ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

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SCHOOL OF CHEMICAL AND BIO ENGINEERING

Synthesis of Anionic Surfactant from Jatropha Oil

By

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ADDIS ABABA, ETHIOPIA

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Synthesis of Anionic Surfactant from Jatropha Oil

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

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ACRONMYS

AES	Alcohol Ether Sulfate
ANOVA	Analysis of Variance
AOS	Alfa-olefins sulfonates
AV	Acid Value
CCD	Central Composite Design
EV	Ester Value
FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
FT-IR	Fourier Transform Infrared Spectroscopy
GC	Gas Chromatography
ISO	International Standards Organization
LABSA	Linear alpha benzene sulfonic acid
LAS	Linear alpha salfonate
ME	Methyl ester
MESA	Methyl ester sulfonic acid
MESS	Methyl ester sodium sulfonate
RSM	Response Surface Methodology
PAS	Primary Alcohol Sulfate
SG	Specific Gravity
SV	Saponification Value

ABSTRACT

Due to the high cost of surfactant production caused by petrochemical feed stocks, considerable attention has been given to non-edible vegetable oils as an alternative source of feedstock. In this paper, a new non-edible oil derived surfactant based on Jatropha plant is synthesized. In this study the objective is synthesis and characterization of anionic surfactant from Jatropha Oil to substitute petroleum based anionic surfactant.

The oil of jatropha was extracted by using Mechanical press and characterization of the oil has been done in order to make sure the oil is best fit for synthesizing anionic surfactant. Using transesterification process the extracted oil reacts with methanol by using catalyst sodium hydroxide to produce methyl ester. The molar ratio of H_2SO_4 to methyl ester, reaction temperature, reaction time and agitation speed on the sulfonation process of methyl ester produced was statistically investigated and important conditions are determined.

A four-factor central composite design (CCD) combined with response surface modeling (RSM) and optimization was employed for maximizing the yield of sulfonated methyl ester based on 20 different experimental data. Analysis of variance (ANOVA) and other tests were used to test the significance of the independent variables and their interactions. Adequacy of the model was tested by the correlation between experimental and predicted response and enumeration of prediction errors. The predicted maximum active mater (68.3%) was found under the optimum conditions of the process variables (1:1 molar ratio of H_2SO_4 to methyl ester, 65^{o}C of reaction temperature and 1.5 hours of reaction time) the result is close to the experimental value (69%) determined.

1. INTRDUCTION

1.1. Background

Fatty acids and their derivatives play an important role in the chemical industry because they are used as raw materials for a wide variety of industrial products utilized in different aspects like, textile, paints, rubber, cosmetics, food, pharmaceuticals and surfactants. The production of fatty acids from non-edible oil resources upgrades them to be suitable for the manufacture of all types of surfactants and other products, this characteristic turns attention to *Jatropha* which grows in tropical and subtropical climates across the developing world. Cultivation of *Jatropha* has been found to be viable due its drought resistance and potential to produce oil from marginal semi-arid lands. The genus Jatropha contains approximately 170 known species. The plant is planted as a hedge (living fence) by farmers all over the world around Homesteads, gardens, and fields because it is not browsed by animals. The use of *Jatropha* seed oil for biodiesel and surfactant production has been reported in many literatures. [2, 3]

All organic surfactants comprise a specific character, in their molecular structure. The molecule must contain a portion which has affinity to oil (lypophilic.), whereas the opposite end of the molecule, at the same distance has an attraction for water or aqueous solutions (hydrophilic). This ability within the same molecule will be a dual affinity for substances of entirely different natures; such character gave these substances surface active property in quite dilute solutions. This function is done to the tendency of the molecules to concentrate at interfaces between the solvent and a gas, solid or other immiscible liquids. From this phenomenon, the tern of surface active agents or surfactants was derived. At the boundaries of the solvent, the molecules are

oriented in such that; the hydrophobic hydrocarbon chain or “tail” of the molecule is directed towards the hydrophobic or oily phase and the hydrophile or polar “head” is directed or embedded into a gas or polar phase. This property leads to the ability of these materials to reduce surface tension, to cause foaming, and to exhibit other unique properties. Therefore, surfactants find utility in many fields, the principle use being as detergents, wetting agent, dispersing agents and floating agents. Consequently, they are widely incorporated in house hold cleaning products and in such diverse applications as agricultural sprays, cosmetics, floatation, foods, emulsifiers, lubricants, leather manufacture, inks, synthetic elastomeric production and oil recovery operations. [2]

It is observed that the acids obtained by hydrolysis of vegetable fats are very largely saturated or unsaturated acids containing more than 18 carbon atoms. The work done in this thesis synthesis of anionic surface active agents obtained from the non-edible ***Jatropha oil*** which is available in Ethiopia were, considered because of the remarkable properties and wide variety of uses of these seeds.

1.2. Statement of the Problem

In Ethiopia Linear Alpha Benzene Sulphonic Acid(LABSA) is widely used anionic surfactant for detergent products by detergent producers all over the country. This anionic surfactant is all imported from different countries like United Arab Emirates, India and China. So it requires high currency which is considered as the main problem and it has poor biodegradability of surfactants under anaerobic condition may sometimes result in a high surfactant sludge load as compared with that of naturally synthesized surfactants. This research is an attempt to come up with a method to help resolve the problem mentioned.

1.3. Objectives

1.3.1.General Objective

The general objective of the study is to synthesis and characterization of anionic surfactant from Jatropha Oil to substitute petroleum based anionic surfactant.

1.3.2.Specific Objectives

The specific objectives of the studies are to:

- Extraction of non-edible oil from Jatropha seed by mechanical pressing.
- Characterization of the extracted Jatropha oil such as acid value, saponification value, unsapponifable matter, Iodine value and hydroxyl value and fatty acids content.
- Synthesis of anionic surfactant using the extracted oil.
- Characterization of synthesized anionic surfactant.

1.4. Significance of the Project

Ethiopia is among the largest Jatropha seed plant grown countries the Government has identified almost 24 million ha of land suitable for Jatropha tree cultivation in the states Oromia, BenishangulGumuz, Gambella, Somali, Amhara Southern Nations, Nationalities and Peoples Region (SNNPR) and Tigray and Afar Regional states. Experts estimate the current land under Jatropha cultivation as 1,700 ha. Therefore producing anionic surfactant from Jatropha oil in Ethiopia enable the country to reduce the foreign currency to import the anionic surfactant called Linear Alpha Benzene Sulfonic Acid (LABSA) which is widely used in the country for detergent production and anionic surfactant from non-edible oils are characterized by a good biodegradability, low toxicity and mildness to skin, making them useful in cleansing products.

1.2. Scope of the Research

The thesis work generally covers Jatropha oil extraction, Jatropha oil characterization, methyl ester preparation and synthesis of anionic surfactant methyl ester sulfonate acid through modified sulfonation process, characterization of produced SME, refining, characterization of jatropha oil,preparation of ME and characterization of the produced methyl ester sulfonic acid using astandard procedures and test methods.

2. LITERATURE REVIEW

2.1. Introduction

The literature review of this research covers the available raw materials for synthesis of anionic surfactant from non edible oils, anionic surfactant production technologies, parameters that affect anionic surfactant production, physicochemical properties and specifications of anionic surfactant and finally sulfonation process.

2.1.1. Surfactant

Surfactants (or 'surface active agents') are organic compounds with at least one lyophilic ('solvent-loving') group and one lyophobic ('solvent-fearing') group in the molecule. If the solvent in which the surfactant is to be used is water or an aqueous solution, then the respective terms 'hydrophilic' and 'hydrophobic' are used. In the simplest terms, a surfactant contains at least one non-polar group and one polar (or ionic) group. [2]

2.1.2. Classification of Surfactant

From the commercial point of view surfactants are often classified according to their use.However, this is not very useful because many surfactants have several uses, and confusions mayarise from that. The most acepted and scientifically sound classification of surfactants is based ontheir dissociation in water. [2]

1. **Anionic Surfactants**

Anionic surfactants are dissociated in water in an amphiphilic anion, and a cation, which is in general an alkaline metal (Na^+, K^+) or a quaternary

ammonium. They are the most commonly used surfactants. They include alkylbenzene sulfonates (detergents), (fatty acid) soaps, lauryl sulfate (foaming agent), di-alkyl sulfosuccinate (wetting agent), lignosulfonates (dispersants) etc… Anionic surfactants account for about 50 % of the world production. [2]

2. Nonionic Surfactants

Non ionic surfactants come as a close second with about 45% of the overall industrial production. They do not ionize in aqueous solution, because their hydrophilic group is of a nondissociable type, such as alcohol, phenol, ether, ester, or amide. A large proportion of these nonionic surfactants are made hydrophilic by the presence of a polyethylene glycol chain, obtained by the polycondensation of ethylene oxide. They are called polyethoxylated nonionics.In the past decade glucoside (sugar based) head groups, have been introduced in the market, because of their low toxicity. As far as the lipophilic group is concerned, it is often of the alkyl or alkylbenzene type, the former coming from fatty acids of natural origin. The polycondensation of propylene oxide produce a polyether which (in oposition to polyethylene oxide) is slightly hydrophobic. This polyether chain is used as the lipophilic group in the so-called polyEOpolyPO block copolymers, which are most often included in a different class, e.g. polymeric surfactants, to be dealt with later. [2]

3. Cationic Surfactants

Cationic Surfactants are dissociated in water into an amphiphilic cation and an anion, most often of the halogen type. A very large proportion of this class corresponds to nitrogen compounds such as fatty amine salts and quaternary ammoniums, with one or several long chain of the alkyl type, often coming from natural fatty acids. [2]

4. Polymeric Surfactant

Polymeric Surfactant the past two decades have seen the introduction of a new class of surface active substance, so-called polymeric surfactants or surface active polymers, which result from the association of one or several macromolecular structures exhibiting hydrophilic and lipophilic characters, either as separated blocks or as grafts. They are now very commonly used in formulating products as different as cosmetics, paints, foodstuffs, and petroleum production additives. [2]

2.2. Raw materials for surfactant synthesis

Many kinds of surfactant structures are today available on the market and the raw materials are extremely varied and come from diverse origins, with a transformation ranging from a simple hydrolysis to multistep high pressure synthesis processes. With the single exception of rosin and tall oils the surfactant raw material market does not depends significantly on the surfactant manufacturing business. A consequence of this is that raw material costs can vary considerably because of factors external to the surfactant business. This volatile situation has produced changes and altered competitive margins in the surfactant industry.

For the sake of simplicity the raw materials for surfactant manufacturing are classified according to their origin (natural or synthesized from a petroleum cut). [2]

2.2.1. Raw Materials from Petroleum

Other sources of lipophilic materials such as petroleum refining were considered in order to lower the cost, particularly for detergents. A proper

lipophilic group exhibits a hydrocarbon chain containing from 12 to 18 carbon atoms. Such substances are found in light cuts (gasoline and kerosene) coming from atmospheric distillation and catalytic cracking. It is also possible to make such a chain by polymerization of short chain olefin, particularly in C_3 and C_4. The main examples are

1. Alkaylates for Alkyl benzene Production
2. Linear Paraffins, Olefins and Alkylates
3. Aromatics

2.2.2. Natural Oils & Fats: Triglycerides

Most oils and fats from animal or vegetal origin are ***triglycerides***, i.e., trimesters of glycerol and fatty acids, as for instance the structure indicated in the following formula.

CH_2-OCO-$C_{17}H_{35}$ Stearic acid ester

CH-OCO-$(CH_2)_7$-CH=CH-$(CH_2)_7$-CH_3 Oleic acid ester

CH_2-OCO-$C_{15}H_{31}$ Palmitic acid ester

Figure 2.1 -Oleyl-palmityl-stearine

In some cases esterification is not completed, leading to mono and diglycerides. Some natural products include poly alcohols which are more complex than glycerol as for instance in C5 and C6 mono-sugar compounds. In all cases, the hydrolysis reaction allows the separation of the poly alcohol from the fatty acids.

Natural triglycerides contain the five most common fatty acids in various proportions: palmitic acid (symbolized as C16:0, i.e. 16 carbon atoms, no

double bound) and the 4 main acidscontaining 18 carbon atoms: stearic (C18:0), oleic (C18:1), linoleic (C18:2) and linolenic(C18:3), with 0, 1, 2 and 3 double bounds, respectively.

It is worth noting that natural oils and fats contain an even number of carbon atoms, and that they are linear with the acid group at one end. Natural oils exhibit an uncommon conformation, i.e., most of the C=C in saturations are of the ***cis*** type, and in poly unsaturated chains the double bonds are not conjugated, whereas the ***trans*** conformation and the double bond conjugation are more stable from the thermodynamic point of view.

Fatty acids in the C12-C18 range, particularly those from natural origin, are quite important in the manufacture of soaps and personal care specialties, because they carry a lipophilic group which is completely biocompatible and well adapted to the preparation of surfactants for cosmetics, pharmaceuticals or foodstuffs. [2]

2.2.3. Jatropha Oil

Jatropha is a great potential industrial oil seed crop. It is considered to be the best sustainable source. It is a multipurpose, drought resistant shrub belonging to the family of Euphorbiaceae. The seeds of Jatropha are considered to be the good source of lipids. They contain approximately 20 to 39% of oil and this makes their use as an energy source for fuel production very attractive. In addition to this, the oil from its seeds has been found useful for manufacture of candles and soap, in cosmetic industry and also as for medicinal purposes. [3]

2.2.3.1. Description of Jatropha plant

Jatropha (physic nut) is a large shrub or small tree up to 5m tall and has a life expectancy of about 50 years. It is originated in Central and South America but now has spread around the world. The plant develops a deep taproot and initially four shallow lateral roots. Normally Jatropha flowers only once a year during the rainy season. Jatropha flowers almost throughout the year in permanently humid regions or under irrigated conditions (Heller, 1996). The seeds become mature when the capsule changes from green to yellow. Jatropha has a deciduous nature, shedding its leaves during the dry season. The plant components contain toxic elements, mainly phorbol esters. [3]

Figure2.2 Jatropha seeds

2.2.3.2. Extraction of Jatropha oil

The oil from Jatropha seeds can be extracted by two different methods; mechanical extraction using a hydraulic or screw press machine (through heating), and solvent extraction.

Mechanical: To prepare the seeds for mechanical extraction, the seeds are solar heated for several hours or roasted for 10 minutes, without overheating. The process breaks down the cells containing the oil and eases the oil flow. The heat also liquefies the oil, which improves the extraction process. A hydraulic press machine is then used to compress a measured amount of seeds and extract the oil.

Solvent: Solvent extraction yields the maximum seed oil, that is 38% by weight of the seed, or 99% of the total available vegetable oil. The process involves the use of solvents, such as Hexane and Isopropanol, applied in varying proportions to extract oil from crushed Jatropha seeds. [3]

2.2.3.3. Chemistry of Jatropha oil

Jatropha curcas consist of saturated fatty acid especially palmitic acid(17.81%), stearic acid (10.95%) and archidic acid(1.00%) whereas monounsaturated fatty acid was oleic acid (37.03%)and polyunsaturated fatty acid was linoleic acid (21.60%).[4]

Table 2-1 Physical and Chemical Properties of Jatropha oil

Sr. No	Physicochemical parameter	Values for Oil
1	Specific gravity	0.913 at 28°C
2	Refractive index	1.496 at 28°C
3	Acid value (mg KOH/g)	3.74±0.07
4	Iodine value (mg/g)	104.90±0.25
5	Saponification value (mg/g)	203.36±0.36
6	Unsaponifiable matter (%)	1.76±0.03

(Source: from www.ijabpt.com)

2.2.3.4. Application of Jatropha oil

Jatropha plant has been found for using on different aspects in different communities in the world. It has been found that the plant is used as an ornamental purpose, chiefly in Africa and America, growing in gardens for their ornamental foliage and flowers. It is also commonly grown as a live hedge around agricultural fields as it can be easily propagated by seeds or branch cutting as is not browsed by goats or cattle. It can be cut or lopped at any desired height and is well adapted for hedges around agricultural fields. However, on the basis of different literatures, some of the economic activities through the use of Jatropha can be broadly classified as follows,[5]

- Potential as an oil crop
- Potential for industrial use
- Potential as medicinal plant
- Potential as raw material for dye
- Potential for enrichment of soil
- Potential as a feed stoke
- Potential as insecticide/pesticide
- Potential as profitable agro forestry crop
- Potential as non conventional energy crop

2.2.4. Sulfuric Acid

The oldest and still widely used, acid in the detergent industry is sulphuric acid of various strengths. The chemical formula of sulphuric acid is H_2SO_4, molecular weight of 98.08. For sulphonation processes either the so called monohydrate of 98/99 percent is acid strength is used.

