Addis Ababa University

Addis Ababa Institute of Technology

School of Chemical and Bio Engineering

Process Engineering Stream

Synthesis of Ethyl Ester Sulfonate Surfactant (EESS) from Castor Oil via Transesterification and Sulfonation for Detergent Application

A Thesis Submitted to the School of Chemical and Bioengineering of Addis Ababa Institute of Technology, Department of chemical engineering in Partial Fulfillment of the Requirements for the attainment of the Degree of Master of Science in Chemical Engineering under Process Engineering Stream.

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ABSTRACT

Due to the need to preserve natural resources, there is a growing need for renewable and biodegradable raw materials for industrial production. According to oleochemistry research, renewable resources have advantages over petrochemicals that make them ideal for making ecologically and consumer-friendly goods. In this investigation, unusual and environmentally friendly methods were used. Transesterification of castor oil was followed by sulfonation with sulfuric acid to produce anionic ethyl ester sulfonate (EES) surfactant. The synthesis of fatty acid esters from castor oil utilizing ethanol as a transesterifying agent and an alkaline catalyst was improved using a box behnken experimental design that took into account variables (reaction duration, catalyst quantity, and oil:ethanol molar ratio). Using a response surface curve and analysis of variance, the impacts and significance of the models on the response variable and ethyl ester yield produced from castor oil were investigated. The best yield was obtained using an oil:ethanol molar ratio of 1:16, a catalyst concentration of 1.00 wt.%, and an 80-minute reaction period. The effects of the EESS sulfonation reaction variables (sulfonation temperature, sulfonation duration, and sulfonating agent/ethyl ester (EE) molar ratio) on yield were studied using a one variable at a time experimental design (OVAT). According to the OVAT study, the best sulfonation settings for synthesizing EESS from castor oil were 80°C sulfonation temperature, 3.00 hours sulfonation duration, and a molar ratio of 1:1 H2SO4/EE, resulting in an EESS yield of 78.4%. The FTIR and NMR (-CH) groups, as shown by the FTIR and NMR (-CH) groups, were verified in the synthesized product, indicating the intended EESS product. EESS had a critical micelle concentration of 1.57 mol/L and an active matter concentration of 64.35%.

Key words: Ethyl ester sulfonate surfactant, sulfonation, transesterification

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ACRONYMS

AES	Alcohol ether sulfonates
AM	Active matter
ANOVA	Analysis of variance
AOS	α-olefin sulfonates
AS	Alkyl sulfates
ASTM	American Society for Testing and Materials
BBD	Box Behnken design
CMC	Critical micelle concentration
EE	Ethyl ester
EESS	Ethyl ester sulfonate surfactant
FAES	Fatty acid ester sulfonate
FTIR	Fourier-transform infrared spectroscopy
HLB	Hydrophilic lipophilic balance
LABS	Linear alkylbenzene sulfonates
MES	Methyl ester sulfonate
NMR	Nuclear magnetic resonance
OVAT	One parameter at a time
RSM	Response surface methodology
SEFMES	Sesame fatty methyl ester sulfonate
SMES	Sodium methyl ester sulfonate
WCO	Waste cooking oil

CHAPTER ONE

1. INTRODUCTION

1.1. Background

Surfactants are important in many industries, including agriculture, manufacturing, and common domestic uses. They are mass-produced to fulfill the demands of many applications. Washing and cleaning account for more than half of overall surfactant consumption across the various applications Surfactants in detergent formulations are categorized into four types depending on their polar head group: anionic, nonionic, cationic, and amphoteric surfactants. Among them, anionic surfactants are the most extensively utilized, owing to their ease of manufacture and low cost. Petrochemicals, such as benzene, linear paraffin, olefins, and alcohols, are used as intermediates in the production of anionic surfactants. Anionic surfactants having a hydrophobic and a hydrophilic (polar) group include alkyl sulfates (AS), a-olefin sulfonates (AOS), and linear alkylbenzene sulfonates (LABS) (yu, zhao, and Bayly 2008). These anionic surfactants are appropriate for a wide range of detergent applications due to their outstanding cleaning and foaming characteristics. Their low-cost manufacturing and varied performance lead to their extensive usage in the detergent industry and other related industries (Knepper and Berna 2003).

Linear alkylbenzene sulfonate (LABS), which is manufactured from petroleum derivatives, is the most extensively used anionic surfactant in both residential and industrial uses. According to data from the chemical development institute, Ethiopia has purchased more than 15 billion tons of LABSA from various foreign nations during the previous eight years. While natural petroleum reserves are diminishing, petroleum use is increasing. Because of the rising need to conserve scarce resources, scientists have focused their efforts on the quest for renewable and biodegradable raw materials for industrial activities. (Ranji, Babajanzadeh, and Sherizadeh 2019). Renewable resources have regularly demonstrated benefits when compared to petrochemical raw materials in order to provide a high degree of product safety for customers and the environment, and may thus be regarded as the optimal raw material base. Using vegetable fats and oils, according to oleo chemical research, allows the production of robust, competitive goods that are both ecologically and consumer-friendly. (Hill 2001).

The oleochemical process of trans-esterifying and sulfonating vegetable oils produces anionic surfactants called fatty acid ester sulfonates. They have a variety of positive properties that make them suitable for a variety of uses. Because of their outstanding skin friendliness, they are extremely advantageous for laundry detergent, body care formulations, and hand dishwashing formulations. They also have high water hardness stability and biodegradability, allowing them to be used in hard water. The two major processes involved in the synthesis of fatty acid ester sulfonate surfactants are transesterification and sulfonation reaction. Because of its high reactivity and petroleum origin, other forms of alcohol can be utilized to carry out the transesterification reaction, although methanol is the most commonly used. However, ethanol is an environmentally beneficial alternative alcohol that may be produced from a range of agricultural wastes. The sulfonation reaction follows transesterification and is carried out using various sulfonating agents such as sulfuric acid, sulfur trioxide, and chlorosulfuric acid depending on numerous conditions. (Ivanova et al. 2017).

The castor seed plant is one of Ethiopia's natural resources for oilseeds. Ethiopia also produces a large volume of castor seed (15,000 tons) each year. Castor oil is a non-edible oil derived from the castor seed plant (Ricinus communis L.), having several uses in the chemical industry. This plant, which is native to various areas of the nation, belongs to the Euphorbiaceous family. Several procedures, including solvent extraction and mechanical pressing, can be used to obtain castor oil from castor seed. One of Ethiopia's natural oil seed resources is the castor seed plant. Ethiopia also produces a significant amount of castor seed (15,000 tons) each year. Castor oil is a non-edible oil produced from the castor seed plant (Ricinus communis L.). It has numerous applications in the chemical industry. This plant is native to numerous parts of the country and is a member of the Euphorbiaceous family. Castor oil may be extracted from castor seeds in several ways, including solvent extraction and mechanical pressing. (Bekele et al. 2018).

Transesterification and sulfonation of non-edible castor oil accessible in Ethiopia were used in this work to make ethyl ester sulfonate anionic surfactant. This can be used in place of the more often used linear alkyl benzene sulfonate. Because of its cheap cost, low toxicity, accessibility, point of reaction for varied chemical processes, and position as a renewable agricultural resource, this non-edible castor oil was chosen as a viable raw material for this inquiry.

1.2. Statement of the Problem

In the face of rising demand for ecologically benign surfactants, the manufacture of fatty acid ester sulfonate surfactants to replace LABSA poses tremendous obstacles. These surfactants are meticulously produced using a varied variety of vegetable oils such as sesame oil, coconut oil, and palm oil in a painstaking procedure including transesterification and sulfonation processes. However, the use of edible oils as the principal feedstock for surfactant synthesis raises serious concerns about possible conflicts with the global food supply and increasing food security concerns. Furthermore, the common practice of using methanol as the transesterifying agent throughout the transesterification process creates serious environmental concerns. Currently, the manufacturing of methanol is primarily reliant on fossil fuels such as natural gas or coal, which contributes to the current ecological crisis.

However, the use of edible oils as the principal feedstock for surfactant synthesis raises serious concerns about possible conflicts with the global food supply and increasing food security challenges. Furthermore, the common practice of using methanol as the transesterifying agent throughout the transesterification process creates substantial environmental concerns. Currently, the manufacturing of methanol is primarily reliant on fossil fuels such as natural gas or coal, contributing to the current ecological crisis. Furthermore, the study aims to use an ecologically favorable strategy by using ethanol, a renewable and environmentally beneficial alcohol, as an alternative transesterifying agent. This admirable endeavor reflects a paradigm change toward the synthesis of ethyl ester sulfonate surfactants, which is distinguished by a less ecological imprint and a greater dedication to sustainability. This project marks a substantial change in the synthesis of ethyl ester sulfonate surfactants, with a focus on minimizing environmental effect and a strong commitment to sustainability.

1.3. Objectives

General Objective

- The main objective of this study was synthesizing and characterizing of sulfonated fatty ethyl ester surfactant from castor seed oil as an alternative surfactant for detergent application.

Specific Objectives

- To extract, refine and characterize castor oil from castor seed.
- To synthesis, optimize and characterize ethyl ester from extracted castor oil.
- To synthesis and characterize ethyl ester sulfonate surfactant and ethyl ester sulfonate surfactant-based detergent.

1.4. Significance of the Study

The production of ethyl ester sulfonate surfactants from castor oil for detergent applications is significant. The study is a first in the field, going into uncharted terrain and improving understanding in surfactant chemistry and sustainable detergent composition. The study tackles the increasing demand for ecologically friendly procedures in the detergent sector by exploiting castor oil as a feedstock This emphasis on sustainable detergent composition becomes a prominent issue in the thesis, emphasizing the significance of lowering cleaning products' environmental effect. The research also includes an in-depth examination of the environmental consequences of ethyl ester sulfonate surfactants generated from castor oil, revealing important information about their ecological impact, biodegradability, and toxicity. The thesis study contributes to a thorough knowledge of their potential environmental advantages by analyzing their performance as greener alternatives to conventional surfactants. Furthermore, process improvement and the study of new reaction conditions and characterisation methodologies contribute to technical developments in the sector. The thesis' results have practical applicability, providing significant information for detergent makers looking for sustainable alternatives..

1.5. Scope of this Study

This study generally covered extraction and characterization of castor oil. Preparation, optimization and characterization of ethyl ester. And synthesis of ethyl ester sulfonate surfactant through sulfonation process and characterization of produced EESS using standard procedures and test methods. Finally, synthesis of EESS-based liquid detergent and characterization of EESS-based liquid detergent.

CHAPTER TWO

2. LITRETURE REVIEW

2.1. Background

Surfactants have amphiphilic structures with hydrophilic and hydrophobic components. Surface-active properties such as surface concentration, surface tension decrease, and micelle formation in bulk solution are attributed to these distinct structures. As a result, they are often found in cleaning, wetting, emulsifying, and dispersing compositions. The most prevalent type of surfactant-containing product used in the household is laundry detergents, cleaning agents, and personal care products (Joshi 2017). The hydrophilic functional group of surfactant molecules prefers interaction with polar substances such as water, metals, and other ions. The hydrophobic component, which is nonpolar, prefers interaction with hydrophobic substances such as the hydrocarbon phase. Surfactants are used in vast amounts in households and business every day, and most of them end up in different environmental compartments (soil, water, sediment). In 2006, the production of surfactants climbed to 12.5 million tons. These statistics will very certainly climb as the detergent and cosmetics businesses grow. Based on the nature of their head groups, surfactants are categorized into four types: anionic, cationic, nonionic, and zwitterionic. To preserve charge neutrality, anionic and cationic surfactants are charged, and a counterion of opposite charge is attached to the head group; metal cations are common anionic surfactant counterions, and halogen ions are common cationic surfactant counterions. Nonionic surfactants have no charge on their head group, whereas zwitterionic surfactants have two distinct and opposing charges (positive and negative) on the molecule at either adjacent or nonadjacent positions. (Ivanković and Hrenović 2010).

2.2. Classification of Surfactants

Surfactants are commonly utilized in liquid solutions, hence categorization based on hydrophilic group type is appropriate. Surfactants were categorized according to their hydrophilic group as follows: (Piorr 1987):

- Anionic surfactants
- Cationic surfactants
- Nonionic surfactants
- Amphoteric surfactants

2.2.1. Anionic Surfactants

These surfactants are the most often used class in industrial applications due to their low manufacturing costs and extensive use in practically every sector. An anionic surfactant with a hydrophobic chain length of 12-16 carbon atoms for optimal detergency. Because linear chains are more efficient and biodegradable, they are suggested for use in various detergent compositions. The most common hydrophilic groups are carboxylates, sulphonates, phosphates, and sulphates. The following is a general formula for an anionic surfactant: (Tadros, 2005)

- Carboxylates
- Sulphates
- Sulphonates
- Phosphates

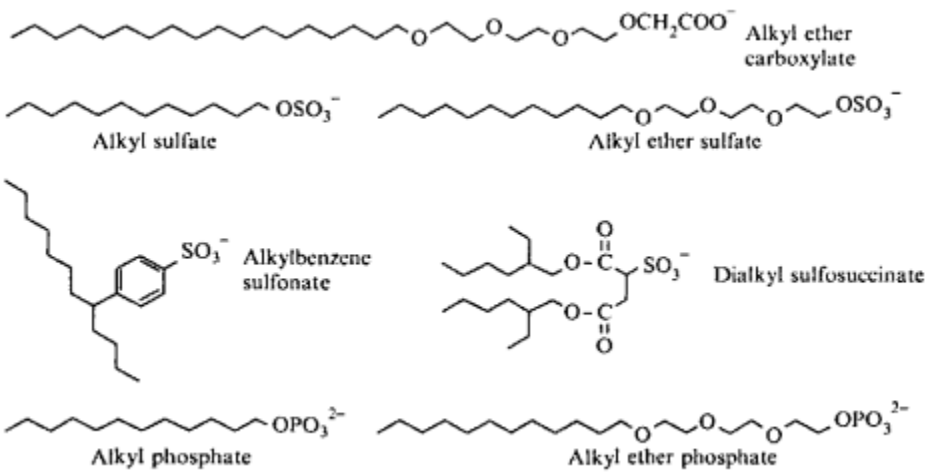

Figure 2-1 Structures of some anionic surfactants

2.2.2. Cationic surfactants

In aqueous media, cationic surfactants that additionally include a hydrophobic hydrocarbon group and one or more hydrophilic groups dissociate into cation and anion. In this scenario, however, the cation is the carrier of surface-active properties. The majority of cationic surfactants used in detergent compositions have a positively charged nitrogen atom in their core. In general, the preferred solubilizing anion is a halide or methosulfate ion. Quaternary ammonium compounds (quats), notably dioctadecyl dimethylammonium chloride, are used as antistatic agents due to their high antistatic action. Fabric softeners like quaternary ammonium and ethoxylated quats are commonly used. It works by reducing friction between fibers and between fibers and the skin, making it an excellent hair conditioner. (Yu, Zhao, and Bayly 2008).

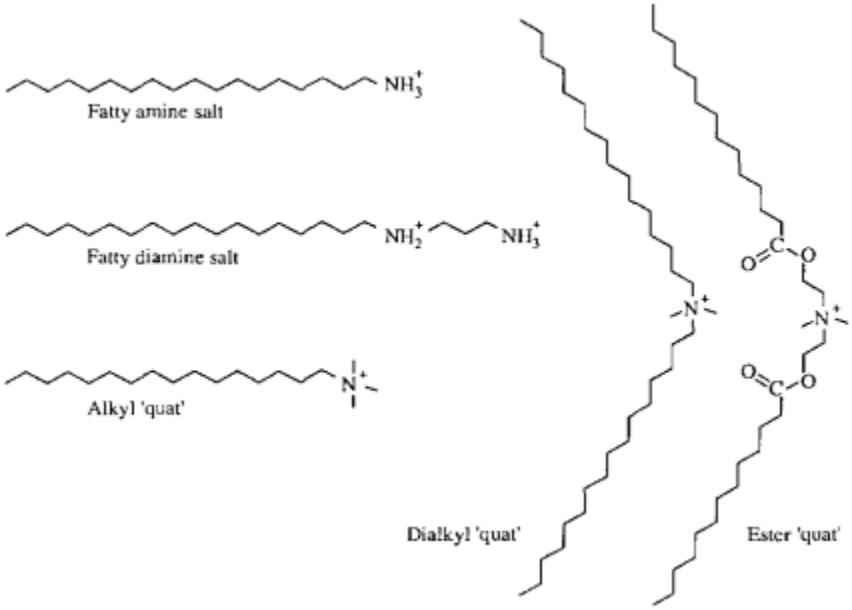

Figure 2-2 Structures of some cationic surfactants

2.2.3. Nonionic Surfactants

Because of their hydrophilic group, alcohol, phenol, ether, ester, or amide are non-dissociable surfactants that do not ionize in aqueous solution. These surfactants are resistant to water hardness deactivation because they lack an electrical charge. They are powerful grease removers that may be found in laundry detergents, household cleaners, and hand dishwashing solutions. Because of the existence of a polyethylene glycol chain formed by Because of ethylene oxide polycondensation, a high fraction of these nonionic surfactants are hydrophilic. Nonionic surfactants are expected to be the most often used in medicine delivery applications. Nonionic surfactants include polyol esters, polyoxyethylene esters, poloxamers, and pluronics. Polyethylene glycol (PEGs) make up the majority of polyoxyethylene esters. Nonionic surfactants that are commonly utilized are ethers of fatty alcohol. Non-ionic surfactants help to reduce the hardness sensitivity of the surfactant system. (Joshi 2017).

2.2.4. Amphoteric Surfactants

Amphoteric surfactants feature a lengthy hydrophobic hydrocarbon chain and a spacer group that connects the hydrophilic positive and negative charged centers. As a result, this surfactant preserves overall charged neutrality. Amphoteric surfactant characteristics are essentially determined by the length of the hydrophobic hydrocarbon chain, the number of methylene segments in the spacer, the positive and negative charged groups, and their relative location. The ionic activity of amphoteric surfactants is affected by the pH of the solvent. They exhibit cationic behavior below the isoelectric points and anionic behavior above the isoelectric points. In the isoelectric point region, they assume the form of zwitterions. (Sarkar et al. 2021).

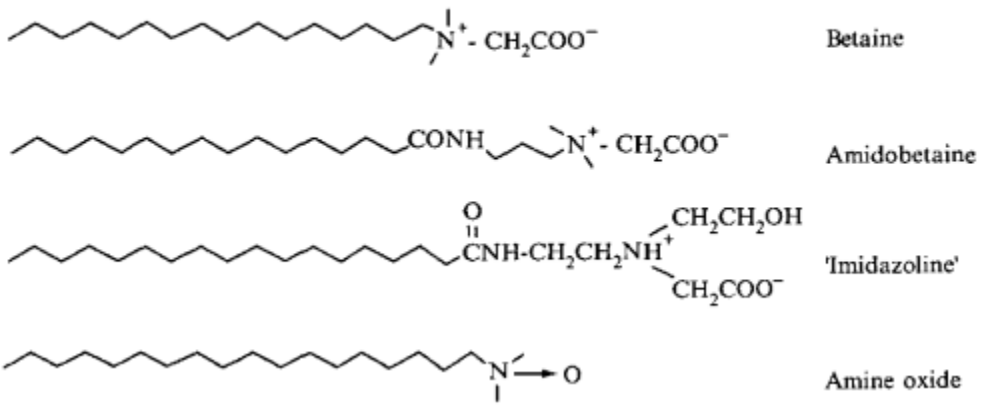

Figure 2-3 Structures of some amphoteric surfactants

2.3. Application of Surfactants

Surfactant is a significant component of personal care products, laundry detergent, oil recovery industries, food, agriculture, and nanotechnology, among others. Surfactants come in a variety of forms, but the most common are cationic, anionic, and nonionic, which are utilized in a variety of applications.

2.3.1. Detergent

Detergent is an effective cleaning solution because it contains one or more surfactants as well as other compounds. Surfactants are used to remove filth off clothes, skin, and household items, particularly in the kitchen and bathroom. It breaks down the contact between oil and water, allowing filth and oil to be suspended and therefore removed. (Duarte et al. 2010).

2.3.2. Oil Recovery

Surfactants of many types have been used in the oil recovery process. Some of the most common surfactants used in laboratories. In oil recovery, anionic surfactants are the most often used surfactants. Anionic surfactants used in the oil recovery process include carboxylates, sulfates, and sulfonates. Petroleum sulfonates, internal olefin sulfonates, synthetic sulfonates, and alkoxy sulfonates have been the most widely used surfactants. (Levitt et al. 2006).

2.3.3. Agriculture

Surfactants lower the surface tension of herbicide, pesticide, and fungicide spray solutions, allowing for closer contact between plant surfaces and spray droplets. Pesticides come into close contact with the surface of the leaf, hence they are used as crop protectors. Ethoxylated alcohol, alkylphenols, alkylamines, and sorbitan are typical pesticide surfactants. Organosilicone-derived surfactants have been used in commercial sprays (Zelená and Veverka 2007).

2.3.4. Food

Surfactants are used in food manufacturing for oil solubilization, liquor emulsification, and cholesterol extraction. Nonionic surfactants are the most common type of surfactant used as a food emulsifier in the food business. Low mass surfactants are very mobile at the interface and can help to reduce interfacial tension. As a result, during the emulsification process, they normally cover the newly created oil-water interface. Common examples include lecithin, monoglycerides, and glycolipids. A surfactant with a large molecular weight protects the protein and carbohydrate groups. The protein's opposing charge binds to the surfactant's head group. (Shachi Tiwari 2018).

