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DETERMINATION OF OPTIMUM CONDITION FOR THE PRODUCTION OF COMMERCIALLY VIABLE GLUE FROM TANNERY SOLID WASTE

By Hanna Berhanu

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Advisor Dr. Ing. Belay Woldeyes

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List of Acronyms

CI – Cost index

DC – Depreciable cost

DF_n– Discounted cash flow

DPC – Direct product cost

ELICO – Ethiopian Leather Industry

EPA – Environmental protection Agency

FC – Fixed cost

FCI – Fixed capital investment

GP – Gross profit

IWM – International waste management

mP – Milli poise

NCF_n – Annual net cash flow

NP – Net profit

NPV – Net present value

PBP – Payback period

PCE – Purchase equipment cost

PPC – Total physical plant cost

PV – Present value

TPC – Total product cost

TCI – Total capital investment

WCI – Working capital investment

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Abstract

Glues are an adhesive which are collected by persistent boiling of animal skin, hide trimmings and flesh from the slaughter houses. They can also be gathered from the scrap of animal skin and hide residues of leather industry. This study was aimed at determining the optimum condition for the production of high quality glue from tannery solid waste. In other word, the effect of type of reagents used (such as lime and sulfuric acid), concentration of reagents, boiling time, soaking time and boiling temperature were investigated. The pelt was treated with 2.5% and 10 % concentration of reagents. Under sulfuric acid solution the pelt was soaked overnight and boiled for 2 and 4 hrs at 70^{o}C and 80^{o}C, whereas it was kept for 2 and 4 weeks under lime solution and boiled for about 4 hrs at 70^{o}C and 80^{o}C. Generally, the glue produced by using lime showed relatively high quality than the one produced from sulfuric acid. It was possible to extract high amount of glue within a short period of time from sulfuric acid treated pelt as compared to lime treated one. Under lime medium, the adhesive strength of glue was increased with the concentration and soaking time and decrease with temperature. Soaking of the pelt, in 10% lime solution, for 4 weeks and boiling at 70^{o}C were found to be the optimum conditions for the production of commercially viable glue. At this condition, the viscosity, yield and mass of residue was 255.05 mP, 0.1357g / g of pelt and 0.32287 g/ g of pelt, respectively. The economic feasibility study, carried out in this work, showed that the project is to be financially viable with the rate of return of the project 27.9%, the payback period of 3.08 year and the net present value of 40,036,155.25 birr.

Key word: Glue, Protein, Quality, Tannery solid waste and viscosity

1. Introduction

1.1.Background

Tannery is among the largest industries in the world producing a wide range of products. The primary raw material is hide and skin. Tannery use byproducts of meat industry and slaughter as a raw material i.e., skin and hide. Therefore, the tanning industry can be considered one of the first industries to use and recycle secondary raw materials [1, 2].

Tannery involves converting the raw hide or skin, highly putrescible material in to leather, a stable material. The whole process involves a sequence of complex chemical reaction and mechanical process [3]. The production process of leather can be split in to four main categories, these are, pre tanning operation (beam house operation), tanning operation, post tanning operation and finishing operation [4].

The tanning industry categorized as one of potentially pollution intensive industry [5]. Due to the bad smell, organic wastes and high water consumption leather industry from primitive to modern all round the world have negative impact on the environment [2]. The pollution is originated from liquid, solid and gaseous waste stream. The wet processing in beam house, the tan yard and the post tanning operation are the main source of waste water. The dry finishing processes and generation of gases such as NH_3, CO_2 and H_2S are the main source of gaseous emission. The main source of solid wastes originated from raw trimming, fleshing, buffing dust, splitting, keratin waste and shaving. The other potential source of solid waste is the sludge from effluent treatment plant [3, 6].

Tannery solid waste constitutes protein as the main component. If these protein which is present in solid waste, are not utilized properly it will results hazardous pollution problem to the environment [6]. On the other side this solid waste can be converted to generate value added product [7].

1.2. Problem statement

Leather industry has been categorized as one of the highly polluting industries and it has adverse impact on environment because of the generation of huge amount of liquid and solid waste also emits offensive odor because of degradation of proteinous material of skin and generation of gases such as NH_3, H_2S and CO_2.

Accumulation of solid waste such as raw trimmings, fleshing, chrome shavings, buffing dust and keratin wastes lead to sludge problem and choking of treatment pipes and finally results in reduction in efficiency of treatment plant. On the other hand treatment of solid waste also is not cost effective. In cognize to/ from the solid waste there is a potential to produce secondary products. Glue, gelatin, fertilizers are some of secondary product which produced after some treatment or without any treatment.

1.3.Objective

1.3.1. General objective

The general objective of this work is to determine the optimum condition for production of commercially viable glue from tannery solid waste

1.3.2. Specific objective

- To reutilize tannery solid waste by producing commercially viable glue.
- To see the effect of some parameters such as temperature, time and concentration of lime and sulfuric acid on the product quality.
- To test some of the property of glue such as viscosity, pH, ash content and moisture content.
- To carry out technical and economical feasibility of glue production from tannery waste.

1.4.Limitation

Jelly strength cannot be analyzed due to the absence of reliable measuring instrument.

2. Literature Review

2.1.Production process of leather

Leather production process transform animal hides and skin, the derma, epidermis and flesh of raw hide, to non putrescible / stable material called leather by using water, chemicals and mechanical process. In this process raw hide and skin is the preliminary input. The process involves cleaning and washing off the dirt, blood, flesh etc., from raw hides and skins after being flayed and preserved with salt till the hide is transported to the tannery [8, 9]. Due to bacterial and chemical action hides and skins begin to decay within an hour or two after the death of the animal. The hides and skins are subjected to various processes such as soaking, liming, deliming, bating, pickling and final chrome tanning after salt are removed from the skin and the hide as much as possible [6, 10].

2.1.1. Sorting and Trimming

Sorting and trimming are the first step in leather processing which may do on receipt. Hide and skin may be sorted in to several grades by size, weight or quality and also hides are sorted by sex. Trimming are generally carried out in the course of the sorting process. Some of the edges (legs, tails, face, udders, etc) of the raw hides and skins can be cut off. Usually the abattoir carried out this process step. However it can also be done in tanneries [2, 11, and 12].

2.1.2. Curing

The inside of the living animal skin contains bacteria and other micro organism and these micro organisms are controlled by metabolic defense of the living animal and external side of the skin is covered with dirt. Hence, when the animal is killed the process of decaying starts immediately [13]. Curing is a process that prevents the decaying of hide and skins from the time they are flayed in the abattoir till the processes in the beam house are started. If the raw material cannot be processed immediately it must be cured [11].

There are different curing methods. Curing by drying, curing by salting, curing by pickling and short time curing without salt are some of curing techniques [13].

2.1.3. Beam house

In the beam house operation, the raw hides are prepared for the subsequent tanning process. Unwanted parts such as hair, skin, hoof, etc. are removed from raw hides. In beam house there are liming, unhairing with sulfide, fleshing, trimming, deliming and bating [9].

After the pre-treated hide is split, the top part of the hide, called upper hide or grain, is used for production of finished leather. The lower part is called lower hide or split [9].

2.1.3.1.Soaking

Soaking is the first major step in beam house operation. It is carried out to allow the hide and skin to reabsorb any water which may have been lost after flaying, to clean the hides and skins (removal of dung, blood, dirt etc), and to remove inter fibrillary material[10, 11 and 12].

Soaking is mainly carried out in two steps which are a dirt soak to remove the salt and dirt and a main soak. The process is done in processing vessel such as mixers, drums , paddle, pits, or race ways. Surfactants, enzyme preparations and bactericides are some of soaking additives which are used depending on the type of raw material used [11].

2.1.3.2.Unhairing and liming

Liming and unhairing are the main and important step in leather making process [10]. The function of liming and unhairing is to remove hair wool, inter fibrillary components and epidermis and to open up the fiber structure. Hair removal is performed by chemical and mechanical means. The keratinous material (hair, hair roots, epidermis) and fats are eliminated from the pelts mainly with sulphides (NaHS or Na_2S) and lime. The process of liming and unhairing can be done in process vessel such as drums, peddles, mixers or pits [11].

2.1.3.3.Fleshing

Fleshing is a mechanical removal of the unwanted excess flesh, fat and organic material from the hide such as connective tissue, fat, etc. Fleshing can be done before soaking, after soaking, after liming or after pickling. If the fleshing is done prior to liming and unhairing it is called green fleshing. If fleshing is performed after the liming and unhairing it is called lime fleshing [2, 11].

2.1.3.4.Splitting

The thickness of hides and skins is regulated by mechanical splitting. Hides and skins are split horizontally in to a grain layer and if the hides are thick enough, a flesh layer. Splitting is carried out on splitting machines, fitted with a band knife. Splitting can be done in limed condition or in the tanned condition [11].

2.1.4. Tanyard operation

In tanyard operation there are deliming, bating, degreasing and pickling. The purpose of tanyard operation is to prepare the pelt to next tanning operation.

2.1.4.1.Deliming

The purpose of deliming is removal of mechanically deposited and chemically bound lime and capillary lime by conversion into readily soluble salts [13]. The hide after fleshing is full of lime and has a pH of about 12 the fibers are swollen and distended, a hide contains undesirable chemicals and hide degradation products from liming [10, 12]. Before the hide and the skin taken for tanning, it is necessary to remove the lime from the pelt, and the pelt takes to the optimum condition for bating. This involves gradual lowering of the pH (by the means of washing and addition of some mild acids and acid salt) and increases the temperature and the removal of residual chemicals and degraded skin component [11].

2.1.4.2.Bating

The purpose of bating is to partially degrade the non collagen protein achieved by enzymes to improve grain of hide and the subsequent run and stretch of leather. In this process the rest of the unwanted hair roots and scud can be removed. Trypsin, mould fungus proteases, bacteria proteases are some of proteases (Enzymes, which act especially on proteins) that used as bating agents [10, 11, 12, 13]

2.1.4.3.Degreasing

The purpose of degreasing is to the formation of insoluble chrome soap or prevents the formation of fat spues at the later stage. Degreasing is most relevant in processing of sheep skin, where the natural fat content is about 10%-20% on dry weight. The nature of this fat makes it difficult to remove because of the presence of cerides and high melting temperature [11].

2.1.4.4.Pickling

The purpose of pickling is to acidify the pelt to certain pH before mineral tanning and some of organic tanning such aschrome tanning, gluterdialdhyde tanning and vegetable tanning [11, 13]. The delimed and the bated pelts have a pH of about 8, and by pickling the pH is brought down to pH of about 2 to 3.5 depending on the amount of acid used. It mainly involves conditioning the pelt for tanning (especially in chrome tanning) and preservation of the pelt for a longer time prior to tanning [10, 12].

2.1.5. Tanning

The purpose of tanning is to stabilize the collagen fiber by tanning agents such that the hide is no longer vulnerable to putrefaction. In this process the collagen fibers can also stabilized by the cross linked action of tanning agents [11].

In other word, the main objective of tanning is to convert the putrefiable raw hides and skins in to a non putrefiable substance known as leather [8].

The following table shows input/ output over view of chrome tanning process.

Table 2.1: Input/output over view for conventional chrome tanning process [11]

In put	Out put
Chemical: 500 kg Water: 15-50 m^3	Leather: 200-250 kg Water: 15-50m^3 • COD: 230-250 kg • BOD :100 kg • SS: 150 kg • Chrome: 5-6 kg • Sulphide: 10 kg

Cont’d table 2.1

Raw hide: 1ton Energy: 9.3- 42 GJ	Solid waste: 450-730 kg • Un tanned ❖ Trimmings: 120 kg ❖ Fleshing: 70-350 kg • Tanned: splits, shaving and trimming: 225kg • Dyed finish ❖ Dust: 2kg ❖ Trimmings: 30 kg • Sludge from waste treatment (40% dry matter content): 500 kg Air: Organic solvent: 40 kg

2.2.Waste in Leather Industry

Animal waste primary comprise solid manure and liquid effluent generated from farm and feed lot. Slaughter house and poultry processing factory also produce large quantities of animal wastes containing high levels of organic pollutants. Waste streams from meat processing such as blood, hides or skin, bone and offals are potential contributors both in terms of solid waste, also called animal biomass, and liquid effluent [14]. Byproduct emitted from meat processing industry used as a raw material for leather industry [1, 2].

Leather industry emit large amount of waste in terms of their Varity and quantity. A variety of chemicals are used in the tanning industry, including lime, sodium chloride, sodium carbonate, ammonium chloride, sulfuric acid, tannins and dyes. All tanneries need large amount of water for processing leather [15]. High amount of reusable wastes are generated in the leather industry [2].

Leather industries emit all the three type of waste in the form of waste water, solid waste and air emission [16].

From the wet salted hide purchased by the tannery only 30-35% is theoretically convertible in to leather and of this amount , only some 30% is eventually converted in to high quality leather with further 10% yielding lower grade material. The remaining part of the hide with excess processing chemicals and large volumes of water employed from the solid and liquid residues [16].

2.2.1. Gaseous waste

Tanneries discharge odorous gas, smoke and dust in to the atmosphere. Rehydration of salted hides and skins generally emit odor of volatile fatty acid and amino acid evolved in the course of biological decomposition in presence of water. Hydrogen sulfide and ammonia are the major gases emitted during the washing of drum with ammonia, effluent of deliming agent and mixing of tanning and deliming effluent [16]. Nitrogen and sulfur compounds are also the main source of bad odor in a tannery. Ammonia escaping from deliming operation is odorous and pungent. The end product of anaerobic decomposition or decaying of protein is odorous. Sulphide, fatty acids like butyric acid, valeric acid and caproic acid and caproic acids, solvents, lacquers, formalin and some of the chemicals used finishing operations are also some of source of bad odor in leather industry. The stinky odor is increased because of unhygienic practice in skin and hide processing and delayed disposal of liquid and solid waste. In many tanneries it is the foul of odor which emits from the putrescrible solid and liquid wastes which account for much of the smell traditionally associated with the tanneries. Phenolics (monohydric, dihydric and trihydric) are emitted in to air during the processes like post tanning and finishing operations [6, 8]. In addition, emission of hydrogen Sulphide and ammonia gases which are emitted during different processes are a health hazard for the workers [16].

2.2.2. Waste water

Tanneries consume large quantity of water. Approximately 30-40 liters of water is used for processing 1kg of raw hide to finished leather. The liquid waste from tannery contains vegetable tannins, non tannins and high amount of protein, especially when a hair pulping unhairing system is used [8].

Chrome tanning process associated with generation of heavy metal containing solid wastes and toxic effluents. During these processes, only 75- 80% commercial chrome sulfate exhausted in leather industry the remaining goes to liquid waste [17].

Waste water which is emitted from tannery process consists of pollution of varying pH values. Similarly a large variation exists in every parameter BOD, COD, Chloride, Sulphate, etc. Discharge of these chemicals into wastewater is hazardous for the environment. Tannery’s wastewater is highly contaminated and the contamination observed is many times beyond the limits set by Environmental Quality Standards for all wastewater parameters [16].

2.2.3. Solid waste

The major solid wastes in tannery consist of dusted curing salt, wet trimmings, dry trimmings, wet shaving, buffing, non proteinous waste; non collagenous protein wastes, untanned collagen and tanned collagen. These wastes are generally separated at the source. During handling of raw skins, adhered dusted salt, which is contaminated with blood, hair, dirt and certain type of bacteria is removed and dumped. Trimmings are cuttings of edges of raw skins. Fleshing is the flesh material of the limed skins generated during fleshing operation. Chrome wet shaving is produced when skins are shaved for proper thickness after chrome tanning [8].

Except dusted salt, most of the solid wastes have a potential to generate valuable product due to its protein content. The main problem with these wastes is their high Chromium content. The Chrome tanned waste contains Chromium in trivalent form but it was found that when the solid wastes are used in making poultry feed the Chromium is converted to hexavalent form which is carcinogenic. The mixing of this metal in poultry feed could produce serious human health problems. It is estimated that for a tannery producing on an average 10,000 kilograms of skins per day, a total of about 5,500 kilograms of solid waste would be produced per day. Some of this solid waste or by-product is used in gelatin, glue, textile and artificial leather industries. It is estimated that 33% of the original protein material leaves the tannery in the form of effluent sludge, fleshing, trimmings, shavings etc., of which the greater part would appear as solid wastes [8].

Solid wastes which are disposed to the environment produced in different quantity from the following processes. The salted, “green” or dried hides are trimmed to remove irregular matter which will produce raw trimmings. Salted hides are then dusted. This operation will produce salt dust containing impurities like blood, dung etc. Again in the soaking process the skin and the hides are again trimmed. Lime, sulphide, enzyme, or dimethylamine using method determine the type of waste produced whether the hair will be recovered as solid waste or pulped in to the effluent. Lime sludge is produced in the lime pits which is either discharged in to the effluent drains or removed as solid wastes [8].

The tanning material is either vegetable, chrome or other agents. In the case of vegetable tanning, solid wastes generated are spent tan liquor sludge. After tanning, the leather undergoes a number of machine shop operations, such as shaving, splitting, buffing, trimming etc., resulting in tanned solid wastes such as split pieces, trimmings and buffing dust. Sludge is obtained as solid waste from equalization and settling of waste waters from different sections of tannery and the biological treatment of tannery solid wastes. All these solid wastes have to be either utilized or disposed off safely without affecting the environment [8].

About 35% of all tannery solid waste is trimming and shaving of various types. 2% of tannery solid waste account for Finished waste. Waste water screenings and sludge account for about 60% of tannery solid waste. 3% of tannery solid waste is floor sweeping [17]. Historically, shavings, trimmings and splits from the chromium tanning of hides and skins have been disposed off in landfills. However, increasing local restrictions on land disposal and the high cost of incineration have stimulated the search for alternative treatments [18]. Solid waste generation in tannery is shown in table 2.2.

Table 2.2. Solid waste in tanneries [16]

Type of solid waste	Rate of generation	Characteristics of solid waste	Comments
Dusted Salt	0.1 kg/skin	Contains around 120 gm/kg of moisture, 120 gm/kg of volatile matter, and 450 gm/kg of salt.	Contaminated with blood, hair, dirt and bacteria. Partly reused in curing and the rest is indiscriminately dumped in undeveloped lands near the tanneries.
Raw Trimmings	0.024 kg/skin	Proteins	The skins are trimmed (especially at legs, belly, neck, and tail parts) in order to give them a smooth shape. The trimmings are usually sold to soap and poultry feed production.
Fleshing	0.25 kg/skin	Contains around 240 gm/kg of proteins, 200 gm/kg of fats, 3gm/kg of sulfide.	This is the flesh material of limed skins. It is usually sold to soap and poultry feed makers.
Wet Trimming/ Wet shaving	0.14 kg/skin	Contains around 240 gm/kg of proteins, 30 gm/kg of fats, 15 gm/kg of chromium oxide	After chrome tanning, skins or split hides are shaved to proper thickness. This operation produces solid waste containing chrome. Secondary users including poultry feed makers; usually collect these shaving from the tanners.

Cont’d table 2.2

Dry Trimmings/ Dry Shaving/ Buffing Dust	0.06 kg/skin	Contains around 300 gm/kg of proteins, 130 gm/kg of fats, 30 gm/kg of chromium oxide	Secondary users, including poultry feed makers, collect cuttings and dry trimmings and buffing dust of the leather from the tanneries.
Assorted Refuse	No consistent Quantity	Primarily cartons, bags, drums, etc.	This is normally sold separately (in bulk) in the retail.

2.3.Solid waste management

Solid waste consists of all solid and semi solid materials which are discarded to the environment. Solid waste management is a complex process because it involves many technologies and regulations. These include technologies related with the generation (including source reduction), on-site handling and storage, collection, transfer and transportation, processing, and disposal of solid wastes. Disposal of solid wastes is described as placement of the waste so that it no longer impacts society or the environment. The wastes are either digested so that they can no longer be identified in the environment, as by incineration to ash, or they are hidden well enough so that they cannot be readily found. Solid waste may also be processed so that some of its components may be recovered, and used again for a beneficial purpose [19, 20].

The management of solid and contaminants which is removed by treatment has been continues to be one of the most difficult and expensive problem. There are regulation for reuse and disposal of solid wastes. So that selecting of the appropriate methods for solids processing and reuse and disposal must consider the regulations. The regulations were designed to protect public health and environment from any reasonable expectation of harm full pollutants present in the solid waste [21].

