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Chemical and Bio Engineering

Manufacturing of synthetic tanning agent from kraft lignin

By

Tewodros kassa

September, 2014

Addis Ababa

Addis Ababa University
School of Graduate Studies
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Department of Chemical Engineering

A Thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in Partial Fulfilment of the Requirements for the Attainment of the Degree of Masters of Science in Chemical Engineering Under leather technology Stream.

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Tewodros Kassa

Advisor
Dr. J RaghavaRao
(Chief Scientist, Chemical Laboratory, CSIR – CLRI)

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Approved by the Examining Board:

_____	_____
Chairman, Department's Graduate Committee	
_____	_____
Advisor	
_____	_____
Internal Examiner	
_____	_____
External Examiner	

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List of abbreviation

GDP	Growth domestic product
Fe ²⁺	Ferrous ion
H ₂ O ₂	Hydrogen per oxide
RPM	Revolution per minute
EA	Ethyl acetate
DCM	Dichloromethane
FT-IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
GPC	Gel permeation chromatography
ANOVA	Analysis of variance
CCD	Central composite design
SD	standard deviation
Syntan	synthetic tanning agent
DLS	Dynamic light scattering
Temp	Temperature

Abstract

In chromium tanning adsorptive processes are minimal and leading to empty inter fibrillar spaces. Of these, the phenolic syntans are used which prepared from petroleum by products such as phenol, naphthalene and cresol. Being petroleum by products, the cost of these products is highly fluctuating. Therefore there is a need to evaluate alternatives for these products. In the current work, an effort has been made to develop phenolic synthetic tanning agent from waste of paper and pulp industry. Black liquor from pulp and paper waste was obtained and fully characterized. The treatment of this lignin with ferrous sulfate and hydrogen peroxide (5, 15 and 25 mmol of the reagent) and reaction temperature (25 °C, 45 °C and 65 °C) induces an extensive degradation in the native lignin. The effects of amount of H₂O₂ concentration, Fe²⁺ concentration and reaction temperature on percentage of were determined by using Design Expert 7.0.0 software three factor Central Composite Design. As observed from optimized design at H₂O₂ concentration of 25 mmol, Fe²⁺ concentration of 15 mmol and 45 °C the maximum percentage of lignin degradation was found 76.91%. Syntan preparation stage were investigated viz, sulphonation temperature, type of sulphonation agent, duration of reaction and amount of formaldehyde. The combined sulphonation product of sulphuric acid and sodium meta bisulfite (SS2) show better softens, roundness and grain smoothness and colour. Emission load of TS for commercial phenolic syntan is 43.61, whereas there is reduction in TS load by 41.7%-24.1% has been observed using lignin based syntan.

Key word: *Lignin degradation; Kraft black liquor; syntans; Hydrogen peroxide; Ferrous ion; free formaldehyde*

Chapter one

Introduction

1.1 background

The Ethiopian GDP is predominated by its agriculture (42%) and service sector (46%) as of 2010/11. Manufacturing accounts for 13% of its GDP, with leather industry occupying a predominant position amongst the manufacturing sectors (1). Thanks to the predominant role for agriculture and a large rural population, Ethiopia has 53.4 million cattle, 25.5 million sheep and 22.7 million goats. 6% of the total employment in Ethiopian manufacturing sector is in leather industry (2). Most of the tanneries are equipped to process available raw material, but working to below their capacity. This has been attributed to acute shortage of quality hides and skins; poor animal husbandry and veterinary services; traditional ways of slaughtering and poor collection and handling of hides/skins (3). There is thus a serious need to upgrade the quality of the leather through processing methodologies.

Ease of processing, shorter duration of processing, versatility for multitude of applications ranging from gloves to uppers has made chrome tanning the most predominant method of tanning. In this method, basic chromium(III) sulfate is offered to hides/skins, at a pH where its aspartic and glutamic acid residues are masked (4). Following the diffusion of chromium(III), the pH is increased, whereby Cr(III) forms coordinate covalent linkages with these groups. In other methods of tanning such as vegetable tanning, the process is dominated by adsorption of large quantities of polyphenols, which form H-bond networks with protein alongside filling of inter fibrillar spaces (5). In chromium tanning, such adsorptive processes are minimal – leading to empty inter fibrillar spaces. Such types of leathers are classified as lacking fullness and could lead to wrinkles on wear, which is enhanced further due to poor quality of the raw material. To prevent this and enhance the quality of the leather, chrome tanned leathers are retanned with natural polyphenols and phenolic auxiliaries for improved fullness (6).

In the case of lightweight leathers, like those meant for garments, softy upper etc., the use of natural polyphenols for retanning applications is limited as they add weight to the leather (7). The retanning in such cases is composed of combination of phenolic and polymeric resins. Of

these, the phenolic syntans are prepared from petroleum byproducts such as phenol, naphthalene, cresol etc. These low molecular weight compounds are condensed and sulphonated to yield high molecular weight water-soluble products for retanning. Being petroleum byproducts, the cost of these products is highly fluctuating. Therefore there is a need to evaluate alternatives for these products. This includes biopolymers amongst several others. Incidentally, biopolymers like polysaccharides and lignin have been employed as fillers in synthetic tanning agents (8).

Of the three major natural polymers that make up ordinary plants, viz., lignin, cellulose and hemicellulose, lignin is the second abundant and only biomass constituent with aromatic units (9). It acts as essential glue for providing the structural integrity in plants (10). Pulp and paper industry is one of the polluting industry in the world, more so in developing nations where there is no much technology and financial preparedness. The conversion of wood chips to pulp for manufacturing paper by Kraft pulping process generates huge quantities of kraft lignin as byproducts (11). The effluent of the paper industry contains varying quantities of organics depending on the type of process adopted by the paper industry. For instance, cook of paper grade contains about 29-45% lignin compared to that from a liner grade cook that contains 8-16% lignin (10). Composition of the black liquor is detailed in Table 1.1.

Table 1.1:- Composition of black liquor (12)

Elements	Weight (%)	Organic matter	Weight (%)
Carbon	34-39	Lignin	29-45
Oxygen	33-38	Hydroxyl acid	25-35
Sodium	17-25	Extractive	3-5
Hydrogen	3-5	Acetic acid	3
Sulphur	3-7	Methanol	1
Potassium	0.1-2	Formic acid	5
Chlorine	0.2-2		

1.2 Statement of problem

Ethiopian leather industry stands to grow in leaps and bounds over the next decade or so. All the ingredients required for achieving high export targets such as raw material, human resources, favorable government policies etc. are available for this industry. Based on these, the Ministry of Industry has set an ambitious target of USD 500 million by the year 2015 for this industry. One of the limiting factors for this industry is the dependence on imported chemicals for leather processing. Substitution of imported chemicals with indigenous products based on locally available material, preferably of low/negligible cost would be ideal.

Substituting conventional aromatic compounds such as phenol, naphthalene, dicyandiamide, melamine etc. with lignin present in the black liquor laying emphasis on the monitored degradation of lignin so as to avoid condensation employing formaldehyde, a suspected carcinogen of category 3 as classified by European Union leading to an indigenous synthetic tanning agent is the background of this research.

There are also other syntan such as acrylic polymeric tanning agent which do not contain formaldehyde however, they cannot fulfill specific property like fullness especially the loosely structure area of the hide. In this course of study the degradation process will be monitor in order to meet final molecular weight for phenolic based syntan by adjusting its duration and catalytic agent. one of multidimensional benefits of this study is to eliminate or minimize the application of formaldehyde in manufacturing of syntan without compromising specific property such as softness, fullness and grain tightness of final leather.

1.3 Objective

1.3.1 General objective

The general objective of this study is to develop a synthetic tanning agent, with performance comparable to commercial phenolic products based on lignin obtained from black liquor, waste of the paper and pulp industry laying emphasis to the avoidance of condensation using formaldehyde

1.3.2 Specific objective

Specific objective of this study are:-

- To characterize black liquor from pulp and paper industry waste.

- To Degrade Kraft lignin in black liquor to produce phenolic compounds by using chemical oxidation.
- To study the effect of hydrogen peroxide concentration on the degradation process.
- To investigate the effect of iron (II) sulfate concentration on degradation process.
- To study effect of reaction temperature on degradation process.
- To prepare and characterize synthetic tanning agent from degraded kraft lignin by using sulphonation and condensation polymerization process.
- To study the effect of sulphonation agent (sulfuric acid, sodium metabisulfite) on syntan manufacturing process.
- To evaluate the performance of the syntan on the leather.
- Characterization of waste water by comparing the lignin based syntan with commercial available phenolic syntans.

1.4 Significant of the research

Quantitative and qualitative finding of this research will enhance knowledge and understanding on the potential utilization of Kraft lignin for syntan manufacturing. This study should be significant in a way that it will:-

- Add value on pulp and paper industry byproduct (Kraft lignin) and produce input raw material (syntan) for leather industry.
- Provide alternative source (kraft lignin) to expensive raw material like naphthalene for the preparation of synthetic tanning agent.
- Minimize the significant environmental aspect and impact of Kraft lignin.
- Avoid treatment cost in pulp and paper industry.
- Minimize the amount of free formaldehyde present in the syntan due to limited usage of formaldehyde in condensation polymerization process.
- Help as a base line for other researchers who further study on this area beyond the scope of this study.

1.5 Scope of the project

This thesis work covers collection of black liquor from local pulp and paper industry and conduct experimental analysis on degradation and extraction of Kraft lignin from black liquor. Then the extract kraft lignin would be used as raw material for preparing syntan and evaluate its performance on leather.

CHAPTER TWO

Literature review

2.1 lignin overview

2.1.1 Chemistry of lignin

Wood is composed of many chemical components, primarily extractives, carbohydrates, and lignin, which are distributed non uniformly as the result of anatomical structure where it mainly consists of cellulose, hemicellulose and lignin. The proportions differ depending on the type of wood (see Table 1.1). Another component group in wood is extractives, which constitutes several percent of the wood. The composition of extractives varies considerably between wood types, and their function primarily is to protect the tree against fungi and insects (13, 14).

Table 2.1:- chemical composition of different types of wood (13)

Wood type	Cellulose (%)	Lignin (%)	Hemicellulose (%)
Soft wood	40-45	25-30	25-30
Hard wood	40-45	20-25	30-35
Eucalypt	45	30	20

2.1.1.1 Cellulose

Cellulose is the most common polymer in nature and the main constituent in lignocellulosic materials, representing 40-60% of its total weight in wood (15). It is a linear polymer, built up of β -D-glucopyranose units linked to each other by glucosidic bonds (16). The average degree of polymerization for wood cellulose is between 8 000 and 10 000 (17). The cellulose chains can aggregate together by forming intra- and intermolecular hydrogen bonds, thus forming microfibrils, in which highly ordered (crystalline) regions alternate with less ordered regions (18). According to the degree of crystallinity, cellulose is classified into crystalline and paracrystalline (amorphous) cellulose (19)

2.1.1.2 Hemicellulose

Hemicelluloses are a group of hetero polysaccharides with shorter chains and are more branched as compared to cellulose and found in the primary and secondary cell walls constituting the second most abundant polysaccharide in nature. Hemicelluloses function as a supporting material in the cell walls. The average degree of polymerization for hemicelluloses is approximately 200 (16). They are classically defined as alkali soluble material after removal of peptic substances, and have a much lower degree of polymerization compared with that of cellulose (20). The structure of hemicelluloses is different in softwoods and hardwoods. The softwood hemicelluloses mainly consist of galactoglucomannans and arabinoglucuronoxylan. In hardwoods, the main hemicellulose is glucuronoxylan, but glucomannan also exists (16, 21).

2.1.1.3 Lignin

The term lignin is derived from the Latin word for wood *lignum*. Lignin is a major constituent in structural cell walls of all higher vascular land plants. Its polyphenolic structure is well known for its role in woody biomass to give resistance to biological and chemical degradation (22).

Lignin can be found into two form such as lignosulfonates and Kraft lignin. Lignosulfonates is lignin resulting from the sulfite pulping process have been the only type of lignin extensively used in the industry. The polymeric character and the high content in sulfonic acid groups give them surface- active and binding properties (23, 24). These properties have been used in several applications developed for lignosulfonates, such as dispersants (25, 26) about 90% of commercialized lignin is used as concrete additive due to this property, emulsifiers (16) and ion-exchange resins (23).

Kraft lignin is a polymer byproduct of the Kraft pulping process, which accounts near the 85% of total lignin production in the world, is mainly used as fuel to recover part of the energy of the pulping process. Apart from that, lignin is the raw material to obtain low molecular weight compounds like vanillin (16), widely used in cosmetics, simple and hydroxylated aromatics, quinones, aldehydes, aliphatic acids.

2.1.2 Structure of lignin

Lignin is a complex chemical compound most commonly derived from wood, and an integral part of the secondary cell walls of plants and some algae (27). Structure of lignin is very complex and

consists of a three dimensional randomized net linked to hemicelluloses, which are formed from monolignols: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (12).

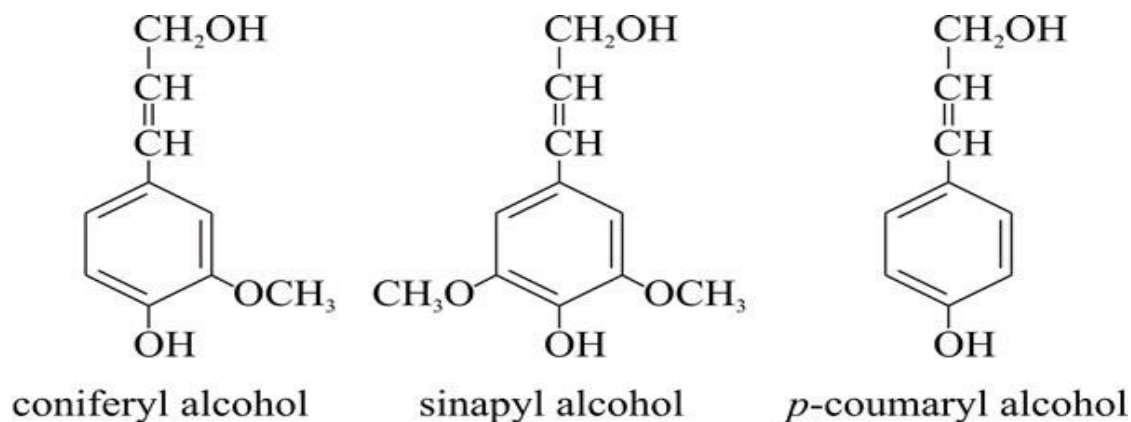


Figure 2.1.2:- Most common monolignol in lignin (29)

Lignin contains a range of chemical functional groups, which is partly the result of the extraction method. The main groups in unmodified lignins are hydroxyl (aromatic and aliphatic), methoxyl, carbonyl, and carboxyl. The solubility of the lignin is affected by the proportion of these functional groups; most lignins are quite soluble in alkaline solution due to the ionization of hydroxyl and carboxyl functional groups. The presence of the hydroxyl group, both phenolic and aliphatic, in lignin has enabled its utilization as a partial substitute for phenol in the synthesis of products with lots of application (29).

Plant lignins can be broadly divided into three classes: softwood (gymnosperm), hardwood (angiosperm) and grass or annual plant (graminaceous) lignin (30). Three different phenylpropane units, or monolignols are responsible for lignin biosynthesis (16). Guaiacyl lignin is composed principally of coniferyl alcohol units, while guaiacylsyringyl lignin contains monomeric units from coniferyl and sinapyl alcohol. In general, guaiacyl lignin is found in softwoods while guaiacyl-syringyl lignin is present in hardwoods. Graminaceous lignin is composed mainly of *p*-coumaryl alcohol units.

The monolignols are linked together by different ether and carbon-carbon bonds forming a three-dimensional network. In the lignin structure, the monolignols are presented in the form of *p*-hydroxyphenol, guaiacyl and syringyl residues as have been shown in Figure 2.1.2.1

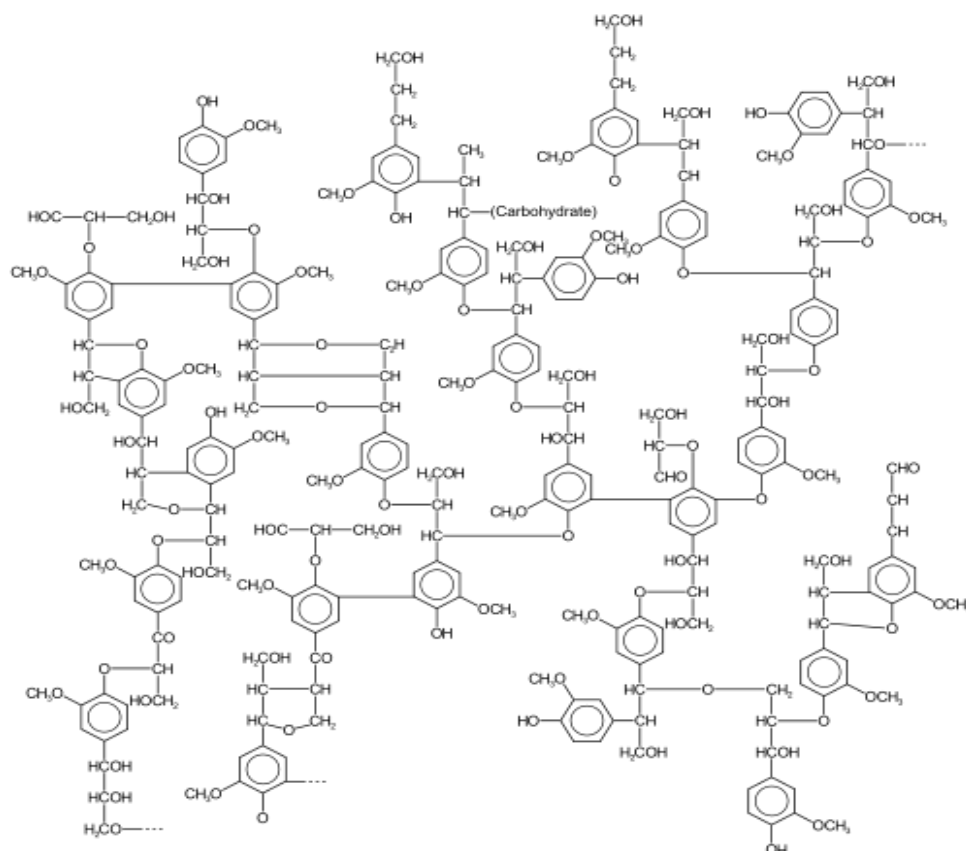


Figure 2.1.3:- Structure of native lignin (29)

The lignins of softwoods, hardwoods and grasses differ with regard to their content of guaiacyl(3-methoxy-4-hydroxyphenyl), syringyl(3,5-dimethoxy-4-hydroxyphenyl) and 4-hydroxyphenyl units. Softwood are predominantly polymers of coniferyl alcohol, hardwood lignin are composed of coniferyl and syringyl units in various proportions, while lignin obtained from grasses contains all three units (16).