2.4. Raw Materials for Production of Surfactants

Surfactants can be produced using both petrochemical feedstocks and renewable resources (plant and animal oils). They are an extremely interesting product group since they were originally derived from renewable resources, even though the majority of surfactants produced now are chemically manufactured from petroleum. Such synthetic tension active chemicals, however, are frequently toxic and difficult to breakdown by microbial activity. Renewables, however, remain essential, and technology for manufacturing surfactants from both types of feedstocks are widely used today. Patel, Theiß, and Worrell (Patel, Theiß, and Worrell, 1999). Crude oil, aromatics, alkaylates, linear paraffins, and olefins comprise the first class, whereas palm oil (+kernel oil), tallow, and coconut oil are the most prominent members of the group of renewable resources. Natural oils are used to create sulfonated ethyl esters. (Knepper and Berna 2003).

2.5. Fatty Acid Ester Sulfonate Surfactant

FAESs are anionic surfactants derived from vegetable oil by transesterification and subsequent sulfonation. Linear alkylbenzene sulfonates (LASs), alkyl sulfonates (ASs), and alpha olefin sulfonates (AOSs) are extensively used as detergent surfactants. However, as a result of the two oil crises in the 1970s, detergent makers were interested in natural fat- and oil-based surfactants rather than petroleum-based surfactants, and FAESs as a viable detergent component were investigated. FAESs offer strong surface-active properties and excellent detergency performance as a significant component in laundry detergent. (Tobori and Kakui 2019).

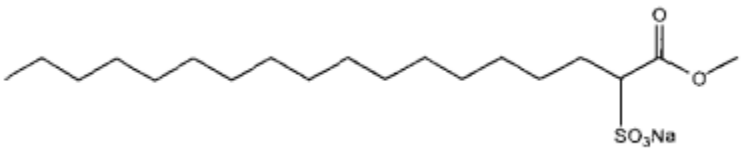

Figure 2-4 General structure of fatty acid ester sulfonate

2.5.1. Rationale for Fatty Acid Ester Sulfonate Surfactant Production

The most prevalent petrochemical-based surfactants are linear alkyl benzene sulfonates (LABS), alpha-olefin sulfonates (AOS), alcohol sulfates (AS), and alcohol ether sulfonates (AES). LABS was renowned as the detergent industry's workhorse in the twentieth century because to its widespread use in laundry detergent and home cleaning products (Akyüz and Roberts 2002). However LABS was under continual pressure to reduce its usage due to a significant spike in crude oil prices around the turn of the millennium. LABS became much less competitive than other surfactants when crude oil prices soared in the first decade of the new century. (Siwayanan et al. 2021).

Furthermore, the buzzwords "green" and "eco-friendly" were popular phrases in detergent marketing between 2000 and 2010, aggravating the need to limit the usage of LABS (Guala and Merlo 2013). This innovation poses a substantial problem for detergent formulators in terms of developing strategies to boost green oleochemical-based surfactants while lowering harmful detergent components such phosphates in detergent formulations (Kohler 2017). Furthermore, this problem has raised concerns regarding the environmental impact of LABS on aquatic ecosystems. In these cases, detergent makers shift their attention to detergent solutions that address financial, environmental, and sustainability problems. (Siwayanan et al. 2015).

2.5.2. History of Sulfonated Fatty Acid Ester Synthesis

The early 1950s saw the beginning of the development of oleo chemical-based sulfonated ester. The first study on MES was undertaken by researchers at the United States Department of Agriculture's (USDA) Eastern Regional Research Laboratory. Initially, the USDA's MES study concentrated on the C16/C18 fatty acid compositions of bovine tallow. Due to its comparable composition to beef tallow, extensive research on palm oil was undertaken from the 1960s until the 1990s. Various industries and academic laboratories explored the processes, techniques, approaches, and characteristics of -MES reactions throughout this time. (Siwayanan et al. 2021).

FAES is associated with a number of early development restrictions, including low solubility, a high proclivity to hydrolyze, a lengthy processing time, irritancy, dark hue, and the presence of skin sensitive components. Due to the unfavorable characteristics of FAES at the time, the detergent industry was cautious to scale-up FAES technology into large-scale manufacturing.

However, these technological challenges were addressed by many FAES technology providers via ongoing research and excellent manufacturing practice. As a result, the technology for producing high-quality FAES became commercially available in the early 1990s. However, due to a lack of manufacturers for FE and its consequent FAES, there has been little progress in the creation of FAES-based laundry detergent powders. -MES became a key focus of interest in the detergent business throughout the 2000s. It was propelled by the rise of palm oil-based biodiesel in Southeast Asia, which offers abundant chances for palm oil-based saturated C16 carbon chain ME (C16ME) at a cheap cost. (Ahmad et al. 2007).

In early 2010, the technology for economically producing high-quality MESs became available thanks to advances in sulfonation, bleaching, and neutralization. This innovative technology was introduced in Japan in 1991, and a new compact detergent was created. Additional tiny goods were created using the improved MESs. In terms of environmental friendliness, performance, manufacturing cost, and sustainability, C16MES created from C16ME outperformed LABS. Furthermore, C16MES is noted for its higher detergency (ability to remove stains from fabric) as compared to -MES formed from ME with other carbon chain lengths, such as C14 and C18 carbon chains. As a result, C16MES has tremendous potential not only as a single surfactant but also as a co-surfactant in the production of laundry detergent powders. (Tobori and Kakui 2019).

2.5.3. Recent Works on Sulfonated Fatty Acid Ester Production

Many studies have studied the synthesis of sulfonated fatty acid ester surfactant via transesterification and sulfonation. Some literatures on FAES production are summarized below:

(Soy, Kipkemboi, and Rop 2020) trans-esterified sesame oil to produce sesame fatty methyl esters (SEFAMEs), which were then used to make sesame fatty methyl esters sulfonate (SEFAMES). The FTIR spectra of SEFAME exhibited methyl ester peaks at 1418-1376 cm-1, suggesting successful oil trans-esterification. SEFAMES revealed spectrum bands corresponding to sulfonic groups at 1419, 1129, and 1048 cm-1, suggesting successful surfactant synthesis. The existence of saturated and unsaturated chains in SEFAMESO and its precursor, as verified by the HNMR spectra, indicated that oil was effectively trans-esterified. The predicted HLB value was lower than that of SDS, but the Krafft point and foam stability were comparable to those reported for methyl esters sulfonates-containing cleaning and wetting agents. CMC and SEFAMESO values were lower than SDS values, indicating that performance might improve. However, because the evaluated solution characteristics were based on a freshly synthesized surfactant, an evaluation of its stability over time should be done. Other application attributes, such as wetting and emulsifying capabilities, should also be investigated for medical and cosmetic uses, according to the research.

Waste cooking oil (WCO), a low-cost raw source, was esterified to produce the environmentally friendly anionic surfactant fatty acid methyl ester sulfonate (MES), which was subsequently sulfonated using chlorosulfonic acid. Yields from WCO MES production (W-MES) achieved 78%. After a successful preparation, the finished product had an a-MES concentration of 66.60% and a disalt content of 4.7%. The chemical structures of W-MES and S-MES are substantially comparable, according to FTIR and NMR data. Surface tension measurements and an examination of MES's physio-chemical properties indicated that it had a low CMC. When compared to other anionic surfactants, W-MES is more resistant to calcium ions. Because of its outstanding detergency and constant foamability, MES is a potential detergent material.

The method of producing synthetic MES, according to Slamet, Ibadurrohman, and Wulandari (2017), includes esterifying and transesterifying crude palm oil, as well as sulfonation, refining, and neutralization. TiO2 nanoparticles are added to surfactants to improve their capacity to remove dirt and break down organic compounds. To create MES, the mole ratios of the reactants in the esterification and transesterification processes, as well as the mole ratios of methyl esters to NaHSO3 in the sulfonation reaction, are modified. Despite a 14.1% mass loss, the methyl ester sulfonate is thermally stable at reservoir temperature. FTIR spectra verified the sulfonate group (S=O) at 1158 cm-1, indicating that this chemical is unquestionably methyl ester sulfonate.Castor Oil as a Potential Feedstock for EESS.

Castor oil has long been used in the chemical industry as a highly renewable feedstock. It is a vegetable oil derived from the seeds of the castor oil plant (Ricinus communis L.). Castor is a flowering plant in the Euphorbiaceous genus of spurges. It is native to Eastern Africa, India, and the Southeast Mediterranean Basin, although being found across tropical climates. Castor seeds are used to make castor oil, which has several uses. Between 40% and 60% of the oil in the seeds is triglyceride-rich ricinolein. The seed contains the toxin ricin, which is found in lower concentrations throughout the plant. The growth pattern and appearance of the castor oil plant can vary greatly. Breeders have selected a range of cultivars for leaf and flower color as well as oil output, increasing diversity. It is a fast-growing perennial shrub that can reach the size of a small tree (12 meters or so). Globally, a million tons of castor seeds are produced each year. With India, China, and Brazil producing over 60% of the world's supply, Ethiopia also produces a substantial quantity (15,000 tons). Castor may be cultivated in areas like as lower and middle Awash, Kobo, Afar, and Metema where bread wheat, maize, and tef cannot since it is resistant to moisture stress in Ethiopian circumstances. Perennial castor can be grown as hedges and shelters for humans, animals, or coffee. Only coconut has a greater oil content than castor, which has a higher output than noug, linseed, and Ethiopian mustard. Oil may be found in castor seed. Ricinoleic acid accounts for 90% of the oil's constituents. The high ricin oleic acid content of the oil makes it special, and the ricin oleic acid's hydroxyl functionality gives the oil good oxidation stability, a long shelf life, and a site of reaction for several chemical reactions. Based on those properties and high availability castor oil was selected for this study.

Figure 2-5 Castor plant and seed

2.6. Production Process of Sulfonated Fatty Acid Ester Sulfonate Surfactant

sulfonated fatty acid ester sulfonate surfactant produced in four steps:

1. Extraction of vegetable oil
2. Transesterification of vegetable oil
3. Sulfonation of fatty acid ester
4. Bleaching and Neutralization

2.6.1. Extraction of Vegetable Oil

Many plants contain extractible oils, which have been used for centuries as food or in cosmetic formulations. Some of these plant-based oils have recently aroused scholars' interest as a source of renewable energy, notably for biodiesel fuel manufacturing. The oil content of oleaginous seeds, nuts, kernels, or fruit pulps ranges from 3% to 70% by weight and has chemical structures similar to animal fats. Among the 40 recognized plant oil sources that provide edible oils are soybean, sunflower, groundnuts, rapeseed, coconut, and oil palm. additional oilseeds that are less economically important but are highly regarded because to their critical roles in one or more of the following processes: Castor, safflower, shea, neem, and tung oils, among others, are used in the creation of soap, chocolate, margarine, and biodiesel. Extraction is one of the most significant unit activities in the extraction of oils from oilseeds since it determines the quality and amount of oil produced. The initial oil content is an important consideration when choosing grain processing and extraction processes for various oil seeds. (Reginaldo et al. 2013).

2.6.1.1. Oil Extraction Methods

Extraction is the method of extracting triglycerides from oilseeds. This is achieved by using several chemical, biological, and mechanical strategies to improve yields while minimizing product quality changes. It is the most essential element of oil processing and is dependent on whether the oil is in the kernel, seed, or pulp (Baskar et al. 2018). The following are examples of regularly used extraction methods:

2.6.1.1.1. Mechanical Extraction

Mechanical extraction was one of the first methods of extracting oil. In general, the seeds are placed between barriers where the volume available to the seed is limited by pressing and squeezing the oil out of the seeds. Mechanical extraction is widely used in rural areas since it needs highly experienced persons to operate the machines and has a lower initial investment cost. The acid value, phosphorus content, water content, and iodine value of the oil generated by this technique are regularly examined. (Subroto et al. 2015).

Mechanical extraction has several advantages over solvent extraction, including the production of high-quality oil and the possibility to reuse the cake. Hydraulic presses or motor-driven screw presses are used. Even while mechanical pressing is efficient, it yields relatively little oil. The screw press produces somewhat greater yields than the hydraulic press and may be set up for continuous operation. (Heriawan, Indartono, and Kartika 2018).

2.6.1.1.2. Solvent Extraction

The process is based on the solvent's ability to break down oils and remove them from seeds, among other things. The solvent must be able to solubilize the oil in order for the extraction to be successful. It is the most often utilized method, and it is frequently carried out as a batch or continuous process. Oilseed washing and conditioning, oil extraction, and miscella separation are the three major processes in solvent extraction. The solvent used, the reaction temperature, and the kind of pretreatment given to the oilseed all have a significant impact on the quality of crude oil and meal. The solvent-extraction method is chosen because it is straightforward to use. The technique necessitates an extra refining step or operation in order to get oil of the specified grade. CSE has an oil recovery rate of 90%-98%, but it requires a lot of energy and money, and the most often used solvent (hexane) is toxic and can cause health problems with long-term exposure (Oniya et al. 2017).

2.6.2. Transesterification of Vegetable Oil

Triglycerides and alcohol undergo a chemical reaction known as transesterification in the presence of a catalyst. It entails a series of three concurrent, reversible reactions in which triglycerides are changed into diglycerides are changed into monoglycerides, and then monoglycerides are changed into glycerol. Three ester molecules are created from one triglyceride molecule by producing an ester in each of the steps. Out of these three processes, transesterification is the most feasible for lowering viscosity. Glycerol, a commercially valuable byproduct, is also generated (Sharma, Singh, and Upadhyay 2008). One of the most exciting potential uses for saturated fatty acid ester is the manufacture of anionic surfactants known as fatty acid ester sulfonates. Fatty acid ester sulfonate is one of the least costly surfactants that can be made from oleochemicals. (Ahmad et al. 2007).

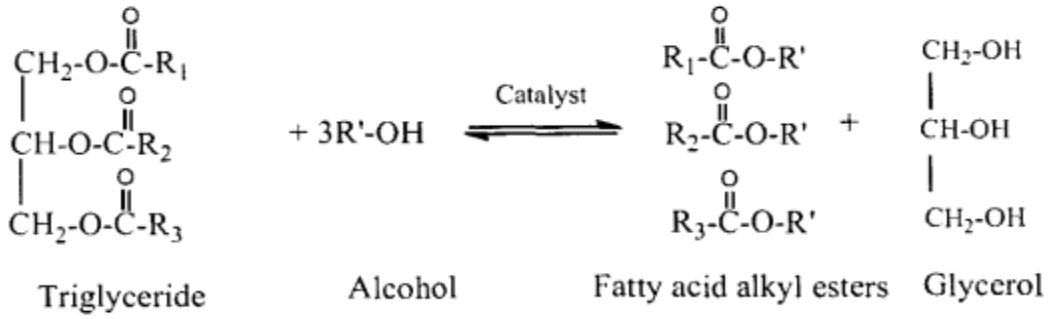

Figure 2-6 General reaction of transesterification reaction

The environment is safe since the fatty acid ester is biodegradable, harmless, and non-toxic. Raw materials utilized for commercial purposes include edible fatty oils derived from plants such as rapeseed, soybean, palm, sunflower, coconut, and linseed (Ramezani, Rowshanzamir, and Eikani 2010). The following are some recent fatty acid ester studies:

H. C. Joshi, Toler, and Walker (2008) used ethanol and potassium hydroxide (KOH) to transesterify cottonseed oil. Using a central composite design with six center and six axial points, the effect of catalyst concentration, ethanol to cottonseed oil molar ratio, and reaction temperature on percentage yield and percentage initial absorbance of the biodiesel was investigated.

Brhane tsegaye Seed et al. (2019) converted castor seed oil to biodiesel by transesterification using methanol and ethanol. The biodiesel was created using a reactant combination of methanol and ethanol via calcium oxide catalyzed transesterification. The reaction parameters studied were the methanol-to-ethanol volume ratio, total alcohol-to-oil molar ratio, and catalyst loading, and their effects on biodiesel yield were explored. The results show that combining methanol and ethanol to make biodiesel has a great potential.

Tinsu Gebreyohans (2018) created a transesterification process using K2O/fly ash as a heterogeneous catalyst and refined Jatropha curcas seed oil extracted from the Jatropha seed. Certain critical factors, such as the molar ratio of methanol to oil, reaction temperature, and catalyst loading, were investigated in order to achieve a high percentage yield of biodiesel fuel that fulfills the standards of standard processes.

Tafere, aga (2018) used a transesterification procedure in a laboratory environment to make biodiesel from waste avocado peel oil. The experimental findings evaluate the effect of the key optimal process parameters for base catalyzed transesterification on biodiesel production and properties. The two most critical factors determining methyl ester yield during the transesterification reaction are the molar ratio of alcohol to oil and the reaction temperature.

Transesterification is defined as either acid or base catalyzed. In transesterification processes, acid catalysts such as sulfuric, sulfonic, phosphoric, and hydrochloric acids and base catalysts such as metal hydroxides, metal alkoxides, alkaline-earth oxides, or hydrotalcites can be utilized. Basic catalysts are typically used over acid catalysts due to their higher activity and lower process temperatures required for transesterification (Gryglewicz 2000). The majority of industrial applications are currently performed in batch or continuous stirred tank reactors at temperatures ranging from 60 to 200 °C, using homogeneous basic catalysts such as alkaline hydroxides or metal alkoxides. (Georgogianni et al. 2009).

The most often used homogeneous catalysts in the transesterification process are sodium hydroxide (NaOH) and potassium hydroxide (KOH). Effective conversion is obtained by transesterifying refined and crude oil with 1% sodium hydroxide or potassium hydroxide catalyst (Acid 2019). The following are the reasons why NaOH and KOH were chosen: (Verma, Sharma, and Dwivedi 2016):

- The ability to accelerate the reaction at lower temperatures and pressures. Higher yield can be attained in lesser time.
- Abundant availability at a lower cost

2.6.3. Factors Affecting the Transesterification Process

The molar ratio of alcohol, alcohol type, catalyst concentration, reaction duration, and reaction temperature all influence the transesterification reaction. Each parameter's impact is discussed more below.

2.6.3.1. Alcohol Type

Methanol and ethanol are the most often used alcohols, although higher alcohols such as 1-propanol, n-butanol butan-2-ol, and iso-propanol are also used, and it has been demonstrated that these branched-chain esters lower the crystallization temperature of biodiesel. Because of its low cost and high reactivity, methanol is frequently used in industry. However, because methanol is obtained from fossil fuels such as natural gas, methanol-derived biodiesel cannot be considered renewable in nature. On the other hand, the use of ethanol is particularly promising because it is created by fermentation from agricultural wastes such as biomass (Oliveira et al. 2010). Furthermore, because ethanol is more soluble in oil than methanol, the mass transfer constraint during the transesterification process is reduced. (Verma, Sharma, and Dwivedi 2016).

2.6.3.2. Reaction Temperature

The reaction temperature has a significant impact on biodiesel yield. Because of the lower viscosity of the oil, higher reaction temperatures shorten the reaction time. Raising the reaction temperature over the optimal range, on the other hand, reduces biodiesel yield because higher reaction temperatures increase triglyceride saponification. Furthermore, to avoid alcohol evaporation, the transesterification reaction temperature should be lower than the boiling point of alcohol. The optimal reaction temperature may range from 50°C to 70°C depending on the oils or fats used. (Leung and Guo 2006).

2.6.3.3. Reaction Time

As with the other factors, reaction time had a considerable impact on the yield of the transesterification process. When the reaction time is prolonged, the fatty acid ester yield and conversion of fatty acid esters rises. The reaction will be sluggish at first due to the mixing and dispersion of the alcohol and oil. Most published research expected that the maximal ester conversion would occur within 90 minutes. Furthermore, due to the reversible reaction of transesterification, which results in ester loss and soap generation, longer reaction periods result in a lower end product (ester). (Dairo et al. 2013).

2.6.3.4. Molar Ratio of Alcohol to Oil

The molar ratio of alcohol to oil is another important element determining ester formation. The reaction stoichiometry needs three moles of alcohol per mole of triglyceride to create three moles of fatty esters and one mole of glycerin. Because this is an equilibrium process, adding more alcohol leads the equilibrium to shift to the right, resulting in more ester conversion. However, applying a larger molar ratio of alcohol to vegetable oil makes separating glycerol and ester more difficult due to increased solubility, and excess alcohol facilitates di-to-monoglyceride conversion. The best results were observed when molar ratios ranged from 9:1 to 16:1. (Encinar et al. 2002).

2.6.3.5. Catalyst Concentration

The concentration of catalyst has an effect on biodiesel production as well. The most often used catalysts for biodiesel production are sodium hydroxide (NaOH) or potassium hydroxide (KOH). The conversion of triglycerides to biodiesel increases as the concentration of catalyst in oil samples increases. Inadequate catalyst, on the other hand, leads to insufficient conversion of triglycerides into fatty acid esters. However, when the NaOH concentration reaches 1.5 wt.%, the product yield (biodiesel) is optimum, confirming that increasing the catalyst concentration has a negative influence on the product yield. Because an excess of alkali catalyst combines with triglycerides, more soap is produced. (Mathiyazhagan and Ganapathi 2011).