There are two major processes used in the production of H_2SO_4, the lead chamber process and the contact process. The lead-chamber process is the older of the two processes, and its product is aqueous sulfuric acid containing 62% to 78% H_2SO_4. The contact process yields pure sulfuric acid. In both processes, sulfur dioxide, SO_2, is oxidized to sulfur trioxide, SO_3, and the SO_3 is dissolved in water.

Sulfur dioxide is obtained by burning sulfur,

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

By roasting pyrite (iron sulfide) or other metal sulfides prior to smelting,

$$4\ FeS(s) + 7\ O_2(g)\ 2 \longrightarrow Fe_2O_3(s) + 4\ SO_2(g)$$

Or by burning hydrogen sulfide,

$$H_2S(g) + O_2(g) \longrightarrow SO_2(g) + H_2O(g)$$

The sulfur dioxide is oxidized to sulfur trioxide catalytically.

$$2\ SO_2(g) + O_2(g)\ 2 \longrightarrow SO_3(g)$$

Without the catalyst, the oxidation of SO_2 is quite slow. In the old lead-chamber process, the catalyst is nitrogen dioxide gas. In the contact process, the catalyst is vanadium (V) oxide, V_2O_5, mixed with an alkali metal sulfate. The mixture is supported on small silica beads, and at the high temperature inside the reactor, the mixture is a liquid. The product SO_3 is dissolved in 98% sulfuric acid. The dissolved SO_3 reacts with the 2% water, forming H_2SO_4.

$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(l)$$

Pure sulfuric acid is a colorless, odorless, oily liquid. It freezes at 10.5^{O}C. It fumes when heated, because some of the H_2SO_4 decomposes to H_2O and SO_3.

The H_2O is retained in the liquid, while SO_3 gas is released. Therefore, the concentration of H_2SO_4 decreases, reaching a concentration of 98.33%. [6]

Table 2-2 Physical & Chemical properties of Sulfuric Acid

Property	**Sulfuric Acid**
Molecular weight	98.07
Color	Colorless liquid
Physical state	Liquid
Melting point	10.3^{o}C (100%)
Boiling point	350(100%)
Density	1.841(96-98%)
Odor	Odorless
Organic solvent(s)	Decomp. Alcohol
Vapor Pressure	1mm Hg at 145.8^{o}C
Flammability limits	No flammable
Conversion factors	1ppm= 4.08mg/m^3

2.3. Production of Methyl Ester or Transestrification Process

Transesterification is the most used method of conversion and refers to the reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to produce alkyl esters and glycerol. The alkyl esters are what are called biodiesel. The purpose of the transesterification process is to lower the viscosity of the oil. The transesterification reaction proceeds well in the presence of some homogeneous catalysts such as potassium hydroxide (KOH)/ sodium hydroxide (NaOH) and sulfuric acid, or heterogeneous catalysts such as metal oxides or carbonates. Transesterification is the general term used to describe he important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the transesterification process is called alcoholysis. The term transesterification is synonymous to alcoholysis of carboxylic esters. The transesterificationis an equilibrium reaction and the transformation occurs

essentially by mixing the reactants. However, the presence of a catalyst (typically a strong acid or base) accelerates considerably the adjustment of the equilibrium. In order to achieve a high ester yield, alcohol has to be used in excess. In the transesterification of vegetable oils, a triglyceride reacts with an alcohol in the presence of a strong acid or base, producing a mixture of fatty acids alkyl esters and glycerol. The overall process is a sequence of three consecutive and reversible reactions, in which di- and mono-glycerides are formed as intermediates. The stoichiometric reaction requires one mole of a triglyceride and three moles of the alcohol. However, an excess of the alcohol is used to increase the yields of the alkyl esters and to allow its phase separation from the glycerol formed. Several factors are there the type of catalyst (alkaline or acid), alcohol-oil molar ratio, temperature, purity of the reactants (mainly water content) and free fatty acid content affect the transesterification process. The types of catalysts often used are discussed below. [7]

2.3.1. Acid-Catalyzed Processes

Transesterification process is catalyzed by acids, preferably by sulphonic and sulphuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100 °C and more than 3 hr to reach complete conversion. The methanolysis of soybean oil, in the presence of 1 mol% ofH_2SO_4, with an alcohol/oil molar ratio of 30:1 at 65 °C, takes 50 h to reach complete conversion of the vegetable oil (> 99%), while the butanolysis (at 117 °C) and ethanolysis (at 78 °C), using the same quantities of catalyst and alcohol, take 3 and 18 hrs., respectively. The alcohol/vegetable oil molar ratio is one of the main factors that influence the transesterification. An excess of the alcohol favors the formation of the products. On the other hand, an excessive amount of alcohol makes the recovery of the glycerol difficult, so that the alcohol/oil ratio has to be established empirically, considering each

individual process. The mechanism of the acid-catalyzed transesterification of vegetable oils is shown below for amonoglyceride. [7]

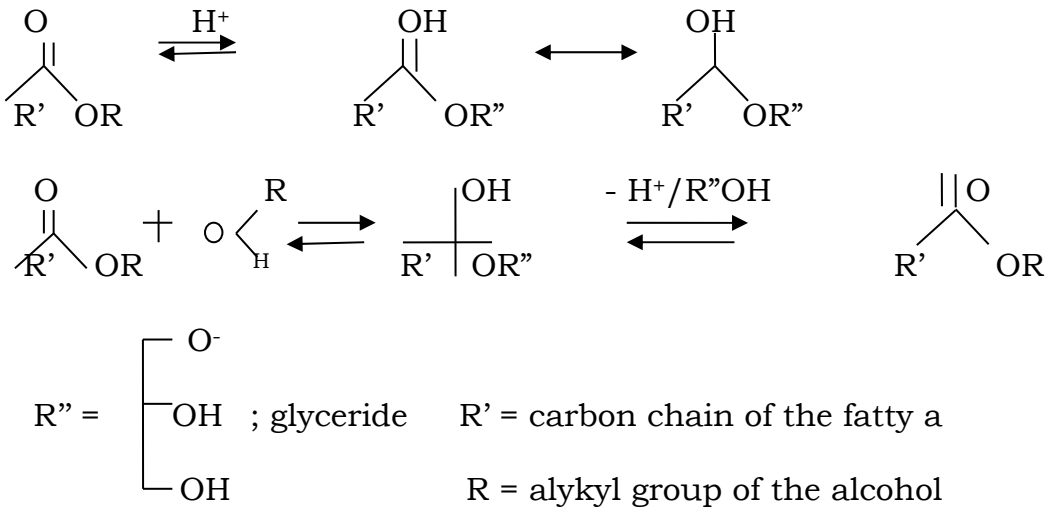


Figure 2.3 Mechanisms of acid catalyzed transesterification of vegetable oil

The protonation of the carbonyl group of the ester leads to the carbocation II which, after anucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminatesglycerol to form the new ester IV, and to regenerate the catalyst H+.According to this mechanism, carboxylic acids can be formed by reaction of the carbo cation II with water present in the reaction mixture. This suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.

2.3.2. Base-Catalyzed Processes

The base-catalyzed transesterification of vegetable oils proceeds faster than the acid-catalyzed reactions. Due to this reason, together with the fact that the alkaline catalysts are less corrosive than acidic compounds, industrial processes usually favour base catalysts, such as alkaline metal alkoxides and

hydroxides as well as sodium or potassium carbonates. The mechanism of the base-catalyzed transesterification of vegetable oils is as shown.

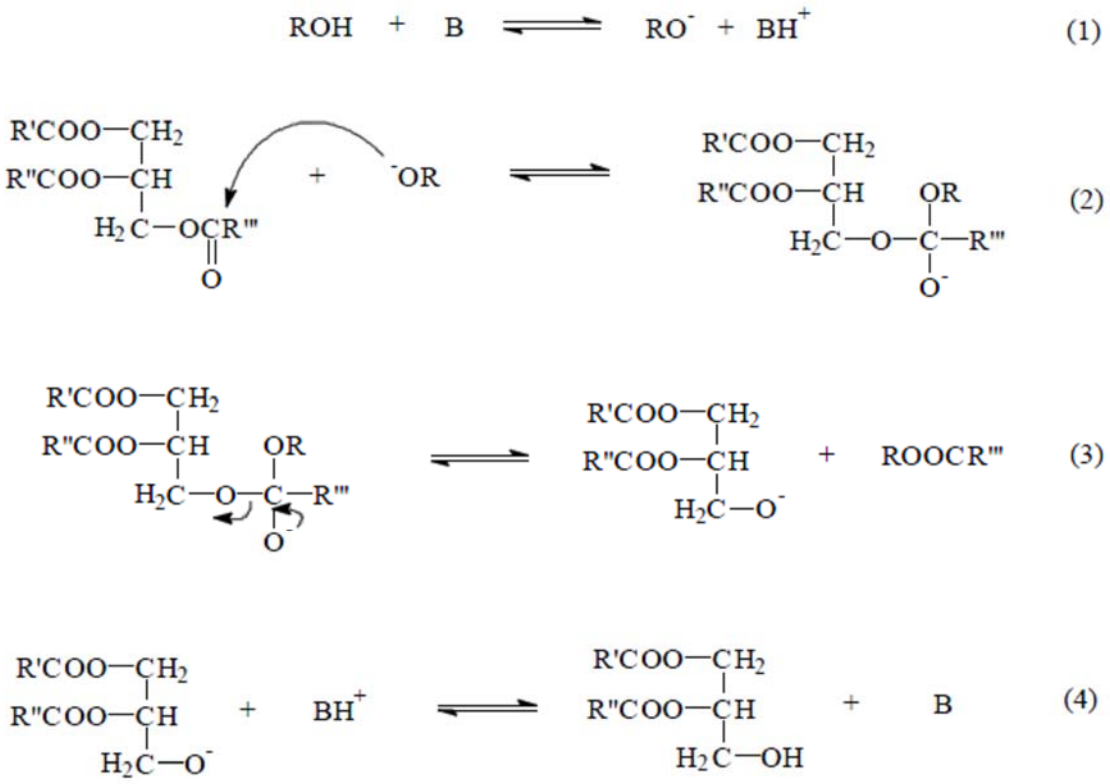


Figure 2.4 Mechanisms of base catalyzed transesterifications of vegitable oil

2.4. Anionic Surfactant Production Technologies

Anionic surfactants are the key component in a detergent formulation. A molecule of anionic surfactant is composed of a lipophilic oil soluble “tail” (typically an organic molecule C12-C14) and a hydrophilic water soluble “head” (such as $SO3^{-}$). Mixtures of organic molecules, either form non-renewable resources, such as crude oil or from renewable sources, such as vegetable oils, are currently used as raw materials for house hold detergents. The cleaning

process performed by anionic surfactants (active detergents) is described in the following way:

i. Wetting of the substrate and dirt due to reduction of surface tension;
ii. Remotion of dirt from substrate;
iii. Retaining the dirt in a stable solution or suspension.

Sulfonation is the term that identifies an electrophilic chemical reaction where a sulfonic group SO_3H is incorporated into a molecule with the capacity to donate electrons. The product of this chemical reaction is recognized as sulfonic acid if the electron donor molecule is a carbon. Sulfuric anhydride reacts easily with delocalized electronic densities as those present in aromatics groups or alkenes in general. These reactions produce a variety of products, including derivate polysulfones. On the other hand, the sulfating process involves the incorporation of the SO_3H molecules to an oxygen atom in an organic molecule to form C−O−S bonds and the sulfate group (Figure 2.4). Sulfates acids can be easily hydrolyzed, and for this reason an immediate neutralization is required after the sulfate group is formed. Although sulfonation and sulfating processes are employed industrially to obtain a wide range of products from hair dyes to pesticides and organic intermediates, their main applications are in the production of anionic surfactants.

Figure 2.5. Functional groups: (a) sulfonate ─SO3H and (b) sulfate ─OSO3H

2.4.1. Types of anionic surfactant produced with different raw materials

2.4.1.1. Linear alkyl benzene sulfonate (LABS)

Linear alkyl benzene is the most common organic feedstock employee in the detergent industry (Figure 2.5). LABS of low molecular weight (230 – 245) lay in the category of anionic surfactants most used in all ranges of household detergent formulations. Dish washing liquids are prepared from LABS of low molecular weight in combination with other anionic surfactant as Lauryl Ether Sulfate (LES) promoting high detergency, foam stability, degreasing capacity, and high stability in hard water. Common concentrations of active detergents in liquid products are: LABS 10-15% (30%), Primary alcohol sulfate/LES 3-5% (10%), where values in brackets are the maximum for concentrated products (Table 1). LABS of high molecular weight (245-260) are the anionic surfactants more used in all ranges of household detergents formulation, but especially in heavy duty laundry products, sometimes in combination with nonionics alcohol sulfates from tallow and soaps. [9]

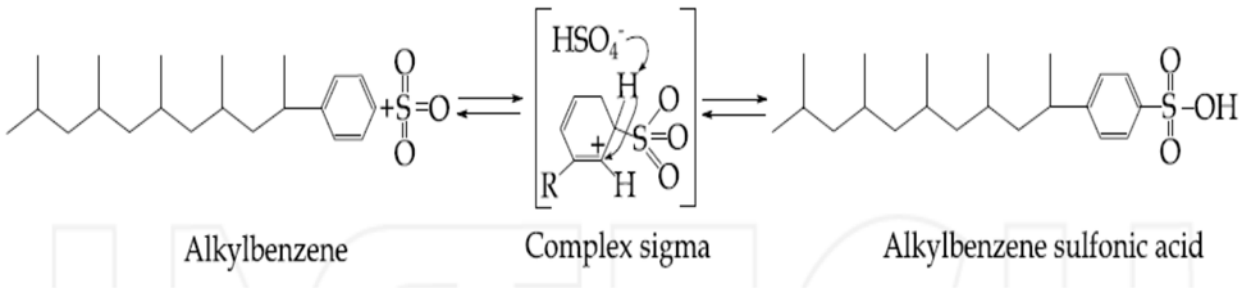


Figure 2.6. Sulfonation of alkylbenzene

Primary alcohol sulfates (PAS)

PAS are categorized in different groups regarding the number carbon that compose them: The so called lauryl alcohol sulfates C12-C14, the "tallow" alcohol sulfates (TAS) C16-C18, and the broader cut C10-C18 alcohol sulfate comprising coconut fatty alcohol sulfates. The broad cut (C10-C18) alcohol sulfates presents cost/performance equilibrium in terms of detergency, solubility and foaming properties. This product can partially or totally substitute other anionic surfactants either in liquid or powder detergent formulations with adequate biodegradability and low "defatting action", which is important for human tissue and delicate natural or synthetic fibers. The narrow cut (C12-C14) alcohol sulfates find their main application in a wide range of personal care products such as shampoos, bubble bath products, tooth pastes, dishwashing liquid, delicate products for laundry wash. The C16-C18 alcohol sulfates ("tallow") are used as sodium salts in the formulation of heavy duty laundry products for hand and machine washing. Their detergency power is up to 10% higher than LABS in a wide range of detergent formulations (de Groot, 1991). Furthermore, TAS shows controlled foam, which is important mainly at high temperatures, still keeping the advantage of softness in the wash of sensitive natural and synthetic fibers [10].

The physical detergency and biodegradability of primary alcohols can be affected by the carbon chain length distribution. Therefore, each new supply may require testing to determine whether the desired properties in the chosen application can be achieved. The mechanism for alcohol sulfation is thought to be similar to that for linear alkylbenzene sulfonation with ΔH = -150 kJ/mol (Figure 2.7)

$$ROH + 2SO_3 \xrightarrow{\text{Fast}} ROSO_2OSO_3H \text{(alkyl hydrogen pyrosulfate)}$$

$$ROSO_2OSO_3H + ROH \xrightarrow{\text{less fast}} 2ROSO_3H \text{ (alkyl hydrogen sulfate)}$$

Figure 2.7. Mechanism of alcohol sulfation

2.4.1.2. Alcohol ether sulfates (AES)

Primary alcohol ethoxylates are made by the addition of ethylene oxide to a primary alcohol in the presence of an alkaline catalyst (Boskamp & Houghton, 1996). The addition of the second ethylene oxide molecule to the alcohol is kinetically favored in comparison with the addition of the first ethylene oxide; hence the product of ethoxylation contains a distribution of ethylene oxide chain lengths attached to the alcohol along with the starting alcohol itself.

