4}\ \text{g NaOH/g oil}$$

For 2745.125 kg degummed oil, the amount of NaOH needed is equal to 2.273 kg.

2% of the oil feed to the degumming section is removed as gum and wax. The crude oil feed to degumming section

$= 2745.125 \times 1.0204 = 2801.148$ kg

The amount of gum and wax removed from degummer

$= 0.02 \times 2801.148 = 56.023$ kg

The amount of hot water feed to the degummer (5%)

$= 0.05 \times 2801.148 = 140.057$ kg

The total amount of spent wash, gum and wax out from degumming section

$= 56.023 + 140.057 = 196.080$ kg

The separator removes around 14.58% suspended solid. So the amount of extracted oil feed to the separator will be

$= 2801.148 \times 1.1707 = 3279.265$ kg

The amount of oil extracted is 35% of feed Vernonia seed including the suspended solids. The amount of cleaned Vernonia seed feed to the extractor

$= 3279.265 \times 2.8571 = 9369.328$ kg

Amount of Vernonia seed required where 1.35% by weight is removed as a waste

$= 9369.328 \times 1.0137 = 9497.545$ kg

All the other unknowns can be simply solved from the material balance for respective unit operation.

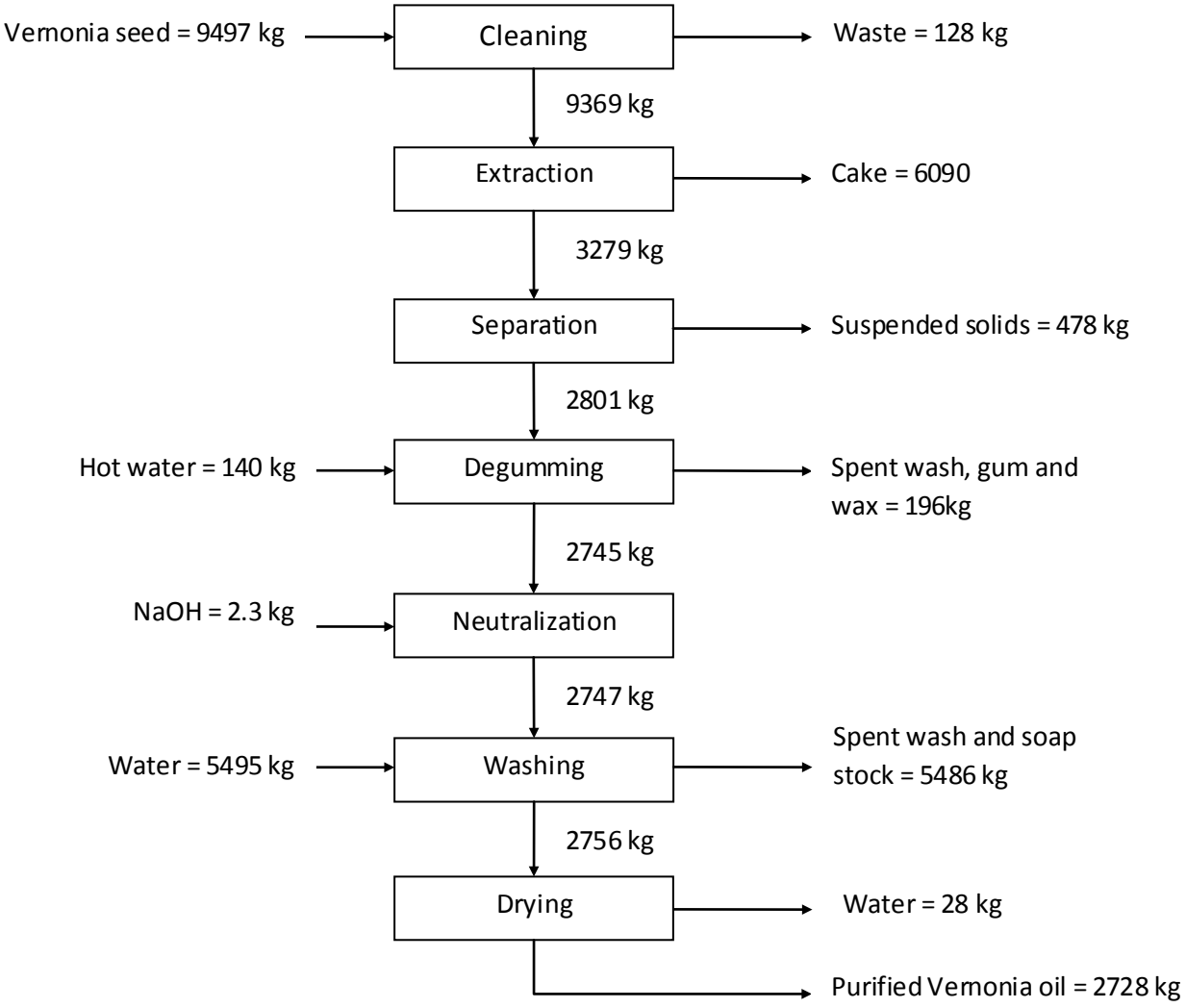


Figure 5.3: Vernonia oil preparation, extraction and purification MB block diagram

5.3 Energy Balance

- **Sulphitation Reactor**

Reactors can be classified in a variety of ways based on the size, method of operation and the phase involved in the process, namely homogenous and heterogeneous reactors. For this study a homogenous semi-batch reactor type is selected. The main reason for selecting a semi-batch reactor is that oxidation and sulphitation reaction is conducted simultaneously so that all the reactants will be feed at the reaction temperature and air is blown constantly in to the reactor. Due to the nature of the reaction, the heat is absorbed during the reaction, thus it is hard to imagine a chemical reaction that has a reaction heat of zero. Normally to bring in isothermal condition, the reaction is brought immediately to that of the surroundings by heating (for endothermic reaction) i.e., the temperature of the reacting mixture is maintained constant throughout the course of reaction. This happens with the assistance of the heat transfer medium under perfectly stirring condition.

In isothermal operation, the reaction temperature is not changing, i.e., constant temperature (dT = 0). If the reactor is to be operated isothermally, the rate of reaction can be expressed as a function of concentration only, not as a function of temperature, then the energy balance equation becomes,

$$\Delta H_R (rV) = KA(T_S - T_R) \quad (5.1)$$

Where K is overall heat transfer coefficient,

A is effective area for heat transfer,

T_S is surrounding (heating) temperature,

T_R is the temperature of the reaction mixture and

ΔH_R is heat of reaction.

From general mole balance:

$$(rV) = n_{A0}dX_A \quad \text{……} (5.2)$$

Substituting, integrating and rearranging equation (5.1) gives,

$$T_S = T_R + \frac{\Delta H_R n_{A0} dX_A}{KAt_r} \quad \text{……} (5.3)$$

From the experimental results the heat of reaction and enthalpy change is calculated as shown below.

$$q = \dot{m} \times Cp \times \Delta T \quad \text{……} (5.4)$$

Where $\dot{m}$ is the total mass of the reaction mixture,

Cp is the specific heat for the composition mixture and

ΔT is the change in temperature in K.

Table 5.2: Heat capacities of feed materials to the sulphitator reactor

Material	Cp (kJ/kgK)
Vernonia oil	1.99
FAME	2.34
$NaHSO_3$	1.93

Therefore, $q = 0.039\ \mathrm{kg/s} \times 2.057\ \mathrm{kJ/kgK} \times 50\ \mathrm{K} = 4.011\ \mathrm{kJ/s}$

The molar flow rate of feed mixture into the reactor

$$\dot{n} = \frac{\dot{m}}{MW_{mix}} \quad \text{……} (5.5)$$

$$= \frac{0.039\ \mathrm{kg/s}}{737\ \mathrm{kg/kmol}} = 0.000053\ \mathrm{kmol/s} = 0.053\ \mathrm{mol/s}$$

The enthalpy change in kJ per mole of a given reactant for the sulphitation reaction is

$$\Delta H = \frac{q}{\dot{n}} \quad \ldots\ldots (5.6)$$

$$= \frac{4.011 \text{ kJ/s}}{0.053 \text{ mol/s}} = 75.68 \text{ kJ/mol}$$

Now, from the above equation the isothermal reaction temperature is set to T_R = 343 k and 85% conversion.