2.6.4. Sulfonation of Fatty Acid Ester

Fatty acid ester surfactant is created by sulfonating fatty acid ester. Sulfonation is the most common process for producing anionic surfactants. Sulfonation is the name given to an electrophilic chemical process in which a sulfonic group is incorporated into a molecule capable of giving electrons. The chemical reaction produces sulfonic acid if the electron donor molecule is carbon. Sulfuric anhydride reacts quickly with aromatic groups or, more broadly, delocalized electronic densities in alkenes. These reactions produce a diverse range of compounds, including polysulfone derivates (Akyüz and Roberts 2002). Sulfonating agents such as gas SO3, H2SO4, and ClSO3H can be used to create fatty acid ester sulfonate

Sulfonation of fatty acid ester is mainly affected by:

- Sulfonation temperature
- Sulfonation time
- Sulfonating agent molar ratio to fatty acid ester

2.6.4.1. Sulfonation Temperature

Temperature is critical in the sulfonation process, and changes in temperature throughout the reaction are related to process efficiency. With increasing reaction temperature, the yield of fatty acid ester sulfonate increased. The sulfonation temperature was thought to affect the extent of heat transfer in order to facilitate sulfonating agent penetration into the fatty acid ester and therefore increase the reaction rate (Yusuff et al. 2021a). Temperatures ranging from 70 to 90°C were optimal for the sulfonation process (Mushtaq, n.d.)..

2.6.4.2. Sulfonation Time

Sulfonation time is one of the most important factors determining the sulfonation process. The sulfonation duration has a substantial influence on the yield and interfacial property of the product. Both fatty acid ethyl sulfonate production and surface tension increase as sulfonation time increases (Slamet, Reza, and Permadani 2018).

2.6.4.3. Sulfonating Agent Molar Ratio to Fatty Acid Ester

The molar ratio of sulfonating agent to fatty acid esters has a considerable impact on sulfonation product yields. Because of its reactive nature, the molar ratio of sulfonating agent to fatty acid esters must be closely managed. Any excess sulfur-containing material produces side reactions and the creation of undesirable compounds. The yield of fatty acid ester sulfonate reduced as the sulfonating agent/methyl ester molar ratio grew (Yusuff et al. 2021).

2.6.5. Bleaching and Neutralization

Bleaching is the removal of colored pigments via the use of different bleaching agents. Bleaching agents are formulations that whiten or lighten a substrate by changing the light-absorbing capabilities of color-producing compounds. Hydrogen peroxide and activated carbon are two typical bleaching agents (Gierer 1990). Following that, bleached fatty acid ester sulfonate must be neutralized to a pH of around 7-8. 2021) (Yusuff et al.

2.7. Characterization of Fatty Acid Ester Sulfonate

2.7.1. FTIR Spectroscopy Analysis

FTIR stands for "Fourier transform infrared" and is the most common type of infrared spectroscopy. All infrared spectroscopies are based on the assumption that some infrared (IR) light is absorbed as it travels through a material. The sample's radiation output is measured. Used to specifically identify the chemical functional groups in a surfactant (Berthomieu and Hienerwadel 2009).

2.7.2. NMR Spectroscopy Analysis

Nuclear magnetic resonance (NMR) is a spectroscopic method used to determine the amount of energy absorbed by changes in nuclear spin state. It can offer information on the structure, content, and purity of the surfactant (Nmr and Nmr 2011).

2.7.3. Krafft Point

The kraft temperature is the lowest temperature at which micelle synthesis begins. The name honors Friedrich Krafft, a German chemist. The critical micelle concentration (CMC) and solubility at the krafft point have been shown to be almost similar. Micelles cannot form below the krafft temperature because the surfactant's maximum solubility is smaller than the critical micelle concentration. Even in an aqueous solution, the surfactant does not change phase and remains crystalline below the krafft temperature. Going below the Krafft point has the same visual effect as going over the cloud point: the solution becomes opaque or hazy due to the surfactant molecules flocculating (Moroi 1992).

2.7.4. Critical Micelle Concentration (CMC)

When surfactant monomers combine at a given concentration, they form a closed aggregate (micelle) with the hydrophilic heads facing the water and the hydrophobic tails shielded from it. The critical aggregation concentration (CMC) is the concentration at which micelles form in an aqueous medium. It signifies the point at which surface activity is at its maximum and monolayer adsorption is complete. Above the CMC, monomer concentrations are mostly constant. As a result, because the monomers are responsible for the surface activity, there are no discernible changes in the solution's surfactant properties (Farn 2007).

2.7.5. Active Matter

The active surfactant matter, usually given as a percentage, shows how much of an active component is present in the surfactant. Understanding the ASM of surfactants is especially important because they are frequently diluted with water. The two phase titration technique can be used to compute it (Farn 2007).

2.7.6. Foamability and Foam Stability Analysis

The active surfactant matter, which is often reported as a percentage, shows how much of an active component is present in that surfactant. Understanding the ASM of surfactants is especially important because they are often diluted with water. It may be estimated using the two-phase titration technique (Farn 2007). The height or volume of the foam column and the volume of the solution draining from the foam are often used to make measurements. Several parameters may be determined from these numbers, but the most common and important ones are as follows (Malysa and Lunkenheimer 2008):

- Hmax, the maximum height of the foam column
- The foam height after a set period (typically five to ten minutes)

2.7.7. Emulsifying Power

Because of liquid-liquid phase separation, an emulsion power is a combination of two or more liquids that are ordinarily immiscible (unmixable or unbendable). Emulsions are a type of colloids, which are a type of two-phase system of matter. Although the terms colloid and emulsion are frequently used interchangeably, emulsion should be used when both phases are liquids, distributed and continuous. One liquid (the dispersed phase) is distributed in another (the continuous phase) in an emulsion. The emulsifying capabilities of the surfactants were determined by dissolving them in water and then adding paraffin oil (Asselah et al. 2017).

2.8. Synthesis of Liquid Laundry Detergent

During the washing process, a surfactant and other substances found in laundry detergent are utilized to clean garments. Laundry detergent has traditionally been a solid that is either granular or powdered, but over time, liquid detergent use has increased to the point that it is now on par with or even higher than that of solid detergent. Laundry detergents come in two varieties: phosphate detergents and surfactant detergents. To increase the capacity for wetting, foaming, dispersing, and emulsifying, surfactant detergents are employed. Laundry detergents use phosphate detergents to soften hard water in the suspension of dirt. According to Bajpai and Tyagi (2007), the laundry detergent's properties include active matter content, pH, foaming ability, viscosity, and detergency power.

2.8.1. Composition of Liquid Laundry Detergent

Surface-active agents are long-chain, heterogeneous molecules that include both hydrophilic and hydrophobic moieties. One of the properties that sets surfactants apart is their propensity to adsorb at surfaces and interfaces largely in an oriented way. The orientation of the surfactant molecules at the surface/interface determines how the surface/interface responds to the adsorption of surfactant, determining whether it becomes more hydrophilic or hydrophobic (Farn 2007).

2.8.1.1. Surfactants

The most important ingredient in any laundry detergent formula is a surfactant since it improves the wetting qualities of water, which helps to dissolve, emulsify, or suspend filth particles in the wash solution (O'Rear 2015)..

2.8.1.2. Builders

Since they increase or "build" the surfactant's cleaning effectiveness, builders are the second-most crucial component of detergent. Builders are intended to accomplish the following (Bajpai and Tyagi 2007):

- Bind the hard water minerals to soften the water.
- Encourage surfactants to concentrate on washing dirt out of materials.
- Increase the surfactant's effectiveness.
- Give the desired amount of alkaline to help with cleaning.

2.8.1.3. Alkaline Agents

When applying negative charges to dirt and substrates, an alkaline condition in a cleaning solution is advantageous. Two typical examples of alkaline agents are sodium silicates and carbonate. In alkaline solutions, fatty acid-containing oily soil may be naturally removed (Bajpai and Tyagi 2007).

2.8.2. Characterization of laundry detergent

2.8.2.1. pH

pH is an important factor that influences the detergent's efficacy and efficiency. The capacity of a detergent solution to get rid of stains, oil, and grime can be affected by its pH. Detergents with certain pH ranges may be needed for certain cleaning jobs in order to maximize their cleaning potential. For instance, mineral deposits may frequently be removed with acidic detergents, whereas oils and grease can be easier to remove with alkaline detergents. The stability and shelf life of liquid detergents can also be impacted by pH. Inappropriate pH values in detergents can lead to chemical reactions or degradation over time, which might decrease their efficacy or make them less stable (Bajpai and Tyagi 2007).

2.8.2.2. Active Matter

The amount of an active component in the detergent is indicated by the term "active matter," which is usually represented as a percentage. Comprehending the detergent's AM is crucial, since it usually denotes the active ingredients accountable for eliminating filth (Farn 2007).

2.8.2.3. Rinsing Property

The capacity of a detergent to be readily and thoroughly removed from the surface being cleaned during the rinsing process is referred to as its "rinsing property." This feature is crucial since any detergent residue left behind might potentially irritate skin or have other negative consequences in addition to affecting the surface's cleanliness and attractiveness (Shachi Tiwari 2018).

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Materials and Equipments Used

In this study, castor seed, sodium hydroxide, sulfuric acid (98%), hydrogen peroxide, sodium tripolyphosphate, sodium carbonate, and analytical grade ethanol (99%) were used. Phenophetalin indicator, hyamine 1622 solution, dam's reagent, sodium thiosulfate, potassium hydroxide, potassium iodide, hydrochloric acid, and potassium hydroxide were used to determine the majority of the physiochemical parameters.

The primary laboratory instruments used in this investigation included a screw press extractor, digital viscometer, three-necked bottom flask, mechanical stirrer, condenser, separating funnel, balance, oven, refrigerator, and water bath.

3.2. Experimental Methods

Overall experimental framework of synthesis of ethyl ester sulfonate surfactant

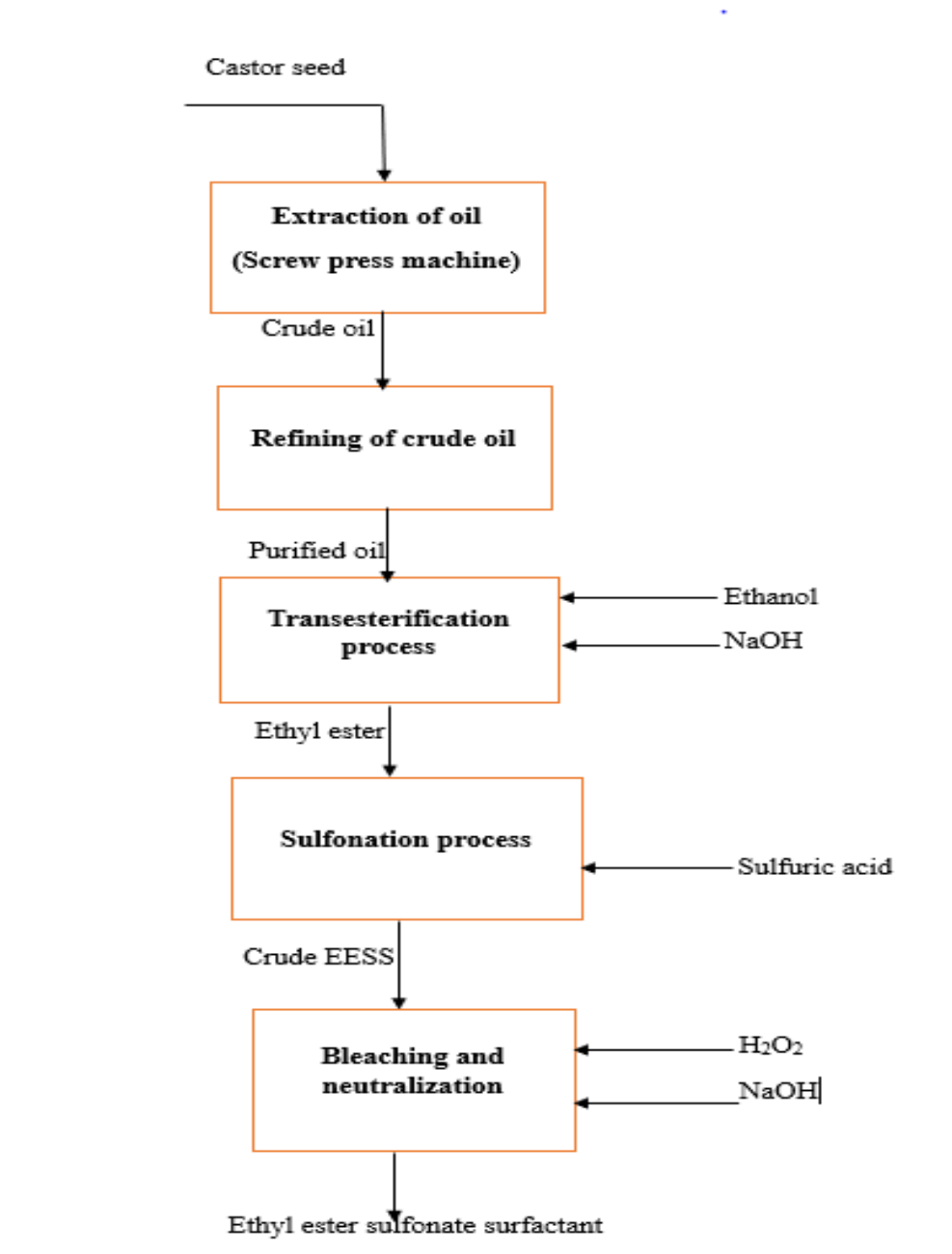

Figure 3-1 General block diagram of EESS production

3.2.1. Extraction of Castor Oil

The mechanical extraction approach was chosen as the extraction method. Extraction was carried out in the food engineering laboratory at Addis Abeba Science and Technology University (AASTU) using a screw press. The screw press machine was cleaned first, then the feed material (castor seed) was continuously supplied to the top of the screw press machine. During the extraction process, the oil is continuously withdrawn in the oil-out part, and the cake is continuously removed in the cake-forming section.

The amount of oil extracted was calculated using the equation below:

$$\%\text{yield of oil} = \frac{mass\ of\ oil\ obtained}{mass\ of\ seed\ used} \times 100\% \quad \text{.....Eq 3.1}$$

3.2.2. Purification of Crude Castor Oil

3.2.2.1. Filtration

Several contaminants were present in the oil that was produced during screw pressing. Certain pollutants, such meal particles and broken seeds, are easily filtered out since they are not soluble in oil. The pollutants were impurities, and vacuum filtering was used.

3.2.2.2. Degumming

Crude extracted or pressed vegetable oils include phospholipids, which must be removed during the purification procedure. Common oilseeds are rich in phospholipids. Phospholipids are eliminated from crude oil during purification by a procedure called degumming, which presents a number of problems for the storage and processing of crude oil. During the degumming process, phospholipids that fall into the hydratable (HPL) or nonhydratable (NHPL) categories are extracted from oil. Water degumming is a useful technique for removing the majority of the hydratable phospholipids found in crude castor oil. The crude castor oils were degummed by heating them to 80 °C and then adding boiling water to them. The liquid was allowed to settle in the separating funnel after two minutes of stirring. Next, the aqueous layer was removed. The method was repeated to guarantee that the majority of phospholipids were removed (Zufarov, Schmidt, and Sekretár 2008).

3.2.3. Characterization of Purified Castor Oil

3.2.3.1.Determination of Moisture Content of the Seeds

After the sample had been washed, 20g was weighed and dried for two hours at 105°C. Until the weight was constant, the procedure was repeated. After two hours, the sample was taken out of the oven and allowed to cool for thirty minutes in a desiccator. Then, it was taken out and weighed once again. The percentage of moisture in the seed was calculated using the following formula:

Moisture $= \frac{w1-w2}{w2} \times 100\%$.....Eq 3.2

Where W1 = Original weight of the sample before drying; W2 = Weight of the sample after drying

3.2.3.2.Determination of Specific Gravity (ASTMD 1298)

A 25 ml pycnometer had a thorough cleaning using soap and water, followed by drying and weighing. After adding the oil sample, the bottle was weighed. A material's density may be defined as its mass per unit volume of that substance. The process of dividing the obtained density by the density of water yields the specific gravity of oil.

3.2.3.3.Determination of Viscosity (ASTMD 445)

A viscometer was used to measure the oil's viscosity. After submerging the tube's thinner arm into the liquid sample and applying suction force up to the viscometer's upper timing mark, the instrument was moved to its normal vertical position and the temperature was adjusted to 40°c. This charged the viscometer with the sample. After then, the value was noted on the viscometer display.

3.2.3.4.Determination of pH Value

A 250 ml beaker was filled to the brim with 100g of the sample. After that, it was cooled in a cold water bath to 25°C. Before the pH electrode was put into the sample and used to measure and record the pH value, it was normalized using buffer solution.

3.2.3.5.Determination of Acid Value (ASTMD 664)

Jimoh et al. (2012) presented a technique for evaluating the acid value of castor seed oil. 25 milliliters each of ethanol and diethyl ether were mixed in a 250 milliliter beaker. Three drops of phenolphthalein and five grams of oil were added to the resultant mixture in a 250 milliliter conical flask. The liquid took on a pink hue and a volume of 0.1M NaOH (V0) after being titrated with 0.1M NaOH until the end point while shaking steadily.

Acid value (AV) = $56.11 \times \frac{v \times c}{m}$……Eq 3.3

FFA = AV/2……Eq 3.4

Where m = sample weight, v = volume of NaOH (ml), C= concentration of NaOH, 56.11= molecular weight of NaOH

3.2.3.6.Determination of Saponification Value (ASTMD 5558)

The method for determining the saponification value provided by Akpan, Jimoh, and Mohammed (2012) was utilized. A conical flask was filled with 2g of the substance and 25ml of 0.1N ethanolic potassium hydroxide. For sixty minutes, the continuously stirred contents were allowed to boil gently. A reflux condenser was placed on top of the flask that contained the mixture. The heated solution was mixed with a few drops of phenolphthalein indicator, and the end point was obtained by titrating with 0.5M HCl until the indicator's pink tint disappeared. The remaining samples and the blank were treated using the same methodology.

Saponification value (S. V) = $\frac{56.11 \times N(vo - v1)}{m}$……. Eq 3.4

where V0 = the volume of the solution used for blank test; V1= the volume of the solution used for determination; N = Actual normality of the HCl used; M = Mass of the sample.

3.2.3.7.Determination of Iodine Value (ASTMD 1959)

Iodine levels are commonly used to assess the degree of unsaturation in fats and oils. For this analysis, the methodology proposed by Akpan, Jimoh, and Mohammed (2012) was utilized. To dissolve the oil, 0.4g of the sample was placed in a conical flask and 20ml of carbon tetra chloride was added. The flask was then filled with 25ml of Dam's reagent using a safety pipette in the fume room. The cork was then inserted, and the contents of the flask were vigorously swirled.

The flask was then left in the dark for a duration of two hours. At the conclusion of this period, 20ml of 10% aqueous potassium iodide and 125ml of water were added using a measuring cylinder. The content was titrated with 0.1M sodium-thiosulphate solutions until the yellow tint almost completely disappeared. After vigorous shaking, the titration was continued by adding thiosulphate drop by drop until the blue coloration disappeared. First, a little amount of 1% starch indicator was applied. The identical procedure was followed for the other samples and the blank test.

$$\text{Iodine value (I. V)} = \frac{12.6(v1-v2)\times N}{m} \quad \text{..... Eq 3.5}$$

where C = Concentration of sodium thiosulphate used; V1 = Volume of sodium thiosulphate used for blank; V2 = Volume of sodium thiosulphate used for determination, m = Mass of the sample.

3.2.4. Transesterification Process

A 1000 ml three-necked round-bottom flask with a reflux condenser and a mechanical stirrer submerged in a hot water bath were used for the transesterification procedures. This allowed the reaction to be maintained at a steady 65°C. In this experiment, the transesterifing agent was a 99.5 percent ethanol, with 25 milliliters of castor oil added to each run. Before the oil was added to the three open round-bottom flasks, the temperature was first adjusted to the required level. After adding the alcohol catalyst (NaOH) mixture to the reactor and continuing to stir the reaction mixture at 500 rpm for the required amount of time, the oil reaches the correct level.

However, when ethanol is utilized as a trasesterifying agent, phase separation between the ester and glycerol phases is challenging. This disadvantage was formerly a common processing problem when ethanol was used. After the transesterification process was finished, 0.05% weight of analytical-grade glycerol was added to remedy the phase separation issue. After being moved into a separatory funnel, the product was given a full day to settle. The phase separation was evident after a whole day. Centrifugation was used to remove any leftover catalysts from the top layer, which contained the produced ethyl ester, after the bottom phase, which included glycerol and other impurities, was removed. Ultimately, the synthesized ethyl ester was dried for two hours at 105° C to remove any remaining water and unreacted alcohol.

3.2.4.1.Preliminary Experiments

To evaluate process components one at a time instead of several at once, one-variable-at-a-time (OVAT) was used to show the impact of a single parameter and choose parameter ranges for optimization trials.

