Formulation and Characterization of Beeswax-Based Shoe Polish

By

Birhan Teshome Beyene

A Thesis Submitted to Chemical Engineering Program in Partial Fulfillment of the Requirement of the Degree of Master of Science in Chemical Engineering

(Specialization in Process Engineering)

School of Mechanical, Chemical and Materials Engineering

Office of Graduate Studies

Adama Science and Technology University

Adama Ethiopia

March 2021

Formulation and Characterization of Bees Wax-Based Shoe Polish

By

Birhan Teshome Beyene

Advisors: Dr. Tatek Temesgen

Dr. Mulugeta Yilma

A Thesis Submitted to Chemical Engineering Program in Partial Fulfillment of the Requirement of the Degree of Master of

Science in Chemical Engineering

(Specialization in Process Engineering)

School of Mechanical, Chemical and Materials Engineering

Office of Graduate Studies

Adama Science and Technology University

Adama, Ethiopia

March 2021

APPROVAL OF THE BOARD OF EXAMINERS

We, the undersigned, members of the board examiners of the final open defense by **Birhan Teshome Beyene**, have read and evaluated her thesis entitled "**Formulation and characterization of beeswax-based shoe polish**" and examined the candidate. This is therefore to certify that the thesis has been accepted in partial fulfillment of the requirement of the degree of master's in chemical engineering.

Name	signature	Date
Birhan Teshome Beyene Name of the student	_____	_____
Tatek Temesgen (Ph.D.) Advisor	_____	_____
Mulugeta Yilma (Ph.D.) Co-Advisor	_____	_____
Dr.P.Selva kumer (Ph.D) Internal Examiner	_____	_____
Elias Wagari (Ph.D.) External Examiner	_____	_____
Melaku Tesfaye (Ph.D.) Chairperson	_____	_____
Hunegnaw Baylie (M.Sc) Head of Department	_____	_____
Tatek Temesgen(Ph.D.) School Dean	_____	_____
_____ Post Graduate Dean	_____	_____

DECLARATION

This is to declare that this thesis entitled **"Formulation and characterization of beeswax-based shoe polish"** and submitted in partial fulfillment of the requirements for the award of the degree of Master of Science in a chemical engineering program for specialization in process engineering at Adama University, prepared by **Birhan Teshome** which is an original work and done by our own effort.

Name of student: Birhan Teshome

Signature_____ Date_____

This MSc Thesis has been submitted for examination with our approval as thesis advisors.

1, Dr. Tatek Temesgen

Signature_____ Date_____

2, Dr. Mulugeta Yilma

Signature_____ Date_____

ACKNOWLEDGMENT

I would like to give thanks to my Lord Jesus for helping me in any condition that I have passed through my career life. Without the blessing of God, it would not be possible for all my wishes to come into reality.

This thesis would not have been completed without the support of my advisor, Dr. Tatek Temesgen, and my deep thanks for his endless support and direction at each progression of this work. I am again thankful to my co-advisor, Dr. Mulugeta Yilma who provided me his valuable support, guidance, and endless tolerance.

I would like to Acknowledge Adama University department of Chemical Engineering for accepting me to pursue my MSc. program and providing precious supports and cooperation during my stay in laboratory analysis.

The last but not least, I would like to heartedly acknowledge my lovely families. And, many thanks deserve to my husband, Mr. Samuel Salomon, for being with my side and my little baby Naol Samuel for his patience in waiting for me to give time for him. Moreover, my optimistic mother Buzunesh Chiquala, for her affection and prays make me able to get such success and honor. Thankfulness also goes to everyone involved directly or indirectly in the compilation of this thesis.

ABSTRACT

Shoe polish is a wax-based product that is put on the surface of the shoe leather to enhance waterproofing, restore, and improve the appearance of leather to make the finished leather smooth and glossy. The main intention of this research thesis is to formulate and characterize shoe polish from beeswax. Beeswax is one of the natural waxes from which shoe polish is produced. Ethiopia has the potential to produce beeswax and one of the beeswax exporters to the world market but amounting to less than 10% of the total estimated beeswax production of the country exported per year. The remaining huge amount of beeswax is wasted due to different reasons. Therefore, this work was conducted primarily to evaluate the physicochemical properties of beeswax, which is the most important input to shoe polish formulation. The physicochemical analysis was conducted according to the standard protocols of the Ethiopian Beeswax specification ET-1203-2005 developed by Quality Standard Authority of Ethiopia QSAE, 2005. According to the laboratory results, the average values for each parameter are melting point (61.43ºC), specific gravity (0.9711), refractive index (1.4403), ash content (0.123), total volatile matter (0.69), acid value (22.44), saponification value (96.31), ester value (73.87), fat and fatty acids (passed), and paraffin and other waxes (passed). The result showed that the compositional content of beeswax sample falls within the range of quality parameters set for national standards. Hence, it is suitable to utilize beeswax in Ethiopia for shoe polish formulation. Additionally, activated carbon (AC) was prepared from sugar cane bagasse and its characteristics were investigated. Sugar cane bagasse activated carbon was produced using potassium hydroxide as an activating agent and at 500 ºC for 2 hours of carbonization. Sugarcane bagasse AC was used as a colorant agent in the shoe polish formulation. Its proximate analysis were done and compared with commercially available AC by SEM to determine the surface morphology of activated carbon FTIR analysis to examine the functional group of materials. The external surfaces are full of cavities and aggregate structures. And FTIR spectroscopy showed presence of significantly different peak frequencies in sugarcane and commercial A.C by different functional groups. The chemical surface characterization result showed that sugar cane bagasse AC and the commercially available activated carbon have almost similar properties. Hence, instead of using commercially available activated carbon the possibility of sugar cane bagasse AC was confirmed. Finally, four shoe polishes were formulated from beeswax and sugar cane bagasse AC alone in addition to other ingredients (castor oil, naphtha, stearic acid), and the properties of the four samples were tested and compared with the standard commercially available shoe polish (kiwi).

The viscosity, density, melting point as well as physical testing like gloss, fade resistance, rub resistance, and dust absorption of the properties were investigated and the sample with a proportion of 14.4% beeswax, 25% castor oil, 43.6% naphtha, 7% stearic acid and 10% activated carbon was found to be the best blending ratio and its comparison favors close to the standard kiwi shoe Polish.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ACRONYMS/ABBREVIATIONS

Acronyms/abbreviation	Full expression
AC	Activated carbon
ASTM	American Society for Testing and Materials
CAC	Commercial Activated carbon
CIF	Cost, insurance, and freight
CSA	Central Statistical Agency
DOE	Design of Experiment
FT-IR	Fourier Transformed-Infrared Spectroscopy
IUF	International Union Fastness
QSAE	Quality and Standards Authority of Ethiopia
UOM	Unit of measurement

CHAPTER ONE

1. INTRODUCTION

1.1. Background of the study

Leather footwear, requires protection against the effect of water, drying out and forming of unpleasant cracks of the shoe uppers.

Shoe polish is a product that is put on the surface of the shoe leather used to result in water proofing, quality restoration, and improve the appearance of leather to make the finished leather smooth and glossy. It also maintains the flexibility of the leather and increases the leather's resistance to weathering, scuffing, and rubbing (Gumel and Umar 2011).Whether inexpensive or expensive, all leather shoes want good polishing to prolong their service and keep them looking new.

The history of shoe polish was started using natural substances like wax, ash, and tallow. Polishes in modern time are formulated by substituting different liquids and suspended solids, while their composition had no exact difference from that produced before, but some products have been added to improve the quality and serve as alternatives to other ingredients, and some products of that era are still in use till today (Altahir 2018).

The polish industry is a huge global economy worth of which the shoe polishes industry as a surface coating enables earning in the very important venture. Mainly, 26% of turnover of shoe polishes is accounted by pastes, 24% by creams, 23% by aerosols, and 13% by liquids. The manufacture of surface coating materials of which shoe polish is a part has been estimated with more than 10,000 million USD yearly. This is in essence meaning that its usage is widespread and in terms of employment, gives lot of opportunities (Alene, Munwyelet et al. 2018).

In Ethiopia, the demand for polishes is largely met through imports. Ethiopia imports a variety of polishes and creams used in different applications. Ethiopian Revenue and Customs Authority classify the imported polishes and creams under the following headings.

34051000 – Polishes, creams, and similar preparations for footwear or leather.
34052000 – Polishes, creams, and similar preparations for maintenance of woodwork; and
34053000 –Polishes, creams, and similar preparations for coachwork.

Among the above three types of polishes and creams imported by Ethiopia, only the first two types are intended for use in footwear and wood (Betrework 2017).

The number of polishes, creams, and similar preparations for footwear or leather that Ethiopia imported during 2020 is presented in Table-1.1.

Table1.1 Import data of Ethiopia for footwear polish (hs code 34051000) during 2020

Product description	Country	Quantity	UOM	Net weight in Kg	CIF value in USD
Polishes, creams and similar preparations for footwear or leather	Turkey	4,378	L	5,745.6	23,034.17
	Italy	1,000	L	1,135.14	7,623.04
	Kenya	650	L	11,700	7,343.03
	China	36,000	L	870	1,775.79

Source: Ethiopia revenues and customs authority

As it can be observed on the above table the annual import of polishes, creams and similar preparations for footwear or leather is 19,450.74 Kg which accounts 39,776.03 CIF value in USD as of 2020.

Waxes are mainly used industrially as components of complex formulations often for coatings. Therefore, shoe polish is, a protective and decorative surface coating product, usually wax-based or a sequence wax-based and when applied to shoe leather it gives a sequence protection and makes it smooth and shiny. The concern of modern-day engineering is carrying out research trying to minimize the number of useful resources from being wasted. This study is one of such works in terms of using some locally available useful resource like beeswax which is wasted by different reasons.

This research is aimed to formulate and characterize shoe polish mainly from beeswax and the properties of produced shoe polish were compared with standard commercial shoe polish (kiwi).

1.2. Statement of the problem

Waxes are an ester of long-chain aliphatic fatty acid and alcohol, and they are used for many purposes. Wax contains special properties such as malleability, hydrophobicity, and ability of solubility in organic nonpolar solvents. Consequently, waxes gained increased use of various industries such as pharmaceuticals, cosmetics, textiles, paints, polishes, and packaging.

One of the dominant uses of waxes in footwear is to preserve and protect the leather from water, dust and at the same time gloss it. Both natural and manufactured waxes are finding applications in the manufacture of polish. Beeswax is one of the natural waxes from which shoe polish is produced. It is used for the formulation of shoe polish due to its organic raw nature, non-toxicity, flexibility of operation, and easy availability compared to other types of waxes in Ethiopia (Betrework 2017)

Ethiopia has the potential to produce beeswax. It is because of the existence of a favorable environment and biodiversity which favored diversified honeybee flora and a huge number of honeybee colonies kept in traditional hives. About 6.52 million hives are estimated to be found in the rural sedentary areas of the country ((CSA) 2017/18 /2010 e.c) It is estimated that the country has the potential to produce 500,000 tons of honey and 50,000 tons of beeswax per annum. Due to the diverse agro-climatic zones, the average honey and beeswax production estimates are about 45,000 and 5,000 tons per year, respectively. Such an amount puts the country 10^{th} in honey and 4^{th} in beeswax production worldwide (Kenesa 2018).

The country has a lifelong history in the beeswax trade and one of the beeswax exporters to the world market but amounting to less than 10% of the total estimated beeswax production of the country exported per year. Despite this fact, the export trends of beeswax are gradually increasing from time to time. The remaining larger portion of wax is either used as candle making (Tuaf) for religious purposes or wasted. Even though it is difficult to give the exact statistics of beeswax consumption locally, it is either used for candle making or a large amount is lost (Addisu Bihonegn, Begna et al. 2017).

According to various works literature mentioned in different parts of the country, there are so many factors assigning to this wastage and challenge of beeswax production. Much of the beeswax produced from bees could be harvested by beekeepers is wasted due to beekeepers lack of knowledge on how to collect, handle, and extract to make marketable beeswax (Tesfu, Asaminew et al. 2020).

Additionally, in many parts of Ethiopia huge amount of crude beeswax is lost or thrown away at the beekeepers back yard because of the fact that many honey hunters and beekeepers do not know that beeswax can be traded or used for a locally made high-value product, and the presence of market demand for this product is not well known (Yeshitila and Tekeba 2018). It is therefore, necessary to change this huge waste of beeswax for making a useful product such as shoe polish. In the country, it has been an opportunity to use beeswax for shoe polish production and changing this situation.

1.3. Objective of the study

1.3.1. General Objective

The main objective of this study is formulation and characterization of beeswax-based shoe polish.

1.3.2. Specific objectives

- Analyzing the chemical and physical properties of sample local beeswax, its relevance to shoe polish formulation.
- Preparation and characterization of activated carbon from sugar cane bagasse
- Formulation and production of beeswax-based shoe polish
- Characterization of produced beeswax-based shoe polish
- Comparison of produced shoe polish with commercial polish (KIWI)

1.4. The Significance of the study

In Ethiopia, there is no factory manufacturing shoe polish but few informal sectors producing it. The demand for shoe polishes is mostly met through imports. Ethiopia imports a variety of shoe polishes in different types and colors. This research project intends to investigate local alternatives to these imported products. It will equally be an avenue for finding means of increasing our domestic national product.

Importantly, developing the benefit offered by this research work will help in making the shoe polish industry a viable system whose product could be exported and there by serving as a foreign exchange earner for the country and create employment opportunities. Additionally, beeswax usage/consumption can produce a market chain with beekeepers and make them advantageous.

1.5. Scope of the study

This study has four components: the first part deals with analyzing the chemical and physical properties of local beeswax for the relevant quality parameters. Then activated carbon was prepared and tested for its physical and chemical properties. After that, the wax and activated carbon are used alone in addition to other ingredients to prepare shoe polish. Finally, prepared shoe polishes were characterized and compared with the properties of commercially available shoe polish (Kiwi).

CHAPTER TWO

2. LITRATURE REVIEW

It has been known for many years to apply thin films of protective substances to shoe and leather goods to preserve them from the effects of water vapor, dirt and to improve their appearance. Thin films of wax are used today to accomplish the protection of shoe surfaces and to increase their aesthetic appeal by imparting more luster or gloss to them. Most polishes depend on wax or oil for their polishing properties. Oil polishes are easy to apply but the polished surface easily attracts dust and finger marks. However, wax polishes are harder to apply on the surface of the shoe but no dust is attracted and no finger marks are shown (Altahir 2018).

Shoe polish consists of a waxy colloidal emulsion, a substance composed of some of the partially immiscible liquids and solids mixed. It has typically a specific gravity of 0.8 that is negligibly soluble in water, and available in many colors. It is applied to leather products to repel other solvents or dust from the film surface and impart elasticity without destroying the hardness of leather (Gumel and Umar 2011).

Shoe polish consists of various toxic substances of petroleum-based products, turpentine, and carbonates of sodium and potassium. The burning of shoe polish results in the yielding of carbon dioxide, carbon monoxide, and traces of oxides of nitrogen and various toxic materials depending upon the chemicals and solvents used to make the shoe polish (Betrework 2017).

Basically, there are two types of shoe polishes. Solvent-based (whose paste polish is non-aqueous and clear or translucent), and the other is water-based (whose emulsion polish is milky in appearance and aqueous) (Ameh 2011).

In recent years environmental, toxicological, and cost considerations have stimulated research into shoe polishes formulated from no or low content of organic solvents. The only realistic alternative to reduce the level of organic solvent is to change organic solvents with water. Water acts as a solvent as an external or water continuous phase in terms of oil-in-water (o/w) and an internal discontinuous phase in terms of water-in-oil (w/o) emulsion. An emulsion is a dispersion of droplets of one liquid in another when the two liquids are immiscible such as wax and oil in water (Altahir 2018).