Land application, surface disposal, pathogen and vector reduction in treating biosolid and incineration. Land application is reuse of biosolids in all form to land for beneficial uses at agronomic rate that is rates designed to provide the amount of nitrogen needed by crop or vegetation while minimization the amount that passes below the root zone [22]. Repeated applications of tannery wastes as soil amendment material, millet crops could accumulate heavy metals to toxic levels [23]. Surface disposal is the other method to treat solid waste. Surface disposal does not include placement of solids for storage or treatment purpose. Alternatively biosolids can be treated by pathogen and vector reduction processes that reduce pathogens beyond detectable level [22].

2.3.1. Integrated waste management system

Integrated waste management (IWM) can be defined as the selection and application of suitable techniques, technologies, and management programs to achieve specific waste management objectives and goals. The EPA has identified four basic strategies for IWM these are source reduction, recycling and composting, combustion (waste-to-energy facilities), and landfills. As proposed by the EPA, these strategies are meant to be interactive. It should be noted that some states have chosen to consider the management options in a hierarchical order [20]. Figure 2.1 shows interactive and hierarchical integrated waste management system.

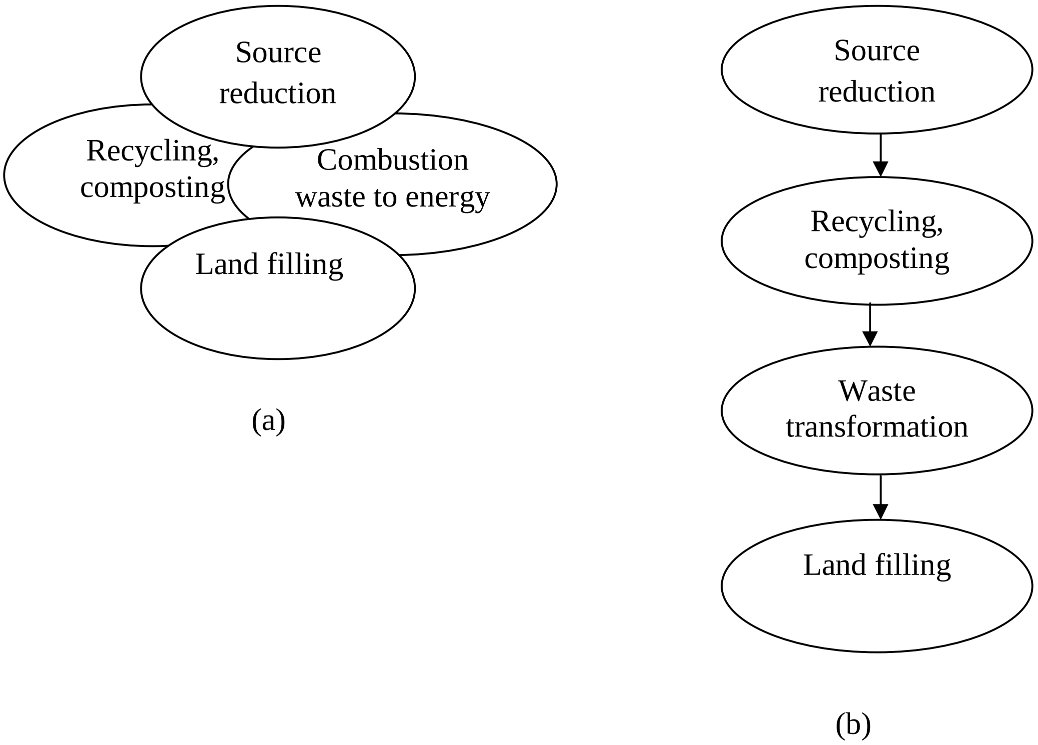


Figure 2.1. A sketch describing an integrated solid waste management: (a) interactive; (b) hierarchical

2.4.Utilization of tannery solid waste

Tannery solid waste include small pieces of animal hides, hooves, horns, bones, shaving and splitting including fleshing sludge and dried excess sludge from the waste water treatment system. Raw hides are transformed to several products and by-products after passing through different process steps of a leather tannery, including the utilization of hide residues. In Thailand hide residues such as, fleshing, splitting and trimmings are use for the production of fish feed, dog chew, gelatin, glue and fertilizer [24].

a) Fleshing and trimming wastes and limed splits

About 50-60%of total waste generated in leather industry is from fleshing. It has been explored for the possible utilization in to useful end products [6].

Green fleshings can be used in rendering plants for the recovery of grease and meat meal. These products must be clean, and contain minimal quantities of minerals. More importantly, green fleshings are a main source of high quality tallow, a basic commodity with added value. In contrast to limed fleshings, green fleshing produces much higher yield and good quality product, because the fleshings are not previously subjected to prolonged alkaline treatment. Lime fleshing needs little pH adjustment prior to enzyme process [25].

Limed fleshings have been utilized for stabilizing the delimed pelt, which has been named as reactive protein (RP) [6, 26]. The green and limed trimmings can be used with limed splits for tallow or gelatine production. Limed trimming and fleshing also used as fertilizer and fish feed [6].

Limed flesings have been used for production of gelatin, glue, sausage casing, pet chews and compositing [9, 22, 25, 27]

b) Keratin waste

Keratin, which is rich in cystine, is difficult to hydrolyze and highly resistant towards enzymes and most of the chemicals. It has been hydrolyzed using concentrated NaOH and HCl. Studies shows that the hydrolysate prepared from keratinous material helps to improve the chrome exhaustion of tanning bath and rechroming bath. The physical strength properties are also altered [6].

c) Chrome shaving wastes

Chrome tanned leather, splits and trimmings have been utilized to obtaining glue, gelatin, protein flavor and reconstituted collagen [6]. Two processes were developed to treat chromium containing solid waste, to isolate gelatin, hydrolyzed protein and chromium sulfate. In the first step process the chrome shavings are processed directly with enzyme and a hydrolyzed product is isolated. The uses of this protein are several e.g. animal foods, fertilizer e.t.c [27].

In the second step process the chrome shavings are treated with alkali to isolate gelatin and in a second step, the enzyme is used to recover the remaining protein so the chrome cake can be treated to be recycle [27]. Chrome tanned leather waste also hydrolysate utilized as a biodegradable packing material (Packing for agriculture chemicals including herbicides, insecticide, pesticides, fertilizer etc). One of the more realistic possibilities consists in using leather waste hydrolysates for manufacture of surfactants of lamepon type [28].

d) Recovered Hair

There are a number of reported promising uses for the recovered hair from hair-save processes. These include: felt production, slow degrading plant containers, keratin hydrolysate, cosmetics and pharmaceutical products (i.e. shampoo, amino acids, etc) [25].

Hair recovered through a hair-save process can be incorporated into existing composting processes, as it is a valuable source of nitrogen and organic carbon [25].

Hair can be directly used as slow release source of organic nitrogen and carbon for fertilizing purposes [22, 25].

e) White Splittings and white shavings

As for lime splits, the wet white process produces splits that can be partially denatured to produce gelatin or collagen additives. However their use in human food production is restricted [25].

Wet white chemistry options can create environmentally friendly tanned waste; aldehyde tanned, syntan tanned, marginally vegetable tanned materials have little associated hazard. These shavings are particularly suitable for use as fertilizer or as a source for collagen hydrolysate. Aluminum containing shavings can be applied to non acidic agricultural land, according to local regulations [25]. Figure 2.2 shows solid waste utilization in leather waste.

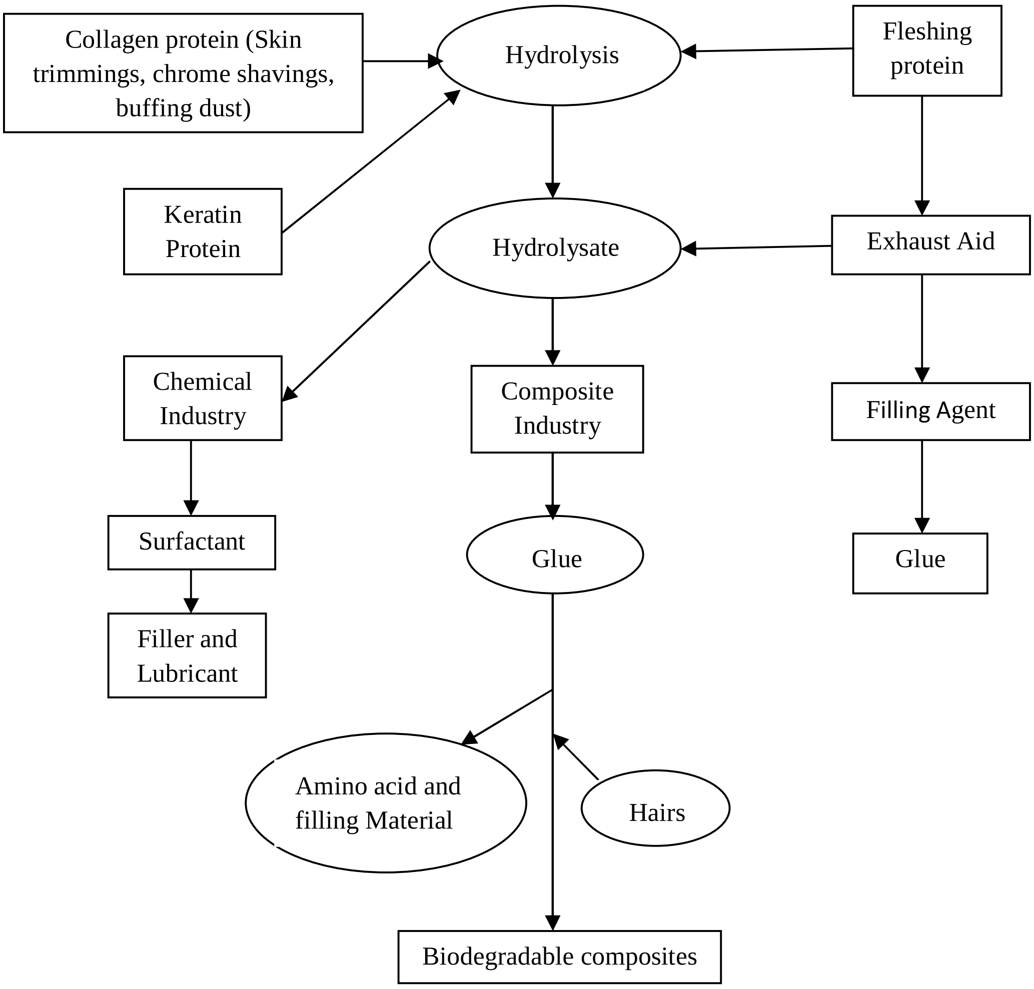


Figure 2.2: Solid waste utilization in leather industry

2.5.Glue production

2.5.1. Historical back ground of glue production

Animal glues have been used for thousands of year in traditional adhesive and sizing application [29]. The earliest indication of use of glue can still be observed in the cave paintings made by our Neanderthal ancestors in Lascaux, France. Egyptian remnants unearthed in their graves show many uses of glues; perhaps the most striking are the coat and inlays in wood furniture, which was made using glue as early as 3,000 B.C. The Egyptians also use glue to produce papyrus. Greek and Roman artists used glues widely; mosaic floors and tiled walls and baths are still undamaged after thousands of years [18, 30]. The earliest known use of animal glue, for veneering, dates to the period 1500–2000 B.C. in ancient Egypt and has been referred to in literature from biblical times [22, 31].

Furniture-making depends heavily on glues. All of the great furniture makers from the sixteenth through the nineteenth centuries used glue in furniture construction. The glues used by these furniture makers were made from animal hides, hooves, and other parts that had been used to produce glue. The glue was ground into power or flakes. It was remixed with water and heated gently in a glue pot. This product was brown, brittle, hard, and not waterproof. Yet this glue was the only glue available until World War I. At that time, casein glues made of milk and nitrocellulose glues were first manufactured [18].

Commercial manufacture dates back to about A.D. 1690 in England and Holland. Numerous patents relating to the manufacture of animal glues were issued during the period 1754–1844. The first manufacture of animal glue in the United States was early in the nineteenth century. In the 1930s, advances in the chemical and plastics industries led to development of a wide range of materials called adhesives and plastic or synthetic resin glues. These were used by the military and were not available for commercial use until the late 1940s or 1950s. Since that time, highly specialized, waterproof adhesives have been developed for many industries and unique applications including construction of the Space Shuttle. Glues are still used in woodworking and the manufacture of abrasives like sandpaper. They are also used as a colloid in industrial processes; colloids are added to liquids to cause solid particles that are suspended in the liquid to separate out so they can be recovered, either to clean the liquid or process the solids. Philanthropist, Peter Cooper was a creative inventive genius and a highly successful manufacturer. Cooper bought the rights to a glue-making process, improved it with his own invention, began operating a glue factory, and secured a virtual monopoly of the American glue business [18].

2.5.2. Type of glue

There are many kinds of glue, some of which have been known for a long time. Liquid glue, vegetable glue, casein glue, blood albumin glue and animal glue are some of glue type [30].

2.5.2.1.Liquid glue

Liquid glue are commonly made from the head, skins bones, and swimming bladders of fish. Some liquid glue, however, are made from animal glue and from other materials. They are ready for immediate use [18, 30]. Liquid animal glues can be modified with clays or calcium carbonate as fillers, and wetting and dispersing agents, plasticizers, and other modifiers as required [29].

2.5.2.2.Vegetable glue

Vegetable glues are made from starch, usually cassava starch, and sold in powdered form. Ordinarily they required heating with water and alkali for preparation [30].

2.5.2.3.Casein glue blood albumin glue

Casein glues are made from casein, lime and certain other chemical ingredients. They are commonly sold in powdered form requiring only the addition of water [30].

Blood albumin glues are made from black soluble blood albumin, a product recovered from the blood of animal. These glues must be mixed just before use, since they deteriorate rapidly in standing [30].

Casein and albumen produce fair adhesives that will bond strongly too many substrates, these adhesives are brittle because they lack the built in “springs” of the helix coil of hide glue [31].

2.5.2.4.Animal glue

Animal glue is one of the several adhesive which exist so far. It is distinguished from other adhesives by the fact that it comes from organic compound while adhesives are chemical based. Glue is produced by persistent boiling of animal connective tissue, bones and hides in a meat packing and tanning industries. These wastes could be processed to remove collagen, the protein in the tissues. The collagen is sticky and useful for holding things together [32, 33]. The term animal glue refers broadly to all gelatin type adhesive substance used to form a surface attachment between discrete materials [18].

There are two major types of animal glue, hide glue and bone glue, differing in the type of raw materials used. Although process conditions may differ, both are obtained by hydrolysis of the collagen in the hide and of connective tissue or bone structure of the raw material. Both types of glue manufacturer obtain the raw material such as bone and tissues of animals from slaughter house, tanneries and meat packing companies [27, 29].

Animal glue is a protein derived from the simple hydrolysis of collagen which is a principal protein constituent of animal glue [31]. The chemical responsible for adhesive properties of glue is collagen, the primary structural protein of animals. It exists as a long fibrous polymer molecule made up of amino acids in a complex, order configuration collagen, referred to as a structural protein, and is a basic “building block” in the construction of animals [29, 31]. Animal contain two groups of proteins: chondrin, which account for its adhesive strength and glutin which contributes jelly strength [34, 35].

2.5.3. Uses of glue

Animal glue currently used for book binding and directory/ catalog binding, paper manufacture and converting, industrial abrasives, emulsifying agent, emulsion stabilizer, ore and metal refining, paper box manufacture, matches, gummed tape, wood working, luggage, case covering and lining, rubber compounding, textiles, glass chipping, picture frame and decorative molding composition, and leather manufacturing [29]. Animal glue also used as gesso, a mixture of glue and whiting [36].

2.6.Manufacturing of glue from tannery solid waste

The raw materials for hide glue include salted, limed, or pickled hide trimmings or splits, and chrome-tanned leather scrap. Tanned leather scrap requires special processing because of the chrome tannage [31].

Hide glues from hide trim and splits are prepared by initial washing with water. Hide glues from hide trim and splits are prepared by initial washing with water. The stock is then soaked in lime (calcium hydroxide) and water for a period of weeks, which dissolves and removes extraneous protein-related materials, as well as conditioning the collagen for subsequent glue extraction, by hydrolysis. The conditioned collagen is then washed with water, followed by acidulation with dilute acid hydrochloric or sulfurous, for pH adjustment, followed by a final water rinse [31, 32].

The treated collagen is transferred to extraction kettles or tanks, where it is heated with water to convert the collagen and extract the glue. Several hot water extractions at progressively higher temperatures are made under carefully controlled conditions. Separate, successive dilute glue solutions are removed from the stock until the glue is completely extracted, usually in four extractions [31]. Cooking at the correct temperature and for the right length of time breaks down the collagen and converts it into glue. If the temperature or timing is off, the quality of the glue will be ruined. Large steam coils in the open tanks heat the water and product to 160°F (70°C) - 176°F (80°C). The dilute glue extractions, ranging from 2 to 9% glue solids, are filtered and concentrated by vacuum evaporation to 20 to 60% concentration prior to drying [31, 32, 33].

When cooled, this material looks like jelly and is solid; although it looks like the kind of gelatin used in food, it contains impurities. To remove the impurities and make the glue clear, chemicals like alum or acid followed by egg albumin may be added. These chemicals cause the impurities to precipitate, or fall out, of the glue. Mechanical methods can also be used to clean the glue. These include passing the glue through a series of mechanical filters or through paper filters or ground bone called bone char. Different additives are mixed with the glue liquor to make brown, clear, or white glue. Sulfurous acid, phosphoric acid, or alum is among these additives. Zinc oxide is added to produce white "school glue" [32, 33].

To this point, the glue is a weak, runny liquid. It is made more concentrated in vacuum evaporators and dried in one of several methods. The glue can be chilled into either sheets or blocks then suspended on nets to dry and become still more concentrated. The glue can also be dropped as beads or "pearls" into non-water bearing liquor that further dries the concentrated beads. The pearls, blocks, or sheets are then mixed to the right consistency and pumped into bottles or jars for sale [18]. With only slight variations, the same basic processes are used to make bone glue, hide or skin glue, and fish glue [30, 31]. Figure 2.3 shows the production process of animal glue

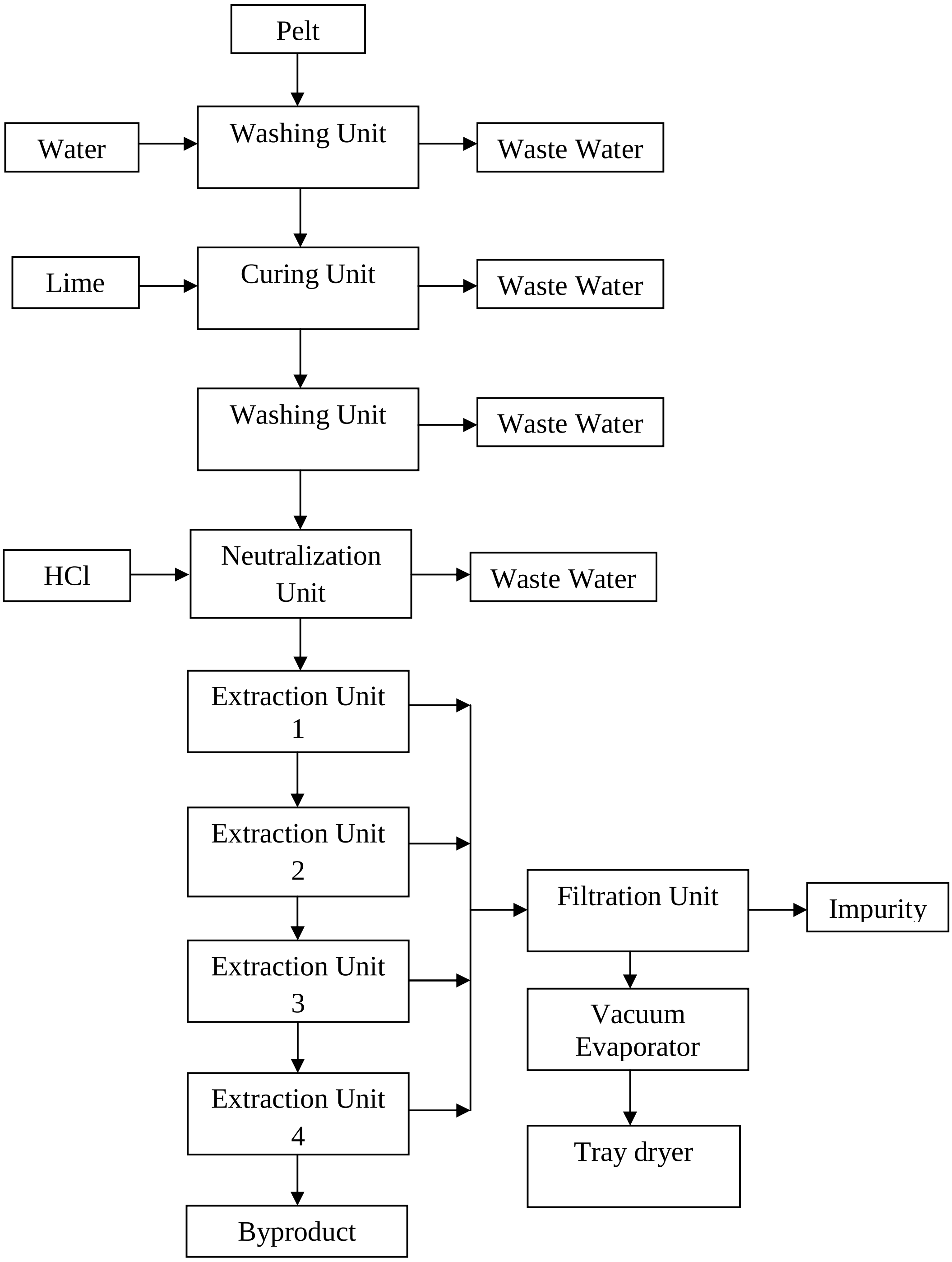


Figure 2.3: production process of commercially viable glue from tannery solid waste

2.7.Classes and grades of animal glue

As stated before, glues are derived from different raw materials. Glue made from hides is generally, of higher grade, according to acceptable standard, than glue derived from bones and tendons. However, there is considerable variation in the grade of glue from hides as well as from other source [24].