Table 3.1 OVAT experimental design

run	Alcohol to oil molar ratio	Reaction Temperature (°C)	Catalyst Conc (%wt)	Reaction time (minute)
1	9:1	65	1	60
2	12:1	65	1	60
3	15:1	65	1	60
4	15:1	65	0.5	60
5	15:1	65	0.75	60
6	15:1	65	1	60
7	15:1	60	1	60
8	15:1	65	1	60
9	15:1	70	1	60
10	15:1	65	1	60
11	15:1	65	1	90
12	15:1	65	1	120

3.2.4.2.Response Surface Methodology Experimental Design

The trials were designed using Design Expert software 13.0.0 using box benten design (BBD) to investigate the effects of process variables on the transesterification reaction-mediated synthesis of ethyl ester. The outcomes of OVAT tests were used to identify the working range of the process variables, which included the alcohol to oil molar ratio, catalyst concentration, and reaction time. A balanced design is provided by BBD, guaranteeing an equal number of tests at various factor values.

This balanced distribution is essential because it makes it possible to estimate main effects and interactions more precisely, which produces more dependable optimization outcomes. Bias-Blind Distribution (BBD) reduces potential biases caused by unequal factor distributions by offering a fair portrayal of the experimental circumstances. Stirrer speed and temperature, however, were taken to be constants.

Table 3.2 Factors and levels for RSM

Factors	**Levels**	
	high	low
Alcohol to oil molar ratio	16:1	12:1
Catalyst concentration	1%	0.5%
Reaction time	60	100

Table 3.3 BBD experimental design

Std Order	Run order	Alcohol to oil molar ratio	Catalyst conc % wt.	Reaction time (minute)
1	14	12.00	0.50	80.00
2	17	16.00	0.50	80.00
3	15	12.00	1.00	80.00
4	10	16.00	1.00	80.00
5	5	12.00	0.75	60.00
6	16	16.00	0.75	60.00
7	11	12.00	0.75	100.00
8	4	16.00	0.75	100.00
9	1	14.00	0.50	60.00
10	12	14.00	1.00	60.00
11	9	14.00	0.50	100.00
12	2	14.00	1.00	100.00
13	13	14.00	0.75	80.00
14	8	14.00	0.75	80.00
15	3	14.00	0.75	80.00
16	7	14.00	0.75	80.00
17	6	14.00	0.75	80.00

$$\%\text{yield of ethyl ester} = \frac{mass\ of\ ethyl\ ester\ obtained}{mass of\ oil\ used} \times 100\% \quad \text{.....Eq 5}$$

3.2.4.3.Purification of Ethyl Ester

During the purification stage, by-products and the unreacted catalyst from the produced ethyl ester were eliminated by repeatedly washing with boiling water. to eliminate unreacted glycerol, fatty acids, mono- and diglycerides, and ethanol.

3.2.5. Characterization of Ethyl Ester

Characterization study was performed to ascertain whether the ethyl ester produced at the optimal point in RSM fulfills the requirements for standard ethyl ester characteristics. The ethyl ester's physiochemical qualities were ascertained using the same methods that were employed to evaluate the oil's numerous physiochemical characteristics, such as specific gravity, viscosity, acid value, and saponification values.

3.2.5.1.Cloud Point Determination (ASTMD 2500)

The cloud point (CP) is the temperature at which the heavier fatty acid esters start to precipitate when the fluid cools. As the solid phase develops in the liquid mass, the solution becomes hazy. For this investigation, the CP determination procedure described by Lopes et al. (2008) was used. After filling a 250 ml conical flask with a sample of ethyl ester and noting the level at which it climbed, the flask was placed inside a chiller. The temperature of the flask was monitored with a thermometer as soon as the sample started to form a cloud, and the measurement was noted as the ethyl ester cloud point.

3.2.5.2.Pour Point Determination (ASTMD 97)

The pour point of biodiesel is the lowest temperature at which it starts to flow. It also measures the ethyl ester's performance in cold temperatures. Jimoh et al. (2012) reported the pour point determination method used in this study. After being placed in the refrigerator, the ethyl ester was allowed to reach –50°C. After the obtained ethyl ester was taken out and placed on a heating plate at the temperature where the biodiesel starts to melt and flow, the pour point of the ester was measured and noted.

3.2.5.3.Flash Point Determination (ASTM D93)

An open cup technique was used to determine the castor oil ethyl ester's flash point. The cup was filled with ethyl ester and heated on a heating plate. When the surface of the open cup containing the sample is repeatedly exposed to an external flame until it burns, the temperature at which the ethyl ester begins to burn was determined and is known as the ethyl ester flash point.

3.2.6. Sulfonation Reaction

A 1000 ml three-necked round-bottom flask with a mechanical stirrer immersed in a water bath of varying temperatures was used to perform the sulfonation process. A different volume of concentrated sulfuric acid and 30 milliliters of ethyl ester were used in each run. First, ethyl ester was added to the three-necked flask and heated for half an hour. Sulfuric acid was then added to the mixture dropwise and stirred for the necessary duration of time. As soon as the sulfonation reaction was finished, 50% hydrogen peroxide was used for 30 minutes at 60 °C to begin the bleaching procedure. The bleached product was then washed with hot distilled water and put into a separatory funnel. Finally, dropwise additions of 30% NaOH solutions were made while stirring to raise the pH of the bleached product to 6-7.

3.2.6.1.Experimental Design for Sulfonation Process

The sulfonation process experimental procedure was carried out by altering process variables (molar ratio of H2SO4 and ethyl ester, reaction temperature, and reaction time) using a one variable at a time experimental design.

Table 3.4 Factors and levels for sulfonation process

Factors	**Levels**	
	Low	High
H_2SO_4 to ethyl ester molar ratio	0.5:1	1.5:1
Reaction temperature	60	80
Reaction time	1	3

3.2.6.2. Characterization of Ethyl Ester Sulfonate Surfactant

3.2.6.2.1. FTIR Analysis

The chemical structure of EESS was determined using FTIR studies. Using KBr windows, the FTIR analysis was performed at 25°C with a resolution of 4 cm-1 and a range of 4000-400 cm-1.

3.2.6.2.2. NMR Analysis

NMR studies were performed to ascertain EESS's chemical structure. Using a BBO ATM 5 mm-gradient probe and a Bruker Avance Hg400b spectrometer tuned to 400 MHz, NMR spectra were obtained. Using standard Bruker parameter configurations at 298.15 Kunder steady-state conditions, all free induction decays were recorded.

3.2.6.2.3. Foam-ability and Foam Stability Test

A 500 mL measuring cylinder containing varying quantities of ethyl ester sulfonate surfactant was quickly shaken at 25°C to agitate an aqueous solution of the surfactant. The initial and ultimate foam heights were recorded five minutes later. Until clear foam heights were reached, this procedure was used. According to Soy, Kipkemboi, and Rop (2020), the end foam height was subtracted from the starting foam height that remained stable for five minutes in order to determine the foam stability.

3.2.6.2.4. Krafft Point

Usually, a 0.2% (w/v) aqueous ethyl ester sulfonate surfactant solution was heated gradually until the clear dispersion temperature was reached. Multiple iterations of this procedure were carried out (Soy, Kipkemboi, and Rop 2020).

3.2.6.2.5. Active Matter Determination

The active substance of EESS was determined using a two-phase titration technique. After weighing, the first 0.5 g of EESS were added to a 250 ml volumetric flask. After dissolving the sample in 100 milliliters of distilled water, a few drops of phenophetalin indicator were added. After that, the solution was neutralized with 5N NaOH solution until a pink hue was seen. Next, 10 milliliters of the diluted solution were put to a 100 milliliter stopper cylinder, along with 20 milliliters of methylene blue solution, 10 milliliters of chloroform, and two minutes of vigorous shaking.

Two minutes later, the top aqueous phase was almost colorless, but the chloroform phase had become blue. After that, the solution was titrated with 0.004M of hyamine 1622 until the chloroform phase's color intensity was seen. According to Tsubochi, Yamasaki, and Matsuoka (1979), the amount of hyamine solution eaten was also noted.

$$\text{Active matter of EESS} = \frac{v \times mol.wt\ of\ EESS \times molarity\ of\ Hyamine}{weight\ of\ sample} \quad \text{.....Eq 6}$$

Where v is volume of hyamine consumed during titration

3.2.6.2.6. Critical Micelle Concentration Analysis

To find the CMC value, the electrical conductivity technique was applied. The conductance was measured using a digital conductivity meter and a dipping-type conductivity cell with platinized electrodes. A concentrated solution was constantly diluted to test the conductivities of surfactant solutions, and aqueous KCl solutions were used to calibrate the cell constant. Measurements of conductivity were taken at 25°C in relation to the EESS surfactant concentration. The conductivity value was measured when the variation was less than 1% in a span of two minutes (Domínguez et al. 1997). To find the intersecting lines (CMC point), the conductivity values were plotted versus the concentration of surfactant. The following represents the linear relationship between a surfactant's concentration and specific conductivity:

$$k = k_o + sC \quad \text{.....Eq 3.7}$$

where k0 is the specific conductivity at infinite dilution, k is the specific conductivity of the surfactant, s is the slope, and C is the concentration of surfactant.

3.2.6.2.7. Emulsification Power Test

By violently shaking 10 ml of a variable surfactant concentration solution and 10 mL of paraffin oil for five minutes at 30°C, the emulsification power of the surfactants generated was ascertained. The emulsification power was determined by measuring the amount of time needed to separate 10 milliliters of surfactant solution (Asselah et al. 2017).

3.2.7. Synthesis of Liquid Laundry Detergent

In this work, one litter of each EESS- and LABSA-based detergent was created utilizing sodium tripolyphosphate (STPP) and sodium carbonate (Na2CO3) as builders. The process was as follows:

To guarantee adequate mixing and dissolving, a suitable quantity of surfactant and sodium hydroxide solution are mixed together for 30 minutes while making a surfactant-based liquid detergent. After that, the mixture is added to weighed builders such sodium carbonate and sodium tripolyphosphate (STPP), which are briskly agitated for an hour to aid in their dispersion and dissolution. The necessary amount of distilled water is then added, and the mixture is well mixed to ensure even mixing. Stirring is kept up until the reaction stops producing as much intense froth, which is a sign that the right mixing and reaction have taken place. This procedure guarantees that every component is effectively included and results in the creation of a stable, well blended liquid detergent solution. For selecting best formulation of EESS based liquid laundry detergent five experiments were performed by varying only the concentration of EESS as shown in table 3.5.

Table 3.5 Formulations of EESS- based liquid detergents

Sample	**%EESS**	**%Sodium tripolyphosphate (STPP)**	**%Sodium carbonate (Na2CO3)**	**%Sodium hydroxide (NaOH)**	**%Distilled water**
1	4	3	6	2	85
2	6	3	6	2	85
3	8	3	6	2	85
4	10	3	6	2	85
5	12	3	6	2	85

Table 3.6 Formulation of LABSA based liquid detergent

Sample	%LABSA concentration	%Sodium tripolyphosphate (STPP)	%Sodium carbonate (Na2CO3)	%Sodium hydroxide (NaOH)	%Distilled water
1	8	3	6	2	85

3.2.8. Characterization of EESS Based Laundry Detergent

3.2.8.1. pH (ES ISO 4316:2001)

A 100 mL amount of the liquid detergent sample is made in a dry, clean beaker in order to ascertain its pH. The sample is then well mixed by adding 25 mL of a 0.1 mol/L sodium hydroxide (NaOH) solution and stirring for about 30 seconds. The mixture is then given a minute to equilibrate in order to stabilize. Next, a pH meter is used to determine the mixture's pH. One can use an appropriate formula or calculation technique to determine the pH of the original liquid detergent based on the observed pH, which should be between 4 and 9.

3.2.8.2. Active Matter (BCTL/SOP/M057:01)

The material was first homogenized to create the liquid detergent sample, and any contaminants were then removed by passing the mixture through a 0.22 μm filter. The filtered sample is centrifuged for 10 minutes at 1500 rpm in order to separate the active ingredients from the inactive ones. To guarantee that the inactive substance is completely removed, this procedure is carried out three times. The necessary active ingredients are found in the supernatant, which is collected. A protein concentration device, such as a centrifugal filter or precipitation device, is used to further concentrate the active matter. In order to determine and measure the amount of active matter in the liquid detergent sample, the concentrated supernatant is then analyzed using appropriate detection techniques, such as physical measurements or biochemical tests (Standard 2018).

3.2.8.3. Rinsing Property (CES 268:2020)

The cleaning agent is dissolved at a certain concentration in distilled water to create the test solution. The features and planned usage of the test surfaces with the cleaning agent are taken into consideration. The surfaces are pre-treated with a mild detergent solution to ensure cleanliness by eliminating any impurities and residues. Next, using a spray nozzle, the prepared test solution is administered to the surfaces that have already been treated. To remove any remaining residue from the test solution, the surfaces are thoroughly washed with distilled water after a predetermined amount of time, usually between 10 and 1 minute. Rinse water through many times until it runs clean. Using a spectrophotometer to detect the residue that remains on the test surfaces, the cleaning chemical's rinsing efficacy is assessed. The quantity of residue left behind determines the rinsing index, which provides a quantitative indicator of how well the cleaning agent rinses off surfaces (Standard 2018).

CHAPTER FOUR

4. RESULT AND DISCUSSION

4.1. Extraction and Characterization of Castor Oil

4.1.1. Extraction of Castor Oil

The oil extraction process was performed by using a screw press machine for 2 hours to extract 3.34 liters of oil from 10 kg of dried castor seed. 33.4% yield was obtained, which is in the range of 30–55% as Akpan, Jimoh, and Mohammed (2012) reported. This assures castor oil can be a selective raw material for fatty ethyl ester sulfonate surfactant. During filtration and centrifugation, 300-gram suspended solid were removed from 3.34 litter crude oil extracted mechanically.

4.2. Characterization of Purified Castor Oil

Physio-chemical characteristics determined for extracted castor seed and oil were moisture content of seed, specific gravity of oil, viscosity, pH, acid value, %FFA, iodine value and saponification value. Their values and comparison with ASTM standard value were listed in table 4.1

Table 4.1 Physiochemical properties of extracted castor oil

Property	**Unit**	**ASTM standard value**	**Experimental values of this study**
Moisture content	……	1.83-5.4	4.25±0.04
Specific gravity at 25°C	g/ml	0.957-0.968	0.965
Kinematic Viscosity at 40°C	mm^2/sec	…….	253
pH	……..	6.00–7.00	6.14
Acid Value	mg KOH/g	0.4-4.0	0.85±0.02
%FFA	……..	0.3–0.7	0.425
Iodine Value	mg I_2/100g	82-88	79.09±1.28
Saponification Value	mg KOH/g	175-187	174.84±5.58

Table 4.1 presents an examination that sheds light on whether the extracted castor oil is suitable for transesterification. With a specific gravity of 0.965 g/ml, the oil satisfies the necessary density requirements and is within the range of the ASTM quality standard. Furthermore, the viscous character of the castor oil is shown by its kinematic viscosity of 253 mm/s2, which is favorable for further reaction. The free fatty acid (FFA) concentration and low acid value make them ideal for transesterification since they do not require a significant oil pretreatment. On the other hand, elevated amounts of acid and FFA may cause the catalyst to be consumed more quickly and result in the production of long-chain soaps, which might hinder the effective separation of pure glycerol in the last stage. The refined castor oil's designation as nondrying oil is supported by the iodine value, which is close to the ASTM norm and indicates a high concentration of unsaturated fatty acids (double bonds). Castor oil and other non-drying oils have various benefits for transesterification. Due to the high amount of unsaturated fatty acids, they offer reactive sites that easily conduct the required chemical reactions with alcohol. Without requiring a significant oil preparation, its reactivity enables an efficient conversion into biodiesel. Non-drying oil-based biodiesel has favorable qualities including better cold flow characteristics and good lubricity. The ASTM standard's moisture content and pH ranges further lend credence to the refined castor oil's appropriateness for transesterification. The refined castor oil satisfies all requirements for effective transesterification, according to the average findings.Transesterification Process Analysis

4.2.1. Preliminary Experiments Analysis

Some preparatory experiments were carried out in order to identify the ranges of optimization parameters and evaluate the influence of a particular parameter individually before moving on to the optimization experimental design (RSM). Preliminary tests were carried out using the OVAT experimental design, with reaction parameters such as the alcohol-to-oil molar ratio, reaction temperature, and catalyst concentration chosen based on previously published literature. The outcomes from the OVAT experimental design are displayed in Table 4.2.

- **Results of OVAT experimental design**

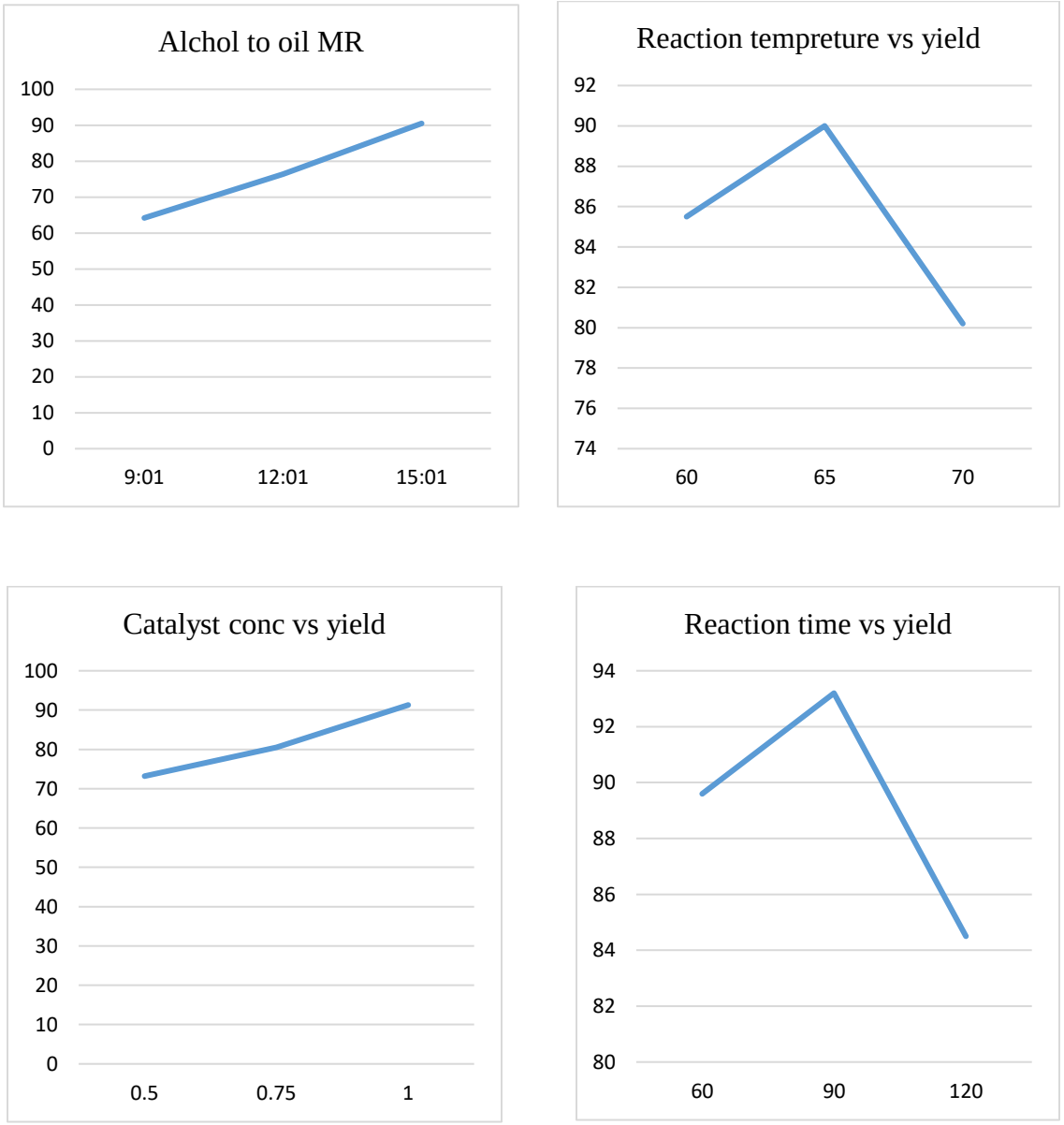

Figure 4-1 OVAT Analysis Results

OVAT investigations looked into whether the molar ratio of alcohol to oil affected the production of ethyl ester in a beneficial way. As the alcohol to oil molar ratio grew, the production of ethyl ester increased as well.Because low yield levels were produced at a 9:1 alcohol to oil molar ratio, the working range of the alcohol to oil molar ratio for optimization study was determined based on this finding (12:1–16:1). The yield was positively impacted by both catalyst concentration and the alcohol to oil molar ratio. From 0.5 to 1 weight percent, there was a noticeable rise in the production of ethyl ester. The results indicated that ethanolysis over this range of catalyst concentration was determined to be undesirable due to soap production, hence the working range of catalyst concentration for optimization study was fixed at (0.5–1) wt%. When the temperature climbed from 60°C to 65°C, the yield of ethyl ester was seen to rise and then progressively decline to 70°C. The working temperature was set at 65 °C for optimization study based on this finding, which corroborated earlier studies that the yield of esters declines when working temperatures approach the alcohol's boiling point (Ferella et al. 2010). The yield of ethyl ester was found to rise as reaction time rose from 60 to 90 minutes, but it was shown to fall at 120 minutes. The working range for optimization analysis was decided upon as 60–100 minutes based on this outcome.