Table 2.1.2:- linkage found in lignin

Linkage type	Dimer structure	Total linkage (%)
β -O-4	Phenylepropane β -aryl ether	45-50
5-5	Biphenyle and Dibenzodioxcin	18-25
β - 5	Phenyle lcoumaran	9-12
β - 1	1,2-Diaryl propane	7-10
α - O - 4	Phenylpropane α -aryl ether	6-8

4-O-5	Diaryl ether	4-8
$\beta - \beta$	$\beta - \beta$ -linked structure	3

2.1.3 Kraft pulping process

Pulp has basically been produced from wood. Pulp is predominantly used for paper making but also processed to various cellulose derivatives. The main purpose of the pulping processes is to liberate the fibers, which can be accomplished either chemically or mechanically or by combining these two types of treatments (13). The most common chemical pulping process of wood today is the sulfate or kraft pulping process, a process using sodium sulfide under alkaline conditions. The principal behind the chemical pulping processes is to liberate the cellulose by dissolving other macromolecules like hemicellulose and lignin into the cooking liquor (26). The most important bond in lignin is the β -O-4' linkage, which is shown in Figure 3 check figure numbers. To dissolve the lignin, nucleophiles such as hydrogen sulphide and hydroxide ions are introduced. The sulphide ion reacts with the β -O-4' linkage and largely degrades the lignin. The cleavage of ether bonds increases the amount of free phenolic groups (19).

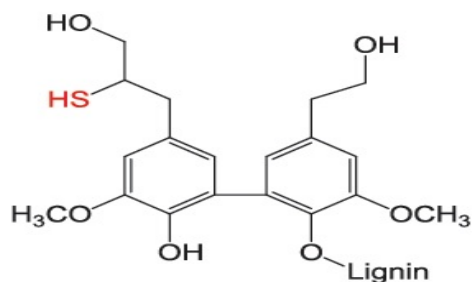


Figure 2.1.3:- Simplified structure of kraft lignin (29)

2.1.4 Black liquor

Black liquor is produced as a by-product from the sulphate process when digesting wood into pulp, removing lignin, hemicelluloses and other extractives from the wood to free the cellulose fibers with sodium-based alkali compounds, such as sodium hydroxide and sodium sulfide [12].

The environmental impact of black liquor results not only from its chemical nature, but also from its dark coloration that reduces oxygen availability and negatively affects aquatic habitants.

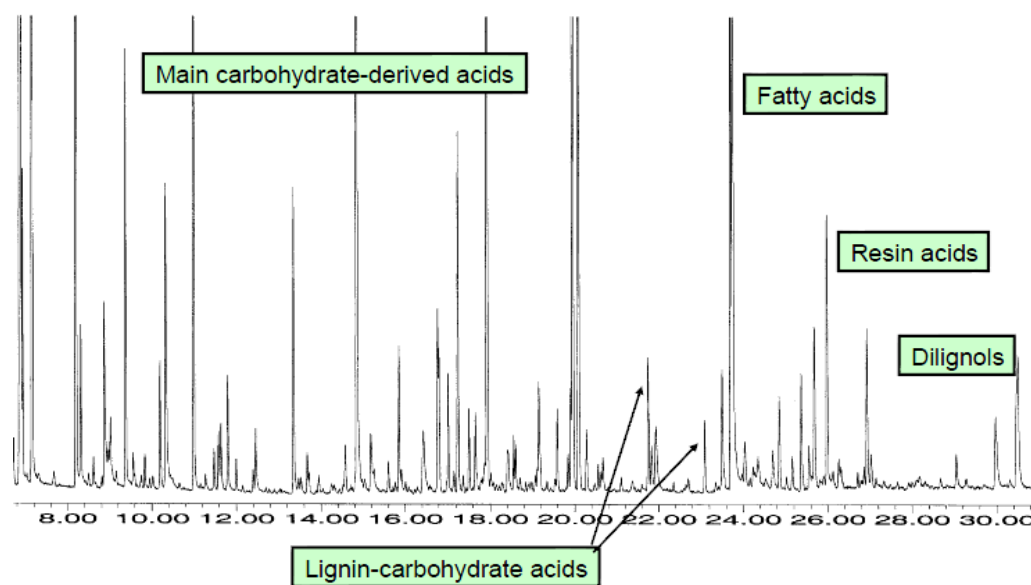


Figure 2.1.4:- GC/MS analysis of black liquor (31).

The organic content in black liquors differs with processing. Black liquor from a cook of paper grade contains about 29-45% lignin (Table 1.1), which is more degraded compared to black liquor from a liner grade cook, containing 8-16% lignin (22).

2.1.5 Lignin depolymerization

The aromatic structure of lignin has to be exploited in the sense of producing low molecular weight compounds that can be used as building blocks or platform chemicals to turn them into fine chemicals. Lignin depolymerization can be achieved by different strategies – oxidation, hydrolysis, hydrogenation, pyrolysis, enzymatic reactions (32)

2.1.5.1 Hydrolysis

Hydrolysis can depolymerize lignin by tearing off the ether and C-C bonds which bind the phenyl-propane units together, thus to obtain low-molecular phenolic compounds. Water at near and supercritical conditions is a unique solvent for degradation of swelled biomass and solid waste polymers. Degradation of lignin in near and supercritical water at temperatures 623 and 673 K was studied using a batch type reactor (33). Alkaline hydrolysis of industrial lignin could yield

reactive degradation products that could be used to synthesize phenolic resins. The phenolic hydroxyl content of the hydrolyzed lignin increased when the severity of the treatment increased, and therefore improved the reactivity of lignin toward formaldehyde (34). Technical lignin could be hydrolyzed to small molecule after treating with a 5% NaOH solution at 180°C for 6h. The resulting compounds were mainly -methoxyphenol, 2, 6-hydroxy-3,5-dimethoxybenzaldehyde(35).

2.1.5.2 Oxidation

Lignin oxidation has been performed to obtain various chemicals, such as vanillin, syringaldehyde and 4-hydroxybenzaldehyde dissolved alkaline lignin in a warm acetic acid solution (90%), that is inert to the oxidative agent NaIO_4 (36). The oxidative agent was added and mixed rapidly. Then the reaction was stopped quickly by adding a reductant. The reaction could be controlled by removing the reaction system from heat. NaIO_4 first oxidized methoxyl groups to quinone groups, and then SO_2 reduced the quinone to hydroxyl groups.

2.1.5.3 Pyrolysis

Lignin thermally decomposes over a broad temperature range, because various oxygen functional groups from its structure have different thermal stabilities, their scission occurring at different temperatures (23). The cleavage of the functional groups gives low molecular weight products, while the complete rearrangement of the backbone at higher temperatures leads to 30-50 wt% char and to the release of volatile products. The cleavage of the aryl-ether linkages results in the formation of highly reactive and unstable free radicals that may further react through rearrangement, electron abstraction or radical-radical interactions, to form products with increased stability(37,20).

2.1.5.4 Enzymatic reaction

Biomimetic systems, with a metalloporphyrin catalyst, mimic the catalytic mechanism of lignin degrading peroxidases (22) causing oxidative C-C bond cleavage reactions in lignin model compounds (17). Hemin, a natural porphyrin, has been shown to exhibit catalytic activity in the oxidation of various lignin model compounds (38). It is chloropropo-porphyrin IX iron (III) the reddish-brown crystalline chloride of haem, produced when hemoglobin reacts with glacial acetic

acid and sodium chloride. Hemin is more closely related to the haemoprotein LiP than a synthetic porphyrin and it is more effective than synthetic porphyrin catalysts, such as tetraphenylporphyrin iron (III) chloride (39).

2.2 Post tanning operation

The term “post tanning” refers to the wet processing steps that follow the primary tanning reaction. This might refer to followed tannage with chromium (III) as is usually the case in industry, but equally it applies to vegetable tanning or indeed any other tannage used to confer the primary stabilizing to pelt. The combination of post tanning processes may not always be the same for all tannages the choice of post tanning processes depends on the primary tannage and the type of leather the tanner is attempting to make .but in general they can be classified into three .such as re-tanning, dyeing and fatliquoring

2.2.1 Retanning

There are many variations in syntan ingredient the relative quantities used and the method of making. They are more or less akin to vegetable tannins but lower molecular weight or size. The syntans may be categorized in to the following group (40)

- Pre-tanning syntans
- Retanning syntans
- Bleaching syntans
- White light fast syntans
- Chrome syntans
- Leveling syntans

ACRYLIC RESIN RETANNING LIQUID SYNTAN;-

- Strong and selective filling action on loose belly areas and flanks areas.
- Excellent light and heat resistance
- Fine, tight grain, mellow and round handle.
- It is compatible with water proofing system.
- it is normally used in a mixed retannage of wet blue, after neutralization.

Sample Applications;-

- Use 3.0 to 5.0 % on the shaved weight, depending upon the articles required and characters.

POLYMER RETANNING LIQUID SYNTAN

- Its excellent selective filling action on loose belly areas and flanks areas
- Fine, tight grain, mellow and round handle.
- Good dyeing properties
- Excellent light and heat fastness properties.

Sample Applications;-

- Use 6.0 8.0 % based on the shaved weight, depending on the required leathers.

MELAMINE RESIN POWDER

- Very good filling & tightening effect on the chrome retanned leathers
- Strong and level dyeing.
- Good softness and round handle.
- Good light fastness and heat resistance.
- Its selective uptake and filling action ensures that loose structured areas are filled and tightened, while the leathers retain softness and round handle. For suede leathers a short and fine nap is produced with very good buffing properties

Sample Applications;-

- Use 4.0 to 6.0 % based on the shaved weight, depending on the required leathers.

DICYNAMIDE SYNTAN ;-

- Good fullness and selective filling action especially in more open structured areas.
- Excellent levelness of the dyeing with no bleaching action.
- Good embossing properties.

Sample Applications;-

- use 4.0 to 6.0 % based on the shaved weight, depending on the required leathers.

REPLACEMENT SYNTAN

- To produce shrunken grain effect.
- Good bleaching action
- Good light and heat fastness.

- grain effect can be controlled.

Sample Applications;-

- Use retanning of chrome tanned leathers & vegetable tanned leathers 8.0 to 12.0 % based on the required leathers and character.
- Use for shrunken grain articles 10 to 20 % based on the shaved weight depending on the required leathers and characters.

FILLING SYNTAN-

- Selective and good filling effect.
- Improved uniformity of the handle by preferentially filling the loose and open structured areas of the hides and skins.

Sample Applications;-

- use 3 to 4 % based on the shaved wt, depending on the required leather and characters.

PHENOLIC REPLACEMENT SYNTAN

- It is particularly suitable for the production of extremely soft leathers and it is highly recommended for top quality upholstery leathers, hand bags fancy leather goods, softy nappa, garment type of leathers.
- very soft and round handle
- Good light fastness.
- Level dye shades.

Sample Applications;-

- Use 6 to 12% based on the shaved wt, depending on the required leathers and characters.

2.2.2 Dyeing

It is the coloring step. Almost any color can be struck on any type of leather, despite the background color, although the final effect is influenced by the previous processes. Coloring almost invariable means dyeing. Applying in solution or pigment to confer dense opaque color, can be performed in the drum or coloring agents may be sprayed or spread by hand (padding) onto the surface of the leather. It need short-rang interaction to get brilliant color and for having through and through color need penetration (41).

CLASSIFICATION OF THE DYES

- ACID DYES –Smaller molecules and very good penetration.
- DIRECT DYES –Larger molecules and surface dyeing.
- BASIC DYES –Larger molecules, poor solubility in water, used for top dyeing for Black & Brown and it will create BRONZINESS and poor fastness.
- METAL COMPLEX DYES –There are two metal complex dyes are available.
1; 1 –metal complex dyes (chalky & light colours. Good solubility in water.
1; 2 –metal complex dyes (poor solubility in water & used as solvent soluble dyes in finishing.
- SULPHUR DYES –Good fastness, through & through penetration, less expensive and used as restricted pastel colours only.

2.2.3 Fatliquoring

This step is primarily applied to prevent fiber sticking when the leather is dried after completion of the wet processes. The nature of the synthetic or natural fatty matter or polymers, the type of the emulsion or their mixture directly influences certain properties of the leather valued by the consumers.

ANIONIC FATLIQUORS;

These are negatively charged. When treated with vegetable tanned leathers, they have less affinity and good penetration and treated with chrome tanned leathers, and they have good affinity (41).

CATIONIC FATLIQUORS;

The cationic fat liquors if finally given after treating with anionic fatliquors, gives good surface lubrication.

SYNTHETIC FATLIQUORS;

It gives light weight without overloading, is stable to variation in PH, does not oxidise, does not spue and it can be used for white and pastel shades. The main advantage is we can mix with combination of other fat liquors.

It will impart softness for the leather which bring by reducing the surface charge of the leather .oil is preferred to reduce surface charge but the problem is oil can't dissolved in water (40) .in order to dissolve in water

- Softness the surface feel and the handle (mellowness, light weight)
- Tensile strength and stretch
- Grain break
- Water-barrier characteristics (water proof, shower-proof)
- Air and water vapour permeability

The most important step before commencing to retanning, dyeing and fatliquoring is the adjustment of an appropriate PH or ionic charge in the leather in order to suit the subsequent operations to be followed .for chrome or mineral tanned leather the process is known as neutralization which ,in reality is the removal of protein-bound acid from the surface as well as interior of leather upto certain depth depending on penetration or the retanning material used in the retanning system(pH 4.5-6).for example for upper leather neutralizing pH will be 4.5-5.3 and for garment leather pH will be 5.0-5.5 (42).

2.2.4 Mechanism of post tanning

All post tanning process steps involve the fixation of a solute in solution onto a solid substrate .The reaction are made more complicated by the fact that the tanner is dealing with a substrate that has finite thickness. Therefore, to control the outcome of these steps it is necessary to understand the parameter come into play. First, it is important to understand that there is a general mechanism that must be taken into account, which is the step by which fixation occurs (42).The steps involved in any general reaction in which a reagent in solution is fixed onto a solid substrate

- 1) Transfer of the reagent from solution into substrate
- 2) Hydrophobic bonding
- 3) Electrostatic interaction between the reagent and the substrate
- 4) Covalent reaction between the reagent and the substrate

2.3 chemistry of Synthetic tanning agent

The word syntans is the abbreviation of 'Synthetic Tannins'. Syntans are defined as high molecular weight compounds or mixtures of such compounds, which are made water soluble by the introduction of suitable groups by process such as sulphonation, sulpho methylation,

amino methylation etc. that are capable of converting animal skins into leather. These syntan are used for pretanning, retanning, bleaching, mellowing, filling, mordenting for dyes, neutralizing and for grain tightening (40). The commercial syntans do not structurally resemble the natural tannins though they react similarly.

2.3.1 Classification of syntan

There are several methods of classification of syntans are classified based on their molecular weight distribution into the following 3 classes

- Auxillary syntans.
- Combination syntans.
- Exchange or Replacement syntans

2.3.1.1 Auxiliary syntans

They are low molecular weight syntans and relatively unreactive in tanning sense, which include non-swelling acid, bleaching and neutralizing syntans fall into this categories. They are also used for solubilizing higher molecular weight syntans or vegetable tannins to allow more uniform surface reaction. The tanning power of this type of syntans are depend upon mostly on the presence of free sulphonic acid group and is totally lost if the latter neutralized completely and even when the solution is subsequently acidified with organic acids. In the phenolic syntan, the hydroxyl group contributes toward tanning potency. The hydroxyl group shows no ionization at pKa value less than 8-9.

2.3.1.2 Combined syntans

The name implies they are medium molecular weight, mildly astringent syntans typically used in post-tanning operation. They also aid vegetable tannin and dye to react with collagen by reducing the reactivity of substrate to promote penetration through cross section. This class shows buffering action on titration curve in the alkaline range and possess weak acid group similar to those of vegetable tannins. The pKa values fall in the range 7-8 (43). These syntans are less acidic and are sensitive to acid and salt.

2.3.1.3 Replacement syntans

They have high molecular weight and astringency, which are designed to replace vegetable tannins and can act as solo tanning agent. They acquire better light fastness as comparing with

vegetable tannins. This kind of syntan have same titration curve as those of vegetable tannins with pKa value of 7-9 and do not get titrated in the strong acidic range. In this class of syntan, which contain just enough sulphonic groups to impart water solubility, phenolic hydroxyl group are responsible for tanning action. These are further sub-classified into: replacement syntan for self-tanning and for retanning.

Table 2.3.1.3:- Properties of syntan (43)

	Auxiliary syntans	Combination syntan	Replacement syntan
pH of decinormal solution	1.3-1.5	-	
pH of analytical solution	1.5-2.0	2.4-3.0	3.1-3.8
pH of product	1.8±0.2	3.2±0.2	4.0±0.2
Fraction precipitation at 1/3 rd saturation of the syntan solution with sodium chloride (70-90% must ppt with NaCl)	6%	20%	60%
Tannin content	20%	40%	60%
Amount that replace vegetable tannins	2-5%	25%	100%
Other properties			
Ash content	-	-	< 10%
Iron content	-	-	0.05-0.1%
Calcium as CaO	-	-	1%
Magnesium as MgO		-	0.5%
Aluminium as Al ₂ O ₃	-	-	1.5%
Free phenol	-	-	Nil

2.3.2 Preparation of syntan

Phenols are the most widely used material in the manufacture of syntans. The other raw materials that are commonly used are Naphthalene, Resorcinol, Naphthalol. The first syntan prepared by condensing phenol or cresol sulphonic acid with HCHO. This patent was taken over by BASF, Germany and the product was named as “Neradol-D” (41). Generally the raw material used for the manufacturing of syntan are of technical grade and should be determined before use as the chemical differ in purity from company to company, grade to grade and sometimes even from batch to batch of the same company. It is therefore necessary that every raw material belonging to a particular batch used in the manufacturing of syntan has to be subjected to assay. Attempts were made to prepare syntans of greater tanning property and with no drawbacks, which were observed with Neradol type. This was possible only if % of HSO₃ groups in comparison to –OH groups in the syntans could be reduced it is called “NOVALAK” was produced in order to replace the Neradol. There are two steps in manufacturing of syntan:-

2.3.2.1 Sulphonation

The raw material, phenol or naphthalene, are usually subjected to sulphonation, which introduce the hydrophilic group (–SO₃H) tanning action and degree of sulphonation are inversely proportional. The sulphonation of phenol is done at 100±2°C in a mild steel reactor with 98-99% concentration sulfuric acid and moisture content less than 10% in order to facilitate smooth sulphonation (43).

Naphthalene based syntan sulphonation is done with concentrated sulfuric acid at 160-165°C and at low temperature like 120-125°C by employing a suitable catalyst like zinc sulphate. Syntan based on condensation of naphthalene sulphonic acid and formaldehyde are widely used as bleaching agent for chrome and vegetable tanned leather. At temperature higher than 150°C the main product of sulphonation are naphthalene 2-sulphonic acid, however if it is less than that unstable product will produce. The tanning power of syntan depends among other thing, on the degree of sulphonation and is inversely proportional to it. Sulphonation must therefore be kept to a minimum if good tanning action is required. However, recent finding (44) indicates, contrary to earlier observation, that an increase in the degree of sulphonation would increase the reaction

of syntan with collagen. Generally the sulphonation of phenol is done at $100\pm 2^{\circ}\text{C}$ in a mild steel vessel.