Mostly these types of shoe and leather polishes have a problem of consistency and become thick, which affects the ease of application and spreadable effect of the product. It also requires a lot of work to shine and becomes dry out (Wiersema, Boonman et al. 2007). Due to the above reasons, the consumer is forced to use solvent-based shoe polish. Solvent-based shoe polish represents sixty percent of the market for leather polish (Kamalu 2005).

There are different shoe polish brands found in the world market such as kiwi, Woly, TiT, Lude, Coxy but Kiwi remains the predominant shoe polish brand in most of the world, being sold in over 180 countries and holding a 53% market share worldwide.

2.1. Ingredients & Product Composition

There are different types of polish compositions that are used to polish shoes and leather goods. These types are paste compositions, cream, liquids, and aerosol spray. Each polish compositions differ in detail but all consist of three fundamental groups of materials that contribute to the formula properties: solvents, wax blends, and dyes. A balanced formula is required to produce a shoe polish that possesses mandatory attributes such as the ability to give a smooth, hard, shiny surface, ease of application, quick buffing, scuff coverage, high spectral reflectance, and satisfactory paste-surface physical characteristics (Buke 2000) .

Additionally, a good shoe polish must possess the following characteristics: it has to be good in heat stability and should have a sufficiently high softening temperature so that polishes do not liquefy in hot summer weather. Because it forms a thin - layer on the surface of shoe, it serves as a barrier between the polished surface and the moisture-filled environment. It has to be transparent, uniform in color, adhesive and resistant to corrosion (Altahir 2018).

In this study, in the formulation of shoe polishes beeswax, oil, solvent, thickening agent, and pigment were used to obtain the desired result.

2.1.1. Wax

The most critical decisions during the formulation are the selection of wax components, wax ratios, and total wax concentration in the product. When a shoe polish is applied, the coating that remains on the shoe reflects by the interactions between the wax components and the pigment after the vaporization of the solvent. Both natural and synthetic waxes are used together for making polish. Natural wax-based polishes have long-lasting properties, but more difficult to apply on the surface of the leather/shoe.

2.1.1.1. Beeswax

Beeswax is a product of the metabolism of a honeybee class (Apismellifera, L. Fam*Apidae*), which belongs to the *Apis* genus. This species of the honeybee is found and domesticated worldwide. Bees need wax as the construction material for their combs. They produce it in their wax glands, which are fully developed in 12 to 18 days old workers (Bogdonov 2016)

Beeswax is a very complex material containing different substances. It is composed of esters of fatty acids (67%) such as monoester (35%), diester (14%), tri ester (3%), hydroxyl monoester (4%), hydroxyl polyester (8%), various hydrocarbons (14%), free acids (12%), long-chain alcohols (1%) and other substances (Tesfu, Asaminew et al. 2020).

Beeswax is a very stable substance with high plasticity at a relatively low temperature and its properties change little over time. It is resistant to hydrolysis and natural oxidization. It is insoluble in water, very slightly soluble in cold alcohol, and completely dissolves in volatile oils, chloroform, ether, benzene at 30°C, and carbon disulfide at 30°C. However, at room temperature, it does not fully dissolve in any of these solvents, but upon heating above the wax melting point, it is readily soluble in all of them, and also in ethanol in the same way (Addisu Bihonegn, Begna et al. 2017).

It is solid at room temperature, becomes brittle once the temperature drops below 18 °C, and quickly becomes soft and pliable at around 35 to 40 °C. Its melting point is not stable, since the composition varies slightly depending on its origin. A typical value of the beeswax melting point is between (61 to 65 °C) while it does not boil but decompose at 120^{O}c (Bogdonov 2016). Beeswax, with its exclusive characteristics, is now being used in the development of new products in various fields such as cosmetics, foods, pharmaceuticals, engineering, and industry (Gemechis Legesse 2014). When applied to finished shoe leather, it can create a durable, lasting, and glossy finish.

Beeswax is a valuable product that can provide a worthwhile income in addition to honey. In the world, the beeswax market commands a much higher unit price, (three times more than honey). In this country, rural beekeepers are the primary source of crude beeswax from traditional hives, and crude beeswax was obtained from the honeycombs after the removal of honey. Also, tej brewers are the chief suppliers of beeswax in its ‘Sefef’ after the beverage production (Gemechis Legesse 2014).

Before using beeswax for any process, it must be rendered and purified to remove dirt and contaminations that occur in the hive. The process by which the crude beeswax is changed into blocks of clean wax is known as rendering. There are several ways of rendering and purifying beeswax. All the processes involve a combination of melting and filtering (Gemeda and Kebebe 2019). Wax has been melted by boiling water, steam, electrical or solar power. After it melted, if the wax is still not pure enough, it has to be filtered. Filtration is carried out by a tightly woven cotton cloth, paper filters and sack (Bogdonov 2016). For industrial purposes, the beeswax is purified by filtration and centrifugation.

2.1.2. Oil

Oil in the prepared products used as softeners and water-repellent agents. It blended with waxes to plasticize and provide a suitable film when applied to the shoe leather. Castor oil is inedible oil, like other seed oils, extracted from the ripe or matures seeds of the plant. It consists of triglyceride molecules, each containing three esters of ricin oleic acid or ricinoleates (in place of three hydroxyl groups) on a glycerol backbone (Nangbes, Nvau et al. 2013). It is the only commercial source of a hydroxylated fatty acid (ricinoleic acid). This high level of purity (by single fatty acid content) makes the oil unique among all naturally occurring fats and oils. The presence of a hydroxyl group makes castor oil excellently solubile in alcohols, and its ability to plasticize a wide variety of natural and synthetic waxes (A.K. Yusuf 2015). It is viscous, pale yellow, non- volatile, and non-drying oil with a bland taste. Relative to other vegetable oils, it has a good shelf life and does not turn rancid unless subjected to excessive heat.

2.1.3. Solvent

Solvents are volatile liquids added to polishes to dissolve the waxes and oils. Essentially, a solvent act to solubilize wax components in a form that permits the development of a relatively uniform, thin-film coating on the leather substrate. Upon evaporation, a thin waxy film can be buffed to give a desirable gloss. The selection of solvents is driven by the chemical property of the gloss components and ranges from water to volatile organic solvent.

In solvent-based shoe polish, many different organic solvents like mineral and petroleum-derived solvents and oil includes turpentine, mineral spirits, naphtha, Stoddard solvent, petroleum ether, and benzene utilized.

Generally, in various polish formulations, turpentine is considered the solvent of choice due to its relatively high kauri-butanol value and its volatility but, all of the above solvents are used in shoe polish applications in the past time and still popular (Buke 2000).

Organic solvents in solvent-based shoe polishes have multiple functions. They assist in achieving ease of application of the product, and they perform a role in cleaning the leather and used to make the footwear water-repellent. After application, the solvents evaporate and leave a water-repellent membrane on footwear (Wiersema, Boonman et al. 2007). The solvent must have an evaporation rate that works well in the environment. Organic solvents are selected to match the waxes and are used to soften the wax and make it easy for the product application. Preferably, the solvent should also be nontoxic (low toxic) of low cost and have an acceptable odor. In this study, naphtha was used as a solvent. Naphtha is a light solvent produced by the processing of crude oil in petroleum refineries. It can be reddish-brown or colorless to pale yellow color with a gasoline-like odor. It is used as a solvent in making varnish, adhesives, coatings, and many other chemicals.

2.1.4. Activated Carbon (as pigment)

Activated carbon is solid, porous black carbonaceous material with a large internal surface area and highly developed porous structure. It consists of 87-97% carbon and the rest of the components oxygen, hydrogen, sulfur, nitrogen, and other elements depending on the processing method used and raw material derived from (Altahir 2018).

Activated carbon can be differentiated from elemental carbon by the oxidation of the carbon atoms found on the outer and inner surfaces. Activated carbon like carbon blacks is lightfast, insoluble in acids and alkalis, and is resistant to solvents. It provides good opacity, even at low addition levels and better texture. It has higher tinting strength compared to iron black or organic pigments. The main difference between carbon black and activated carbon is that the surface-area-to-volume ratio of carbon black is lower than that of activated carbon.

Activated carbon produced by carbonization and activation of carbonaceous materials. The carbonization process is heat treatment that converts the raw materials to carbon by minimizing the content of volatile matter and increasing the carbon content of the material. Activation is used for enhancing porosity and creates structures that lead to the formation of fine solid cavities in carbonized carbon. Carbonaceous materials can be activated through one of two distinct methods, namely, chemical activation and physical activation (Udeh 2018).

Physical activation is done by carbonization of raw materials followed by activation of the resulting char at elevated temperature in the presence of suitable oxidizing gases such as carbon dioxide, steam, air, or their mixtures. In the chemical activation process, both steps are carried out simultaneously, with the raw material mixed with chemical activating agents. In chemical activation, activating agents are used such as phosphoric acid, sulfuric acid, zinc chloride, potassium hydroxide. Among the above activators, potassium hydroxide due to its ability to produce activated carbon with a high surface area, its distribution of good pore size, low environmental pollution, less corrosiveness, and lower costs is widely used (Heidarinejad, Dehghani et al. 2020). Chemical activation compromises several advantages over physical activation: higher yield, simplicity, lower temperature of activation, and better porous structure (Bachrun, AyuRizka et al. 2016).

Activated carbon is a black solid that contains fixed carbon content and other minor contents such as ash, moisture, and volatile matter. It exists in different forms. Two of the most popular form is powder activated carbon and granular activated carbon. Powder AC is particularly a powder or fine that has a large surface area to the volume ratio. It also contains micropores (< 2 nm), mesopores (2nm-50 nm), and macropores (>50 nm) within its pore sizes. Activated carbon may contain different atoms such as hydrogen, oxygen, nitrogen, phosphorus, and sulfur within the delocalized electron of the carbon on the surface will form certain functional groups that will determine the chemical properties of its surface. Surface chemistry, particle size, and structure properties are the main parameters for activated carbon pigment and have a large effect on the properties of the dispensability and blackness of activated carbon when they are mixed with waxes or resins (Jebur (2018)).

Activated carbon has occurred as potential materials with extensive applications. Because activated carbon contains remarkable characteristics, for example, high specific surface area, high porosity, and favorable pore–size distribution, it is a good adsorbent for gaseous and liquid. AC is widely used in the purification, decolorization, and removal of toxic substances and the treatment of wastewater. The most common sources of activated carbon on a commercial scale are bituminous or lignite coal and petroleum residue. However, due to long-term availability, environmental impacts, and high cost have encouraged researchers to have studied the production of activated carbons from cheap and renewable raw materials (Yahya, Mansor et al. 2018).

This research emphasizes on, instead of using commercial activated carbon, sugar cane bagasse was examined to produce an AC through the chemical activation process since it was available and inexpensive material with high carbon content. Several works for developing high surface area activated carbon from sugar cane bagasse can be used as versatile adsorbents but, in this study, can be used as a black pigment.

Sugar cane bagasse is a by-product of sugar cane industries obtained after the extraction of sugar cane juice to produce sugar. Sugar cane bagasse consists of cellulose, pentose, and lignin. The high cellulose content in bagasse is important for using it as raw material carbon production. It is currently used as a fuel for boilers or supplied as raw material for the manufacturing of pulp paper and building boards. It also is a suitable resource for the preparation of activated carbon (Dwiyaniti, Barruna et al. 2020).

2.1.5. Stearic acid

An essential ingredient in the shoe polish formulation is a thickener without this the polish will be too runny making it difficult to use. Stearic acid is a substance commonly used to increase the viscosity of the product. Stearic acid is long-chain fatty acids comprising oils and fats. It exists in animal fats, oil, and the same kinds of vegetable oils as the form of glycerides. It is white or colorless, wax-like solid and soluble in alcohol, ether, chloroform, and insoluble in water.

2.2. Related works

Various substances have been used as raw materials for polish formulation. There is a direct link between the function and quality of the shoe polish and the ingredients used during formulation. Today, shoe polish is made from a composition of natural and synthetic materials, including naphtha, turpentine, lanolin, waxes (often Carnauba wax), benzene, dyes, and gum Arabic using straight forward chemical engineering processes.

Several studies have been carried out to produce shoe polish from waste. Wastes are like polyethylene films, shopping bags, plastics, and water sachets littering. These wastes pollute the environment if it is not properly disposed and managed. These days, the waste polyethylene (often called used water sachets) was pyrolyzed at various temperatures to obtain polyethylene wax.

(Betrework 2017) investigated the conversion of used water sachets to a useful product. Used water sachets were pyrolyised at various temperatures to obtain polyethylene (sachet) wax. The author formulated a shoe polish from polyethylene wax with beeswax, olive oil, and stearic acid. During his formulation, a blend of bee wax and a wax obtained from used water sachets was melted and stearic acid was added and stirred. Thereafter, Olive oil was introduced while still stirred to ensure a proper mix. Finally, the mixture was allowed to cool to 41°C and poured into a container. His formulation has three different shoe polishes and compared it with the standard polish (Kiwi) by its density, melting point, viscosity, and physical testing such as gloss, rub resistance, fade resistance, dust absorption resistance, and crease resistance, of the polish formulated.

(Kamalu 2005), revealed four different black shoe polishes from castor oil. In his study, a castor oil undergoes hydrogenation (the addition of hydrogen element) to a double bond that changes the physical and chemical properties of fat to form a castor wax. Castor wax is used for the production of leather polish with carbon black, benzene or ethanol as a solvent.

According to his study, two of the trials polishes were benzene based while the remaining two were ethanol based. In his formulation, weighted, grinded and sieved carbon black was dissolved in the required volume of solvent by applying heat (40-45^{0}c) using hot plate. After that the solution (solvent and dye) was continually stirred and castor wax was added while heat was continuously applied for about three minutes then it was poured into the container. Finally, the author concluded that the benzene-based formulation gives satisfactory result in terms of gloss, color, drying rate, dust attraction, and texture compared to ethanol-based polish. Additionally, the wax he obtained from hydrogenated castor oil gives a good penetration and good protection polishes. The high surface area of carbon black that was used as a pigment adds the gloss of the finished product.

(Altahir 2018), conducted a study on the formulation of black shoe polish by using activated charcoal as a colorant agent. He produced two types of black shoe polishes, one to be used for cleaning and the other for shining. Both types of polishes were produced from activated carbon as colorant agent, gum Arabic as an emulsifying agent, and oily phase from paraffin oil, white wax, and Vaseline. The author studied and compared the produced shoe polishes based on some physical parameters (conductivity, pH, relative density, and viscosity) with standard shoe polishes (kiwi, Nikwax, and Woly).

Other researchers investigated a simple formulation without using mineral solvents, comprising a wax and oil from nontoxic organic constituents. A scholar **(Anderson, Anderson et al. 2017),** formulated water in oil emulsion composition from soya oil, beeswax, and water. His composition comprises from about 40 % (w /w) to about 60%(w/w) of soya oil; from about 1 % (w /w) to about 15 % (w/w) of a beeswax and from about 20 % (w\ w) to about 50 % (w /w) of water. It concludes that one advantage of the compositions avoids the inclusion of toxic, synthetic, and petroleum products.

2.3. Wax characterization

Characterization is important in the formulation especially in the wax analysis. It allows prediction of properties and quality of the final product. There is a relationship between wax properties and their performance in the end application. Each type of wax has its own specific composition and physical properties, but the composition and the physical characteristics of the wax are influenced by adulteration with various materials. It is therefore necessary to characterize waxes quality or properties before the wax applications.