4.2.2. Optimization of Ethyl Ester Analysis

The Box-Behnken design (BBD), with a three-level, three-factor design that addressed reaction temperature, oil-to-ethanol molar ratio, and catalyst amount, was chosen to optimize the reaction parameters for the castor oil transesterification reaction. Based on the BBD experimental design, these experimental parameters and their outcomes are shown in Table 4.2. To improve accuracy, 17 planned experiments were carried out in triplicate. Design-Expert 13.0.0 software was used to evaluate the findings using multiple regressions.

Table 4-2 Response surface methodology

Std order	Run order	Alcohol to oil molar ratio	Catalyst conc % wt	Reaction time (minute)	Actual yield (%)	Predicted Yield (%)
1	14	12.00	0.50	80.00	73.30	73.49
2	17	16.00	0.50	80.00	89.50	90.04
3	15	12.00	1.00	80.00	80.20	79.66
4	10	16.00	1.00	80.00	94.50	94.31
5	5	12.00	0.75	60.00	75.50	76.04
6	16	16.00	0.75	60.00	89.50	89.69
7	11	12.00	0.75	100.00	69.50	69.31
8	4	16.00	0.75	100.00	87.40	86.86
9	1	14.00	0.50	60.00	83.50	82.77
10	12	14.00	1.00	60.00	88.50	88.50
11	9	14.00	0.50	100.00	78.50	78.50
12	2	14.00	1.00	100.00	82.50	83.22
13	13	14.00	0.75	80.00	84.50	84.86
14	8	14.00	0.75	80.00	84.40	84.86
15	3	14.00	0.75	80.00	84.60	84.86
16	7	14.00	0.75	80.00	84.40	84.86
17	6	14.00	0.75	80.00	84.40	84.86

4.2.3. Analysis of variance (ANOVA)

Analysis of variance (ANOVA) for the yield of ethyl ester obtained using box benken design (BBD) is shown in table 4.4 below.

Where A; Alcohol to oil molar ratio

B; catalyst concentration

C; reaction time

Table 4.3 Analysis of Variance (ANOVA)

Source	**Sum of squares**	**Df**	**Mean Square**	**F Value**	**Prob > F**	
Model	640.58	9	71.18	140.76	<0.0001	Significant
A	486.72	1	486.72	962.58	*<0.0001*	
B	54.60	1	54.60	107.98	*<0.0001*	
C	45.60	1	45.60	90.18	*<0.0001*	
A^2	11.19	1	11.19	22.12	*0.0022*	
B^2	5.52	1	5.52	10.92	*0.0130*	
C^2	31.96	1	31.96	63.20	*<0.0001*	
AB	0.90	1	0.90	1.78	0.2234	
AC	3.80	1	3.80	7.52	*0.0288*	
BC	0.25	1	0.25	0.49	*0.5047*	
Residual	3.54	7	0.51			
Lack of fit	2.35	3	0.78	2.63	*0.1870*	Not Significant
Pure error	1.19	4	0.30			

The model's F-value of 140.76 shows that it is significant, as shown in table 4.3. a "model F-value" that only seldom has noise (0.01%). In cases when "Prob > F" is less than 0.0500, model terms become relevant. The alcohol to oil molar ratio, catalyst concentration, reaction time, square of the alcohol to oil molar ratio, square of the catalyst concentration, square of the reaction time, and the interaction between the alcohol to oil molar ratio and reaction time are all pertinent model terms in this situation. Compared to the pure error, the "Lack of Fit F-value" of 2.63 suggests that the lack of fit is not significant. Due to noise, a "Lack of Fit F-value" of this magnitude has an 18.70% probability of happening. A non-significant fit deficiency is advantageous since the model must fit. Furthermore, the model coefficients' p-values (catalyst concentration, reaction time, and the linear interaction between the catalyst and the oil molar ratio and reaction time) are all less than 0.0001. This illustrates how all process factors and the interplay between the molar ratio of alcohol to oil and reaction time impact the yield of ethyl ester.

4.2.4. Model Adequecy Checking

By ensuring that the model is adequate, the variation in the yield of ethyl ester as a percentage of process variables is explained. R-Squared, Adj R-Squared, Pred R-Squared, and Adeq Precision are used in its execution.The figures are displayed below.

Table 4-4 Model adequacy check

Std. Dev.	0.71	R-Squared	0.9945
Mean	83.34	Adj R-Squared	0.9874
C.V.	0.85	Pred R-Squared	0.9388
PRESS	39.42	Adeq Precision	45.840

The "Pred R-Squared" value of 0.9388 is quite close to the "Adj R-Squared" value of 0.9874, as table 4.5 illustrates. "Adeq Precision," indicating a variation of 0.0557, which is less than 0.2. The model and real data are plotted above, and the resulting R-squared value is quite near to 1. This graph shows the yield variation that the model was able to capture. The signal-to-noise ratio is evaluated using the "Adeq Precision" parameter. A ratio greater than 4 is ideal; a signal of 45.840 is suitable. When traversing the design world, this paradigm comes in handy. The table presented the regression coefficient along with the 95% high and low confidence intervals (CI) to illustrate how process factors affect the yield of ethyl ester. The regression coefficient's effect on the process increases with its value.

4.2.5. The Regression Model Equation

The model equation which relates the response to independent variables in terms of coded factors is given below:

The final equation in terms of coded factor is:

$$\text{Yield} = 84.86+7.80*A+2.61*B-2.39*C-1.63*A^2+1.14*B^2-2.75*C^2-0.48*A*B+0.98*A*C-0.25*B*C$$

Where A; Alchol to castor oil molar ratio

B; Catalyst concentration

C; Reaction time

The link between the coded components and the yield of biodiesel production is explained by the model equation. The coefficients show how each component affects the yield, whereas the intercept term shows the predicted yield when all factors are set to zero. An rising influence is indicated by positive coefficients, whereas a diminishing effect is implied by negative coefficients. The response surface's curvature is represented by the quadratic terms, and the total impacts of all the components are shown by the interaction terms. The equation makes it possible to anticipate the yield depending on the factor levels by entering the coded values. All things considered, the equation offers insightful information about the impacted variables and how they interact with the ethyl ester yield.

4.2.6. Graphical Analysis

Through graphical studies such as expected vs. actual yield, residual vs. projected yield, and a residual normal plot, the suitability of the produced model was evaluated. The experimental data closely matched the model's predictions, as seen by the near alignment of data points on the predicted vs. actual yield graph. The residual vs. expected yield graph showed dispersed residuals, indicating that systematic errors were not present and the model was reliable. The experimental data points roughly followed a straight line, as seen by the residual normal plot, supporting the normal distribution of errors. Together, these graphical studies provide evidence for the model's accuracy and dependability, confirming its capacity to forecast the yield of biodiesel production in relation to the chosen parameters.

Predicted vs Actual yield

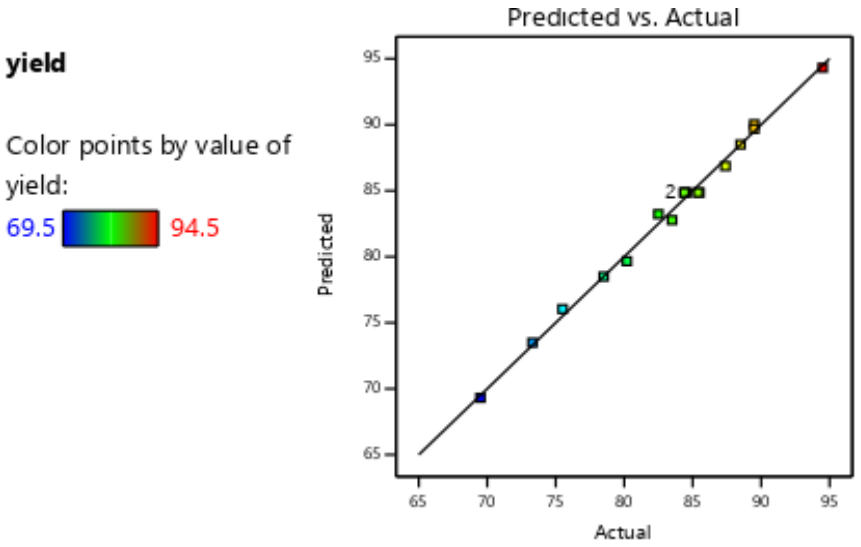

Figure 4-2 Predicted vs actual yield graph

Residual vs Predicted yield

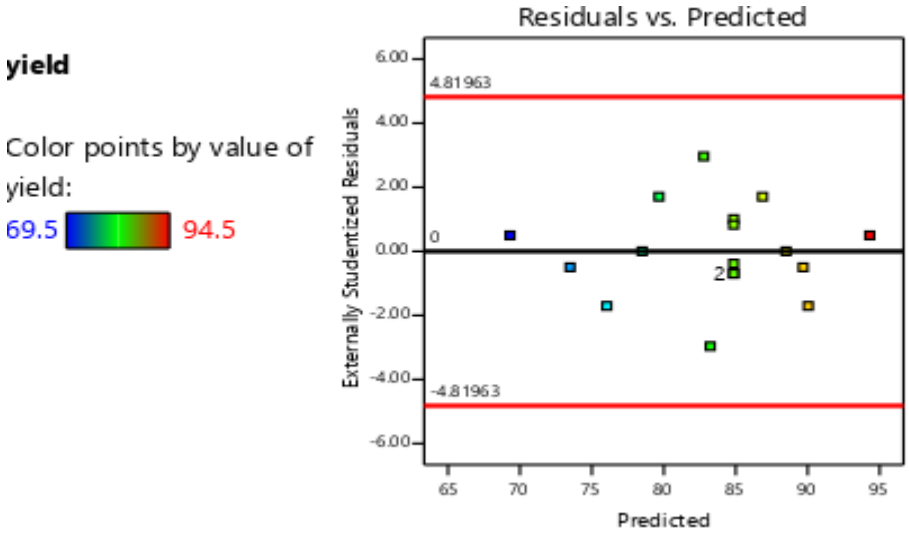

Figure 4-3 Residual versus predicted yield graph

Normal plot of residuals

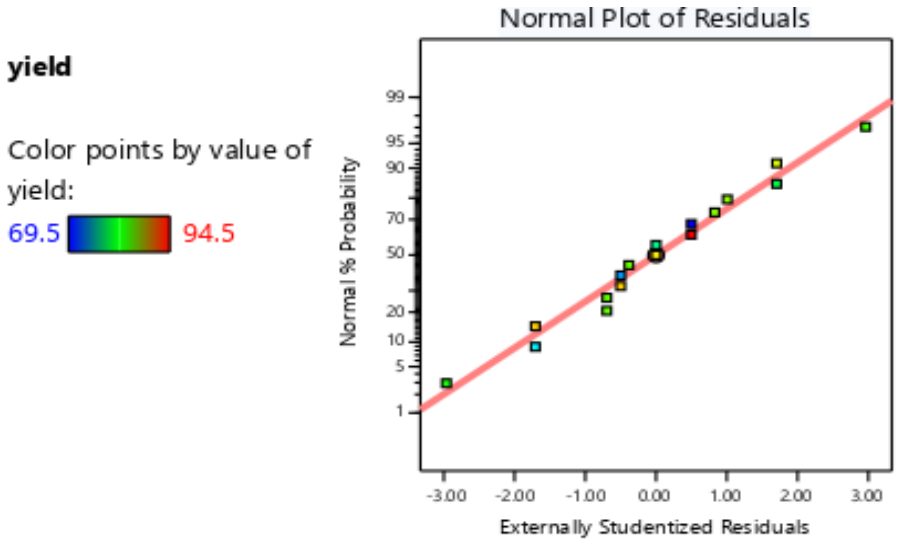

Figure 4-4 Normal plot of residuals graph

4.2.7. Effect of Process Parameters on Yield of Ethyl Ester

The analysis of variance (ANOVA) demonstrates how the catalyst concentration, reaction temperature, and alcohol to oil molar ratio were significant process factors that affected the reaction process. ... there was a substantial interaction between the molar ratio of alcohol to oil and the reaction time. Below was a discussion of each process variable's consequences.

4.2.7.1. Effect of Alcohol to Oil Molar Ratio

The alcohol to oil molar ratio was one of the key factors affecting the production of ethyl ester. Moreover, larger molar ratios are required to enhance miscibility and the interaction between the alcohol molecule and the triglyceride since the transesterification reaction is reversible and the stoichiometric molar ratio of alcohol to oil is 3:1 (Musa 2016). As shown in figure 4.4, the greatest yield of ethyl ester (94%) produced at a 16:1 alcohol to oil molar ratio, the yield of ethyl ester grows linearly with increasing alcohol to oil molar ratio from 12:1 to 16:1. This result supports earlier findings that the molar ratio of alcohol to oil increased with an increase in ethyl ester synthesis (Mathiyazhagan and Ganapathi 2011).

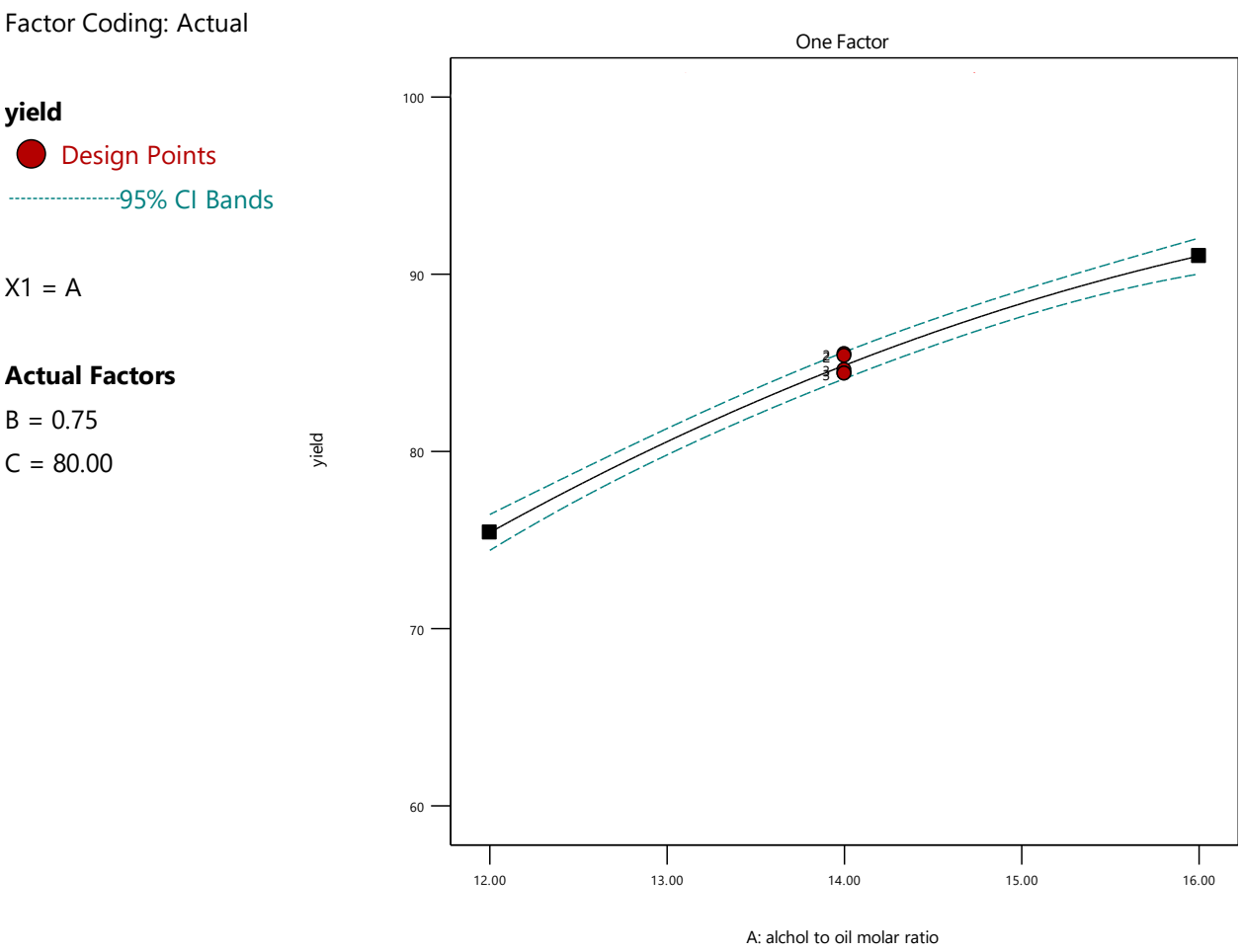

Figure 4-5 Effect of alcohol to oil molar ratio graph

4.2.7.2. Effect of Catalyst Concentration

The yield of ethyl ester was significantly impacted by the catalyst concentration as well. The maximum yield of ethyl ester was achieved at 1 weight percent catalyst concentration, as seen in figure 4.5. The yield of ethyl ester increased as the catalyst concentration increased from 0.5 weight percent to 1 weight percent. This result is in line with the findings published by Mathiyazhagan and Ganapathi (2011), which reported that between 0.5 and 1.5 weight percent of triglycerides were converted to ethyl ester. Applying a significantly higher catalyst concentration, however, proved to be harmful to the ethyl ester yield. because triglycerides react when there is a high concentration of alkali catalyst, producing more soap.

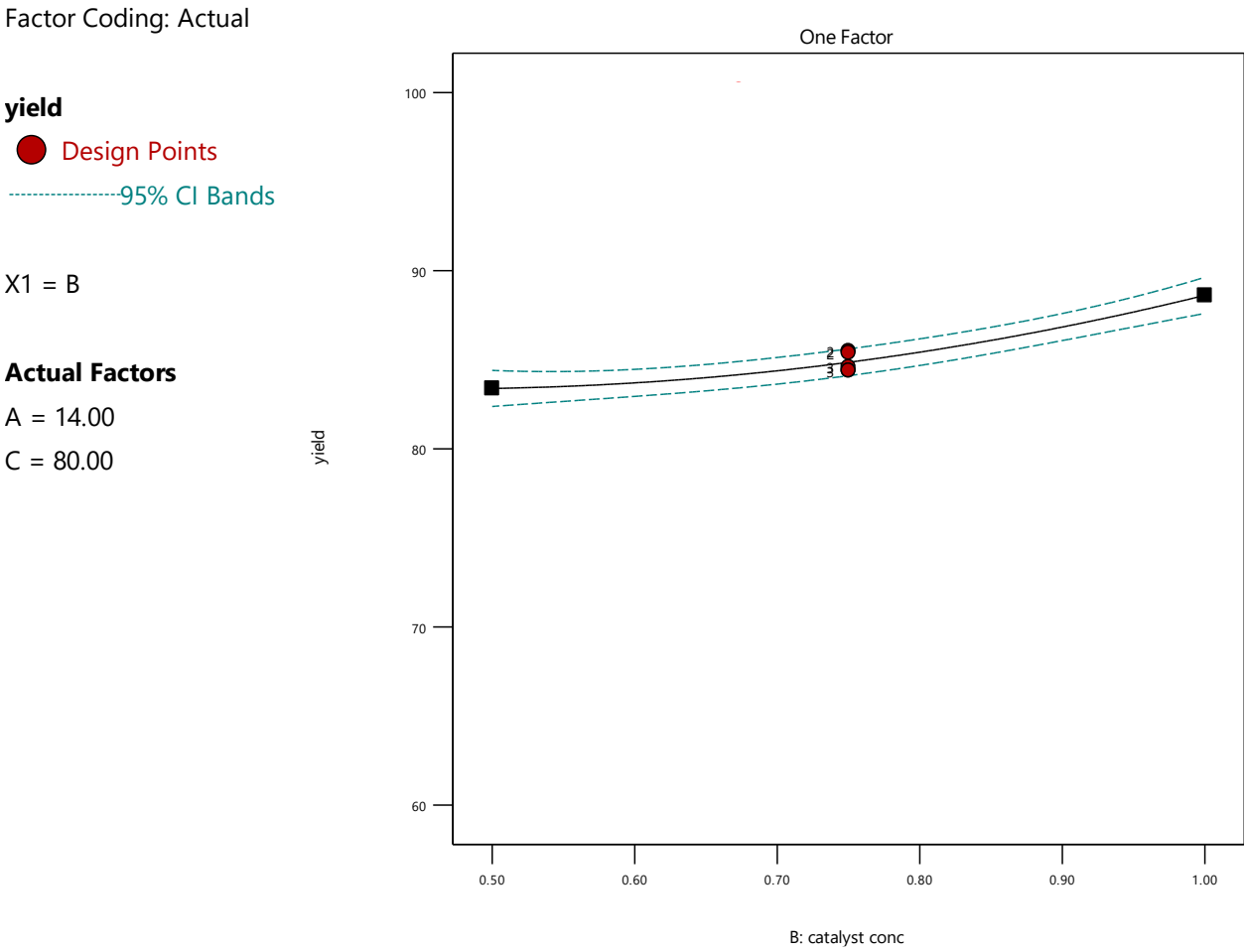

Figure 4-6 Effect of catalyst concentration graph

4.2.7.3. Effect of Reaction Time

The yield of ethyl ester was significantly impacted by reaction time as well. Fatty acid esters are converted at a rapid rate as reaction time increases. The reaction begins very slowly and proceeds quickly as a result of the oil and alcohol mingling and dispersing. The yield of ethyl ester rose as the reaction time increased from 60 to 80 minutes, as shown in Figure 4.6. However, the ethyl ester yield began to fall after 80 minutes. After 80 minutes, the highest yield was reached. Given that transesterification is a reversible process that results in the loss of esters and the production of soap, a longer reaction time was not advantageous, as the data show (Mathiyazhagan and Ganapathi 2011).