For sulphonation of phenol concentrated sulphuric acid of 98-99% strength is required. Under these condition 90 per cent of para sulphonic acid is formed. At lower temperature the quality of para isomer formed is less. Higher temperature of about 100°C , do not seem favorable as more and more of disulphonics are formed. Chlorosulphonic acid, at a temperature of about 100°C , can also be used to obtain the parphenol sulphonic acid but due to the cost and handling problems, it is very much in practice. As para phenol acid is more conducive for polymerization with formaldehyde, condition for the formation of para isomer are prepared for syntan manufacturing.

2.3.2.2 .Condensation

Condensation with formaldehyde in acid medium generally yields better result than alkaline medium, which can act as the bridging agent between two phenolic nuclei resulting in the formation of methylene bridge ($-\text{CH}_2-$). By changing the cross linker several trial were conducted such as methylene($-\text{CH}_2-$), dimethyle carbamid ($-\text{CH}_2\text{NHCONHCH}_2$), sulpho methyl ($-\text{CH}_2-\text{SO}_2-$) and found the light fastness of the methylene group was poor as this group helped further formation of quinone structure due to oxidation effect, whereas of the group suggested exhibit better light fastness.

CHAPTER THREE

Material and method

3.1 Material

The black liquor which is used as sources of kraft lignin can be collected from pulp and paper industry. All chemical and reagent used in degradation, extraction of lignin, preparation and characterization of sytan are analytical grade. Wet-salted sheep skin was used for testing the performance of sytan on the leather and all leather processing chemical were commercial grade.

3.1.1 Equipment and apparatus

Leather processing equipment

Leather processing involve sample drum, fleshing machine, shaving machine, setting out machine and weighing balance.

3.1.2 Laboratory equipment and apparatus

- Analytical weighing balance
- Digital pH meter
- Graduated cylinders
- Micropipette
- Water bath shaker
- Sampling tube
- Thermostats
- Filter paper
- Round bottom flask
- Magnetic stirrer
- Oven and desiccators
- UV-Vis spectroscopy
- FT-IR spectroscopy
- Particle size analyzer
- Thin layer chromatography paper

- Thermometer
- Autoclave
- Vacuum pump
- Leather strength taster
- Crockmeter (fastness to dry and wet rub)

3.1.3 Chemicals and reagents

- Hydrogen per oxide(H_2O_2):- to perform oxidation reaction
- Hydrochloric Acid(HCl):- to adjust the pH in the degradation process
- Iron sulphat ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$):- for chemical degradation process
- Chloroform(CHCl_3):- used as alternative solvent in degradation experiment
- Ethanol($\text{CH}_3\text{CH}_2\text{OH}$):- used as alternative solvent in degradation experiment
- Dichloromethane(CH_2Cl_2):- used as alternative solvent in degradation experiment
- Ethyl acetate :- used as solvent in extraction process
- Sodium bicarbonate(NaHCO_3):-used in extraction process
- Sodium sulfate(Na_2SO_4):- used in extraction process to concentrate phenolic of degraded lignin
- Sulfuric Acid(H_2SO_4):-used for in sulphonation process to increase the solubility of the syntan
- Sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$):- used as alternative sulphonation agent in syntan preparation
- Sodium hydroxide(NaOH):- used for neutralize the syntan to working pH
- Formaldehyde(CH_2O):- used in condensation polymerization process

3.2 Methods

3.2.1 Characterization of black liquor

3.2.1.1 Determination of solid content

The empty dish was weighed with and without the amount of sample and dried in an oven at 105°C for 6hr, weighing each two hours till constant weight is obtained and finally the weight was taken and compared with the initially recorded weight. The percentage weight of sample was calculated using the formula:

$$\text{Solid content \% (w/w)} = \frac{(W_1 - W_2)}{W_1} \times 100$$

Where:

W1 = Original weight of the sample before drying

W2 = Weight of the sample after drying



Figure 3.2.1.1: - Heating oven

3.2.1.2 Determination of ash content

Ash content of black liquor was determined using muffle furnace. A 10 g of black liquor was added in a crucible. Then, the sample was placed in a furnace. A furnace was located at a temperature of 511^oC for 2 hour and after burning the residue sample was weighted and ash content was calculated.

$$Ash (\%) = (A * 100)/B$$

Where

A=the weight of ash in grams

B= the weight of moisture free test sample in grams

3.2.1.3 Determination of klason lignin

Klason lignin is defined as the solid residual material obtained after a sample has been subjected to hydrolysis treatment with 72% sulphuric acid. The detailed method, which is presented in (45). 4.8 g of filtrated liquor is weighed and 12 mL of 72% sulfuric acid is added to the sample. The sample is then evacuated for 15 min and placed in a water bath at 40 °C for 1 hour. 140 ml of deionized water is added to the sample and then heated to 125 °C in an autoclave for 1 hour. After hydrolysis, the sample is filtrated and the insoluble solid residue,

which is referred to Klason lignin, is measured gravimetrically. In order to minimize experimental error, klason lignin estimation was repeated for three times and average value was noted.

3.2.1.4 Acid soluble lignin

The acid-soluble lignin can be determined in a solution, after filtering off the insoluble lignin, by a spectrophotometric method based on absorption of ultraviolet radiation. The most often used wavelength is 205 nm using the 1-cm light path cuvette where a 4% of H_2SO_4 will used as a reference blank 46). If the absorption reading exceeded 0.7, the sample must be diluted until resulting absorbance reading become between 0.2 and 0.7. An absorptivity value of 110 L/g-cm is used to calculate the amount of acid –soluble lignin present in black liquor.

3.2.1.5 Fourier Transform Infrared (FTIR) spectroscopy analysis

FT-IR spectroscopy were employed to acquire information on the chemical structure of the black liquor. Through measurement and analysis of the resulting spectra analyze the functional group present in lignin can be distinguished, which help in identifying binding site (i.e:- hydroxyl group) in sytan preparation stage. The spectrum of the sample was recorded on ABB MB3000 Fourier transform infra-red (FTIR) spectroscopy. All spectra were performed with the resolution of 4 cm^{-1} and recorded at 45° incident angle using potassium bromide in the region 4000 to 6000 cm^{-1} .

3.2.2 Degradation of kraft lignin in black liquor

The black liquor which consists of large biopolymeric molecule used as starting material for the design experiments along with different level of iron(II) sulphat and hydrogen per oxide concentration. Glass stire tank reactor (STR) was used as reaction vessel. The raw material was f from pulp and paper industry was collected and conducting degradation process using chemical oxidation process.

Processes variable for the degradation experiment are temperature, concentration of iron (II) and hydrogen per oxide. In order to find optimum value of degradation the reaction pH, reaction duration and rotation speed was set to pH=4-6, four hours and 250 rpm. In course of experiments Fenton's reagent were used to degrade the organic moites via oxidation method by releasing free radical to the reaction.



Figure 3.2.2:- Glass reactor setup

Processes variable for the degradation experiment are temperature, concentration of iron (II) and hydrogen per oxide. In order to find optimum value of degradation the reaction pH, reaction duration and rotation speed was set to pH=4-6, four hours and 250 rpm. In course of experiments Fenton's reagent were used to degrade the organic moites via oxidation method by releasing free radical to the reaction. The pH during the course of reaction was between 6-4 otherwise can be adjust via 1N HCL .

3.2.3 Experimental design

During this work the degradation of lignin on black liquor was study using reaction temperature, Fe^{2+} concentration and H_2O_2 concentration.

Experimental design was analyzed and done by the Design Expert 7.0.0 software application. Experimental design selected for this study is CCD and the output measured is percentage of lignin degraded.

Process variables revised are reaction temperature, H_2O_2 concentration and Fe^{2+} concentration. To get maximum degradation; reaction period and rotation Speed was set at 4 hours and 250 rpm respectively and at constant atmospheric pressure. The operating limits of the degradation process conditions are reasons to choose Levels of the variables.

Three level three factors CCD was made use of in the optimization study, needing 20 Experiments to be done. H_2O_2 concentration, Fe^{2+} concentration and reaction temperature were the independent variables selected to optimize the conditions for degradation of lignin in black liquor which solely treated by Fenton's reagent. The percentage of lignin degraded were expires on the function of viscosity since it is the main parameter which can explain changes in molecular weight of biopolymer.

Table 3.2.3.1: - complete design matrix for degradation experiment

variable	Factor code	Units	Levels		
			-1	0	+1
Iron(II) sulphate	Y_1	mmol	5	15	25
Hydrogen peroxide	Y_2	mmol	5	15	25
Reaction temperature	Y_3	$^{\circ}\text{C}$	25	45	65

Twenty experiments were done and the data was statistically analyzed by the Design Expert 7.0.0 software and to get suitable model for the percentage of lignin degraded as a function of the independent variables. Order in which the runs were made was randomized to avoid errors which are caused by systematic. The maximum percentage of lignin degradation among the degradation process option were used for further utilization in syntan manufacturing. Upscaling of experimental result were done in order to find reasonable amount of degraded lignin for leather application.

Table 3.2.3.2:- Experimental design matrix

Run Code	Coded factor			Actual factors			Percentage of lignin degradation
	Y1	Y2	Y3	H ₂ O ₂ (mmol)	Fe ²⁺ (mmol)	Temperature (°C)	
D1	+1	0	-1	15	15	45	
D2	+1	+1	-1	25	25	25	
D3	0	-1	0	15	5	45	
D4	+1	+1	+1	25	25	65	
D5	+1	0	0	25	15	45	
D6	0	0	0	15	15	45	
D7	0	0	0	15	15	45	
D8	+1	-1	+1	25	5	65	
D9	+1	-1	-1	25	5	25	
D10	0	+1	0	15	25	45	
D11	-1	-1	-1	5	5	25	
D12	0	0	+1	15	15	65	
D13	-1	-1	+1	5	5	65	
D14	0	0	0	15	15	45	
D15	-1	+1	-1	5	25	25	
D16	0	0	0	15	15	45	
D17	0	0	0	15	15	45	

D18	-1	0	0	5	15	45	
D19	-1	+1	+1	5	25	65	
D20	0	0	-1	15	15	25	

3.2.4 Identification of degrade product

3.2.4.1 UV-Vis spectroscopy analysis

In identification of degrade product control (in the absence of reactant) and the degraded kraft lignin was analyze using a Lambda 3B (PerkinElmer®) spectrophotometer in order to record the absorption wave length and to examine the degradation process.



Figure 3.2.4.1:- UV-visible spectroscopy

3.2.4.2 Determination of Phenolic group

UV-spectroscopic methods were used in order to estimate amount of phenolic group based on the wave-length shift between ionized and protonated phenolic hydroxyl groups. The intensities of the absorbance in the ionization difference spectrum are proportional to the content of phenolic hydroxyl groups. The method chosen for this work is based on the intensities of two maxima (ca. 300 and 350 nm) in the ionization difference UV spectrum. Therefore, it is rather insensitive to structural differences in lignin related to differences in the content of α -conjugated phenolic structures (48), and thus superior to several other modifications of the UV method. The

calculation was made using Kubelka-Munk equation (1) for their difference in absorbance at specific wave length in acidic and alkaline medium.

$$\text{phenolic group } \left(\frac{g}{L}\right) = 0.425\Delta\lambda_{305nm} + 0.182\Delta\lambda_{350} \dots \dots \dots (1)$$



Figure 3.2.4.2:- phenolic group estimation

3.2.4.3 Determination of particle size

The particle size was measured in DLS with high performance particle seizer (Zetasizer Nano series, Malvern) at 25°C using the technique of photon correlation spectroscopy. With this technique the fluctuations in the intensity of light scattered by the particles were analyzed using a digital correlate to determine the diffusion coefficients. The diffusion coefficient is inversely proportional to the size of the particle and size was obtained from the Stokes Einstein equation. The obtained diffusion constant values were converted to intensity average particle size and number average particle size using CONTIN software employing Mie theory(49). The ions in the medium and the total ionic concentration can affect the particle diffusion speed by changing the thickness of the electric double layer called the Debye length (K⁻¹). Thus a low conductivity medium will produce an extended double layer of ions around the particle.



Figure 3.2.4.3:- dynamic light scattering

3.2.4.4 Absolute Viscosity

The viscosity of degraded reaction mixture were measure using viscometer which explicitly show trends cause due to change in amount of high molecular weight entities . The temperature was kept at 30°C for all treatments and before subjected to viscometer filtration were conduct in order to remove precipitate form during reaction. When sample preparation was completed, immediately the spindle was inserted into the reaction mixture. L1 type of spindle were selected and operated at 1

3.2.5 Solubility of black liquor in organic solvent

Different set of experiment was taken to check the solubility of black liquor in organic solvent, where eight different solvents were used. Black liquor and solvent mixture where gently rotate using vortex mixture and kept for some time. The response variable in this experiment was physically observed and picture was taken using Nikon s6200 digital camera.

Table 3.2.5: - solubility of black liquor in solvent

s.no	Solvent	Solubility
1	Water	
2	Acetone	
3	Ethyl acetate	

4	Hexane
5	Chloroform
6	THF
7	DCM
8	Ethanol

3.2.6 Extraction of degraded lignin from black liquor

3.2.6.1 Extraction of degraded lignin using ethyl acetate

The black liquor after degradation contain both organic (degraded lignin) and inorganic moities. Initially neutralize the pH of black liquor with mineral acid such as hydrochloric or sulfuric acid. Then separating the aqueous part of solute by filtration. After separating residue and filtrate then extract the aqueous filtrate using ethyl acetate via number of times to enhance the extraction process and wash with water until we get pure product. The pka value for phenol and carboxylic acid will be on pH 9.9 and 4.5 respectively.

3.2.6.2 Rotary evaporator

The separation of solvent mixture from the degraded lignin was done using buchi R-134 rotary evaporator. It works by vacuum distillation where rotating the pot provides better agitation, keep contact among the solvent and degraded lignin mixture with warming bathe and increase the surface area of the solvent which is evaporating, It fundamentally boils under the reduces pressure , so the solvent removed as gas. Then efficient spiral condenser allow to cools the gaseous solvent to returns into liquid phase.

3.2.7 Phase II

3.2.7.1 Preparation of syntan

The preparation stage was the cumulative effect of two major process, sulphonation and condensation polymerization. In this course of work sulphonation followed by condensation was taken as alterative operation. In order to investigate the effect of sulphonation agent the degraded product was sulphonated using sulfuric acid and sodium meta bisulfite in 250 ml round bottom flask at different temperature suchlike 60 °c ,80 °c , 100 °c and 120 °c for about six hours. A known amount concentrated degraded lignin was dissolved in 90ml of water and 2.5 ml of 98% sulfuric acid for a total six hour , however every one hour sample were taken in order to

investigate the interaction effect of time and type of sulphonation agent . In the combined sulphonation experiment the ratio of sulfuric acid to sodium Meta bisulfite were 50:50. The condensation experiment were conduct using the same amount of formaldehyde for all sulponated product under reaction of 50°C while doing the experiment 2M NaOH were used to adjust the pH prior to leather application (50).

Table3.2.7.1:- experiment design for syntan preparation

Product code	Sulphonation agent	Condensation agent	Total solid	Total solubility	Particle size
SS1	Sulphric acid	Nil			
SS2	Sodium metbisulfit And sulfuric acid	Nil			
SS3	Sodium metbisulpit	Nil			
SF1	Sulphric acid	015 mol			
SF2	Sodium metbisulfit And sulfuric acid	0.15 mol			
SF3	Sodium metbisulpit	0.15 mol			

3.2.7.2 Characterization of syntan

3.2.7.2.1 Determination of solid content

A known amount of product can weight and put in oven for overnight at 100 °c and measure the dried weight.

3.2.7.2.2 Fastness to natural light

The resistance of syntan toward natural light was analyzed by exposing the product to direct day light for six hour .Control for this analysis will be commercially available phenolic syntan and employing this analysis acquire information on degree of proneness to light.

3.2.7.2.3 Determination of total soluble

Filter the original solution through Whatmen filter paper (No. 1). Reject the first 150 ml of the filtrate and continue the filtration until it is clear from both transmitted and reflected light. Transfer 50 ml of the filtrate to a porcelain dish and evaporate to dryness. Dry the residue in an oven at 98.5° to 100°C for 3 hour and weigh to constant mass.

$$Total\ soluble = \frac{M2}{V2} * \frac{V1}{M1}$$

Where

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

M2= mass in g of the residue,

V1= volume in ml of the originally made up solution, and

V2= volume in ml of the solution taken for the test

3.2.8 Evaluation of product

Conventional post tanning leather processing was apply for assisting the performance of lignin based syntan and product will be compare with leather develop using commercial phenolic syntan.

Table 3.2.8:- Post tanning recipe for Goat upper

ARTICLE ;GOAT UPPER				BATCH NO ;		
COLOUR ;BLACK				NO.OF PCS ;		
THICKNESS ;0.7/0.9MM				SQ.FT ;		
GRADE ;				SHAVED WEIGHT ;		
S.NO	PROCE SS	NAME OF THE CHEMICAL	%	RUNTI ME	PH	Remark
1	ACID WASH	H ₂ O@35 ⁰ C	200			
		Wetting agent	0.5			
		FORMIC ACID	0.3	60*		
Drain /Washing /Drain						
2	NEUTR ALIZA	H ₂ O@35 ⁰ C	100			

		SODIUM FORMATE.	0.5			
		SODIUM BICARB	2.0	2*10*+ 20	4.6/4. 8	
Washed 2 times thoroughly.						
3	RETAN NING	HOT H ₂ O @60° C	50			
		Acrylic syntan	4.0	30*		
		Synthetic fatliquor	0.5	20*		
		SS1/SS2/SS3/SF1/SF2/SF 3/C/D	10.0	60*		
4	DYEING	HOT H ₂ O@60°C	100	20*		
		BLACK GTN	3.0	30*		Check penetration
5	FATLIQ UOR.	Semi-synthetic fatliquor	2.0			
		Synthetic fatliquor	3.0			
		Lecithin fatliquor	2.0			
		FORMIC ACID	3.0	3*10+3 0		
		CATIONIC fatliquor	1.0	10*		
		Collect liquor before D/W/D				

	DRAIN, WAS	PILE FOR 12 HOURS,	SA	M,SETT IN	G(RE V),	VACUM@50 ⁰ C,2 min.hook
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Figure 3.2.8 :- Sample drum

3.2.8.1 Physical strength characteristics

The physical properties such as tensile strength, tear strength, % elongation at break and water vapor permeability will be examine as per standard procedure for both the experimental and control leather (51,52).