Each class of glue is sold in cake, flake, ground, pearl, shredded, and other forms, but the form of the glue is not trustworthy indication of quality. The main difference between the various forms is in the quickness and convenience with which they can be put in solution. The finely divided forms absorb water more rapidly and can be dissolved more easily than the cake and flake forms [24].

The higher grade glues, in flake form, are usually light in color and nearly transparent. Lower grade glues tend to be dark in color and opaque. However color and transparency is not safe indication for the quality of the glue because sometimes lower grade glues are bleached. On the other hand, foreign substance, such as zinc white and chalk are frequently added to transparent glue to produce opaque glue. The added materials have no effect on the quality of glue. Aside from the fact that they give an unremarkable glue line in a joint, the “opaque” or whitened glues have no apparent improvement over other glues of the same grade. Higher grade hide glues are used mostly in joints of thick stock; lower grade glues for veneer work [24].

2.8.Property of animal glue

Animal glues are available in different form. Flake, ground, pearl, shredded are some of the form. However, the quality of the glue is not dependable on the form of the glue. The main difference between the various forms is the speediness and convenience with which they can be put in solution. The finely divided forms absorb water more rapidly and can be dissolved more easily than the cake and flake forms [24]. Animal glues are dry, hard, odorless materials that vary in color from light amber to brown. The density of animal glue is approximately 1.27 and a moisture content of 8-15%. An inorganic ash content of 2 – 5 % and a grease content of 0.2 to 3% are normal range for commercial animal glue. The pH range of commercial glue is 5.5 to 8.0 [29].

Animal glues are soluble only in hot water. They are insoluble in oils, greases, waxes, organic solvent, absolute alcohols, and other solvents [29, 35]. In cold water the glue particles absorb water and swell, resulting in a jelly like sponge. Up on application of heat, the particles dissolve, forming a solution. Up on cooling, the solutions set to an elastic gel. The gelatin is thermally reversible reaction, and on application of heat the gel reverts to liquid form. The melting or gelling point will vary from below room temperature to over 120 ^{o}F, depending on glue concentration, grade, and possible presence of modifiers [29]. Molecular weight of hide glue has a wide range from 20,000-250,000, the high molecular weight the high the gel strength [31].

2.9.Testing of animal glue

The national association of glue manufacturers has approved a standard method of grading based up on test of viscosity and jelly strength. In 1931 a federal specification was adopted for procurement of animal glues for wood working. The grades set up in the federal specification are based on test of viscosity and jelly strength. There are also tests for moisture content, pH, foaming, and odor, and keeping quality and specifies the minimum requirements, considered adoptable to glues for wood working [24].

The dry glue must be also examined test as to color, odor, moisture content, ash content and if in the form of flake, sheer, ribbon or strip, as to the nature of the fracture when a piece is broken between the finger or by other means. The solution must be examined as to odor, acidity and alkalinity, grease, ash, foam and viscosity. The jelly resultant from the solution is tested for strength. The most important test for animal glue is viscosity and jelly strength [37].

2.9.1. Appearance

The dry glue should first be carefully examined for the appearance of the glue. The appearance of the glue tells nothing in regard to its strength, such examination is often sufficient to warrant the rejection of the glue, without the necessity of further tests [37].

The surface of the piece of glue should be free from bubbles. These may be merely the result of the incorporation of some air with the glue; but, if sizeable and irregular in outline, they are evidence of the fact that the stock from which the glue was made, and hence the glue itself, is in an advanced stage of decomposition. Of such glue, the jelly will rapidly putrefy and the solution will have a putrid odor, which, in some instances, may be detected in the glue itself, particularly if the sample be slightly moistened [37].

The piece of glue should break with an even fracture. If the fractured edges are splintery, the glue has not been properly boiled. On the other hand, if glue breaks under a very slight strain, even though the fracture is even, the glue is either very weak or unduly dry [37].

The cut of the glue is at times an indication of its strength. If, for example, the glue is cut very thin and is sufficiently flexible to permit of bending almost double without fracture, it is a glue of great strength [37].

Good glue should present a velvety or glossy surface, although the absence of this does not always condemn the glue. A "dead" surface may be due merely to the fact that dust settled upon the glue while it was drying upon the nets [37].

2.9.2. Odor

The solution of glue must have "sweet" odor. This does not mean that it should be free from any odor whatsoever, as even the solution of the purest gelatin will have a characteristic smell. There should be no trace of putrefaction. If the glue is very greasy, this may impart an odor to the solution, and yet the glue be rated sweet. The odor of the solution will vary according to the stock from which the glue is made. Thus, solutions of common bone glues have a marked "beefy" or "soupy" odor, and yet may be excellent glues of their class. Goat and sheep stocks impart a characteristic odor to the glues prepared from them, while glues from skin or epidermis are more or less odoriferous [37].

It is difficult to describe an "off" odor in glue, but this requires no extended experience to recognize. Frequently glue that exhibits a disagreeable odor upon going into solution loses this completely as the solution becomes hotter. Care must be taken not to condemn the glue because of smell, without first considering whether this is not due only to the stock. Odors due to partial putrefaction and other radical defects are permanent, and heating the solution does not dissipate them. Acid-treated glues, particularly those from junk bone, are, as a rule, very sweet, though some smell strongly of acid [37].

2.9.3. Alkalinity and Acidity

Glues are strictly neutral when in solution, being either acid or alkaline, depending upon the treatment which the stock has received. As previously stated, some manufacturers, after liming the stock, kill the excess of lime by means of a mineral acid. Glues boiled from such stock will be more or less acid in reaction, as will also those prepared by leaching [37].

Unless acid or alkali is present in large excess, it may be disregarded save as indicating, to a certain extent, the treatment which the stock has undergone. It has already been noted that acid glues keep longer than alkaline ones, as the bacteria of decomposition reproduce far quicker in alkaline media than in acid. If the glue has a rather earthy smell, and the solution turns red litmus deep blue, the stock has been over limed. Such glue should be rejected as the excess of alkali in this case will gradually weaken the glue, causing it to rot rapidly. Although the appearance of over-limed glue may frequently give indication of strength, upon test this will be found to be lower than was anticipated, owing to the fact that the lime has already radically weakened the fiber of the glue [37].

2.9.4. Grease

The presence of grease in glue has always met with strenuous objection, more or less justified, upon the part of the consumer. As a matter of fact, its presence is of material advantage for some purposes and of equal disadvantage for others. In any one make of glue, the amount of grease will vary considerably in the course of, say, a year. As has been pointed out, there are times when the manufacturer relies upon the recovery of the bulk of grease in order to reduce the cost of production. At others, when the market value of the recovered and rendered grease is so low as not to warrant the additional labor-cost attendant upon its complete removal [37].

A simple and accurate test for grease is affected by placing upon the corner of a sheet of white paper a few grains of some aniline color such as methyl violet, magenta, or any other readily soluble in water [37].

Glue at times contains free fatty acids resulting from the destruction of lime soaps by mineral acids. These impart a more or less acryline odor to the hot solution. Their presence is sufficient to condemn the glue, as they are markedly hygroscopic, absorbing sufficient atmospheric moisture to radically retard drying of the solution [37].

Of the various glues, that made from sheep stock is the greasiest. Next in order comes glue made from goat; and glues from ox or cow hides are more or less greasy, depending upon the care exercised in the removal of fat. Acid-treated glues seldom exhibit more than a trace of grease [37].

2.9.5. Viscosity

The measure of the viscosity of the glue solution is important. The test for viscosity, or fluidity, is based on the idea that the greater the tenacity of the glue, the greater will be its cohesiveness, and the less will be its flowing power. In other words, the higher will be its viscosity. The viscosity test is not entirely accurate in itself, but taken in connection with the jelly test it forms a very satisfactory basis for grading [testing and grading]. It has been adopted by several prominent Western manufactories as the sole means of determining glue strength. Of itself, it is insufficient for this purpose, but, considered in conjunction with jelly strength, it is of great value in grading the glue [37].

It must not be inferred from this that the higher the viscosity, the stronger the glue. This is true only of certain kinds of glue [37].

By some, notably Western producers, viscosity is taken as the ultimate measure of glue strength. This is a grave error. Viscosity is of importance in the glue test as it indicates the treatment the stock has undergone; and is, further, a reliable index of the value of the glue as a sizing medium. It must, however, be considered side by side, with other factors. The assumption that the strength of the glue is in direct ratio to the viscosity of its solution is true only of certain glues. Those prepared from the same stock, under identical conditions, may exhibit viscosities varying directly as their strength; but these constitute the exception rather than the rule. It will be observed that the higher grades exhibit greater divergence in viscosity than the lower. Such is the case with the majority of glues [37].

Acid-treated bone glues, as well as those from acid-treated hide stock, exhibit viscosities remarkably low in proportion to their jelly strength [37].

The viscosities of opaque and colored glues are always slightly higher than those of clear glues of corresponding strength. Hence, if viscosity is to be taken as the ultimate measure of strength, it is necessary to provide separate standards for comparing opaque or colored glues, separate standards for clear glues, for hide glues, for bone glues, and for acid-treated glues. Even if this were done, the results would not always be accurate [37].

If the glue stock has been incompletely washed, permitting mucin to be present, or if it has been over limed, with the result that soaps are present in the finished article, the viscosity will be disproportionately high. These were hide glues from improperly washed or over limed stock [37].

If the clarification has been effected by means of alum, the viscosity is very high, as alum renders the glue solution stringy. This is to be observed in the case of rabbit glues, the viscosities of which would mislead the observer as to their strength [37].

2.9.6. Foam

Foam, in glue, arises from the incorporation of minute bubbles of air with the solution, when this is beaten rapidly. There may be present in the solution, substances which render the emulsion more or less permanent; or the emulsion may be only temporary, the foam receding and disappearing in a few moments. The same defects which fictitiously increase the viscosity, contribute materially to the foam in glue. Thus, over-limed or poorly washed stock will retain mucin or soaps which make the solution foam badly. Glues from alum-clarified liquors foam, as do also cheap bone glues, because of the impurities they contain. If, however, there is grease present to any extent, it will prevent the foam emulsion from forming. This applies to all makes of glue [37].

Foam, although undesirable in glues, is often demanded in gelatin, particularly that used for the manufacture of confectionery. In making marshmallows, the solution of gelatin, combined with other ingredients, is beaten rapidly in a special machine [37].

2.9.7. Jelly Strength

This is the most important of all the test factors and, unless considered in conjunction with this, the others are of only limited value. The stronger a glue, the greater the resistance offered by its jelly to outside pressure [37].

3. Material and Method

3.1.Material

Beaker, measuring cylinder, boiling pan, Jenway model 3510 digital pH meter, stove, tray dryer, thermometer, model Nov AA 400 AAS and JD 210-4 model31 No. weighting scales, Beschickung-loading model 100-800 type oven, heater, dissector, crucibles, muffle furnace, viscometer, Aluminum foil and plastic bags were used throughout the experiment.

Different types of reagents were used throughout this experiment for curing and for pH adjustment. Reagents such as 98% w/w Sulfuric acid (H_2SO_4) and lime ($CaOH$) were used for curing. In addition to this, 30% w/w Hydrochloric acid (HCl) and sodium hydroxide ($NaOH$) were used to adjust the pH of the pelt. Adequate amount of sample was taken from Ethio leather industry (ELICO) glove and hide unit, and it was kept in the chemical engineering laboratory of Addis Ababa Institute of Technology. Viscosity was analyzed in reaction laboratory of chemical engineering department. Moisture content and ash content was analyzed in the mass transfer laboratory and pH was analyzed in the environmental engineering laboratory of Addis Ababa Institute of Technology. Figure 3.1 shows tannery solid waste obtained from ELICO.

Figure 3.1. Tannery solid waste obtained from ELICO

3.2.Method

3.2.1. Study variable

The experiment was done by using two different types of reagents; these were lime and sulfuric acid. It was done by using 2.5% and 10% of sulfuric acid and lime with boiling temperature of $70^{o}C$ and $80^{o}C$. The pelt was soaked for 2 and 4 weeks in lime solution prior to boiling for about 4 hours. On the other hand, the pelt was soaked overnight in sulfuric acid solution and then the boiling time was optimized between 2 and 4 hour.

The quality of the glue was analyzed by measuring its viscosity. The adhesive strength/ quality of the glue were found to augment with the viscosity, if no additives were used. Physical and chemical characteristics of glue such as pH, moisture content and ash content were analyzed.

3.2.2. Experimental design

Factorial experimental design was adopted in this study. Four factors were considered here. These are type of chemical used, temperature, time and concentration. Each of the factors was with two levels. The whole experiment was carried out in two replications. After doing so, different properties (i.e., response variable) of glue were assessed in terms of yield, mass of residue, moisture content, ash content, pH and viscosity to sort out the type of chemical, optimum boiling temperature, soaking or boiling time and concentration of sulfuric acid and lime for the production of quality glue.

3.2.3. Experimental procedure

3.2.3.1.Production of glue from tannery solid waste

The sample, which has been taken from ELICO, was prepared for extraction by washing and soaking it with 2.5% and 10% concentration of sulfuric acid and lime followed by neutralization. The amount of sample was 500 g and the amount of water used for washing and soaking and neutralization was 1.5 L and 1 L respectively. The time taken for soaking was different for each reagent because of their effect on the pelt.

The pelt was soaked for 2 and 4 weeks in lime solution. During soaking the amount of pelt was increased by 150% of its original weight. Then boiling of the pelt in pure water was followed after washing it with several rounds of tap water and neutralization. Nevertheless, it was necessary to boil the pelt for four times in order to achieve the entire extraction of the glue. The extraction was by using 1:2 ratio of tap water. The first extraction took place at 70°C and 80°C for 4 hour. The second, third and forth extraction were taken place at gradually increased temperature for 2 hours and 1 hour. Finally, the product was dried in tray dryer prior to collection of the final product.

The experiment was also done by sulfuric acid. In this case, the pelt was soaked overnight or about for 14 hrs in sulfuric acid solution and then it was boiled for 2 hr and 4 hr at 70°C and 80°C. Unlike the extraction done by the lime, the entire product was collected in a single extraction, and hence the extraction process was terminated. Then it was dried in the tray dryer and the product was gathered.

3.2.3.2.Viscosity

The measure of the viscosity of the glue solution is important for determining the quality of the glue. The viscosity of 12.5 % glue solution at 60°C was measured by using viscometer.

Apparatus used

Viscometer, beakers, measuring cylinder, thermometer, analytical balance and heater were used.

Procedure

At first, 50 ml of 12.5% glue solution was prepared. The concentration of the glue solution was estimated / calculated from the apparent moisture content. This solution later was subjected to heating until it reaches to the temperature of 60°C. Finally, the sample was run under viscometer for subsequent measurement. Figure 3.2 shows glue sample in the viscometer for viscosity measurement.

Figure 3.2. Samples in the viscometer for viscosity measurement. Arrow points to the container with the sample solution

3.2.3.3.Moisture content and Ash content

I. Moisture content

In this study a standard method was used in the determination of moisture content. In short, it was estimated from the weight loss of the glue upon evaporation at 110^{O}C for 16 hr in an oven. Figure 3.3 shows sample in the oven for moisture content measurement.

Figure 3.3. Sample in the oven for moisture content determination. Arrow points to the sample

II. Ash content

Ash content was estimated from weight loss upon ignition at 600°C for 2 hours in muffle furnace (standard method).

Apparatus used

Crucibles, analytical balance, drying oven (operating at 110 ° C) and Furnace operating at 600 °C were used. Figure 3.4 shows sample in the Furnace for ash content measurement.

Measuring procedure

Aluminum foil and crucibles were cleaned and weighed for tarring purpose. Then 3 gram sample was weighed using the weighed aluminum foil. The sample was dried in an oven at 110°C for 16hrs in order to evaporate the moisture. The remaining sample weight was measured. After that the dried sample was added to the crucible then ignited in the furnace for 2 hr at 600^{O}C. finally the ash was placed in dissector for dry cooling and measure the amount of ash.

Figure 3.4. Ash content analysis in muffle Furnace. Arrow points to the sample

Calculation

The amount of moisture content and ash content is calculated as flow.

— (Equation 3-1)

Where A is the amount of sample before drying, B is the amount of sample after drying

— (Equation 3-2)

Where Y is the amount of sample after drying, Z is the amount of ash after ignition and X is the amount of crucible.

3.2.3.4.pH

pH was measured using Jenway model 3510 digital pH meter.

Procedure

The sample dissolved in distilled water. After being dissolved, pH of the glue solution was determined using Jenwey model 3510 digital pH meter

3.2.4. Optimization of glue

3.2.4.1.Effect of temperature

The samples were boiled at different temperatures such as 70°C and 80°C. Then the glue liquor was collected and concentrated prior to drying. The glues produced at these temperatures were subjected to viscosity, pH, moisture content and ash content analysis.

3.2.4.2.Effect of concentration

The effect of concentration of two reagents viz. sulfuric acid and lime was analyzed. The concentration was ranged from 2.5% - 10%. The yield, viscosity, pH, moisture content, ash content and mass of residue were analyzed for the glues produced at these concentrations.

3.2.4.3.Effect of soaking and boiling time

Effect of soaking and boiling time was analyzed between 2 and 4 week for lime and 2 and 4 hours for sulfuric acid, respectively.

3.2.4.4.Effect of type of chemical use

Two types of reagents (sulfuric acid and lime) were used throughout the experiment. The effect of these reagents on quality and yield of the product were analyzed.

4. Result and Discussion

In addition to viscosity, several other characteristics / properties of the glue, i.e., appearance, yield, mass of residue, pH, ash content and moisture content were taken in to consideration for the present study to optimize the parameters such as temperature, time and concentration for quality production.

4.1.Experimental result

4.1.1. Production of glue

Glues with different characteristics and yield were produced in different conditions. Glues which have high yield were produced in the case of sulfuric acid than lime. When the lime was used the average amount of glue produced was 0.1475 g of glue / g of pelt. On the other hand, 0.1894 g of glue/ g of pelt produced in the case of sulfuric acid.

The amount of glue produced also affected by boiling temperature. When we consider the impact of temperature on the yield it has a positive impact. When the temperature increased from 70^oC to 80 ^{o} C the yield also increased from an average of 0.1571 g/g of pelt at 70^{o}C to 0.179g/g of pelt at temperature of 80^{o}C.

The analysis in annex 1 showed that, the yield of the glue was not affected by the concentration of chemical used and it was also not significantly affected by the boiling and soaking time.

The amount of glue produced and the amount of residue were determined and experimental results of different condition are displayed in table 4.1. The amount of glue produced was high when sulfuric acid was used and it was significantly low in the case of lime.