Consequently the physical, detergency and biodegradation characteristics are affected not only by the carbon chain length distribution as is the case for primary alcohols, but also by the ethylene oxide distribution which in turn can be supplier depend (de Groot, 1991). The most common alcohol ethoxylates found as feed stocks for sulfation have an average of 2 to 3 molecules of ethylene oxide (2EO or 3EO). During the sulfating of alcohol ethoxylates the by products 1,4-dioxane may be formed (Figure 2.5). Although the formation of

1,4-dioxane is governed predominantly by sulfation and neutralization conditions and by the chemical composition of the feedstock, other factors such as the quality of the raw material also contribute. These factors must be considered during the store and handling of the alcohol ethoxylate feedstock. [11]

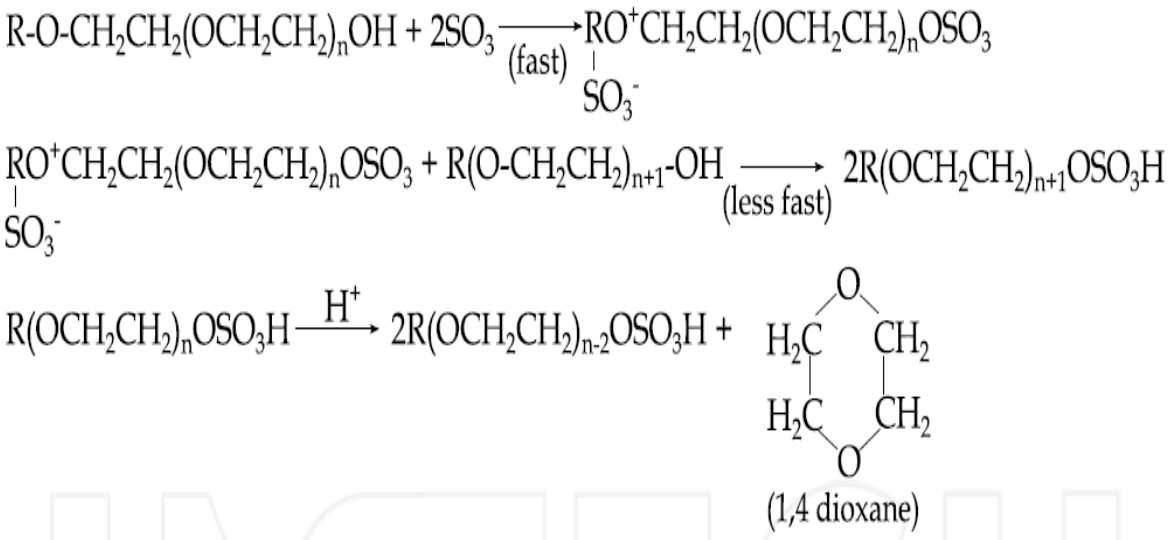


Figure.2.8.reaction scheme of ethoxylated alcohol sulfation

LES (C12-C14/15 2-3 ethylene oxide) can be considered as the most efficient anionic surfactant in terms of: superior detergency power, good tolerance for water hardness, and mildness on hands and fibers. The application therefore is wide: from household to personal care and cosmetic product. Unfortunately, sulfated alcohol ether sulfates show a limited stability to hydrolysis at high temperatures, and this restricts their use in heavy duty laundry powders, where high temperatures occur in the spray drying process of powder manufacture. The high stability to calcium ions permits formulation of liquid detergents with limited or no addition of water “softeners” even in case of use in hard water. The optimum compromise of ethylene oxide addition to keep adequate foam levels and solubility/mildness ratio vary from 2 to 3 moles per

mole of fatty alcohol. The most important worldwide application of AES 2-3 ethylene oxide (EO) are in dish washing liquid detergent, generally combined with LABS and in shampoos/bubble baths. [11]

2.4.1.3. Alfa-olefins sulfonates (AOS)

Alfa-olefins are a potential replacement for alkylbenzenes in detergent applications. Olefin sulfonation is highly exothermic with ΔH = -210 kJ/mol (Roberts, 2001). The neutralized product of alfa-olefin sulfonation requires hydrolysis to remove the sultones, which are skin sensitizers (Figure 2.8). Their exploitation, however, is largely limited to the Far East, Centre on Japan, at present. Commercial supplies of alfa-olefins are produced by the

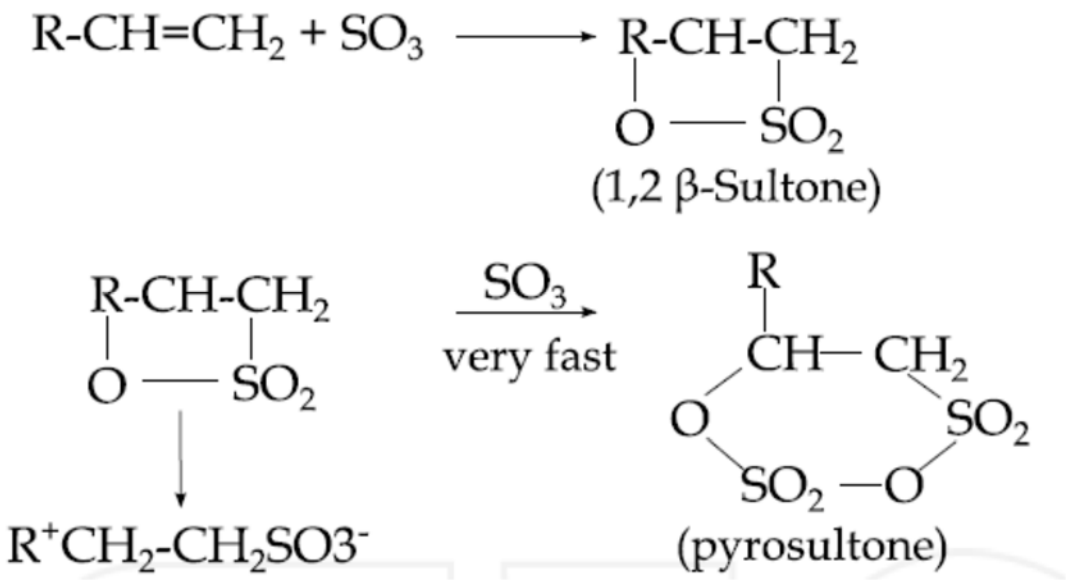


Figure 2.9. Reactions of alfa-olefin sulfonation

oligo merisation of ethylene. The physical, detergency and biodegradation characteristics of alfa-olefins are affected by the carbon chain length

distribution and therefore each new supply may require testing to determine whether the desired properties for the new chosen application can be achieved. The Lion Corporation, Japan, is one of the principal producers and users of alfa-olefin sulfonates. In addition to fabric washing powders, they also market fabric washing liquid, shampoos, tooth paste and foam bath products containing this active. In the USA, Minnetonka has utilized AOS in hand cleaners/liquid soaps. AOS is a potential replacement for alkyl benzene sulfonates in dish wash detergent liquids formulations with performance peaking at C16 chain length.[11]

2.4.1.4. Fatty acid methyl esters sulfonates (FAMES)

FAMES are called to be the main feedstock for detergent formulating in the future due to their applicability in detergent formulations. Moreover, when it is derived from natural oil presents special biodegradable properties that place them over the surfactants derived from petrochemicals compounds. To date, the application of FAMES is under development in various detergent products. The typical cut of FAMES (C16-C18) shows interesting surface activity (about 90% compared to LABS), high detergent, dispersing and emulsifying power in hard water, high lime soap dispersion and moderate foam levels. FAMES show high stability to pH and temperature hydrolysis. Therefore, they can be easily spray dyer and/or incorporated in detergent bars.

Methyl ester sulfonates have a wide range of application and important biological properties. As aggregated value the FAMES can be used in cosmetics, as auxiliary agents in the production of fibers, plastics, and rubber, and in leather manufacture.[11,12,13]

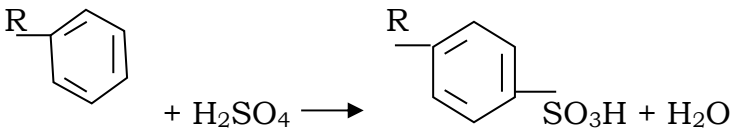
2.4.2. Sulfonation process used for the manufacturing of anionic surfactants

Sulfonation reactions can be carried out in different configurations, either liquid-liquid contact, or gas-liquid contact reactors, and a diversity of sulfonating reagents can be applied for the sulfonation process, such as: Sulfuric acid, SO_3 from stabilized liquid SO_3, SO_3 from sulfur burning and subsequent conversion of the SO_2 formed, SO_3 from boiling concentrated oleum and chloro sulfonic acid.[7]

2.4.2.1. Sulfonation with Sulfuric Acid and/ or Oleum

Sulfonation with sulfuric acid and /or oleum of various free SO_3^- strengths is still widely carried out in the detergent industry. The sulfonation with acid is mainly used for the sulfonation of alkylate. The procedure of sulfonation is described in detail in publication issued by the producers of alkylate.

The chemical reaction is as follows:



Alkylate

As we can seen, water is set free by the reaction. The presence of water retards the sulfonation reaction, or even prevents it altogether. This is the reason why either a very large surplus of H_2SO_4 or a lesser surplus of oleum (H_2SO_4 + SO_3) is required to bring the reaction to completion.

For sulfonation, a glass-lined (or stainless) jacketed vessel with an anchor type of agitator of 120rpm is suitable. During sulfonation, optimum temperature is maintained by cooling with water through the jacket. In hot climates it may be necessary to augment the cooling effect by a refrigeration system and/or a side-arm heat exchanger through which the reaction mass is recirculated by means of a great pump.

After the actual sulfonation step the separation of spent acid (i.e, the greater part of surplus acid) has to be accomplished. Sulfonation without subsequent spent acid separation is rarely carried out, because in this case all the surplus acid has to be neutralized with caustic soda, transforming it to sodium sulfate. This is rather uneconomical and owing to the high reaction temperature for neutralizing considerable amounts of free sulfuric acid, special precautions are required to keep neutralization temperatures under control. We will therefore describe here a sulfonation process with subsequent spent-acid separation.[6]

2.4.2.2. Sulfonation with Chlorosulfonic Acid

Chlorosulfonic acid widely used for the sulfonation of fatty alcohols, fatty alcohol-ethoxylates, alkylphenol-ethoxylates, and related detergent raw materials with OH groups available for the attachment of an SO_3H group. The reaction of lauryl alcohol with chlorosuphonic acid illustrates the chemistry involved:

$C_{12}H_{25}OH + ClSO_3H = C_{12}H_{25}O\text{-}SO_3H + HCl$

The hydrogen chloride must be absorbed to give 30 percent HCl solution as a by-product. One can well consider the HCl in the formula of chlorosulfonic acid as a kind of 'carrier gas' present as liquid bound to SO_3, and set free during the sulfonation reaction. Whereas sulfonation with SO_3 within an inert carrier gas

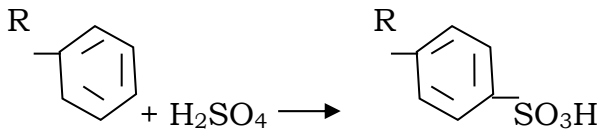
consists of a gas/liquid reaction, sulfonation with chlorosulfonic acid is a liquid/liquid reaction, with liberation of HCl.

Sulfonation with chlorosulfonic acid requires special corrosison-proof equipment, either glass-lined steel or all-glass, the latter especially suitable for small –batch-size sulfonation. The HCl-absorber, too, is built either of glass-lined steel or is all-glass. Some firms use glass-lined steel reactors and all-glass HCl-absorbers.[6]

2.4.2.3. Sulfonation with SO_3

The greatest advance in sulfonation technique in recent years is the use of SO_3 as sulfonating agent, made possible by the commercial availability of this material. Whereas sulfuric acid and/or oleum is mainly used for the sulfonation of alkyl benzene, and chlorosulfonic acid(to be described later) is only suitable for detergent raw materials where an OH-group is present, SO_3 is suitable for practically all types of detergent raw materials.

The reaction with SO_3 takes place without formation of water. The following equation clearly shows this:



The most widely accepted method of using liquid SO_3 as a sulfonating agent is to employ it in its vaporized form diluted with inert carrier gas, mostly dry air, to give a dilute SO_3 gas stream of 7-12 percent (vol) SO_3. Naturally the carrier gas must be as dry as possible; otherwise the SO_3 would react to give H_2SO_4 fumes which would cause poor quality of the finished product. Vaporization of

SO_3 and air-drying is an essential part of process equipment in sulfonation plants using liquid SO_3.[6]

However some reasons why SO3/air in gas-liquid contactor (sulfonator) is becoming the predominant process for the manufacture of anionic surfactants are:

- **Adaptability**: All types of organic feed stocks, like alkylbenzenes, primary alcohols, alcohol ethers, alfa-olefins and fatty acid methyl esters, can be successfully transformed to high-quality sulfonate/sulfate active detergents using SO3/air as sulfonating reagent. Sulfonating reagents like sulfuric acid and oleum are less desirable because only alkylbenzene feedstocks can be converted to high-quality alkylbenzene sulfonic acids.
- **Safety**: Concentrated sulfuric acid, liquid SO_3, and oleum (20 or 65%) are hazardous to be handled, transported, and storage. Sulfur, either in liquid or solid form, although less dangerous option as initial material for the manufacture of SO3, is still risky.
- **Price**: SO_3 obtained directly from the sulfur combustion is the most economical option among all the others options mentioned above regarding transport, handle and storage.
- **Availability**: Liquid SO_3, 65% and 20% oleum and even sulfuric acid are not produced everywhere. Even close to sulfuric acid plants, it is not guaranteed the availability of all the gamma of oleum concentrations.

The SO_3-sulfonation is carried out in tubular reactors where the organic matter (liquid) wets the wall of the tubes while a gas stream containing the sulfonating reagent flows in co-current with the organic matter to avoid over-sulfonation.

The simplest FFR configuration can be described as a two concentric tubes arranged in a vertical way (Figure 2.10).

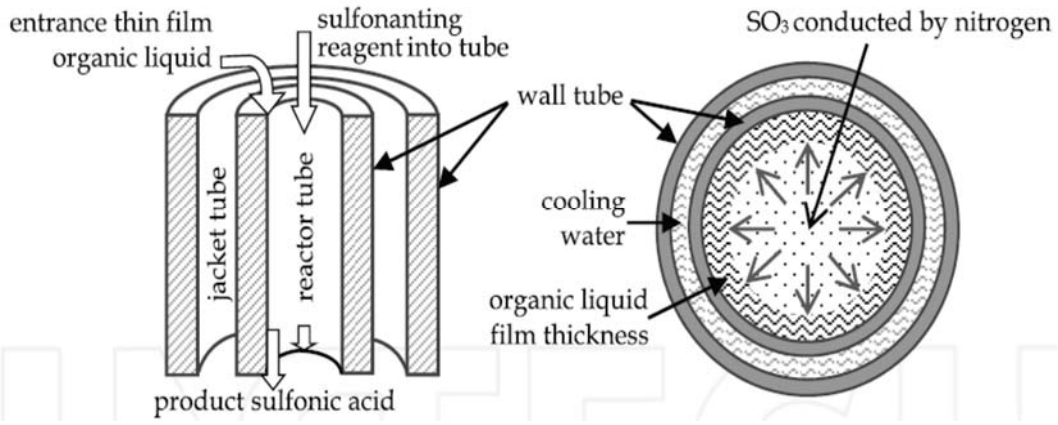


Figure 2.10. Sketch of falling film reactor

Organic matter forms a thin film covering the inner wall of the inner tube. The film descends from the top of the reactor in laminar flow forming an annulus for whose interior a gas stream flows in turbulent regimen. In the first reaction section the concentrated sulfonate reagent get in touch with fresh organic matter. The reaction rate is high as well as the amount of heat released (150 – 170 kJ/mole). A coolant stream flows by the external wall of the inner tube in parallel with the reactant streams. As long as the reaction advances the viscosity of the liquid phase increases (ca. 100 times the initial value). The depletion of reactants reduces the reaction rate and the increase of viscosity slow down the mass transfer process in the film. In this point the co-current coolant, this has already removed a huge amount of heat from the first reactor zone, works as a heating current that controls the viscosity of the film.

Figure 2.10 shows a diagram of film SO3-sulfonation along with an additional step (bleaching) than could be required depending of the feedstock and characteristic of the final product. Depending on the type of organic feedstock

and consequent organic acid, further reaction steps may be required before neutralization. Sulfonic acids of LABS are one of those materials that no require an aging step to reach full conversion. Moreover, a hydrolysis or stabilization step is required to convert anhydrides form during the sulfonation process. Alcohol and alcohol ethoxylate sulfonic acids, as well as FAMES, must be neutralized immediately after a delayed aging to avoid undesired by-products formed in side reactions.