3.2.8.1.1 Tensile strength

Tensile strength is the load per unit area of cross section required to pull apart or break a strip of leather material. The tensile strength of control and experimental leathers were measured as per procedure. A dumb bell shaped leather sample parallel to the direction of backbone of the animal was punched out using a steel press knife of standard dimensions. The samples were of 9cm total length and of 5cm in the experimental region. After condition for 48 hours at temperature $20 \pm 2^{\circ}$ C and $65 \pm 2^{\circ}$ C % R.H., the thickness of the samples at the middle point and at two point's midway between the middle and ends were measured as per procedure given in (52). The samples were tested in an Instron Universal Testing Machine.

$$\text{Tensile Strength (Kg/cm}^2\text{)} = (\text{Breaking load (kg)}) / (\text{thickness x width (cm}^2\text{)})$$

3.2.8.1.2 Tear strength

The tear strength of control and experimental samples were measured following a modified procedure based on (53). A sample of the size 7.5x2.5 cm was slit at right angles to the grain and flesh sides for about half the length. One end of the piece formed by the slit was clamped in the upper jaw of the Instron Universal Testing Machine and the other end was fixed to the lower jaw. When the Instron machine was run, the sample treated. The average load corresponding to the tearing of the tongue was calculated from strip chart recorder. This load is divided by the average thickness of the sample was taken to be the tearing strength of the samples in kg/cm. Control and experimental samples were tested for the determination of tearing strength of the samples in kg/cm. Control and experimental samples were tested for the determination of tearing strength parallel to the direction of the backbone, similar procedure was repeated for equal number of samples taken from direction perpendicular to the direction of backbone.

Tear Strength (Kg/cm) = Load (kg) / Thickness (cm)

3.2.8.1.3 Color measurement

Color measurement (L, a, b, h and c) for control and experimental leather was analyzed using UV-Vis spectrophotometer. The total color difference (ΔE) was calculating using the formula:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2}$$

The L value for each scale therefore indicates the level of light or dark, the a value redness or greenness, and the b value yellowness or blueness. All three values are required to completely describe an object's color.

3.2.8.2 Organoleptic properties

A comparison of the organoleptic properties of commercial and lignin based syntan will be examine based on hand evaluation by an experienced personnel from leather industry, and rate on a scale of 1–10, where higher points indicate better properties .The leather will evaluate for different organoleptic properties such as softness, grain tightness, roundness ,fullness and general appearance.



Figure 3.8.1.3:- color measurement instrument

3.2.8.3 Waste water analysis

Waste water from the both control and experimental process were collected and filtered through Whatman no.1 filter paper and analyzed for various parameters such as TDS, total solid and COD. A direct correlation of the observed COD/TS value with the environment may not give proper consequence .Hence, emission load were calculate by multiplying the concentration with volume of effluent (Lit) per kg of skin processed.

Chemical oxygen demand (COD)

Chemical oxygen demand is defined as the amount of a specified oxidant that reacts with the sample under controlled condition. The quantity of oxidant consume is expressed in terms of its oxygen equivalence. COD often is used as a measurement of pollutants in waste water and natural water. Reagents used for the determination of the COD include standard potassium dichromate 0.25N, COD acid and mercuric sulphate. Take sample of the spent liquor and made upto 100 ml distilled water and from that take 2.5 ml and transferred to clean COD tube, add 1.5ml potassium dichromate and 3.5ml of COD acid. Add spatula of mercuric sulphate. Also the blank was prepared in the same way with 2.5ml of distilled water, 1.5ml of of potassium dichromate and 3.5ml of of COD acid and mercuric sulphate. All tubes were kept in the COD incubator at 150°C for 2 hours. After incubation samples were titrated against ferrous ammonium sulphate in burette for the COD value using few drops of ferroin indicator and the end point is the persistence of reddish brown colour.

$\text{COD (mg/l)} = (A-B) \times N \times 8000 / \text{volume of sample}$

A=Volume of FAS used for titration of the blank (ml)

B=Volume of FAS used for titration of the sample (ml)

8000=Milliequivalent weight of oxygen $\times 1000\text{ml/l}$

N = Normality of FAS

Chapter four

Result and discussion

4.1 Characterization of black liquor

Industrial black liquor were collecting from pulp and paper industry which is by product from kraft pulping process. The type of wood used for kraft pulping such as soft or hard wood have tremendous effect on the content of black liquor. The waste liquor formed in the digestion operation consists of an alkaline aqueous solution that contains organic and inorganic solids and has a distinctive dark coloration. For characterization of black liquor which were used as starting material in sytan making parameters such as kasolin lignin, acid soluble lignin, total solid, ash content and phenolic group analysis were done in accordance with procedures describe from section3.2.1 to 3.2.5 and all values are tabulated in table 4.1.

Table 4.1: - characterization of black liquor

Parameter	Value
Kasolin lignin (%)	21.8
Acid soluble lignin (%)	1.87
Total solid (%)	37.8±2.71
Phenolic group (g/ml)	2.31
Ash content (%)	2.7
Density (g/m ³)	1.201±0.11
pH	13.4±0.00
Viscosity (cP)	11.4±0.21

All values are triplicate means ± SD at 95% Confidence Interval

Estimation on Molecular weight distribution of black liquor was difficult task to perform.

Most observed problems are presence of impurities, interaction between lignin molecules and interaction of lignin with stationary phases in chromatographic systems and the lack of similar and well defined lignin references. Gel permeation chromatograph (GPC) was employed to obtained rapid information on molecular weight distribution of black liquor.

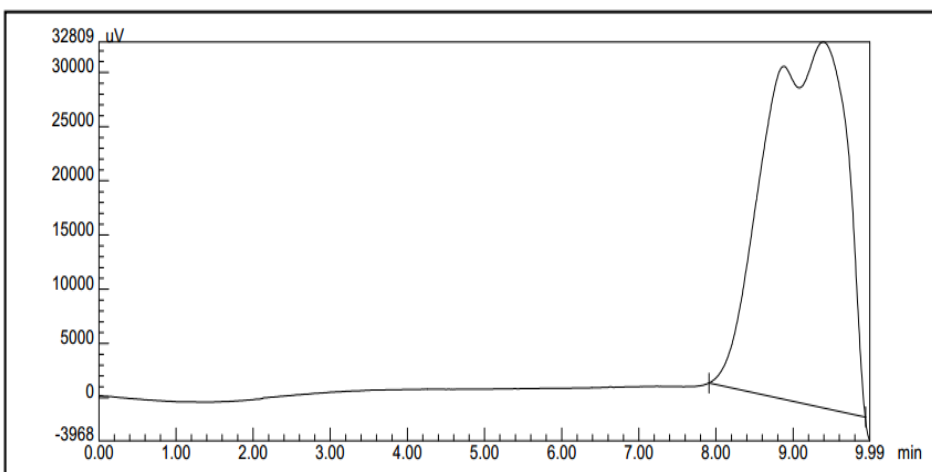


Figure 4.1.1:- GPC result for black liquor

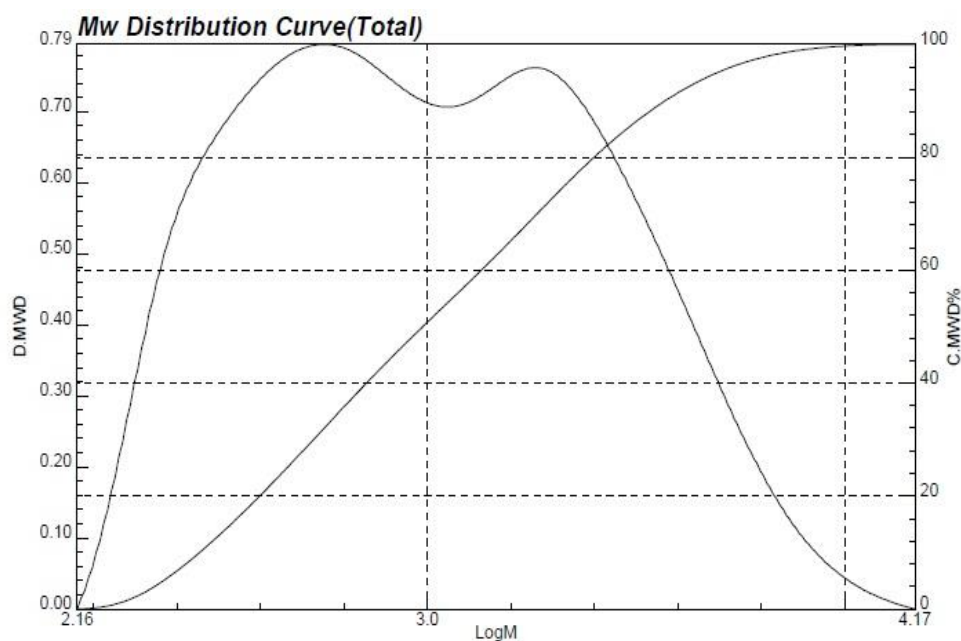


Fig 4.1.2:- Mw distribution curve for black liquor

Total molecular weight calculation was done to display no.average molecular (M_n), weight average molecular weight(M_w), Z average molecular weight (M_z) and dispersity index(D). The

result could show the molecular weight of aromatic structure in black liquor has to be exploited in the sense of producing low molecular weight compounds that can be used as building blocks or platform chemicals to turn them into fine chemicals.

Table 4.2:- Total molecular weight calculation

	Value
No Average molecular (Mn)	675±2.85
Weight Average molecular weight(Mw)	1604±5.75
Z average molecular weight(Mz)	3330±3.51
Viscosity average molecular weight (Mv)	1604
Disperslty index(Mw/Mn)	2.3770
Mz/Mw	2.0759

Analyzing chemical structure of black liquor was used in disgusting binding site viz in degradation and syntan preparation stage. FT-IR spectroscopy was employed to determine structural information about biopolymer in black liquor. The spectrum of black liquor show bands at 1615, 1534 and 1425 cm⁻¹ corresponding to aromatic ring vibrations of the phenyl propane skeleton. A wide absorption band focused at 3400 cm⁻¹ is assigned to aromatic and aliphatic OH groups while bands at 2963, 2935, 2871 and 1469 cm⁻¹ are related to the C–H vibration of CH₂ and CH₃ groups. The cleaves b-O-4 and a-O-4 linkages leaving a lot of non-etherified phenolic OH groups in lignin, visible in spectrum at 1376 cm which is supported by other researcher.

UV spectroscopy were also employed in order to acquire structural information about lignin in black liquor. The UV spectrum was record in a range between 190nm to 1110 nm which explicitly explain the structural conformity and the result is depicted on figure 4.1.3

As evident from the result the UV spectrum of lignin in black liquor show peaks at 204nm, 214nm and 280nm. However, the UV spectrum did not show any absorption between wave lengths 400nm to 1110nm on visible region. This structural analysis both in FTIR and UV spectroscopy will help as to know the possible bond cleavage during degradation process. The disappearance or appearance of new peaks after degradation process will assure the cleavage of bonds.

4.2 Degradation of black liquor

4.2.1 Effect of organic solvent on degradation process

Analyzing the solubility of black liquor on organic solvent will have effect on selecting appropriate medium for degradation reaction. For this purpose various solvent were subjected for solubility analysis. Selection of solvent were done on the basis of their GSK solvent list, polarity and LD₅₀ value. GSK solvent selection guide categorize solvent based on boiling point, environmental impact health, flammability reactivity and life cycle score.

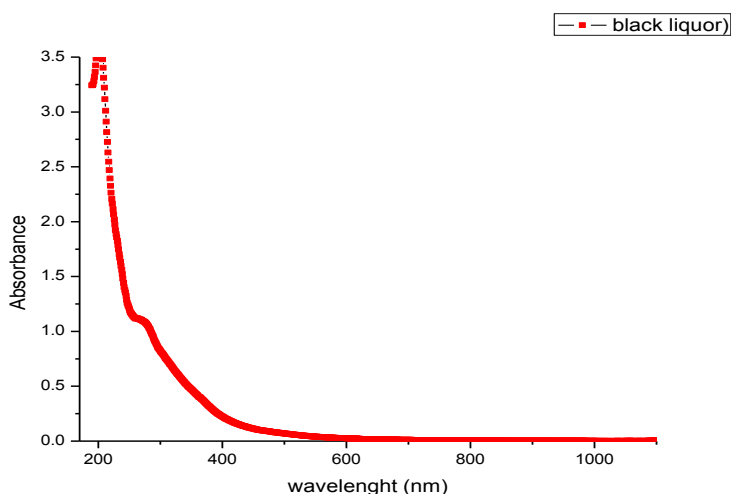


Figure 4.1.3:- UV spectrum of black liquor

The other properties were polarity which represent the relative ability of a molecule too engage in strong interaction with other polar molecule .In all case 3 gram of black liquor was added first, then followed by 30 ml of selected solvent and mixed for 3 minute. Observation are tabulated below on Table 4.2.1.

Table 4.2.1: solubility of black liquor in different solvent

s.no	Solvent	Solubility
1	Water	Soluble
2	Acetone	Insoluble
3	Ethyl acetate	Insoluble
4	Hexane	Insoluble

5	Chloroform	Insoluble
6	THF	Insoluble
7	DCM	Insoluble
8	Ethanol	Partially soluble

Black liquor was not soluble in most of selected organic solvent and 100% soluble in water. This was to deprotonating of functional group at highly alkaline pH which make the solution more polar and cleavage of ether bonds via increases the amount of free phenolic groups. It is evident from table 4.2.1 non polar solvent are completely insoluble whereas slightly polar and polar solvent show better solubility. In the case of water uniform dispersion was observed.

4.2.2 Effect of H₂O₂ on degradation process

4.2.2.1 Effect of H₂O₂ on percentage of lignin degradation

The aromatic structure of lignin has to be degradation in sense of producing low molecular size and weight compound that can be used as building blocks or precursor for synthesis of syntans. Fenton's reagent, a combination of hydrogen peroxide and a ferrous salt, is a potent oxidizing agent of organic compounds in acidic aqueous solution. Aqueous

Industrial Black liquor were used as raw material. The degradation of black liquor consisted of know amount of black liquor with 100 ml of water(solvent) for a duration of 5 hour for all reaction.

The effect of hydrogen per oxide concentration at 5 mmol, 15 mmol and 25 mmol while keeping concentration of iron (II) sulfite at 15 mmol and temperature at 45 °C were present in figure 4.2.2.1.

A certain relation exist s between the viscosity and molecular weight of macromolecule Polymer. Solely from viscosity, we can't get the molecular weight of polymer. But the Viscosity enlarged with the increase of the molecular weight. So in this study, we compared the molecular weight of degraded lignin from the perspective of the viscosity of biopolymer.

$$\text{lignin degradation (\%)} = \frac{(\text{viscosity})_b - (\text{viscosity})_a}{(\text{viscosity})_b} \dots \dots \dots (1)$$

Design-Expert® Software

lignin degradation

• Design Points

X1 = A: H2O2

Actual Factors

B: FeSO4 = 15.00

C: temp = 45.00

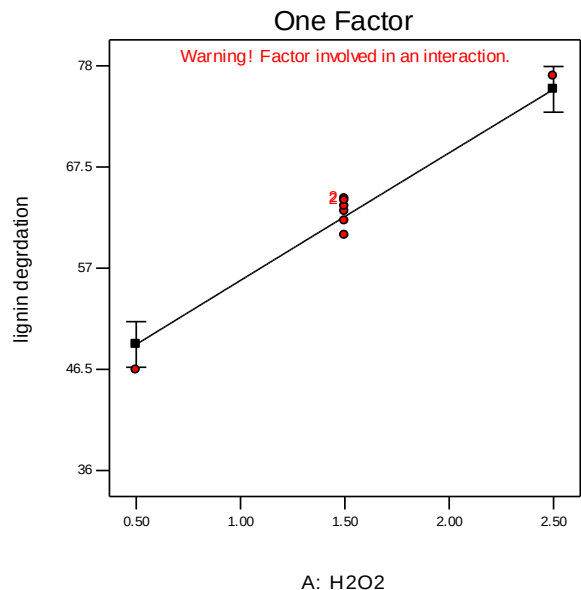


Figure 4.2.2.1:- Effect of H₂O₂ concentration on percentage of lignin degradation

Table 4.2.2.1 effect of H₂O₂ concentration on viscosity

Process	H ₂ O ₂ (ml)	FeSO ₄ .7H ₂ O (mmol)	Temperature (°C)	Viscosity
				CP
D18	5 mmol	15	45	3.71
D1	15 mmol	15	45	1.60
D5	25 mmol	15	45	2.06

The percentage of lignin degradation were increase as increasing concentration of hydrogen per oxide. It has been observed from figure 4.2.2.1 that the maximum and minimum percentage of lignin degradation obtained at hydrogen per oxide concentration of 25 mmol and 5 mmol ml respectively. It is evident from the result that increasing H₂O₂ will increase hydroxyl free radical which has high oxidation potential to degraded lignin in black liquor. The degradation process was shown a higher degree of degradation at 25 mmol of H₂O₂ with irrespective of other factors this will support there was Fenton's like reaction which generating Fe³⁺ and again allows Fe²⁺ regeneration in an effective cyclic mechanism to give rise reactive oxygen species.

4.2.2.2 Effect of H₂O₂ concentration on particle size

The effect of H₂O₂ concentration on hydrodynamic diameter that refer to how a particle diffuses within a fluid was determine using Malvern Zetasizer Nano ZS. The particle size distributions plot for reaction mixture D5, D1 and D18 are depict in figure 4.2.2.2. The increase in H₂O₂ concentration induced a reduction in particle size of black liquor sample treated with Fenton's reagent.

As observed from fig 4.2.2.2, particle size of lignin treated with 25mmol H₂O₂ (D5) have 174.2 nm which enormously decrease (Ca.94 %) and give rise to multiple peaks on DLS measurement. This result confirm formation hydroxyl radical generated by Fenton's reagent and perform high degree of degradation due to increase concentration of H₂O₂.

