

INDIGENOUS SYNTHESIS OF WETTING AGENTS FROM CASTOR OIL FOR THE FINISHING OF COTTON FABRIC

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ABSTRACT

Castor oil is one of the most versatile plant oils. The various grades of the oil and its derivatives are currently used in over a dozen diverse industries. In future, with the rising environmental concerns and the need for bio-based products to replace synthetic feedstocks, castor oil and oil oleo chemicals have the potential to be used in many newer industries.

Many derivatives and oleochemical of castor oil require relatively simple methods for their production. While higher generation derivatives such as sebacic acid or salts ricinoleic and undecylenic acid could require more sophisticated production methods.

This paper carried out experimental study, through sulfation and neutralization of refined castor oil. Concentrated sulfuric acid will be used as solvent for the sulfation process. The oil produced will be neutralized by caustic soda solution. The characterization analysis revealed that tested parameters, which include concentration, acid value, saponification value and iodine value for refined castor oil produced, were within the ASTM standard specifications. In fact the iodine value obtained (82-88) for the refined oil indicates that the oil could certainly be used as lubricant, wetting agent. The oil was modified via sulphation method to produce Turkey – red oil that was tested on cotton cloth. The test revealed that the Turkey – red oil produced is suitable for wetting agent for cotton fabric.

KEYWORDS: Castor Refined Oil, Sulfation, Neutralizing, and Wetting Agent

INTRODUCTION

Research Background

The Vegetable fats or vegetable oils have an essential function in the industrial economy of a developing country as the seed oil provide a huge use in human daily life in order to complete and make the nowadays life more easier. The seed oils are one of the vegetable oil family members. Vegetable oils or vegetable fats are the lipid materials that been derived from the natural plants which physically oil are in liquid state in the room temperature whereas the fat exists in solid state in the room temperature (Ndiaye et. al., 2006). The vegetable oil is composed of triglycerides which lack glycerin in its structure.

Oils that are extracted from plants have been used in this world since the ancient times and already used in many cultures. As an example the castor plant has been known to man for ages. Castor beans have been found in ancient Egyptian tombs dating back to 4000 B.C and during that time, the castor oil was used thousands of years ago in the wick lamps for lighting (Scarpa et. al., 1982). Basically, to obtain the oil from the plants or seeds, the seeds and the plants are

through extraction process and then be distillate to remove the solvent used as to separate the extracted oil and solvent used in order to get the pure oil (Kirk-Othmer, 1979).[1]

Several feedstocks from vegetable source such as soybean, rape seed, canola, palm, corn, Jatropha and castor seeds have been studied as an alternative to oil candidate. Among these sources, castor seeds are a potentially promising feedstock since among vegetable oils, castor oil is distinguished by its high content (over 85%) of ricinoleic acid. There is no other vegetable oil contains so high a proportion of fatty hydroxyacids and castor oil is the most stable viscosity of any vegetable oil (Ogunniyi, 2006).

There are variety processes or the combination of the processes to obtain the oils from the castor seeds. The hydrate presses, continuous screw presses and also solvent extraction are the common methods to obtain the oils from the castor seeds. However, the most satisfactory approach to get the oil is hot pressing the castor seeds by using a hydraulic press and then followed by solvent extraction. This proposal is however focused at not on the extraction but it is about the modification of castor oil by sulphation process.

Identification of Problem

Currently, the leading producers and the countries that seriously involve in the production of castor oils are India, China, and Brazil. [1] Together, these countries account for 90% of the acreage and production of castor beans. It is grown in Costa Rica, Ecuador, Thailand, Philippines, Paraguay, Romania, Sudan, Mexico, Pakistan, Ethiopia, and Tanzania. The world-wide production stood at 1, 227, 669 tonnes in 2000 (FAO). However, India is the world's largest producer of castor seeds and oils that meets most of global demand for castor oil. India contributes about 750, 000 tonnes annually, and accounting for 60% of the entire global production. Essentially, all the castor oil production in the U.S has been eliminated by a combination of economic factors, excessive allergenic reactions of field and the processing workers, and the toxicity of the seed meal. The toxic inside the castor seed which is known as ricin, is a very dangerous to human as it can kill adults if two or three castor seeds were chewed [1]. In Ethiopia there castor plant is adversity planted but there is no as such benefits obtained in this sector. This research will bring initials for the production of wetting agents from castor oil and its effectiveness for the pretreatment of cotton and finally it compares the cost of its derivatives from the normal wetting agent.