The overall heat transfer coefficient K, is largely dependent on the agitator speed and the viscosity of the liquid. For the sulphitator reactor the cold media is mixture of vegetable oil, FAME and sodium bisulphite solution and the heating media is water, the overall heat transfer coefficient is selected to be 200 W/m^{2}K [54].

A simple batch reactor working in the industry is often a vertical cylinder with an elliptical bottom. The material used for its construction is generally suitable for various reaction processes. Most often used is a glass lined steel vessel. The heat transfer area for a 2.48 m^3 capacity reactor is 7.68 m^2 as shown in Appendix F.

From the reactor material balance, the mass production per cycle is calculated as

$$= 3368.694 \frac{\text{kg}}{\text{day}} \times \frac{1\text{day}}{24 \text{ h}} \times \frac{12.5 \text{ h}}{1 \text{ cycle}} = 1754.538 \text{ kg/cycle}$$

In mole using equation (5.5)

$$\dot{n} = \frac{1754.538 \text{ kg/cycle}}{737 \text{ kg/kmol}} = 2.3806 \text{ kmol/cycle}$$

Substitute all the known values into equation (5.3) results

$$T_S = 343 \text{ K} + \frac{75.68 \text{ kJ/mol} \times 2381\text{mol} \times 0.85}{0.2 \text{ kJ/sm}^2\text{K} \times 7.68 \text{ m}^2 \times 45000 \text{ s}} = 346 \text{ K}$$

Therefore the heating temperature will be pumped at 346 K.

The amount of heat supplied to the reactor is calculated as

$$Q = KA(T_S - T_R) \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots \dots (5.7)$$

$$= 0.2\ kJ/sm^2K \times 7.68\ m^2 \times (346 - 243)K = 4.608\ kW$$

- **Transesterification Reactor**

Similarly for transesterification reactor temperature of heating media and the amount of heat supplied is calculated as shown below.

Table 5.3: Heat capacities of feed materials to the transesterification reactor

Material	Cp (kJ/kgK)
Vernonia oil	1.99
Methanol	2.65

From the experimental results the heat of reaction and enthalpy change is calculated as shown below. Substitute all known values into equation (5.4) gives.

$$q = \dot{m} \times cp \times \Delta T = 0.0106 \frac{kg}{s} \times 2.13 \frac{kJ}{kgs} \times 40\ K\ = 0.902\ kJ/s$$

The molar flow rate of feed mixture into the reactor using equation (5.5) results

$$\dot{n} = \frac{\dot{m}}{MW_{mix}} = \frac{0.0106\ kg/s}{708\ kg/kmol} = 0.000015\ kmol/s = 0.015\ mol/s$$

The enthalpy change in kJ per mole of a given reactant using equation (5.6) for the

transesterification reaction is

$$\Delta H = \frac{q}{\dot{n}}\ = \frac{0.902\ kJ/s}{0.015\ mol/s} = 60.13\ kJ/mol$$

The isothermal reaction temperature is set to T_R = 333 K and 85% conversion.

Similarly the overall heat transfer coefficient is selected to be 200 W/m^2K [54]. The heat transfer area for a 0.24 m^3 capacity reactor is 1.83 m^2 as shown in Appendix F.

From the reactor material balance, the mass production per cycle is calculated as

$$= 914.578\,\frac{\text{kg}}{\text{day}} \times \frac{1\text{day}}{24\ \text{h}} \times \frac{3\ \text{h}}{1\ \text{cycle}} = 114.322\ \text{kg/cycle}$$

In mole

$$\dot{\text{n}} = \frac{114.322\ \text{kg/cycle}}{708\ \text{kg/kmol}} = 0.16147\ \text{kmol/cycle}$$

Substitute all the known values into equation (5.3) results

$$\text{T}_\text{S} = 333\ \text{K} + \frac{60.13\ \text{kJ/mol} \times 161.47\ \text{mol} \times 0.85}{0.2\ \text{kJ/sm}^2\text{K} \times\ 1.83\ \text{m}^2 \times 10800\ \text{s}} = 336\ \text{K}$$

Therefore the heating temperature will be pumped at 336 K.

The amount of heat supplied to the reactor is calculated using equation (5.7) as

$$\text{Q} = \text{KA}(\text{T}_\text{S} - \text{T}_\text{R}) = 0.2\ \text{kJ/sm}^2\text{K} \times 1.83\ \text{m}^2 \times (336 - 333)\text{K} = 1.098\ \text{kW}$$

- **Distillation Column**

From the material balance the amount and composition of feed, distillate and bottom is

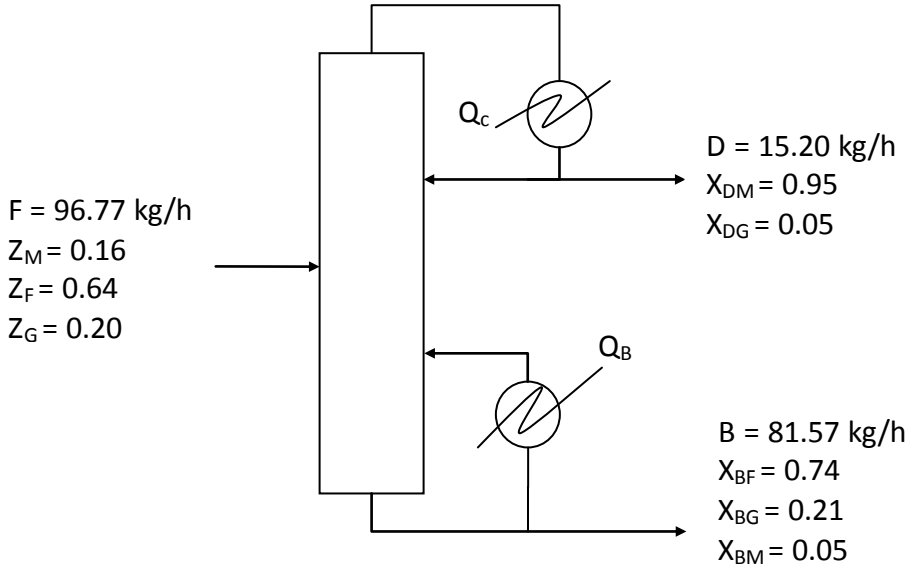


Figure 5.4: Flow rate and composition of feed, distillate and bottom products of distillation column

Assume steam is available at 25 psig, the rise in cooling water temperature is limited to 30^0C and column operates at 1 bar.

The kinetic and potential energy of the process streams will be small and can be neglected.

The heat losses from the system will be small if the column and exchangers are properly lagged and will be neglected.