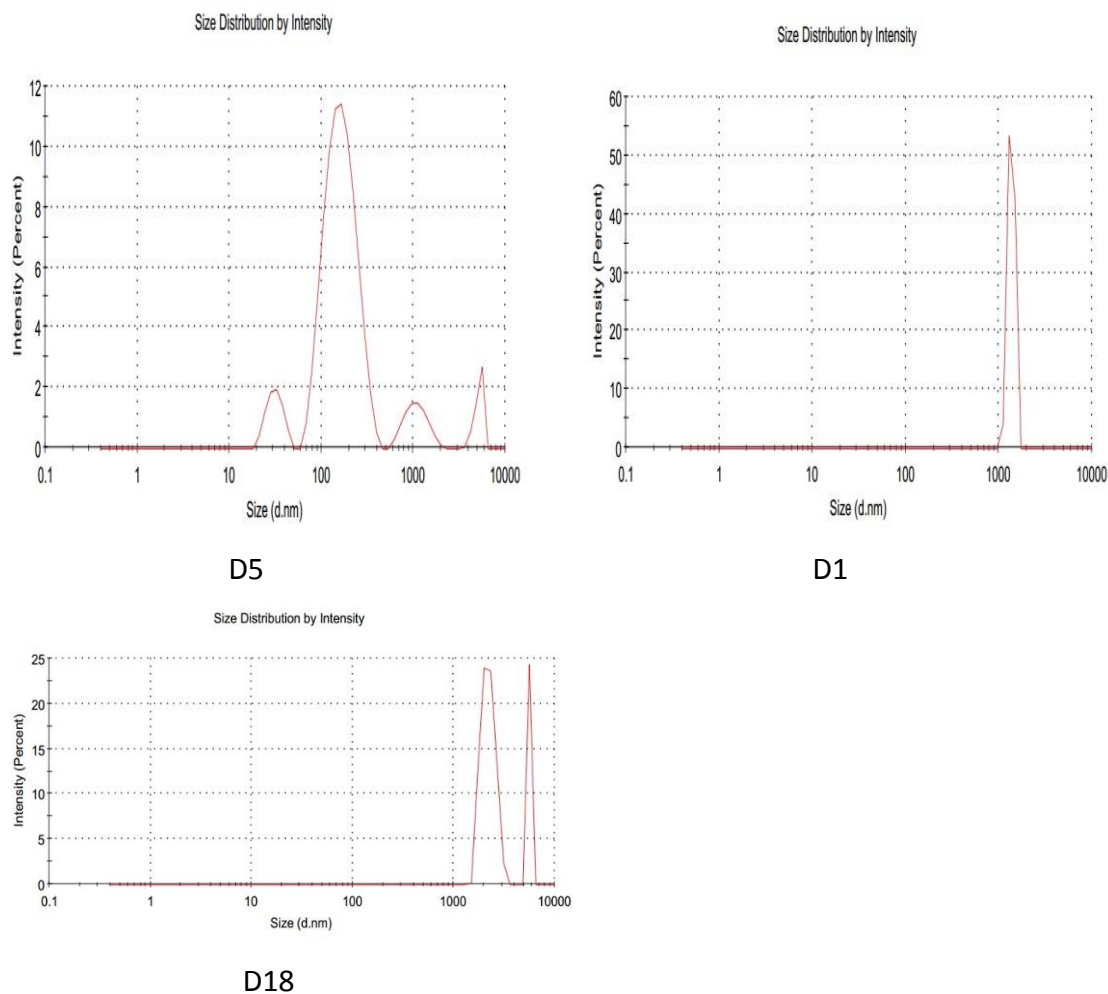


Figure 4.2.2.2:- effect of H₂O₂ concentration on particle size distribution

Whereas for D1 and D18 are 1330 nm and 2194 nm respectively. It is noteworthy to underline the particle size determination of lignin structure cannot be solo response variable to examine degradation process where, lignin cannot give structurally intact precursor due to presence of many reactive sites, but this principle fail to confirm using DLS measurement also there is possibility of formation in low hydrodynamic diameter with high molecular weight particle which gives us false positive result in particle size analysis. However, it is possible to examine the trend being followed in degradation process.

4.2.2.3 Effect of H₂O₂ concentration on absorbance maximum

In order to find out the effect of H₂O₂ concentration on absorbance maximum the UV spectrum of black liquor treated with Fenton's reagent were recorded using Lambda 3B (PerkinElmer®). As shown in figure 4.1 native lignin structure in black liquor show peak at 201 nm, 203 nm and 276 nm. This absorption are typical for lignin (11). Whereas the effect of H₂O₂ concentration on absorbance maximum were shown in fig 4.2.3a and fig 4.2.3b

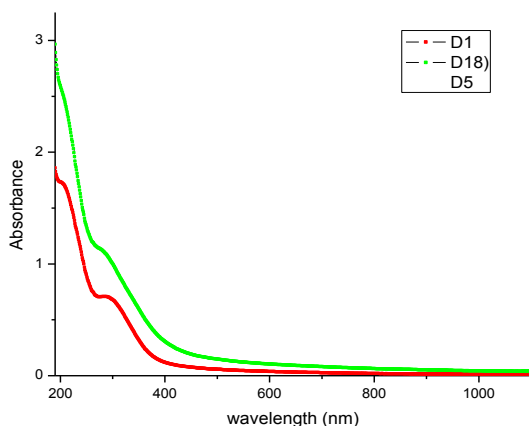


Figure 4.2.2.3a:- UV spectra for D1 and D18

As depict above the increase in H₂O₂ concentration caused a reduction in the maximum of lignin absorbance of black liquor samples treated with Fenton's reagent. This indicate the lignin structure profoundly modified by Fenton's treatment and cause explicit degradation.

The UV spectrum for reaction mixtures D5 and D1 didn't shows absorbance belonging to lignin structure rather show shoulder at 310 nm this may be arise from carbonyl group which will support the presence of braking down of C–C bond cleavage between the α-and β-carbon chain.

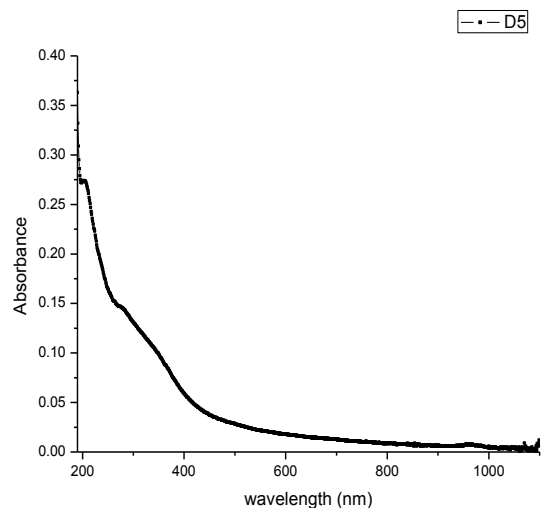


Figure 4.2.2.3b: - UV spectra for D5

4.2.3 Effect of iron (II) sulfate on degradation process

4.2.3.1 Effect of iron (II) sulfate on percentage of lignin degradation

The $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ system play a vital role in degradation of lignin by chemical oxidation path. Analyzing the efficacy of iron (II) sulfate on degradation were conduct by keeping constant H_2O_2 concentration and temperature at 15 mmol and 45°C while increasing Fe^{2+} concentration from 5mmol to 25 mmol. The result are depict on figure 4.2.3.

Design-Expert® Software

lignin degrdation

● Design Points

X1 = B: FeSO4

Actual Factors

A: H2O2 = 1.50

C: temp = 45.00

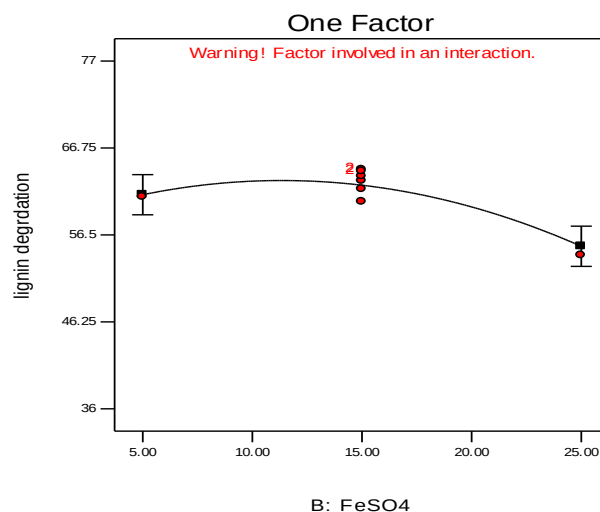


Figure 4.2.3.1:- Effect of Fe^{2+} concentration on lignin degradation

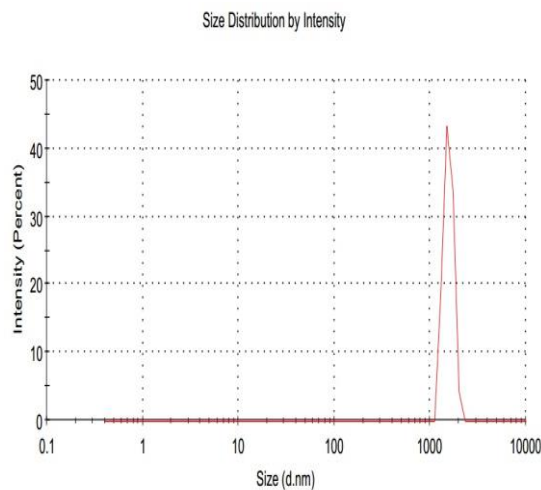
It has been observed that percentage lignin degradation for 5 mmol Fe^{2+} is ca.60.98 % whereas for 15 mmol and 25 mmol are ca.64% and ca.54.1% respectively. Degradation phenomena was directly proportional to Fe^{2+} concentration from 5 mmol to 15 mmol and inversely proportional from 15 mmol to 25 mmol. This may be due to the presence of unreacted Fe^{2+} give rise to increase viscosity of the reaction mixture. This will support the rate limiting reaction was the regeneration of Fe^{2+} in Fenton's like reaction. Fe^{2+} at 5 mmol have percentage lignin degradation of ca.60.98 %, quit big value, this will tell as there was trace amount of iron in the black liquor sample, which react with H_2O_2 , then degraded lignin into lower molecular weight moites .

Process	H_2O_2 (mmol)	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (mmol)	Temperature ($^{\circ}\text{C}$)	Viscosity
D2	15	5	45	1.71
D3	15	15	45	1.91
D1	15	25	45	1.60

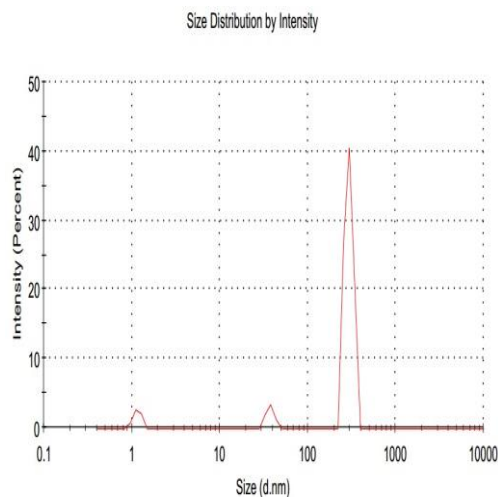
Table 4.2.3.2:- absolute viscosity for product D1, D2 and D3

4.2.3.2 Effect of iron (II) sulfate on particle size distributions

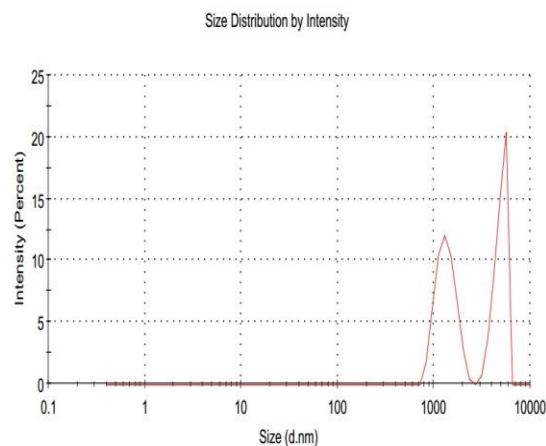
The particle size distributions at different concentration offer for reaction mixture D1, D2 and D3 were estimated and illustrate on fig 4.2.3.2(a) - (c). As observed from the result the increase in Fe^{2+} concentration from 5 mmol to 15 mmol induced degradation of lignin in black liquor. The hydrodynamic diameter for 5 mmol and 15 mmol is 1547 nm and 878 nm respectively which is much lesser than that of untreated black liquor particle size. However, when Fe^{2+} concentration increase from 15 mmol to 25 mmol there increasing in particle size diameter from 1574nm to 1987nm with 100% intensity respectively. This will support the finding in percentage lignin degradation.



D3



D2



D1

Figure 4.2.3.2:- particle size distribution for reaction mixture D1, D2 and D3

4.2.3.3 Effect of Fe^{2+} concentration on absorption maximum

The UV spectrum will deduced on if there is degradation of lignin in black liquor occurs due to change in Fe^{2+} concentration. As evident from fig 4.2.3.3 the reaction mixture D2 didn't show absorption belonging to native lignin structure. However there is increase in absorption at 380 nm which clear show us there is occurrence of bond cleavage and bring degradation phenomena. The increasing in Fe^{2+} concentration from 15 mmol to 25 mmol, the UV spectrum resemble from one another, therefore further addition of Fe^{2+} above its threshold amount cause negative effect on degradation process.

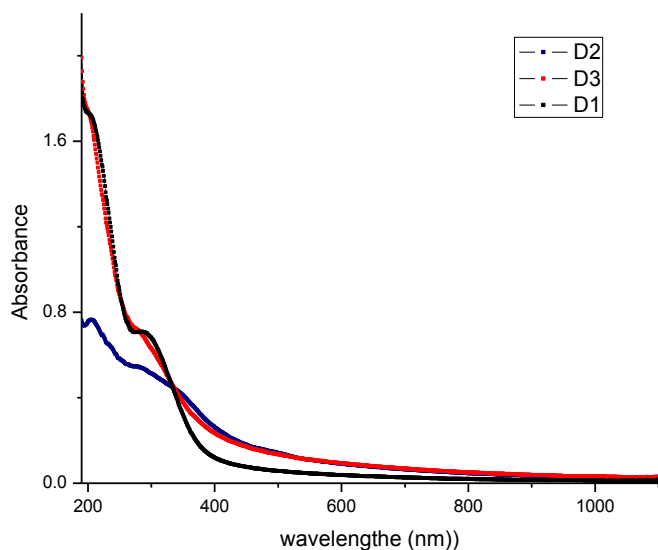


Figure 4.2.3.3:- Effect of Fe^{2+} concentration on UV spectrum

4.2.4 Effect of temperature on degradation process

4.2.4.1 Effect of temperature on percentage of lignin degradation

The effect of temperature on percentage of lignin degraded in black liquor initiated by Fenton's reagent has been study in order to analysis there effect on reaction mechanism. Different reaction temperature were selected in order to investigate its effect on percentage of lignin degradation. The concentration of H_2O_2 and Fe^{2+} kept constant at 15 mmol and 15 mmol respectively, while changing temperature from 25 °C to 65 °C. The results are depict on figure 4.2.4.1.

As evident from the result in general increasing trend showed as the reaction temperature increase from 25 °C to 65 °C. The percentage of lignin degradation of reaction mixture D20, D7 and D12 are 58.3%, 63.4% and 67.3% respectively. When the temperature from 25 °C to 45 °C there is 13.7 % increase in overall efficiency and increasing of temperature from 45 °C to 65 °C cause urges only 8.1 % increment in efficiency.

This will support the fact the temperature in Fenton's reaction manly participate in thermal decomposition of H_2O_2 into H_2O^+ and OH^+ . Therefore, further increasing in temperature at this $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ concentration will not have significant improvement in percentage of lignin degradation.

Design-Expert® Software

lignin degrdation

● Design Points

X1 = C: temp

Actual Factors

A: H₂O₂ = 1.50

B: FeSO₄ = 15.00

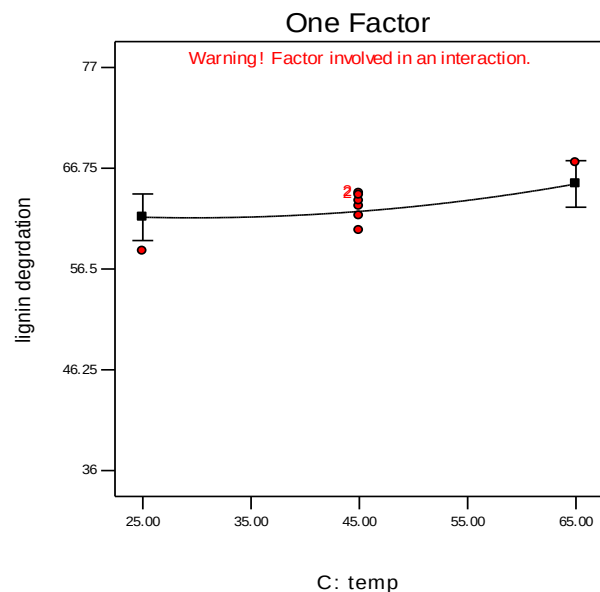


Figure 4.2.4.1:- Effect of temperature on percentage of lignin degradation

Process	H ₂ O ₂ (mmol)	FeSO ₄ .7H ₂ O. (mmol)	Temperature (°C)	Viscosity
D20	15	15	25	4.37
D7	15	15	45	2.47
D12	15	15	65	2.69

Table 4.2.4.1:- Effect of temperature on dynamic viscosity

4.2.4.2 Effect of temperature on particle size distribution

The effect of temperature on hydrodynamic diameter of lignin molecule were investigated in order to strengthen the result found on percentage lignin degradation. The particle size distributions for reaction mixture D20, D7 and D12 were estimated and depict on fig 4.2.4.2. As observed from the result the particle size distribution is decrease as temperature increase which conform the occurrence of degradation. When the temperature increase from 25 °C to 45 °C the particle size tremendously reduce from 1779 nm to 955 nm with 100% intensity. This automatically support the result found on percentage of lignin degradation. However when the

temperature increase from 45 °C to 65 °C the particle size reduce slightly from 955 nm to 520 nm but give rise two peaks with different intensity.

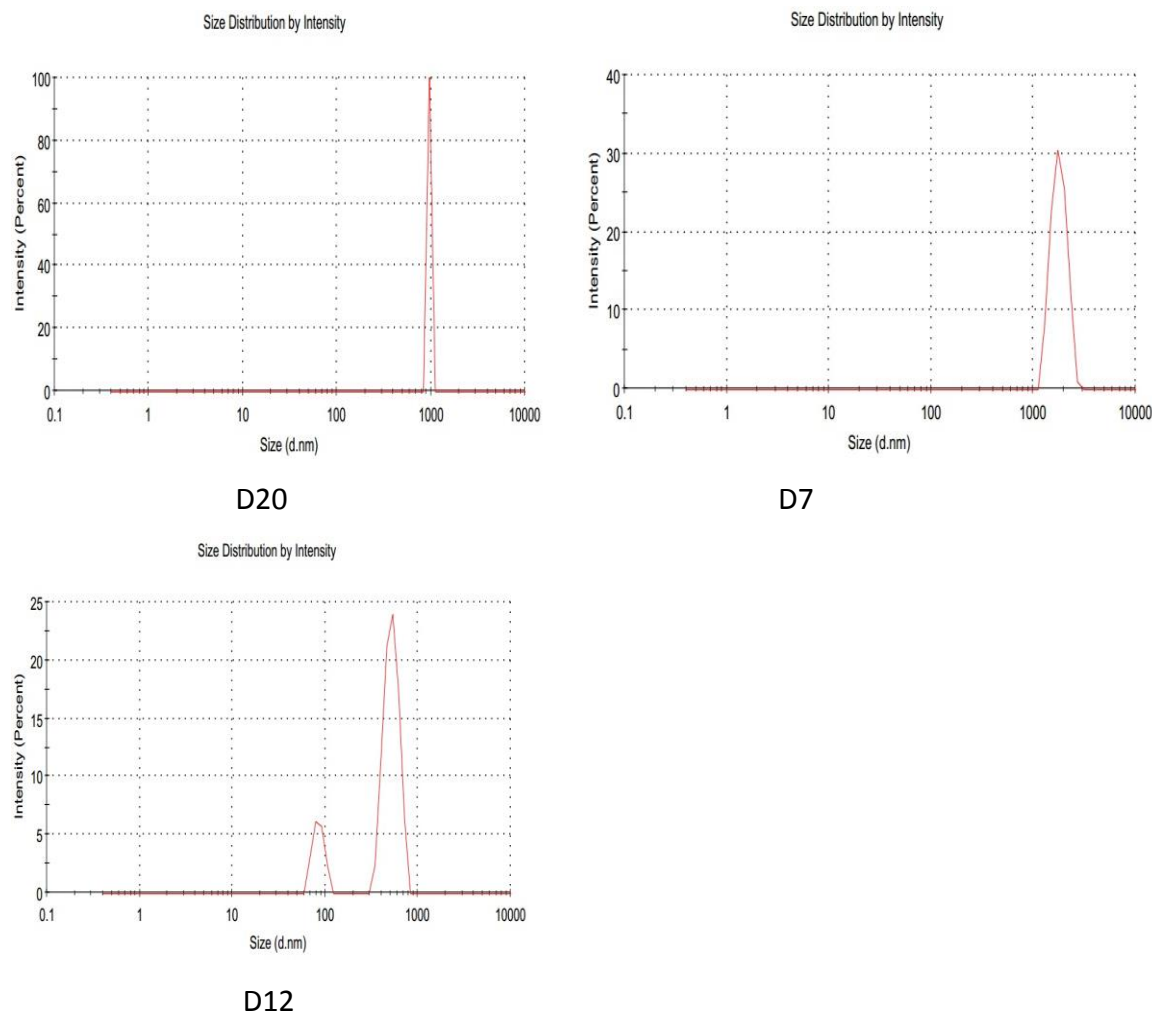


Figure 4.2.4.2:- Effect of temperature on particle size distribution

4.2.4.3 Effect of temperature on absorption maximum

The UV spectrum will show upon if there is degradation of lignin in black liquor occurs due to change in temperature. As evident from fig 4.2.4.3 the reaction mixture D12 didn't show absorption belonging to native lignin structure. However there is increase in absorption at 380 nm which clear show us there is occurrence of bond cleavage and bring degradation phenomena. The increasing in temperature from 45°C to 65°C there is decrease in absorption in ultra-violet region. Therefore further increasing of temperature positive effect on degradation process.