Rationale and Significances of Study

Due to the importance of the vegetable oils in the industrial (especially textile industry) pharmaceutical, food industries, and also medical, there is an urgent need to produce more oil from the natural plant. In view of this, castor oil is a promising vegetable oil because it has several advantages; it is renewable, environmental friendly and produce easily in the rural areas, where there is an acute need for modern forms of energy. The primary use of the castor oils is as the basic ingredient in the production of nylon 11, sebacic acid, plasticizers and engine jet lubricant. Castor oil's high lubricity which reduces the friction is superior to other vegetable oils and petroleum-based lubricants. It is really clings to metal, especially hot metal, and the castor oils is used in production nylon 6-10, heavy duty automotive greases, coating and inks, surfactants, polyurethanes, soaps, polishes, synthetic resins, fibers, paints, varnishes, dyes, leather treatments, hydraulic fluids and also sealants[1]. The industrial type maybe divided into three types of quality. 'First' quality is the oil that obtains from only one pressed castor oil and extracted without solvent. This kind of oil normally produced in Europe, is

virtually colorless and has very low acidity. 'Second' and 'third' quality of castor oil is commercial names, meaning that the oil has been extracted using solvent [1].

Wetting agent in the market is very costly and Owing to our team efforts, we are able to offer our clients optimum quality Sulphonated Castor Oil (T.R.O) or Turkey Red Oil which is very prominent in international market. Our product is offered to the clients in convenient packs and is well known for its quality. This is used across the industry as a powerful surface agent. Our bio-degradable and eco friendly product is based on vegetable oils.

Some applications of our product are listed below:

As a softener for Sizing in the textile industry

For Vat and Naphthol dyeing of cellulose

As an anionic wetting agent and emulsifier

As a defoamer in Sugar, Paper and Brewery industry. As an Emulsifier in the pesticide industry. As an Additive in the lubricant and petroleum industry. Also used extensively in the Rubber, Ball bearing and leather industries

LITRATURE REVIEW

Introduction

The castor plant is a robust annual that may grow 6 to 15 feet (2-5 meters) in one season with full sunlight, heat and adequate moisture. In areas with mild, frost-free winters it may live for many years and become quite woody and tree-like. The large, palmately lobed leaves may be over 20 inches (50 cm) across and resemble a tropical aralia. There are several cultivated varieties with strikingly different foliage colorations, including black-purplish, dark redmetallic, bronze-green, maroon, bright green with white veins, and just plain green. Although it grows very rapidly with little care or insect pests and produces a mass of lush tropical foliage, its use in cultivation should be discouraged because of the extremely poisonous seeds or "beans." This is particularly true where small children might be attracted to the large, beautifully-mottled seeds which are produced in prodigious numbers. Castor bean plant showing large, tropical, palmately-lobed leaf and cluster of spiny red fruits. [2]

The Vegetable fats or vegetable oils have an essential function in the industrial economy of a developing country as the seed oil provide a huge use in human daily life in order to complete and make the nowadays life more easier. The seed oils are one of the vegetable oil family members. Vegetable oils or vegetable fats are the lipid materials that been derived from the natural plants which physically oil are in liquid state in the room temperature whereas the fat exists in solid state in the room temperature. The vegetable oil is composed of triglycerides which lack glycerin in its structure.

Oil is any neutral chemical substance that is a viscous liquid at ambient temperatures, is immiscible with water but soluble in alcohols or ethers. Oils have a high carbon and hydrogen content and are usually flammable and slippery (no polar). Oils may be animal, vegetable, or petrochemical in origin, volatile or non-volatile.

Castor oil is pale amber viscous liquid derived from the seeds of the plant *Ricinus Communis*, sometimes known as ricinus oil. Castor oil is one of the few naturally occurring glycerides that approach being a pure compound, since the fatty acid portion is nearly nine-tenths ricinoleic.

A crude Castor oil is a pale straw colour but turns colorless or slightly yellowish after refining and bleaching. The crude oil has distinct odour, but it can easily be deodorized in the refining process. Like any other vegetable oils and animal fats, it is a triglyceride, which chemically is a glycerol molecule with each of its three hydroxyl group esterified with a long chain fatty acid. Its major fatty acid is the unsaturated, hydroxylated 12-hydroxy, 9-octadecenoic acid, known familiarly as Ricinoleic acid. The fatty acid composition of a typical castor oil contains about 87% of ricinoleic acid.

Castor plant (*Ricinus Communis*) from which castor beans and oil are subsequently derived grows naturally over a wide range of geographical regions and may be activating under a variety of physical and climatic regimes. The plant is however essentially a tropical species, although it may grow in temperate regions. Literature revealed that Castor beans contains about 30-35 percent oil which can be extracted by variety of processes or combination of processes, such as hydrate presses, continuous screw presses and solvent extraction. However the most satisfactory approach is hot pressing using a hydraulic press, followed by solvent extraction.