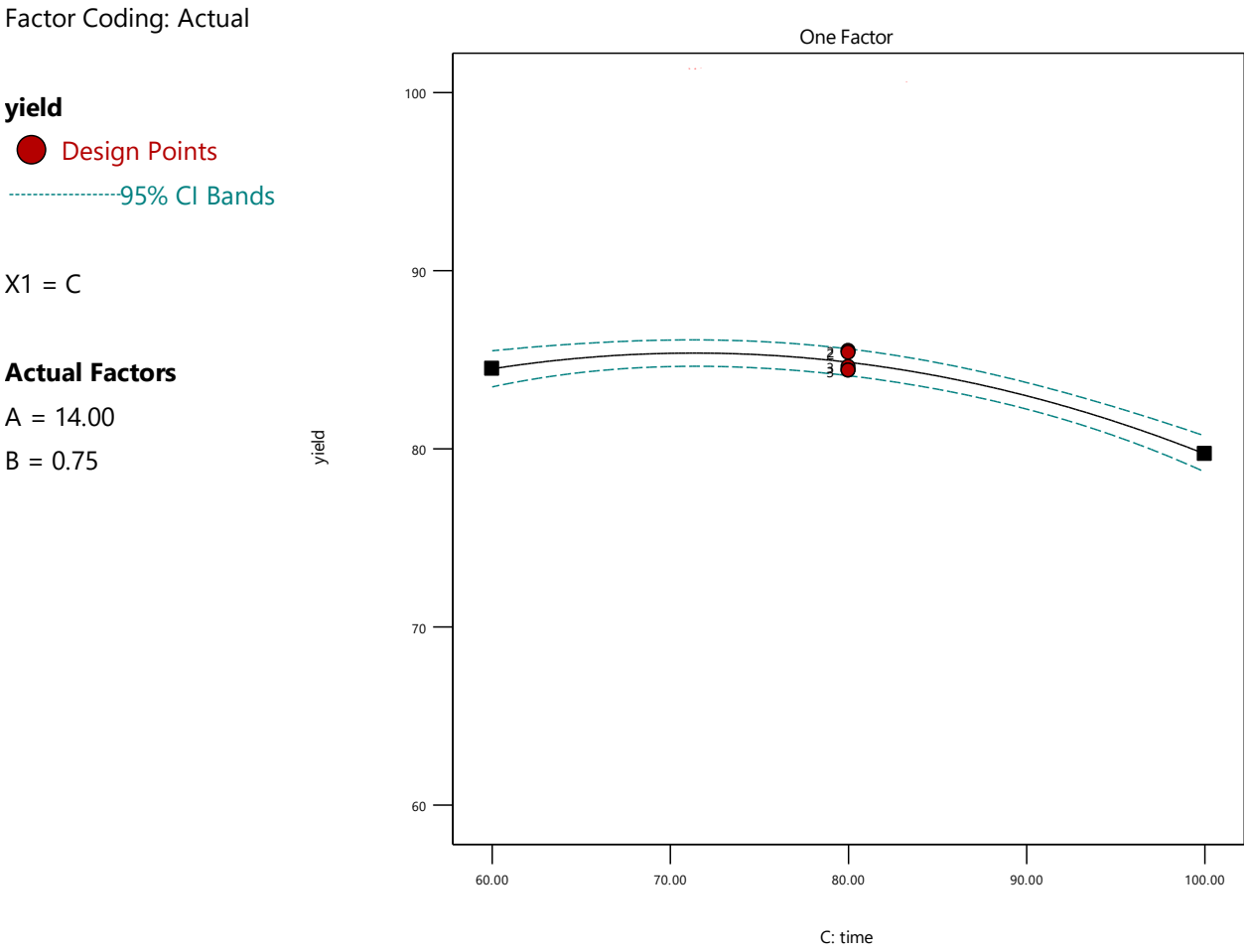

Figure 4-7 Effect of reaction time graph

4.2.8. Effect of Interaction between Process Parameters

The analysis of variance (ANOVA) revealed that the yield of ethyl ester was significantly influenced by the interaction between the alcohol to oil molar ratio and reaction time. The influence of the interaction between process factors on ethyl ester yield was investigated using response surface (3D) and contour plots, where the third variable was displayed with a fixed constant at its center point.

4.2.8.1. Effect of Interaction between Alcohol to Oil Molar Ratio and Reaction Time

The response surface (3D) and contour plots produced by determining the yield of ethyl ester as a function of alcohol to oil molar ratio and reaction time are displayed in Figures 4.7 and 4.8. Catalyst concentration was set at 1 weight percent. Given that the alcohol to oil molar ratio rose from 12:1 to 16:1, the reaction time went from 60 to 80 minutes, and the yield of ethyl ester increased from 73.2% to 94.5%, according to both figures. However, as can be seen in both figures, when the reaction time was raised from 80 to 100 minutes, the ethyl ester yield fell. With a 60-minute reaction period and a 12:1 alcohol to oil molar ratio, the lowest ethyl ester yield was achieved. However, an 80-minute reaction period and a 16:1 alcohol to oil molar ratio were found to produce the highest yield. These findings suggested that there was a substantial relationship between the alcohol to oil molar ratio and reaction time.

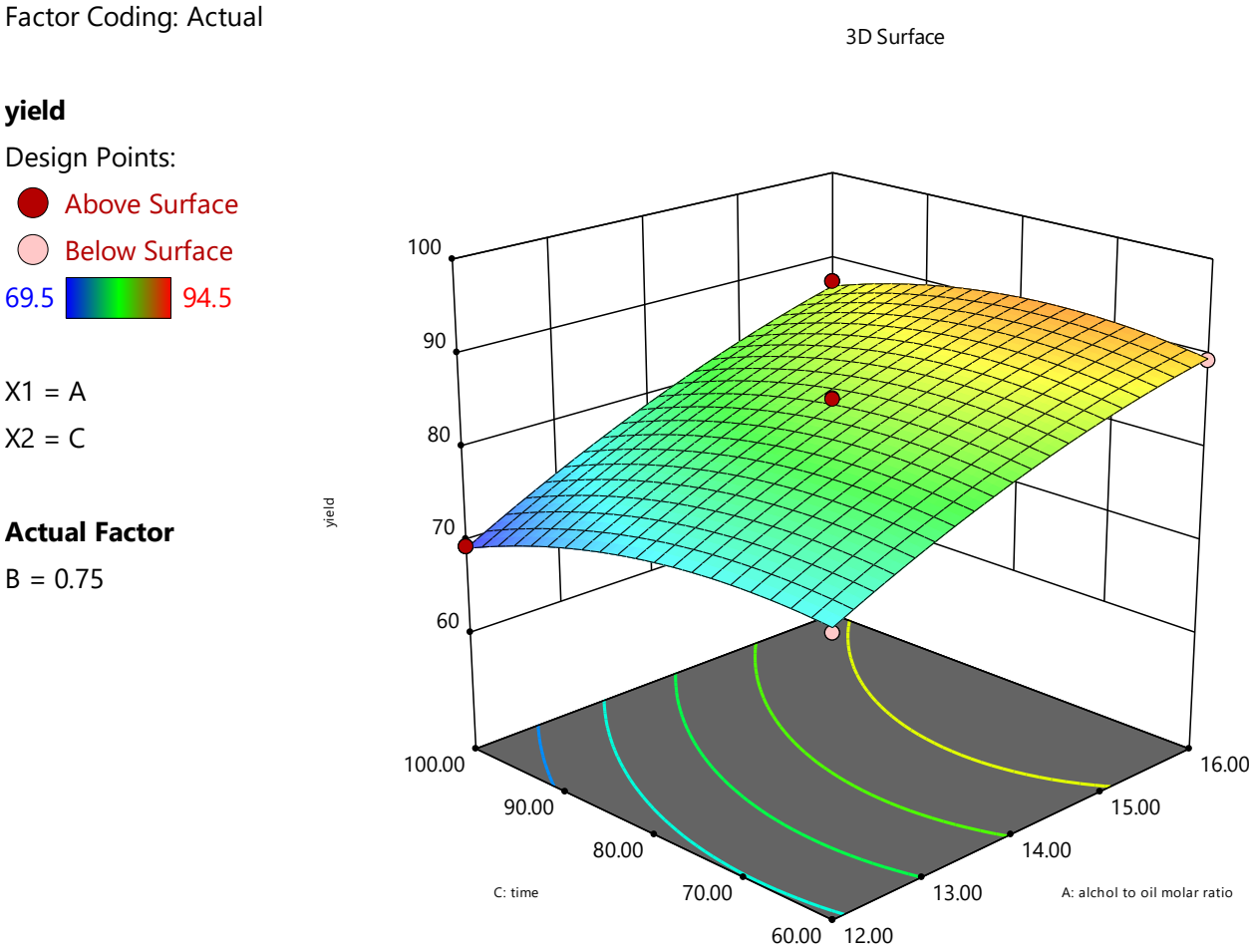

Figure 4-8 Interaction between alcohol to oil molar ratio and reaction time 3D plot

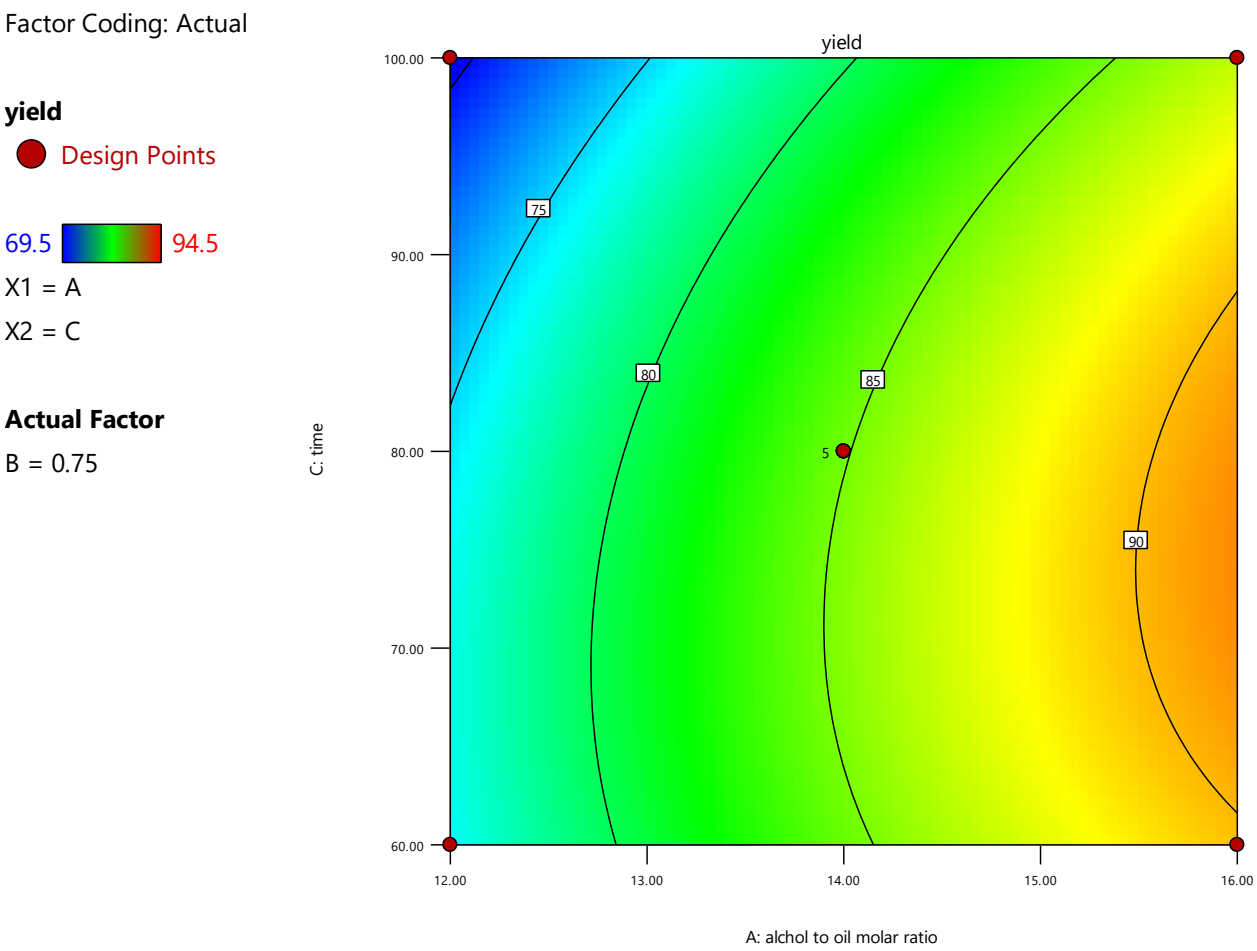

Figure 4-9 Interaction between alcohol to oil molar ratio and reaction time counter plot

- **Optimization of Process Variables of Transesterification Reaction using RSM**

The model-identified ideal configuration produced an EE yield of 94.54% at an alcohol to oil molar ratio of around 15.99:1, a catalyst concentration of 1.00 wt%, and a reaction time of 73.077, all of which are within the desirable range of 1.Therefore, the result suggested that the best yield was achieved when the values of each variable were placed at their ideal values, which was confirmed by additional trials using the projected responses.

4.2.9. Characterization of Ethyl ester

The ethyl ester generated at the optimal point in the RSM analysis was found to have the following physiological-chemical properties: specific gravity, viscosity, pH, acid value, iodine value, cloud point, pour point, flash point, and saponification value. Table 4.5 presented their values along with a comparison to the ASTM standard value.

Table 4-5 Physio-chemical properties of ethyl ester

property	**Unit**	**ASTM standard value**	**Experimental values of this study**
Specific gravity at 25°C	g/ml	0.86-0.90	0.908
Viscosity at 40°C	mm^2/sec	1.9-6	23.04
Acid Value	mg KOH/g	<0.8	0.71±0.17
Iodine Value	g I_2/100g	<120	80.51±1.13
Cloud point	°C	-3 to 12	6.2
Pour point	°C	-15 to 10	-7.5
Flash point	°C	≥130	176.31

The average specific gravity and cloud point values, as shown in table 4.6, were within the range of the ASTM Standard for ethyl ester. Additionally, the average viscosity of ethyl ester demonstrated that the transesterification reaction reduced the viscosity of castor oil from 253 mm2/sec to 23.04 mm2/sec. Even though ethyl ester's average viscosity was still higher than the ASTM requirement, its viscosity had a significant influence when it was employed in engines, thus it could be utilized to make ethyl ester sulfonate surfactant. The produced ethyl ester's cloud point was found to be 6.2°C, suggesting that it can be used at low temperatures. The synthesized ethyl ester's flash point was found to be 176.31, a higher flash point that confirms the ethyl ester's safety for handling and use. The average acid value of the ethyl ester was found to be within the ASTM standard range. A lower acid value also suggests a lower FFA concentration.

The ethyl ester created at the optimal point in RSM analysis satisfies the predicted conditions for employing it for subsequent product synthesis, as confirmed by comparisons between the synthesized ethyl ester and the ASTM standard for ethyl ester.

4.3. Sulfonation Reaction

Dark-colored ethyl ester sulfonate surfactants were produced via the sulfonation reactions between ethyl ester and sulfuric acid, as described in Chapter 3. After bleaching and neutralization, the generated ethyl ester sulfonate surfactant changed to a pale yellow color, as seen in figure below 4.9, which was the color anticipated by Jin et al. (2016).

(a) (b)

Figure 4-10 Ethyl ester sulfonate surfactant before bleaching process and after bleaching process

4.3.1. Experimental Process Analysis of Sulfonation Process

The influence of process factors on the production of ethyl ester sulfonate surfactant and the ideal point at which the maximum yield of ethyl ester sulfonate surfactant was achieved were evaluated using the OVAT experimental design, as indicated in Chapter 3. Based on a reported study by Yusuff et al. (2021b), the working range for H2SO4 to ethyl ester molar ratio (0.5:1-1.5:1) molar ratio and sulfonation duration (1-3) hours were fixed. Furthermore, sulfonation temperature range () °C was selected in accordance with the conclusions made by Stein et al. (2000).Table 4.6 displayed the findings of the experimental design.

Table 4-6 OVAT experimental design

run	**H_2SO4 to ethyl ester molar ratio**	**Sulfonation Temperature (°C)**	**Sulfonation Time (hour)**	**Ethyl ester sulfonate yield (%)**
1	1:1	70	1	66.4
2	1:1	70	2	71.2
3	1:1	70	3	75.5
4	0.5:1	70	3	68.3
5	1:1	70	3	75.1
6	1.5:1	70	3	70.2
7	1:1	60	3	72.5
8	1:1	70	3	75.2
9	1:1	80	3	78.4

The maximum yield of 78.4% was achieved at a molar ratio of 1:1 sulfuric acid to ethyl ester, 80°C reaction temperature, and 3 hours reaction period, according to the OVAT experimental study on the synthesis of ethyl ester sulfonate surfactant. The lowest yield of 66.4% was obtained at a molar ratio of 1:1 sulfuric acid to ethyl ester, 1 hour reaction period, and 70°C reaction temperature. These results highlight the important impact that certain parameters like the molar ratio, reaction temperature, and reaction duration have on the surfactant production. Based on the OVAT result, the effects of several parameters on the production of ethyl ester sulfonate surfactant were discussed below.

4.3.1.1. Effect of Sulfonation Time

The infulence of sulfonation time were analyzed by varying reaction time from 1-3hour at fixed temperature 70°c, agitation speed 400rpm and 1:1 sulfuric acid to ethyl ester molar ratio.

Table 4-7 Effect of sulfonation time

run	H_2SO4 to ethyl ester molar ratio	Reaction Temperature (°C)	Reaction Time(hour)	Ethyl ester sulfonate yield (%)
1	1:1	70	1	66.4
2	1:1	70	2	71.2
3	1:1	70	3	75.5

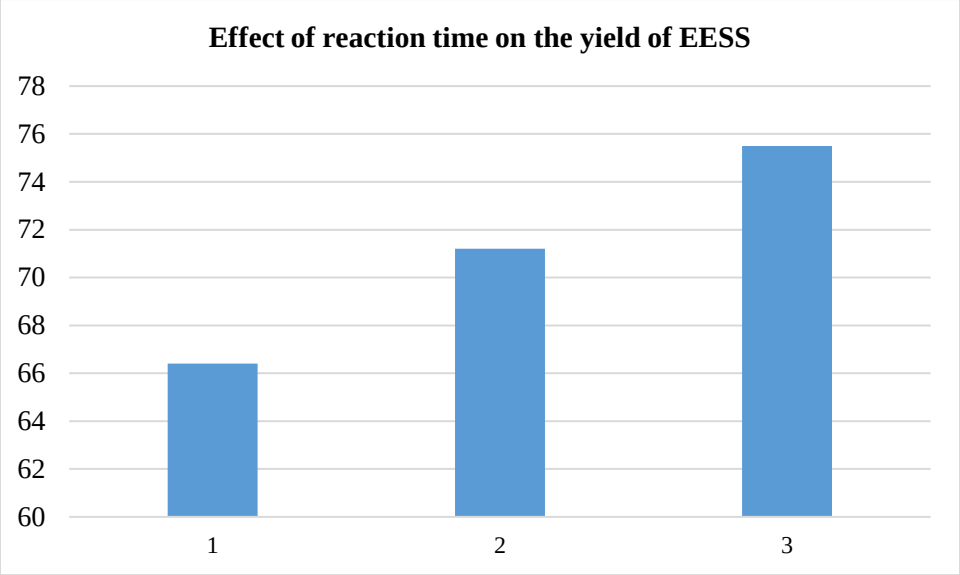

Figure 4-11 Yield of EESS vs reaction time graph

Reaction time had an impact on the production of ethyl ester sulfonate surfactant, as Figure 4.10 illustrates. The yield increased from 66.4% to 71.2% when the reaction time was extended from one to two hours. In a similar vein, increasing the sulfonation period from two to three hours resulted in a further 75.5% rise in yield from 71.2%. These results showed that the production of ethyl ester sulfonate surfactant is significantly influenced by the sulfonation period. The lengthier reaction periods resulted in a larger production of the required surfactant, indicating that a longer duration permits more thorough sulfonation of the ethyl ester. The longer reaction period between the sulfonating chemical and the ethyl ester probably made the conversion process more effective. The results of Yusuff et al.'s earlier research are in line with the observations observed in this investigation.

4.3.1.2. Effect of Sulfuric Acid to Ethyl Ester Molar Ratio

The effect of sulfuric acid to ethyl ester molar ratio were analyzed by varying the ratio 0.5:1-1.5:1 at fixed sulfonation temperature 70°c and sulfonation time 3 hours.