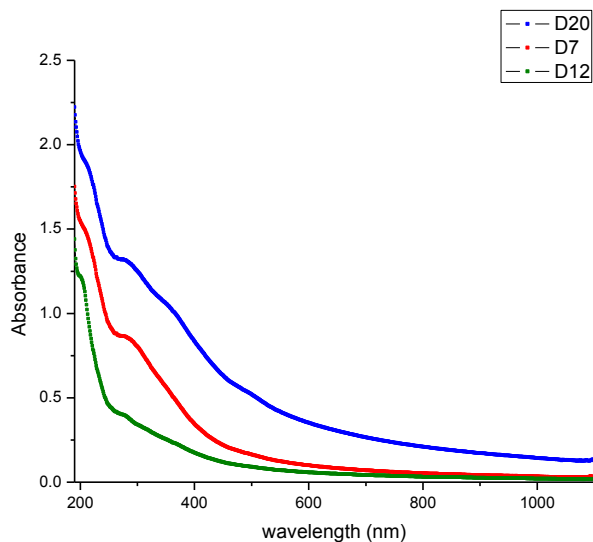


Figure 4.2.4.3:-Effect of temperature on UV spectrum

4.3 Analysis on degradation process

4.3.1 Statically analysis

Experimental design was selected for the statistical analysis of the study by selecting Central Composite Design (CCD) and the response measured is the percentage lignin degradation from the perspective of change in viscosity before and after degradation. The extent of degradation on lignin in black liquor were investigating by selecting three factor over three level suchlike H_2O_2 concentration, Fe^{2+} concentration and reaction temperature.

Regression analysis and analysis of variance (ANOVA) was done by using Design Expert 7.0.0 Program. The software program was used to generate surface plots, using the fitted Equation obtained from the regression analysis, keeping one of the independent variables Constant.

Response of the degradation process was used to develop a mathematical model that correlates the percentage of lignin degradation to degradation process constituent were investigating. Design Expert software version 7.0.0 was used for the regression analysis of the experimental data and also for evaluation of the statistical significance of the equation developed. The central composite design results and responses, and the statistical analysis of the ANOVA are given in tables 4.3.1 and 4.3.2 respectively. The actual percentage of lignin degradation at different process parameters. The model was tested for adequacy by analysis of variance.

$$\text{lignin degradation (\%)} = \frac{(\text{viscosity})b - (\text{viscosity})a}{(\text{viscosity})b} \dots \dots \dots (1)$$

Run	Process code	H ₂ O ₂ (mmol)	Fe ²⁺ (mmol)	Temperature (°C)	Actual value (%)	Predicted value (%)	Residual
1	D1	15	15	45	62.87	62.35718	0.51
2	D2	25	25	25	72.3	71.40682	0.89
3	D3	15	5	45	60.98	61.23473	-0.25
4	D4	25	25	65	75.21	76.58082	-1.37
5	D5	25	15	45	76.91	75.55273	1.36
6	D6	15	15	45	64	62.35718	1.64
7	D7	15	15	45	63.4	62.35718	1.04
8	D8	25	5	65	70.9	71.61182	-0.71
9	D9	25	5	25	70.2	70.36782	-0.17
10	D10	15	25	45	54.1	55.15873	-1.06
11	D11	5	5	25	54.5	52.80082	1.70
12	D12	15	15	65	67.3	65.14873	2.15
13	D13	5	5	65	53.83	54.39482	-0.56
14	D14	15	15	45	64.2	62.35718	1.84
15	D15	5	25	25	36.72	35.67982	1.04
16	D16	15	15	45	61.9	62.35718	-0.46
17	D17	15	15	45	60.4	62.35718	-1.96
18	D18	5	15	45	46.41	49.08073	-2.67

19	D19	5	25	65	41.7	41.20382	0.50
20	D20	15	15	25	58.3	61.76473	-3.46

Table 4.3.1:- Experimental values for percentage of lignin degradation

As evident from table 4.3.1 ,the maximum percentage of lignin degradation was Ca 76.91% at experiment number 5 or product code D5, while the minimum percentage of lignin degradation was ca.41.7%, at experiment number 9 (D9). Also from the table experiment numbers 3, 5, 7, 13, 14 and 19 were maximum amount of yield gained. Therefore it was concluded that the maximum percentage of lignin degradation was gained at 25 mmol of H₂O₂ concentration, 15 mmol of Fe²⁺ concentration and 45^oC reaction temperature. The minimum yield was obtained at a 5 mmol of H₂O₂ concentration, 25 mmol of Fe²⁺ concentration, and temperature of 65^o C on experiment number 19(D19).

4.3.2 Development of Regression Model Equation

The practical deployment of a CCD often arises through sequential experimentation which makes it very efficient design for fitting second order model. The model equation that correlates the response on extent of degradation of lignin in black liquor treated by Fenton's reagent to process variables in terms of actual and coded value after excluding the insignificant terms was given below in equation.

Final Equation in Terms of Coded Factors:

$$\text{Percentage of Lignin degrdation} = 62.36 + 13.24 * A - 3.04 * B + 1.69 * C + 4.54 * A * B - 0.087 * A * C + 0.98 * B * C - 0.040 * A^2 - 4.16 * B^2 + 1.10 * C^2$$

A= H₂O₂ concentration

B= FeSO₄.7H₂O concentration

C= Degradation temperature

Final Equation in Terms of Actual Factors:

$$\text{Percentage of Lignin degrdation} = 52.60321 + 0.67442 * H2O2 + 0.042274 * FeSO4 - 0.22992 * temp + 0.045400 * H2O2 * FeSO4 - 4.37500E-004 * H2O2 * temp + 4.91250E-003 * FeSO4 * temp - 4.04545E-004 * H2O2^2 - 0.041605 * FeSO4^2 + 2.74886E-003 * temp^2$$

Table 4.3.2:- Analysis of variance fro experimental result

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	2111.41	9	234.60	50.97	< 0.0001
A-H ₂ O ₂	1751.92	1	1751.92	380.65	< 0.0001
B-FeSO ₄	92.29	1	92.29	20.05	0.0012
C-temp	28.63	1	28.63	6.22	0.0318
AB	164.89	1	164.89	35.83	0.0001
AC	0.061	1	0.061	0.013	0.9104
BC	7.72	1	7.72	1.68	0.0243
A ²	4.501E-003	1	4.501E-003	9.779E-004	0.9757
B ²	47.60	1	47.60	10.34	0.0092
C ²	3.32	1	3.32	0.72	0.4152
Residual	46.02	10	4.60		
Lack of Fit	35.69	5	7.14	3.45	0.1

The Model F-value of 12.18 implies the model is significant. There is only a 0.01% chance that a model F-value this large occurs due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AB, AC, B² and C² are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

The adjusted R-square were 0.907 whereas predicted R-square were 0.873 which are reasonably equal.

4.3.3 Interaction effect between Process Variables

The process variables were found to have significant interaction effects. From Figure 4.3.3.2 to 4.3.3.4-and 4.3.3.6 shows the interaction between H₂O₂ concentration and Fe²⁺ concentration, H₂O₂ concentration and reaction temperature and Fe²⁺ concentration and reaction temperature respectively, on percentage of lignin degradation. Generally, an increase in H₂O₂ concentration is found to increase percentage of lignin degradation up to some optimal value in all three cases. Additionally it was observed that at lower value of H₂O₂ concentration, Fe²⁺ concentration and higher reaction temperature, always resulted in higher lignin degradation than when using lower Fe²⁺ concentration and reaction temperature. This phenomenon is further supported by the fact that H₂O₂ concentration is the most significant process variable that affects the percentage of lignin degradation as indicated by graphs.

Design-Expert® Software

lignin degradation

● Design Points

76.91

36.72

X1 = A: H2O2

X2 = B: FeSO4

Actual Factor

C: temp = 45.00

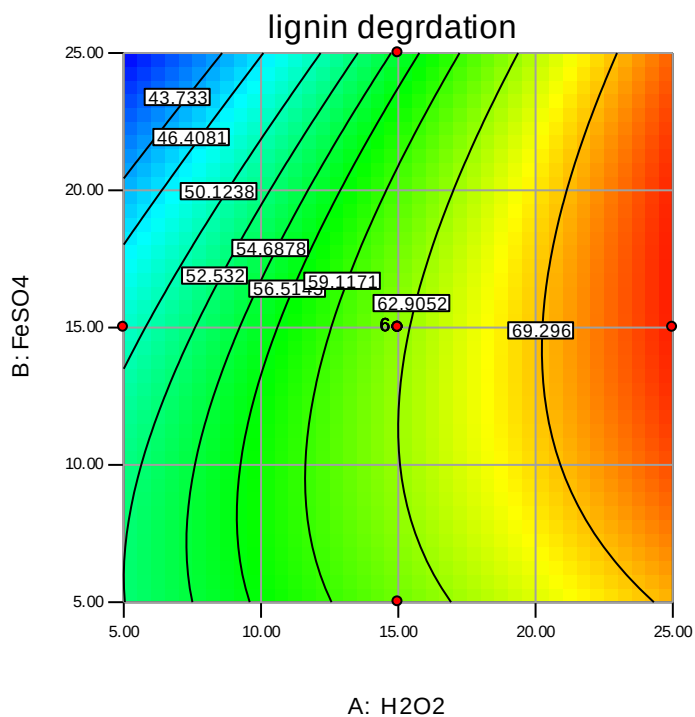


Figure 4.3.3.2: Contour plot for interaction effect of H_2O_2 and Fe^{2+} concentration

Design-Expert® Software

lignin degradation

76.91

36.72

X1 = A: H2O2

X2 = B: FeSO4

Actual Factor

C: temp = 45.00

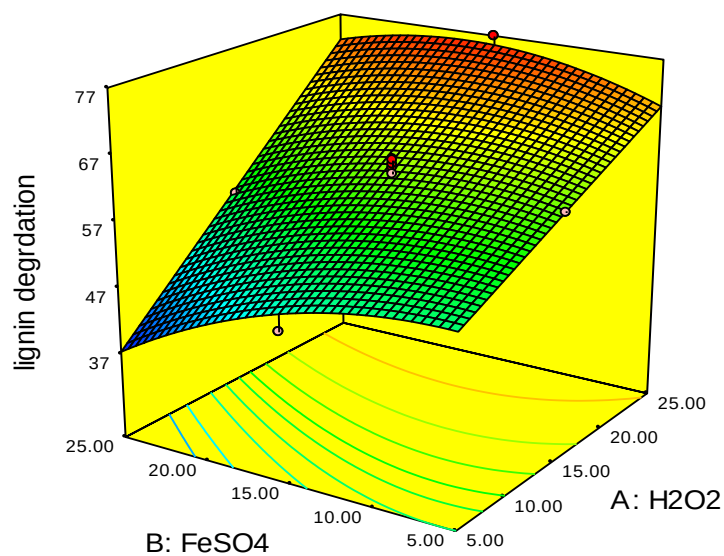


Figure 4.3.3.3:- surface plot for interaction effect of H_2O_2 and Fe^{2+} concentration

Design-Expert® Software

lignin degrdation

● Design Points

76.91

36.72

X1 = A: H2O2

X2 = C: temp

Actual Factor

B: FeSO4 = 15.00

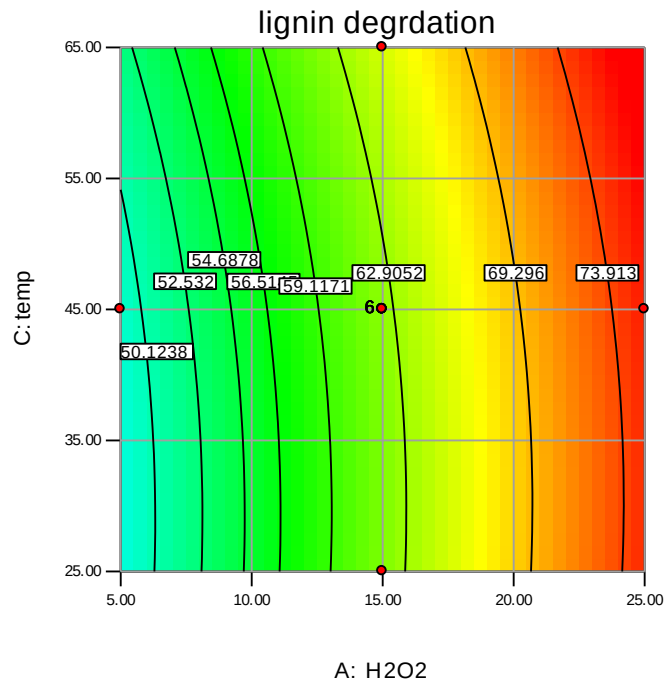


Figure 4.3.3.4:- Contour plot for interaction effect of H₂O₂ concentration and temperature

Design-Expert® Software

lignin degrdation

76.91

36.72

X1 = A: H2O2

X2 = C: temp

Actual Factor

B: FeSO4 = 15.00

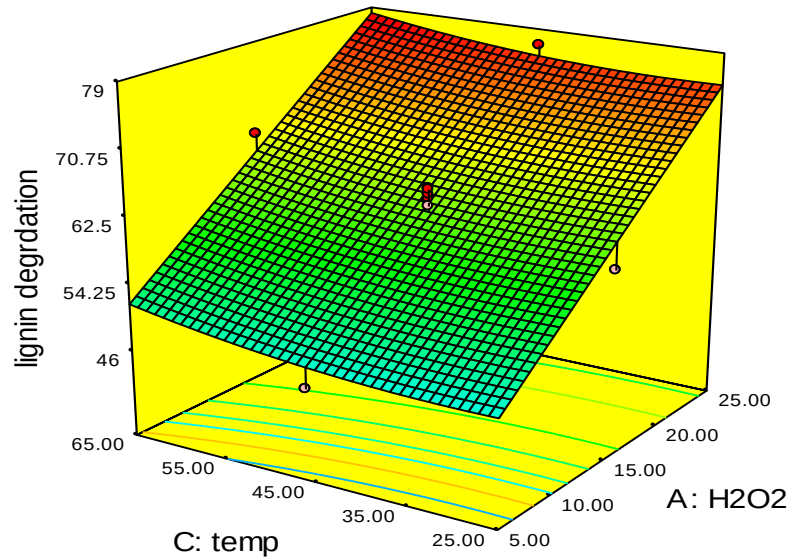


Figure 4.3.3.5:- surface plot for interaction effect of H₂O₂ and temperature

Design-Expert® Software

lignin degradation

● Design Points

76.91

36.72

X1 = B: FeSO4

X2 = C: temp

Actual Factor

A: H2O2 = 15.00

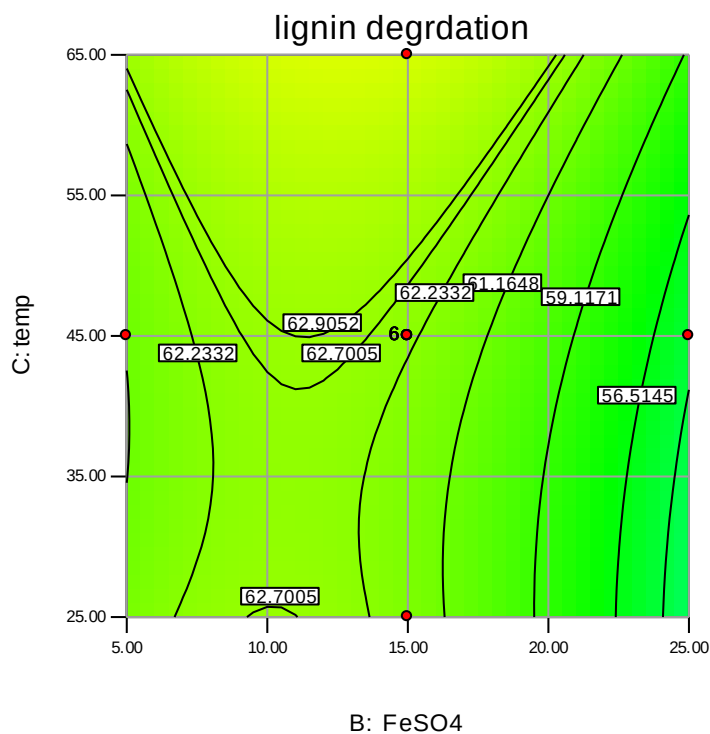


Figure4.3.3.6:- Contour plot for interaction effect of Fe^{2+} concentration and temperature

Design-Expert® Software

lignin degradation

76.91

36.72

X1 = B: FeSO4

X2 = C: temp

Actual Factor

A: H2O2 = 15.00

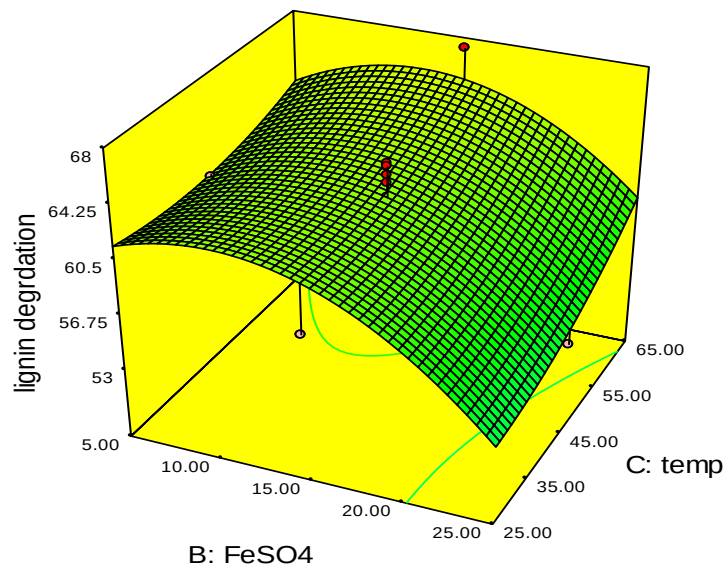


Figure 4.3.3.7:-surface plot for interaction effect of Fe^{2+} concentration and temperature

4.3.4 Optimization of process variable

Our ultimate goal is to maximize the percentage of lignin degradation as much as possible so that the possibility of scale formation is minimized. The above results have shown that the three degradation process variables and their interactions among the variables affecting the percentage of lignin degraded. Therefore, the next step is to optimize the process variables in order to obtain the highest lignin degraded using the model regression developed.