Basis: 25^0C and 1 h

Table 5.4: Heat capacity data of feed material for distillation column

Material	Cp (kJ/kgK)
Methanol	2.65
FAME	2.34
Glycerol	2.55

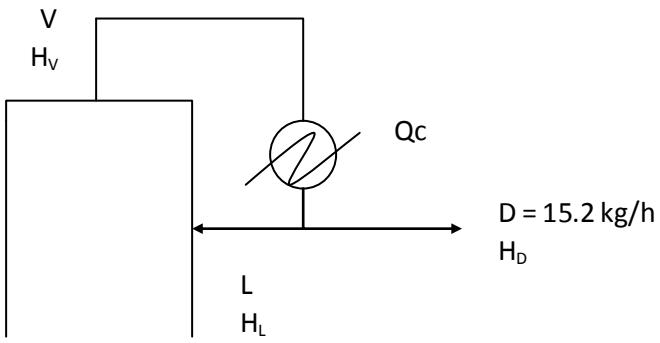
Heat capacities can be taken as additive

Feed: $(0.16 \times 2.65) + (0.64 \times 2.34) + (0.20 \times 2.55) = 2.432\ \text{kJ/kgK}$

Top: $(0.95 \times 2.65) + (0.05 \times 2.55) = 2.645\ \text{kJ/kgK}$

Bottom: $(0.74 \times 2.34) + (0.21 \times 2.55) + (0.05 \times 2.65) = 2.40\ \text{kJ/kgK}$

Qc must be determined by taking a balance round the condenser



Take the reflux ratio R = 10

$$R = \frac{L}{D} = 10$$

Therefore, $L = 10 \times 15.2 = 152\ \text{kg/h}$

$V = L + D = 167.2\ \text{kg/h}$

Boiling point of 95% methanol and 5% FAME is 65^0C.

At steady state: $\text{Input} = \text{Output}$

$H_V = H_D + H_L + Q_C$ ……(5.8)

Hence rearranging equation (5.8), $Q_C = H_V - H_D - H_L$

Assume complete condensation,

$\text{Enthalpy of vapor } HV = \text{ latent } + \text{ sensible heat}$ ……(5.9)

Values of the latent heat of methanol and water as functions of temperature

Latent heat of methanol = 1317 kJ/kg

Glycerol = 974 kJ/kg

Taking latent heat as additive and substitute values into equation (5.9):

$$\mathrm{H_V} = 167.2[(0.05 \times 974) + (0.95 \times 1317) + (65 - 25) \times 2.645] = 235025\ \mathrm{kJ/h}$$

The enthalpy of the top product and reflux are zero, as they are both at the base temperature. Both are liquid, and the reflux will be at the same temperature as the product.

Hence, $Q_C = H_V$ =235025 kJ/h = 65.3 kW

Q_B is determined from a balance over complete system.

$$\mathrm{Input} = \mathrm{Output}$$

$$\mathrm{Q_B} + \mathrm{H_F} = \mathrm{Q_C} + \mathrm{H_D} + \mathrm{H_B} \quad \ldots\ldots\ldots\ldots (5.10)$$

$$\mathrm{H_F} = 96.77 \times 2.43 \times (25 - 25) = 0$$

$$\mathrm{H_B} = 81.57 \times 2.4 \times (65 - 25) = 7829.41\ \mathrm{kJ/h}$$

Hence from equation (5.10),

$$\mathrm{Q_B} = \mathrm{Q_C} + \mathrm{H_D} + \mathrm{H_B} = 235025 + 0 + 7829.41 = 242855\ \mathrm{kJ/h} = 67.5\ \mathrm{kW}$$

Q_B is supported by condensing steam:

Latent heat of steam = 2174 kJ/kg

$$\mathrm{Steam\ required} = \frac{242855}{2174} = 111.71\ \mathrm{kg/h}$$

Q_C is removed by cooling water with a temperature rise of 30^0C.

$$\mathrm{Q_C} = \mathrm{waterflow\ rate} \times 4.2 \times 30$$

Hence,

$$\mathrm{water\ flow} = \frac{235025}{4.2 \times 30} = 1865.28\ \mathrm{kg/h}$$

5.4 Preliminary Equipment Specifications and Sizing

- **Selection of Pressing Machine**

Continuous screw pressing machine is to be used for extraction of vernonia oil. A pressing machine having a capacity of 390 kg/h and power consumption 18.5 kW is selected [55].

- **Selection of Filter Press**

Oil filter having size 350 mm×350 mm, 25 pieces filter plates and 1.1 kW power consumption filter press is selected [56].

- **Oil Degummer**

The volume of degumming tank is determined as follows.

From material balance the total mass feed to the degummer = 2801.148 kg/day.

Density of crude Vernonia oil = 920 kg/m^3

Hence,

$$V = \frac{m}{\rho} \quad (5.11)$$

$$= \frac{2801.148}{920} = 3.05 m^3$$

The volume of degumming tank per cycle

$$= \frac{3.05 m^3}{day} \times \frac{1\ day}{24\ h} \times \frac{1\ h}{cycle} = 0.13\ m^3/cycle$$

Accounting 10% for safety, the volume of degumming tank per cycle

$$= 0.13 + (0.1 \times 0.13) = 0.143\ m^3$$

- **Oil Neutralizer**

Similarly the volume of neutralization tank is determined as follows.

From material balance the total mass feed to the neutralizer = 2745.125 kg/day.

Density of crude Vernonia oil = 910 kg/m^3

Hence using equation (5.11),

$$V = \frac{m}{\rho} = \frac{2745.125}{910} = 3.07\ m^3$$

The volume of neutralizer tank per cycle

$$= \frac{3.07\ m^3}{day} \times \frac{1\ day}{24\ h} \times \frac{1\ h}{cycle} = 0.13\ m^3/cycle$$

Accounting 10% for safety, the volume of degumming tank

$$= 0.13 + (0.1 \times 0.13) = 0.143\ m^3$$

- **Transesterification Reactor**

The reactor volume, assuming 3 h reaction time, operation at constant temperature and pressure of 60^0C and 1 atm respectively.

The volume of reactants per day

$$V_f = \left(\frac{m}{\rho}\right)_{Vernonia\ \ oil} + \left(\frac{m}{\rho}\right)_{methanol\ \ +NaOH} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.12)$$

From material balance the amount of reactant feed to the reactor is known. And the density of methanol and NaOH mixture is determined from additive property of density.

$$\rho_{mix} = (\%\ methanol \times \rho\ methanol) + (\%\ NaOH \times \rho\ NaOH) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.13)$$

$$= (0.996 \times 720) + (0.034 \times 2120) = 767.6\ kg/m^3$$

Substitute all known values into equation (5.12)

$$V_f = \left(\frac{914.578}{880}\right) + \left(\frac{295.092}{767.6}\right) = 1.42\ m^3/day$$

The volume of reactants for one reaction cycle

$$V_f = 1.42\frac{m^3}{day} \times \frac{1\ day}{24\ h} \times \frac{3\ h}{cycle} = 0.1775\ m^3/cycle$$

The volume of reactor accounting the safety factor

$$V_r = \frac{4}{3} \times V_f \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.14)$$

$$= \frac{4}{3} \times 0.1775 = 0.24\ m^3/cycle$$

- **Sulphitator Reactor**

A specially designed sulphitator which will allow air to blow in to the reactor will be used. So that oxidation and sulphitation reactions can be done simultaneously. Besides, the reactor volume, assuming 12.5 h reaction time, operation at constant temperature and pressure of 70^0C and 1 atm respectively.

The volume of reactants per day from equation (5.12)

$$V_f = \left(\frac{m}{\rho}\right)_{\text{Vernonia oil}} + \left(\frac{m}{\rho}\right)_{\text{FAME}} + \left(\frac{m}{\rho}\right)_{\text{NaHSO}_3}$$

Using the results of material balance and density of reactants

$$V_f = \left(\frac{1813.912}{880}\right) + \left(\frac{777.391}{840}\right) + \left(\frac{777.391}{1330}\right) = 3.57\ \text{m}^3/\text{day}$$

The volume of reactants for one reaction cycle

$$V_f = 3.57\frac{\text{m}^3}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{12.5\ \text{h}}{\text{cycle}} = 1.86\ \text{m}^3/\text{cycle}$$

The volume of reactor accounting the safety factor using equation (5.14)

$$V_r = \frac{4}{3} \times V_f = \frac{4}{3} \times 1.86 = 2.48\ \text{m}^3/\text{cycle}$$

- **Separating Tank**

For sulphited fatliquor production three separating tanks will be needed. One is for separating the neutralized oil from spent wash and the other is for separating the FAME from crude glycerol. The third one is for washing the sulphited fatliquor.