Nowadays, adulteration and contamination are the main beeswax quality issues. Mostly, beeswax product quality has always been low due to its high demand in the global market. Beeswax is adulterated with cheaper materials like animal fat, plant oils, and petroleum spirits. In our country beeswax mostly adulterated with animal tallow which is many times cheaper than beeswax (Adgaba 2007). On the other hand, due to prolonged overheating throughout rendering, there has been quality deterioration and compositional change of natural beeswax.

Beeswax adulteration was detected by measures of sensory and Physico-chemical characteristics methods. Examination of the sensory characteristics (e.g., odor and color) of beeswax allows a simple and quick quality check, but this does not guarantee that the beeswax has not been adulterated. Because of this physical and chemical property that is commonly used to evaluate the beeswax quality and distinguish possible adulterations.

Ethiopian government sets quality standards for beeswax produced in the country after investigating the physical and chemical properties of samples of beeswaxes collected from different parts of the country. The physical and chemical properties that are relevant to beeswax quality include melting point, specific gravity, refractive index, volatile matter, ash content, saponification cloud point, acid value, ester value, and ester to acid ratio was analyzed.

CHAPTER THREE

3. MATERIAL AND METHODS

3.1. Material and Equipment

The types of equipment used for this analysis was a digital thermometer- an accuracy of 0.1°C, Test-Tube, Water-Bath, Specific Gravity Bottle - 25 ml capacity, Abbe digital refractometer, silica dish - having a capacity of 100 ml, Oven, Analytical balance, Metal or aluminum dish, conical Flasks - 250 to 300 ml capacity, Reflux condenser- at least 65 cm long, hot plate, cotton, Bunsen Burner, Watch glass, Laboratory furnace (muffle furnace), Desiccator, electrical stirrer (fluid mixer), viscometer, oven, ball mill machine

Material used for this analysis was, Beeswax, Benzene, Rectified Spirit, Standard Potassium hydroxide Solution 0.5N and 1M, Phenolphthalein Indicator Solution, Alcohol, Methyl Ethyl Ketone, Alcoholic Potassium Hydroxide. Hydrochloric Acid 0.5 N and 0.1M solution, Sodium hydroxide Solution - 10 percent, dilute hydrochloric acid 4N, Ethanol *95%*, sugar cane bagasse, Castor oil, paraffin wax, distilled water, Stearic acid, Activated carbon, naphtha, and commercial shoe polish (Kiwi).

3.2. Beeswax sample collection and preparation

Beeswax samples were obtained from southwest Ethiopia (Masha) in June 2020 from beekeepers and honey cooperatives. The sampling area was selected for this study based on the high potential of beeswax production and availability and samples were collected randomly.

Before any analysis, the beeswax sample was purified. This study used the simplest method of hot water extraction using immersion. In the first step, wax samples were placed in a tied tightly woven cotton cloth and placed in a recipient (beaker) and submerged in a water bath at a temperature of 75-80°C. It is then melted and filtered through the woven cotton and rises to the surface of a beaker. After all, wax was melted and the pot was cooled down. Finally, the wastes remaining on the woven cloth was discarded.

3.3. Bees wax characterization

The Physico-chemical properties including melting point, specific gravity, refractive index, total volatile matters, ash content, saponification point, acid values, ester values, paraffin and other waxes, fats and fatty acids were investigated based on the detailed procedures of Ethiopian Beeswax quality specifications ET-1203-2005 (QSAE) 2005) as listed below and For each analysis**,** the measurements were collected in triplicated and the average data was reported.

3.3.1. Determination of melting point

The beeswax was melted by warming it in water -bath at a temperature just sufficient to melt and then dip the thermometer and withdraws with the melted material to get the bulb thinly coated with the wax and let it stand for 24 hours. After doing that insert this thermometer (with an accuracy of 0.1 °C) into the test-tube through the bored cork and then place the test -tube in the water-bath. The temperature gradually rose, at the rate of 1°C in 3 minutes at which a transparent drop forms at the end of the thermometer bulb. Finally, this temperature is recorded as the melting point of the material (QSAE) 2005)

3.3.2. Determination of Specific Gravity

Two grams of the beeswax was melted in a porcelain crucible at a temperature of about 100°C.The solidified beeswax was removed from the crucible by allowing it to cool to room temperature and warming it slightly (if necessary). During weighing, beeswax was attached to tarred silk or similar item that thread was suspended. The sample was stored for 2 hours at a temperature of 20 ± 1^0c. The mass of the sample was determined, first in the air, and then in a rectified spirit maintained at 20± 1°C. The specific gravity at 20°C/20°$_C$ of the rectified spirit was determined by means of the specific gravity bottle (QSAE) 2005)

The specific gravity of beeswax was calculated by the following formula:

$$\text{Specific gravity at } 20\ ^oC = \frac{M_1 d}{M_1 - M_2} \quad \text{... ... ...Equation 3.1}$$

Where,

M_1 = mass in g of the material in air

d = specific gravity of rectified spirit,

M_2 = mass in g of the material in alcohol

3.3.3. Determination of refractive index

The sample was melted and filtered through fast filter paper to remove any impurities and last drops of moisture. A digital refractometer was used to measure the refractive index. The temperature of the refractometer was adjusted by circulating water from the water bath at 75 $\pm 1^0_C$. Few drops of the sample were placed in the lower prism and the prism closed and tightened firmly was allowed to stand for one or two minutes. Finally, the refractive index of the sample was read and recorded after it attained the test temperature (QSAE) 2005)

3.3.4. Determination of ash

The silica dish was heated to redness and cooled to room temperature in a desiccator and weighed. Then after 50 g of beeswax was taken in a watch-glass and weighed accurately. About three-quarters of this quantity was transferred to the silica dish and heated on a Bunsen burner so that the material burns gently at the surface and when about half of the material was burnt away heating stopped and cooled. After that, the remainder of the material was added to the silica dish. The dish heated again as before until the material completely charred and after that, the sample was incinerated in a muffle furnace at 550 to 650 °C for 1 hour and cooled to room temperature in a desiccator and weighed. By repeating the incineration, cooling, and weighing of it was, done until the difference between two successive weightings was less than one milligram (QSAE) 2005).

The ash content of beeswax was calculated by the following formula:

$$\text{Ash percent by mass} = \frac{M_2}{M_1} * 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\text{Equation 3.2}$$

Where,

M_2=mass in g of the ash and

M_l = mass in g of the material taken for the test.

3.3.5. Determination of total volatile matter

Ten grams of the beeswax was weighed accurately in a previously dried and weighed suitable dish and placed it in an oven maintained at 105.2 ^{o}C for 6 hours. Then, the dish was cooled in a desiccator and weighed. The dish heated again in the oven for 30 minutes and the process was repeated until the loss in mass between two successive weightings was less than one milligram. The lowest mass obtained was recorded as a result (QSAE) 2005).

The calculation for determining total volatile matter was done by the following formula:

$$\text{Total volatile matter at 105.20C percent by mass} = \left(\frac{M_1 - M_2}{M_1 - M_3}\right) * 100 \quad \text{... ... ... Equation 3.3}$$

Where,

M_1 = mass in gram of the material before heating

M_2= mass in gram of the dish after heating.

M_3 = mass in gram of the empty dish

3.3.6. Determination of acid value

Five grams of the beeswax was weighed in a 250 m1 conical flask then after 75 ml of a mixture of two parts of benzene and one part of rectified spirit were added. The solution was heated under reflux until the sample was dissolved and allowed to cool to room temperature. Then the mixture was titrated with standard potassium hydroxide solution of 0.5 N and using phenolphthalein as indicator until pink color is observed. The formula for determining acid value of beeswax was indicated as follows (QSAE) 2005)

$$\text{Acid value} = 56.1\ \frac{VN}{M} \quad \text{... ... ... Equation 3.4}$$

Where

V= volume in ml of standard potassium hydroxide solution used,

N= normality of standard potassium hydroxide solution and

M = mass in g of the material taken for the test.

3.3.7. Determination of saponification value

Accurately 2g of beeswax was weighed in a tarred conical flask and 25 ml of methyl ethyl ketone was added, followed by *25* ml of alcoholic potassium hydroxide solution. Then after adding a few pieces of pumice stone in a reflux condenser it was connected to the flask and heated on a water-bath or electric hot-plate for about 2 hours to boil steadily but gently. After the flask and condenser were cooled, the inside of the condenser was washed down with about 10 ml of rectified spirit. About 1ml of phenolphthalein indicator solution was added and the residual potassium hydroxide was titrated with 0.5 M standard hydrochloric acid. Finally, the blank assay or titration was also performed with 25ml of 0.5 M alcoholic

potassium hydroxide. The formula for determining the saponification value of beeswax was indicated as follows (QSAE) 2005)

$$\text{Saponification value} = 56.1\frac{(B-S)N}{M} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 3.5}$$

Where,

B=volume in ml of standard hydrochloric acid required for the blank,

S = volume in ml of standard hydrochloric acid required for the material,

N = normality of standard hydrochloric acid and

M = mass in g of the material taken for the test.

3.3.8. Determination of ester value

The ester value was obtained when the acid value was subtracted from the saponification value (QSAE) 2005)

3.3.9. Test for fats and fatty acids

Five grams of beeswax was boiled for about 10 minutes with 80 ml of 10% sodium hydroxide solution replacing the water lost by evaporation. The solution was cooled and filtered through glass wool and the filtrate solution was acidified with 4N dilute hydrochloric acid. The beeswax should been taken to pass the test if the solution does not become turbid after acidification (QSAE) 2005)

3.3.10. Test for paraffin and other waxes

One gram of beeswax was weighed and placed in a conical flask fitted with water - cooled reflux condenser. Then 10 ml of alcoholic potassium hydroxide solution was added and boiled under reflux for one hour. Then after detaching the flask from the condenser, a thermometer was inserted suitably into the liquid in the flask and allowed to cool by stirring constantly. The beeswax has been taken to pass the test if the following conditions were satisfied:

i. The liquid does not become cloudy at a temperature higher than 61°C but
ii. becomes cloudy at a temperature between 61°C and 59°C and precipitation of large flocks occurs at not more than 2°C below the temperature at which the liquid becomes cloudy (QSAE) 2005).

3.4. Preparation of activated carbon

Sugar cane bagasse A.C preparation was performed according to (Joan Na Lee 2014, Tadele 2016). Sugar cane bagasse was collected from Wonji/Shoa Sugar factory and dried in an oven at 110^{o}c for four hours until it reaches a constant weight and dried bagasse was crushed by using a ball milling machine and sieved to the particle size of the range between 2 to 4 mm. Then the raw material was subject to digestion with 1M KOH overnight by 1:2 ratio of mass of raw bagasse pith to KOH. The resulting mixture was dried in an oven overnight at 110 °C to remove water. After that, the dried materials were carbonized at 500 °c for two hours in a muffle furnace. Then the activate sample was cooled and washed with distilled water and a 0.1 M HCL to remove residual potassium hydroxide and other impurities until a pH value of 6 to 7 is obtained. Then the product was dried in an oven at 105° C for 12 hours and then crushed to powder form by using a ball milling machine and sieved. Finally, the samples were stored in plastic bags and ready for analysis and shoe polish preparation.

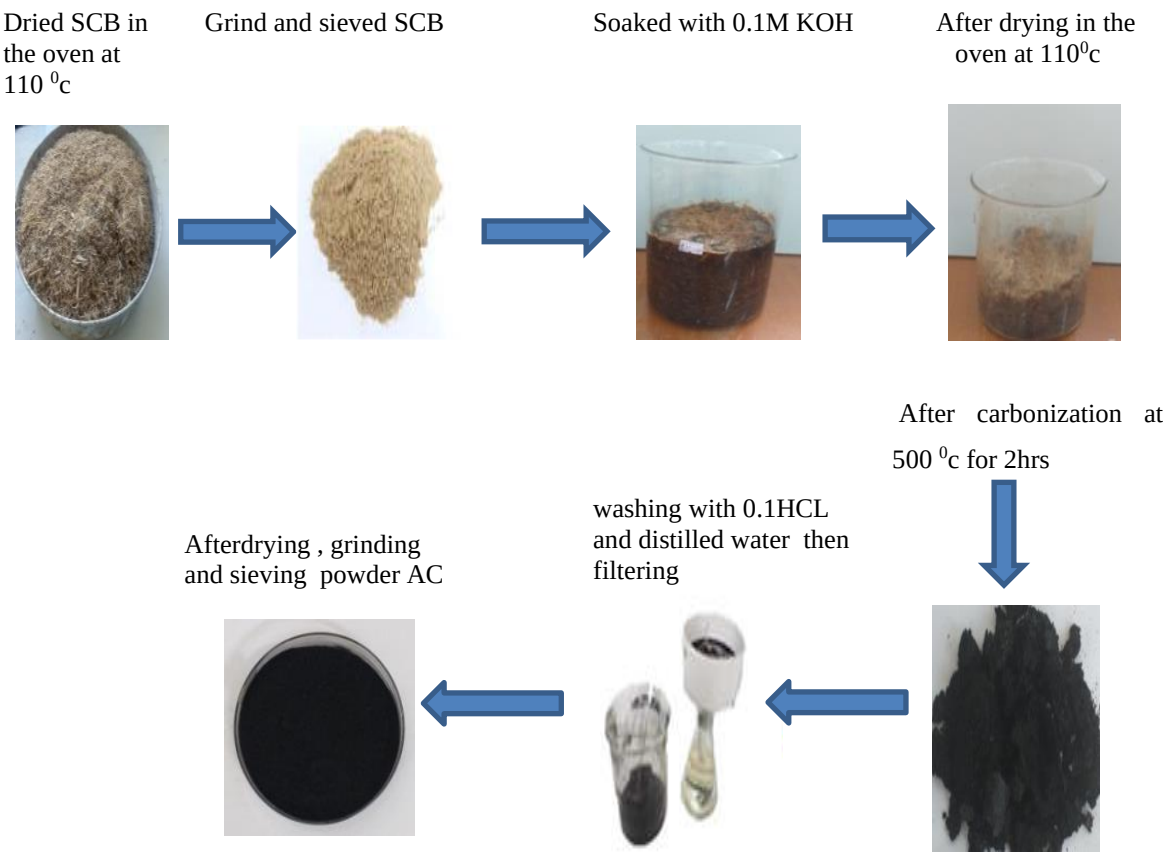


Figure 3. 1: The stage of sugar cane bagasse activated carbon preparation

3.5. Characterization of Produced sugar cane bagasse Activated Carbon

3.5.1. Proximate analysis

The prepared activated carbon sample was characterized for proximate analysis by using the American Society for Testing and Materials standard to determine the moisture content (ASTM D 2867-99), the presence of volatile matter (ASTM D 5832-98), the ash content (ASTM D 2866-94 and particle size (ASTM C136-06) for Sieve Analysis of Fine and Coarse aggregates.

3.5.1.1. Activated carbon yield

The activated carbon yield was obtained by the following equation

$$\text{Yield \%} = \frac{W1}{W0} * 100 \quad \text{…….. Equation 3.6}$$

Where: W_1 is the mass dry activated carbon and W_0 is the mass of dry bagasse

3.5.1.2. Moisture Content Determination

A gram of the dried activated carbon was placed in washed, dried, and weighed crucible, then put in the oven at 105°C for 3hrs. Then the sample was cooled and reweighed again. This test was repeated until constant moisture content was obtained. The difference between the initial and final mass of the carbon represents the water content in the sample.

$$\text{Moisture content} = \frac{W1 - W2}{W1} * 100 \quad \text{……. Equation 3.7}$$

Where:

W_1 = Initial weight of the sample before drying (g)

W_2 = Final weight of sample after drying (g)

3.5.1.3. Ash Content Determination

0.1g of activated carbon was placed into weighed ceramic crucibles and the samples were heated in an electrical furnace at 650 ^{0}C for 3hours. Then the crucibles were cooled to ambient temperature in a desiccator and weighed. The percent of ash was evaluated using Equation 3.8

$$\text{Ash\%} = \frac{W_3 - W_1}{W_2 - W_1} * 100 \quad \text{…….. Equation 3.8}$$

Where w_3= the weight of crucible containing ash,

w_2= the weight of crucible containing heated sample

w_1= the weight of empty crucible.