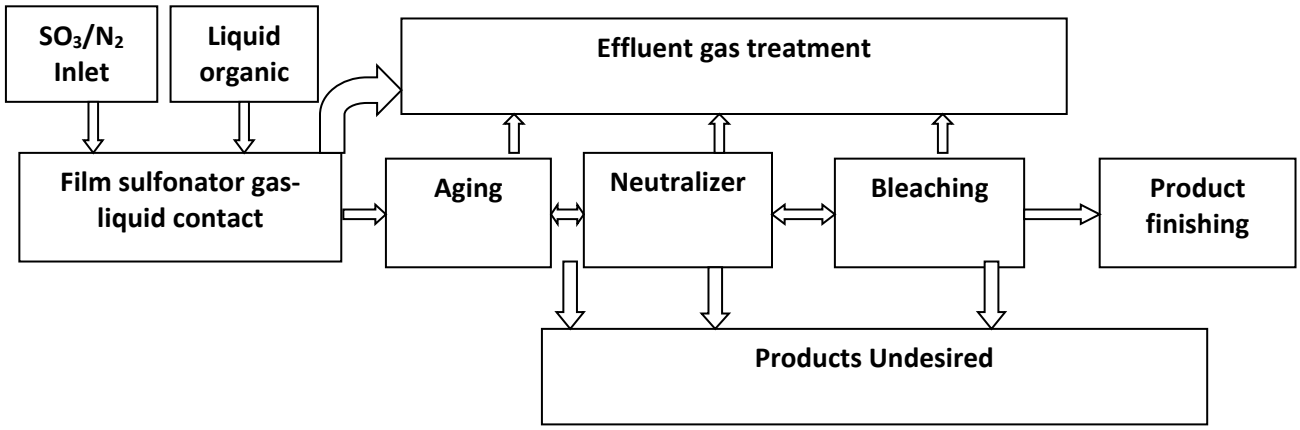


Figure 2.11. Process diagram for film SO3-sulfonation

After aging and hydrolysis a stable product is obtained, and then the neutralization stage can be carried out with many alkaline chemicals like caustic, ammonia and sodium carbonate. Neutralization with diluted caustic is recognized as instantaneous and highly exothermic it may form gel at high temperatures or undesired reactions may occur if micro-dispersion of organic acid in the diluted caustic phase fails. Various loop-type reactors, consisting of a circulation pump, homogenizer (where the acid is introduced in the circulating alkaline paste), and heat exchanger, are used for the complex neutralization step [7].

2.4.3. Main parameters affecting anionic Surfactant Production

An experimental set was developed to study the effect of follows factors:

- mole ratio between Sulfonating agent and feedstock
- Reaction temperature and,
- Reaction time

The variables representing the quality of the sulfonated product are: active matter. [8]

2.4.3.1. Molar ratio between sulfonating agent and feedstock

In the sulfonation process the molar ratio of H_2SO_4 to ME is controlled to achieve optimum conversion to sulfonic acid without increased side reaction or color degredation. It is an important parameter for anionic surfactant production. As this ratio increases, the final yield i.e. (w/w) % of MESA increases and formation of undesired byproducts, sulfones can be reduced by using an optimum value of the ratio. [14]

2.4.3.2. Reaction Temperature

As temperature rises the final yield of MESA also rises. But that the product quality (in terms of color) deteriorates at highest temperature. So the temperature should be kept normal, by varying the reaction temperature we can achieve the optimal point of temperature.[14]

2.4.3.3. Reaction Time

The methyl ester sulfonic acid is formed by a slower process, parallel to the diminishing of the anhydride. When no more free methyl ester is present, the concentration of the anhydride no longer declines. A further increase in the reaction time does not improve the yield (degree of sulfonation). At the end of

the reaction, therefore, a mixture of sulfo methyl ester acids, anhydrides and free fatty acids present. Although the reaction time in the methyl ester sulfonation may be substantially shortened by a higher sulfonator, the resulting increase in the disodium salt content would lead to diminished properties of the end products. [18]

2.5. Characterization of Anionic Surfactant

2.5.1. Specification of methyl ester sulfonic acid

Table 2-3 Specification of methyl ester sulfonic acid

Appearance , 25°C	Yellowish paste
Total active matter, %	68-72
Krafft Point, ºC	17-30ºC
pH value (25°C, 1% Am. aq.sol)	4.5-7.0

[12]

2.5.2. Characterization of anionic surfactant methyl ester sulfonic acid

2.5.2.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

A FTIR spectrophotometer was used to determine the chemical functional groups present in the surfactant. Different functional groups are susceptible to absorb characteristic frequencies of IR radiation.

2.5.2.2. Emulsifying Power

The concentration of the emulsifying agent, it is not possible to rate specific surfactants as general emulsifying agents in any particular order. However, there are some general guidelines that can be helpful to act as an emulsifier:

1) It must show good surface activity and produce a low interfacial tension in the particular system in which it is to be used. This means it must have a tendency to migrate to the interface, rather than to remain dissolved in either one of the bulk phases. It must therefore have a balance of lyophilic and lyophobic groups such that it will distort the structure of both bulk phases to some extent, although not necessarily equally. Too great solubility in either bulk phase will make its usefulness dubious.
2) It must form, at the interface, either by itself or with other adsorbed molecules that are present there, an interfacial film that is condensed because of lateral interactions between the molecules comprising the interfacial film.
3) It must migrate to the interface at a rate such that the interfacial tension reduces to a low value in the time during which the emulsion is being produced. Since the rate of migration to the interface of a particular surfactant usually varies, its emulsifying behavior often depends on the phase in which it is placed prior to emulsification.

2.5.2.3. Foaming Power and Stability

Foam is highly dependent on the concentration of the surfactant, impurities, temperature, and many other factors. In addition, a complete characterization of the foam capacity should take into account the intial amount of foam, its stability, and its texture. The amount and quality of foam is dependent on the alkyl length. Surfactants with C12-14 alkyl chains produce the richest creamy foam with small bubbles. The most widely appreciated property of the surface active substances in aqueous solution is their ability to encourage the formation of foam and bubbles. These behaviors could be endorsed to the physical nature and bubble development. [14]

3. MATERIALS AND METHODS

3.1. Materials

The major raw materials used during the experimental work ware Jatropha seed, sodium hydroxide, methanol and Sulfuric Acid. Jatropha seed was acquired from Beta Engineering, Wolkite All the other chemicals were analytical reagent grade and bought from different chemical stores in Addis Ababa.

3.2. Equipments

The equipments used during the experimentations includes mechanical pressing machine, a glass reactor equipped with a mechanical stirrer, water bath, condenser, separating funnel, balance, oven, different size conical and Erlenmeyer flasks, beakers, measuring cylinders and burette.

Extraction of Jatropha oil using mechanical press oil extractor was done at School of Mechanical and Industrial Engineering Workshop. preparation of Methyl Ester, synthesis of Anionic surfactant and characterization of the refined oil and synthesized Anionic surfactant were done at School of Chemical and Bio Engineering Laboratory, AAiT. The overall structure of the experimental works is shown in Figure (3.1).

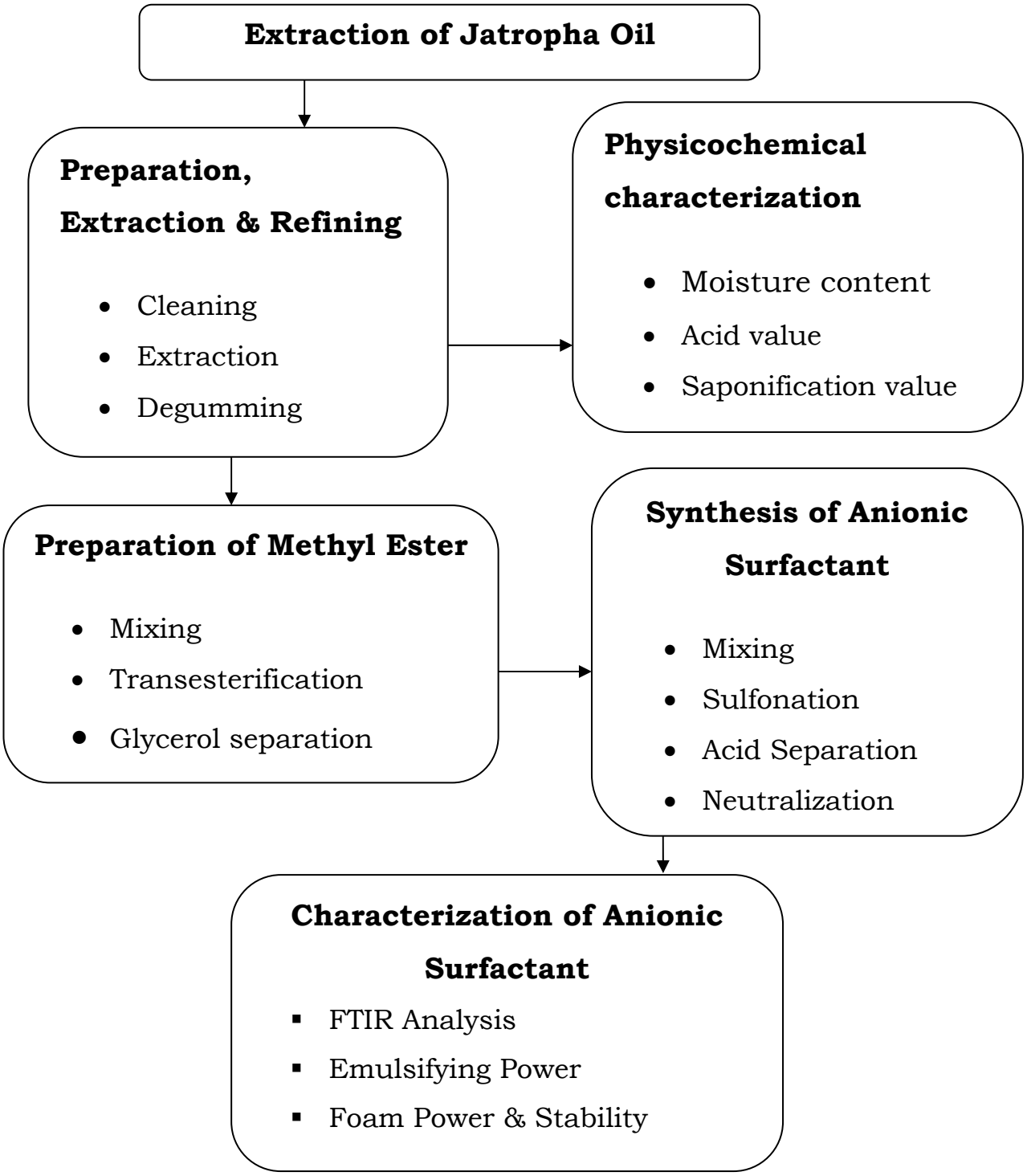


Figure 3.1. Frame work of the Experiment

3.3. Experimental Methods

3.3.1.Preparation of Jatropha Seed

Jatropha seeds were first cleaned from dirt, dust, sand and small stones manually. Then the clean seeds were weighed and 2 kg Jatropha seeds were further dried in an oven at 90^0C for an hour.

3.3.2.Extraction of Jatropha Oil

Mechanical extraction method was applied for Jatropha oil extraction. The pressing machine was cleaned and the prepared seed feed in to the screw pressing machine. The crude Jatropha oil was collected at the bottom and the cake was removed. A typical pressing machine pressing Jatropha seeds is shown in Figure (3.2) below.

Figure 3.2. Pressing Machine

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

$$\text{Yield of Oil} = \frac{Mass of Oil}{Intial mass of seed} \text{ X } 100\% \quad \text{.....(3.1)}$$

3.3.3.Purification of Crude Jatropha Oil

3.3.3.1. Settling

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

3.3.3.2. Degumming

Degumming was done to avoid the interference of phosphatides, gums and other complex compounds during reaction and to avoid rancidity (increase in free fatty acid) of oil during storage. Distilled water 3 wt% of oil at 70^0C was mixed with the oil. Then the mixture was stirred at speed of 200 rpm for 1 h heated at 70^0C. Finally the mixture was separated using centrifuge at 3500 rpm for 30 minutes.

3.3.4.Characterization of Jatropha Oil

The Jatropha seed Viscosity, acid value, saponification value, ester value and iodine value of purified Jatropha oil was determined for the physicochemical property.

3.3.4.1. Determination of Moisture Content

First the empty dish was weighed. Then accurately weigh about 4 g of Jatropha seeds into an empty dish. The sample was dried in an oven at 105^0C for 7 h,

weighing each 2 h till constant weight is obtained and finally the weight was taken and compared with the initially recorded weight. The percentage weight in the seed was calculated using the formula:

$$\text{Moisture content} = \frac{W1 - W2}{W2} X\ 100 \quad \text{(3.2)}$$

Where W1 is original weight of the sample before drying and W2 is weight of the sample after drying.

3.3.4.2. Determination of Acid Value

Material

- Fat or Oil
- Absolute ethanol alcohol
- Phenolphthalein
- 0.1 N KOH

Procedure

1. Place 5.0 g of fat or oil in a dried conical flask.
2. Add 25 ml of absolute ethanol alcohol and add (2-3) drops of phenolphthalein
3. Heat with shaking in water bath (65%) for 10 minutes ,then cool Titrate the solution against 0.1 N KOH until pink color appears (end point).
4. Record your observations.
5. Calculate the acid value (AV) and free fatty acid (%FFA) using above laws.

Result

During titration the end point (pink color appears) with volume of 9.1ml KOH

solution of 0.1N.

The total acidity in mg KOH/gm was calculated using the following equation:

$$\text{Acid value} = \frac{56.1xVxN}{W} \quad \text{..... (3.2)}$$

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

N is concentration of ethanolic KOH and

W is weight in gram of the test portion.

3.3.4.3. Determination of Iodine Value

Materials Used

- Oil or fat
- Hanus solution (it's prepared by dissolving 18.2 g of iodine in 1L of glacial acetic acid and then add 3 ml of bromine water for increasing the halogen content.
- 15% potassium iodide solution
- 1% starch solution
- 0.1 N Sodium thiosulfate solution.

Procedure

1. Weigh approximately 0.25 g of the fat or oil into a 250 mL conical flask.
2. Add 10 ml of chloroform.

3. Add 30 ml of Hanus solution and close the flask completely by Para film, then leave the solution for 30 minutes with shaking continuously.
4. Add 10 ml of 15% potassium iodide solution and then shake.
5. Add 100 ml of distilled water (DW).
6. Titrate the iodine solution against 0.1 N Sodium thiosulfate solution till yellow color formed , then add 2-3 drops of starch solution where blue solution formed and then continue with titration till the blue color is disappeared (Volume (ml) of $Na_2S_2O_3$ - at end point represents S)
7. Do same above procedure but without sample (Volume (ml) of $Na_2S_2O_3$ at end point represents B).
8. Calculate the iodine number by using the following law:

$$\text{Iodine Value} = \frac{1.269\,x(a-b)}{W} \quad \text{..... (3.3)}$$

Where a = titration end volume with oil

b = titration end volume with out oil

3.3.4.4. Determination of Saponification Value

Materials Used

- Fat or Oil
- 0.5 N alcoholic potassium hydroxide (alcoholic KOH) (prepared by dissolving 30 g potassium hydroxide in 20 mL of water and make the final volume to 1 L using 95 % ethanol. Leave the solution to stand for 24 h before decanting and filtering the solution.
- 0.5 N Hydrochloric acid
- Phenolphthalein.

Procedure

1. Weigh approximately 2 g of the fat or oil into a 250 mL conical flask.
2. Add 25 mL of alcoholic potassium hydroxide solution (0.5 N).
3. Attach a reflux condenser and heat the flask contents on a boiling water bath for 1 hour with occasional shaking.
4. While the solution is still hot, add 3 drops of phenolphthalein indicator and titrate the excess potassium hydroxide with the 0.5 N hydrochloric acid (Vml of hydrochloric acid at end point represents Va).
5. Do same above procedure but without sample (Vml of hydrochloric acid at end point represents Vb).
6. calculate the saponification number by using the following law:

$$\text{Saponification value} = \frac{56.1\ x\ N\ x\ (Vb - Va)}{W} \quad \text{..... (3.4)}$$

Where W is weight of oil taken in gram,

N is normality of HCL solution,

Va is volume of HCL solution used in the test in milliliter and Vb is volume of HCL solution used in blank in milliliter.

3.3.4.5. Ester Value

The ester value is defined as the mg of KOH required to react with glycerin (glycerol / or glycerin) after saponify one gram of fat. It is calculated from the saponification.

Ester Value (EV) = Saponification Value (SV) – Acid Value (AV)..... (3.5)

3.3.5.Transesterification Process

The extracted oil triglycerides react with methanol to produce methyl esters with transesterification reaction in the presence of a catalyst. However, this process is greatly affected by the free fatty acid (FFA) content of the raw material. The presence of high FFA (i.e. high acid value) in the raw material results in soap formation that could decrease the methyl ester yield and complicate the separation and purification of the product of interest. This problem can be avoided by pre-treating the oil with an acid catalyst esterification to convert the FFAs into esters before the alkali catalyst is used. Hence, fatty acid methyl ester is produced via a two-step transesterification Acid-catalyzed transesterification and Alkaline-catalyzed transesterification but in this case base catalyst which is alkaline catalyzed transesterification is chosen because alkaline catalysts are much faster than other type of catalyst and it is less corrosive than acid-catalyzed. And sodium hydroxide is chosen as it is the cheapest one.