Using the optimization function in Design Expert 7.0.0, it was predicted that at the following conditions; 25 mmol of H_2O_2 concentration, 15 mmol of Fe^{2+} concentration and 45°C of reaction temperature an optimum degradation 75.55% was obtained. In order to verify this prediction, experiments were conducted and the result of ca.76.9% degradation was found which will agree with the predicted value. The optimization result showed that the same result as the ANOVA output. The ANOVA output shows that the degradation process is highly and significantly affected by the H_2O_2 concentration, Fe^{2+} concentration, reaction temperature, interaction effect between H_2O_2 concentration and Fe^{2+} concentration, interaction effect between H_2O_2 concentration and temperature.

4.4 Extraction of degraded lignin from black liquor

The extraction process was conducted to separate degraded lignin from black liquor which is going to be used for accomplishing synthesis of syringic acid. It is a crucial step since it will decide the overall yield of the process. The selection criteria of solvent for extraction process was selected on the basis of solubility of black liquor in that specific solvent which is explained under section 4.2.2. Ethyl acetate was selected as solvent medium which is virtually insoluble in water, can dissolve large number of organic compounds both polar and non-polar and has a low boiling point, in order to extract degraded lignin from black liquor. As shown in Figure 4.4 the organic layer was extracted repeatedly until we get a pure organic layer.

The phenolic group in black liquor was protonated at pH 9.8, however the degradation process was conducted between pH 4-6. This will explicitly explain that the extracted organic layer is predominantly consists of phenolic compounds and its derivatives. Whereas other constituents of black liquor such as inorganic compounds (mostly sodium salt), hemicellulose, sugar and un-degraded lignin

are drawn into aqueous. The removal of solvent was done using rote vapor till concentrated product. The concentrated product were acquired foe sytan making process.

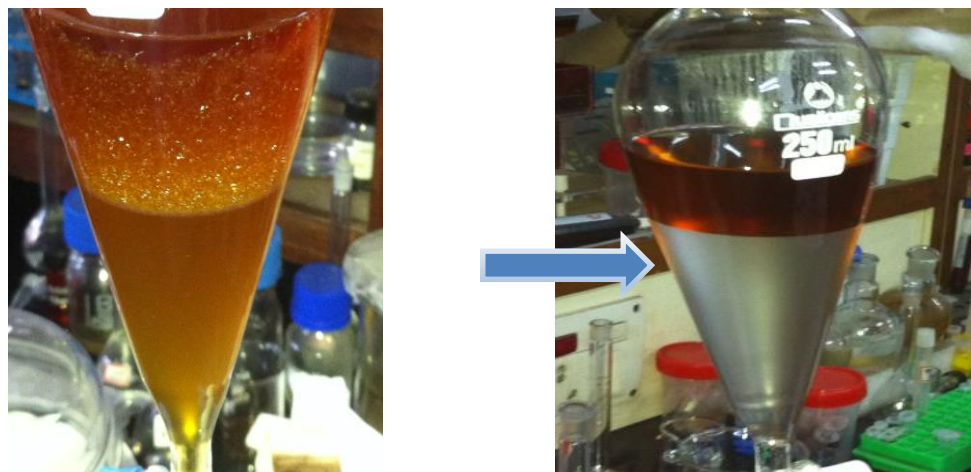


Figure 4.4:- Extraction of degraded lignin with ethyl acetate

4.5 preparation of sytan

The extracted degraded lignin was taken as starting material in order to prepare sytan for post tanning application based on phenolic compound. The primary requirement of sytan were achieve via sulponation using sulphonation agent suchlike sulfuric acid and sodium metabisulphite and condensation by formaldehyde. In order to understand the effect of each component on the performance of sytan and to provide alternative to commercially available phenol-formaldehyde based sytan, six product were prepare, sytan prepared using degraded lignin and sulfuric acid (SS1); sytan prepare using degraded lignin and combination of sulfuric acid and sodium meta bisulfite (SS2) and sytan prepare using degraded lignin and sodium meta bisulfite (SS3). Sytan prepare using degraded lignin, sulfuric acid and formaldehyde (SF1); Sytan prepared using degraded lignin formaldehyde with combination of sulfuric acid and sodium meta bisulfite (SF2) and sytan prepare using degraded lignin, sodium meta bisulfite and formaldehyde (SF3).

4.5.1 Effect of sulphonation temperature

The tanning power of sytan depend on the degree of sulphonation which highly affected by sulphonation temperature. A know amount extracted degraded lignin were taken then sulphonation was done using concentrate sulfuric acid under different temperature .The

sulphonation time and mixing speed were kept six hour and 250 rpm respectively. The effect of temperature at 60 °c, 80 °c 100 °c and 120 °c on total solubility of syntan were tabulated in table 4.5.1

Table 4.5.1:- Effect of sulphonation temperature on solubility of syntan

Temperature	Total soluble	Percentage of total solubility
60 °c	28.40±0.75	71.36
80 °c	32.12±0.31	80.71
100 °c	36.41±0.11	91.49
120 °c	36.65±0.16	91.78

All values are standard deviation of two sample

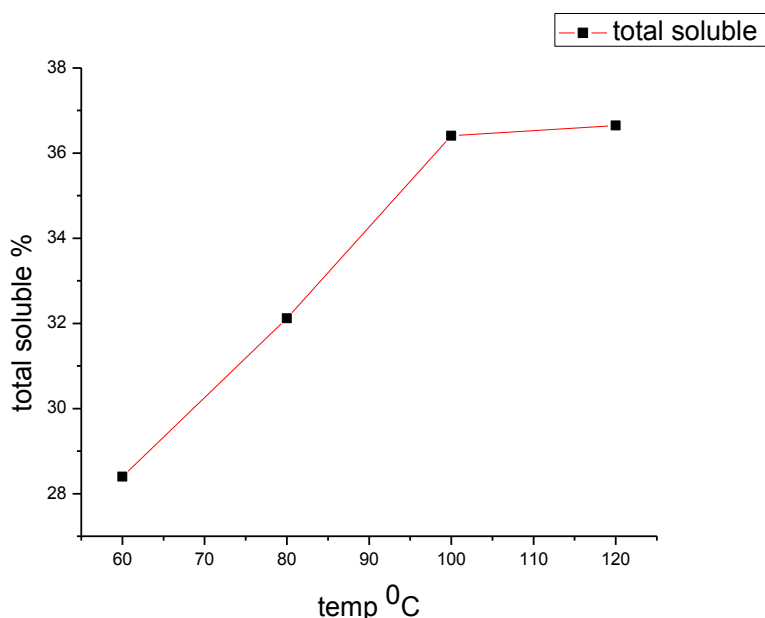


Figure 4.5.1:- Effect of temperature on total solubility of syntan

It has been observed from fig 4.5.1 that the minimum total solubility of syntan was for a temperature of 60 °c is about 28.4% and the maximum value at 120 °c which is 36.65 %.

It clearly show that total solubility of syntan were directly proportional with increasing temperature but as observed from the figure 4.5.1 increasing temperature from 100 °c to 120 °c was having nominal impact on solubility this may be due to less formation of paraphenol sulphonic acid this phenomena indicates that further increasing in temperature gives no

contribution on total solubility. In the course of the experiment reactions more than 100 °c were difficult to handle and need more precaution which makes less practical.

4.5.1.2 Interaction effect of time and type of sulfonation agent

Water soluble biopolymer syntan have been obtained depending on the type of sulphonation agent used. In order to determine the effect of sulphonation agent on performance of syntan a known amount sulfuric acid and sodium meta bisulfite were taken as potential sulfonation agent. The sulphonation was carried out in glass lined reactor at a temperature of 100°C which allow us to be sure all sufon- group enter into degraded lignin molecule. The resultant products were then neutralization using sodium hydroxide to a pH of 4.5-5.0. Sample were taken every one hour interval in order to analysis change in response variable. In order to understand the effect on type of sulfonation agent on degree of sulfonation comparison were made among three product via, 100% sulfuric acid (SS₁) , 50:50 of sulfuric acid to sodium meta bisulfite(SS₂) and 100% sodium metabisulfite(SS₃) The total solid, total soluble and particle size of product were determine while characterizing the syntan. Effect of type of sulfonation agent on total solid and soluble content are tabulated in table 4.5.2.

Table 4.5.1.2. Effect of sulfonation agent

H ₂ SO ₄ : NaS ₂ O ₅	Total solid (%)	Total soluble (%)	Percentage of total soluble (%)	pH
100:0	39.2	36.41	91.4	1.85
50:50	41.5	36.22	87.3	2.54
0:100	46.7	38.24	81.9	3.94

The percentage of total soluble from total solid was increase as the amount of sulfuric acid increase in sulfonation reaction. It has been observed from table 4.5.2 the percentage of total soluble in 100% sulfuric acid reaction was 91.4, whereas in 0% sulfuric acid reaction was 81.9%. From this data we can conclude sulfonation degraded lignin using sulfuric acid yield better total soluble matter than other trial this is due to easy liberation of sulfon group during the reaction. In addition to that , from physical observation product sulfonated by sodium meta bisulfite show lighter and clear tint than the one made by sulfuric acid and combination, this will give us access to use the product for pestle shade leather.

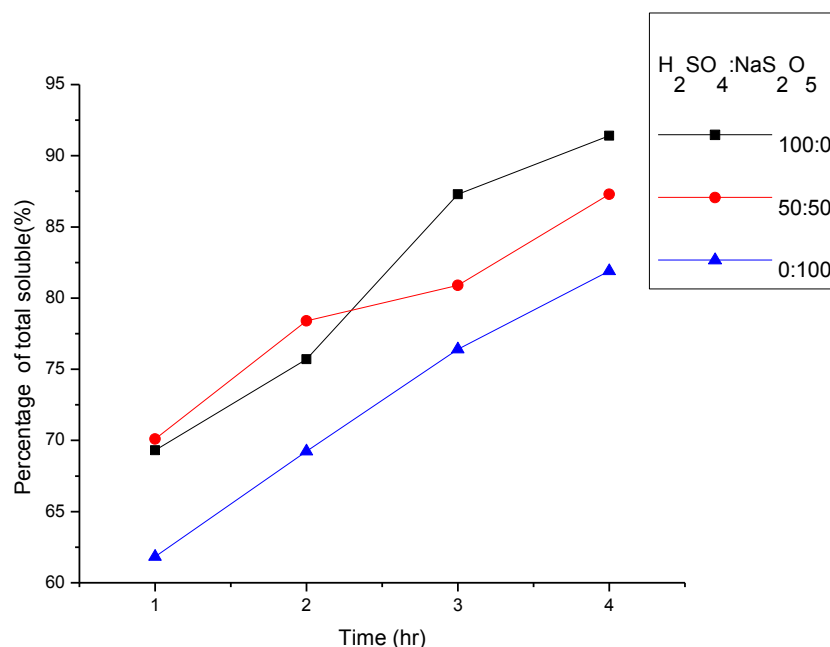


Figure 4.5.2.2:- total soluble matter on different time interval

As observed from result in figure 4.5.2.2 effect of time on total soluble while varying type of sulfonation agent 50% sodium meta bisulfite reaction show better total soluble content on the first two hours, this is due to the contribution of both sulfonation agents toward increasing the hydrophilic group into aromatic nucleus make the product reasonably soluble in water. In general we can conclude from the result there is directly proportional relationship between time and total soluble content. But the total soluble matter affect by time in lesser increment over varying temperature than type of sulfonation agent.

Particle size of a 10% aqueous solution of the product was obtained through a particle size analyzer instrument. The pH profile of product have effect on their average diameter of the particle, so the measurement where taken at pH generally employed for retanning operation. As observed from figure 4.5.2.3 the 10% solution of product SS₁ had particle size of 437 nm. It is therefore expected the product SS₁ would penetrate into the matrix and provide for the fullness and body of the leather.

It has been seen from result in figure 4.5.2.4 the product SS₂ had particle size of 819 nm which expected to penetrate through matrix while product SS₃ had 1222nm would fill up the intermediate layers, thereby provide necessary compactness to the leather

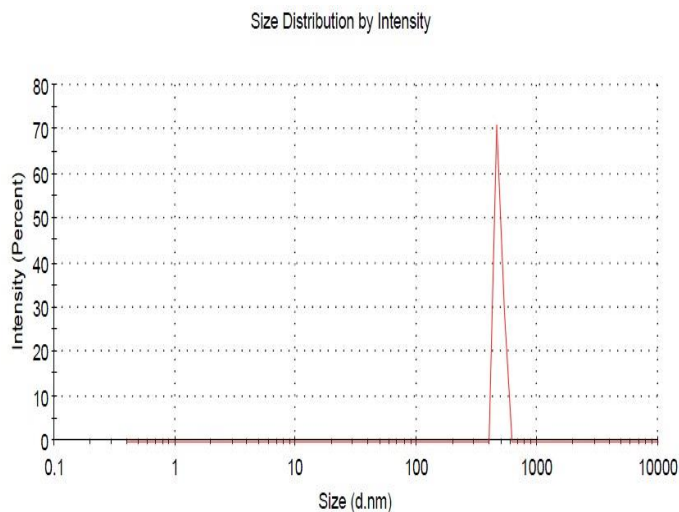
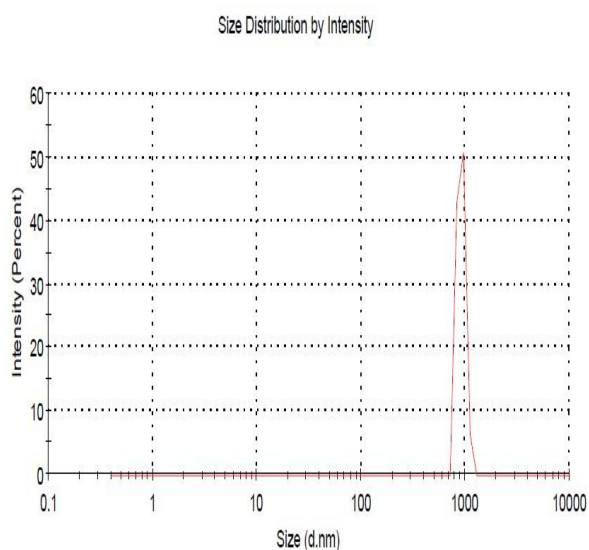
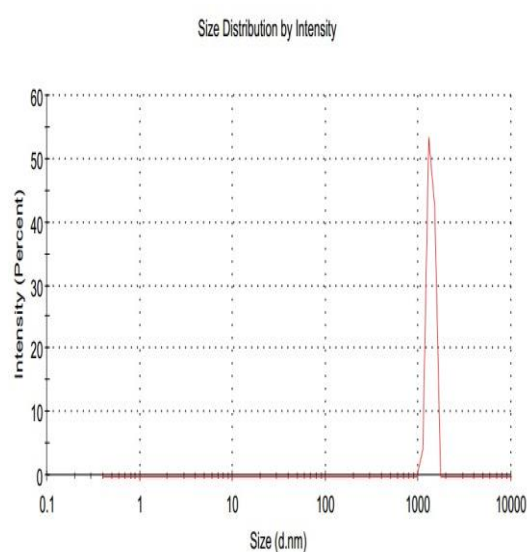


Figure 4.5.2.3:- particle size distribution for SS1

. Most of the time the particle size of syntan were affected by condensation process which impart bridge connected between aromatic molecules. However, particle size of product only may not be enough to predict penetration and bindability of product toward skin matrix. As native lignin structure reach in phenolic moities where degradation process may promote the formation hydrogen bond interaction with collagen which makes the sulfonated product of degraded lignin resistance to prolong washing with water.



SS2



SS3

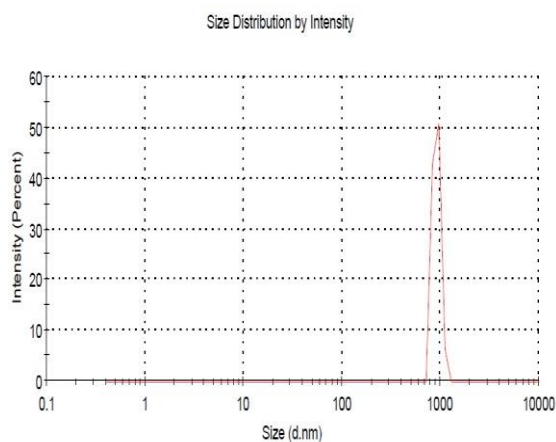
Figure 4.5.2.4 particle size distribution for product SS2 and SS3

The resistance of products towards natural light was assessed by exposing the prepared syntan for six hour on day light as a result there was no major change in colure of products.

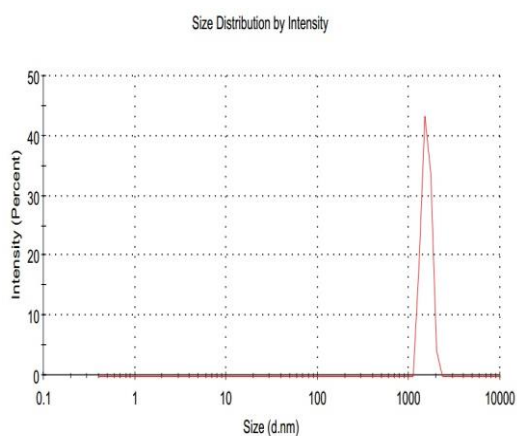
4.5.3 Effect of formaldehyde on syntan

In syntan preparation formaldehyde were used for condensation polymerization reaction since it will withdraw Methylene Bridge between aromatic organic compounds. Formaldehyde usually increase number of phenolic group per chain which is predominate functional group from tanning aspect. The effect of formaldehyde on syntan prepared from degraded lignin were investigating using product SS1, SS2 and SS3 by further treatment of all product with 0.15 mol for formaldehyde under 50°C temperature for 3 hour. Particle size distribution for polymerize product were analyses and the result are depicted on figure 4.5.3. Where Syntan prepare using degraded lignin, sulfuric acid and formaldehyde (SF1); Syntan prepared using degraded lignin formaldehyde with combination of sulfuric acid and sodium meta bisulfite (SF2) and syntan prepare using degraded lignin, sodium meta bisulfite and formaldehyde (SF3).