However, castor oil and its derivatives are used in the production of paints, varnishes, lacquers, and other protective coatings, lubricants and grease, hydraulic fluids, soaps, printing inks, linoleum, oil cloth and as a raw material in the manufacturing of various chemicals sebacic acid and undecylenic acid, used in the production of plasticizer and Nylon.

This paper is however aimed at extraction, characterization and modification of castor seed oil. This will be achieved through the realization of the following objectives:

Extraction of Castor Oil from Castor beans through solvent extraction process;

Characterization of crude and refined castor oil for easy identification, and also to assess its quality;

Modification of the refined castor oil. [2]

Basic Facts about Castor Oil

The trade in castor oil as an item of commerce goes back to antiquity (Ogunniyi, 2006). The castor oil is obtained from the extracting method or pressing the castor seed which known with botanical name *Ricinus Communis*. This oil is inexpensive, environmentally friendly and also a naturally-occurring resource. The oil that comes from castor is a viscous, pale yellow color, non-volatile, and also non-drying oil with a bland taste and sometimes used as a purgative. Furthermore, the oil has a slight characteristic odour while the crude oil tastes slightly acid with a nauseating after-taste. The oil is one of the relative in the vegetable oil family which has a good shelf life and it does not turn rancid unless the oil subjected to excessive heat. The largest exporter of castor oil is India and the other major producers of castor oil are China and Brazil as shown. The total world production of the extracted castor oil is about 500, 000 tones and the production of seeds are estimated at one million tones. [1].

The Castor Oil Properties

Relative to other vegetable oils, castor oil has different physical and chemical properties which vary with the method of extraction the oil. The castor oil that obtain from the cold pressing has low acid value with low iodine value and has slightly higher saponification value compared to the solvent-extracted oil, and the oil is lighter in color (Ogunniyi, 2006). The chemistry of castor oil is focused on its high content of ricinoleic acid and also the other three points of function that exist in the castor molecule. One of the molecule functions is the carboxyl group that can give a huge and

wide range of the esterification. Second one is the single points of unsaturation which can be altered using the hydrogenation process or the epoxidation process or the vulcanization process. The last one is the hydroxyl group in the castor oil can be acetylated or alkoxyated maybe can be remove from the oil molecule by using the dehydration process to increase the unsaturation of the oil compound to provide the semi-drying castor oil. By high-temperature pyrolysis and by caustic fusion, the hydroxyl position of oil which is so reactive the molecule can be split at that point to yield useful product with shorter chain length. Actually, the presence of the hydroxyl group on the castor oil is adding the extra stability to the castor oil and also preventing the formation of hydroperoxides. [1]

Features of Castor Seeds

The castor plant grows in the wild in large quantities in most tropical and sub-tropical countries. The plant is available at the low price and it is known to tolerate in varying weather condition. Normally, the castor plant needs a temperature between 20 and 26 °C with low humidity throughout the growing season in order to give maximum yield. Moreover, the weather conditions for its growth limit its cultivation to tropical areas of the developing world. There are different types of castor seeds all around the world but on the average, the castor seeds contain about 30 to 55% of oil by weight. The seeds are very poisonous to human and also animals as the seeds contain ricin, ricinine and certain allergens which are toxics. The effects if the castor seed is accidentally ingested, the victims will face abdominal pain, vomiting and diarrhea and as little as 1 mg of the ricin can bring the human to death. The fear of accidental ingestion of the poisonous castor seed by the children does not encourage the use of the castor plant for ornamental purpose. Besides that, the seed cake is poisonous and consequently not suitable for animal feed. Some people who worked with the meal highly develop allergic reaction such as asthma. The main reason why the US farmers no longer grow the castor plant is because of the toxicity of castor seed extensively. However, the pure castor oil if used in right and recommended quantities can be used as the laxative. The quality of the seed oil is hardly affected by the variation in good or poor seeds. The oil from the castor seed is non-edible oil which can be used and can free up some edible oils used in industries for human consumption. [3]

General Products and Use

The uses of castor oil have changed over the years. Sixty years ago, castor oil was used for lamp oil, medicinal purposes and as a general industrial lubricant. Soon afterwards, chemical

Engineers were able to produce derivatives of the oil that were of even more benefit to man.

The chemical structure of castor oil is of great interest because of the wide range of reactions it affords to the oleochemical industry and the unique chemicals that can be derived from it.