Volume of separating tank for purification of vernonia oil

Density of mixture feed into the separator

$$\rho_{mix} = (\%\ \text{Vernonia oil} \times \rho\ \text{Vernonia oil}) + (\%\ \text{water} \times \rho\ \text{water})$$
$$= (0.333 \times 880) + (0.666 \times 1000) = 959.707\ \text{kg/m}^3$$

The volume of separating tank will be

$$V = \frac{m}{\rho} = \frac{8242.194}{959.707} = 8.588\ \text{m}^3$$

The volume of separating tank per cycle

$$= \frac{8.588\ \text{m}^3}{\text{day}} \times \frac{1\ \text{day}}{24\ \text{h}} \times \frac{2\ \text{h}}{\text{cycle}} = 0.72\ \text{m}^3/\text{cycle}$$

Accounting 10% for safety, the volume of separating tank

$$= 0.72 + (0.1 \times 0.72) = 0.792\ \text{m}^3$$

Similarly the volume of separating tank for separation of FAME and crude glycerol and volume of separating tank for sulphited fatliquor washing is found to be 0.11 m^3 per cycle and 1.11 m^3 per cycle respectively.

- **Mixing Tank**

The volume of mixing tank for mixing methanol and sodium hydroxide using data from material balance and densities of feed material is found to be 0.053 m^3 per cycle and the construction material will be carbon steel.

- **Storage Tanks**

Select storage capacity of tanks for seven days. The volume of storage tanks is calculated from the material balance and respective density of materials as shown in Table (5.5) below.

Table 5.5: The capacities of storage tanks used in production of sulphited fatliquor

Storage Tank	Volume (m^3)
Vernonia oil	21.7
Sodium bisulphite solution	4.09
FAME	6.48
Methanol	2.77
Brine	36.44
Crude Glycerol	1.53
Sulphited Fatliquor	19.44

5.5 Total Capital Investment

The purchased equipment cost is determined from the capacities and construction material of the respective equipments [55, 56, 57].

Table 5.6: List of equipments and purchased price

Item	Capacity (m^3)	Cost ($)
Sulphitator	2.48	37500
Transesterification Reactor	0.24	1090
Distillery	-	18000
Condenser	-	13300
Reboiler	-	9300
Screw Press	-	14000
Filter Press	-	17600
Degummer	0.143	17900
Neutralizer	0.143	17900
Separating Tanks		
Purification of vernonia oil	0.792	3700
FAME separator	0.11	1300
Sulphited fatliquor washing	1.11	4300
Mixing tank	0.053	6700
Storage Tanks		
Vernonia oil	21.7	14900
Sodium bisulphite solution	4.09	11600
FAME	6.48	6800
Methanol	2.77	3900
Brine	36.44	20800
Crude Glycerol	1.53	2700
Sulphited Fatliquor	19.44	13800
Dryer	-	37600

Accounting the cost of auxiliary equipments cost to be $ 150000. The total purchased equipment cost is $ 424690 or Birr 8408862. The sulphited fatliquor production factory is a solid-fluid processing plant.

Table 5.7: Ratio factors for estimating CI items based on delivered equipment cost

1. Direct cost		
	Ratio	**Cost (Birr)**
Purchased equipment cost	100	8408862
Purchased equipment installation	39	3279456.2
Instrumentation and controls	13	1093152.1
Piping (installed)	31	2606747.2
Electrical (installed)	10	840886.2
Buildings (including service)	29	2438570
Yard improvements	10	840886.2
Service facilities (installed)	55	4624874.1
Land (if purchased)	6	504531.7
Total direct plant cost	**293**	**24637965.7**
2. Indirect cost		
Engineering and Supervision	32	2690835.8
Construction expenses	34	2859013.1
Total direct and indirect cost	359	30187814.6
Contractor's fee	18	1513595.2
Contingency	36	3027190.3
Fixed capital investment (FCI)	**413**	**34728600**
Working capital (WC)	**74**	**6222558**
Total capital investment (TCI)	**487**	**40951157.9**

5.6 Production Costs

5.6.1 Raw Material Cost

The major raw material in production of sulphited fatliquor is Vernonia seed and sodium bisulphite and auxiliary raw materials include methanol, sodium hydroxide and sodium chloride. Annual estimated cost of main raw material is presented in Table (5.8) below.

Table 5.8: Annual raw material requirement and cost estimates

Raw material	Unit price (Birr/kg)	Quantity per annum (kg/year)	Total cost (Birr/year)
Vernonia seed	2	2849263	5698526
Sodium bisulphite	14	93287	1306018
Methanol	80	28635	2290800
Sodium hydroxide	12	3090	37080
Sodium chloride	1.2	171803	206163.6
		Total	**9538588**

5.6.2 Operating Labor

In our country the cost of labor is not high. For production of sulphited fatliquor a total of 55 skilled and unskilled workers are required. Total unskilled worker required is 40.

Average salary per worker is 2000 Birr /month$= 2000 \times 40 = 180000$ Birr/month

Total skilled worker required 15.

Average salary per worker is 5000 Birr/month$= 5000 \times 15 = 75000$ Birr/month

Total salary for both skilled and unskilled workers is 155000 Birr/month.

Salary per year $= 155000 \times 12 = 1860000$ Birr/month

5.6.3 Utilities Cost

Electricity and water are the two major utilities used for production process of sulphited fatliquor production. The annual consumption and cost estimates at full plant capacity utilization from the energy balance and specification of equipments.

Table 5.9: Annual utilities requirement and cost estimates

	Unit	**Unit cost (Birr)**	**Quantity per year**	**Total cost (Birr)**
Electricity	kWh	0.4736	10000	4736
Water	m^3	3.25	3500	11375
			Total	**16111**

The annual raw material used, utilities and operating labor of the process is estimated as shown above. The other costs can be estimated as a function of fixed capital investment, total capital investment and/or total product cost as shown below in Table (5.10).

Table 5.10: Total product cost estimate

I – Manufacturing Costs (Birr)		
1. Direct production costs		
Raw materials	Calculated	9538588
Operating labour	Calculated	1860000
Direct supervisory and clerical labor	15% OL	279000
Utilities	Calculated	16111
Maintenance and repairs	5% FCI	1736430
Operating supplies	0.5% FCI	173643
Laboratory charges	10% OL	186000
Total direct production costs		**13975772**

2. Fixed charges		
Depreciation	10% FCI	3472860
Local taxes	2% FCI	694572
Insurance	0.5% FCI	173643
	Total fixed charges	**4341075**
3. Plant overhead costs	60% OL	1119600
	Total manufacturing costs	**19436447**
II – General Expenses		
1. Administrative cost	15% OL	279000
2. Distribution and Selling	10% TPC	2379998
3. Research and development	2% TPC	476000
4. Financing (Interest)	3% TCI	1228535
	General Expenses	**4363533**
	Total product cost	**23799980**

$$\text{Total product cost per kg} = \frac{\text{Annual TPC}}{\text{Capacity of the plant}} \ldots \ldots \ldots \ldots (5.15)$$

$$= \frac{23799980 \text{ Birr/year}}{825000 \text{ kg/year}} = 28.85 \text{ Birr/kg}$$

5.7 Financial Appraisal

Once the total product cost has been estimated, evaluation of the attractiveness of the proposed process using such measures of profitability net profit, rate of return, payback period, profitability index, internal rate of return and present worth is the next step.