3.5.1.4. Volatile content determination

A gram of dried activated carbon was weighed into a closed crucible of a known weight and heated at 950 ^{0}c for 7 minutes in a muffle furnace. The difference in weight between the weight of samples before and after heating was used to determine the amount of volatile matter in the sample. The percentage volatile matter content was determined from the equation 3.9

$$\text{Volatile content (\%)} = \frac{\text{Loss in weight on drying}}{\text{Initial weight of sample}} * 100 \quad \text{…… …. Equation 3.9}$$

3.5.1.5. Fixed carbon content determination

The fixed carbon content was determined by subtracting the sum of the percentage composition of moisture content, volatile matter content, and ash content from 100.

3.5.1.6. Particle Size

For the particle size determination, lots of samples were weighed and placed on top of a set of sieves. The sieves were shaken electrically for ten minutes, after which the weight percent of the active carbon taken on the sieves and bottom pan was determined.

3.5.1.7. Scanning Electron Microscopy

The morphological structure and pore size of sugar cane bagasse and activated carbon was analyzed through a scanning electron microscope.

3.5.2. Chemical surface characterization

3.5.2.1. Fourier Transform Infra-Red (FT-IR) Analysis

Fourier transform infrared spectroscopy (FTIR) was used to study the functional groups of sugar cane and commercial activated carbon. An FT-IR spectrophotometer measured using potassium bromide (KBr) pellet for wavelength ranged from 4000 to 400 cm−1.

3.6. Formulations of shoe polishes

Shoe polish was prepared from selected ingredients and formulation was performed using a procedure made by (Buke 2000, Betrework 2017). In the formulation of shoe polish, the beeswax was melted at 80 ^{0}c then stearic acid was added into the molten wax and melted together and stirred using a fluid mixer. Thereafter, castor oil was introduced into the mixture. After which the molten mass is added to warm solvent (60^{0}c) before being hardened. Then some pigment was added by keeping stirring to ensure a proper mix for 15 min with 1500 rpm of a fluid mixer. Finally, the mixture allowed to cool and poured into a container for storage.

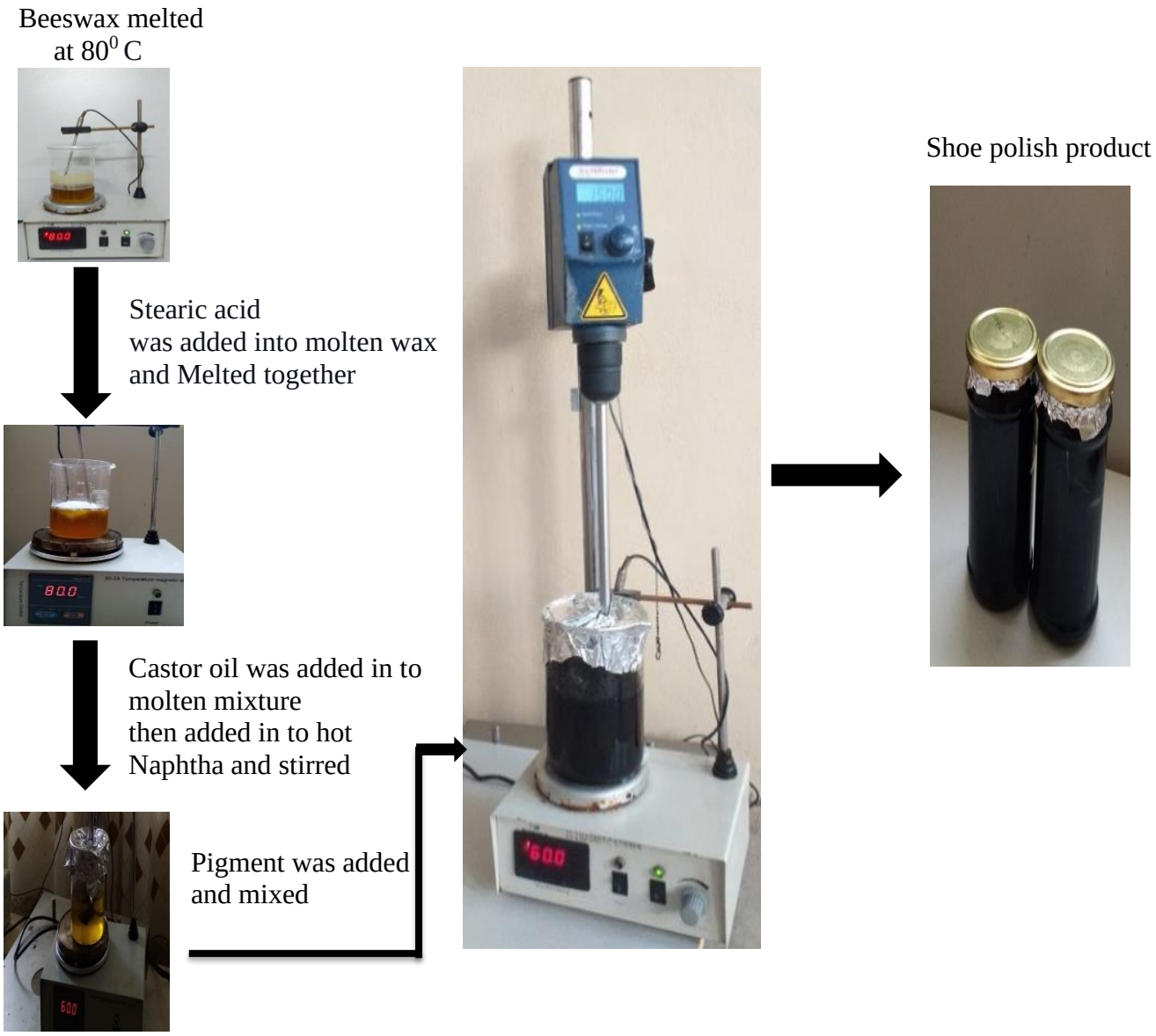


Figure 3.2 : Shoe polishes ingredient heating and blending

3.7. Experimental design

The statistical analysis was executed using Design-Expert version 11.1 software. Design Expert was used to check the effects of various variables and their relationship on the end-product. It is an effective method for optimizing the ultimate properties of the coating.

Mixture D- optimal special cubic model was used for this study to see the influence of the proportion of a constituent in the mixture with components having different ranges varying all at the same time.

The mass of wax, oil, solvent, and pigment was selected as variable factors and put in software based on the primary standard formulation and ranges based on different articles. In the formulation, the thickening agent (stearic acid) was kept constant due to the mass variation of it directly affect the response.

This formulation has four factors and two levels. The output of the software revealed twenty-four experimental runs to be carried out. The variables and their range (high and low levels) are listed in the table below.

Table 3.1Mixture components for two levels

Ingredients	**Range % by weight**	
	Low	**High**
Beeswax	5.0	15
Castor oil	25	45
Naphtha	30	45
Activated carbon	5.0	10
Stearic acid	7.0	7.0

Table 3. 2 Runs order and formulations of shoe polish proposed by mixture design expert

	Component 1	Component 2	Component 3	Component 4
Run	**A: Beeswax**	**B: Castor oil**	**C: Naphtha**	**D: Activated carbon**
	%	%	%	%
1	15.0	38.0	30.0	10.0
2	11.5	37.8	38.7	5.0
3	5.0	38.0	45.0	5.0
4	14.4	25.0	43.6	10.0
5	8.2	36.8	38.0	10.0
6	5.0	45.0	38.0	5.0
7	13.0	45.0	30.0	5.0
8	10.0	41.8	31.2	10.0
9	10.1	30.0	45.0	7.9
10	14.4	25.0	43.6	10.0
11	5.0	33.0	45.0	10.0
12	5.0	45.0	38.0	5.0
13	10.8	31.9	40.3	10.0
14	15	37.1	34.5	6.4
15	15	31.4	36.6	10.0
16	15	28.0	45.0	5.0
17	5.0	45.0	33.0	10.0
18	5.0	38.0	45.0	5.0
19	14.0	33.0	41.0	5.0
20	13.0	45.0	30.0	5.0
21	5.0	38.1	41.9	8.0
22	5.0	33	45	10.0
23	10.0	42.9	35.1	5.0
24	5.0	41.4	37.2	9.4

3.8. Application on Shoe Leather

Tanned and finished shoe leather (black) was obtained from KOLBA Tannery PVT.LTD.CO, Modjo. The prepared and commercial (Kiwi) shoe polish was separately applied on finished black shoe leather for each test. Equal size of the shoe leather sample was prepared and an equal weight of two grams of the prepared and the commercial shoe polishes were applied on it.

3.9. Characterization of produced shoe polish and its comparison with Commercial shoe polish product

Newly formulated polishes were compared with standard commercial polish by its density, viscosity, and melting point and other physical tests.

3.9.1. Determination of Viscosity

The viscosity of shoe polishes was determined by Using VK-2000 MYR KREBS Viscometer. The sample was measured to have 250ml and the spindle was adjusted on 200rpm. Based on the internal resistance to rotation provided by the shear stress of the shoe polish, the shoe polish dynamic viscosity was measured and displayed in the digital reading in centipoise.

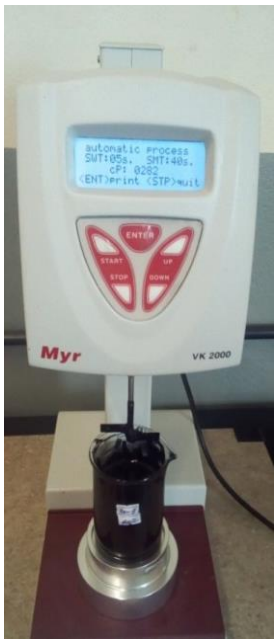


Figure3. 3: Viscosity determination

3.9.2. Determination of density

Based on the method on ASTM 1475, the specific gravity or density for coating, pastes, or similar liquids the density of shoe polish was determined using specific gravity cups.

During the determination of density of shoe polish, the density cup was weighed when it was empty using electronic balance and weighed by filling with the sample of the shoe polish, and after that the lid was placed on the cup. The cup was weighed after it was filled with the sample then the difference between the two weight was divided by the volume of the cup to determine the specific gravity of the sample.

3.9.3. Determination of melting point

A quantity of shoe polish was put in a dish and placed on the heat source and then the melting point of the shoe polish was measured and recorded using a digital thermometer.

3.9.4. Physical Testing of the Polished Leathers

The polished leather samples and the row leather samples were tested for some physical parameters as follows to check the properties of the shoe polish:

3.9.4.1. Luster/Gloss:

Based on ISO 2813, 60° geometry the polished samples were examined for their gloss/luster by comparing them with one another.

3.9.4.2. Fading Resistance:

Based on colorfastness of leather to light (IUF 401) or ISO105-B01 with the grey-scales, color change to daylight (sun light) was checked to test fade resistance. To test fading resistance, the polished leather samples were exposed to the sun for 74hrs under glass, and finally, a change in shade was assessed by using imagej software.

3.9.4.3. Rub Resistance:

Based on ISO 11640 (Leather – Tests for colorfastness – Color fastness to cycles of to-and-fro rubbing), polished leather samples were rubbed with white and clean cotton material for about 40 times under constant pressure with a given number of forwarding and backward motions. Finally, changes in hue and level of staining were examined by using imagej software.

3.9.4.4. Dust Absorption Resistance

The polished leather samples were exposed to an open environment in which dust can get easy access to them for 24hrs. The level of dust adsorption was examined by assessing the quantity and size of dust particles on exposed polished leather.

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Beeswax characterization

The Physico-chemical quality analysis, including melting point, refractive index, ash content, total volatile matter, acid value, ester values, saponification value, paraffin and other waxes, fats, and fatty acids of the examined sample result is presented here below.

4.1.1. Melting point (°C)

The melting point of the beeswax sample was determined by measuring the temperature at which the first drop of liquid wax appears during heating. It is one of the most significant quality parameters used to detect the adulteration of beeswax. The melting points of beeswax gradually decrease with increased proportion of adulteration with animal tallow (Adgaba 2007). The melting point of examined samples obtained with an average value of 61.43°C. All the tested trials showed the acceptable limits of the Ethiopian national quality standard.

4.1.2. Specific Gravity at 20 ^{0}C

The specific gravity of beeswax is the ratio of the weight in air of a unit volume of beeswax at a specified temperature to the weight in air of an equal volume of rectified spirit at the specified temperature. It indicates changes in the material (beeswax) or possible contamination. The specific gravity of the sample was obtained with an average value of 0.9711. The obtained result shows the specific gravity of beeswax falls within the acceptable limit of national standard.

4.1.3. Refractive index, at 75^{0}C

Refractive index is one of the most important quality parameters used to detect the contamination of beeswax. The refractive index of a substance is the ratio of light in the air to that of a sample. The average refractive index of beeswax sample was found to be 1.4403 at 75 ^{0}c. The present result well met the limit of national quality standard. The result indicates it was free of contamination.

4.1.4. Volatile matter, % by mass, max

The volatile matter of the sample is the weight loss percent of beeswax when heated in a reducing atmosphere (out of air contact). The amount of volatile matter lost occurs during rendering or further wax processing when excessive heating is used. This effect changes the structure of wax and alters the beneficial characteristics of many of its minor compounds, not only the volatile compounds. The maximum limit for an acceptable total volatile matter of beeswax in the Ethiopian Standard is 0.75. The volatile matter for beeswax in the current study is found to be with the value of 0.69. The current result is within the national requirement.

4.1.5. Ash content% by mass, max

The ash represents a mineral content of the sample remaining in the residual after ignition. The maximum limit for acceptable ash content of beeswax in the Ethiopian Standard is 0.2%. The ash content of the beeswax sample with an average value of 0.123 was obtained. The present result shows that the beeswax collected has low ash content compared to the standard expected.

4.1.6. Acid value max, (mgKOH/g)

The acid value is the amount of potassium hydroxide (KOH) milligrams required to neutralize the free acidity present in one gram of beeswax. It is a relative measure of rancidity as free acidity is normally formed during the decomposition of beeswax glycerides. It is also determined by direct titration of the beeswax in an alcoholic medium against the standard potassium hydroxide solution. The acid value of the examined samples had an average value of 22.44 and test results were within the range of national requirements of 17-24.

4.1.7. Saponification Value min, (mgKOH/g)

The saponification value (number) is the number of milligrams of potassium hydroxide required to hydrolyze 1g of the sample. It is a measure of saponifiable matter present. The testing of saponification value indicates the number of acids and ester groups found in beeswax. The saponification value of the beeswax sample was obtained with an average value of 96.31. This result well met the national standard range.

4.1.8. Ester value

Long- time heating of the wax or higher temperatures leads to degradation and loss of esters. These changes also influence the physical characteristics of the beeswax. The ester value is equal to subtracting the acid value from the saponification value. The results obtained had an average value of 73.87. The obtained result shows it falls within the acceptable limit of national standards.

4.1.9. Fats and fatty acids

In this study beeswax sample boiled with 10% NaOH and acidified with 4N HCl dilute hydrochloric acid, the result shows a clear solution and tested sample was within the standard of national requirements.