These derivatives are considerably superior to petrochemical products since they are from renewable sources, biodegradable and eco-friendly. [3]

Castor oil forms a clean, light-colored soap, which dries and hardens well and is free from smell. Sulfonated (sulfated) castor oil, or Turkey Red Oil, was the first synthetic detergent after ordinary soap, and other forms of the oil became important for the treatment of leather, industrial lubricants, and other industrial uses. Castor oil is regarded as one of the most valuable laxatives in medicine. Castor oil is an excellent solvent of pure alkaloids and such solutions of atropine, cocaine, etc., as are used in ophthalmic surgery. [3]

Today, there are many uses of castor oil and its derivatives such as: polyamide 11 (Nylon 11) engineering plastic, lubricating grease, coatings, inks, sealant, aircraft lubricants, surfactants, emulsifiers, encapsulators, plastic films, plasticizer for coatings, and components for shatterproof safety glass. It is an essential component in some artificial rubbers, in various descriptions of celluloid, and in the making of certain waterproof preparations, and one of the largest uses is in the manufacture of transparent soaps. It also furnishes sebacic acid which is employed in the manufacture of candles, and caprylic acid, which enters into the composition of varnishes. Castor oil has even made its way into cosmetics and related products. [3]

Partial oxidation of Castor oil at 100° C produce "blown oil", an oil that stays fluid at low temperatures and is used a lot for hydraulic brake fluid, and as weakener in ink, varnishes and leather. Nowadays it is an important resource for very high quality lubricants. They are used for engines working under extreme conditions, like jet engines for airplanes. [3]

Castor oil qualities with regard to lubrication: For any fluid to act as a lubricant, it must first be "polar" enough to wet the moving surfaces. Next, it must have a high resistance to surface boiling and vaporization at the temperatures encountered. Ideally the fluid should have "oiliness", which is difficult to measure but generally requires a rather large molecular structure. Castor oil meets these rather simple requirements in an engine, with only one really severe drawback in that it is thermally unstable. This unusual instability is the thing that lets castor oil lubricate at temperatures well beyond those at which most synthetics will work.

Castor oil is roughly 87% triglyceride of ricinoleic acid $[(CH_3(CH_2)_5CH(OH)CH_2CH=CH(CH_2)_7COO)_3(OC)C_3H_5]$, which is unique because there is a double bond in the 9th position and a hydroxyl in the 11th position. As the temperature goes up, it loses one molecule of water and becomes "drying" oil. Castor oil has excellent storage stability at room temperatures, but it polymerizes rapidly as the temperature goes up. As it polymerizes, it forms ever-heavier "oils" that are rich in esters.

These esters do not even begin to decompose until the temperature hits about 650 degrees F (345° C). Castor oil forms huge molecular structures at these elevated temperatures - in other words, as the temperature goes up, the castor oil exposed to these temperatures responds by becoming an even better lubricant. [3]

The sulphated compositions may be used on textiles materials derived from natural, manmade and synthetic fibres such as cotton, wool. Silk, jute, sisal, hemp, fur, flax, kapok, rayon, cellulose acetate, nylon, polyesters and acrylic. [4].

Extraction of Castor Seed Oil

There are many ways to obtain the oil from the castor seeds. The extraction of oil from the castor seed is one or combination of processes, such as mechanical pressing and solvent extraction. The examples of the mechanical pressing are hydrate presses and continuous screw presses. However, the most effective way to obtain the oil from the seed is hot pressing using a hydraulic press and followed by solvent extraction. In the mechanical pressing, the seeds are crushed to remove the seed from the shell and the adjusted to low the moisture content by warming in a steam-jacketed vessel or in the oven. After that, the crushed seeds are placed into the hydraulic presses and the seeds are pressed by until become the cake to extract the oil. The properties of oil from the mechanical pressing are the oil has the light colour and low free fatty acids (Ogunniyi, 2006). However, about 45% of oil present by the mechanical pressing and the remaining oil in the castor cake can be recovered only by the solvent extraction method. During extraction method using solvents such as heptanes,

hexane and petroleum ethers, the seed cakes are extracted with the solvent in the Soxhlet extractor or the commercial extractor.

Castor Oil and its Chemistry

Vertellus supplies a variety of castor oil grades whose uses are dictated by acid value, moisture level, color and purity. Castor Oil, also known as ricinus oil, is a triglyceride of fatty acids which occurs in the seed of the castor plant, *Ricinus communis* (India, Brazil).