Table 4.1: Raw data of the experiments and results for full factorial experimental design

Ru.	Type of chem.	Tem. (^{o}C)	Boil. Time (hr)	Soak. Time (week)	Conc. (%)	Visc. (mP)	Yeild (g)	Resi. (g)	Moist. Conte. (%)	Ash cont. (%)	pH
1	Sulf.acid	70	2	ON	2.5	33	90.8	81.52	13	3.52	5.7
2	Sulf.acid	70	2	ON	2.5	38.1	98.4	73.2	13.2	3.4	6.1
3	Sulf.acid	70	2	ON	10	37.5	95.2	3.2	14.7	5.67	5.01
4	Sulf.acid	70	2	ON	10	34.5	75.1	1.5	13.1	4.5	5.23
5	Sulf.acid	70	4	ON	2.5	42.2	92.2	52.7	14.1	3.45	6.4
6	Sulf.acid	70	4	ON	2.5	40.4	73.5	8	13.1	3.3	6.34
7	Sulf.acid	70	4	ON	10	46.4	79.4	4.2	12.4	3.9	5.21
8	Sulf.acid	70	4	ON	10	62.1	137.6	30.7	13.17	4.03	5
9	Sulf.acid	80	2	ON	2.5	54	85.3	45.1	15.17	2.309	6.7
10	Sulf.acid	80	2	ON	2.5	60.1	84.6	5.4	14.42	3.1	5.8
11	Sulf.acid	80	2	ON	10	29.01	92.9	27.8	13.53	4.74	5.2
12	Sulf.acid	80	2	ON	10	27.9	81.6	2	12.57	5	6.4
13	Sulf.acid	80	4	ON	2.5	19	134.1	10.6	15.12	3.96	6.3
14	Sulf.acid	80	4	ON	2.5	25.1	111.1	12.4	14.02	4.7	5.6
15	Sulf.acid	80	4	ON	10	23.8	102.2	1.2	11	4.92	5.4
16	Sulf.acid	80	4	ON	10	28.1	82.2	3.4	13.6	5.2	5.32
17	Lime	70	4	2	2.5	183	57.5	240.3	13.04	2.3	7.9
18	Lime	70	4	2	2.5	174	60.3	262	12.7	2.727	7.89
19	Lime	70	4	2	10	250	60.8	206	15.78	3.726	6.8
20	Lime	70	4	2	10	255	72.2	204.9	15.6	1.23	7.2
21	Lime	70	4	4	2.5	195	55.4	224.9	14.1	3.14	8.1
22	Lime	70	4	4	2.5	194	64.5	217.1	14.7	2.07	7.56
23	Lime	70	4	4	10	278	75.7	142.2	14.3	4.67	6.83
24	Lime	70	4	4	10	234	72.4	155.2	13.3	3.634	7.2
25	Lime	80	4	2	2.5	153	82.9	154.2	13.48	2.2	7.4
26	Lime	80	4	2	2.5	135	79.14	243.2	14.46	1.23	6.8
27	Lime	80	4	2	10	193	90.71	115.9	15.38	1.2	7.2
28	Lime	80	4	2	10	210	71.5	103	15.97	5.59	7.7
29	Lime	80	4	4	2.5	221	84.1	138.6	12.8	4.56	6.9
30	Lime	80	4	4	2.5	230	84.8	144.9	12.7	2.727	7
31	Lime	80	4	4	10	180	83.34	68.5	12.5	3.65	7.6
32	Lime	80	4	4	10	193	85.05	59.6	12.1	2.928	7.86

ON: Over Night

4.1.2. Appearance of the glue

The appearance of the glue has been observed and the experimental results are displayed in figure 4.1. The surface of piece of glue in figure 4.1 (A), (B), (G), (M), (O) were not free from bubble. These is the result of the integration of some air with the glue or this is the evidence of the fact that the stock from which the glue was made, and hence the glue itself, is in an advanced stage of decomposition. Glue sample as presented in figure 4.1 (C), (D), (H), (I), (J), (L), (N), (O) had shiny and smooth surface these is the indication of quality glue. On the other hand, glues with transparent surface were obtained in figure 4.1 (C), (D), (H), (J) and (L) this is also the indication of quality glue, contrary wise, glues with opaque surface were observed as in case in figure 4.1 (G), (K). Glues in figure 4.1 (E), (G), (K), (M), (O) are brittle and some of the glue in figure 4.1 (C), (D), (H), (J), (L), (N) are sufficiently flexible these is the indication of great strength [37]. Most of the glue breaks with an even fracture. This is the indication of the glue has been boil properly. The following figure shows different glue which was produced in different condition.

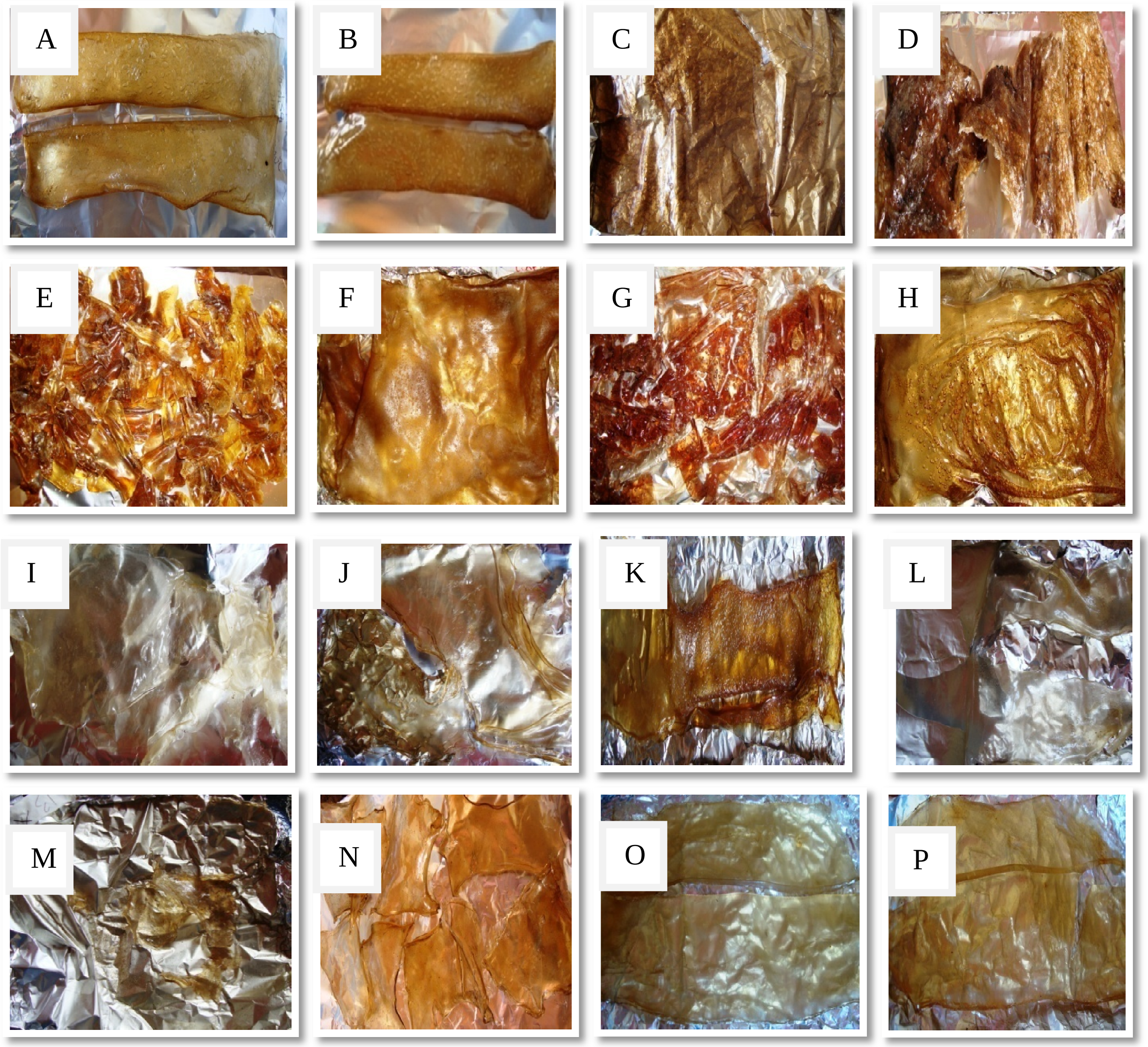


Figure 4.1: Appearance of the glue (A)10% H_2SO_4, 2hr, 70°C, (B) 10% H_2SO_4, 4hr, 70°C, (C) 2.5% H_2SO_4, 4hr, 70°C, (D) 2.5% H_2SO_4, 2hr, 70°C, (E) 2.5% H_2SO_4, 4hr, 80°C, (F) 2.5%H_2SO_4, 2hr, 80°C, (G)10% H_2SO_4, 4hr, 80°C, (H)10% H_2SO_4, 2hr, 80°C (I) 10 % lime, 2week, 70°C (J)10% lime, 2week, 80°C (K)10% lime, 4week, 80°C (L)10% lime, 4week, 70°C, (M) 2.5% lime, 2week, 70°C, (N)2.5% lime, 2week, 80°C, (O) 2.5% lime, 4week, 80°C, (P)2.5% lime, 4week, 70°C.

4.1.3. Viscosity

The viscosity of 12.5 % glue solution at a temperature of 60 °C has been determined and the experimental results are displayed in table 4.1.

Higher value of viscosity was shown in the glue which was soaked in 10% lime for 4 week then boiled at a temperature of 70°C. The value was 256±22 mP. Glue which was soaked in 10 % sulfuric acid and then boiled at 80°C for 4 hr was shown lower viscosity. The value was 25.95±2.15 mP. Generally glues made from sulfuric acid have low viscosity than lime. This result was the same as the results in literature [29].

4.1.4. Ash content, Moisture content and pH

An average moisture content of glue which was made from sulfuric acid and lime was 13.5 ± 1.6741 and 13.975 ± 1.625 respectively. Its ash content was 4.07 ± 0.667 and 2.85 ± 0.65 respectively and the pH range was between 5.2 and 7.8. The pH of glue solution must be in range between 5.5 and 8 [29, 37].

Ash content of the glue was significantly affected by concentration of lime and soaking time. However, it was slightly affected by the temperature. When the concentration of lime increased from 2.5% to 10 % the ash content increased from an average of 2.80987 – 3.3285.

The reduction in ash content from an average of 3.12775 % to 3.01062% was observed when the temperature increased from 70°C to 80°C.

The ash content of the glue increased from an average of 2.41% to 3.28 % when the soaking time increased from 2 week to 4 week.

The ash content of the glue is affected by the curing method used. The standard value for ash content is 2% - 5% [29, 37].

Moisture content is the amount of water in the glue. The high amount of water in the glue makes the glue easily putrefied. The glue will be brittle in little amount of moisture. The standard value for moisture content of the glue is 8% - 16% [29].

Moisture content of the glue was affected by concentration and time. However, it was not affected by boiling temperature. The moisture content of the glue increased from an average of 13.755 % to 14.9662% when the concentration of reagent augmented from 2.5 %- 10%.

The moisture content of the glue was negatively affected by time. When the time was increased from 2hr to 4 hr the moisture content of the glue decreased from an average of 14.905 % to 13.8162 %.

4.2.Optimization of parameters

Optimization is the act of obtaining the best result under given circumstances. In design, construction, and maintenance of any engineering system, engineers have to take many technological and managerial decisions at several stages. The ultimate goal of all such decisions is either to minimize the effort required or to maximize the desired benefit. Since the effort required or the benefit desired in any practical situation can be expressed as a function of certain decision variables, optimization can be defined as the process of finding the conditions that give the maximum or minimum value of a function [38].

4.2.1. Effect of temperature

Among the major factor affecting the quality and quantity of glue, temperature is considered to be the most important. According to the result of the experiment conducted as shown in chapter 3, the quality and the quantity of the glue has been affected by the temperature significantly. In the case of sulfuric acid, the viscosity of the glue decreased from an average of 41.775mP to 33.37mP when the temperature was increased from 70^{o}C to 80 ^{o} C, respectively. On the other hand, the viscosity of glue solution was decreased from an average of 220.3mp at 70^{o}C to an average of 189.3 mp at 80^{o}C in the case of lime.

The viscosity increment at low temperature, i.e. 70^{o}C, is probably due to linking of glue molecule to form aggregate. In other word, at high temperature the protein molecule may denature [39]. Figure 4.2 shows the effect of temperature on the viscosity of the solution.

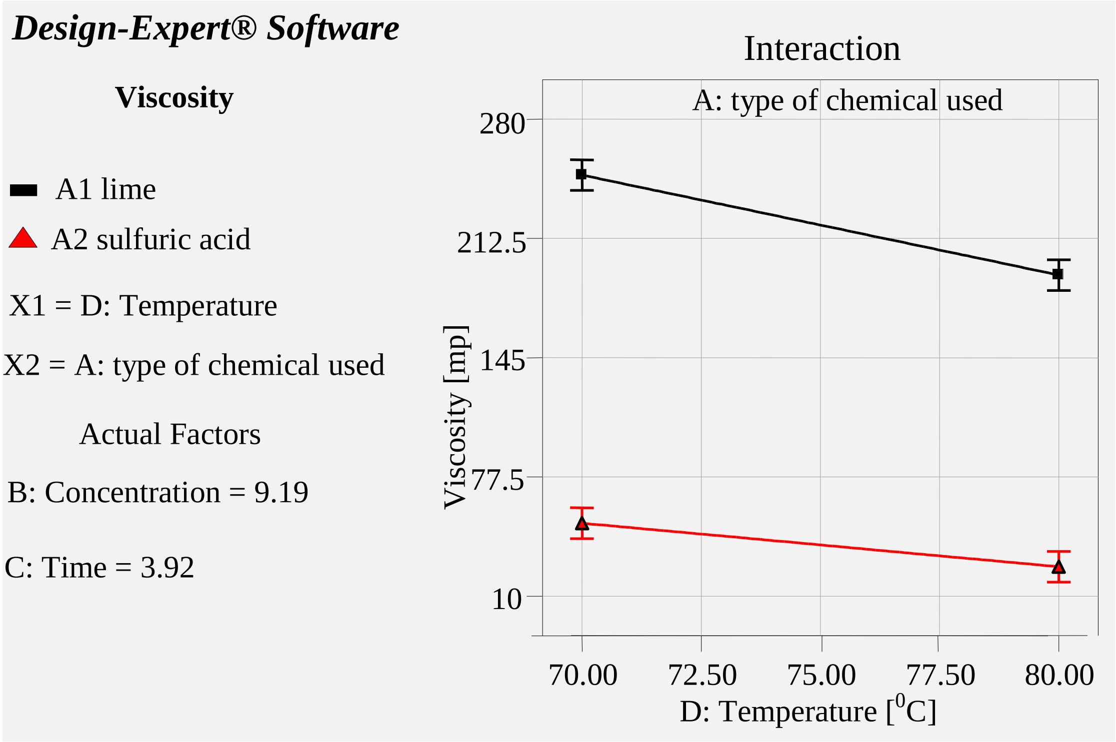


Figure 4.2: Viscosity of glue solution by using different chemicals verses boiling temperature

Contrariwise, temperature has a positive impact on the yield. When the temperature was increased from 70^{o}C to 80 ^{o} C the yield also increased from an average of 67.85 g of glue / 500 g of pelt at 70^{o}C to 78.85 g of glue / 500g of pelt at 80 ^{o} C. It is because elevated temperature (i.e., 80^{o}C) breaks high amount of collagen in the pelt, which in turn facilitates the conversion of collagen in to glue than low temperature [31]. The optimize value of temperature was 70^{o}C. Figure 4.3 shows the effect of temperature on the amount of product.

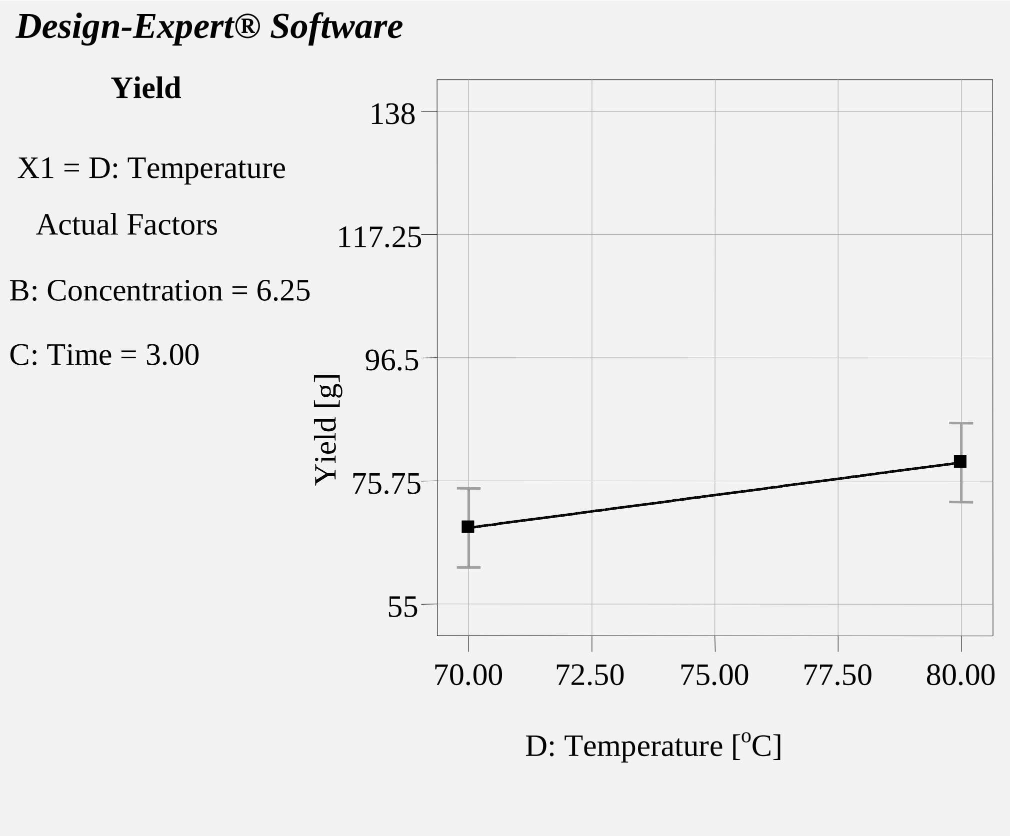


Figure 4.3. Effect of Temperature on the yield

4.2.2. Effect of concentration

The viscosity and the yield of the glue at different concentration of reagent such as lime and sulfuric acid have been investigated and the results are plotted in figure 4.4.

The result shows that, the viscosity of the glue solution was decrease from an average of 38.98mp to an average of 36.16 mp when the concentration of sulfuric acid increased from 2.5% to 10%. On contrary, the viscosity of glue solution was increased from an average of 185.625% to an average of 224.12% when the concentration of lime solution was increased from 2.5% to 10%. It is due to high concentration of sulfuric acid damage the collagen and ruins the quality of the glue [31]. Figure 4.4 shows the effect of concentration of reagent on the viscosity of glue solution.