3.3.6.Experimental Design for Sulfonated methyl ester

In this work the SME was prepared using purified Jatropha oil, ME and concentrated sulfuric acid (98%). Experimental data analysis was done using Design- Expert 6.0.0 software. The experimental design selected for this study was three-level-three-factor face-centered central composite design (CCD) and the response variable measured was the active matter of SME. In addition analysis of physicochemical properties of SME was done at School of Chemical and Bio Engineering laboratory, AAiT. The three independent variables studied for the modified sulfonation process were reaction temperature, Molar ratio of H_2SO_4 to ME and reaction time. The independent variables interaction effect was analyzed to obtain maximum active matter of sulfonation. In addition to achieve maximum yield of sulfonation rotational speed was set at 300 rpm.

Three-level-three-factor face-centered CCD was used in the optimization study which requires 20 experiments to be conducted. The twenty experiments were done and the data was statistically analyzed using Design-Expert Software 6.0.0 to obtain a suitable model equation for the active matter of SME as a function of the independent variables.

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

Table 3-1 Independent variables and levels used in the CCD for the SME production

Variables	Factor Coding	Unit	Levels		
			-1	0	+1
Reaction Temperature	X_1	^oC	60	65	70
Mole ratio of H_2SO_4 to ME	X_2	Ml	0.2	0.6	1.0
Reaction time	X3	Hr	1	1.5	2

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

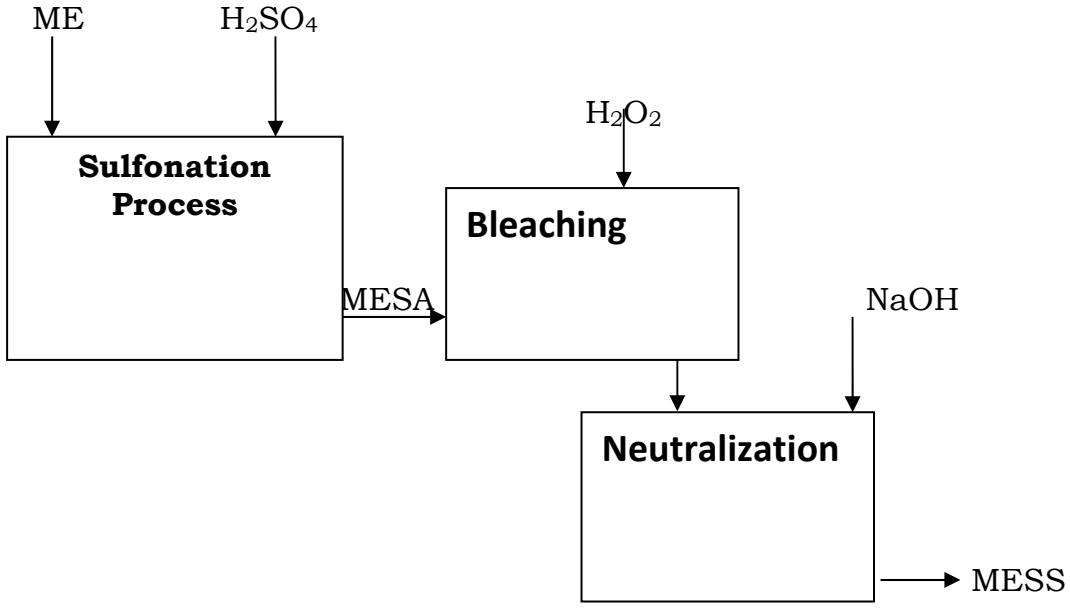
Table 3-2 the complete experimental design matrix

Coded Factor				**Actual Factor**		
Run	**X_1**	**X_2**	**X_3**	**Temperature(^{O}C)**	**Molar Ratio of H_2SO_4 to ME**	**Reaction Time(hr)**
1	0	-1	0	65.00	0.20	1.50
2	+1	-1	-1	70.00	0.20	1.00
3	0	0	0	65.00	0.60	1.50
4	0	0	0	65.00	0.60	1.50
5	-1	-1	+1	60.00	0.20	2.00
6	-1	0	0	60.00	0.60	1.50
7	+1	+1	-1	70.00	1.00	1.00
8	0	0	0	65.00	0.60	1.50
9	+1	0	0	70.00	0.60	1.50
10	0	+1	0	65.00	1.00	1.50
11	0	0	0	65.00	0.60	1.50
12	-1	-1	-1	60.00	0.20	1.00
13	-1	+1	+1	60.00	1.00	2.00
14	+1	-1	+1	70.00	0.20	2.00
15	0	0	0	65.00	0.60	1.50
16	0	0	-1	65.00	0.60	1.00
17	0	0	+1	65.00	0.60	2.00
18	+1	+1	+1	70.00	1.00	2.00
19	-1	+1	-1	60.00	1.00	1.00
20	0	0	0	65.00	0.60	1.50

3.3.7.Experimental Setup

Mixture of Jatropha oil, caustic soda and methanol will be done on a water bath equipped with a motor stirrer. For sulfonation reaction a 500 ml glass reactor equipped with agitator in all experiments. The sulfonation reaction system was employed for MESA production as shown in the schematic diagram below.

Figure 3.3. Schematic diagram of experimental setups for methyl ester sulfonic acid production



3.3.8.Methyl ester sulfonic acid Production Procedure

Methyl ester was prepared from refined Jatropha oil at specific conditions (from the literature and previous similar works). The parameters were set at speed 250rpm, 2hr reaction time, 65◦C reaction temperature, 6:1 molar ratio of methanol to oil and 1.125% weight by oil amount of catalyst (NaOH) [16]. Then the produced methyl ester sulphonated with H_2SO_4 in a glass reactor equipped

with motor stirrer with using water bath when and bleaching will continue by adding 50% wt of Hydrogen peroxide after SME formed then the reactor outlet pour into separtory funnel and a volume of 250ml hot water at 60ªC added. The mixture was then immediately separated. Finally, the separated SME will be neutralized by 20% wt of caustic soda for 30min with reaction temperature maintained at 45ºC.

3.3.9.Feed Material Requirement

600ml of ME, 74.18ml of H_2SO_4, 300 ml of H_2O_2 and 105.12gm was used totally for each run.

The amount of Methyl ester required calculated as follows. First the weight of oil was directly measured on balance and the weight of fatty acid methyl ester is estimated from its density.

$$Density\ of\ ME\ (\rho) = \frac{Mass\ of\ ME}{Volume\ of\ ME} \quad \text{..... (3.6)}$$

$$Density\ of\ ME\ (\rho) = 0.876 gm/ml$$

$$Volume\ of\ ME = \frac{26.28 gm}{0.876 gm/ml} = 30 ml$$

3.3.10. Active matter of Methyl ester sulfonic Acid

The active matter after neutralization is determine by titration with (0.004M) Hyamine solution using Methylene Blue as indicator.

CHEMICALS:

1. Hyamine 1622, E.MERCK

2. Chloroform. Analytical reagent.
3. Methylene Blue solution: Dissolve 0.5 gm of BDH standard stain Methylene Blue in 100 DM water. To 5 ml of this solution, add 50 gm anhydrous Sodium Sulfate (dissolved in water). Add 120 ml of 2N Sulfuric acid and dilute to 1000 ml with with D.M water.

APPARATUS:

1. 10 ml pipette.
2. 100 ml graduated measuring cylinder with glass stopper.1922233F 0.004(M)

SULFONIC ACID

PROCEDURE:

1. Weight about 0.3-0.5gm of the representative sample in a 500 ml volumetric flask.
2. Add about 150 ml of DM water dissolve the sulfonic acid sample by swirling then add a few drop of phenolphthalein indicator solution.
3. Neutralize this solution with 5(N) NaOH solution to pink colour and make up to the mark.
4. Pipette 10 ml of this dilute solution into 100 ml stopper cylinder.
5. Add 25 ml methylene blue solution and 15 ml chloroform.
6. Replace the stopper and shake; the upper aqueous phase will be almost colourless, and the chloroform phase dark blue.
7. Add 2 ml Hyamine solution from a burette replace the stopper and shake for about 10 seconds.

8. Continue making 2 ml addition of Hyamine solution, shaking for 10 seconds after eachaddition, until the blue colour begins to appear in the aqueous phase.
9. Compare the colour of the two phases after each addition.
10. As the end point is approached, add progressively smaller volumes of hyamine solution and shake for 30 seconds, after each addition, allow to settle and judge the colour intensity f the phases.
11. The end point is obtained when the colour intensity of the chloroform phase. The addition of a further drop of Hyamine solution will develop a paler tinge in the chloroform layer.

$$Active\ matter\ of\ MES = \frac{V\ x\ mol.wt\ of\ MES x\ Molarity\ of\ Hyamine}{Weight\ of\ sample} \quad \text{..... (3.7)}$$

Where

V is the volume in ml of Hyamine consumed for titration.

Molecular weight of MES = 226

3.3.11. Yield of Methyl ester sulfonic acid

After the separating the SME from the sulfuric acid the yield of SME calculated as follow

$$\text{Yield, percent} = \frac{Mass\ of\ the\ SME}{Mass\ of\ ME + Mass\ of\ H2SO4 + Mass\ of\ H2O2} X\ 100 \quad \text{.....(3.8)}$$

3.3.12. Characterization of Sulfonated methyl ester

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

3.3.12.1. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR wave number and transmittance data is done at Natural Science University Chemistry Department by taking sample of MESS which is produced with the optimized result. The synthesized surfactant was milled with potassium bromide (KBr) to form a fine powder. This powder was then compressed into a thin pallet and analyzed directly. The FTIR spectrophotometer (Perkin Elmer-Spectrum Two) was used to determine the functional group present in the SMSS surfactant.

3.3.12.2. Emulsifying power

Emulsifying power of the aqueous solutions of MESS was determined for water/liquid paraffin (light) system by measuring the time of separation of aqueous phase from the emulsion.

3.3.12.3. Foaming Power and Stability

The foaming property of aqueous solutions of the MESS product was determined using standard Rose-Miles method at different concentration of the surfactants.

4. RESULT AND DISCUSSION

4.1. Jatropha Seed Preparation, Oil Extraction, Purification and Characterization

4.1.1.Jatropha Seed Preparation

About 24 kg of Jatropha seeds were taken for this research work. First it was cleaned from impurities.

4.1.2.Jatropha Oil Extraction

Mechanical extraction method was used for oil extraction from 10 kg Jatropha seeds 2.3 liter crude Jatropa oil was extracted using mechanical screw pressing machine. The density of crude oil was found 920kg/m^3using hydrometer. Therefore 2.11 kg crude oil was extracted. Yield of oil extraction using mechanical pressing machine is calculated using equation (3.1) as follows.

Yield of oil $=\frac{Mass\ of\ Oil}{Intial\ mass\ of\ seed}$ X 100=21.16%

4.1.3.Jatropha Oil Purification

The total amount of crude oil obtained from mechanical extraction was 2.3 liter. From 2.3 liter crude oil 800 g was removed during the purification process. Higher amount of suspended solid (700 g) were removed by centrifuging. About 123 ml distilled water was used for degumming.

4.1.4.Physicochemical Properties of Purified Jatropha Oil

The viscosity, acid value, Saponification value, ester value and iodine value of Jatropha oil were determined.

4.1.4.1. Determination of Acid Value

The titration was done three times to increase the accuracy. The average titration volume was taken for acid value calculation. The laboratory results are presented in Appendix C. The acid value of purified Jatropha oil is calculated using equation (3.2).

Acid value = $\frac{56.1\ xVxN}{W}$ = $\frac{56.1x\ 3.26x\ 0.1}{5}$=3.66 mgKOH/g oil

FFA = $\frac{AV}{2}$..... (4.1)

FFA= $\frac{3.66}{2}$= 1.83mg KOH/g oil

4.1.4.2. Determination of Iodine value

The iodine value of the oil was calculated using equation (3.3) as shown below.

Iodine Value = $\frac{1.269\ \mathrm{x(a-b)}}{W}$=$\frac{1.269(24.5-1.4)}{0.28}$= 104.69g I_2/100g oil

4.1.4.3. Determination of Saponification value

SV=$\frac{56.1\ x\ N\ x\ (Vb-Va)}{W}$=$\frac{56.1x\ 0.5x\ (19-5.63)}{2}$=187.5mgKOH/g oil

4.1.4.4. Determination of Ester value

The ester value of Jatropha oil can be estimated using the relation given below from equation 3.5.

Ester Value (EV) = Saponification Value (SV) – Acid Value..... (4.2)

Ester value = 196.35-10.212 = 186.14KOH/g Oil

Table 4-1 physicochemical properties of Jatropha Oil

Properties	**Experimental Result**	**Unit**
Acid Value	10.02	mg KOH/g Oil
Iodine Value	102.42	g I_2/100g Oil
Saponification Value	182	mg KOH/g Oil
Ester Value	181.14	mg KOH/g Oil

4.2. Analysis of transesterfication process

The extracted oil will lead to transesterifcation process by using parameters taken from previous researches which are:

Reaction temperature = 65^{O}C

Reaction time = 2hr

Agitation speed = 500rpm

Molar ratio of Oil to Methanol = 6:1

- Yield of ME produced = $\frac{MassofOil}{MassofMEOutput} X100 = 90\%$
- Total amount of ME produced = 600ml

4.3. Analysis of Methyl ester Sulfonic Acid

The MESA was prepared using the ME produced from purified Jatropha oil and H_2SO_4, using the specified parameters sulfonation process taking place in 500ml capacity glass reactor which is equipped with a motor stirrer and a water bath. The stirrer rotational speed kept constant at 250rpm and temperature was adjusted to the desired conditions.

The MESA active matter will be done by titration and using the following formula

$$Active\ matter\ of\ MESS = \frac{V\ x\ mol.wt\ of\ MESx\ Molarity\ of\ Hyamine}{Weight\ of\ sample}$$ using equation 3.7

Where, V is the volume in ml of Hyamine consumed for titration.

Molecular weight of MES = 226

Figure 4.1. Methyl ester sulfonic acid separation in a separating funnel

The statistical analysis of the MES synthesis is discussed in the following sections.

4.3.1.Statistical Analysis on Factors Affecting Active matter

The experimental design selected for this study is the Central Composite Design (CCD) and the response variable measured is the Active matter. Three-level-three-factor CCD apply the face-centered cubic design. Having three levels

instead of five was cited as desirable because it reduced the preparation time and complexity of the experiment.

Three-level-three-factor face-centered CCD with a complete 2^K factorial layout, 2K axial (star)points and 6 center points was employed in the optimization study, a total of 20 experiments were conducted, where K is three for three factors (independent variables) used in the analysis. The three Sulfonation process variables are reaction temperature, molar ratio of H_2SO_4 to ME and reaction time.

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

Design-Expert Software 6.0.0 was used in the least squares regression analysis of variance (ANOVA). The statistical software program is used to generate the model equation, interaction effects of the independent variables and surface plots using the fitted equation obtained from the regression analysis holding one of the independent variable constant. The CCD conditions and their respective responses and the ANOVA are given in Table (4.3) and Table (4.4) respectively.

The actual Active matter of the methyl ester sulfonic acid produced at different process parameters is determined by using titration method. The detail calculations and results are discussed in sections below and in Appendix C.