Table 4-8 Effect of sulfuric acid to ethyl ester molar ratio

H_2SO4 to ethyl ester molar ratio	**Reaction temperature**	**Reaction time**	**Ethyl ester sulfonate yield**
0.5:1	70	3	68.3
1:1	70	3	75.1
1.5:1	70	3	70.2

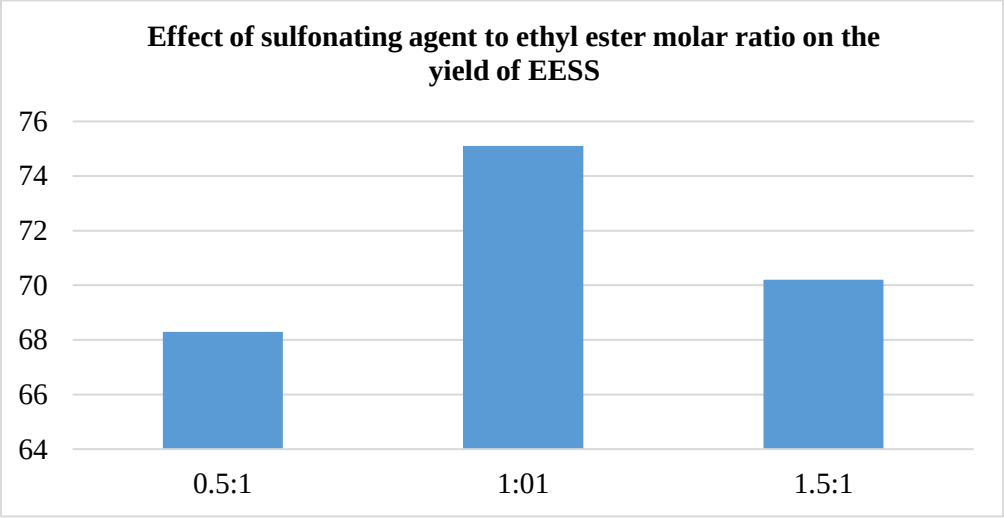

Figure 4-12 EESS yield vs sulfonating agent to EE molar ratio graph

Figure 4.11 shows that the molar ratio of sulfuric acid to ethyl ester affected the production of ethyl ester sulfonate surfactant. The yield increased from 68.3% to 75.1% when the ratio was increased from 0.5:1 to 1:1. But raising the ratio even further—from 1:1 to 1.5:1—caused the yield to drop from 75.1% to 70.2%. These results showed that the production of ethyl ester sulfonate surfactant is significantly influenced by the molar ratio of sulfuric acid to ethyl ester.

The ratio of sulfuric acid to ethyl ester molar ratio that produced the maximum yield was 1:1, while the ratio that produced the lowest yield was 1.5:1. The outcomes of this investigation are consistent with the conclusions made in earlier research by Slamet, Reza, and Permadani.

4.3.1.3. Effect of Sulfonation Temperature

The effect of sulfonation time was investigated by varying the sulfonation temperature from 70-90 at fixed sulfonation time 3 hours and sulfuric acid to ethyl ester molar ratio 1:1.

Table 4-9 Effect of sulfonation temperature

H_2SO4 to ethyl ester molar ratio	**Reaction temperature**	**Reaction time**	**Ethyl ester sulfonate yield**
1:1	60	3	72.5
1:1	70	3	75.2
1:1	80	3	78.4

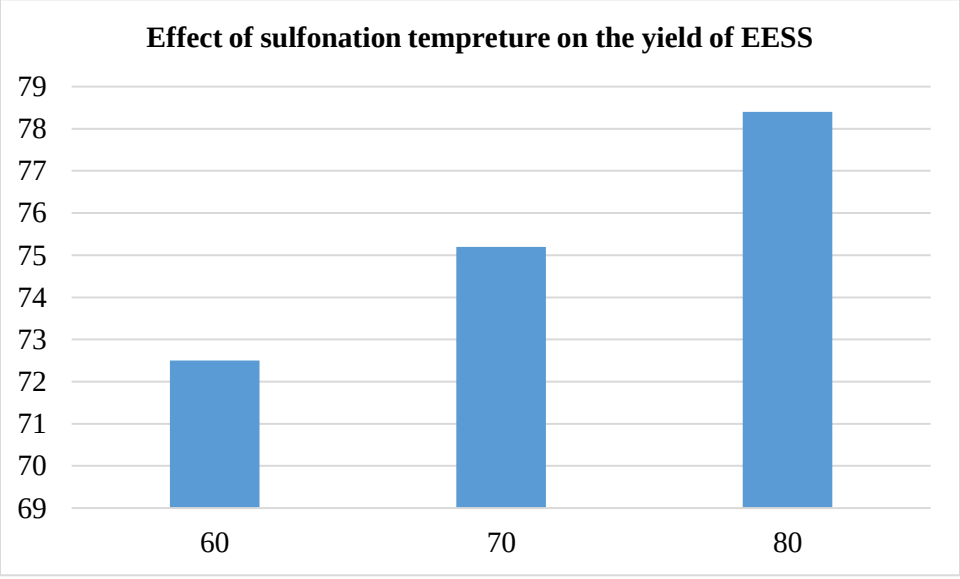

Figure 4-13 Yield of EESS vs sulfonation time graph

As the sulfonation temperature was elevated, Figure 4.12 shows that the production of ethyl ester sulfonate surfactant increased. The yield rose from 72.5% to 75.2% when the sulfonation temperature was raised from 60°C to 70°C. Similarly, the yield rose from 75.2% to 78.4% when the temperature was raised further from 70°C to 80°C. These results suggest that the production of ethyl ester sulfonate surfactant is positively impacted by the sulfonation temperature. The impact of temperature on heat transfer and the penetration of the sulfonating agent into the ethyl ester is responsible for the yield increase that occurs at higher sulfonation temperatures. The sulfonating agent can diffuse into the reactants more easily as a result of increased heat transfer efficiency brought on by rising temperatures. This increases the production of the required ethyl ester sulfonate surfactant and strengthens the sulfonation process. The results presented in Figure 4.12 align with the data documented by Yusuff et al. in their earlier research. Ethyl Ester Sulfonate Surfactant Characterization.

4.3.2. Characterization of Ethyl Ester Sulfonate Surfactant

4.3.2.1. FTIR Analysis

Figure 4.13 displays the infrared spectrum analysis of the ethyl ester sulfonate, which was generated at the optimum point of the OVAT experimental design. The spectrum analysis revealed a number of notable peaks that pointed to the existence of certain functional groups inside the surfactant molecule. The prominent band seen at 3,454 cm-1 represents the stretching vibration of the alcohol group (O-H). This suggests that alcohol groups are present in the ethyl ester sulfonate surfactant. The peaks seen in the 2855.81–2927.49 cm-1 range contain (-CH) groups, which are often associated with the stretching vibrations of carbon–hydrogen bonds. These peaks offer more proof that the surfactant molecule has alkyl chains in it. A carbonyl group (C=O) may be present, as shown by the signal detected at 1,737.19 cm-1. This peak, which is characteristic of ester groups, shows that the ethyl ester sulfonate surfactant has ester bonds. A peak at around 1,180.68 cm-1 further suggests the existence of sulfonate groups (S=O stretching vibration). This signal confirms the presence of the sulfonate functional groups in the surfactant molecule.

These characteristic peaks are mixed together in the infrared spectrum analysis, which is consistent with the expected properties of an ethyl ester sulfonate surfactant. The findings published by Awang and Seng (2008) make it abundantly evident that the produced product is, in fact, an ethyl ester sulfonate surfactant.

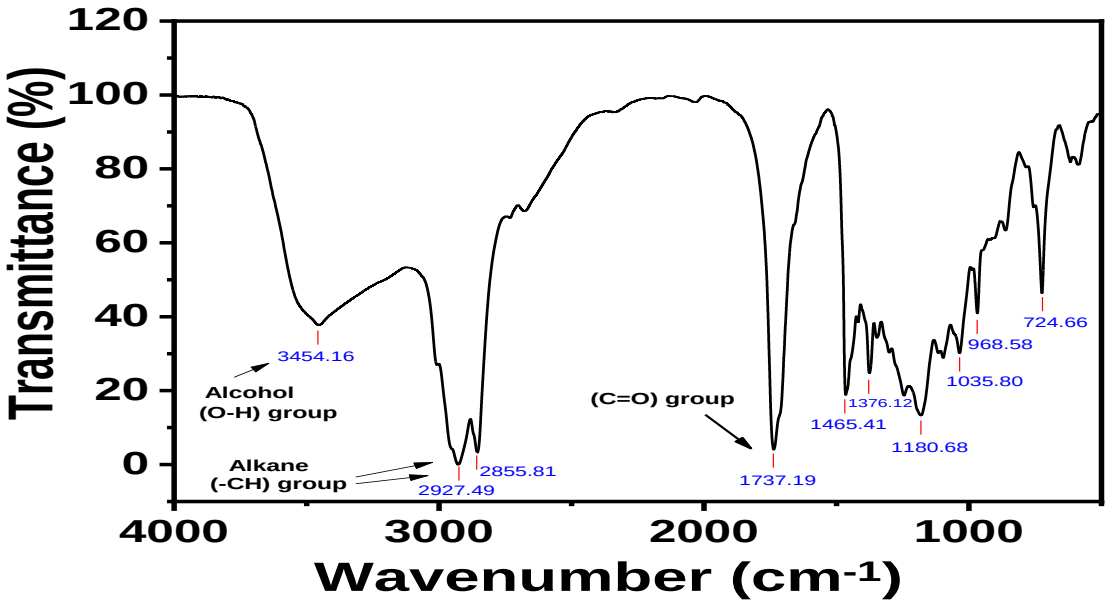

Figure 4-14 FTIR graph

4.3.2.2. NMR Analysis

The proton nuclear magnetic resonance (NMR) spectrum analysis of the ethyl ester sulfonate surfactant was shown in Figure 4.14. Important details on the relative signals and chemical shifts of the various protons in the surfactant molecule were revealed by the spectrum. The signal at δ = 4.00 is indicative of a proton that is joined to the sulfonate group-bearing carbon atom (–SO). This signal showed that the surfactant molecule included a sulfonate group. Within the hydrocarbon chain, signals are seen for protons between δ = 0.84 to 2.26. The protons in the alkyl chain section of the surfactant molecule are represented by these signals. The proton that is affixed to the carbon atom that has an ester group (–COO) is represented by the signal at δ = 2.75. This signal suggests that the ester group is present in the surfactant molecule. The carbon atom that was immediately connected to the sulfonate group was found at δ = 77.13 in terms of carbon atoms.

The carbon atom that is immediately attached to the sulfonate group is represented by this signal. The carbon in the ester group itself is seen at δ = 173.99, but the carbon immediately linked to the ester group shows at δ = 60.12. These signals offer information on the chemical changes in the carbon atom of the surfactant molecule as well as verifying the existence of the ester group.Figure 4.14's observations are consistent with research on sulfonated fatty ester surfactants published in 2016 by Jin et al. and in 2011 by M. Ahmad et al.

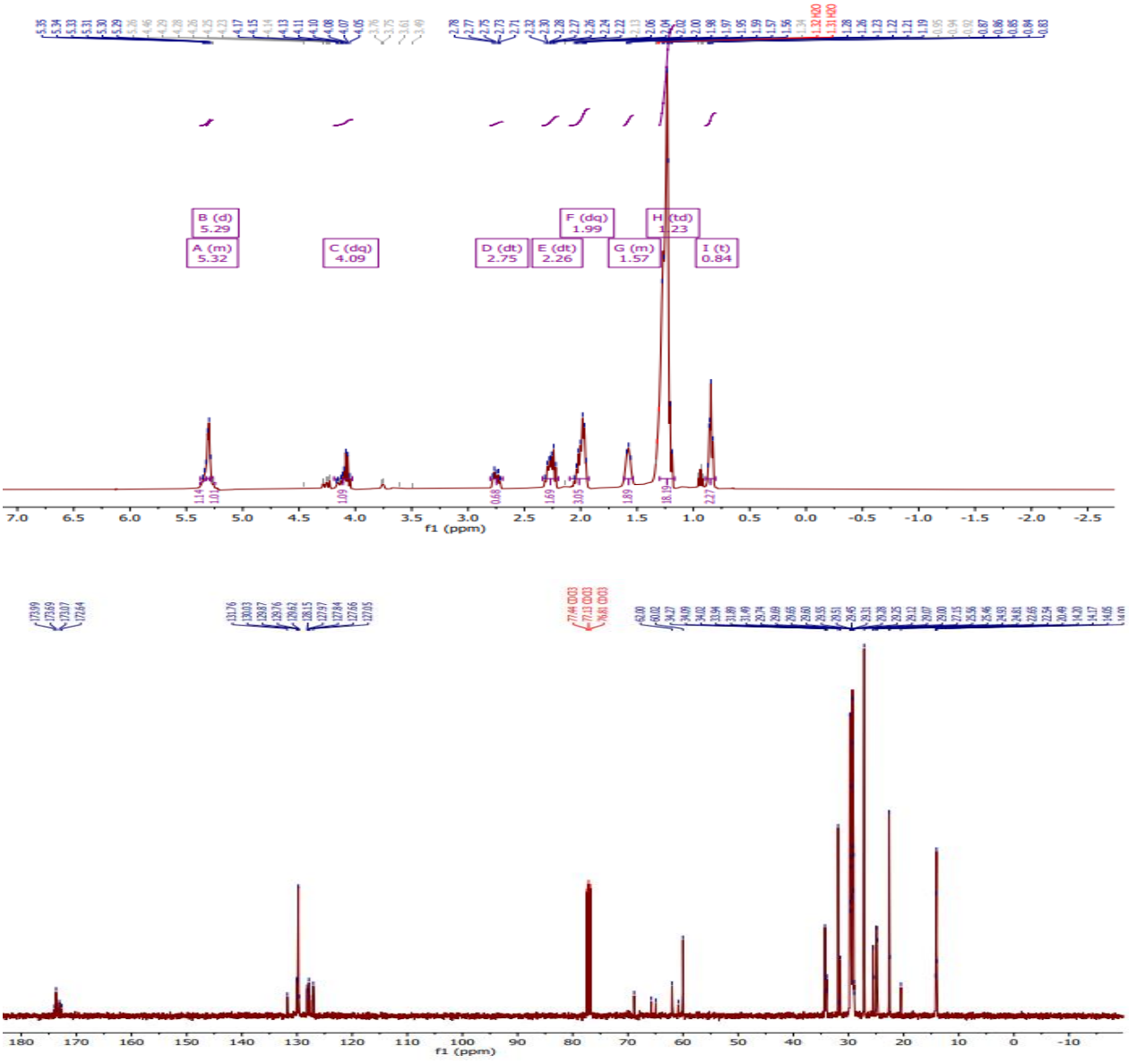

Figure 4-15 NMR analysis graph

4.3.2.3. Foamability and Foam-stability Analysis

Variations in surfactant concentration were used to examine the foamability and foam stability features of the produced ethyl ester sulfonate surfactant. The lowest levels of foamability and foam stability were seen at a surfactant concentration of 0.02 g/L, which led to the development of tiny bubbles and little foam volume. It was observed that the foamability and foam stability improved with increasing concentration, with the best results occurring at 0.08 g/L. These findings are consistent with 2020 research by Soy, Kipkemboi, and Rop on sulfonated ester surfactants, which similarly showed that increased surfactant concentrations improve foam quality. The peculiarities of the ethyl ester sulfonate surfactant are what underlie this behavior. The surfactant molecule's sulfonate group (–SO) makes it easier for it to adsorb at the air-water interface, which lowers interfacial tension and encourages the creation of stable foam. The hydrocarbon chain, which is indicated by the signals in the proton nuclear magnetic resonance (NMR) spectrum analysis, helps the surfactant become hydrophobic, which keeps the foam structure stable and slows down the formation of bubbles. These chemical characteristics work together to give the synthesized ethyl ester sulfonate surfactant good foamability and foam stability. This makes it a good option for a variety of applications where it is desired to generate and retain robust foam, like in detergents, cosmetics, and firefighting foams.

Table 4-10 Foamability and foam-stability analysis

Ethyl ester sulfonate surfactant concentration(g/L)	**Initial foam volume (ml)**	**Final foam volume after 5 minutes (ml)**
0.02	39	7
0.04	131	52
0.06	154	71
0.08	425	254

4.3.2.4. Emulsifying Power Analysis

The chemistry of the ethyl ester sulfonate surfactant, which was created at the optimal point in the OVAT analysis, is responsible for its emulsification power. An essential component of the surfactant molecule's capacity to emulsify is the presence of the sulfonate group (-SO). The surfactant may adsorb at the oil-water interface thanks to this functional group, which lowers the interfacial tension between the two phases. The surfactant's hydrophobic alkyl chain creates a shield over the oil droplets to keep them from clumping together, which results in steric stabilization. The sulfonate group also gives the surfactant an anionic character, which causes electrostatic repulsion between like-charged droplets and increases the emulsion's stability even more. The ethyl ester sulfonate surfactant's ability to emulsify is influenced by the equilibrium between steric and electrostatic stabilization. Moreover, emulsion formation is significantly influenced by the surfactant's concentration. Phase separation may occur immediately at lower concentrations because the surfactant molecules may not be readily accessible to create a stable interfacial layer. But when the concentration rises, more molecules of the surfactant join the emulsification process, resulting in enhanced emulsifying power and emulsion formation.

Essentially, the molecular structure of the ethyl ester sulfonate surfactant controls its ability to emulsify by allowing for interfacial adsorption, interfacial tension reduction, steric and electrostatic stabilization, and concentration-dependent surfactant molecule availability for emulsion. Further supporting the EESS surfactant's efficacy as an emulsifying agent, the study's emulsifying power was found to be similar to that of Asselah et al.'s 2017 findings.

Table 4-11 Emulsifying power analysis

Ethyl ester sulfonate surfactant concentration (g/L)	**Emulsifying power (min)**
0.01	4
0.02	7
0.03	15
0.04	25
0.05	34
0.06	48

4.3.2.5. Kraft Point

The 0.2% (w/v) EESS synthesized at the OVAT analysis's optimal point had an average kraft temperature of 21.8°C, indicating that it may be used as a detergent at room temperature or above. The generated surfactant appears to be devoid of di-salts, as shown by the Kraft temperature value. Reaction byproducts known as di-salts frequently cause oleochemical surfactants to become less soluble or raise their Kraft temperature. Crucially, the 21.8°C Kraft temperature that EESS got is within the range of values that Cohen et al. (2008) reported for sulfonated fatty ester surfactants. Sulfonated fatty ester surfactants were found to have a temperature range of 17–30°C. This implies that the synthesized EESS surfactant displays solubility properties akin to those of other surfactants sulfonated fatty ester. A Kraft temperature that falls within the specified range is ideal since it guarantees the surfactant's functionality and solubility in a range of detergent applications. Better solubility and performance are possible at lower temperatures, especially when the Kraft temperature is lowered.

4.3.2.6. Active Matter Analysis

Based on the two-phase titration findings, the average active matter content of the ethyl ester sulfonate surfactant (EESS) generated at the optimal point in the OVAT study was found to be 64.35%. According to Jin et al.'s 2016 study, this number is in line with the active matter content recorded for other sulfonated ester surfactants including S-MES, R-MES, and W-MES. The produced EESS surfactant is in the normal range of active matter content of sulfonated fatty ester surfactants, as shown by the similarity in active matter content. Achieving effective detergency requires surfactants with the right amounts of active matter since they contribute to the cleaning and foaming qualities needed for a variety of applications. The EESS surfactant's active matter composition closely resembles that of well-known sulfonated ester surfactants, indicating that it has the qualities needed to meet cleaning and foaming criteria in real-world applications.

4.3.2.7. Critical Micelle Concentration Analysis

Figure 4.15's plot of certain conductivity values vs EESS concentration sheds light on the EESS surfactant's critical micelle concentration (CMC) and underlying chemistry. The concentration at which surfactant molecules begin to self-assemble into micelles—organized structures created by the arrangement of hydrophilic heads and hydrophobic tails in aqueous solutions—is known as the critical mass concentration, or CMC. The graph's crossing lines show the CMC point, which denotes a noticeable shift in behavior. In comparison to previously investigated sulfonated fatty ester surfactants like W-MES, micelle production appears to become substantial at a comparatively lower concentration, as indicated by the lower CMC value of 1.57 mol/L obtained for the EESS surfactant at 25°C. The unique chemical structure of EESS is the cause of its reduced CMC. A key component of the self-assembly process is the hydrophobic alkyl chain and the ethyl ester sulfonate group. The hydrophilic character needed is provided by the sulfonate group, whereas the hydrophobic alkyl chain prefers to agglomerate in an attempt to reduce interaction with water. When the concentration of EESS exceeds the CMC, the molecules of surfactant combine to form micelles, which improve its solubility of hydrophobic materials and enable efficient cleaning.

Because of its effective micelle production even at lower concentrations, as seen by its lower CMC values, EESS is a suitable option for detergent compositions when lower surfactant amounts are sought without sacrificing performance.