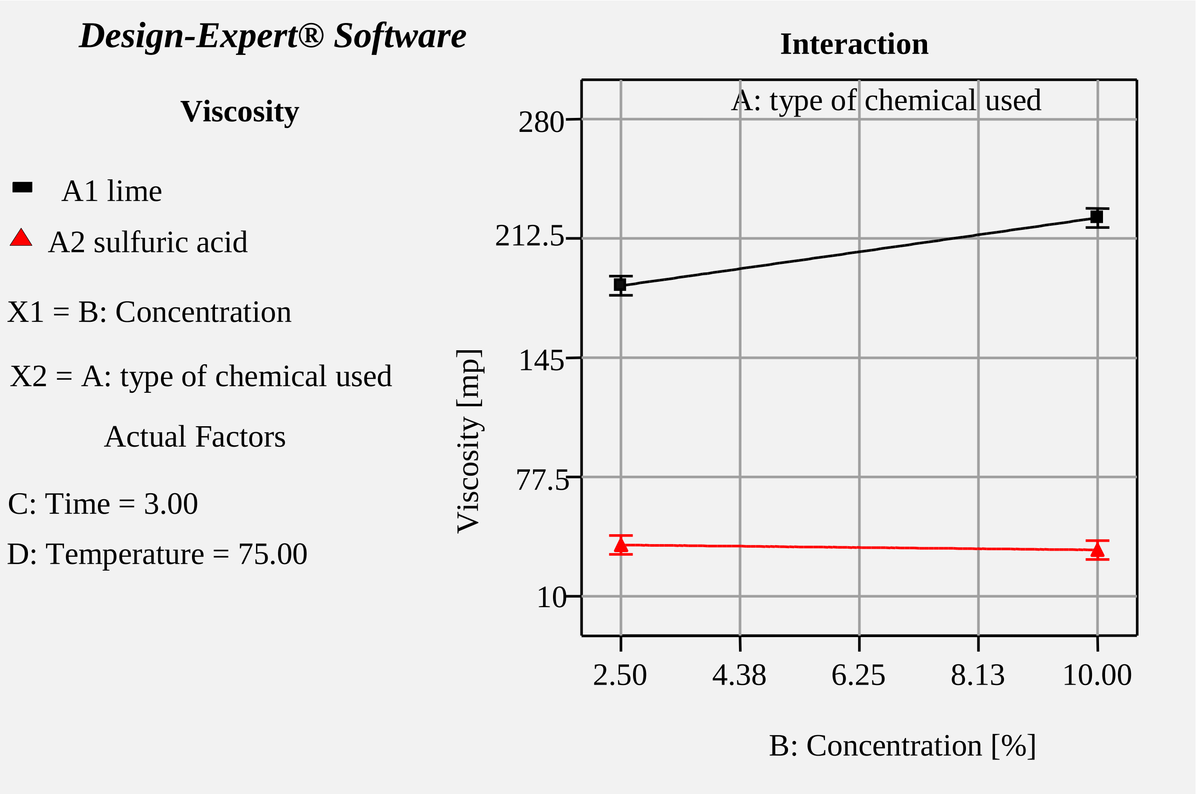


Figure 4.4: The effect of concentration of reagent on the viscosity of glue solution

The analysis of variance in annex 1 showed that, the yield of the glue was not affected by the concentration of chemical used. The optimum value of the concentration is 10 % lime.

4.2.3. Effect of boiling and soaking time

The effect of 2 and 4 week soaking of pelt with lime and 2 and 4 hr boiling of pelt after soaking the pelt in sulfuric acid solution over night on viscosity and yield of glue was studied. The viscosity of glue solution was decrease from an average of 39.2637 mp to an average of 35.887 mp when boiling time was increased from 2 hr to 4 hr. On contrary the viscosity of glue solution was increased from an average of 194.125 mp to an average of 215.75 mp when the soaking time was increased from 2 week to 4 week. The reduction in viscosity of the glue

4 week soaking of the pelt in 10% lime solution has been selected as the best time to obtain quality glue with high yield. Figure 4.5 shows the interaction effect of time and type of chemical used on the viscosity of glue solution.

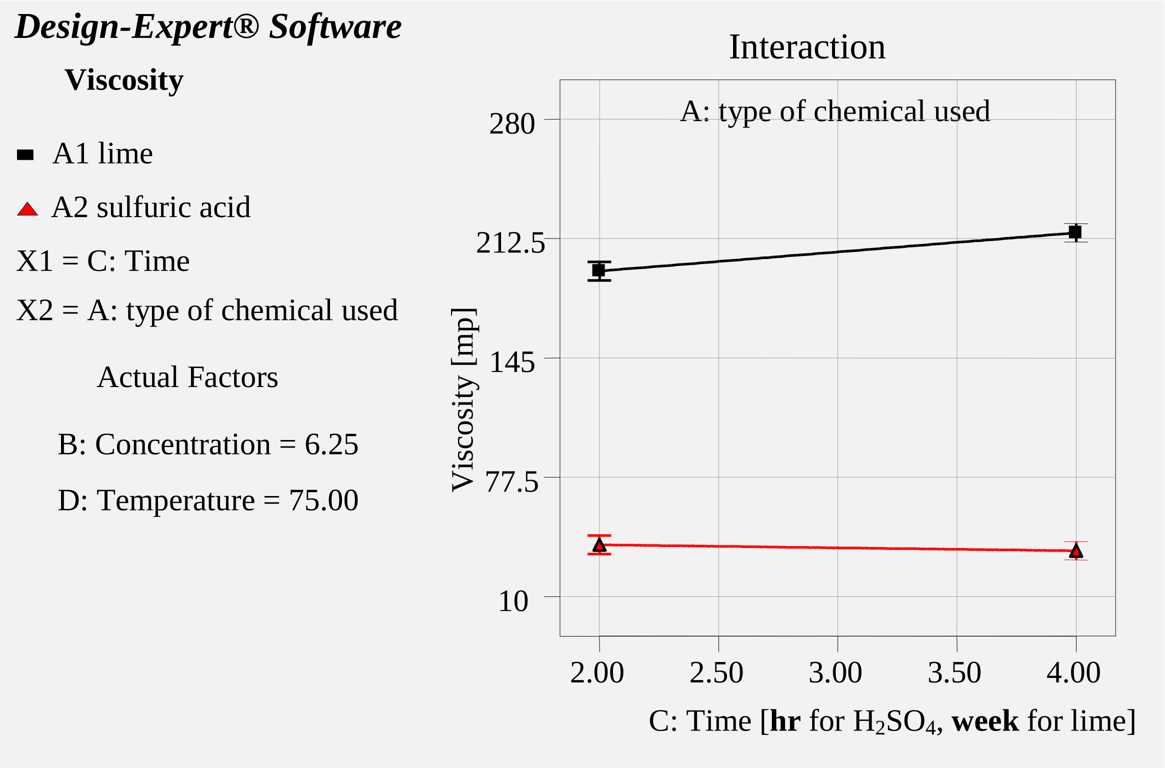


Figure 4.5: The interaction effect of time and type of chemical on the viscosity of the glue

4.2.4. Effect of type of chemical used

The viscosity and the yield of the glue have been highly affected by the type of curing agent used. The viscosity of glue solution varied between 135 mP to 278 mP in the case of lime and from 19 mP to 62.5 mP in the case of sulfuric acid. The viscosity of glue solution was an average of 37.57 mp when sulfuric acid was used. On the other hand the viscosity was an average of 204.875 mp in the case of lime solution. Lime has been selected as the best reagent which results in the production of quality glue.

In contrary the yield of the glue was very high in the case of sulfuric acid than lime. The yield of the glue was an average of 94.745 g of glue / 500 g of pelt and 73.35 g of glue/ g of pelt in the case of sulfuric acid and lime respectively. Figure 4.6 shows the effect of type of chemical on the amount of product.

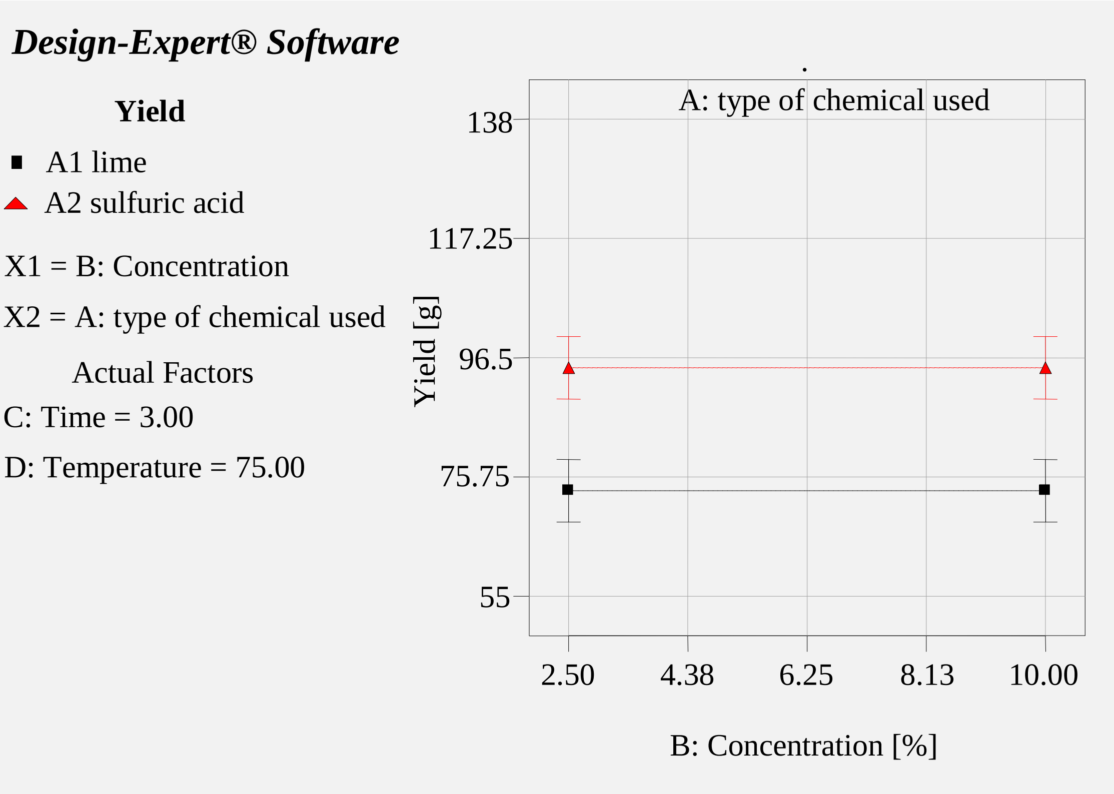


Figure 4.6. The effect of type of chemical used on the amount of product produced

5. Economical feasibility of glue manufacturing from tannery solid waste

5.1. Material balance and energy balance

Material balances (also called mass balance) are essential of process design. It is an application of conservation of mass to the analysis of physical system. If it is taken over the complete process, it will determine the quantities of raw materials required and products produced. If it is over individual process units it determines the process stream flows and compositions [40].

Material balances are also useful tools for the study of plant operation and trouble shooting. They can be used to check performance against design; to extend the often limited data available from the plant instrumentation; to check instrument calibrations; and to locate sources of material loss [40].

The flow chart for production of glue from tannery solid waste is shown in figure 2.2.
In the experiment's it was possible to produce 8.6%, 4.7%, 4.4%, and 3.7% high quality glue in 1st, 2nd, 3rd and 4th extraction respectively.
The processing capacity of Elico is 5000 pic of full hide and skin per day in it's two tanneries, Elico Goat swede and shoe leather unit and Elico Glove and hide unit.
As stated in table 2.2, 0.474 kg solid waste which contains raw trimming, fleshing, wet trimming and dry trimming waste per skin is discarded to the environment.
Therefore, the amount of solid waste is $\frac{5000\text{pic}}{\text{day}} \times \frac{0.474\text{kg}}{\text{pic}} = \frac{2{,}350\text{kg}}{\text{day}}$.
Most of leather industry has 300 working days so $705{,}000\,\frac{\text{kg}}{\text{year}}$ protentious leather waste is disposed to the environment.

The material balances at each section are calculated based on flow sheet in shown in fig 2.2. This process flow sheet was selected with current local glue production unit which says from literature [18].

I Material balance on washer

It is assumed that all of dirt, salt and sulfide are removed in this process with water. As shown in table 2.1 the waste contains 0.962% dirt, salt and sulfide. As shown in section 3 for 1kg of pelt 3 liter of water is needed. Therefore, mass of water is 7110kg/day.

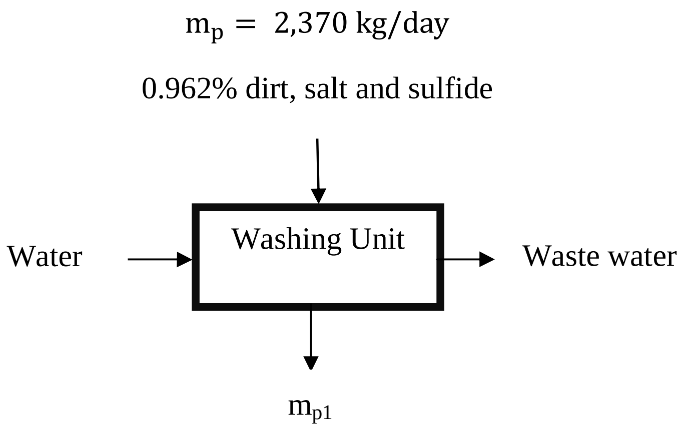


Figure 5.1. Flow diagram for mass balance on washing tank

Material balance on the pelt

The amount of dirt, salt and sulfide = 2370 × 0.00962

= 22.799 kg/day

So, the mass of pelt after washing is m_{p1} = 2370 kg/day – 22.799 kg/day

= 2347.2 kg/day

Total material balance

Mass of pelt before washing + Mass of water = Mass of waste water + Mass of pelt after washing

$m_p + m_w = m_{ww} + m_{p1}$

The mass of waste water removed = 7132.8 kg/day

Where m_p is mass of pelt, m_{p1} is mass of the pelt after washing, m_w mass of water and m_w mass of waste water.

II Material balance on soaking unit

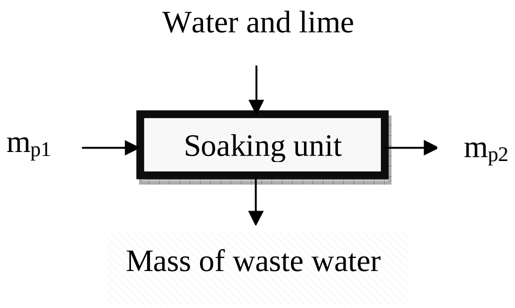


Figure 5.2. Flow diagram for mass balance on soaking tank

Where m_{p1} is mass of pelt after washing, m_{ww} is mass of waste water removed from soaking unit and m_{p2} is mass of pelt after soaking by lime

In this process the hides swallow and the collagen will break. From section 3 for 1 kg of pelt 2 liter of water is needed for soaking. In addition to this, mass of the hide increase by 150% of its weight and 72% of the lime removed with water.

Mass of the pelt after washing is 2347.2 kg/day

Therefore, mass of water = 2 × 2347.2 kg/day = 4694.4 kg/day

From the experimental result 10% lime is found to be the optimum concentration.

Mass of lime = 469.4 kg/day

From the above information mass of pelt after soaking is calculated as

$m_{p2} = 1.5 \times m_{p1} + (0.28 \times \text{mass of lime})$

$= 3652.23\text{kg/day}$

Over all material balance on soaking unit

Mass of the pelt before soaking+mass of water= mass of pelt after soaking + mass of waste water

$m_{p1} + \text{mass of water} = m_{p2} + m_{ww}$

From the above total material balance mass of waste water is calculated as 3389.39 kg/day

III Material balance on washing and neutralization unit

This process involves removal of lime and pH adjustment. From the experimental result to neutralize 1 kg pelt 2 liter of water and 17 ml of 5% HCl is needed.

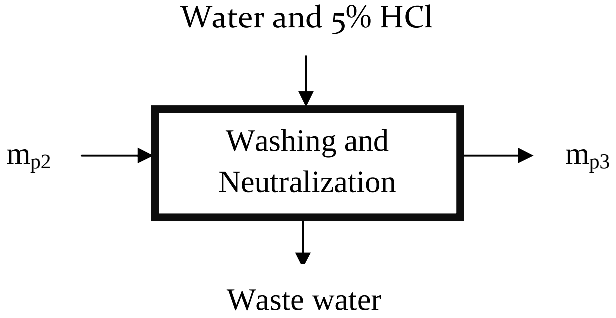


Figure 5.3. Flow diagram for material balance on washing and neutralization tank

m_{p2} *is* mass of pelt after soaking and m_{p3} is mass of pelt after washing and neutralization

Therefore, the amount of HCl needed per day is 3652.23 × 17 = 62,087.91 ml/ day

= 0.0621 m^3/ day 5% HCl

Density of 5% HCl at 20^oC is taken from perry chemical engineering hand book which is

1023 kg/m^3 [41].

Mass of 5% HCl = 1023 kg/m^3 × 0.0621 m^3/ day

=63.52 kg/day

Mass of water = 2 × 3652.23kg/day

= 7304.46 kg/day

Mass of the pelt after neutralization = 3652.23 – (0.28 × 469.4)

= 3520.79 kg/ day

From over all material balance on washing and neutralization unit the amount of waste water removed is 7,500.42 kg/day.

IV Material balance on extraction unit

After neutralization the extraction is done 4 times with pure water. In the first extraction 8.6% glue was extracted and from experimental result 0.8406 kg of residue was obtained from 1kg. As an example the following diagram shows the first extraction. As stated in section 3 for 1 kg pelt 2 kg water is needed.

Mass of pelt after neutralization = 3520.79 kg/ day

Mass of water = 7041.58 kg/day

Mass of residue = 0.8406 × 3520.79 = 2957.45 kg/day

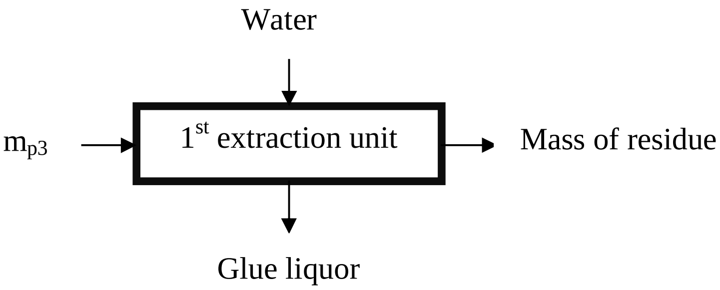


Figure 5.4. Flow diagram for mass balance on 1^{st} extraction unit

Where m_{p3} is mass of pelt after washing and neutralization, m_{gl1} is mass of glue liquor from first extraction and m_{r1} is mass of residue after first extraction.

From total material balance on 1^{st} extraction unit amount of glue liquor is calculated.

Over all material balance

m_{p3}+ water = mass of residue + mass of glue liquor

Mass of glue liquor = 7604.91 kg/ day

Balance on glue

$0.086 \times 3520.79 = 7604.91 \times (X)$

Where X is percentage of glue that found in glue liquor

$X= 0.0398$

Therefore, 3.98% of glue liquor is glue

Material balance on other equipments is done on the same manner and summarized as below in table 5.1.

Table 5.1. Summary of material balance on all equipments

Equipment	**Assumption**	**Input**	**Output**
Extraction unit 2	4.7% glue extracted 0.76 kg residue from 1 kg of pelt	m_{r1} =2957.45 kg/day W= 5914.9 kg/day Where m_{r1} is mass of residue after first extraction and W is mass of water	m_{gl2} = 6620.58 kg/ day m_{r2}= 2251.765 kg/ day Where m_{gl2} is mass of glue liquor from second extraction; m_{r2} is mass of residue after second extraction
Extraction unit 3	4.4 % glue extracted 0.655 kg residue from 1 kg of pelt	m_{r2} = 2251.765 kg/day Water= 4503.53 kg/day Where m_{r2} is mass of residue after 2nd extraction	m_{r3} = 1475.255 kg/day m_{gl3} = 5280.04 kg/day Where m_{gl3} is mass of glue liquor from 3rd extraction; m_{r3} is mass of residue after 3rd extraction
Extraction unit 4	3.7 % glue extracted 0.473 kg residue from 1 kg of pelt	m_{r3} =1475.255kg/day W= 2950.45 kg/day Where m_{r3} is mass of residue after 3rd extraction	$m_{gl4=}$ 3726.96 kg/day m_{r4}= 698.71 kg/day Where m_{gl4} is mass of glue liquor from 4th extraction; m_{r4} is mass of residue after 4th extraction
Filtration	All of impurity is removed from glue liquor.	m_{tgl}= 23,232.4 kg/day 0.54 % impurity Where m_{tgl} = Total mass of glue liquor from all extraction unit.	Mass of impurity= 125.4 kg/day m_{pgl}= 23,107.03 kg/day Where m_{pgl} = mass of purified glue liquor

Cont'd table 5.1.

Evaporator	The glue liquor is concentrated to 60%	m_{pgl}= 23,107.03 kg/day 2.58 % glue	Glue = 993.6 kg/day 60 % glue Water vapor =22,113.42 kg/day
Dryer	The glue liquor is concentrated to 87% glue	Glue = 993.6 kg/day 60 % glue	Drayed glue = 685.24 kg/day 87% Glue

5.2.Energy balance

Energy balances are also essential for process design to determine the energy requirements of the process: the heating, cooling and power required. In plant operation, an energy balance (energy audit) on the plant will show the pattern of energy usage, and suggest areas for conservation and savings [40].