Table 4-2 experimental and predicted values

Run	Reaction Temperature (^oC)	Molar Ratio of H_2SO_4 to ME	Reaction Time(hr)	Experimental Active matter (%)	Predicted Active matter (%)	Residuals
1	65.00	0.20	1.50	58.00	57.72	0.28
2	70.00	0.20	1.00	59.50	59.65	-0.15
3	65.00	0.60	1.50	65.00	65.54	-0.54
4	65.00	0.60	1.50	68.00	67.92	0.082
5	60.00	0.20	2.00	61.40	61.54	-0.14
6	60.00	0.60	1.50	60.00	59.52	0.48
7	70.00	1.00	1.00	65.00	64.91	0.092
8	65.00	0.60	1.50	63.00	63.34	-0.34
9	70.00	0.60	1.50	64.00	63.70	0.30
10	65.00	1.00	1.50	63.80	63.88	-0.078
11	65.00	0.60	1.50	62.00	62.48	-0.48
12	60.00	0.20	1.00	69.00	68.30	0.70
13	60.00	1.00	2.00	64.70	64.38	0.32
14	70.00	0.20	2.00	63.90	64.00	-0.098
15	65.00	0.60	1.50	65.60	65.42	0.18
16	65.00	0.60	1.00	66.00	65.42	0.58
17	65.00	0.60	2.00	65.30	65.42	-0.12
18	70.00	1.00	2.00	65.40	65.42	-0.025
19	60.00	1.00	1.00	65.00	65.42	-0.42
20	65.00	0.60	1.50	64.80	65.42	-0.62

4.3.1.1. Development of Regression Model Equation

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

Yield of methyl ester =+65.42 + 0.090 * A + 2.91* B - 0.19 * C - 1.64* A^2- 0.036* B^2- 1.24 * C^2 + 0.11 * A * B - 0.99* A * C - 1.11* B * C ……. (4.3)

Where, A is Reaction temperature,

B is Molar ratio of H_2SO_4 to ME

C is Reaction time

4.3.1.2. Model Adequacy Check

The model was tested for adequacy by analysis of variance. The regression model was found tobe highly significant with the correlation coefficients of determination of R-Squared, adjusted R-Squared and predicted R-Squared having a value of 0.9810, 0.9639 and 0.8360 respectively.

The quality of the model developed could be evaluated from their coefficients of correlation. The value of R-squared for the developed correlation is 0.9810. It implies that 98.10% of the total variation in the Active matter is attributed to the experimental variables studied. The graph of the predicted values obtained using the developed correlation versus actual values is shown in Figure (4.1).

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

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table (4.4). Based on a 95% confidence level, F – value is a test for comparing model variance with residual (error) variance. If the

variances are close to the same, the ratio will be close to one and it is likely that any of the factors have a significant effect on the response with the P – value less than 0.05. It is calculated by model mean square divided by residual mean square. Here the model F – value of 57.29implies the model is significant. There is only a 0.01%chance that a "Model F – Value" this large could occur due to personal error or disturbance.

Figure4.2. Predicted versus actual Active matter

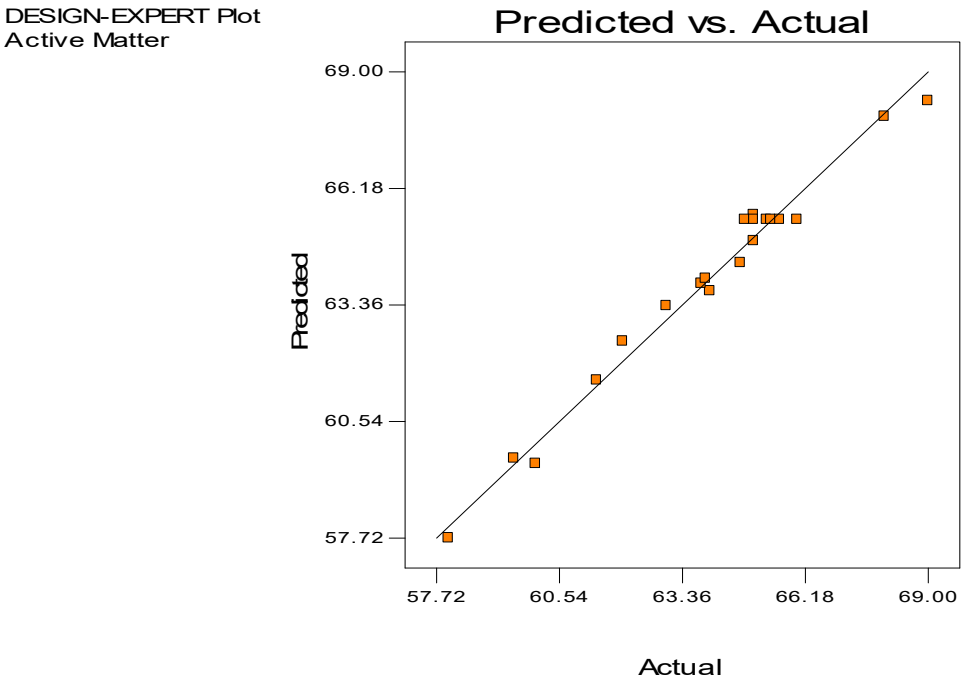


Table 4-3 ANOVA for the regression model equation and coefficients

Source	**Sum of squares**	**df**	**Mean square**	**F – value**	**P – value Prob > F**	**Remark**
Model	136.73	9	15.19	57.29	< 0.0001	Significant
A	*0.081*	*1*	*0.081*	*0.31*	*0.5926*	

B	*84.68*	*1*	*84.68*	*319.36*	*< 0.0001*	
C	*0.36*	*1*	*0.36*	*1.36*	*0.2704*	
A^2	*7.36*	*1*	*7.36*	*27.77*	*0.0004*	
B^2	*3.636E-003*	*1*	*3.636E-003*	*0.014*	*0.9091*	
C^2	*0.10*	*1*	*0.10*	*0.38*	*0.5504*	
AB	*0.10*	*1*	*0.10*	*0.38*	*0.5504*	
AC	*7.80*	*1*	*7.80*	*29.42*	*0.0003*	
BC	*9.90*	*1*	*9.90*	*37.34*	*0.0001*	
Residual	2.65	10	0.27	Residual	2.65	
Lack of Fit	*1.74*	*5*	*0.35*	*1.90*	*0.2494*	*not significant*
Pure Error	*0.91*	*5*	*0.18*			
Cor Total	139.38	19				

This shows that the Molar ratio of H_2SO_4 to ME, square of reaction temperature, square of reaction time, interaction between reaction temperature and reaction time and interaction between Molar ratio of H_2SO_4 to ME and reaction time affects the Active matter significantly.

The "Lack of Fit F – value" of 1.90 implies the Lack of Fit is not significant relative to the pure error. There is a 24.94% chance that a "Lack of Fit F – value" this large could occur due to noise. Non-significant lack of fit is good because we want the model to fit.

4.3.2.Effect of Sulfonation Reaction Process Variables

Based on the analysis of variance, sulfonation reaction was significantly affected by interactions between reaction temperature and time and interaction between molar ratio of H_2SO_4 to ME and time. This result demonstrated that

the advantage of using face-centered CCD for experimental data analysis in capturing the interaction between variables that affects the sulfonation reaction. In addition to the interaction effect, significant individual process variables that affect the sulfonation reaction is reaction temperature, A and Molar ratio of H_2SO_4 to ME, B.

4.3.2.1. Effect of Individual Process Variables

The increase in the percentage of H_2SO_4 is a positive action, probably because it is promoted in the mass transfer in the ME, the change presents the mole ratio H_2SO_4/ME which increase the sulfonation of the ME. The increase in the flow of ME to maintain the percentage of H_2SO_4 constant implies an increase of all the flows. This effect results in an increase of active substance and a decrease of the content in sulfuric acid. Figure 4.2 confirm the effects of the mole ratio H_2SO_4/ME, in which is observed that the sulfonation is a direct product of the generation of active matter compared with increase in the mole ratio SO_3/ME, because the reaction is favored in excess of the sulfonating agent.

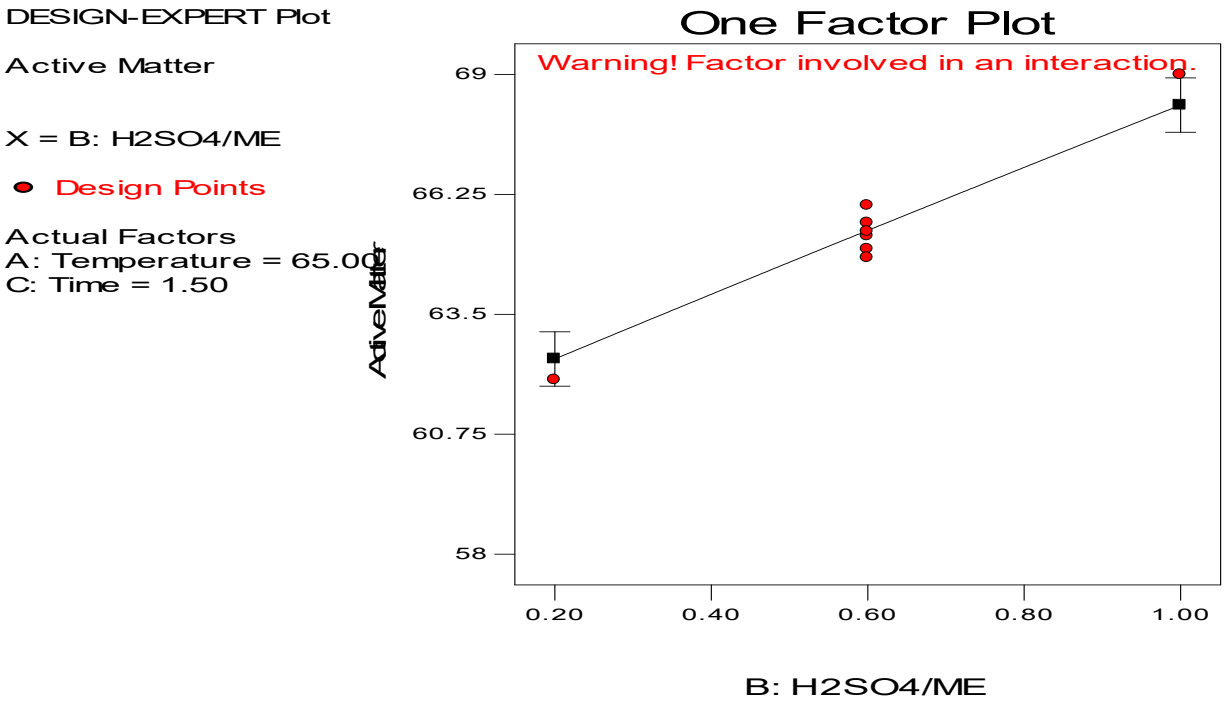


Figure 4.3. Active matter versus Molar ratio of H2SO4 to ME at reaction temperature 65 and 1.5 h reaction time.

As shown in Figure (4.3) below the Active matter is significantly affected by reaction temperature. It can be seen from the figure that with increasing reaction temperature the active matter increases but when it reaches 65°C presents a turning point and reversing its trend due to increased collateral reactions. The change of slope that is submitted with respect to the variable temperature process is due to the generation of side-reactions, and the formation of unlike products, that reduce the percentage of active matter. Therefore, when the reaction temperature becomes higher and higher the percentage of active matter will decrease.

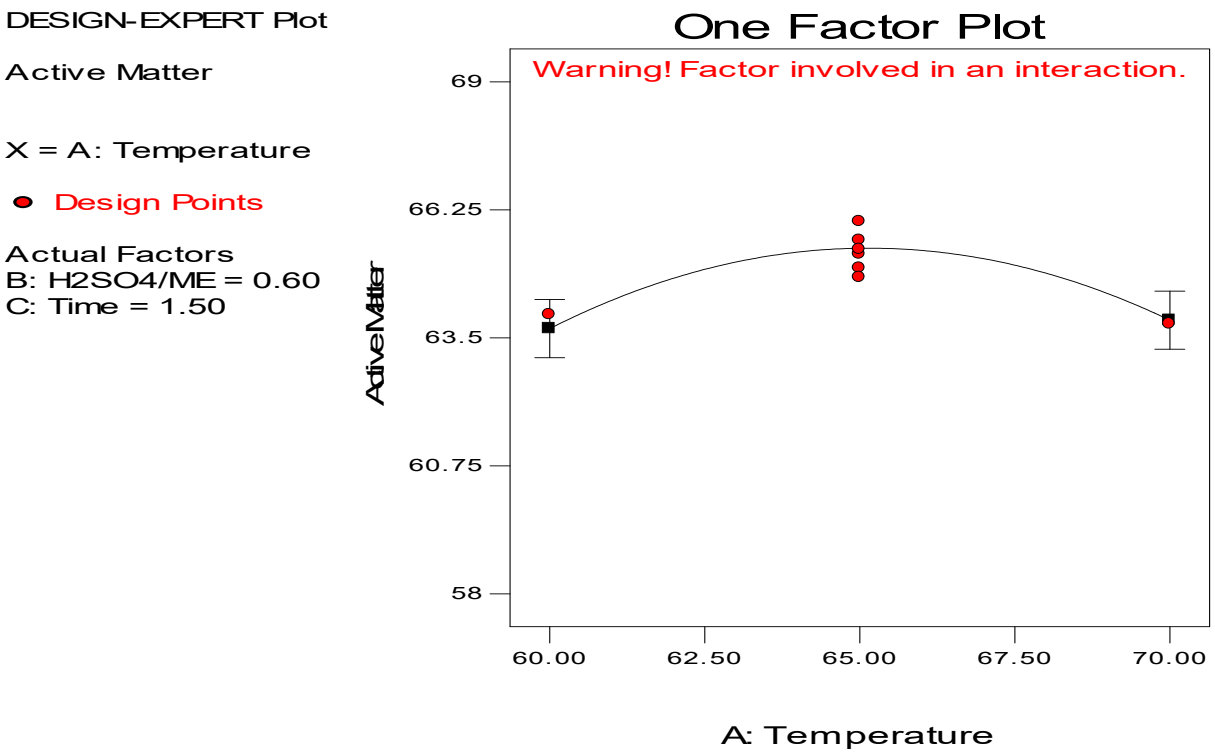


Figure 4.4. Active matter versus reaction temperature at amount of molar ratio of H2SO4 to ME of 0.6 and 1.5 h reaction time.

As shown in figure 4.4 the active matter of methyl ester sulfonic acid is increase with reaction time but when it reaches 1.5hr changes slope and shows side-reactions and the formation of unlike products generates. Therefore the graph concludes excess reaction time will affect the sulfonation process.

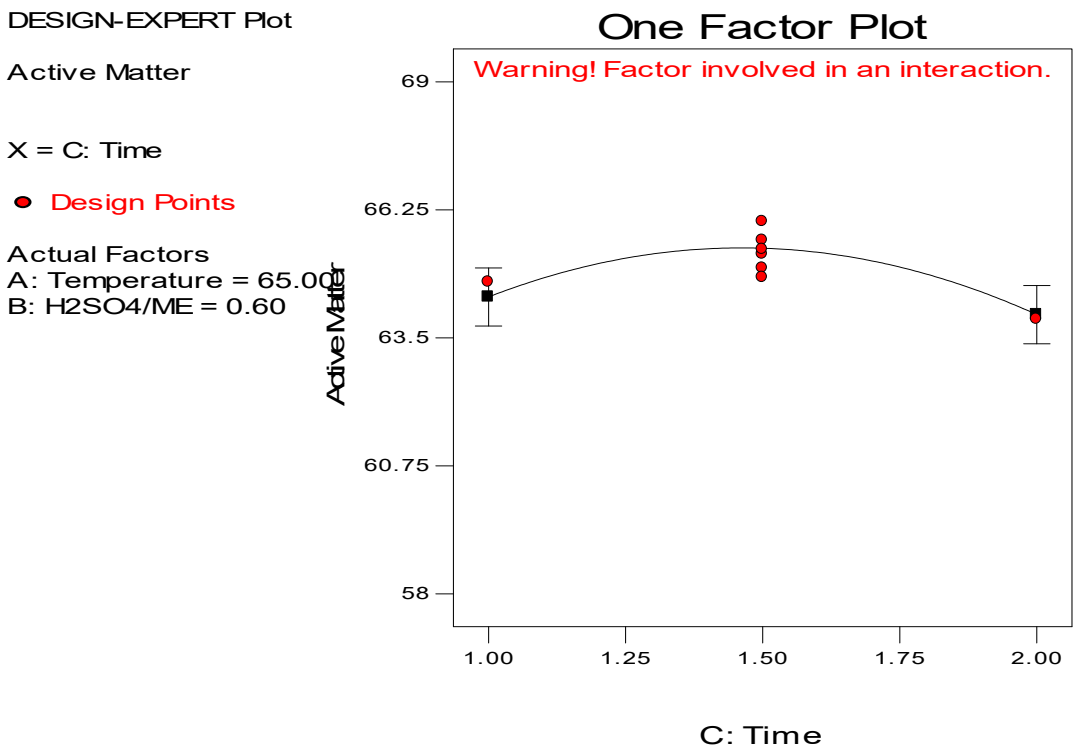


Figure 4.5. Active matter versus reaction time at reaction temperature 65 and H2SO4/ME 0.6

4.3.2.2. Effect of Interaction between Process Variables

The most common way to summarize the results of a central composite design experiment is in the form of a response surface plot and via response contours plot. The process variables were found to have significant interaction effects. Figure (4.5), (4.7) and(4.9) shows the interaction between reaction time and molar ratio of H_2SO_4/ME, reaction temperature and reaction time, and molar ratio of H_2SO_4/ME and reaction temperature on the active matter respectively.