Basis: 1 year full capacity operation

$$\text{Sales} = \text{Selling} \times \text{Capacity} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.16)$$

$$\text{Sales (sulphited fatliquor)} = 54 \text{ Birr/kg} \times 825000 \text{ kg/year} = 44550000 \text{ Birr/year}$$

$$\text{Sales (cake)} = 2 \text{ Birr/kg} \times 1827000 \text{ kg/year} = 3654000 \text{ Birr/year}$$

$$\text{Sales (crude glycerol)} = 3 \text{ Birr/kg} \times 726000 \text{ kg/year} = 217800 \text{ Birr/year}$$

$$\text{Total Sales} = 44550000 + 3654000 + 217800 = 48421800 \text{ Birr/year}$$

- **Gross profit**

$$\text{Gross profit} = \text{Sales} - \text{TPC} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.17)$$

$$= 48421800 - 23799980 = 24621820 \text{ Birr/year}$$

- **Net profit**

$$\text{Depreciation} = 10\% \text{ FCI} = 0.1 \times 34728600 = 3472860 \text{ Birr/year}$$

Assume the factory fully depreciate within ten years.

$$\text{Income tax} = 0.3 \times (\text{Gross profit} - \text{Depreciation})$$

$$= 0.34 \times (24621820 - 3472860) = 7190646.4 \text{ Birr/year}$$

$$\text{Net profit} = \text{Gross profit} - \text{Depreciation} - \text{Income tax}$$

$$= 24621820 - 3472860 - 7190646.4 = 13958314 \text{ Birr/year}$$

- **Rate of return on investment (ROI)**

$$\text{RORI} = \frac{\text{Gross profit} - \text{Depreciation}}{\text{TCI}} \times 100 \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5.18)$$

$$= \frac{24621820 - 3472860}{40951158} = 51.6\%$$

Annual percent return on average investment before income taxes is 51.6 percent, which is preferable value for investment opportunity.

Table 5.11: Cash flow for fatliquor production (× 10^6 Birr)

Year of Operation	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Fixed capital	-34.729										
Working capital	-6.2225										
Sales		48.4218	48.4218	48.4218	48.4218	48.4218	48.4218	48.4218	48.4218	48.4218	48.4218
Direct production costs		-13.976	-13.976	-13.976	-13.976	-13.976	-13.976	-13.976	-13.976	-13.976	-13.976
Gross profit		24.6218	24.6218	24.6218	24.6218	24.6218	24.6218	24.6218	24.6218	24.6218	24.6218
Cumulative Gross profit		24.6218	49.2436	73.8654	98.4872	123.109	147.731	172.353	196.974	221.596	246.218
Depreciation		-3.4728	-3.4728	-3.4728	-3.4728	-3.4728	-3.4728	-3.4728	-3.4728	3.4728	-3.4728
Gross profit – Depreciation		21.149	21.149	21.149	21.149	21.149	21.149	21.149	21.149	21.149	21.149
Income tax		7.1906	7.1906	7.1906	7.1906	7.1906	7.1906	7.1906	7.1906	7.1906	7.1906
Net profit		13.9583	13.9583	13.9583	13.9583	13.9583	13.9583	13.9583	13.9583	13.9583	13.9583
Cumulative Net profit		13.9583	27.9166	41.8749	55.8332	69.7915	83.7498	97.7081	111.666	125.623	139.583
Cash flow	-40.951	17.4311	17.4311	17.4311	17.4311	17.4311	17.4311	17.4311	17.4311	17.4311	17.4311
Cumulative cash flow	-40.951	-23.520	-6.0888	11.3423	28.7734	46.2045	63.6356	81.0667	98.4978	115.929	133.360
Net present value	-40.951	-25.104	-10.699	2.3976	14.3032	25.1266	34.966	43.9109	52.0426	59.4351	66.1556
Cumulative Net present value	-40.951	-66.055	-76.754	-74.356	-60.0532	-34.927	0.0394	43.9503	95.9929	155.428	221.584

- **Payback period**

The payback period from the cash flow table is calculated as shown below.

$$\text{Payback period} = 2 + \frac{5.0134}{17.9688} = 2.349 \text{ year or 2 years and 4 months}$$

The project pays back the original investment within 2 years and 4 months.

- **Profitability index (PI)**

$$\text{PI} = \frac{\text{Discount cash in flow}}{\text{Discount cash out flow}} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.19)$$

$$= \frac{\frac{17.4311}{(1.1)^1} + \frac{17.4311}{(1.1)^2} + \frac{17.4311}{(1.1)^3} + \cdots + \frac{17.4311}{(1.1)^{10}}}{40.9512} = \frac{107.107}{40.951} = 2.6$$

Profitability index 2.6 is a favorable investment since PI > 1.

- **Internal rate of return (IRR)**

IRR is also known as the discount rate or breakeven point that makes the project NPV equals to zero.

$$\text{NPV} = \text{NCF}_0 + \text{NCF}_1 \times \text{DF}_1 + \text{NCF}_2 \times \text{DF}_2 + \cdots + \text{NCF}_{10} \times \text{DF}_{10} = 0 \ldots\ldots (5.20)$$

$$\text{DF}_n = \frac{1}{(1+\text{IRR})^n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5.21)$$

Where CF is the cash flow

DF is the discount factor

n is the number of years

Iterate through various values of IRR to solve the above equation equal to zero.

$\text{NPV} = 0$

$$0 = -40.9512 + \frac{17.4311}{(1+\text{IRR})^1} + \frac{117.4311}{(1+\text{IRR})^2} + \cdots + \frac{17.4311}{(1+\text{IRR})^{10}}$$

Solve for IRR gives $\text{IRR} = 42\%$

Since IRR is greater than the company's rate of return 10% is a good investment opportunity.

6. Conclusion and Recommendation

6.1 Conclusion

In this research, production of sulphited fatliquor from locally available raw material *vernonia galamensis* seed oil via sulphitation reaction has been investigated. The three sulphitation reaction parameters affecting the degree of sulphitation namely reaction temperature, amount of sodium bisulphite and reaction time has been studied. The outputs of the experiment conducted have been analyzed by employing Design-Expert 7.0.0, three-level-three-factor face-centered CCD, through analysis of physicochemical characteristics and through application of synthesized sulphited fatliquor on leather.

Based on the analysis of experimental results, it is found that all the three process variables exhibited significant interaction effect on the degree of sulphitation. This shows that the capability of the design of experimental analysis in successfully capturing these effects. A reaction temperature of 70^0C, 30% by weight amount of sodium bisulphite solution and 12.5 h reaction time results an optimal value of 3.36% by weight degree of sulphitation which is better than a similar work done by El-Shahat H. *et al*. (2011) with 3.2% degree of sulphitation.

The physicochemical properties determined for the sulphited fatliquor and the physical tests determined for fatliquored leather met IS 14488 and BASF specifications respectively. The fatliquoring effect of the synthesized fatliquor on leather shows higher organoleptic and physical properties than that of the imported vegetable oil based sulphited fatliquor.

From the preliminary feasibility study for 2750 kg/day capacity sulphited fatliquor production plant Birr 40.95 million total capital investment (TCI) is required. The product cost was found to be 28.85 Birr/kg. The project was financially feasible with 51.6% rate of return on investment (RORI), Birr 66.16 million net present value (NPV), 2 years and 4 months payback period; and 42% internal rate of return (IRR).

Therefore, from experimental analysis and preliminary feasibility study we can conclude that sulphited fatliquor production using Vernonia oil has a considerable potential application on

leather processing industry as fatliquoring chemical. This is mainly because of its great performance on leather for fatliquoring, the potential of exploiting local resources and an easily affordable, adaptable and environmentally friendly production technology.

Finally it can be concluded that *Vernonia galamensis* seed oil sulphited fatliquor has a great potential for substitution of imported vegetable oil sulphited fatliquor in leather processing industry.

6.2 Recommendation

Further research has to be conduct on Vernonia oil fatty acid composition and its physicochemical characteristics using either GC or HPLC; and analysis of Vernonia oil sulphited fatliquor using FT-IR Spectroscopy, since it will help to know the exact composition of percent SO_3 and degree of fixation.