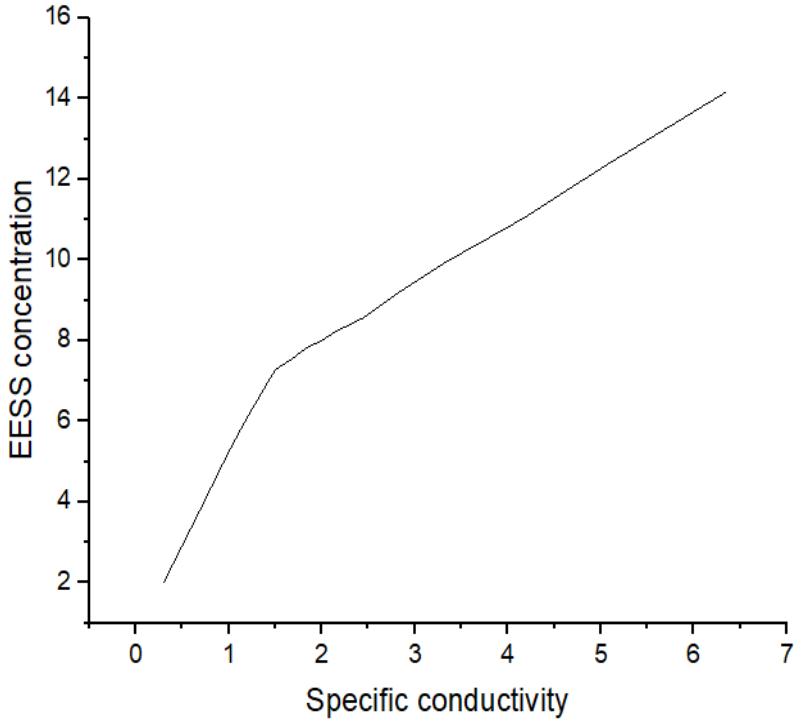

Figure 4-16 Specific conductivity against EESS concentration at 25°C

4.4. Analysis of EESS-Based Liquid Laundry Detergent

EESS based liquid laundry detergents were synthesized by procedure mentioned in chapter three. From synthesized detergents by varying surfactant concentration best formulation were selected by comparing all samples with synthesized LABSA-based liquid detergent based on their characteristics of foamability and detergency test by using testing procedures stated in chapter three.

Table 4-12 Foamability and detergency test of EESS-based liquid detergents

Sample	**Foamability test of EESS-based liquid detergent (cm)**	**Detergency test of EESS-based detergent (Good, not good and Excellent)**
1	3.2	Not good
2	8.1	Good
3	11.5	Excellent
4	13.5	Excellent
5	17	Excellent

Table 4-13 Foamability and detergency test of LABSA based detergent

Sample	**Foaamablity test of LABSA-based liquid detergent (cm)**	**Detergency test of LABSA-based liquid detergent (good, not good and excellent)**
1	14.5	Excellent

The findings in Table 4.12 showed that the foamability and detergency of laundry liquid detergents containing EESS grew in tandem with the quantity of EESS. The detergent's capacity to generate foam improved, as seen by the measurement of foamability rising from 3.2 cm to 16 cm. Additionally, the detergent's detergency power rose in tandem with the amount of EESS, indicating improved cleaning efficacy. Out of all the samples that were evaluated, samples 3, 4, and 5 showed positive traits. Sample 4 was determined to be the optimal formulation for the production of a liquid detergent based on EESS after examination. Sample 4 showed sufficient detergency strength while retaining foamability levels similar to a liquid detergent based on LABSA, which led to this decision. Despite the great foamability of sample 5, it should be remembered that applying a large amount of surfactant is not cost-effective. As a result, sample 4 was chosen as the best formulation because of its foamability and balanced detergency power, which made it an excellent option for the synthesis of a liquid detergent based on EESS.

4.4.1. Characterization of EESS-Based Surfactant

As shown in table 4.14 characteristics of the selected EESS-based and LABSA-based liquid detergents were evaluated in terms of pH, active matter, and rinsing property. The detailed test reports for these characteristics can be found in Appendix D.

Table 4-14 Properties of synthesized Liquid Detergents

No	Parameters	EESS-based liquid detergent	LABSA- based Liquid detergent	Standard
1	pH	9.25	9.4	7-9.5
3	Active matter	25.44	27.54	>15
4	Rinsing property	Free rinsing	Free rinsing	Shall be free- rinsing

pH

The pH values of 9.4 for the liquid detergent derived from Linear Alkylbenzene Sulfonic Acid (LABSA) and 9.25 for the liquid detergent derived from ethyl ester sulfonate surfactant are both within the normal range of 7-9.5. These pH readings show that the two detergents have a slightly alkaline composition. The pH range of 7-9.5, encompassing the detergents under comparison, is often regarded as suitable for both residential and commercial cleaning agents. This range minimizes any harm to fabrics or surfaces while guaranteeing efficient cleaning. For a variety of reasons, an alkaline pH in detergents is preferred since it increases cleaning efficacy. Alkaline solutions are excellent for removing stains and grime because they have a greater ability to dissolve and break down grease, oils, and other organic materials. Alkaline pH levels can also help with the emulsification of oils and the elimination of mineral buildup.

Active matter

The liquid detergent made from ethyl ester sulfonate surfactant has an active matter concentration of 25.44, which has important effects on its foamability, emulsion power, and cleaning efficacy. This detergent is anticipated to have exceptional foamability due to its greater active matter concentration, producing copious amounts of durable foam while in use. This foam makes cleaning easier by helping to suspend and remove grime. Furthermore, the detergent's strong emulsion power, which is linked to a larger concentration of active matter, facilitates the efficient dispersion and emulsification of oily and greasy substances, hence facilitating their removal from surfaces. This quality is very helpful for cleaning away grease accumulation and tough stains. Additionally, a greater active matter content indicates better cleaning performance since the surfactant concentration allows for more efficient interaction with the dirt particles, which in turn facilitates their separation and subsequent washing away. It is significant to remember that, although the active matter content plays a major role, other aspects including the detergent's composition, compatibility with various surfaces, and inclusion of other cleaning agents can also have an impact on its overall cleaning performance. Consequently, in order to properly analyze the detergent's cleaning powers, a thorough evaluation of these components is required.

Rinsing property

The "shall be free rinsing" feature of liquid detergent made from ethyl ester sulfonate surfactant signifies that the detergent is made to rinse off quickly and leave the least amount of residue on surfaces after washing. The entire cleaning process and the caliber of the outcomes are greatly impacted by this attribute. A detergent that has good rinsing qualities makes sure that the product may be easily and completely removed from the surfaces it is cleaning after the cleaning process. This is especially crucial since detergent residue can cause problems like stains, hazing, or sticky films on surfaces. The detergent reduces the possibility of these unfavorable effects by being "free rinsing," which improves the general cleanliness and look of the cleansed surfaces. Additionally, the "free rinsing" feature helps with water saving initiatives. Because less water is needed to remove the detergent, there is less of an environmental effect during the cleaning process.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

In this work, inexpensive, renewable feedstock castor oil was used to synthesize an ethyl ester sulfonate surfactant for use in liquid detergent applications. EESS was produced by synthesising ethyl ester from castor oil using ethanol as an alcohol and NaOH as a catalyst in a transesterification process. The synthesis of ethyl ester from castor oil via alkali transesterification was effectively optimized by the use of the box Behnken experimental design of the RSM. The findings of the RSM experiment indicated that in order to achieve 94.5% FAEE content in the transesterification process, the ideal conditions were 1:16 oil to ethanol molar ratio, 1.00% weight% NaOH catalyst, and 65ºC reaction temperature. With an R2 value of 0.994, the ANOVA statistics showed that the model was very significant and that there is a strong association between the experimental data and the projected model. The castor oil was entirely transformed into FAEE, as demonstrated by chemical structures based on FTIR results. The produced ethyl ester was converted to EESS by a sulfonation process employing sulfuric acid as the sulfonating agent. Using the OVAT experimental design, the optimal point and the impact of sulfonation parameters on the yield of EESS were examined. At a ratio of 1:1 sulfonating agent to ethyl ester, a sulfonation temperature of 80°C, and a sulfonation period of three hours, a high yield of 78.4% was produced. The resulting surfactant had strong surface-active characteristics, and the sulfonate group (S=O) at 1180 cm-1 was verified by the FTIR spectra, proving that the chemical was an ethyl ester sulfonate surfactant. As the surfactant concentration rose, so did the conductivity of the produced surfactant. Furthermore, EESS's average active matter of 64.35% was found to be comparable to that of sulfonated ester surfactants that had been previously investigated. Additionally, the EESS performed well as LABSA in the formation of liquid detergents, indicating that it may be a viable surfactant for these formulations.

5.2. Recommendation

Considering results obtained in this thesis the following recommendations are suggested for future works:

- Because other sulfonating agents are not readily available, the impact of sulfonating agent type on the yield of EESS was not taken into account in this work. Gaining knowledge about the possible effects of various sulfonating agents on the yield of EESS may be extremely helpful in streamlining the production procedure and perhaps enhancing the overall effectiveness of EESS synthesis. Consequently, in order to deepen our comprehension of this crucial step in the surfactant synthesis process, it is advised that future research investigate and assess the impact of various sulfonating agents on the yield of EESS.
- The goal of the current investigation was to determine how sulfonation factors affected the amount of ethyl ester sulfonate surfactant (EESS) produced. It is advised, nonetheless, that future research broaden the scope to encompass the impact of these sulfonation variables on the surfactant's surface tension characteristics and critical micelle concentration (CMC).

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APPENDIX

Appendix A Extraction and Characterization of Castor Oil

Figure 0-1 Screw press machine

Figure 0-2 Purified castor oil

Figure 0-3 moisture content analysis

Figure 0-4 filtration process

Figure 0-5 degumming process

Figure 0-6 pH analysis

Figure 0-7Acid value test

Figure 0-8 Saponification value test

Table 0-1 Moisture content of castor oil

Trial	Seed weight Before drying(g)	Seed weight after drying(g)	Moisture content %
1	20.73	19.87	4.32
2	20.12	19.31	4.19
3	20.52	19.68	4.26
Average moisture content			4.25

Table 0-2 Acid values of castor oil

Trial	Titration volume	Acid value
1	0.5	0.562
2	0.8	0.891
3	0.9	1.01
average acid value		0.85

Table 0-3 Saponification values of castor oil

Trial	Titration volume of sample	Titration volume of blank solution	Saponification value
1	7.6	20	173.92
2	7.1	19	180.9
3	5.3	17.4	169.7
Saponification value			174.84

Table 0-4 Iodine values of castor oil

Trial	**Volume of sodium thiosulphate used for blank**	**Volume of sodium thiosulphate used for determination**	**Iodine value**
1	28	3.5	77.72
2	28	2.7	80.26
3	28	3.0	79.31
Average iodine value			79.09

Appendix B Synthesis and Characterization of Ethyl Ester

Figure 0-9 Experimental setup for transesterification reaction

Figure 0-10 phase separation between ethyl ester and glycerol

Figure 0-11 Degumming of ethyl ester

Figure 0-9 Centrifugation process

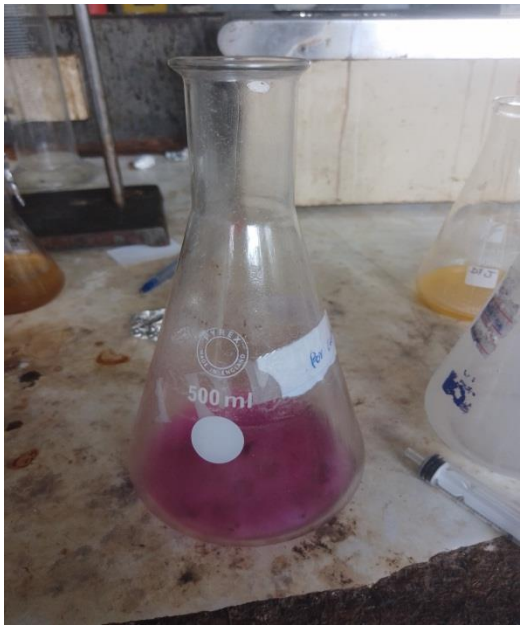

Figure 0-10 Acid value test

Table 0-5 Regression coefficient and corresponding 95% CI

Factor	**Estimated coefficent**	**DF**	**Standard error**	**95% CI low**	**95% CI High**	**VIF**
Intercept	84.86	1	0.32	84.11	85.61	
A-alchol to oil molar ratio	7.80	1	0.25	7.21	8.39	1.00
B-catalyst conc	2.61	1	0.25	2.02	3.21	1.00
C-time	-2.39	1	0.25	-2.98	-1.79	1.00
A^2	-1.63	1	0.35	-2.45	-0.81	1.01
B^2	1.14	1	0.35	0.33	1.96	1.01
C^2	-2.75	1	0.35	-3.57	-1.94	1.01
AB	-0.48	1	0.36	-1.32	0.37	1.00
AC	0.98	1	0.36	0.13	1.82	1.00
BC	-0.25	1	0.36	-1.09	0.59	1.00

Table 0-6 Acid values of ethyl ester

Trial	**Titration volume**	**Acid value**
1	0.6	0.673
2	0.8	0.897
3	0.5	0.561
average acid value		0.71

Table 0-7 Iodine values of ethyl ester

Trial	**Volume of sodium thiosulphate used for blank**	**Volume of sodium thiosulphate used for determination**	**Iodine value**
1	28	2.8	79.32
2	28	2.4	80.64
3	28	2.1	81.58
Average iodine value			80.51

Appendix C Synthesis and characterization of Ethyl Ester Sulfonate surfactant

Figure 0-11 Sulfonation process

Figure 0-12 pH of EESS before neutralization

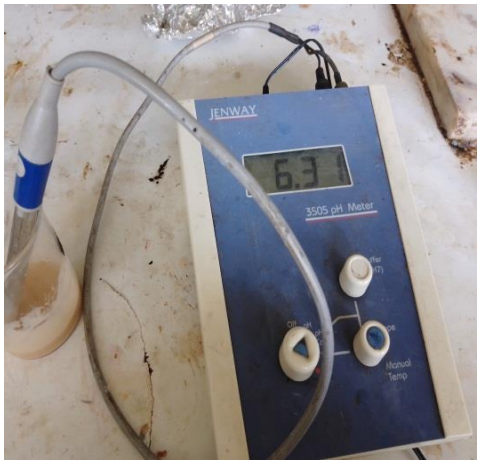

Figure 0-13 pH of EESS after neutralization

Table 0-8 Specific gravity of EESS

EESS concentration (mol/L)	**Specific conductivity k (mScm-1) (± 0.02) at 25°C**
0.20	1.95
0.60	3.55
1.00	5.15
1.35	6.05
1.65	7.20
1.85	7.35
2.05	7.76
2.20	7.95
2.40	8.15
2.80	9.15
3.20	9.85
4.05	10.85
5.00	12.15
6.15	14.05

Figure 0-14 EESS based liquid detergent

Appendix D Characterization of EESS based laundry detergent

ECAE

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Ethiopian Conformity Assessment Enterprise

Document No: TLD/F7.08-1 | Copy No: - | Rev No: 3 | Page No: 1 of 1 | Effective Date: 26 Oct 22

Title: **TEST REPORT** የፍተሻሪፖርት

Name and address of client:	Dibora Marie, Addis Ababa	Test Report No:	CTR/0275/16
Tel:	+251-965-22-68-84	Test Order No:	---
Fax:	---	Reported date:	22/09/2023
E-mail:	---	Date of sampling:	Not Specified
Date sample Received:	15/09/2023	Place of sampling:	Not Specified
Client Sample code:(Brand)	EESS Based Detergent	Sampled and submitted by:	Client
Type of sample:	Synthetic liquid laundry detergent for hand wash	Date tested:	18-21/09/2023
Lab Designated number:	16004010	Method/Specification:	CES 268:2020

S/N	Characteristics tested	Test Method/Specification	Standard Requirements			Test result	Comment
			Min	Nom	Max		
1.	pH value	ES ISO 4316:2001	7		9.5	9.25	Passed
2.	Active matter, % by mass	BCTL/SOP/M057.01	15			25.44	Passed
3.	Rinsing property	CES 268:2020	Shall be free - rinsing			Free rinsing	Passed

Remark :

1 This test report relates only to the specific sample product which has been tested by ECAE testing laboratory.

Test report authorized by, Name Fitsum G/medhin Position Analyst -II Sign

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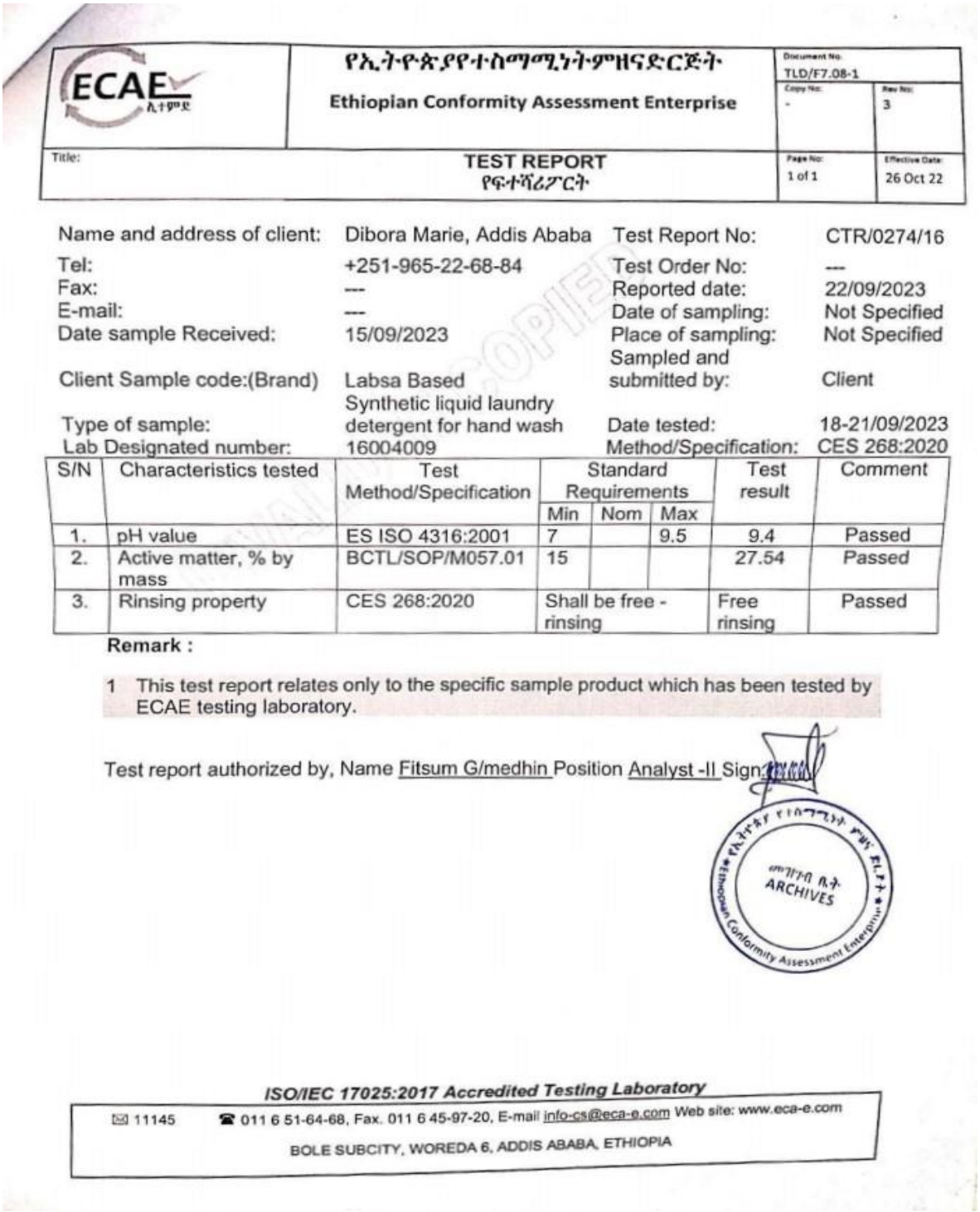
BOLE SUBCITY, WOREDA 6, ADDIS ABABA, ETHIOPIA

Figure 0-18 Test report of EESS based liquid detergent



ECAE ኢተምኗ

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Ethiopian Conformity Assessment Enterprise

Document No: TLD/F7.08-1 | Copy No: - | Rev No: 3 | Page No: 1 of 1 | Effective Date: 26 Oct 22

Title: TEST REPORT
የፍተሻሪፖርት

Name and address of client:	Dibora Marie, Addis Ababa	Test Report No:	CTR/0274/16
Tel:	+251-965-22-68-84	Test Order No:	---
Fax:	---	Reported date:	22/09/2023
E-mail:	---	Date of sampling:	Not Specified
Date sample Received:	15/09/2023	Place of sampling:	Not Specified
Client Sample code:(Brand)	Labsa Based	Sampled and submitted by:	Client
Type of sample:	Synthetic liquid laundry detergent for hand wash	Date tested:	18-21/09/2023
Lab Designated number:	16004009	Method/Specification:	CES 268:2020

S/N	Characteristics tested	Test Method/Specification	Standard Requirements			Test result	Comment
			Min	Nom	Max		
1.	pH value	ES ISO 4316:2001	7		9.5	9.4	Passed
2.	Active matter, % by mass	BCTL/SOP/M057.01	15			27.54	Passed
3.	Rinsing property	CES 268:2020	Shall be free - rinsing			Free rinsing	Passed

Remark :

1 This test report relates only to the specific sample product which has been tested by ECAE testing laboratory.

Test report authorized by, Name Fitsum G/medhin Position Analyst -II Sign:

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Figure 0-19 Test report of LABSA based liquid detergent