4.1.10. Paraffin and other waxes

The paraffin and other waxes indicate the contamination or adulteration of natural beeswax with other waxes sources. According to the test result for paraffin and other waxes of the examined sample have passed the test that the liquid becomes cloudy at a temperature lower than 61^0C. If it were adulterated with other waxes the solution would have turned clear only at a higher temperature.

Finally, all beeswax analysis result showed that the mean values of compositional content of the sample fall in the range of national standards. According to various studies recognized the quality status of beeswax produced in a different area of the country is found to be within the acceptable range of national and international standards in its most parameters (Bekele Tesfaye 2016, Addisu, Begna et al. 2017, Tesfu, Asaminew et al. 2020). Therefore, it is necessary to make use of high-quality beeswax resources out of waste. This research work tends to use high-quality waste beeswax as approval by converting them to other useful product.

Table 4. 1 Comparison of Physico-chemical quality characteristics of beeswax sample with national standards

S/N	Characteristics (specification)	Current study result (average)	Ethiopian standard (ET1203/2005)
1	Melting point, 0_c	61.43	61-66
2	Specific gravity, at 20 ^{0}c	0.9711	0.9550-0.9800
3	Refractive index	1.4403	1.4400-1.4450
4	Ash % by mass, max	0.123	0.2
5	Total volatile matter,%max	0.69	0.75
6	Acid value, max	22.44	17-24
7	Saponification value, min	96.31	85-105
8	Ester value	73.87	70-80
9	Fat and fatty acids	Passed	To pass test
10	Paraffin and other waxes	Passed	To pass test

4.2. Characterization of Produced sugar cane bagasse Activated Carbon

4.2.1.1 Proximate analysis of activated carbon

Carbonization is a process that involves the thermal decomposition of carbonaceous material to eliminate non-carbon species. Thus, after carbonization, the char will contain more than 90% of carbon content. Carbonization temperature and carbonization time play a significant role in the yield of activated carbon. Several works on, carbonization of sugar cane bagasse were conducted with the activated agent of potassium hydroxide at 500^{0}c temperatures. ((Dwiyaniti, Barruna et al. 2020), revealed the carbonization of sugar cane bagasse activation was at a temperature of 500^{0}c. According to the study, this temperature is chosen based on the degradation of the chemical composition of sugar cane bagasse consisting of hemicellulose, cellulose, and lignin. Hemicellulose is degraded by heat at temperatures of 220-315^{0}C, cellulose is degraded at temperatures of 315-400^{0}C, and lignin is slowly degraded with a temperature range of 160-900 ^{0}C.

According to the study done by (Joan Na Lee 2014) carbonization of sugar cane bagasse was carried out from 500 -700 ^{0}c and holding it for 2hrs. According to the authors result, a high surface area of activated carbon was produced at 500^{0}c for 2hrs, when compared to other carbonization temperatures. Accordingly, this thesis used the above parameters for carbonization temperature and time, and the required black pigment activated carbon was obtained.

Many researchers indicated activated carbon yield decreased with an increase in the carbonization temperature and time due to the loss of volatile matter and the higher the temperature the more the carbon turns to ash. In this study, the carbonization temperature of 500 °C for two hours produces activated carbon with a % yield of 29.4 Similarly, this research obtained a yield in the range done by researchers namely (Kalderis, Bethanis et al. 2008), (Dwiyaniti, Barruna et al. 2020) having a % yield ranging between 20-30 of the carbonization process of sugar cane bagasse.

Activated carbon is usually priced on a moisture-free basis. Some activated carbon when stored under humid conditions will absorb a considerable amount of moisture over some time and dilutes the carbon. In most countries, the standard moisture content of activated carbon allowed is not more than 15%. The obtained result of moisture content of the sugar cane bagasse activated carbon of this thesis is shown in the pie chart (Figure 4. 1**)** below which is 10%.

The ash content of the activated carbon is the total amount of inorganic constituents which varies from one carbon to another depending on the source of materials and activating agents added during preparation. In this study, the ash content of activated carbon from sugarcane bagasse was 20 %, which is still higher than some countries activated carbon standards in the range between 2 and 10%. A publication by (Zulkania, Hanum et al. 2018) described activated carbon-based on soft by-product materials such as sugarcane bagasse, rice straw, and rice husk have higher ash content due to their high mineral content. The high ash content of activated carbon is undesirable since it reduces the mechanical strength of carbon.

The particle size value obtained in this work by sieve analysis of the sample was < 230 meshes (< 63μm) at 500^{O}C activation temperatures. Particle size influences the color strength of a pigment. Higher color strength is obtained with smaller particles, and the small size allows better polishing and smoother surfaces. Color strength is a colored pigment which maintains its color characteristic when mixed with another shoe polish components. Generally, the minimal size particle becomes the maximal blackness of activated carbon.

The Proximate characteristics of the powdered activated carbon produced in this work from sugar cane bagasse are presented in pie chart (Figure 4. 2**)** below

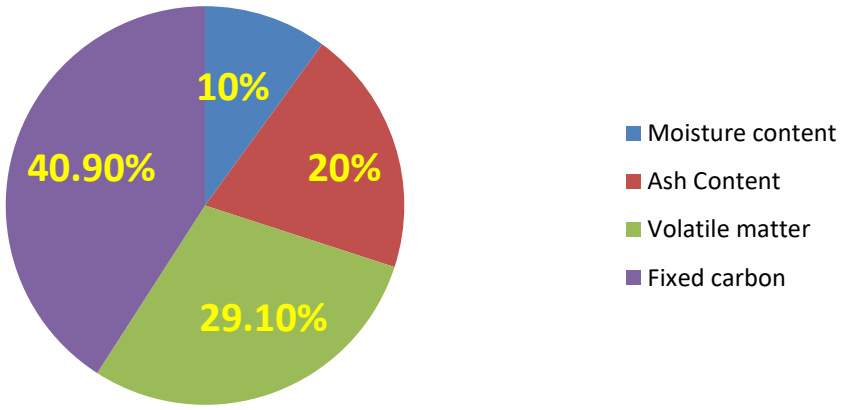


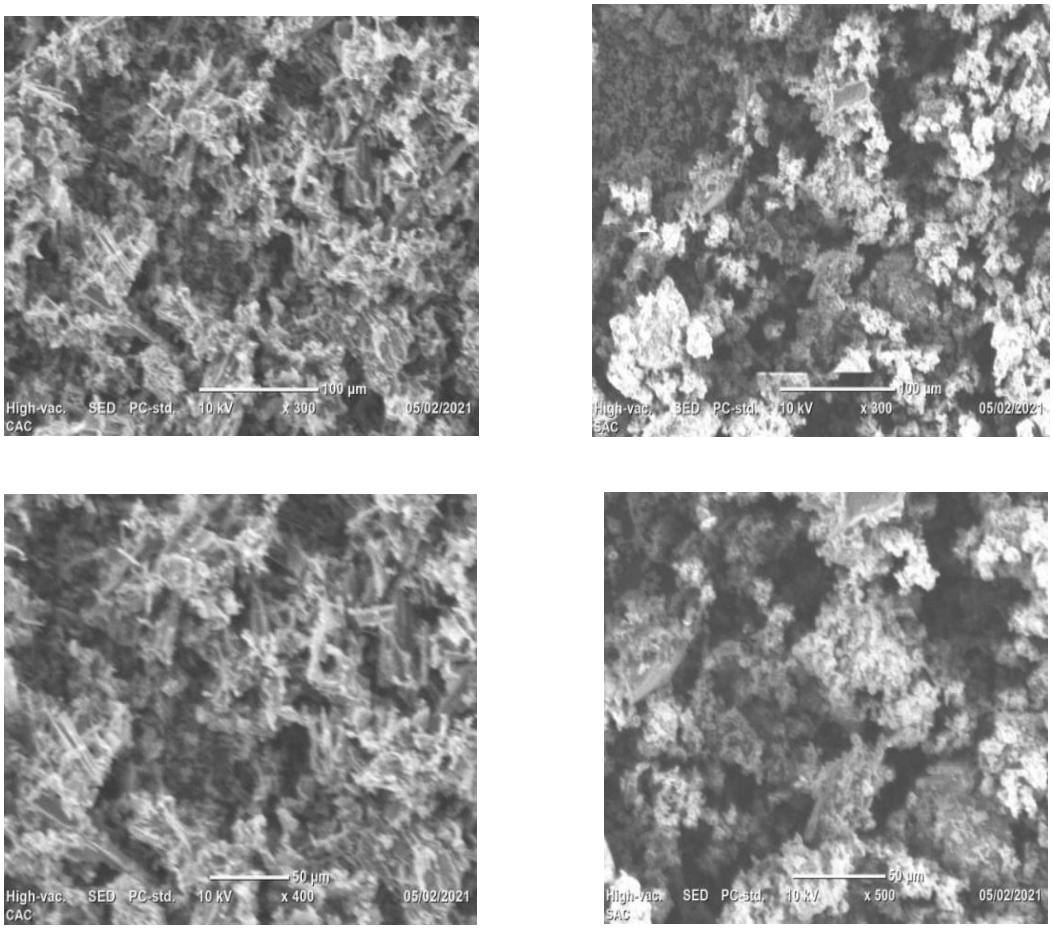
Figure 4. 3: A pie chart showing proximate analysis result of sugar cane bagasse activated carbon

4.2.1.2 Scanning Electron Microscopy

The morphology structure of sugar cane bagasse activated carbon was observed using the scanning electron microscope. The SEM micrographs showed the activated carbon particle cavities, pores, and surfaces on the carbon samples.

Figure-4.2: refer to SEM images of commercial activated carbon and activated carbon produced from sugar cane bagasse at different magnification. The SEM results have revealed that the sugarcane bagasse-based activated carbon prepared with potassium hydroxide as an activating agent had less visible pores character and have a very fine particulate aggregates structure.

While the morphology of CAC showed a rough and uneven surface having irregular cavities with pores of different sizes.



A, Commercial activated carbon B, Sugar cane bagasse activated carbon

Figure4. 4: SEM images of SCB and commercial activated carbon at different magnification

4.2.2. Chemical surface characterization

Activating sugar cane bagasse with potassium hydroxide transformed the structure and surface chemistry of the resulting activated carbon. This study includes a comparison of chemical properties of sugar cane bagasse activated carbon with the commercial one.

4.2.2.1. Fourier Transform Infra-Red (FT-IR) Analysis

Figure- 4.3: shows the elemental analyses of commercial activated carbon and SCB activated carbon produced at 500^0c carbonization temperatures. Results indicate the presence of many elements with a predominance of carbon in the sample.

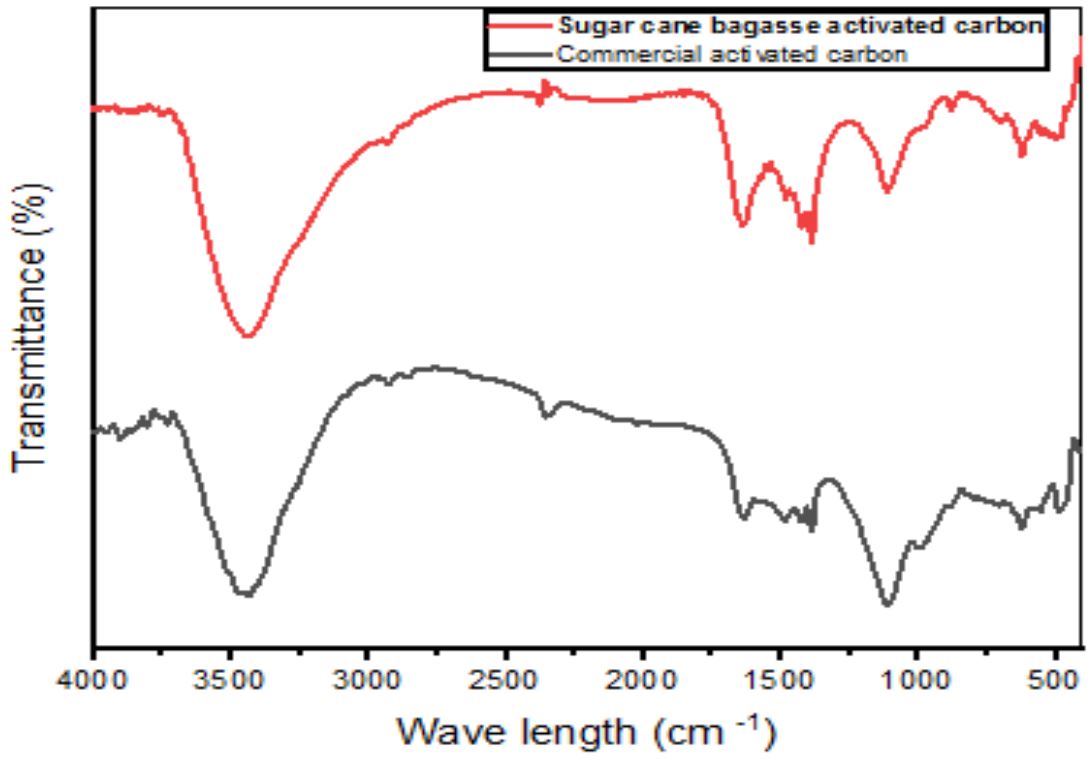


Figure4. 5: FT-IR spectra of the SCB activated carbons and commercial activated carbon

The FTIR spectroscopy provides information on the functional group of SCB AC at 500^0c and the commercial activated carbon. In Figure- 4.3 shows, SCB activated carbon and commercial activated carbon displaying the broadband values at 3441 cm^{-1} and 3434 cm^{-1}, which reveals the presence of (O–H) vibrations in hydroxyl groups due to the absorption of a water molecule (Taha, Abdelhafez et al. 2016). In Sugar cane bagasse activated carbon, the activation process with KOH increases the surface area. The increase in surface area enables the activated carbon to easily absorb moisture from the environment.

The two peaks appear in SCB activated carbon at 2373 and 2342 cm^{-1} in FTIR result indicate the presence of (C–O) vibrations for carbon monoxide or carbon dioxide derivative (Khalil, Jawaid et al. 2013). In sugar cane bagasse activated carbon this implies thermally broken down of cellulose and hemicellulose in the raw material. A similar band was observed at 2353 cm^{-1} in commercial activated carbon. In the region of 1632-1651 cm^{-1} assigned to C=C aromatic vibration. This band is normally found in the lignin aromatic structure of sugar cane bagasse (Taha, Abdelhafez et al. 2016). The FT-IR spectra observed at the band 1384 -1481 cm^{-1} could be C-H aliphatic adsorption bands. This indicates the presences of methyl groups in KOH SCB AC and commercial activated carbon. However, at 1384 cm^{-1} C-H aliphatic bending more intense in both activated carbons. This indicates the presence of alkane attributed to the saturated hydrocarbons. The moderate band visible at 1110 cm^{-1} corresponds to C-O, Si–O–Si stretching mode as a result of the existence of silica within the sugar cane bagasse (Bachrun, AyuRizka et al. 2016) and also it exists in the commercial activated carbon. Some narrow bands like 474-618 cm^{-1} is associated with C-H vibrations in olefin or aromatic structure and C-C stretching.

Furthermore, the FTIR spectra of commercial AC which displayed a close resemblance between the FTIR spectra of potassium hydroxide activated sugarcane bagasse. Almost similar functional groups were observed with slight wavelengths shift. Therefore, activated carbon from sugar cane bagasse has a possibility to be used instead of commercially available activated carbon in the formulation of shoe polish.

4.3. Mixture experimental design results and Optimization of shoe polish formulation

Twenty-four experimental runs were conducted by design expert software and based on viscosity as a response variable. In the formulation, viscosity is very significance parameter due to its importance in making the product easy to apply, easy to dispense, and flow property during polishing. The viscosity of prepared shoe polish and the standard polish (Kiwi) was determined at different temperatures based on (Betrework 2017). These temperatures are at 40^0c, 50^0c, and 60^0c, out of which the prepared polishes favorably were comparable to control polish at 40 ^{0}c because it was easier to control the viscosity at this temperature.