Castor Oil is unique among all fats and oils in that:

It is the only source of an 18-carbon hydroxylated fatty acid with one double bond

Ricinoleic acid (12-Hydroxyoleic Acid) comprises approximately 90% of the fatty acid composition

Product uniformity and consistency are relatively high for a naturally occurring material

it is a nontoxic, biodegradable, renewable resource

The hydroxyl groups in castor oil account for a unique combination of physical properties:

Relatively high viscosity and specific gravity

Solubility in alcohols in any proportion

Limited solubility in aliphatic petroleum solvents

The uniformity and reliability of its physical properties are demonstrated by the long-term use of castor oil as an absolute standard for viscosity. Because of its higher polar hydroxyl groups, castor oil is not only compatible with but will plasticize a wide variety of natural and synthetic resins, waxes, polymers and elastomers. Castor Oil also has excellent emollient and lubricating properties as well as a marked ability to wet and disperse dyes, pigments and fillers. In the form of its chemical derivatives, castor oil's application versatility is further enhanced.

Castor Oil Grades & Derivatives Production

- While castor oil by itself is used in diverse applications, chemical derivatives of castor oil find numerous uses in industrial applications and their domains of use are increasing rapidly.
- The global market for generation II castor oil derivatives, which include sebacic acid, undecylenic acid, heptaldehyde, polyols and dimer acid, is estimated at about \$300 million.
- For generation III derivatives, where half of the generation II derivatives are converted, the estimated market worth is close to \$350 million.
- Generation III derivatives include the esters and salts of generation II derivatives as well as derivatives such as methyl-12-hydroxystearate while generation I derivatives include hydrogenated castor oil, 12-hydroxy stearic acid, dehydrated castor oil acid, and ethoxylated castor oil among others.
- Quite naturally, the prices and profit margins

Table 1: Generic Chemical Reactions of Castor Oil

Reaction Type	Nature of Reaction	Added Reactants	Type of Products
Ester Linkage	Hydrolysis	Acid, enzyme or Twitchell reagent catalyst	Fatty acids, glycerol
	Saponification	Alkalies, alkalis plus metallic salts	Soluble soaps, insoluble soaps
Hydroxyl Group	Caustic fusion	NaOH	Sebacic acid, capryl alcohol
	Sulphation	H ₂ SO ₄	Sulphated castor oil

Of higher generation castor derivatives are significantly higher than the basic grades. The generation I derivatives such as HCO and 12-HSA respectively cost about 20% and 50% more than the basic castor oil grades.

Table 2: Key Derivatives of Castor Oil, Starting Products & Methods of Production

Product Name	Castor Seed	Crushing and Expelling
Commercial Castor Oil	Commercial castor oil	Degumming
First pressed Degummed Grade Castor Oil	Commercial castor oil	Degumming
Refined Castor Oil	Commercial castor oil	Bleaching
Refined Castor Oil (Pale Pressed Grade)	Commercial castor oil	Neutralizing and bleaching
Turkey Red Oil	Commercial castor oil	Sulphonation and neutralization

Sulfonated Castor Oil

Treatment of castor oil with concentrated sulfuric acid yields the sulfonated (actually; sulfated) ester known as "Turkey-red" oil. This product is an anionic wetting agent widely used in textile drying and finishing. [5]

Turkey-red oil is widely used as an anionic wetting agent in the dyeing and finishing of cotton and linen. It is manufactured by treating raw castor oil at room temperature (less than 35°C.) with concentrated sulfuric acid for a period of 3 - 4 hours. Acid in the amount of 15 – 30% of the weight of the oil is used. The exact quantity depending on the product desired.

Following the reaction period. The mass is diluted with water forming two layers. The oil layer is decanted and neutralized with caustic solution. It is then washed again with water to remove traces of caustic. [5]

This oil is obtained thru the process of adding salt of sulfuric acid to ordinary castor oil, often called Turkey Red Oil. The addition of the sulfuric acid makes this oil completely water soluble, thus when added to water it will disperse evenly without needing a suspension agent. For this reason it's often used in blooming bath oil recipes, or as a co-emulsifier for oils into water.

Turkey red oil is deep red in color, and thick in texture, similar to standard castor oil. This oil holds differences of opinions as to the benefit for skin use, some studies show that direct skin contact over a period of time can mildly irritate the skin. Other studies show no toxicity or skin related issues. [6]

Sulfated castor oil, also known as turkey---red oil, represents one of the earliest chemical derivatives of castor oil.

The traditional method of preparing turkey---red oil is to add concentrated sulfuric acid at a controlled rate to castor oil over a period of several hours with constant cooling and agitation of the reaction mass to maintain a temperature of 25-30°C. After acid addition is complete, the reaction mass is washed then neutralized using an alkali solution or an amine.