Industrially different types of fatliquor were used in blend for best outcome. So it is recommended to see the effect of Vernonia oil sulphited fatliquor in combination with other fatliquors.

In addition, further study is recommended on the potential application of vernonia oil sulphited fatliquor as emulsifier, anti-foaming agent and surfactant.

Further study on improvement of the sulphitation process reaction time and degree of sulphitation is also suggested. This can be achieved by using phase transfer catalysis (PTC). The two frequently prepared phase transfer catalysts are benzyl-tri-phenyl phosphonium chloride (BTPP) and tri-ethyl-benzyl ammonium chloride (TEBA).

Finally, it is also recommended to investigate the potential for commercialization of vernonia seed plantation for raw material supplement.

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Appendices

Appendix A: Composition of Vernonia Oil

Table A1: Fatty acid composition of Vernonia oil

Fatty Acid	Systemic Name	Formula	Structure	Wt%
Vernolic	Cis-12, 13-epoxycis-9-octadecenoic	$CH_3(CH_2)_{12}(CH)_4OCOOH$	18:1:1	72 – 80
Linoleic	Cis-9,cis-12-octadecadienoic	$CH_3(CH_2)_{12}(CH)_4COOH$	18:2	12 – 14
Oleic	Cis-9-Octadecenoic	$CH_3(CH_2)_{14}(CH)_2COOH$	18:1	4 – 6
Palmitic	Hexadecanoic	$CH_3(CH_2)_{14}COOH$	16:0	2 – 3
Stearic	Octadecanoic	$CH_3(CH_2)_{16}COOH$	18:0	2 – 3

(Source: Carlson *et al.* (1981) and Ayorinde *et al.* (1988))

Table A2: Vernonia oil characteristics

Property of Oil	Value
Iodine value, $gI_2/100g$ oil	104 – 108
Saponification value, mg KOH/g oil	165 – 210
Unsaponifiable, wt%	1.0 – 8.0
Refractive Index at 25^0C	1.4740 – 1.4860
Relative Index at 25^0C	0.9050 – 0.9730
Boiling temperature, ^0C at 760 mmHg	183 – 190
Heat of vaporization, kJ/kmol	24.32
Calorific value, kJ/g	33.33 – 35.55

(Source: Manuel des crops gras, AFCEG, Paris, (1992))

Table A3: Fatty acid composition of the major fatty oils and fats

Product	Saturated				Unsaturated		
	Lauric	**Myristic**	**Palmitic**	**Stearic**	**Oleic**	**Linoleic**	**Linolenic**
Beef tallow	-	3	24	19	43	3	1
Castor oil	-	-	1.0	1.0	3.0	4.2	0.3
Coconut oil	47	18	9	3	6	2	-
Coconut oil	45	20	5.0	3.0	6.0	-	-
Cod liver oil	-	8	17	-	22	5	-
Corn oil	-	-	11	2	28	58	1
Cottonseed oil	-	-	23.4	-	31.6	45.0	-
Linseed oil	-	3	6.0	-	-	74.0	17.0
Olive oil	-	-	14.6	-	75.4	10.0	-
Palm kernel oil	55	12	6.0	4.0	10.0	-	-
Palm oil	-	1	45	4	40	10	-
Peanut oil	-	-	8.5	6.0	51.6	26.0	-
Sesame oil	-	-	9	4	41	45	-
Soy bean oil	-	-	11.0	2.0	20.0	64.0	3.0
Sunflower oil	-	-	7	5	19	68	1

(Source: *J. Lewkowltsch, Chemical Technology and Analysis of Oils, Fats and Waxes* (London, Macmillan, 1922, 3 vols., 6th edition))

Table A4: Characteristic average values of the main fatty substance

Product	Density (g/ml)	Saponification value (mg KOH/g oil)	Unsaponifiable value (wt%)	Iodine value (g I_2/100g oil)	Solidification range (^{0}C)
Beef tallow	0.936 – 0.953	190 – 200	0.1 – 0.3	32 – 47	+30 to +38
Bees wax	0.950 – 0.966	99 – 100	52 – 55	6 – 15	+60 to +63
Castor oil	0.950 – 0.974	176 – 191	0.3 – 0.4	81 – 86	- 18 to - 10
Coconut oil	0.920 – 0.938	246 – 268	0.2 – 0.3	8 – 10	+ 14 to + 25
Cod liver oil	0.921 – 0.928	179 – 193	0.7 – 3.0	140 – 181	-10 to 0
Cotton seed oil	0.913 – 0.927	191 – 199	1.0 – 2.0	101 – 121	- 6 to - 1
Ground nut oil	0.916 – 0.921	188 – 197	0.3 – 1.0	83 – 103	- 3 to 0
Linseed oil	0.930 – 0.936	187 – 195	0.5 – 2.0	172 – 196	- 27 to - 16
Neat's-foot oil	0.913 – 0.919	192 – 196	0.1 – 0.6	68 – 81	- 12 to - 6
Olive oil	0.914 – 0.929	191 – 195	0.5 – 1.4	80 – 85	- 6 to 0
Palm oil	0.921 – 0.948	196 – 210	0.2 – 0.3	51 – 57	+ 31 to + 41
Rape oil	0.911 – 0.918	172 – 176	0.5 – 1.6	94 – 105	-10 to 0
Sesame oil	0.921 – 0.925	187 – 195	0.5 – 1.0	103 – 112	- 6 to - 3
Soy bean oil	0.922 – 0.934	188 – 195	0.5 – 1.5	124 – 133	- 18 to - 8
Sperm oil	0.875 – 0.890	125 – 149	35 – 44	71 - 93	+7 to +10

(Source: Pocket Book for the Leather Technologist, 4th edition, 2002)

Appendix B: Standard Specification of Sulphited Fatliquor

Table B1: Specification of sulphited fatliquor according to IS 14488

Characteristic	Sulphited Fatliquor Requirement
Chemical Property Requirement	
pH of emulsion (1:10 dilution in distilled water)	6.5 – 7.5
Total fatty matter, percent by mass	≥ 60
Unsaponifiable matter, percent by mass	≤ 15
Total alkalinity in mg equivalent per 10 g	≤ 5
Total sulphur as sulphites (SO_3) as, percent by mass	≥ 1.8
Total Ash, percent by mass	≤ 4.5
PCP content, mg/kg	≤ 5
Physical Property Requirement	
Pouring temperature, ^0C	≤ 25
Emulsion stability (1:10 ratio) for application, minutes	≥ 40
Odor	Shall be free from rancid or putrefactive odor of oil
Emulsion stability (1:10 ratio)	Shall remain stable for 40 minutes when mixed with 5% solutions of sodium chloride, calcium chloride magnesium sulphate and 5% basic chromium sulphate solution in separate containers without creaming and oil separation.
Sulphited fatliquor	Shall be capable of being readily washed out with water without leaving any oily feeling to hand.