The response value of twenty- four runs, design dependent on viscosity at 40^0c are shown in table 4.2:

Table4. 2 Mixture response values for shoe polish samples

	Component 1	Component 2	Component 3	Component 4	Response 1
Run	**A: Beeswax**	**B: Castor oil**	**C: Naphtha**	**D: Activated carbon**	**Viscosity at 40 ^{0}c)**
	%	%	%	%	Poise
1	15.0	38.0	30.0	10,0	11.63
2	11.5	37.8	38.7	5.0	2.58
3	5.0	38.0	45.0	5.0	1.1
4	14.4	25.0	43.6	10	2.82
5	8.2	36.8	38.0	10	1.82
6	5.0	45.0	38.0	5.0	1.4
7	13.0	45.0	30.0	5.0	3.61
8	10.0	41.8	31.2	10	4.2
9	10.1	30.0	45.0	7.9	1.54
10	14.4	25.0	43.6	10.0	2.82
11	5.0	33.0	45.0	10.0	1.2
12	5.0	45.0	38.0	5.0	1.4
13	10.8	31.9	40.3	10.0	2.38
14	15.0	37.1	34.5	6.4	2.82
15	15.0	31.4	36.6	10.0	11.18
16	15.0	28.0	45.0	5.0	2.87
17	5.0	45.0	33.0	10.0	1.5
18	5.0	38.0	45.0	5.0	1.1
19	14.0	33.0	41.0	5.0	2.18
20	13.0	45.0	30.0	5.0	3.61
21	5.0	38.1	41.9	8.0	1.35
22	5.0	33.0	45.0	10.0	1.2
23	10.0	42.9	35.1	5.0	3.81
24	5.0	41.4	37.2	9.4	1.6

As shown in the above table the response (viscosity) of all experimental runs is between 1.1 to 11.63 poise and the viscosity of the control polish (Kiwi) measured was obtained 2.68 poise.

Analysis of variance (ANOVA) was performed to determine the influence of each component on the response. Each components of the shoe polish ingredient has an impact on viscosity. An analysis of variance (ANOVA) is an important technique to find out whether the experimental result is significant or not. P-value and F-value were used to evaluate the significance of the DOE proposed model and the interaction of each factor. The model F-value of 89.43 implies the model is significant. P-values less than 0.0500 indicate model terms are significant. From the ANOVA result, it can be confirmed that the contribution of the linear factor is significant with P-value less than 0.0500. Most importantly, in this case, B, C, AD, BC, CD, ABC, ABD, ACD, BCD are significant model terms that imply castor oil, naphtha, and the binary interaction between beeswax-activated carbon, castor oil-naphtha, naphtha-activated carbon respectively had a significant effect on response. Additionally, the p-value of the three interactions between bees wax-castor oil-naphtha, beeswax–castor oil-activated carbon, beeswax-naphtha-activated carbon, castor oil-naphtha-activated carbon had a significant effect on the viscosity response. The term AB, AC, and BD interaction are not significant model terms due to their values are greater than 0.500. ANOVA for a special cubic model which implies the interaction between beeswax- castor oil, beeswax–naphtha, and castor oil- activated carbon respectively do not affect the viscosity response.

The result of model fitting and analysis of variance (ANOVA) are presented in the Table: 4.3.

Response 1: Viscosity

Table 4. 3: ANOVA results for viscosity response for beeswax-based shoe polish formulations

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	173.36	13	13.34	89.43	< 0.0001	Significant
[(1)]Linear Mixture	95.18	3	31.73	212.77	< 0.0001	
AB	0.0052	1	0.0052	0.0351	0.8551	
AC	0.1975	1	0.1975	1.32	0.2766	
AD	8.7	1	8.7	58.37	< 0.0001	
BC	5.71	1	5.71	38.29	0.0001	
BD	0.5093	1	0.5093	3.42	0.0943	
CD	1.39	1	1.39	9.35	0.0121	
ABC	3.82	1	3.82	25.6	0.0005	
ABD	10.72	1	10.72	71.87	< 0.0001	
ACD	13.43	1	13.43	90.03	< 0.0001	
BCD	9.67	1	9.67	64.82	< 0.0001	
Residual	1.49	10	0.1491			
Lack of Fit	1.49	5	0.2982			
Pure Error	0.000	5	0			
Cor Total	174.85	23				

Different response surface plots were generated by the software. Each plot shows the effect of each mixture component on the response and the effect of the different formulation of shoe polish on the viscosity. Figure: 4.4 shown a trace graphs which express how viscosity changes as the function of mixture components.

As seen in the trace graph below, among the main variables, the amount of beeswax affects a response (viscosity). More proportion of beeswax in the shoe polish formulation, results in viscosity value increases since beeswax is hard natural wax but as the amount of solvent was increased in the formulation the viscosity value decreases.

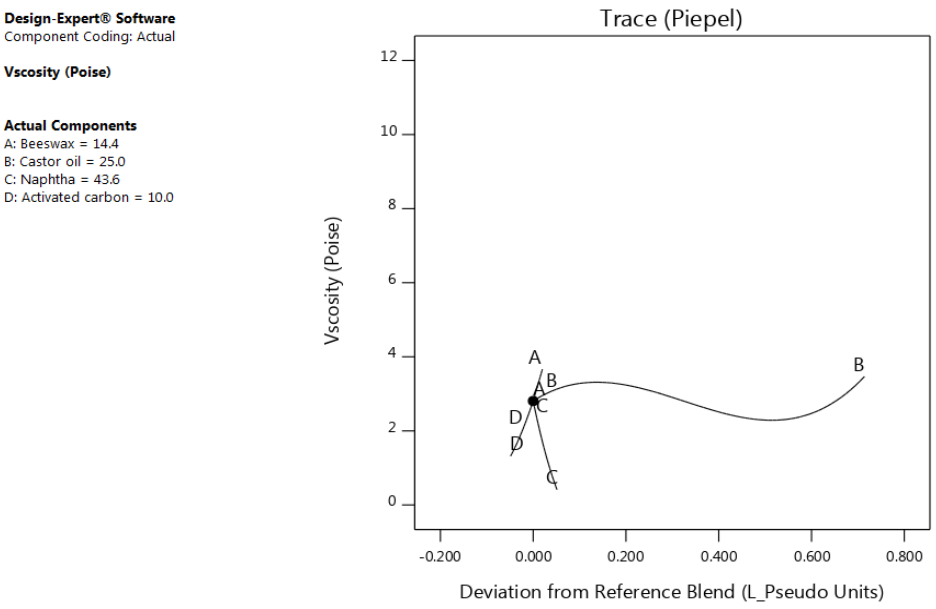
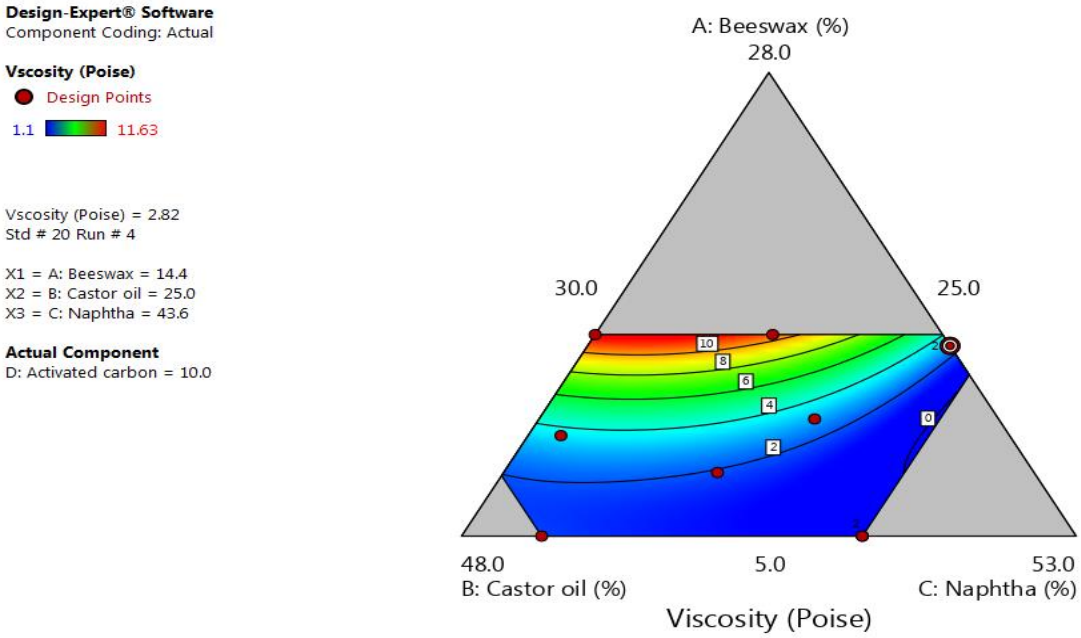
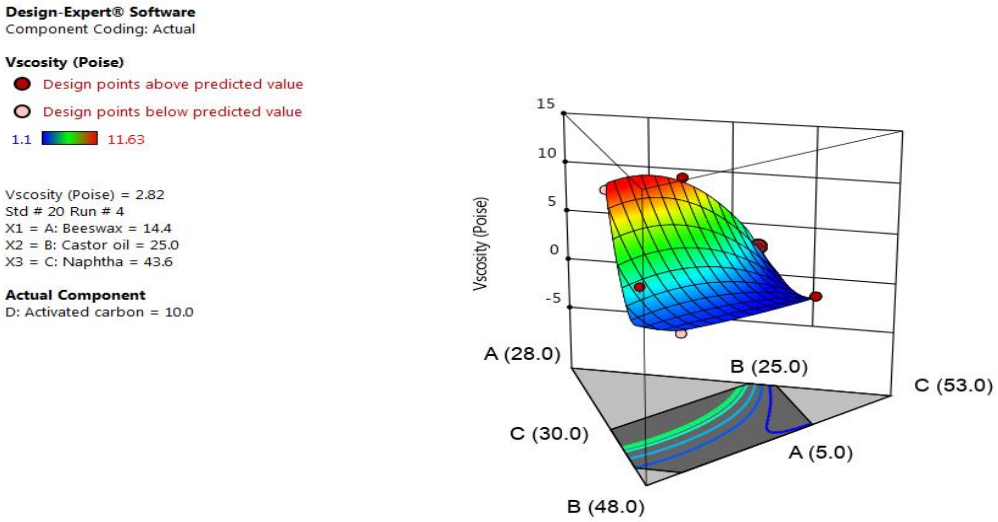


Figure 4. 6: Trace graph for the selected run viscosity as a function of different level of shoe polish ingredients

The effect of the mixture component on the response is also shown in the contour plot and the three-dimension surface of the response model. The contour plots show how the response changes as a function of the three mixture components at the constant level of the fourth component. In each plot, the color change shows from blue area to red area the viscosity changes from 1.1- 11.63 poise by variation in A, B, and C components (at a constant level of the fourth component D).



a. Viscosity contour plots



b. Viscosity of 3D response surface

Figure 4. 7: Viscosity of contour plots and 3D response surface

Optimization of shoe polish formulation from all experimental runs was measured on the range from 2.68 ±0.5 poise which is based on control shoe polish viscosity. In figure 4.6 the yellow zone shows the amounts of the materials that should be used for the preparation of optimized beeswax-based shoe polish samples. The optimum viscosity products for a given runs obtained by Mixture design response surface method are run 2, run 4, run13, run14, run16, and run19.

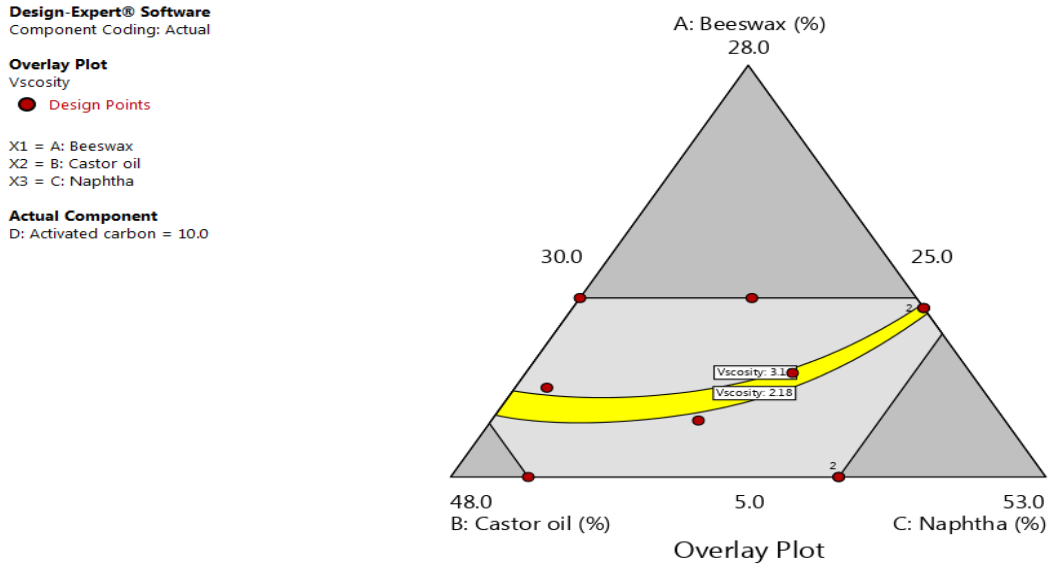


Figure 4. 8: Shoe polishes formulations by DOE software in optimized zone

The response equation of viscosity and the amount of the components can be modeled as equation:

Viscosity = - 14.71*A+ 11.82*B + 21.70*C +16.67*D – 2.80*AB – 21.84*AC + 541.55*AD -64.53*BC -71.65*BD -132.54*CD + 151.28*ABC – 649.72* ABD-798.98 *ACD+ 341.12*BC … Equation 4. 1

Where A, B, C and D represented the % by weight effect of beeswax, castor oil, naphtha and activated carbon, respectively on the response.

The special cubic model for viscosity with the coefficients' from data fitting is presented in the equation 4.1. Among the main factors the % by weight of beeswax-activated carbon interaction has the largest effect on viscosity.

Beeswax-naphtha-activated carbon interactions have antagonistic effect which means it decreases the viscosity of the prepared shoe polish due to the presence of naphtha.

The other optimization criteria were used to select the best four shoe polishes formulation out of the six formulations obtained from the above optimization formulation based on raw material cost (not production cost). The purchased cost of raw material in birr as shown in the table 4.4 below:

Table 4. 4: Cost of ingredients

Cost Analysis			
Ingredients	**UOM**	**Amount**	**Cost(Birr)**
Beeswax	G	1000g	120
Castor oil	Ml	500ml	800
Naphtha	Ml	1000ml	20
Activated carbon	G	500g	450
Stearic acid	G	500g	750

In Table 4.5 below each ingredients of in each shoe polish formulation cost and a total ingredient cost in 100 gram weight of shoe polish product in Table 4.6 is presented respectively.