Castor oil sulfation results largely in sulfuric acid esters in which the hydroxyl group of ricinoleic acid has been esterified. However, the other reactions can also take place. For example, the double bond can be attacked to produce an ester or the hydroxysulfonic acid. Hydrolysis of the sulfuric acid esters occurs during the reaction and subsequent treatment forming hydroxy acids and sulfuric acid. These hydroxyl acids can be further sulfated.

Commercially sulfated castor oil contains ca 8.0---8.5 wt % combined SO₃, indicating that the surfactant properties result from the sulfation of only one of the reactive points in the unmodified triglyceride. The sulfate group acts as a hydrophile imparting excellent wetting, emulsification, and dispersing characteristics to the oil. The anion---active product is used in the textile industry for fiber wetting ability and as dye agent to obtain bright, clear colors. Sulfonation of castor oil using anhydrous SO₃ yields a product having better hydrolytic stability than that from the sulfuric acid reaction. The organically combined SO₃ is low compared to the amount of SO₃ introduced to the reaction: the final product contains only 8.0---8.5 wt % combined SO₃ although 17 wt% SO₃ is added. The product contains less inorganic salts and free fatty acids than the sulfuric acid product.

What is Turkey red Oil?

Turkey Red Oil is also known as Sulfated Castor Oil. It is the only oil that will completely disperse in water. The oil is expressed from the seed. Sulfated castor oil is created by adding sulfuric acid to castor oil, and is considered the first synthetic detergent. Turkey Red Oil has a distinct and heavy scent. It is a surfactant and therefore makes a wonderful base for bath oil as it mixes well with water, producing a milk bath.

Uses: Used in Textile industries, Sugar industry, as a defoaming agent, as an Emulsifier. In cosmetics it is used as humectants and as an Emulsifier for Oil Bath.

Turkey red oil is used in agriculture as organic manure, in textiles as surfactants and wetting agents, in paper industry for defoaming, in cosmetics as emulsifiers, in pharmaceuticals as undecylenate, in paints inks and as lubricants.

For e.g. it is used to emulsify essential oils so that they will dissolve in other water-based products, or for superfatting liquid soap if you want the soap to remain transparent. This means that the oil will combine with the water in the tub, and not leave those little oil bubbles floating on the top of the water. It is of medium viscosity and is usually used in bath oil recipes along with fragrance or essential oils, or in shampoos. This oil also has great moisturizing abilities.

Applications

Sulfated Castor Oil was the first synthetic detergent after ordinary soap. It is also used in formulating lubricants, softeners, and dyeing assistants.

Being an anionic surfactant, it is an active wetting agent (a chemical agent capable of reducing the surface tension of a liquid in which it is dissolved). As such, it is used extensively in dyeing and in finishing of cotton and linen. Generally, the ability of castor oil and some of its derivatives to wet surfaces make them useful as excellent carriers of pigments and dyes.

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Sulfonated castor oil is also used in agriculture as organic manure, in paper industry for defoaming, in pharmaceuticals as undecylenate, in paints, inks, softeners and in lubricants. [6]

MATERIALS AND METHODS

Materials

For this project cotton fabric with epc 21, ppc 26 and GSM of 150 were used. In this experiment castor oil used as a raw material which was purchased from local market. Just like other vegetable oils, castor oil is a triglyceride of various fatty acids and about 10% glycerine. It has the following specifications. Minimum concentration 99%, viscosity (20oc) 0.950-1.050 mpas, saponification value 160 (min.), iodine value 82-88, acid value 1(max) and unsaponifiable value of 1 %(max.)

Methods

Turkey-red oil is widely used as an anionic wetting agent in the dyeing and finishing of cotton and linen. It is manufactured by treating raw castor oil, at room temperature (less than 35oC.), with concentrated. Sulfuric acid, for a period of 3 - 4 hours. Acid in the amount of 15 - 30% of the weight of the oil is used. The exact quantity depending on the product desired.

Following the reaction period. The mass is diluted with water, forming two layers. The oil layer is decanted and neutralized with caustic solution (1.2-2.4% of the weight of oil). It is then washed again with water to remove traces of caustic.

This reaction is a very simple one, requiring only an open vessel fitted with cooling, water coils and a high-speed agitator. The acid is run in continuously over the reaction period so as to avoid an excess which might char the oil, and the reaction temperature is controlled by regulating the flow of water to the cooling coils. This can be done manually, or by automatic controls.

Modification of the Refined Castor Oil: Sulphation

20g of oil was warmed at 35°C. 15ml of concentrated sulphuric acid (98%) was then added and the reaction was allowed to completion with constant stirring. After, the product was washed with hot distilled water and left to stand for 2 hrs, after which water was then removed. And the sulphuric acid ester formed was finally neutralized with 10ml of 0.1M Sodium Hydroxide.