A. Energy balance on 1st extraction unit

Energy balance on extraction unit calculated as follow:

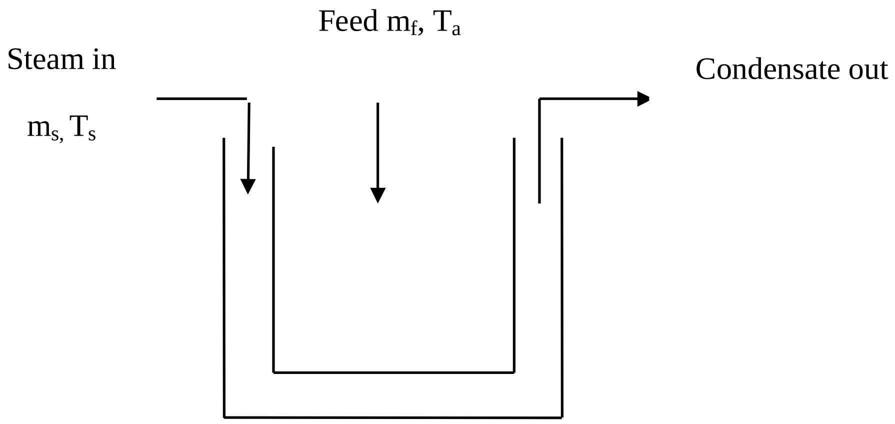


Figure 5.5. Flow diagram of extraction unit

Datum temperature = 25°C

Specific heat of pelt = 2.9 kJ/kg k

$$m_f \times C_P \times \frac{dT}{dt} = U \times A(T_s - T) \qquad \text{(Equation 5-1)}$$

$$\int_{T_a}^{T_b} \frac{dT}{(T_s - T)} = \frac{U \times A}{m_f \times C_p} \times \int_0^t dt \qquad \text{(Equation 5-2)}$$

Where: m_f = Mass flow rate of the feed in kg/day

T_a = Temperature of the feed = 25 °C

T_b =Target temperature = 70 °C

T_s = Temperature of the steam = 121 °C

C_p = Heat capacity of the feed in kJ/kg K

t = Extraction time = 4hr for 1st extraction

U = Heat transfer coefficient in kJ/h m^2 K

l_s=Heat of vaporization

H_c = Enthalpy of condensate = 580.46 kJ/kg at 121 °C

H_s= enthalpy of saturated vapor = 2,707.9 kJ/kg at 121 °C

A = Heat transfer area

m_s = Mass flow rate of steam in kg/day

$$\text{Mass of feed } m_f = 3{,}520.79\frac{kg}{day} + 7041.58 kg/day = 10{,}562.37\ kg/day$$

$$= 440.09 \text{ kg/hr}$$

Assume that U= 190 kJ/h m^2 K

$$\ln\frac{T_s - T_a}{T_s - T_b} = \frac{UA}{m_f C_P} t \qquad \text{(Equation 5-3)}$$

$$A = 1.42 m^2$$

$$m_s \lambda_s = UA\Delta T \qquad \text{(Equation 5-4)}$$

The heat of vaporization, λ_s, is the difference between the enthalpy of saturated vapor H_s and the enthalpy of condensate H_c leaving (Assumed here to be saturated liquid).

Enthalpy of saturated vapor H_s and the enthalpy of condensate H_c were found in smith unit operation of chemical engineering [41].

$$\lambda s = H_s - H_c = 2{,}199.4 \text{ kJ/kg} \qquad \text{(Equation 5-5)}$$

By using equation 5-3 mass of steam can be calculated as

$$m_s = \frac{UA\Delta T}{l_s} = 142.7\,\frac{kg}{day}$$

Energy balance on 2nd, 3rd and 4th extraction unit is calculated in the same manner.

B. Energy balance on 2nd extraction unit

Extraction time = 2 hr

Assume that the inlet temperature is $T_a = 50^{o}C$

Target temperature $T_b = 78^{o}C$

m_p is mass of the pelt = 2957.45 kg/day

Mass of water = 5914.9 kg/day

Mass of steam m_s=118.9 kg/day

C. Energy balance on the 3rd extraction

Extraction time = 1hr

Assume that the inlet temperature $T_a = 55^{o}C$

The target temperature $T_b = 85^{o}C$

m_{p3} mass of pelt after 2nd extraction = 2251.76kg/day

Mass of water = 4503.53 kg/day

By using the above information area is calculated as:

Mass of steam m_s=234.4kg/day

D. Energy balance 4th extraction unit

Extraction time = 1hr

Assume that the inlet temperature $T_a = 60^oC$

The target temperature $T_b = 90^oC$

m_{p4} mass of pelt after 3rd extraction = 1475.225 kg/day

Mass of water = 2950.45 kg/day

By using the above information area is calculated as:

Mass of steam m_s=171.6 kg/day

E. Energy balance on evaporator

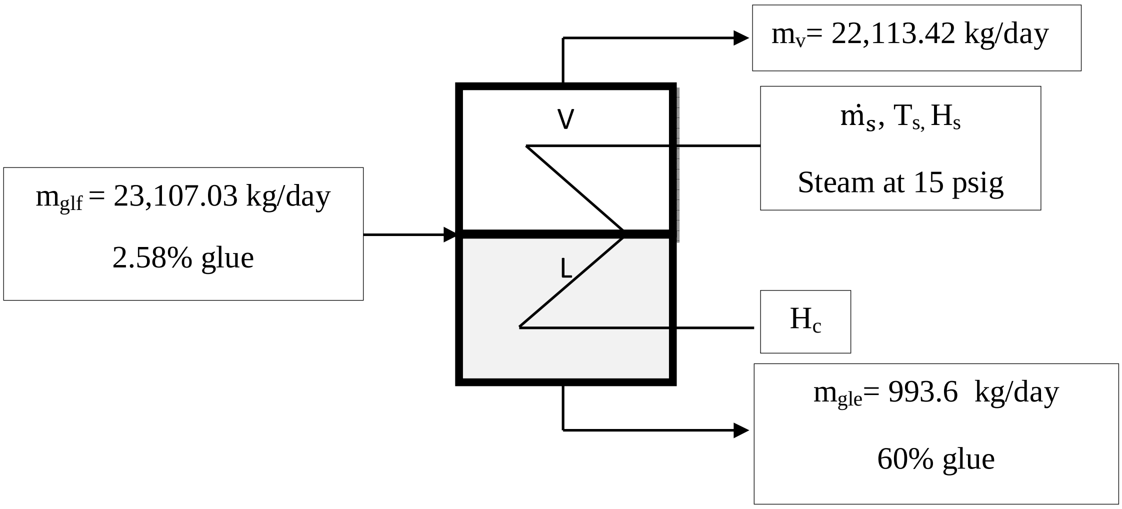


Figure 5.6. Flow diagram for energy balance on evaporator

Where m_{glf} = Mass of glue liquor after filtration kg/day

m_v = Mass of vapor in kg/hr

m_s= Mass of stream in kg/hr

m_{gle}= Mass of glue after evaporation in kg/hr

T_s = temperature of steam= 121 ^oC

T_a = Temperature of the feed = 25 ^oC

T_b =Target temperature = 70 ^oC

C_p = Heat capacity of the feed in kJ/kg K

U = Heat transfer coefficient in kJ/h m^2 K

ls=Heat of vaporization

H_c = Enthalpy of condensate = 580.46 kJ/kg at 121 ^oC

H_s= enthalpy of saturated vapor = 2,707.9 kJ/kg at 121 ^oC

A = Heat transfer area in m^2

P = Vacuum pressure

q= heat duty of heat exchanger in kJ/hr

H_f = Enthalpy of feed = $104.88\ kJ/kg$

To keep the boiling temperature low enough keep the vapor space under vacuum [41].

$$P = 4\ in\ Hg = 1.959\ lbf/in^2$$

The heat duty of the heat exchanger is just the heat gained by the feed in terms of enthalpies of the stream.

$$q = (m_v)H_v + (m_{gle})H - (m_{glf})H_f \qquad \text{(Equation 5-6)}$$

Neglect boiling point elevation and heat of dilution for high molecular weight substance [41]. Glues have high molecular weight so we can neglect boiling point elevation and heat of dilution.

Then the enthalpies of the feed and the liquid are essentially the properties of pure water under that condition.

At 25 ℃ = 77°F $\quad H_f = 45.09\ Btu/lb = 104.88\ kJ/kg$

Since the liquor is in equilibrium with the vapor, their temperature and pressure should be the same.

Since the vapor is just saturated steam at 4 in Hg, its temperature is take from steam table.

$H_v = 2{,}595 \frac{kJ}{kg}$ at $T = 51.7℃$ Were found in smith, unit operation of chemical engineering [41]

$$H_{ge} = 216.55\ kJ/kg$$

q = 55,176,023.67 kJ/day

= 2,299,000.986 kJ/ hr

The area required is calculated by using design equation

$$\mathrm{q = UA\Delta T_m} \qquad \text{(Equation 5-7)}$$

The driving force for heat transfer is the difference in temperature of saturated steam and saturated vapor.

$$\Delta \mathrm{T_m} \approx \mathrm{T_s} - \mathrm{T} = 69.33\ ℃$$

The pressure of steam is 15 psig = 29.7 psia

T is boiling temperature of concentrated liquid at p in vapor space

The heat of vaporization λs is the difference between the enthalpy of saturated vapor H_s and the enthalpy of condenset H_c leaving (Assumed here to be saturated liquid)

$$\lambda s = H_s - H_c = 2199.4\ kJ/kg$$

For long tube vertical evaporator with forced circulation heat transfer coefficient is range between 2000-5000 $w/m^2\ ^oC$ [41].

Assume that U= 3000 $w/m^2\ ^oC$

From the design equation the area is calculated as A = 11.053 m^2

$$m_s = \frac{q}{ls} = 1{,}045.28 \text{ kg/hr}$$

Capacity is just the rate of evaporation which will be the flow rate of vapor

$$\text{capacity} = m_f - m_{ge} = 22{,}113.42 \text{ kg/day}$$

The economy is the mass of vapor produced per mass of steam consumed

$$\text{economy} = \frac{m_f - m}{m_s} = 0.881 \qquad \text{(Equation 5-8)}$$

F. Energy balance on dryer

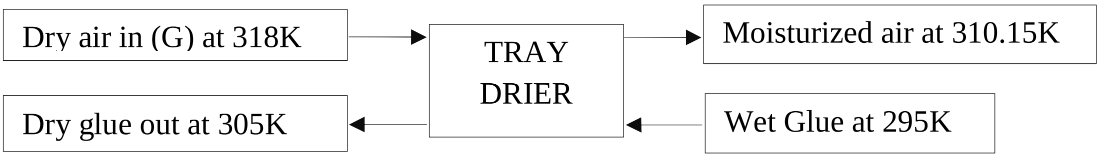


Figure 5.7. Flow diagram for energy balance on drier

In let condition: m_t = 993.6 kg/day with 40% moisture content at 295 K

Out let condition: m_g = 685.24 kg/day with 13% moisture content at 305 K

Assume that the air supplied which contain 0.6 % water vapor enters at 318.15K and the air leaves the dryer at 310.15 K.

Latent heat of water vapor at 295 K= 2449 kJ/kg

Specific heat capacity of dried glue is assumed to be 0.88kJ/kg K

Latent heat of water vapor and specific heat capacity of dried glue were estimated based on smith unit operation of chemical engineering [41].

Where m_t = mass of glue liquor before draying

m_g = mass of dry glue

C_{pair} = Heat capacity of dry air = 1kJ/kg K

C_{pw} = Heat capacity of water vapor = 2.01 kJ/kg K

G = mass of dry air

Air

G kg/hr air enters with 0.006 G kg/ s water vapor and hence the heat content of stream

$= [(1 \times \mathrm{G}) + (0.006 \times \mathrm{G} \times 2.01)(318.15 - 273) = 45.69\ Gkw$

Where G is mass flow rate of air

Wet solid

Mass flow rate of water = 397.44 kg/day=16.56 kg/hr

Mass flow rate of solid = 596.16 kg/day =24.84 kg/hr

Hence the heat contain of this stream is

$= [(16.56 \times 4.18) + (24.84 \times 0.88)](295 - 273) = 2{,}003.76\ \mathrm{kJ/hr}$

Outlet

Heat in the exit air

$= [(1 \times G) + (0.006 \times 2.01)](310 - 273)$ =37.44 Gkw

Mass flow rate of dry solid= 596.15 kg/day= 24.84 kg/hr

Leaving water in dried solid = $\left(\frac{0.13 \times 24.84}{1+0.13}\right)$ =2.86 kg/hr

The water evaporated in to the gas stream= $16.56 - 2.86 = 13.7\ kg/hr$

Assume that evaporation takes place at 295 K, and then heat the water vapor.

$= 13.7$ $[2.01(310 - 295) + 2449 + 4.18(295 - 273)]$ = 35,224.2kw

The total heat in this stream = $35{,}224.2\ +\ 37.44G$

Heat in dried solid

The dried solid contain 2.31 kg/hr water and hence heat content of this stream is

$= [(24.84 \times 0.88) + (2.86 \times 4.18)] \times (305 - 273) = 1071.9\ kw$

By using total heat balance equation

$\mathrm{G} = 4156.6\ \mathrm{kg/hr}$ and water in the out let stream = $41.67\,\frac{\mathrm{kg}}{\mathrm{hr}}$

5.3.Sizing of equipment

a) Sizing of washing tank

Mass of the pelt m_p = 2370 kg/day

Mass of water m_w = 7110.1 kg/day

Density of pelt = 980 kg/m^3

Density of the pelt is taken from perry chemical engineering hand book [43].

Volume water is calculated as 7.11 m^3/day

Volume of pelt is calculated as 2.418 m^3/day

$$\text{Total volume} = \text{volume of water} + \text{volume of pelt} = \frac{9.528\mathrm{m}^3}{\mathrm{day}} = 0.397\ \mathrm{m}^3/\mathrm{hr}$$

$$\text{The actual volume required} = \frac{0.397}{0.85} = 0.467\ \mathrm{m}^3 \approx 0.5\mathrm{m}^3$$

b) Sizing of soaking tank

Mass of the pelt m_{p1} = 2347.2 kg/day

Mass of water = 4694.4 kg/day

Mass of lime m_l = 469.4 kg/day

Density of lime = 963.87 kg/m^3

Density of lime was found in perry chemical engineering hand book [43]

Volume of the pelt V_{p1} =2.39 m^3/day

Volume of water = 4.69 m^3/day

Volume of lime = 0.486 m^3/day

$$\text{Total volume } = \text{ volume of water} + \text{volume of lime} + \text{volume of pelt } = 7.57m^3$$

$$\text{Actual volume required } = \frac{7.57}{0.85} = \ 8.9 \text{ m}^3 \approx 9\text{m}^3$$

c) Sizing of extraction unit

Sizing of the 1st extraction unit

$\mathrm{m_p} = 3{,}520.79 \text{ kg/day}$

$m_w = 7{,}041.58kg/day$

Volume of pelt = 3.6 m^3/day

Volume of water = 7.04 m^3/day

$$Total\ volume\ =\ 10.63\frac{m^3}{day} = 0.4429m^3/hr$$

1st extraction continue for 4 hr

Volume of glue = 1.771 m^3

Actual volume required = 1.94$\approx 2m^3$

$\text{Actual volume required for second extraction unit} = \ 1\text{m}^3$

$\text{Actual volume required for thrid extraction unit } = \ 0.5\text{m}^3$

$\text{Actual volume required for forth extraction unit} = 0.3\text{m}^3$

d) Sizing of filtration

$\frac{1}{\mathrm{A}}\frac{\mathrm{dV}}{\mathrm{dt}} = \frac{-\Delta\mathrm{P}}{\mathrm{r\mu l}}$ The basic filtration equation and r is termed as the specific resistance which is seen to depend on e and s.

$$r = \frac{5(1-e)^2 S^2}{e^3} \qquad \text{(Equation 5-9)}$$

Assume that r is constant

Where: V = The volume of filtrate which has passed at time t

A = The total cross sectional area of filter cake

l = The cake thickness

S = The specific surface of the particle

e = The void space

μ = The viscosity of filtrate

ΔP = The applied pressure difference

Viscosity of glue liquor taken as 10m.Ns/m2

Take that $\Delta P = 780\ \mathrm{kN/m^2}$ and $r = 11\times10^5\ \mathrm{m^{-2}}$

ΔP and r was found in coulson and Richardson's chemical engineering [42]

$$\frac{dV}{dt} = 2.702\ \times 10^{-4}\,\frac{m^3}{sec}$$

A is calculated as $23.9\mathrm{m^2}$

$$\text{Actual area required } = 28.11\mathrm{m^2} \approx 30\mathrm{m^2}$$

e) Sizing of dryer

Mass of glue liquor after evaporation = 993.6 kg/day

Density of glue liquor = 1080 $\mathrm{m^3}$/day

Volume of glue liquor after evaporation = 0.92 $\mathrm{m^3}$/day

The actual volume = $\frac{0.92}{0.85} = 1.08\ \mathrm{m^3} = 38.139\mathrm{ft^3} \approx 40\mathrm{ft^3}$

5.4.Plant cost estimation and cost analysis

To determine the cost benefit and feasibility of implementing glue production in ELICO leather factory, several factors must be considered. First, the raw material used for soaking must be determined (lime and sulfuric acid) as well as the concentration must be determined.

Next, an appropriate equipment and material must be selected. Finally the market for the glue product of each quality level must be considered. The selling price of glue is determined by the quality and grade of glue in addition to production and labor cost.

The equipment capacity and cost is shown in the following table. The equipment cost is taken from coulson and Richardson's volume 6 table 6.2.

$$\mathrm{C_e} = \mathrm{CS^n} \qquad \text{(Equation 5-10)}$$

Where: C_e = Purchased equipment cost

S= characteristic size parameter in units given in table 6.2 of coulson and Richardson

C= Constant from table 6.2

n= index for that type of equipment

Equipment cost which is found in coulson and Richardson is cost in 2004. To get the cost of equipment in 2011

$$\text{Cost in } 2011 = \text{Cost in } 2004 \times \frac{\text{Cost index in } 2011}{\text{Cost index in } 2004} \qquad \text{(Equation 5-11)}$$

Cost index in 2004 = 1340 and cost index in 2011 = 1550 [44]

Table 5.2: Equipment capacity and cost

Equipment type	**No**	**Capacity**	**Cost $**	**Total $**
Washing unit	2	0.5 m^3	623.6	1,247.25
Soaking unit	30	9 m^3	419.8	12, 594.32
Evaporator	1	25 m^2	127,988.09	117,803.96
Drier	1	40ft^3	11,404.66	11,404.66
Filter	1	30 m^3	48,294.52	45,294.52
Boiling vessel	4	2 m^3	7,481.4	15,616.6
		1 m^3	4,134.86	
		0.5 m^3	2,331.95	
		0.3 m^3	1,668.42	
			Total	203,961.31

Total equipment cost $ 203,961.31= 3,678,315.5 birr

Estimation of fluid solid fixed capital cost is taken from Coulson and Richardson's volume 6, table 6.1. [40].

The major direct costs to be added to PCE are listed below.

Equipment erection f_1=0.45, Piping f_2=0.45, Instrumentation f_3=0.15, Electrical f_4 = 0.1, building process f_5=0.1, Utility f_6 = 0.45, Storage f_7 = 0.2

Therefore, the total physical plant cost (PPC) or direct cost

$$\mathrm{PPC} = \mathrm{PCE}\,(1 + f_1 + f_2 + f_3 + f_4 + f_5 + f_6 + f_7) \qquad \text{(Equation 5-12)}$$

$$\mathrm{PPC} = 10,667{,}114.95\ \mathrm{birr}$$

The major indirect cost are design and engineering (f_{10}) = 0.25, contractor fee (f_{11}) = 0.05, contingency (f_{12}) = 0.10

$$\text{Fixed capital} = \mathrm{PPC}(1 + f_{10} + f_{11} + f_{12}) \qquad \text{(Equation 5-13)}$$

FCI= 14,933,960.93 birr

Working capital investment, 15% fixed capital investment

WCI = 10 % × 14,933,960.93 birr

= 1,493,396.09 birr

TCI = FCI + WCI = 16,427,357.02 birr

Annual operating cost,

Assuming operating day is 300 day/ year, and there are two basic cost in annual operation cost.