Table 4. 5: Ingredient cost in the product

Ingredients	**Run-2**	**Run-4**	**Run 13**	**Run 14**	**Run 16**	**Run 19**
Beeswax	1.38	1.728	1.296	1.8	1.8	1.68
Castor oil	60.48	40	51.04	59.36	44.8	52.8
Naphtha	0.774	0.872	0.806	0.69	0.9	0.82
Activated carbon	4.5	9	9	5.76	4.5	4.5
Stearic acid	10.5	10.5	10.5	10.5	10.5	10.5

Table 4. 6 : cost of 100-gram product

Total cost (in birr)	Run-2	Run-4	Run 13	Run 14	Run 16	Run 19
for100 gram product	77.638	62.1	72.642	78.11	62.5	70.3

Finally, out of the six optimized shoe polishes selected from design expert the four formulations are selected. The selection was made from two nearly raw materials bases on cost the lowest cost is selected out of them. Then, one a raw material with the larges cost was selected. This method of selection enables to distinguish the effect of cost of raw materials on the product. These are Run-2, Run-4, Run-14 and Run19. These four runs or prepared shoe polish was labeled samples A, B, C, D and the control polish labeled E.

Table 4. 7 : Shoe polishes formulation

Ingredients (%)	Sample A	Sample B	Sample C	Sample D
Beeswax	11.5	14.4	15	14
Castor oil	37.8	25	37.1	33
Naphtha	38.7	43.6	34.5	41
Activated carbon	5	10	6.4	5
Stearic acid	7	7	7	7

4.3. Physical Properties of Shoe Polish

4.3.1. Melting Point of shoe polish

Four different formulations of polishes were prepared and labeled Samples as A, B, C and D while sample E is the control sample which is Kiwi. In analysis, sample C had the highest melting point followed by D, A and then B. The melting point of shoe polish sample B is comparable with that of samples E (control polishes) which is Kiwi. Sample C has the highest melting point since it contains more wax and lower solvent than the others polish.

Table 4. 8: Melting point of shoe polish

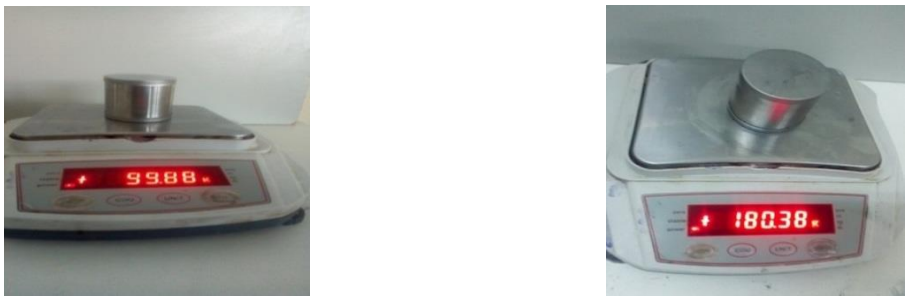
Formulated and control shoe polish	**Melting point(0c)**
A	34.2
B	32.8
C	35.4
D	33.5
E	32

4.3.2. Density of Shoe Polish

The effect of temperature on density is highly significant and varies with the type of product. Because of this, the density cup (Figure 4.9:a) and test sample were maintained at the standard temperature of (23+ 0.5) in the water bath and allowed approximately for 30 min until temperature equilibrium was reached. Table 4.9 shows the density of polishes produced and control standard polish. Density of sample D polish was the highest followed by sample A, C and B. The density of shoe polish sample B was comparable with that of samples E (control polishes) than sample A, C and D.

Table 4.9: Density of shoe polish**.**

S/N	Formulated and control Polish	Density (g/ml)
1	A	0.89
2	B	0.83
3	C	0.85
4	D	0.92
5	E	0.80



a, weight of empty cup b, weight of cup + sample

Figure 4. 10: Density of shoe polishes measurement by using 100ml density cup

4.3.3. Viscosity of Polishes at Different Temperatures

The viscosity of shoe polishes formulated A, B, C, D & the control polishes E determined at different temperatures. Temperature affects the viscosity of the samples and viscosity value decreased with an increase in temperature for all samples. Table 4.10 shows that the two polishes labeled Sample B and C had the same viscosity at 40^{o}C. The viscosity of polish produced sample A compares favorably with control polish sample E at 40^{o}C and sample D at 60^{0}c.

Table 4. 10: Viscosity of polish at different temperature

Temperature (0c)	**Viscosity (poise) of formulated and control polish**				
	A	**B**	**C**	**D**	**E**
40	2.58	2.82	2.82	2.18	2.68
50	0.91	0.66	91	0.41	0.51
60	0.61	0.56	66	0.05	0.01

4.4. Performance comparison of Shoe polishes with Commercial Product

4.4.1. Physical properties of polished leather samples

4.4.1.1. Luster/Gloss:

Mostly the appearance of the surface of shoe leather can be described by its color and gloss characteristics. Gloss is an attribute that causes the surface of the shoe leather to have a shiny or lustrous appearance. It is often measured by directing a constant power light beam at an angle to the test surface and subsequently monitoring the amount of reflected light. The reflected light is dependent on the material and angle of illumination.

Gloss can be measured at three different angles of incidence 20°,60°and 85°standard geometries and have high, intermediate, and low gloss scales. The 60° geometry has been adopted for most materials by the American Society for Testing and Materials in ASTM method D523 using the

instrumental device (gloss meter). Gloss also measured by visual assessment. Visual assessment had a decreased accuracy of measurement due to its difference from person to person. Despite of using measuring gloss by gloss meter alternative instrument is used due to unavailability of gloss meter in a nearby working area.

The polished samples were examined for their gloss/ luster by comparing them with one another by using WL 362 Thermal radiation unit. The thermal radiation unit is intentional for the investigation of radiation laws using thermal and optical radiation. It has a heat source in the form of a black body radiator with a thermopile and a light source with a lux meter to measure luminance. The gloss was determined using the light source to measure the reflected illuminance with a lux meter.

As seen in the Figure 4.11 below, the specularly reflected illumination is measured by the WL-362 thermal radiation unit instrument. During the measurement, the distance between light source, lux meter, and polished leather sample adjusted to 210 mm at an angle of 60 degrees. Since the lux meter is too sensitive to any working area light, this measurement was taken in the absence of another light effect during the night. Generally for the glossier surface, more light was reflected from the surface, and the higher the specular reflection or specular gloss.

The research reveals that most prepared shoe polishes have similar specular reflections. Sample A and D have a higher specular reflection (gloss) while samples B, C, and control polish kiwi E have a similar specular reflection. Based on the result, specular reflection of the produced shoe polishes compared with the control polish, almost all the produced polish has good and similar gloss. This shows that the beeswax gives a good shining and the high surface area of activated carbon that was used as a pigment it adds the gloss of the finished product.

Table 4. 11: Quantitative value of specular reflection (specular gloss)

S/N	Formulated and control shoe polishes	Value of specular reflection (lux)
1	A	12
2	B	11
3	C	11
4	D	12
5	E	11

Figure 4. 12: Specular reflection measurement

4.4.1.2. Fading Resistance

Fading causes the pigment to lose its attraction to an object due to the influence of light. The fade resistance of dyed materials (polished leather) was determined by exposing them to daylight or artificial illumination in an accelerated fading lamp. Daylight (Sunlight) contains visible, ultraviolet, and infrared light. Ultraviolet rays are one of the causes of fading because they break the chemical bond of pigment. Other major contributor of fading includes visible light. When polished leather is exposed to light, its color becomes paler and duller.

This depends on the pigment used in coloration processes and their resistance to light, and it is a good method for measuring the performance of the pigment.

Mostly fade resistance of shoe polish is determined based on color difference (colorfastness) and measured by instrumental and visual assessment. Many researchers' works on shoe polish for this test used visual assessment, but test methods are mostly qualitative such as color fastness analysis on a gray-scale. Visual color difference assessment is not accurate due to the difficulties in the difference between small color changes either at lower or higher shades and influenced by different color sensitivities from person to person. In this study, an image-based technique was developed alternatively and employed to quantify fade resistance.

Fade resistance was used to determine the mean color intensity difference between the polished leather before exposure to sun and the polished leather after exposure to sun light by using imagej software. Each sample image was converted into 8-bit and analyzed for its pixel histogram. In histogram the color intensity has the scale from 0 to 255 gray-scale value. The graph which is close to zero is the darker and which approach to (close to) 255 is the lighter. In the graph the result is obtained in mean, standard deviation and in mode value of color intensity. The mean value is the most common comparison to get the peak of the measurement.

In this study to get fade resistance quantitatively, after the mean color intensity difference of prepared and control polishes was calculated. The mean color difference intensity is calculated by first obtaining the difference in color intensity of polished leather before exposure to sun and after exposure to sun. Nevertheless, the result of the difference of the two-color intensity gave negative, this is due to color change (fade) which is the intensity approach to 255 gray-scales and the color become lighter and the value increase.

Generally, the negative sign shows the presence of color change. Finally fade resistance of prepared shoe polishes is compared with the commercial polish. The result indicates that the higher mean color difference intensity of the shoe polishes indicates lower fade resistance.

A summary of the quantified results for the fade resistance test presented in Table 4.12 which shows the mean color intensity difference value of the prepared and the control polish at a measure of fade resistance.

Table 4. 12: Fade resistance test based on mean color intensity difference

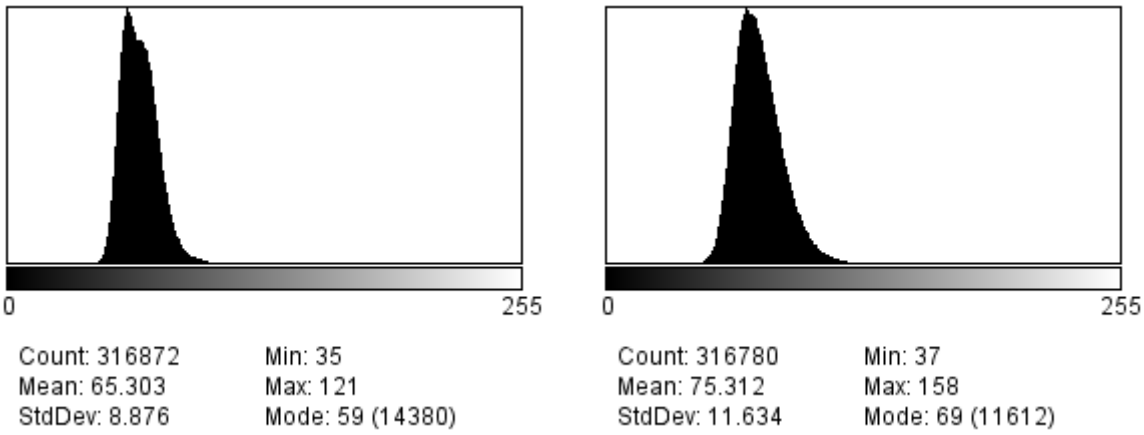
S/N	Formulated and control shoe polishes	Mean Color intensity Before exposed to light	Mean Color intensity after exposed to light)	Mean Color intensity difference
1	A	69.710	85.745	-18.035
2	B	65.303	75.312	-10.009
3	C	67.978	91.456	-23.478
4	D	79.126	91.695	-12.569
5	E	61.686	101.774	-40.088

Based on the results Sample B shoe polish had the best fade resistance compared to the control and other prepared shoe polishes. Based on the result the prepared polishes have high fade resistance than the control polish this may be due to the pigment used. Mostly, commercial polish use dye as a coloring agent, but when it is compared to pigment, a pigment has a high light resistance than dye. Sugar cane bagasse activated carbon A.C pigment shows deep black color characteristics and high tinting strength when employed in shoe polish formulation.

Polished leather sample image

sun light exposed shoe leather sample image

Figure 4. 13: Image of sample result for Fade resistance test



Histogram graph before exposed to sun Histogram graph after exposed to sun

Figure 4. 14: Image J histogram graph for fade resistance test based on color intensity

4.4.1.3. Rub Resistance

Rub resistance is the ability of prepared polish to withstand scuffing actions that tend to disfigure or change the appearance of polished leather surfaces. It is significant to determine the mechanical property of prepared shoe polishes. Rub resistance quantification was done in terms of the degree of change in color of the rubbed areas of polished leather from the original polished leather by using ImageJ software.

During the measurement, before rubbing polished leather was marked in a fixed area and an image was taken. Then the color intensity was measured.

After that, the marked area was rubbed with the white cotton cloth, and an image of it was taken. Like fade resistance calculation, the rub resistance quantified by the difference of the color intensity before and after rubbing. Before the measurement, each sample image was converted into 8-bit and analyzed for its pixel histogram. The mean gray-scale color value can then be determined by the difference in the color intensity between the treated specimen and the original polished sample. Finally, the higher the color value change of the rubbed polish leather, the lower the rub resistance.

Polished shoe leather sample

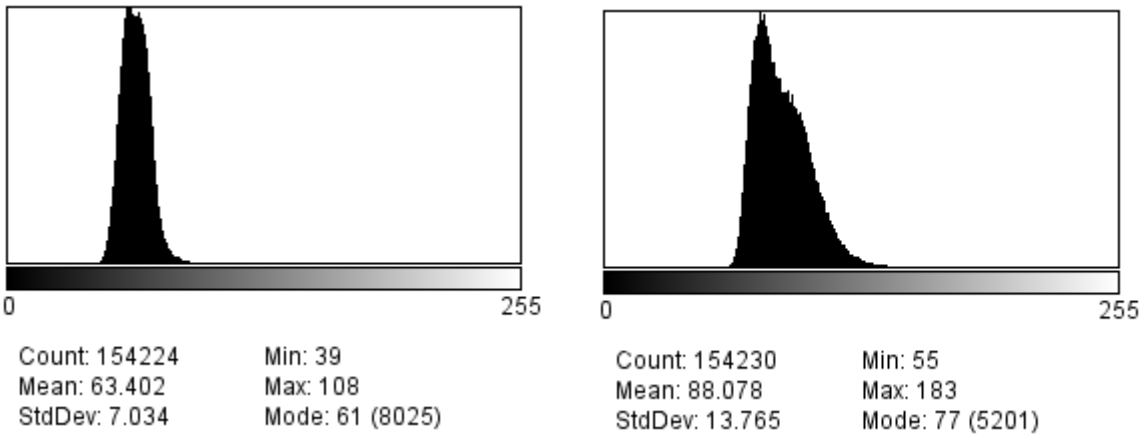
Rubbed shoe leather sample

Figure 4. 15: Image of Sample result for Rub resistance test

Table 4. 13: Rub resistance test result based on mean color intensity difference

S/N	Formulated and control shoe polishes	Before rubbing shoe polish leather mean color intensity	After rubbing shoe polish leather mean color intensity	Color difference intensity
1	A	68.611	93.772	-25.161
2	B	63.402	88.078	-24.676
3	C	65.127	95.876	-30.749
4	D	76.295	109.684	-33.39
5	E	58.016	81.845	-23.83

The results of the shoe polish which is Sample B with the best rub resistance (lowest color change intensity) is the formulation compared to other prepared polish (contains large fraction of wax and small fraction of oil), which indicates that wax has the most significant effect in improving rub resistance than oil.



Histogram graph before rub Histogram graph after rub

Figure4. 16: Image J histogram graph for rub resistance test based on color intensity

4.4.1.4. Dust Absorption Resistance

A good shoe polish applied to leather products repels dust from the film surface. Mostly wax-based polishes tend to attract little dust (Altahir 2018). In this study, image-analysis was done to determine the dust absorption resistance of prepared and commercial shoe polish using a digital microscope.