Generally, an increase in molar ratio of H_2SO_4/ME is found to increase the active matter. This is due to similar explanation given in the previous section.

Higher amount of molar ratio of H_2SO_4/ME with lower reaction temperature and lower reaction time is found to have higher active matter as compared to lower amount of molar ratio of H_2SO_4/ME and higher reaction temperature and higher reaction time.

On the other hand, at higher range of reaction temperature, lower amount of molar ratio of H_2SO_4/ME and lower reaction time is found to have lower active matter as compared to reaction using lower reaction temperature, higher amount of molar ratio of H_2SO_4/ME and higher reaction time.

The above observations can easily be explained as higher molar ratio of H_2SO_4/ME and medium temperature range will drive the reaction forward and medium reaction time will ensure the sulfonation reaction goes to completion which results in higher active matter. Another notable observation is that at higher range of reaction temperature and higher reaction time will decrease the active matter.

This phenomena is further supported by the fact that molar ratio of H_2SO_4/ME is the most significant process variable that affect the Active matter of the sulfonic acid as indicated by the highest F –value in the ANOVA as shown in Table (4.4).

The Response Surface Methodology (RSM) was used to optimize the conditions of sulfonation of methyl ester and to understand the interaction of the factors affecting the production of methyl ester sulfonic acid. Figures (4.5), (4.7) and (4.9) show surface plots between the independent and dependent variable for fixed parameters.

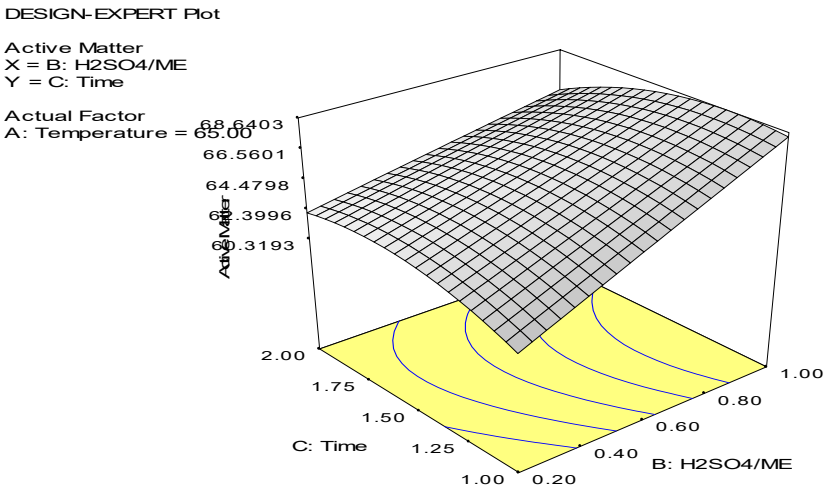


Figure 4.6. Surface plot of the interaction effect of reaction time and mole ratio of H2SO4/ME versus Active matter when the reaction temperature is 65oC

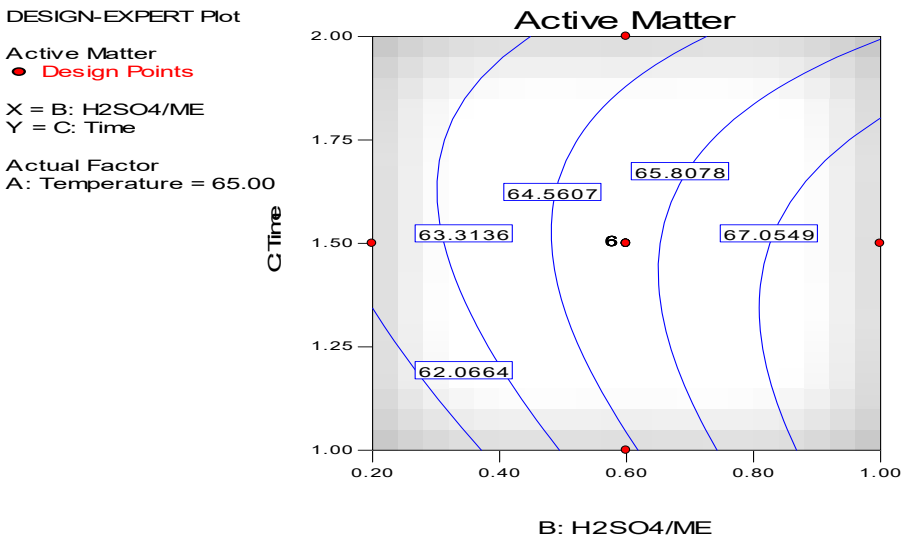


Figure 4.7.Contour plot of the interaction effect of reaction time and mole ratio of H2SO4/ME versus Active matter when the reaction temperature is 65oC.

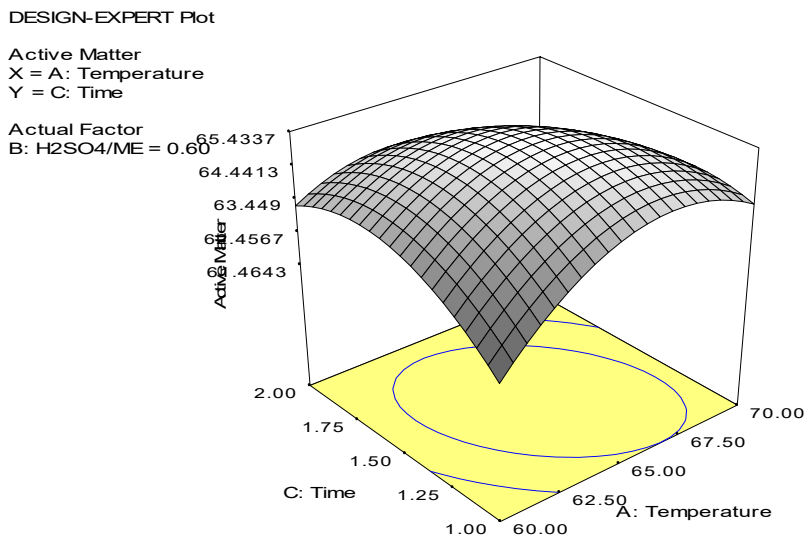


Figure 4.8.Surface plot of the interaction effect of reaction temperature and reaction time versus Active matter when mole ratio of H2SO4/ME is 0.6

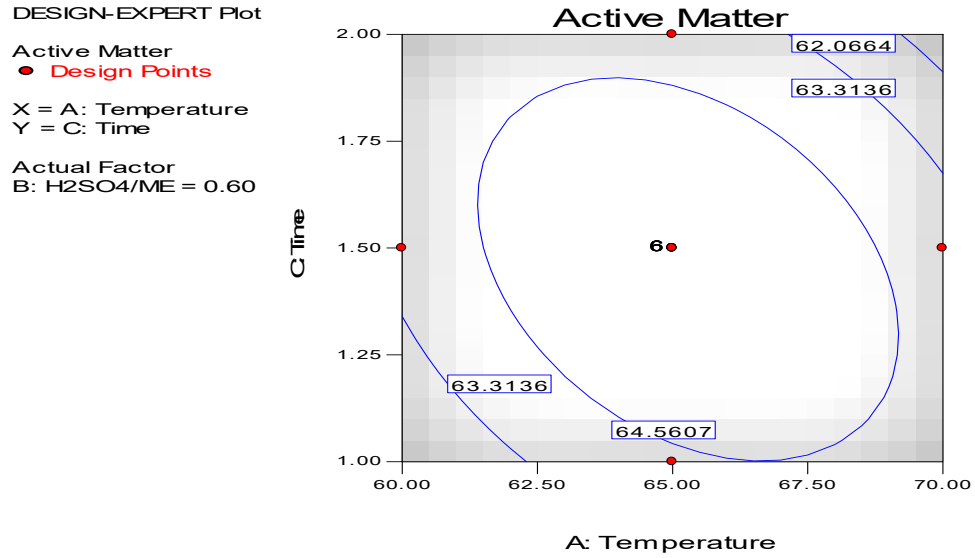


Figure 4.9. Contour plot of the interaction effect of reaction temperature and reaction time versus Active matter when amount mole ratio of H2SO4/ME is 0.6

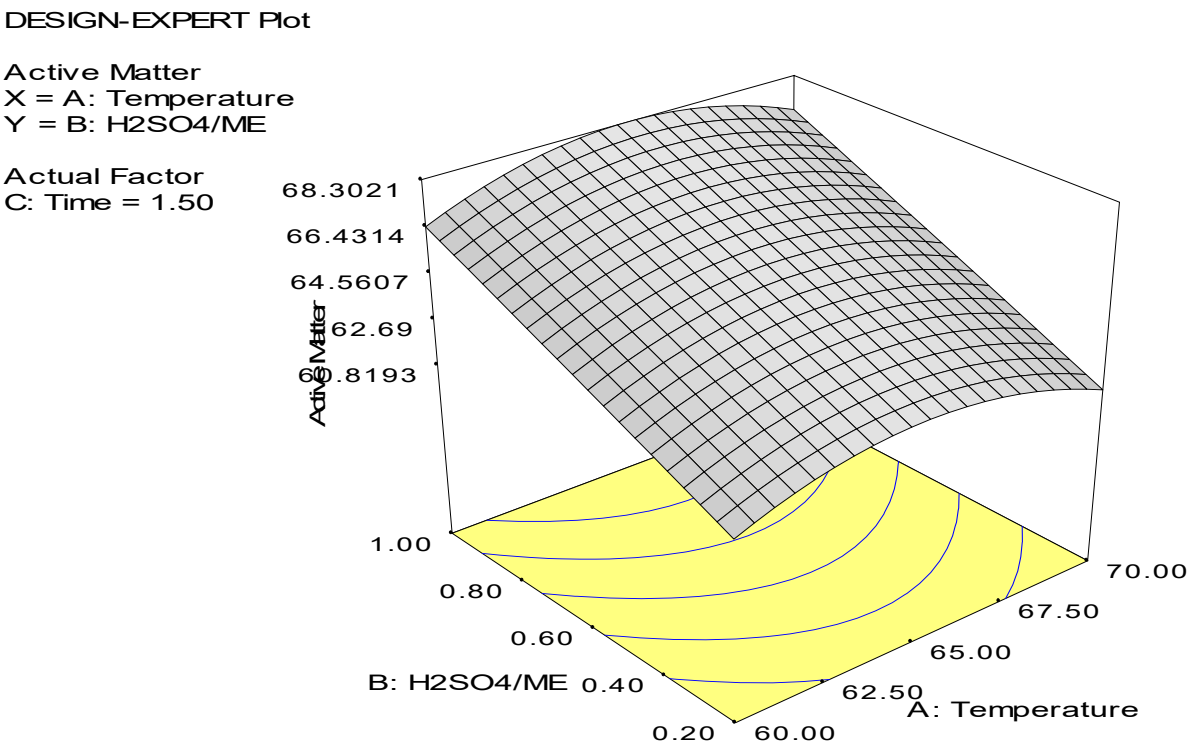


Figure 4.10. Repsonse Surface plot of the interaction effect of molar ratio H2SO4/ME and reaction temperature versus Active matter when reaction time is 1.5hr.

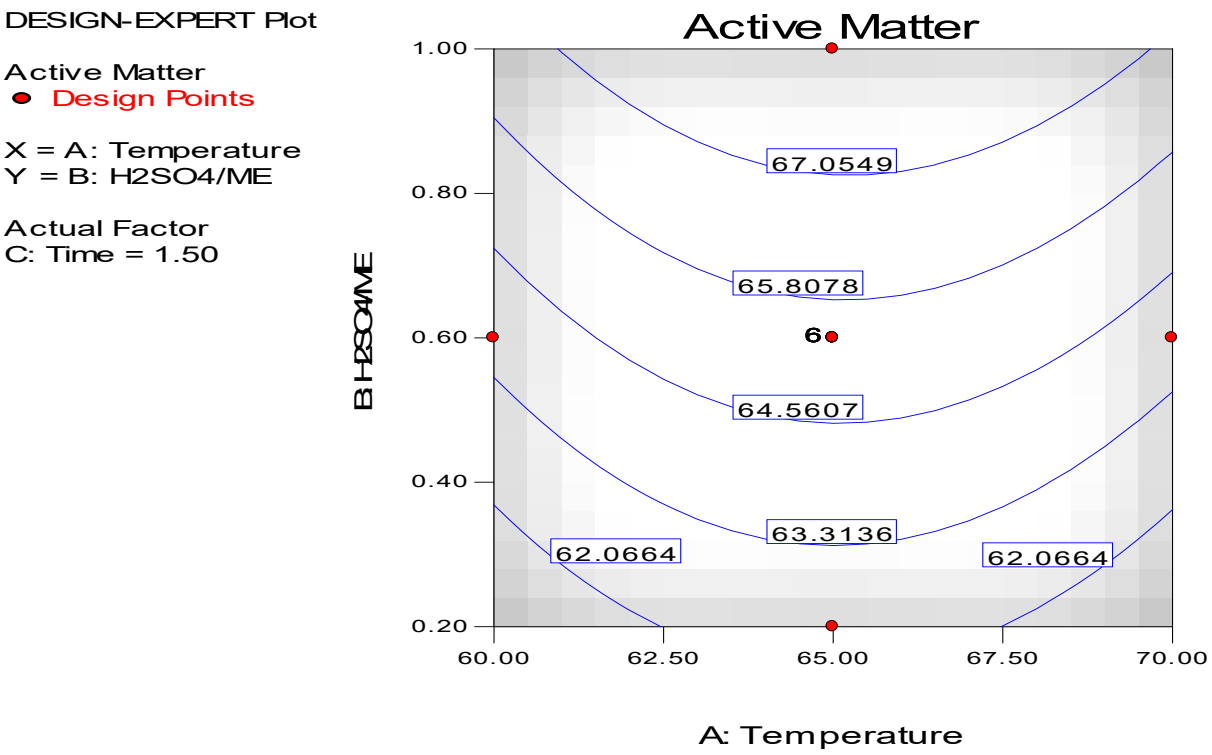


Figure 4.11. Contour plot of interaction effect of molar ratio H2SO4/ME and reaction temperature versus Active matter when reaction time is 1.5hr.

Optimization of Process Variables

The results above have shown that the three sulfonation process variables and the interaction among the variables affect the active matter. Therefore, the next step is to optimize the process variables in order to obtain the highest Active matter using the model regression developed. Using the optimization function in Design-Expert, it was predicted that at conditions of 65^0Creaction temperature, 1:1 molar ratio of H_2SO_4/ME and 1.5 h reaction time, an optimal active matter of 68.3% can be obtained. In order to verify this prediction, experiments were conducted and the results were computable with the prediction. It was found that the experimental value of 69% Active matter

which is well agreed with the predicted value. Therefore, this study shows that jatropha oil methyl ester can definitely be used for synthesis of Anionic surfactant.

4.4. Physicochemical Properties of Methyl ester Sulfonic Acid

4.4.1.Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR data interpreted using the data analysis and graphics software called Origin Spectroscopy. The infrared spectrum of the MESS is shown in **Fig. 4.11**. The peaks appearing at 3442.5cm-1 and 2924 cm-1 are attributed to the symmetric and asymmetric –CH2 stretching. The characteristic absorption band at 1714.5 cm-1 can be assigned to stretching vibration of –C=O and–CH2 bending respectively. Another peak at 1127.5 cm-1 represents the –C-O group functionality.