Fixed cost

Maintenance, take as 5% of fixed capital = 746,698.04 birr

Operating labour, 1 additional professional 3000 birr and 5 labor 1000 birr per each Total 96,000 birr /year

Supervision, no additional supervision would be needed

Plant overheads, take as 50% of operating labour = 48, 000 birr

Laboratory, take as 30% of operating labour = 28,800 birr

Insurance, 1% of fixed capital = 149,339.6 birr

Local taxes neglect

Royalties not applicable

Fixed cost = 1,068,837.6 birr

Variable cost

Raw materials: 5% w/w HCl = 18.63 m^3/ year

= 17,697 birr

Lime = 140.82 ton/year

= 249,768.65 birr

Total raw material cost = 267,447.65 birr

Cost of transport = 30,000 birr/ year

Miscellaneous materials, 10% of maintenance cost = 66,945.3 birr

Utility : Steam $513.86\frac{\text{ton}}{\text{year}} \times 237.048\ \text{birr/ton} = 121{,}810.43\text{birr}$

Electric = $40539.5\text{kJ} \times 0.37\frac{\text{birr}}{\text{kJ}} = 14{,}999.615\ \text{birr}$

Water = $11{,}855.7\ \frac{\text{m}^3}{\text{year}} \times 0.447\text{birr/m}^3$ = 5,301.19 birr

Total utility cost = 142,111.2 birr

Total variable cost = 506,504.2 birr

Sales expense and research and development cost is not considered.

Direct production cost (DPC) = Variable cost + Fixed cost = 1,575,341.7 birr

Production capacity of the factory = 205,572 kg glue/ year

Selling price of finished glue = 30 birr /kg

Sales income = 6,167,160 birr

$\text{Gross profit (Gp)} = \text{sales income} - \text{Total production cost (TPC)}$ (Equation 5-14)

GP = 4,591,818.3 birr

Depreciation cost (DC): Assuming 0 salvage value, 12 year service value and using straight line method

$$\text{DC} = \frac{(\text{Depreciable FCI} - \text{Salvage value})}{\text{Service life}} \qquad \text{(Equation 5-15)}$$

$$\text{DC} = 1{,}357{,}632.8\ \text{birr}$$

$$\text{Net profit (NP)} = 0.65\ \times \text{Gross profit (GP)} -\ \text{DC} \qquad \text{(Equation 5-16)}$$

NP= 2,095,755.454 birr

$$\text{Pay back period (PBP)} = \frac{\text{Depriciable FCI}}{\text{NP+DC}} \qquad \text{(Equation 5-17)}$$

$$= \frac{10{,}667{,}114.95}{2{,}095{,}755.454+1{,}357{,}632.8} = 3.08 \text{ year}$$

$$\text{Rate of return on the investment (ROR)} = \frac{\text{GP}}{\text{Total investment}} \qquad \text{(Equation5-18)}$$

$$\text{ROR} = 27.9\%$$

Financial appraisal of this project is based on the following assumptions

Construction period 1 year

Discount for cash flow (i) 10%

$DF_n = (\frac{1}{1+i})^n$

$PV = TCI \times DF_n$

$NCF_n = PV - 0.35 \times PV - D$

DF_n = Discounted cash flow

NCF_n= Annual net cash flow

Table 5.3: Project net present value

Year	Annual present value	Net present value
0	NCF_0= 16,427,354	-
1	PV= 14,933,958.1 NCF_1= 8,349,439.965	-8,077,914.035
2	PV= 13,576,325.62 NCF_2=7,466,978.853	-610,935.18
3	PV = 12,342,114.2 NCF_3=6,664,741.43	6,053,806.25
4	PV=11,220,103.82 NCF_4= 5,935,434.68	11,989,240.93
5	PV= 10,200,094.38 NCF_5= 5,272,428.54	17,261,669.48

6	PV=9,272,813.07 NCF_6=4,669,695.696	21,931,365.18
7	PV = 8,429,830.06 NCF_7= 4,121,756.739	26,053,121.92
8	PV = 7,663,481.878 NCF_8= 3,623,630.4	29,676,752.32
9	PV = 6,966,801.7 NCF_9= 3,170,788.305	32,847,540.63
10	PV = 6,333,456.098 NCF_{10}= 2,759,113.664	35,606,654.29
11	PV = 5,757,687.3 NCF_{11}= 2,384,863.954	37,991,518.24
12	PV= 5,234,261.258 NCF_{12}= 2,044,637.005	40,036,155.25
		NPV= 40,036,155.25

6. Conclusion and Recommendation

6.1.Conclusion

From this research work of determination of optimum condition for the production of commercially viable glue from tannery solid waste the following conclusion can be drawn.

The type of reagent used was found to be the most important factor affecting the quality and the quantity of glue. Results obtained showed that the better quality was achieved in 10% concentration of lime.

The increment in the concentration of reagent in both lime and sulfuric acid observed to increase the quality of the glue. However, the quality of glue will decline if the concentration goes beyond 10% concentration of sulfuric acid.

The soaking time positively affect the quality of the glue. On the contrary, the quality was negatively affected by boiling time.

The boiling temperature was also observed to affect the quality and the quantity of the glue. The boiling temperature has negative impact on quality of the glue and it has positive influence on the amount of glue produced. A boiling temperature at 70^oC was found to be the optimum boiling temperature.

The pH, moisture content and ash content of the glue were ranged from 5.5- 7.8, 11-15.97, and 1.23- 5.67 respectively. These values are the same as the value in the literature as it described in section 3. The optimum condition for production of commercially viable glue was obtained at 4 week soaking of the pelt with 10% concentration lime then boiled at 70^oC. At this condition the viscosity, the yield and the mass of residue was 255.05 mP, 0.1357g / g of pelt and 0.32287 g/ g of pelt respectively.

In this research economic feasibility of commercially viable glue was done, the total capital investment required is estimated as birr 16.42 million. The project is financially viable with 27.9% rate of return of the project, the payback period of 3.08 year and net present value of 40.036 million birr.

6.2.Recommendation

From the aforementioned outputs obtained from the study on the optimization of glue production, the following points are recommended:

- ✓ In the present study, viscosity was one of the property that was taken into consideration to test the quality of the glue. The absence of equipments/ devices like Bloom Calorie meter makes the determination of other crucial characteristics, i.e., jelly strength, impossible. Hence, future studies should include determination of jelly strength to grade the quality of glue more precisely.
- ✓ Further studies should be designed in the way to produce water resistant glue.
- ✓ The present study only utilizes fleshing wastes and trimmings to recycle and produce glue. However, in this study, it is highly recommended that studies in the future should consider all other leather wastes in the reutilization process.

References

1. Kolomaznik, K., Adamek, M., Andel, L. and Uhlirola, M. (2008). Leather waste-potential threat to human health, and a new technology of its treatment. *J. Hazard. Mater*. **151**(2-3): 514-520.
2. Ozgunay, H., Colak, S., Mutlu, M.M. and Akyuz, F. (2007). Characterization of leather Industry waste. *J. Environ. Stud*. **16**(6): 867-873.
3. European Commission, Integrated pollution prevention and control (IPPC). Reference document on best available techniques for the tanning of hides and skin, February 2003.
4. Karabay, S., Waste management in leather industry, Dokuz Eylul Univerisity, Natural and applied science, thesis, 2008
5. Sayers, R. H., and Langlais, R. J. (Dec 1977). Removal ond recovery of sulfide from tannery waste water. Retrived on January 11/2011.
   URL: http://www.p2pays.org/ref/11/10640.pdf
6. Kanagaraj, J., Velappan, K. C., Chandra Babu, N. K. and Sadulla S. (2006). Solid Waste Generation in the Leather Industry and its Utilization for Cleaner Environemtal - A Review. *J. Sci. and ind. Research*. **65:** 541-548.
7. Aftab, M. N., Hameed, A., Ul-Haq, I., Sheng, R. C. (2006). Biodegradation of leather waste by enzymatic treatment. *J. Chinese process eng.* **6**(3): 462-465.
8. Environmental Pollution and Control in Chemical Process Industries.*1st ed. Bhatia,* S. C., 2003. Khanna Publishers. New Delhi:pp. 776-786.
9. Environmental management guide line for the leather tanning and finishing industry, Environmental Advisory Assistance for industry, 1997, Thailand. PN 2000.2266.5-001.00.
10. *Hand Book of Leather and Leather Products Technology.*EIRI Board of Consultants and Engineers.
11. European commission. 2003. Integrated pollution prevention and control (IPPC), Reference document on best available techniques for the tanning of hides and skin.
12. *Practical Leather Technology,* Thomas, C. T., 1993. Krieger Publisher. Malabar Florida
13. Pocket book for the leather technologist, 4th ed. BASF. Germany: pp 48-85. URL:http://www.basf.com/leather.
14. Idris, A., saed, K. and Hung, Y. T. (2010). Environmental bioengineering: Hand book of environmental engineering. J. springer Science. **11**: 685-699.

15. Anbalagan, K., Karthikeyan, G., and Narayanasamy, N. (1997). Assessing pollution from tannery effluents in south India village. PLA notes 30:3-6
16. An assessment of environmental concerns in the leather industry and proposed remedies: a case study of Pakistan. Dr. Javed Ahmad Chattha and M. Mobeen Shaukat GIK Institute of Engineering Sciences and Technology Topi, Dist. Swabi NWFP,Pakistan
17. Nawaz, H., Solangi, A., Nadeem, U., Nazehra, B. (2010). Preparation of High Exhaust Chrome for Leather Shavings and Hydrocarbons with its Application in Leather Processing for Green Tanning Technology. *J. chem. Soc. Pak.* **32**(4):525-530
18. How product are made: Glue. Retrieved on December 24/2010
    URL: http://www.madehow.com/volume.5/Glue.html.
19. Environmental Engineering. 4th ed. Ruth F. Weiner and Robin A. Matthews. 2003. An imprint of Elsevier science: New York
20. Environmental Engineering. 5th ed. Joseph A. Salvato, Nelson L. Nemerow and Franklin J. Agardy. 2003. John wiley and sons, Inc publisher: New Jersey
21. Tchobanoglous, George, Burton, Franklin L and Stensel, David H, [ed.]. *Waste Water Engineering Treatment and Reuse.* Fourth edition. s.l. : Mc Graw Hill, 2003.
22. Desrochers, P. *(*2001). Market Processes and the Closing of " Industrial Loops" A Historical Reappraisal. *Journal of Industrial ecology*. **4** (1): 29-43
23. Tudunwada, Y. I., Essiet, E. U. and Mohammed, S. G. (2007). The effect of Tannery Sludge on Heavy Metals Concentrated in cereals on small holding forms in Kano Nigeria*.* Not. Bot. Hort. Agrobot. Cluj, **35**(2): 55-60.
24. United States Department of agriculture Forest Service. (1955). Animal Glue: Their Manufacture, Testing, and Preparation. Agriculture , Forest Production Laboratory. USA : University of Wisconsin, 492.
25. IUE: Recommendation for tannery solid waste product management: (2008). URL:http://wwwiultcs.org/pdf/IUE2-2008.pdf
26. Mokrejs, P., Langmaier, F., Mladek, M., Janavcova, D., Kolomaznik, K., and Vasek, V. (2009) .Waste management and research, extraction of collagen and gelatin from meat industry by product for food and non food use. Retrived on January 19/ 2011.
    URL:http://www.sagepub.com/content/27/1/31

27. Cabeza, L. F., Mcaloon, A. J., Yee, W. C., Taylor, M. M., Brown, E. M. and Marmer, W. N. Process simulation and cost estimation of treatment of chromium containing leather waste.
28. Langmaier, F., Mokreis, P., Karnos, R., Mladek, M., and kolomaznic, K. (2005). Modification of chrome tanned leather waste hydrolysate with epichlorhydrin. *J. soc. of leather techno. and chem.* **90**:29-34.
29. Hand World lingo, Animal glue. Retrieved on Nov 27 2010,

    URL:http://www.worldingo.com/ma/enwiki/en/animalglueanf.htm
30. J. Rank, 2010.Glue. Retrieved on Nov 28 2010 from

    URL:http://www.diamondtapes.ae/howgluemade
31. Hand Book of Adhesive Technology. 2nd ed. Charles L. pearson. 2003. Taylor and francis group: USA
32. Allen, S. W. and Truax, T. R. (1922). Glues used in Air plane parts. United state department of agriculture. Repore no 66.
33. Hide glue production. Retrieved on February 2/2011. URL: http://www.bjorn.net/prod.htm.
34. All about Hide Glue. Retrieved on Nov 30 2010 from

    URL:http://www.naturalpigments.com/detail.asp?product_ID=510-21RSGLU
35. Glues. Retrieved on February 22/2011
    URL: http://www.primeryinfo.com/animal-glue.htm.
36. Endt, W. D., and Baker, T. B. (2010). The chemistry of filled animal system. Retrieved on November 23/2011. URL: http:albumin.conservation-us.org/library/c20/vonedtl1991.
37. Testing of glue. retrived on 27 April 2011
    URL:http://www.oldandsold.com/articles30/glue-2,shtml
38. Engineering optimization. Theory and practice 3rd edition singiresu s.rao. A wiley interscience publition. New york 1996
39. Encyclopedia of chemical technology. Thomas, R. K. John Wiley and Sons. Inc. V12.Pp 436-440
    URL: http://www.scribd.com/doc/30116669
40. Chemical engineering design, Coulson and Richardson's engineering series. 4th ed. 2005. Sinnott, R. K., Elsevier publisher. V6. PP

41. Unit operations of chemical engineering. 7th ed.2005. McCabe, W. L., Smith, J. C., Harriott, P., Mc Graw- Hill publisher. Singapore. Pp 486-515
42. Colson and Richardson's chemical engineering, Particle Technology and separation process. 5th ed. 2002. Richardson, J. F., Harker, J. H. and Backhurst, J.R., Elsevier publisher. V2. PP 776-790
43. Perry chemical engineering hand book. 7th ed. Perry, R. H., Green, D. W.
44. Plant design and economics for chemical engineers. 4th ed. 1991. Peters, M. S. and Timmerhaus, K. D. Singapore.

Annex 1

Design expert out puts for the experiments conducted in chapter 3.

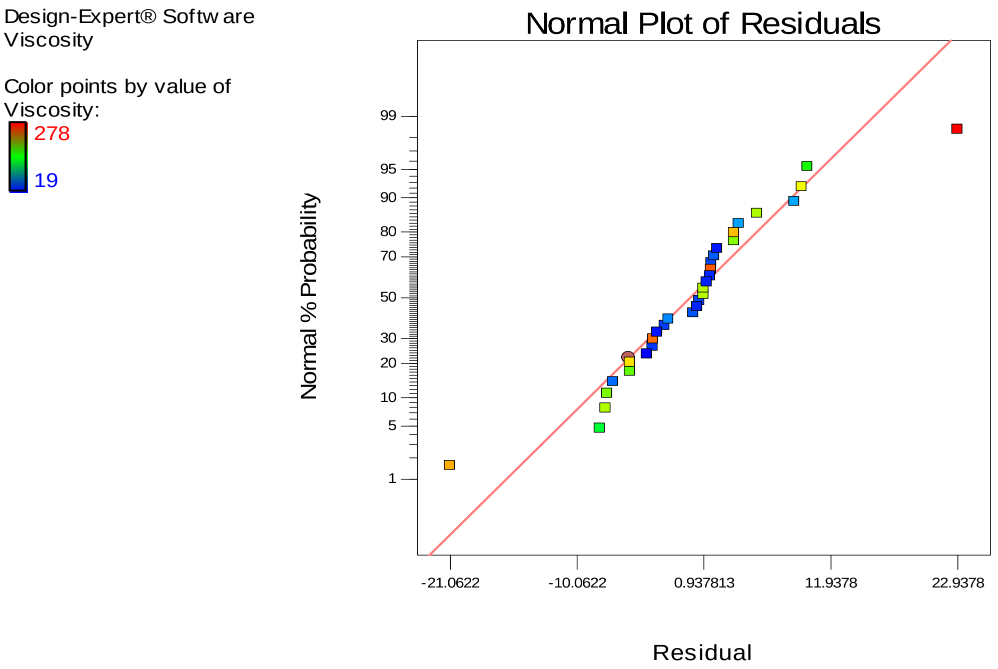
ANOVA analysis result and Residual plot for the experiment 3.2.4

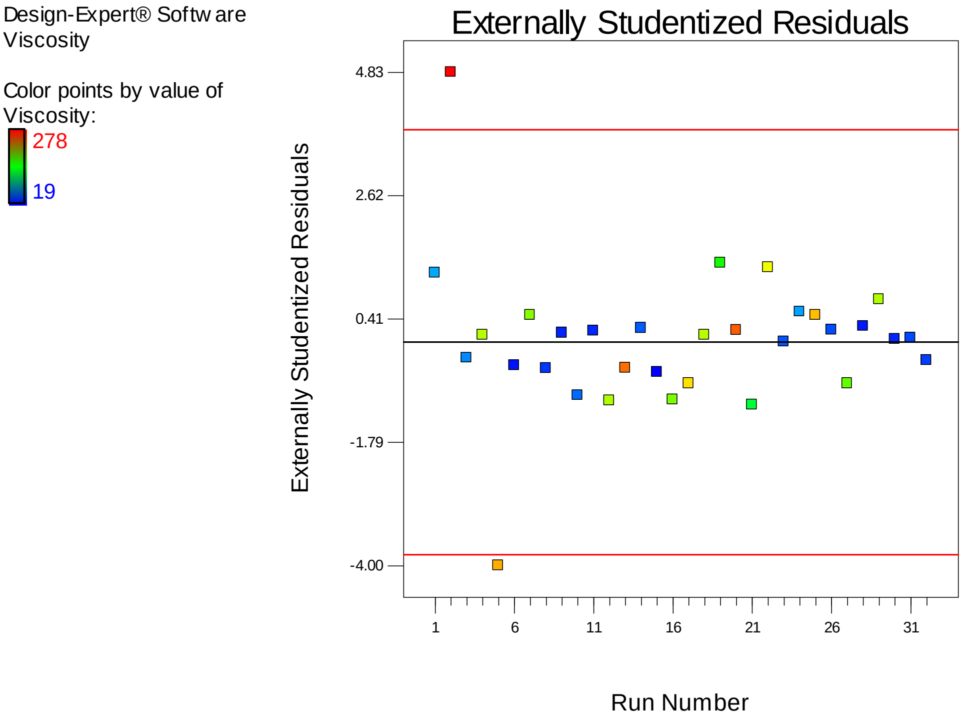
Response 1 Viscosity

ANOVA for selected factorial model

Source	**Sum of squares**	**Df**	**Mean Square**	**F Value**	**p-value Prob > F**
Model	2.466E+005	14	17616.89	179.32	< 0.0001
A-Type of chemical	2.241E+005	1	2.241E+005	2280.94	*significant*
B-Concentration	2527.78	1	2527.78	25.73	*< 0.0001*
C- Time	666.03	1	666.03	6.78	*< 0.0001*
D- Temperature	3124.25	1	3124.25	31.80	*0.0185*
AB	3394.67	1	3394.67	34.55	*< 0.0001*
AC	1250.13	1	1250.13	12.73	*< 0.0001*
AD	1032.96	1	1032.96	10.51	*0.0024*
BC	520.11	1	520.11	5.29	*0.0048*
BD	2987.45	1	2987.45	30.41	*0.0343*
ABC	2983.59	1	2983.59	30.37	*< 0.0001*
ABD	768.42	1	768.42	7.82	*< 0.0001*
ACD	1458.14	1	1458.14	14.84	*0.0124*
BCD	504.11	1	504.11	5.13	*0.0013*
ABCD	1338.90	1	1338.90	13.63	*0.0369*
Residual	1670.08	17	98.24		*0.0018*
Lack of Fit	28.14	1	28.14	0.27	
Pure Error	1641.94	16	102.62		*0.6077 not significant*
Cor Total	2.483E+005	31			

Analysis of variance table [Partial sum of squares - Type III]


Design-Expert® Software
Viscosity
Color points by value of Viscosity:
278
19
Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-21.0622
-10.0622
0.937813
11.9378
22.9378
Residual