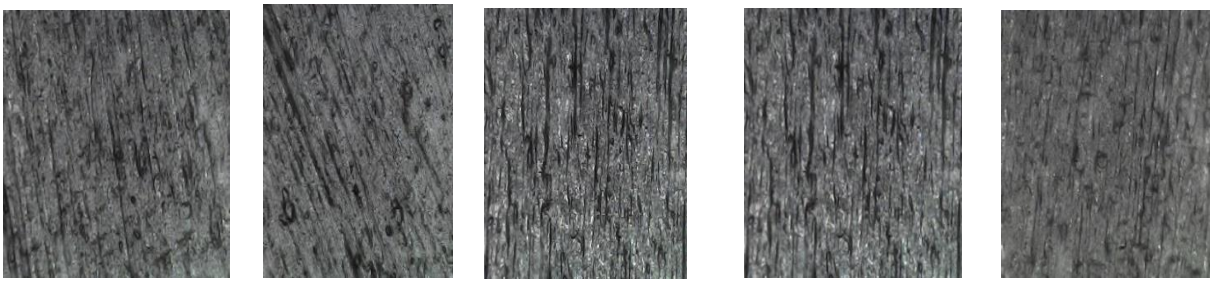
Primarily, the prepared polish and commercial one applied to black shoe leathers and image was taken by digital microscope. Then, the polished leather samples were exposed to an open environment in which dust can get easy access for 24 hours and take the image of it again. During the image analysis, the image was taken from the polished leather (before exposing dust) and marking it and in the same place to recognize how much dust absorption was observed on an image on that spot is taken. Finally, the level of dust absorption was examined by assessing the particle area and size by using ImageJ software.

Figure 4.14 shows the image of polished leather before dust absorption and after dust absorption. On the image of polished leathers after dust absorption when a tiny white particle is revealed, it can be understood that the dust particles are absorbed.

The one with the high amount of dust particle size and area has low dust absorption resistance and vice versa.

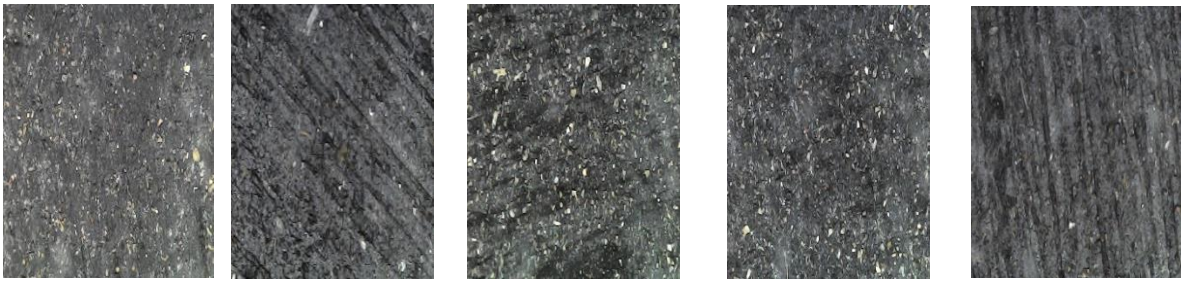
From the result shown on Table-4.14 when the prepared shoe polishes are compared to commercial polish, sample B has good resistance to dust followed by control polish than sample D,C and sample A since sample B has lower oil content than the other prepared shoe polishes.

Figure 4. 17: Image of polished leather sample taken by digital microscope



Sample A Sample B Sample C Sample D Sample E

a, Polished leather before dust absorption



Sample A Sample B Sample C Sample D Kiwi

b, Polished leather after dust absorption

Figure 4. 18: Polished leather before dust absorption and after dust absorption

The summary of the quantified results of dust particle for the dust absorption resistance test is presented in Table 4.14 below

Table 4.14: ImageJ dust particle size and area result

S/N	Formulated and control shoe polish	Count	Total area	Average size	% Area
1	A	847	32130	37.934	4.074
2	B	156	3178	20.372	0.364
3	C	934	35390	37.891	4.051
4	D	797	27847	34.94	3.412
5	E	137	2669	19.482	0.317

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The beeswax analysis result showed that the mean values of compositional content of the sample fall in the range of good quality compared to national standards set for quality determination. Therefore, it is necessary to make use of high-quality beeswax resources out of waste.

Beeswax was found to form compatible and worthy formula in the production of shoe polish. Its shoe polish exhibited good shine and very good rub resistance and fade resistance compared with commercial shoe polish. Additionally, melting point, density, and viscosity of one of the shoe polishes formulated using 14.4% beeswax, 25% castor oil, 43.6% naphtha, 10% activated carbon, and 7% stearic acid was compared favorably with standard commercial polish. The prepared shoe polish has a good opacity, tinting (color) strength because of the pigment of the high surface area sugar cane bagasse activated carbon used. Additionally, activated carbon from sugar cane bagasse was economically important by replacing commercially available AC.

The shoe polish produced has appreciably similar effect on the shoe leather as that of commercially available polish, but it is cheaper. This makes that an economic replacement for commercially available polishes.

5.2. Recommendation

- Beeswax is the main ingredient of shoe polish formulation; hence, it is important to build the knowledge and skills of the beekeeper, how to harvest, handle, process it and enhance awareness on its economic importance.
- By creating the market chain of beeswax, enabling the use of this raw material to produce shoe polish and other useful materials is expected from business organizations and entrepreneurs.
- Instead of importing shoe polish it is better to produce it in the homeland and reduce the hard currency flow.
- When characterizing a shoe polish many researches were done on shoe polish formulation and characterization use visual assessments. In this research instruments and software's are used but further alternative instruments need to be used to enhance the accuracy.
- The shelf life of the produced shoe polish needs to be researched further.

REFERENCES

(CSA) (2017/18 /2010 e.c). "Federal democratic republic of ethiopia central statistical agency, Report on Livestock and livestock Characteristics." Statistical Bulletin 2 (583): 9-13.

A.K. Yusuf, P. m. a. U. A. (2015). "Extraction and Characteriation of Castor seed oil from Wild ricinus communislinn " International Journal of Science, Environment and Technology, Vol. 4, No 5, 2015, 1392 – 1404.

Addisu, B., D. Begna, A. Tassew and Z. Mekuriaw (2017). "Physicochemical properties of Ethiopian Beeswax, the case of South Wollo zone, Amhara Region." Int J Agric Sc Food Technol **3**(3): 061-066.

Addisu Bihonegn, A., D. Begna, A. Tassew and Z. Mekuriaw (2017). "Physicochemical properties of Ethiopian Beeswax, the case of South Wollo zone, Amhara Region." Int J Agric Sc Food Technol **3**(3): 061-066.

Adgaba, N. (2007). "Physical and chemical properties of Ethiopian beeswax and detection of adulteration." Ethiopian journal of Animal production: 39.

Alene, T., N. Munwyelet and E. Anmut (2018). Production of Shoe Polish from Bee Wax and Used Water sachet.

Altahir, S. M. A. (2018). Formulation of a Shoe polish using Activated Charcoal and Gum arabic إذاع ييزعلا غوصلا و طشنولا نحفلا ماذختسإب تيذحأ ءلاط, Sudan university of Science and Technology.

Ameh, C. U. (2011). "Thermophysical Properties of Shoe Polish Manufactured from Pure Water Sachet." AU Journal of Technology 15 (2): 129-132.

Anderson, S., E. Anderson, S. Richert and T. Tate (2017). Compositions and methods for treating leather, Google Patents.

Bachrun, S., N. AyuRizka, S. Annisa and H. Arif (2016). Preparation and characterization of activated carbon from sugarcane bagasse by physical activation with CO2 gas. IOP Conference Series: Materials Science and Engineering, IOP Publishing.

Bekele Tesfaye, B. D., Eshetu Mitiku (2016). "Analysis of Physico-Chemical Properties of Beeswax Produced in Bale Natural Forest, South-Eastern Ethiopia." European Journal of Biophysics 4 (5): 42.

Betrework, W. (2017). "Formulation of shoe polish from wax and used water sachets." international journal of advanced engineering management and science, Ethiopia, 2017.

Bogdonov, S. (2016). "Beeswax-Production-Properties-Composition-Control." Beeswax book. Bee product science.

Buke, P. A. (2000). "Shoe Polishes."

Dwiyaniti, M., A. E. Barruna, R. M. Naufal, I. Subiyanto, R. Setiabudy and C. Hudaya (2020). Extremely high surface area of activated carbon originated from sugarcane bagasse. IOP Conference Series: Materials Science and Engineering, IOP Publishing.

Gemechis Legesse, Y. (2014). "Beeswax production and marketing in Ethiopia: Challenges in value chain." Agriculture, Forestry and Fisheries 3 (6): 447-451.

Gemeda, M. and D. Kebebe (2019). "Evaluation of the Quality of Beeswax from Different Sources and Rendering Methods." International Journal of Research Studies in Biosciences 7 (6): 20-25.

Gumel, S. and A. Umar (2011). "Comparative study of performance of shoe polishes formulated from polyethylene and carbon black (CI Black pigment 7)." ChemSearch Journal 2 (1-2): 42-44.

Heidarinejad, Z., M. H. Dehghani, M. Heidari, G. Javedan, I. Ali and M. Sillanpää (2020). "Methods for preparation and activation of activated carbon: a review." Environmental Chemistry Letters: 1-23.

Jebur, S. K. ((2018)). "Carbon black production analyzing and characterization ".

Joan Na Lee, X. Y. L. (2014). "Production of Activated Carbon from Sugarcane and Coconut Shell."

Kalderis, D., S. Bethanis, P. Paraskeva and E. Diamadopoulos (2008). "Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times." Bioresource technology 99 (15): 6809-6816.

Kamalu, C. (2005). "Formulation-of-a-black-leather-shoe-polish-from-hydrogenated-castor-oil."

Kenesa, T. (2018). "Status of Beekeeping in Ethiopia- A Review." Journal of Dairy & Veterinary Sciences 8 (4).

Khalil, H., M. Jawaid, P. Firoozian, U. Rashid, A. Islam and H. M. Akil (2013). "Activated carbon from various agricultural wastes by chemical activation with KOH: preparation and characterization." Journal of Biobased Materials and Bioenergy 7 (6): 708-714.

Nangbes, J. G., J. Nvau, W. Buba and A. Zukdimma (2013). "Extraction and Characterization of Castor (Ricinus Communis) Seed Oil."

QSAE), Q. S. A. o. E. (2005). "Ethiopian Standard, Beeswax-Specification; ES 1203_2005_Bees_wax_specification."

Tadele, A. A. (2016). "Proximate Analysis of Cane Bagasse and Synthesizing Activated Carbon Emphasis on Material Balance." Journal of Environmental Treatment Technique Volume 4 (Issue 4): Pages: 102-110.

Taha, N., S. Abdelhafez and A. El-Maghraby (2016). "Chemical and physical preparation of activated carbon using raw bagasse pith for cationic dye adsorption." Global Nest Journal 18 (2): 402-415.

Tesfu, S., T. Asaminew and B. Desalegne (2020). "Evaluation of Physico Chemical Qualities of Beeswax in Selected Districts of Kafa Zone, Southern Nations Nationalities and Peoples Region (SNNPR), Ethiopia." Evaluation 12 (1).

Udeh, N. U. (2018). "Production and Characterization of Activated Carbon from Nigerian Bamboo Using the Two Methods of Activation." International Journal of Engineering Inventions e-ISSN: 2278-7461, p-ISSN: 2319-6491 Volume 7, Issue 4.

Wiersema, P.-J., W. F. P. M. Boonman and S. Jin (2007). Shoe and leather care product, Google Patents.

Yahya, M. A., M. H. Mansor, W. A. A. W. Zolkarnaini, N. S. Rusli, A. Aminuddin, K. Mohamad, F. A. M. Sabhan, A. A. A. Atik and L. N. Ozair (2018). A brief review on activated carbon derived from agriculture by-product. AIP Conference Proceedings, AIP Publishing LLC.

Yeshitila, E. and E. Tekeba (2018). "A Review on Crude Beeswax Mismanagement and Lose: Opportunities for Collection, Processing and Marketing in Ethiopia." Research Journal of Food and Nutrition 2 (4): 4-12.

Zulkania, A., G. F. Hanum and A. S. Rezki (2018). The potential of activated carbon derived from bio-char waste of bio-oil pyrolysis as adsorbent. MATEC Web of Conferences, EDP Sciences.

APPENDICES

Appendix I: Methods of chemical solution preparation

Alcoholic Potassium Hydroxide Solution approximately 0.5 N**:** dissolve 30 g of potassium hydroxide in rectified spirit and make up to 1 liter. Allow to settle overnight in a dark place, decant the clear liquid and keep in a bottle closed tight with cork or rubber stopper.

Phenolphthalein Indicator: dissolve 0.1 g of phenolphthalein in 60 ml of rectified spirit and dilute with water to 100 ml.

Standard Potassium Hydroxide Solution 0.5 N**:** dissolve 28.05g of potassium hydroxide in distilled water and make up to 1 liter. This process is exothermic, so add KOH slowly.

Standard Hydrochloric Acid 0.5 N: add 42.4 ml of HCl to a half filled flask and make up to 1 liter.

Sodium Hydroxide Solution - 10 percent: dissolve 100g of NaOH and dissolve in a beaker with about 50 ml of water and make up to 1 liter.

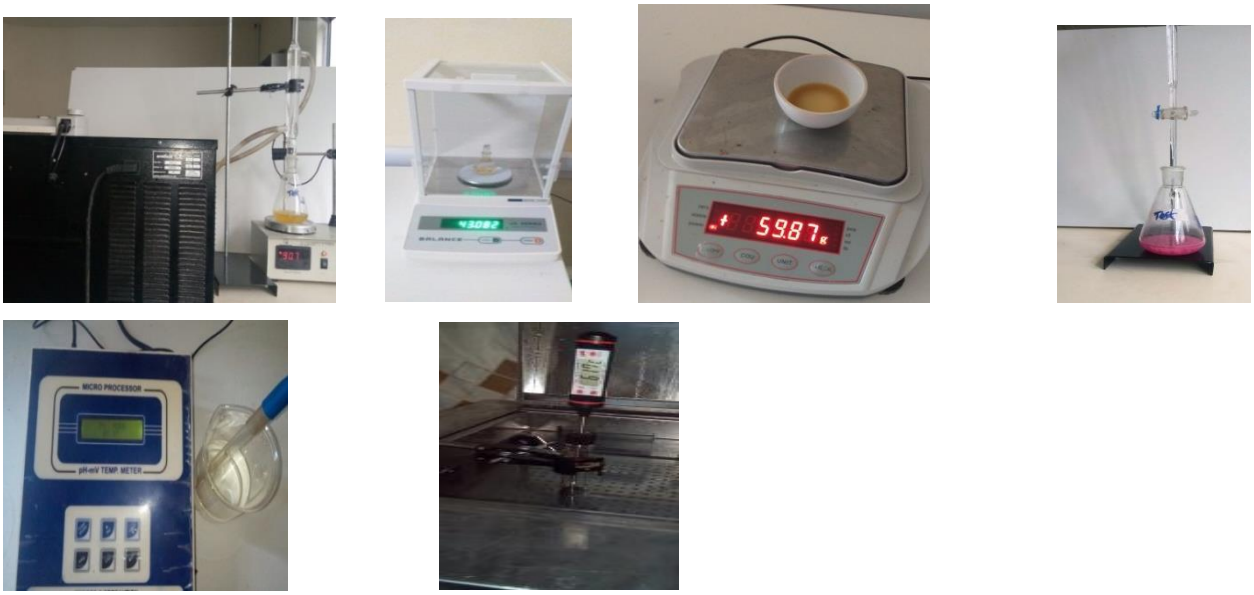
Standard Hydrochloric Acid - approximately 4N**:** add 33.9ml of HCl in a half distilled water filled flask and make up to 100ml.

Potassium Hydroxide Solution 1M- **:** dissolve 56.1g of potassium hydroxide pellet in distilled water and make up to 1 liter.

Appendix II: List of appendix pictures

Picture- I: Bees wax sample preparation for analysis

Picture II: Laboratory analysis of beeswax and data collection



Picture III: .Laboratory analysis of sugar cane bagasse activated carbon

Picture IV: Ingredients used for shoe polish formulation