Characterization of TRO

Specific gravity, pH, acid value, iodine value, saponification value, refractive index and viscosity of the oil were determined

Determination of Specific Gravity

Density bottle was used to determination of density of the oil. A clean and dry bottle of 25ml capacity was weighed (W0) and then filled with the oil, stopper inserted and reweighed to give (W1). The oil was substituted with water after washing and drying the bottle and weighed to give (W2). The expression for specific gravity (Sp.gr) is: $Sp.gr = (W1 - W0)/(W2 - W0) = \text{Mass of the substance} / \text{Mass of an equal volume of water}$ [7].

Determination of PH value

The pH value of oil was determined with the aid of a pH meter (Model Delta 320, Mettler Toledo, China).

Determination of Acid Value

The method was specified by ISO 660 (2009). 25ml of diethyl ether and 25ml of ethanol was mixed in a 250 ml beaker. The resulting mixture was added to 10g of oil in a 250ml conical flask and few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1N KOH to the end point with consistent shaking for which a dark pink colour was observed and the volume of 0.1N KOH (V) was noted [7].

$$\text{Acid value} = (56.1 * V * C) / M$$

Where V is the volume in ml of standard volumetric KOH solution used, C is the exact concentration in KOH solution used (0.1 N); m is the mass in grams of the test portion (1g). 56.1 is equivalent weight of KOH.

Determination of Saponification Value

Indicator method was use as specified by ISO 3657 (2002). 2g of the sample was weighed into a conical flask; 25ml of 0.1N ethanolic potassium hydroxide of was then added. The content which was constantly stirred was allowed to boil gently for 60 min. A reflux condenser was placed on the flask containing the mixture. Few drops of phenolphthalein indicator was added to the warm solution and then titrated with 0.5M

HCl to the end point until the pink colour of the indicator just disappeared. The same procedure was used for other samples and blank. The expression for saponification value (S.V.) is given by: $S.V. = [56.1 N (V_0 - V_1)]/M$, where V_0 = the volume of the solution used for blank test; V_1 = the volume of the solution used for determination; N = Actual normality of the HCl used; M = Mass of the sample [7]

RESULTS AND DISCUSSIONS

Combined pretreatment process of grey fabric with conventional wetting agent and TRO as wetting agent is as shown in the following table at a temperature of 90 oc and at a time of 90 minutes.

Table 3: Combined Pretreatment

Combined Pretreatment	
Chemicals Used	Concentration (Owf)
NaOH	2
H ₂ O ₂	2
stabilizer	1
Sodium per sulphate	0.3
TRO	2,4 &6
Wetting agent	2

For comparison the treatment was performed with controlled without wetting agent.

Evaluation of the pretreated fabric

To test the efficiency of the treated fabric the quality of pretreated fabric was performed.

- Capillary rise test with 2x20 cm stripe fabric sample
- Sinking time test with specimen of 2.5x2.5 cm square fabric sample
- Drop test
- %reflectance (%R)
- Iodine test

The result of the quality test is as follows:

Table 4: Results of Combined Treatment

SN	Wetting Agent %	%R	Capillary Rise (cm)	Drop Test (sec.)	Sinking Time Test (sec.)
1	Controlled	65	3.5	3	10
2	WA	74.25	5.4	0.4	4.56
3	TRO 2%	73.34	5.2	0.5	4.35
4	TRO 4%	77.82	8.2	Difficult to record	3
5	TRO 6%	77.86	8.5	Difficult to record	3

Form this table we can understand that TRO as wetting agent at 4% concentration is better than the synthetic wetting agents.

The refined oil was modified for a specific use by means of sulphation process to produce Turkey – red oil which may be use in polishes, as a dyeing and wetting agent. The sulphated castor oil produced was observed to be of high viscosity. This was due to the fact that sulphuric acid used added itself across and unsaturated bond of the oil, yielding a saturated product. However, a little kind of pungent smell was perceived from the sulphated castor oil. This may be as result of the excess un-reacted acid in the oil which has no effect on the intended end use. The modified sulphated castor oil has been tested on wood, a piece of white cloth and a piece of paper. It stuck to the materials and a shining surface was obtained when the wood dried, while the colour is not easily removed from the cloth.

When ricinoleic acid (castor oil) is treated with concentrated H_2SO_4 , its gives a complex mixture consisting of hydrogen sulphate (OSO_3H) of ricinoleic acid in which the hydroxyl group is esterified and a compound in which the H_2SO_4 has added to the double bond. Esterification and addition do not occur together in the same molecule of ricinoleic.