Appendix C: Experimental Result

Table C1: Moisture content of Vernonia seeds

Run	Sample weight (g)			Moisture content (%)	Average Moisture content (%)
	W_1	W_2	$(W_1 - W_2)$		
1	4.115	3.826	0.189	4.9	**5.15**
2	4.012	3.808	0.204	5.4	
3	4.026	3.785	0.241	6.4	
4	4.014	3.863	0.151	3.9	
5	4.025	3.831	0.194	5.1	
6	4.027	3.826	0.201	5.2	

Table C2: Acid Value of *Vernonia galamensis* oil

Run	Titration Volume, ml	Colour Change
1	1.50	Gray to Pink
2	1.55	Gray to Pink
3	1.50	Gray to Pink
Average value	**1.52**	

Table C3: Saponification value of *Vernonia galamensis* oil

Run	Titration volume, ml	Colour Change
1	4.7	Pink to Red
2	4.8	Pink to Red
3	4.7	Pink to Red
Average value	**4.73**	

Table C4: Experimental processes conditions for sulphited fatliquor production

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	Amount of Vernonia oil (g)	Amount of FAME (ml)	Amount of sodium bisulphite (ml)
1	65	40	12.5	70	35.71	30.07
2	65	30	15	70	35.71	22.56
3	65	20	12.5	70	35.71	15.04
4	70	20	10	70	35.71	15.04
5	60	20	15	70	35.71	15.04
6	70	40	10	70	35.71	30.07
7	70	20	15	70	35.71	15.04
8	60	20	10	70	35.71	15.04
9	65	30	10	70	35.71	22.56
10	65	30	12.5	70	35.71	22.56
11	70	30	12.5	70	35.71	22.56
12	65	30	12.5	70	35.71	22.56
13	65	30	12.5	70	35.71	22.56
14	65	30	12.5	70	35.71	22.56
15	60	40	15	70	35.71	30.07
16	65	30	12.5	70	35.71	22.56
17	60	30	12.5	70	35.71	22.56
18	70	40	15	70	35.71	30.07
19	60	40	10	70	35.71	30.07
20	65	30	12.5	70	35.71	22.56

Table C5: Degree of sulphitation and pH for different processes variables

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	Degree of sulphitation (wt%)	pH Value (10% Emulsion)
1	65	40	12.5	3.17	7.78
2	65	30	15	3.31	6.86
3	65	20	12.5	2.58	7.44
4	70	20	10	2.45	6.84
5	60	20	15	1.83	6.38
6	70	40	10	3.06	6.30
7	70	20	15	2.96	6.59
8	60	20	10	1.81	7.44
9	65	30	10	3.30	6.83
10	65	30	12.5	3.27	7.47
11	70	30	12.5	3.36	7.11
12	65	30	12.5	3.30	7.34
13	65	30	12.5	3.28	7.42
14	65	30	12.5	3.31	7.39
15	60	40	15	2.48	7.61
16	65	30	12.5	3.29	7.49
17	60	30	12.5	2.65	7.57
18	70	40	15	3.23	7.42
19	60	40	10	2.82	7.30
20	65	30	12.5	3.32	7.34

Table C6: Total sulphur as sulphites (SO_3) of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	W_1 (g)	W_2 (g)	W_3 (g)	Degree of sulphitation (wt%)
1	65	40	12.5	2.106	40.0575	40.2521	3.1696
2	65	30	15	2.0765	37.3883	37.5885	3.3071
3	65	20	12.5	2.1481	35.2525	35.4143	2.5837
4	70	20	10	2.1311	23.3841	23.5361	2.4465
5	60	20	15	2.0824	35.2525	35.3635	1.8284
6	70	40	10	2.1181	40.0575	40.2463	3.0575
7	70	20	15	2.0365	37.7848	37.9603	2.9560
8	60	20	10	2.1129	23.3841	23.4956	1.8101
9	65	30	10	2.075	23.3841	23.5837	3.2996
10	65	30	12.5	2.0947	35.2525	35.4523	3.2718
11	70	30	12.5	2.0721	37.7848	37.9880	3.3638
12	65	30	12.5	2.0459	35.2525	35.4496	3.3046
13	65	30	12.5	2.1454	41.4873	41.6926	3.2824
14	65	30	12.5	2.1522	37.4848	37.6918	3.2991
15	60	40	15	2.0721	41.4873	41.6372	2.4814
16	65	30	12.5	2.1792	37.7848	37.9936	3.2866
17	60	30	12.5	2.0016	41.4873	41.6421	2.6528
18	70	40	15	2.0883	37.3883	37.5848	3.2276
19	60	40	10	2.0709	37.3883	37.5586	2.8208
20	65	30	12.5	2.0439	40.0575	40.2553	3.3196

Table C7: Total active ingredient of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	F (g)	E (g)	A (%)	B (%)	Total active ingredient (wt%)
1	65	40	12.5	2.71	0.62	54.23	12.4	66.63
3	65	20	12.5	2.72	0.43	54.43	8.6	63.03
5	60	20	15	2.37	0.58	47.43	11.6	59.03
7	70	20	15	2.66	0.61	53.23	12.2	65.43
9	65	30	10	3.09	0.49	61.83	9.8	71.63
11	70	30	12.5	2.65	0.69	53.13	13.8	66.93
14	65	30	12.5	2.97	0.59	59.42	11.8	71.29
16	65	30	12.5	2.96	0.58	59.18	11.6	70.78
18	70	40	15	2.72	0.71	54.43	14.2	68.63
20	65	30	12.5	2.90	0.62	57.97	12.4	70.37

Table C8: Unsaponifiable matter of Sulphited Fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	A (g)	V (ml)	B (g)	Unsaponifiable matter (wt%)
1	65	40	12.5	0.9151	7.2	0.4061	10.18
3	65	20	12.5	0.9440	8.2	0.4625	9.63
5	60	20	15	0.8606	5.8	0.3271	10.67
7	70	20	15	0.9831	9.0	0.5076	9.51
9	65	30	10	0.8925	6.4	0.3610	10.63
11	70	30	12.5	0.9234	7.4	0.4174	10.12
14	65	30	12.5	0.9328	7.7	0.4343	9.97
16	65	30	12.5	0.9389	7.8	0.4399	9.98
18	70	40	15	1.0140	8.6	0.4850	10.58
20	65	30	12.5	0.9389	7.8	0.4399	9.98

Table C9: Total alkalinity of sulphited fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	V (ml)	A (mg/10 g)
1	65	40	12.5	7.1	3.55
3	65	20	12.5	5.1	2.55
5	60	20	15	2.9	1.45
7	70	20	15	4.2	2.10
9	65	30	10	6.7	3.35
11	70	30	12.5	6.3	3.15
14	65	30	12.5	6.3	3.15
16	65	30	12.5	6.3	3.15
18	70	40	15	7.0	3.50
20	65	30	12.5	6.2	3.10

Table C10: Total Ash of Sulphited Fatliquor

Run	Reaction Temperature (^{0}C)	Amount of sodium bisulphite (wt%)	Reaction Time (h)	W_0 (g)	W_1 (g)	W_2 (g)	Ash content (wt%)
1	65	40	12.5	23.3805	27.4005	23.4960	2.8731
3	65	20	12.5	23.3805	27.3905	23.5160	3.3790
5	60	20	15	23.0788	27.0888	23.2269	3.6933
7	70	20	15	23.2095	27.2095	23.3300	3.0125
9	65	30	10	22.4634	26.4634	22.6038	3.5100
11	70	30	12.5	23.3805	27.3805	23.4998	2.9825
14	65	30	12.5	23.3841	27.3941	23.5093	3.1222
16	65	30	12.5	23.3805	27.4905	23.5109	3.1727
18	70	40	15	23.4634	27.6634	23.5462	1.9714
20	65	30	12.5	23.3841	27.3841	23.5058	3.0425

Appendix D: Calculation Part

D1: Purification of Crude Vernonia Oil

The total amount of crude Vernonia oil obtained from mechanical extraction is 5.0 liter out of 22 kg of Vernonia seed.

- **Degumming**

It is the removal of phosphatides, gums and other complex compounds the extracted crude Vernonia oil. Hence, based on the method discussed in previous chapter 3 wt% of distilled water is required for degumming process of crude oil.

$$\text{Amount of distilled water required} = \text{amount of Vernonia oil} \times 3\%$$

$$= 4.1\ \text{kg} \times 0.03 = 0.123\ \text{liter} = 123\ \text{ml}$$

- **Neutralization**

This step is used to neutralize the free fatty acids using appropriate amount of NaOH. Sodium chloride (about 10% of the weight of the oil) was added to help settle out the soap formed.

Amount of sodium chloride (makes the soap to settle faster) = 10 wt% of oil = 400g

The appropriate amount of alkaline solution (NaOH) required to neutralize the free fatty acid was calculated using molecular weight of triglycerides and the chemical reaction shown below. First of all, the composition of free fatty acid was determined from the acid value.