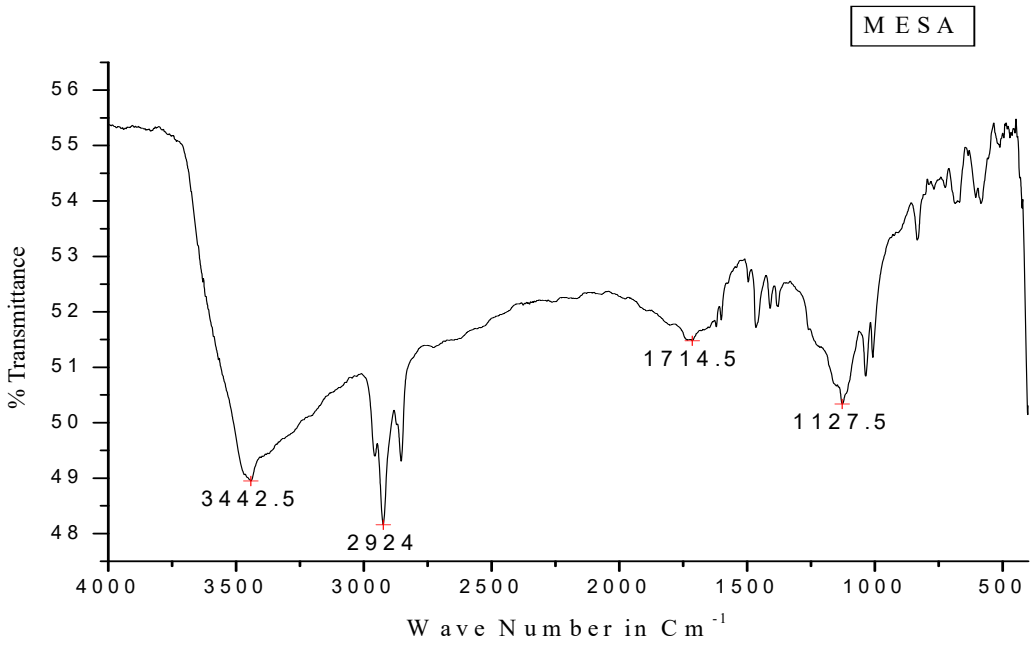


Figure 4.12 FTIR spectra of synthesized MESS

4.4.2.Emulsifying power

Emulsifying power (EP) of the aqueous solutions of MESS was determined for water/liquid paraffin (light) system using different concentration of MESS in (table 4.1) In general, EP increases with increased amount of surfactant in the immiscible binary mixture. The more is the time requiring clearing the two layers, the higher is the emulsifying power of the surfactant. The addition of 0.01g/L of MESS solution in equal volume proportion to the water was found to be ineffective for emulsification since the separation of two phases occurred instantaneously. Besides, further increasing the concentration of MESS solution showed relative emulsification power. At steady storage conditions, it was observed that the emulsion stability gradually decreased as time passed. This may be due to breaking of dispersed droplets within the system and subsequent segregation of two phases [22]. When using higher concentration of MESS (0.05 g/L), a stable creamy emulsion was obtained which took about 38 min to effect separation.

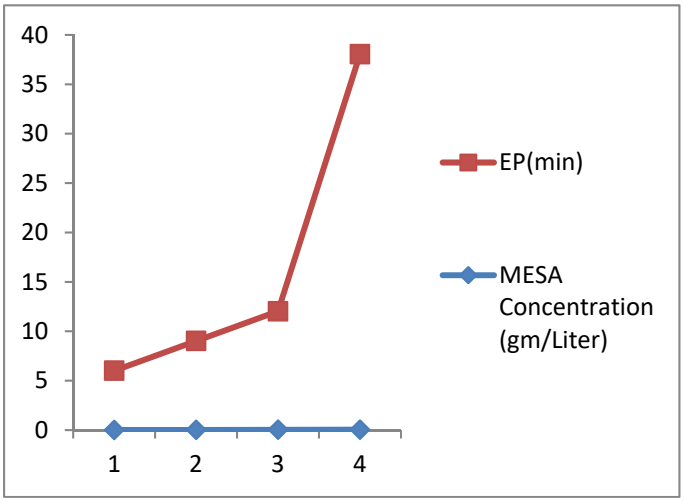
2.5.3. Foaming Power and Stability

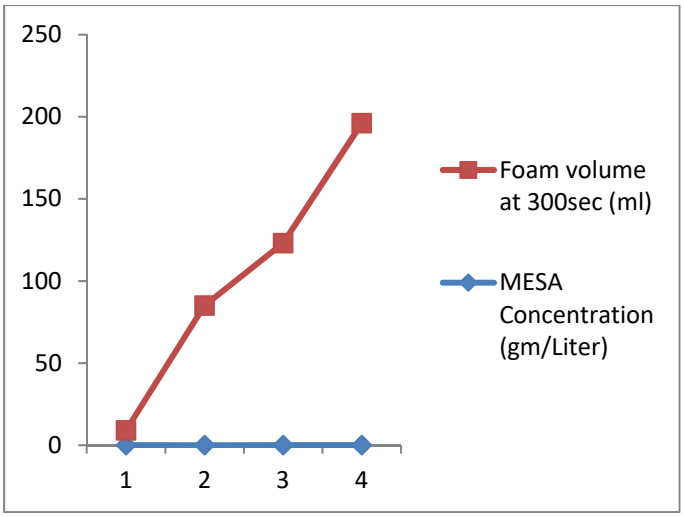
The most widely appreciated property of the surface active substances in aqueous solution is their ability to encourage the formation of foam and bubbles. These behaviors could be endorsed to the physical nature and bubble development. In present case, the concentration of MESS was varied to investigate the effect on the foaming ability. The results obtained for MESS showed that at lower concentration (0.01 g/L) depth of foam formed was least with full of larger bubbles and thus, the foam diminished almost for the given period of observation period. The increasing MESS concentration enhanced the dense foam production with increased depth. At higher concentration (0.05 g/L) of MESS, very thick high quality foam was observed indicating the

dispersion air in the form of small bubbles throughout the solution blend. Besides, a stable foam volume was obtained showing the stability of the MESS foam at that concentration for the experimental period.

Table 4-4 Emulsifying power and foam stability of MESA at different concentration

MESA Concentration (gm/Liter)	EP(min)	Initial foam volume (ml)	Foam volume at 300sec (ml)
0.01	6	48	9
0.02	9	125	85
0.03	12	161	123
0.04	38	468	196





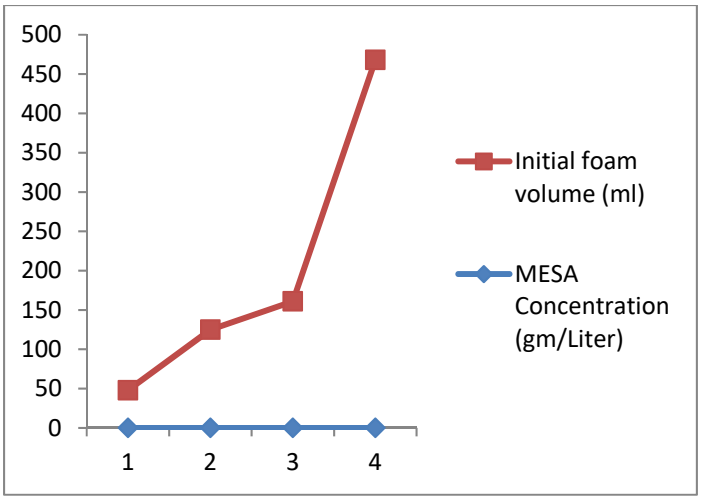


Figure 4.13 Emulsifying power and foam stability of MESA at different concentration

5. CONCLUSION & RECOMMONDATION

5.1. Conclusion

In this research, synthesis of anionic surfactant from locally available raw material *Jatropha* seed oil using transesterification and sulfonation process, further investigation has been done on sulfonation process. The three sulfonation process reaction parameters affecting the active matter of the methyl ester sulfonic acid synthesized namely reaction temperature, molar ratio of H_2SO_4/ME and reaction time has been studied. The outputs of the experiment conducted have been analyzed by employing Design-Expert 6.0.0, three-level-three-factor face centered CCD, through analysis of physicochemical characteristics and through application of synthesized methyl ester sulfonic acid with producing liquid detergent in a small amount.

Based on the analysis of experimental results, it is found that all the three process variables exhibited significant interaction effect on the active matter of the methyl ester sulfonic acid. A mole ratio of 1:1 H_2SO_4/ME, reaction temperature of 65^{o}C and 1.5hr reaction time results an optimal value of 68.3% active matter.

The physicochemical properties determined for the methyl ester sulfonic acid are The FTIR analysis, Emulsifying power, foaming power & foam stability. At higher concentration (0.05 g/L) of MESS, very thick high quality foam was observed and a stable foam volume was obtained showing the stability of the MESS foam at that concentration for the experimental period. The characterization shows the MESS synthesized fit most of the specification of anionic surfactant therefore; it has great potential of exploiting local resources and a perfect substituent of the petroleum based anionic surfactants which are widely used in our country. ME is an inexpensive, natural and renewable

feedstock. Methyl ester sulfonates provide superior surfactant properties at low cost, and therefore a strong economic incentive to substitute MESS for surfactants in many applications.

5.2. Recommendation

In this thesis synthesis of methyl ester salfonic acid from jatropha oil are studied using sulfuric acid as a sulfonating agent even though sulfuric acid is not the best options but due to the unavailability of other sulfonating agents I forced to use it, therefore choise of sulfonating agent effect did not account in this study, and the synthesis of the anionic surfactant was studied only to show the possibility of replacing the petroleum based and other types of surfactant from natural oils.

Considering results obtained in this thesis with the above limitations, the following recommendations are suggested for future works.

- Since type of sulfonating agent have the great effect on the active matter percentage of MESA, it needs further investigation.
- Further research is also recommended in order to confirm jatropha seed oil is the best option for the synthesis of anionic surfactant. Which will lead to more formulation work can be expected utilizing different types of ME feedstock based on the concentrated of MESA.

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APPENDICES

Appendix A: Compositions of Jatropha Oil

Table A-1 Fatty acid Composition of Jatropha Oil

Fatty Acid	**Systemic Name**	**Formula**	**Structure**	**Wt%**
Palmitic	Hexadecanoic	$C_{16}H_{32}O_2$	16:0	11.3
Stearic	Octadecanoic	$C_{18}H_{36}O_2$	18:0	17.0
Oleic	Cis-9 Octadecanoic	$C_{18}H_{34}O_2$	18:1	12.8
Linoleic	Cis-9,cis-12-Octadecedianoic	$C_{18}H_{32}O_2$	18:2	47.3
Arachidic acid	Eicosanoic	$C_{20}H_{30}O_2$	20:1	4.7

Source: [17]

Table A-4 Jatropha Oil Characteristics

Sr.No.	**Physicochemical Parameters**	**Values for Oil**
1	Specific gravity	0.913 at 28^{o}C
2	Refractive Index	1.496 at 28^{o}C
3	Acid number(mg KOHm/g)	36.461
4	Iodine Value (mg/g)	104.46
5	Saponification Value (mg/g)	175.12
6	Unsaponifiable matter (%)	1.02

(Source: www.ijabpt.com)

Table A-2 Fatty acid composition of the major fatty oils and fats

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

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

Appendix B: Standard Specification of Methyl ester Sulfonic Acid

Table B-1 Specification of Methyl ester sulfonic acid

Characteristic	Methyl ester sulfonic acid Requirment
Chemical property Requirment	
Total Active matter, %	68-72
Petroleum ether soluble	≤2.5
Di-Sodium salt	≤ 5
PH(25^{o}C, 1% a.m)	4.5 to 7.0
Physical property Requirment	
Appearance(25^{o}C)	Light yellow

Appendix C: Experimental Results

Table C-1 Moisture content of Jatropha seeds

Run	Before drying weight(W1)gm	After drying weight(W2)gm	(W1-W2) Gm	Moisture Content (%)
1	5.141	4.963	0.178	3.6
2	5.025	4.824	0.201	4.2
3	5.011	4.822	0.189	3.9
Average Moisture Content (%)				3.8

Table C-2 Acid Value of Jatropha Oil

Run	Titration Volume, ml	Colour Change
1	3.20	Pink
2	3.18	Pink
3	3.40	Pink
Average Value	3.26	Pink

Table C-3 Saponification value of Jatropha Oil

Run	Titration Volume, ml	Colour Change
1	5.68	Red
2	5.61	Red
3	5.60	Red
Average Value	5.63	Red

Table C-4 Experimental process conditions for methyl ester sulfonation process

Run	**Reaction Temperature (^oC)**	**Molar Ratio of H_2SO_4 to ME**	**Reaction Time(hr)**	**Amount of Methyl ester(ml)**	**Amount of H_2SO_4 (ml)**
1	65.00	0.20	1.50	30	1.24
2	70.00	0.20	1.00	30	1.24
3	65.00	0.60	1.50	30	3.71
4	65.00	0.60	1.50	30	3.71
5	60.00	0.20	2.00	30	1.24
6	60.00	0.60	1.50	30	3.71
7	70.00	1.00	1.00	30	6.18
8	65.00	0.60	1.50	30	3.71
9	70.00	0.60	1.50	30	3.71
10	65.00	1.00	1.50	30	6.18
11	65.00	0.60	1.50	30	3.71
12	60.00	0.20	1.00	30	1.24
13	60.00	1.00	2.00	30	6.18
14	70.00	0.20	2.00	30	1.24
15	65.00	0.60	1.50	30	3.71
16	65.00	0.60	1.00	30	3.71
17	65.00	0.60	2.00	30	3.71
18	70.00	1.00	2.00	30	6.18
19	60.00	1.00	1.00	30	6.18
20	65.00	0.60	1.50	30	3.71

Table C-5 Yield of Methyl ester sulfonic acid and PH for different Process Variables

Run	Reaction Temperature (^oC)	Molar Ratio of H_2SO_4 to ME	Reaction Time(hr)	Yield of methyl ester sulfonic acid (%)	PH value
1	65.00	0.20	1.50	75.5	6.81
2	70.00	0.20	1.00	74.4	7.00
3	65.00	0.60	1.50	72.3	6.78
4	65.00	0.60	1.50	71.5	7.20
5	60.00	0.20	2.00	73.4	6.91
6	60.00	0.60	1.50	71.07	7.0
7	70.00	1.00	1.00	72.8	7.05
8	65.00	0.60	1.50	71.3	7.20
9	70.00	0.60	1.50	70.7	7.32
10	65.00	1.00	1.50	72.6	6.88
11	65.00	0.60	1.50	71.6	7.01
12	60.00	0.20	1.00	74.8	7.21
13	60.00	1.00	2.00	73	7.32
14	70.00	0.20	2.00	74.9	6.53
15	65.00	0.60	1.50	71.4	7.44
16	65.00	0.60	1.00	70.5	7.50
17	65.00	0.60	2.00	72	7.22
18	70.00	1.00	2.00	74.02	6.92
19	60.00	1.00	1.00	73.7	6.87
20	65.00	0.60	1.50	72.03	7.0

Appendix D: Calculation Part

D1: Purification of Jatropha Oil

The total amount of jatropha oil obtained from mechanical extraction is 2.3 liter out of 10kg of Jatropha Seed.

Degumming

It is the removal of Phosphatides, gums and other complex compounds from the mechanically extracted jatropha oil. Hence, based on the method discussed in Chapter 3 wt% of distilled water is required for degumming process of curde oil.

$$Amount\ of\ distilled\ water\ required = amount\ of\ Jatropha\ oil\ X\ 3\%$$

$$= 2.01\ X0.03 = 60.31ml$$

The acid value is determined by using titration, from equation (3.2)

$$\text{Acid value} = \frac{56.1xVxN}{W}$$

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

N is concentration of ethanolic KOH and

W is weight in gram of the test portion.

$$\text{Acid value} = \frac{56.1\ xVxN}{W} = \frac{56.1x\ 3.26x\ 0.1}{5} = 3.66\ \text{mgKOH/g oil}$$

FFA $= \frac{AV}{2} = \frac{3.66}{2} =$ 1.83mg KOH/g oil

Molecular weight of Jatropha Oil

Table D-1 Molecular Weight of Fatty Acids

Fatty Acid	**Formula**	**Constitutional Formula**	**Molecular Weight (kg/kmol)**
Palmitic	$C_{16}H_{32}O_2$	$CH_3(CH_2)_{14}COOH$	256
Stearic	$C_{18}H_{36}O_2$	$CH_3(CH_2)_{16}COOH$	284
Oleic	$C_{18}H_{34}O_2$	$CH_3(CH_2)_{14}(CH)_2COOH$	282
Linoleic	$C_{18}H_{32}O_2$	$CH_3(CH_2)_{12}(CH)_4COOH$	280
Arachidic acid	$C_{20}H_{40}O_2$	$(CH_2)_{18}COOH$	312

Molecular mass of Triglyceride = Molecular mass of Palmitic Acid

+ Molecular mass Stearic Acid

+Molecular mass of Oleic Acid

+Molecular mass of Linoleic Acid

+ Molcular mass of Arachidic Acid

Molecular mass of Triglyceride $= (256x0.113) + (284x0.17) + (282x0.128) + (280x0.47) + (312x0.047) = \frac{259.568gm}{mol}$

D2: Physicochemical Properties of Purified Oil

Saponification Value

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

Mass of KOH = N × equivalent weight× Volume of solution in liter

= 0.5mol/liter × 1 liter = 28.055gm

Mass of HCL = N × equivalent weight× Volume of solution in liter

= 0.5 × 36.5 × 1 liter = 18.25 g

$V_{HCl} = \frac{m}{\rho} = \frac{18.25}{1.16} =$ 15.73ml

D3:Determination of Active matter of MESA

The active matter after neutralization is determined by titration with (0.004M) Hyamine solution using Methylene Blue as indicator.

$$Active\ matter\ of\ MES = \frac{V\ x\ mol.wt\ of\ MES x\ Molarity\ of\ Hyamine}{Weight\ of\ sample}$$ using equation 3.7

Where

V is the volume in ml of Hyamine consumed for titration.

Molecular weight of MES = 226