The product which is known as Turkey red oil (sulphated castor oil) has good wetting properties. Neutralization of this with aqueous $NaOH$ gave a detergent plus water. The reaction proceeded at temperatures between 35 - 40%. The water was vaporized by further heating and a solid (powdered) detergent was the result. The bleaching agent (H_2O_2) added helped to bleach the color of the castor oil so that milk colored detergent was produced. pH tests showed that the detergent exhibited basic property. The detergent can thus be described as amphoteric. This classification is characteristic of the intrinsic property of castor oil. This pH range is preferable to that of acidic as it is non - corrosive to the skin and cloths.

From the structure of castor oil (Ricinoleic acid) as shown under literature review, the sulphation reaction occurred at the hydroxyl group while the esterification reaction occurred at the ester linkages and this can be used to produce both soluble and insoluble soaps. Hence the detergent produced was the result of the esterification of the ricinoleic acid.

Table 5: Comparison of derived TRO with Standard

Property	Derived TRO	Standard Value
Acid value	3	3-9
Saponification value	179	176-184
Iodine value	85	83-88
Solubility in alcohol	complete	complete
Specific gravity	0.961	0.958-0.968
PH value	8.5	8.0-9.5

ECONOMICS

This process is also conveniently done on a batch scale. Similarly to those described above. Since no heating is involved, there is no fuel requirement in the operation. Power requirement will be very low. Since no recirculation or vacuum systems need be employed.

Labor requirements per batch will be essentially the same as those stated above, or about Birr 100 per batch per day.

Approximately 0.476 kg of castor oil and 0.113kg of concentrated sulphuric acid are needed for the reaction, to produce 0.454 kg of turkey-red-oil. Neutralization will require about 0.00907 kg of caustic soda per 0.454 kg of Turkey red oil.

Turkey red oil in the market is an average of 1200 birr per kg (Us \$20-100/kg) and castor oil in the market is 700 birr per liter. Sulphuric acid and sodium hydroxide cost birr 220 and birr 65 per liter and per kg respectively.

We can produce/we can get castor oil birr 31 per liter from Ethiopian market and the total cost to produce 0.454 kg of Turkey red oil is 40.2 birr.

So raw material cost per liter approximately birr 80.4 based on the current sales prices.

According to the above suggestion the overall profit if it is produced indigenously is approximately 1120 birr per liter of the product. If we assume we can pay 20 birr for the worker per liter we can save 1100 birr per liter of our product.

CONCLUSIONS

The results of the research showed that castor oil derivatives can be used to formulate wetting agent that has comparable characteristics with normal wetting agent.

The refined castor oil was modified by means of sulphation and Turkey-red oil was obtained which can be use as a wetting and dyeing agent and in the finishing of cotton and linen.

This review on the uses of castor oil in the chemical and polymer industry clearly shows that castor oil is a very valuable renewable resource. Apart from a direct use of this OH group functional oil in many applications (e.g. for PU synthesis a series of industrial procedures to yield a variety of different renewable platform chemicals is well established. Especially the industrially available platform chemicals 10-undecenoic acid and sebacic acid in combination with newly available a, o-bifunctional derivatives obtained via olefin metathesis offer the potential to derive a vast amount of different polyesters and PA with different application possibilities from castor oil in a sustainable fashion. Moreover, the manifold uses of castor oil in polymer applications is described and highlighted within this contribution, clearly showing that castor oil is and will be one of the most promising renewable raw materials for the chemical and polymer industries.

The production of wetting agent from castor oil was successively done. The many desirable intrinsic qualities of castor oil makes it very useful in the wetting industry, thus castor oil can serve as a good substitute to synthetic wetting agent, the conventional detergent bases.

Castor plant is easy to establish and can tolerate different types of soils even marginal soil. The oil extracted from castor bean (*Ricinus communis*) already has a growing international market, assured by more than 700 uses, ranging from medicines and cosmetics to substituting petroleum in the manufacturing of biodiesel, plastics and lubricants. Each hectare of castor oil bean plants planted in arid and semi arid regions produces 350-900 kg of oil per hectare. *Ricinus communis* L. oil is critical to many industrial applications because of its unique ability to withstand high and low temperatures. Compared with food crops, the castor-oil plant is an economic crop, Castor bean has been widely accepted as an agricultural solution for all subtropical and tropical locations that addresses the need for commercial crops with low input costs and at the same time provides traditional farming with a viable income from current non productive lands. Castor

bean does not compete with food crops, as Castor bean can be grown on marginal lands, which are not competitive with food production lands.

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