The acid value is determined by using titration. From equation (3.4)

$$\text{Acid value} = \frac{56.1 \times V \times N}{w}$$

Where V is the volume expressed in milliliter of 0.1N solution of ethanolic KOH

N is concentration of ethanolic KOH

w is weight in gram of the test portion

Hence,

$$\text{Acid value} = \frac{56.1 \times 5.4 \times 0.1}{2.5} = 12.12 \text{ mg KOH/g oil}$$

The percent composition of free fatty acid is calculated as

$$\%\ \text{FFA} = \frac{\text{AV}}{2} = \frac{12.12}{2} = 6.06 \text{ mg KOH/g oil}$$

From 4.4 liter (density of degummed vernonia oil = 0.91 g/ml) Vernonia oil

$$\text{FFA} = 4000 \text{ g oil} \times 6.06 \text{ mg KOH/g oil} = 24.24 \text{ g}$$

- **Molecular weight of Vernonia oil**

Table D1: Molecular Weight of Fatty Acids

Fatty Acids	**Elementary Formula**	**Constitutional Formula**	**Corresponding Fatty acid composition (%)**	**Molecular weight (kg/kmol)**
Vernolic	$C_{18}H_{32}O_3$	$CH_3(CH_2)_{12}(CH)_4OCOOH$	72 – 80	296
Linoleic	$C_{18}H_{32}O_2$	$CH_3(CH_2)_{12}(CH)_4COOH$	12 – 14	280
Oleic	$C_{16}H_{34}O_2$	$CH_3(CH_2)_{14}(CH)_2COOH$	4 – 6	282
Palmitic	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{14}COOH$	2 – 3	256
Stearic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{16}COOH$	2 – 3	286

Molecular mass of Triglyceride = Molecular mass of Vernolic acid
+ Molecular mass Linoleic Acid
+ Molecular mass Oleic Acid
+ Molecular mass Palmitic Acid
+ Molecular mass Stearic Acid

Taking average values for the fatty acids except Vernolic acid

Molecular mass of Triglyceride = $(296 \times 0.77) + (280 \times 0.13) + (282 \times 0.05)$

$+ (256 \times 0.025) + (284 \times 0.025)$ = 292.69 g/mol

The calculated free fatty acid was removed by using stoichiometric amount of sodium hydroxide. Hence, amount of NaOH required to neutralize the free fatty acids will be

$$= \frac{\%\text{FFA} \times \text{MW}_{\text{NaOH}}}{\text{MW}_{\text{FFA}}}$$

$$= \frac{40 \text{ g/mol}}{292.69 \text{ g/mol}} \times \%\ \text{FFA}$$

= 0.13667×0.606 %

= 8.28×10^{-4}g NaOH /g oil of was required to neutralize

Amount of NaOH needed for the neutralization of free fatty acid

$$= 4000 \text{ g oil} \times \frac{8.28 \times 10^{-4} \text{g NaOH}}{\text{g oil}} = 3.312 \text{ g NaOH}$$

D2: Physicochemical Properties of Purified Oil

- **Saponification Value**

The Saponification value was determined by using titration. 0.5N alcoholic KOH solution was prepared with the required concentration.

$\text{Mass of KOH} = \text{N} \times \text{equivalent weight} \times \text{Volume of solution in liter}$

$= 0.5\text{mol/litere} \times 1 \text{ liter} = 28.055\text{gm}$

$\text{Mass of HCL} = \text{N} \times \text{equivalent weight} \times \text{Volume of solution in liter}$

$= 0.5 \times 36.5 \times 1 \text{ liter} = 18.25 \text{ g}$

$$\text{V}_{\text{HCl}} = \frac{\text{m}}{\rho} = \frac{18.25}{1.16} = 15.73 \text{ ml}$$

Appendix E: Production Capacity of Leather Factories

Table E1: Production capacity of leather factories

SR.No.	Name of factory	Production capacity per day	
		Hide	Skin
1	Addis Ababa Tannery	1200	2400
2	Hora Tannery	0	300000
3	China Africa Tannery	0	10000
4	Mojo Tannery	500	8000
5	Colba Tannery	500	8000
6	Batu Tannery	0	8000
7	Mesaco Tannery	0	3000
8	Bahir Dar Tannery	0	4000
9	Ethiopian Tannery	1200	12000
10	Bale Tannery	400	2000
11	Friendship Tannery	1000	10000
12	ELICO Tannery	1050	15500
13	Kombolcha Tannery	0	6000
14	Dire Tannery	600	6000
15	Gelan Tannery	0	3000
16	Hafede Tannery	250	6000
17	Mersa Tannery	350	6500
18	East Africa Tannery	0	8000
19	Sheba Leather Industry	600	6000
20	Walia Tannery	1000	5000
21	Debere Birihan Tannery	0	6000
22	Faride Tannery	0	7000
23	United Vesan Tannery	0	5000
24	Habesha Tannery	0	4000
25	Koko Tannery	500	5000
26	DX Tannery	1200	8000

(Source: Ref. [15])

Appendix F: Technical Data

Table F1: Main characteristics of standard reactors available in the market

Capacity (m^3)	8	14	25	32	10	20	25	1	4	10	25	0.7
Diameter (m)	2	2.50	2.80	3.10	2.40	2.80	3.00	1.20	1.80	2.40	3.00	0.90
Total weight (kg)	9450	13900	21300	24100	11000	18000	21800	1830	2500	5200	7900	800
Exchange area (m^2)	18.6	26.6	40.0	45.6	19.8	33	38.8	4.45	10.90	11.15	19.50	3.4
Service Pressure (bar)	1.5	1.5	1.5	1.5	6	6	6	6	6	6	6	1.5
Material	AV	AV	AV	AV	AV	AV	AV	AI	AI	AI	AI	V

Where AV = glass-lined steel, AI = stainless steel and V = glass

(Source: Belay Woldeyes, Chemical Reaction Engineering Reactor Design, 2009)

Table F2: Technical data for oil press machine

Model	Capacity (kg/h)	Power (kW)	Net weight (kg)	Packing (mm)
6YL – 68	40	5.5	130	1050 × 660 × 760
6YL – 80	80 – 125	5.5	330	1320 × 440 × 695
6YL – 95	160 – 200	11	420	1910 × 610 × 765
6YL – 100	160 – 200	7.5	400	1860 × 550 × 695
6YL – 120	200 – 300	11	700	2060 × 610 × 770
6YL – 130	375 – 500	18.5	700	2320 × 700 × 780
6YL – 160	550 – 700	18.5	920	2020 × 700 × 780
6YL – 165	620 – 830	22 – 30	1600	2120 × 800 × 980

(Source: Ref. [55])

Declaration

I declare that the thesis for the M.Sc. degree at the University of Addis Ababa, hereby submitted by me, is my original work and has not previously been submitted for degree at this or any other university, and that all resources of materials used for this thesis have been duly acknowledged.

Name: Senait Gebeyehu Nadew

Signature: _____

Date of Submission:_____

This thesis has been submitted for examination with my approval as a university advisor.

Name: Ato Gizachew Shiferaw

Signature: _____

Date: _____

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SCHOOL OF CHEMICAL AND BIO ENGINEERING

Fatliquor Product Development from *Vernonia galamensis* Seed Oil via Modified Sulphitation Process

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By

Senait Gebeyehu Nadew

Approved by the Examining Board:

Taye Zewdu	Signature	01/01/2015
Chairman Department's Graduate Committee		Date
Ato Gizachew Shiferaw		
Advisor	Signature	Dec. 29/2014 Date
Ato Teshome Worku		
Internal Examiner	Signature	29/12/2014 Date
Ato Lelissa Daba		
External Examiner	Signature	01-01-15 Date