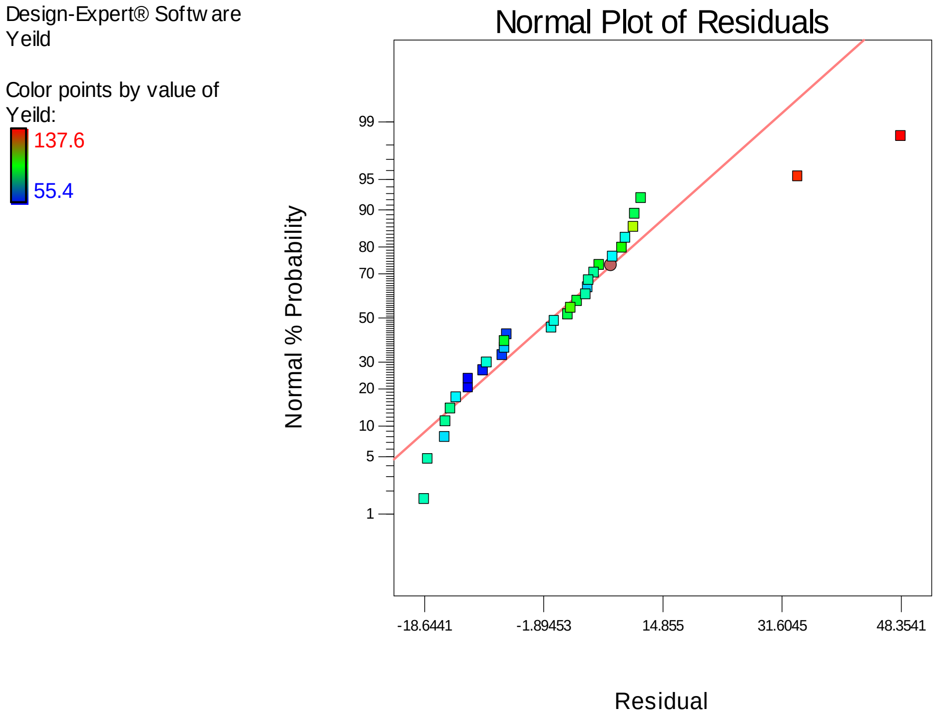

Design-Expert® Software
Viscosity
Color points by value of Viscosity:
278
19
Externally Studentized Residuals
Externally Studentized Residuals
4.83
2.62
0.41
-1.79
-4.00
1
6
11
16
21
26
31
Run Number

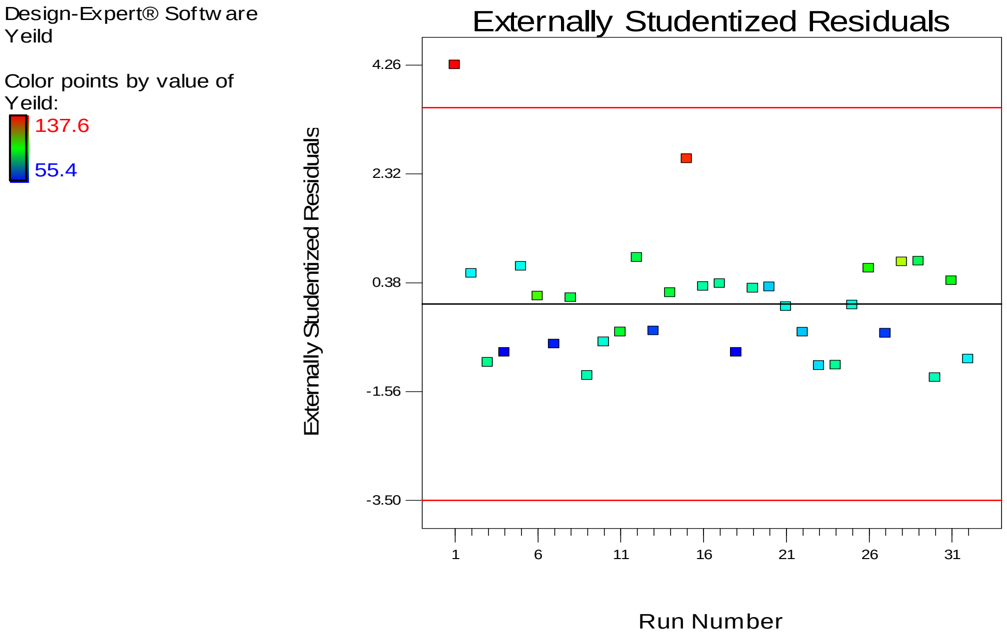
Response 2 Yeild

ANOVA for selected factorial model

Source	**Sum of square**	**df**	**Mean square**	**F value**	**P-value Prob > F**
Model	4628.57	2	2314.28	10.24	0.0004 *significant*
A-type of chemical	3660.90	1	3660.90	16.19	0.0004
D-Temprature	967.67	1	967.67	4.28	0.0476
Residual	6556.40	29	226.08		
Lack of Fit	3623.66	13	278.74	1.52	0.2115 *Not significant*
Pure Error	2932.75	16	183.30		
Cor Total	11184.97	31			

Analysis of variance table [Partial sum of squares - Type III]



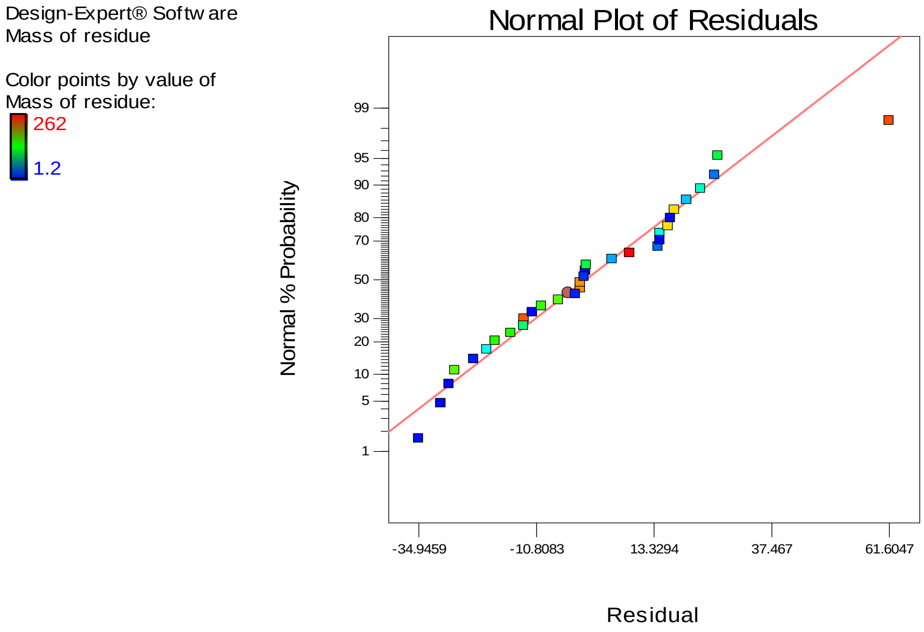


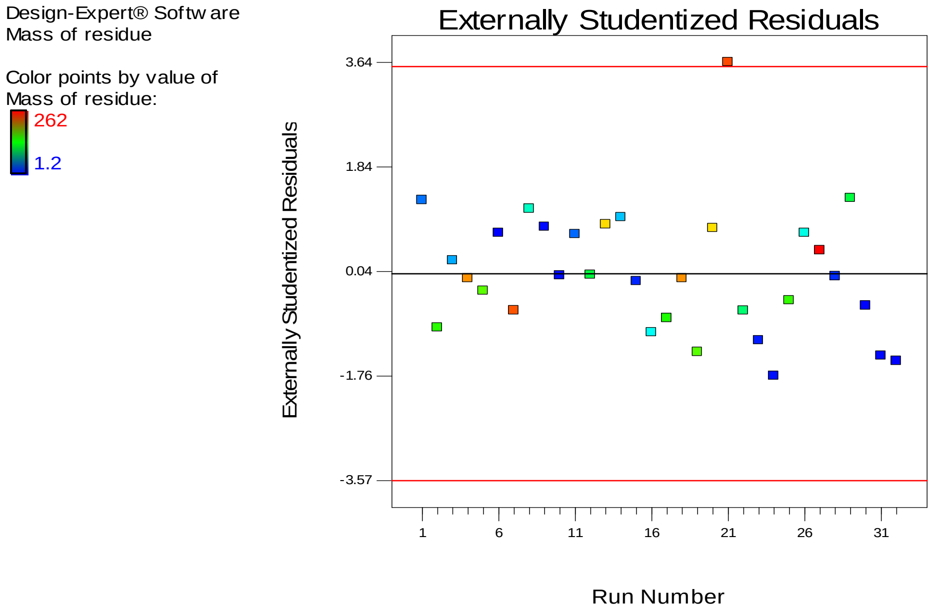
Response 3 Mass of residue

ANOVA for selected factorial model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of square**	**df**	**Mean square**	**F value**	**P-value Prob > F**	
Model	2.251E+005	6	37520.43	68.72	< 0.0001	*significant*
A-type of chemical	1.774E+005	1	1.774E+005	*324.84*	< 0.0001	
B-Concentration	16901.79	1	16901.79	*30.96*	< 0.0001	
C-Time	5822.01	1	5822.01	*10.66*	0.0032	
D-Temprature	16299.60	1	16299.60	*29.85*	< 0.0001	
AB	2956.61	1	2956.61	*5.42*	0.0284	
AD	5777.32	1	5777.32	*10.58*	0.0033	
Residual	13650.07	25	546.00			
Lack of Fit	5666.39	9	629.60	*1.26*	0.3278	*not significant*
Pure Error	7983.69	16	498.98			
Cor Total	2.388E+005	31				


Design-Expert® Software
Mass of residue
Color points by value of
Mass of residue:
262
1.2
Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-34.9459
-10.8083
13.3294
37.467
61.6047
Residual


Design-Expert® Software
Mass of residue
Color points by value of
Mass of residue:
262
1.2
Externally Studentized Residuals
Externally Studentized Residuals
3.64
1.84
0.04
-1.76
-3.57
1
6
11
16
21
26
31
Run Number

Response 4 *pH*

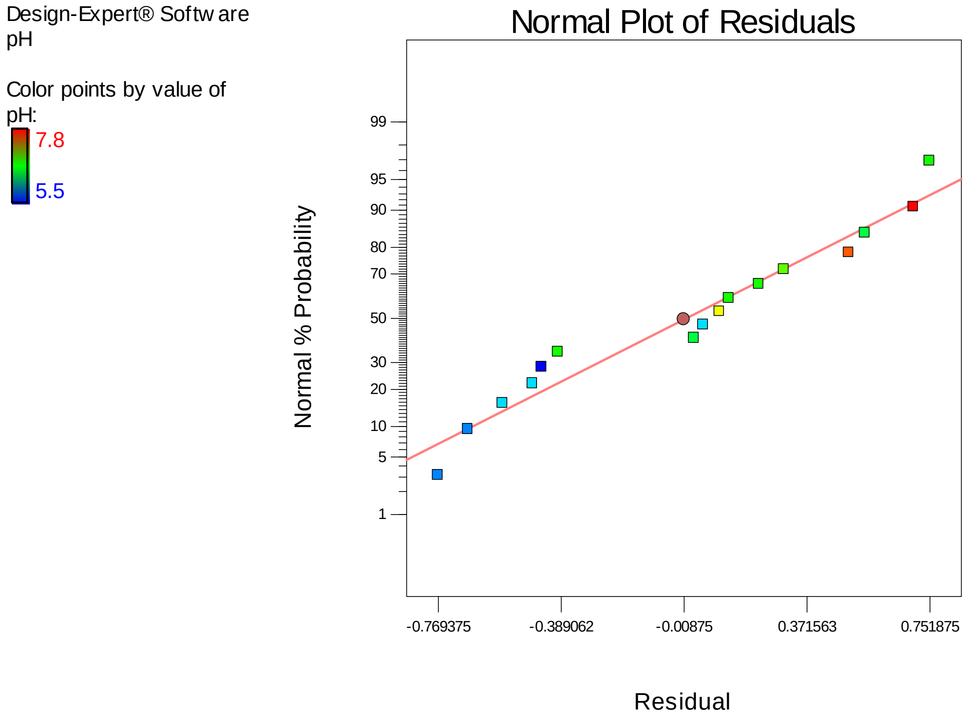
ANOVA for selected factorial model

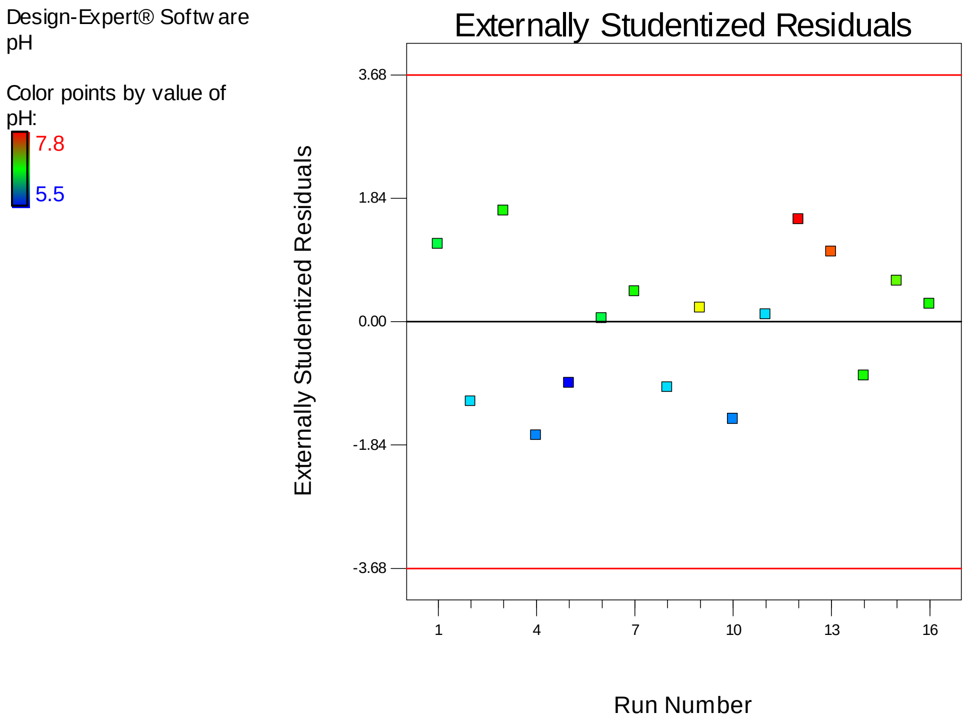
Analysis of variance table [Partial sum of squares - Type III]

Design expert out puts for the experiments conducted in chapter 3.

ANOVA analysis result and Residual plot for the experiment

Source	**Sum of Square**	**Df**	**Mean square**	**F Value**	**p-value Prob > F**	
Model	2.66	2	1.33	4.62	0.0305	*Significant*
C-Time	1.12	1	1.12	3.88	0.0705	
BC	1.54	1	1.54	5.36	0.0376	
Residual	3.75	13	0.29			
Lack of Fit	2.09	5	0.42	2.03	0.1790	*not significant*
Pure Error	1.65	8	0.21			
Cor Total	6.41	15				





Response 5 Moisture content

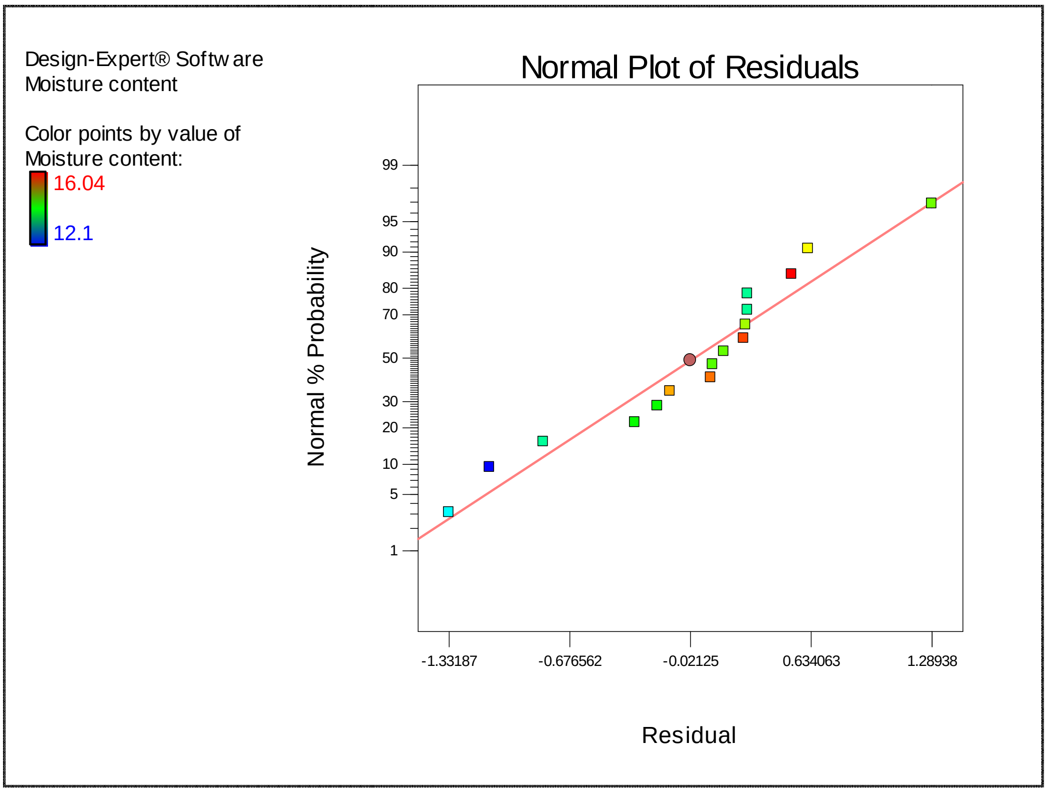
ANOVA for selected factorial model

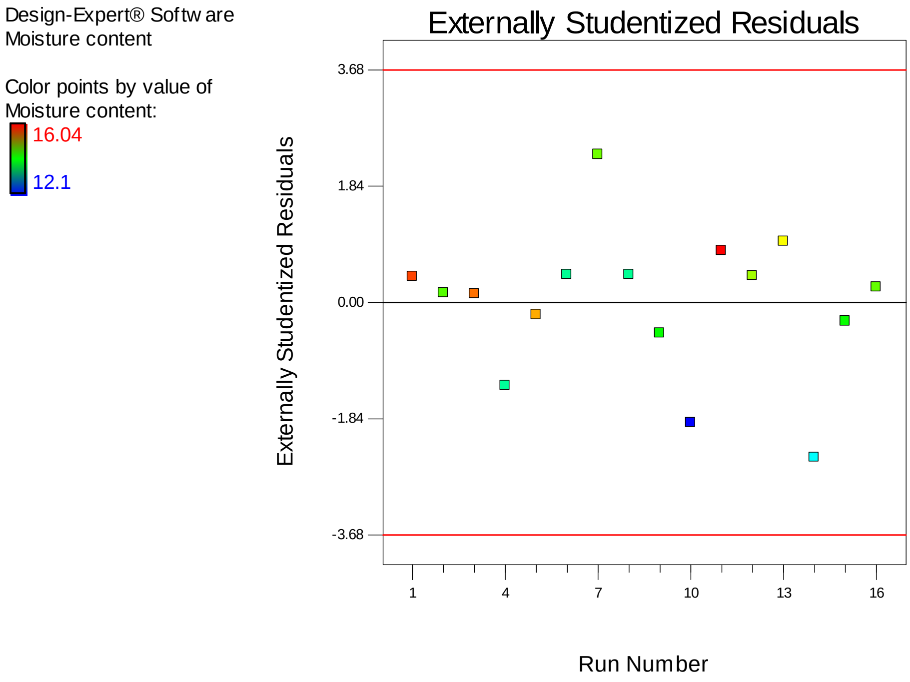
Analysis of variance table [Partial sum of squares - Type III]

Design expert out puts for the experiments conducted in chapter 3.

ANOVA analysis result and Residual plot for the experiment

Source	**Sum of Square**	**df**	**Mean square**	**F Value**	**p-value Prob > F**
Model	10.61	2	5.31	10.57	0.0019 *Significant*
B-Concentration	5.87	1	5.87	11.69	0.0046
C-Time	4.74	1	4.74	9.45	0.0089
Residual	6.53	13	0.50		
Lack of Fit	2.55	5	0.51	1.03	0.4630 *Not significant*
Pure Error	3.98	8	0.50		
Cor Total	17.14	15			


Design-Expert® Software
Moisture content
Color points by value of
Moisture content:
16.04
12.1
Normal Plot of Residuals
Normal % Probability
99
95
90
80
70
50
30
20
10
5
1
-1.33187
-0.676562
-0.02125
0.634063
1.28938
Residual


Design-Expert® Software
Moisture content
Color points by value of
Moisture content:
16.04
12.1
Externally Studentized Residuals
Externally Studentized Residuals
3.68
1.84
0.00
-1.84
-3.68
1
4
7
10
13
16
Run Number