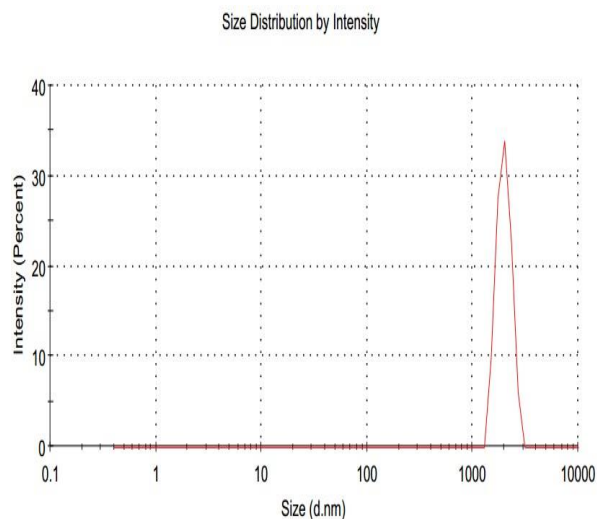
As evident from the figure there is increasing in particle size due to condensation polymerization reaction. The particle size distribution for SS1 were but after treatment with formaldehyde which become product SF1 it increase to 909 nm which expected to penetrate through matrix. Product SF2 and SF3 have particle size distribution 1280 nm and 1980 nm which expected to fill up the intermediate layers, thereby provide necessary compactness to the leather



SF1



SF2



SF3

Figure 4.5.3:-Particle size distribution for product SF1, SF2 and SF3

4.6 Evaluation of product

4.6.1 Physical properties of leather

The both experimental and control crust leathers were subjected to various physical strength measurements in order to study the effect on the bulk properties of crust leathers. The physical strength parameters suchlike tensile and tear strength for leather made using commercial phenolic syntan and lignin derivative syntan both for along and across backbone line. The mean of the value corresponding to along and across backbone was calculated for both strength properties and given in table 4.6.1

Table 4.6.1:- tensile and tear strength characteristics

Sample	Tensile strength		Tear strength	
	Tensile strength(N/mm ²)	Elongation at break (%)	Maximum load (N)	Tear strength (N/mm)
SS1	36.878	82.13	108.975	80.078
SS2	40.383	70.73	108.6278	78.2711
SS3	34.403	63.5	89.5243	76.1927
SF1	23.636	80.56	82.404	55.8876
SF2	28.677	67.3	85.53	59.9508

SF3	28.114	70.7	79.278	65.647
D	28.944	87.9	92.9977	76.7781
C	36.542	83.5	86.051	74.2897

It is evident from table 4.6.1 that the tensile strength increase in the order of SF1<SF2<SF3<D<SS3<C<SS3<SS1<SS2. It possible that all product condensation by formaldehyde show lower tensile strength due to the compaction level offers by this products resulting decreased fiber lubrication. Whereas sulfonate and degrade lignin product are comparable interims of tensile strength. The tear strength properties of leather mainly impart due to fiber lubrication and of all the product influenced the properties in less extent. The trend followed indicated that the product had better closeness to control leather.

Table 4.6.2:- Measurement of distension and strength of grain by the ball burst test

Product code	Average distension crack (mm)	Average load crack	Average distension burst (mm)	Average load burst
SS1	13.93	803.3	14.7	884
SS2	14.3	714.3	15	777
SS3	11.84	514.3	13.4	654
SF1	13.3	465	14.86	544
SF2	13.33s	478.7	15	608
SF3	11	339	12.8	482
D	12.6	430.7	14.3	584.7
C	12.93	563	13.93	641.7

The grain crack strength for the crust leathers were also carried out. The mean values corresponding to each experiment were averaged and the values are given in table 4.6.2.It

has been observed that the distension and grain strength properties of the leather made from synthesis product and that of control are barely comparable and all of them meet the UNDIO specification (54)

4.6.3 Organoleptic properties

Quality standard for upper leather are fullness, uniformity of substance, grain tightness and grain break .The comparisons of bulk properties of control and experimental leathers are provide in figure 4.6.3.1 and 4.6.3.2 based on standard tactical evaluation by experienced experts. The leather were evaluated for various properties suchlike softness, fullness roundness, grain tightness, color uniformity, grain smoothness and general appearance. The average value from two experience experts corresponding to each trials was assessed for each bulk properties.

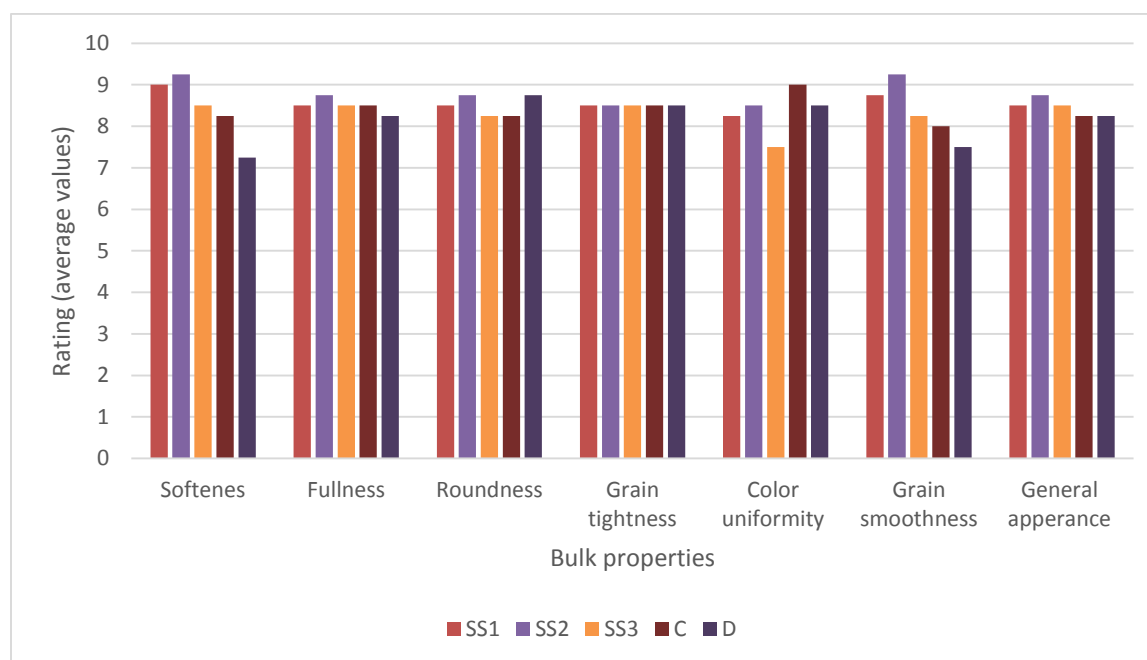


Fig 4.6.3.1:- organoleptic properties of leather retaned with product SS1, SS2, SS3,D VS C

The result obtained in fig 4.6.2.1 indicate that the product SS2 show better softens, roundness and grain smoothness this can be supported the factor sulfonation by sulfuric acid and sodium meta bisulfite will make better penetration into skin matrix and introduce more sulfone group for interaction with collagen. Color uniformity for control leather was much better than all other experiment leathers this may be draw back for lignin based syntans due to uneven affinity of dyes toward leather. The result sated in figure 4.6.2.2 indicate higher level of compactness obtained

when product SF1 and SF2 employed while product C impart better softness and color uniformity properties for product SS2 show improvement after condensation (SF2) reaction this phrase trig the point particle size of syntan have impact on the dye absorption of leather.

The grain tightness properties were influenced by all product on the same extent. This may lead as to conclude the synthesis product and phenol –formaldehyde syntan will not or negligible effect on grain tightening properties rather equal amount acrylic syntan added during retanning trial brought this effect. Therefore in order to satisfy quality standard for upper leather combined usage of degraded lignin based syntan along with acrylic, resin is required. In general the appearance of experiment leathers are comparable to or even better than that of control leather.

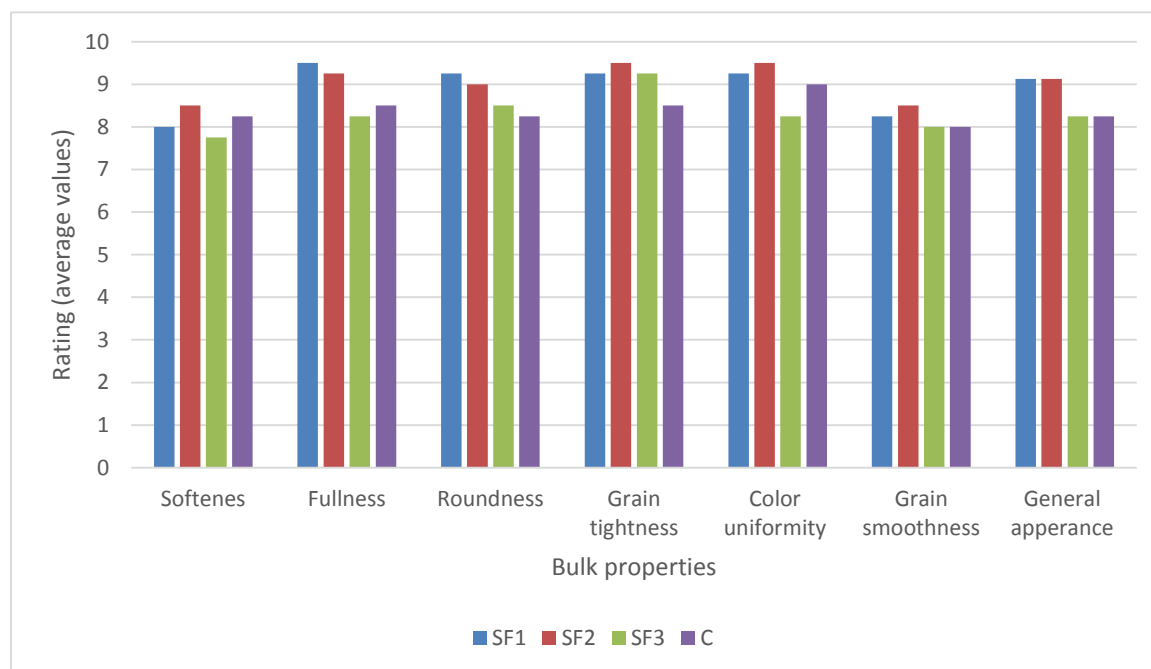


Figure 4.6.3.2 organoleptic properties leather retanned with SF1, SF2, SF3 and C

4.6.3 Color measurement

Color measurement value of leather made by all product are given in table 4.6.3. As observed from the result “L” value of leather made using product

Table 4.6.3:- color measurement of control and experiment leather

Leather	L	a*	b*	
SS1	22.53	-0.27	-0.32	

SS2	24.73	-0.66	-0.81	
SS3	28.16	-0.44	-0.86	
SF1	14.68	-0.19	-2.28	
SF2	18.22	-0.59	-1.76	
SF3	19.48	-0.20	-1.27	
D	20.94	0.10	0.04	
C	22.35	-0.30	-0.78	
Change with control leather				
	ΔL	Δa	Δb	ΔE
SS1	0.18	0.03	0.46	0.494
SS2	2.38	-0.36	-0.03	2.41
SS3	5.81	-0.14	-0.08	5.812
SF1	-7.67	0.11	-1.5	7.816
SF2	-4.13	-0.29	-0.98	4.254
SF3	-2.87	0.1	-0.49	2.913
D	-1.41	0.4	0.82	1.679

The effect of lignin based syntans on the color of the leather has been compared to that of commercially phenolic syntan through color measurement. Color value of crust leather has been shown in table 4.6.3. As observed from the result “L” value of leather made using product SF1, SF2 and SF3 have lower value than that of control leather. This indicate that those lignin based product which undergo condensation reaction are darker in shade than commercial phenolic syntan retanned leather. The value of “b” for almost all leather was lies nearly negative value this indicate that the leather are on bluish shade. The type of dyestuff viz., black hue and blue tint used in retanning trial may have effect on their occurrence on bluish shade. The overall color value (ΔE) for control and experiment leather was less than 5 except for leather retanned by product SF1, indicating that the color difference between samples cannot be distinguish by human eye. The other component of ΔE viz., Δa , Δb shows nearly zero values, which imply the color has not been altered. These result are in agreement with visual inspection.

4.6.4 Waste water analysis

The spent liquor from post-tanning operation has been collected from experiment and control leather. Chemical oxygen demand (COD), total solids (TS) and total dissolved solids (TDS) have been analyzed to know the environmental impact of lignin based syntan in accordance with that of commercial phenolic syntan. Direct interpretation of the observed parameter may not give full picture on their impact in environment. Hence, COD, TDS and TS value have been converted to emission load. The wastewater characterization of the products are presented in table 4.6.4.

Table 4.6.4 waste water characterization

Process	COD (ppm)	TS (ppm)	TDS (ppm)	Volume ^a of effluent (Lit/ton of shaved wet blue)	Emission load ^b (kg/ton of shaved wet blue leather)		
					COD	TS	TDS
SS1	6965.9	21674	18340	2119	14.77	45.93	38.86
SS2	7707.0	12749	12324	1980	15.26	25.24	24.40
SS3	7021.6	18473	16381	2044	14.35	37.76	33.48
SF1	9317.1	24711	22168	1891	17.61	46.72	41.92
SF2	7756.1	16777	16098	1972	15.31	33.08	31.75
SF3	9814.3	21478	20511	1831	17.97	39.32	37.55
D	35687	20820	18340	2245	80.1	46.74	41.17
C	9610	26451	253120	1649	15.84	43.61	41.42

As observed shown table 4.6.4 there is significant reduction in pollution reduction while using lignin base products. Product undergoing sulfonation by sulfuric acid viz, SS1, SF1 show higher value of TDS, this phrase due to the formation of considerable amount of neutral salt while adjusting the final pH of syntan using alkaline. Application of degraded lignin without any modification were brought high COD pollution load than all other product. This will arise from the hemicellulose and sugar constituent of black liquor which contribute to organic load. Emission load of TS for commercial phenolic syntan is 43.61, whereas there is reduction in TS load by 41.7%-24.1% has been observed using SS2 and SF2. The reduction in TS load are due to

improved fixation of syntans, dyes and fat liquor. This also evident from improved fullness, color and softness of the leather retanned by SS2 and SF2 in comparison with control leather.

CHAPTER FIVE

Conclusion and recommendation

5.1 Conclusion

Convectional post-tanning process employs phenol derivative synthetic tanning agent to impart functional properties which chrome tanning system fail to fulfill. In chromium tanning adsorptive processes are minimal and leading to empty inter fibrillar spaces. Of these, the phenolic syntans are prepared from petroleum byproducts such as phenol, naphthalene, cresol. Being petroleum byproducts, the cost of these products is highly fluctuating. Therefor there is a need to evaluate alternatives for these products. In the current work, an effort has been made to develop phenolic synthetic tanning agent from waste of paper and pulp industry.

It was observed from the characterization result the particle size range were 3250 nm and molecular weight of 600 kDa from this we can conclude direct application of black liquor alone for post tanning operation will not be technically feasible. The inorganic content of black liquor were found to be 40% which also give rise to papery leather if it used without modification.

Degradation of lignin in black liquor was performed using fenton reagent at constant reaction time of five hours, mixing rate of 250rpm and at atmospheric pressure. Production of biodiesel was performed by batch process system. The effects of amount of H_2O_2 concentration, Fe^{2+} concentration and reaction temperature on percentage of were determined. By using Design Expert 7.0.0 software three levels; three factor Central Composite Design with full type, when H_2O_2 concentration and reaction temperature were increased, the percentage of degraded lignin increased until the optimal amount. The degradation process was shown a higher degree of degradation at 25 mmol of H_2O_2 concentration with irrespective of other factors , this will support there was Fenton's like reaction which generating Fe^{3+} and again allows Fe^{2+} regeneration in an effective cyclic mechanism to give rise reactive oxygen species. Fe^{2+} concentration at 5 mmol was having percentage lignin degradation of ca.60.98 %, quit big value, this will tell as there was trace amount of iron in the black liquor sample, which react with H_2O_2 , then degraded lignin into lower molecular weight moites. The maximum degradation was attained at H_2O_2 concentration of 25 mmol, 15 mmol Fe^{2+} concentration and at a reaction temperature of 45°C . In contrast, the

average minimum degradation was at H_2O_2 concentration of 5 mmol, 25 mmol of Fe^{2+} concentration and at 25°C .

The liquid–liquid extraction mechanism were employed to extract degraded lignin from black liquor using ethyl acetate. The result showed considerable amount of degraded lignin were extracted from this we can conclude that the type of solvent and extraction pH have effect on the yield of degraded lignin.

In syntan preparation stage were investigate viz, sulphonation temperature, type of sulphonation agent and duration of reaction, amount of formaldehyde. At 120°C of sulphonation temperature show higher total soluble than all other level, however from practical point of view temperature at 100°C were more preferable which have reasonably similar total soluble with that of 120°C . The combined sulphonation product of sulfuric acid and sodium meta bisulfite (SS2) show better softens, roundness and grain smoothness and color of product this will give us access to use the product for pestle shade leather. All product condensation by formaldehyde show lower tensile strength. Whereas sulphonated and degrade lignin product show better and comparable interims of tensile strength. “L” value of leather made using product SF1, SF2 and SF3 have lower value than that of control leather. This indicate that those lignin based product which undergo condensation reaction are darker in shade than commercial phenolic syntan retanned leather. Product undergoing sulfonation by sulfuric acid viz, SS1, SF1 show higher value of TDS, this phrase due to the formation of considerable amount of neutral salt while adjusting the final pH of syntan using alkaline. Emission load of TS for commercial phenolic syntan is 43.61, whereas there is reduction in TS load by 41.7%-24.1% has been observed using SS2 and SF2.

5.2 Recommendation

Depending on the results obtained in this thesis, available resources and technical Feasibility, the following recommendations are suggested:

- The type of wood during pulp and paper making viz soft and hard, have impact on the nature and amount of lignin present in black liquor. Therefore, characterization of black liquor should perform depending upon the type of wood used during kraft process. This will helps to have standardize process for specific wood type.
- The optimized percentage of degraded lignin by Fenton's reagent was found to be 76.8% which is fairly enough for leather application but Other lignin de-polymerization processes involving enzymes could be considered to obtain simple monomeric compounds this can be consider as future area of study.
- The foremost factor in utilizing lignin as precursor of phenolic compound is yield of product. In this course of study extraction were conducted after degradation process which give rise of moderately medium yield obtained .Therefore in order to maximize extraction of lignin should perform prior to degradation process.
- The degradation process were investigate as function of particle size, phenolic group, and viscosity and UV spectrum. It is recommended to use GPC to assess the change in molecular weight and strengthen the result. The use of the GPC was not possible because the equipment was not available in our country.

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Annex

Annex-1

Run	Process code	H ₂ O ₂ (mmol)	Fe ²⁺ (mmol)	Temperature (°C)	Viscosity (cp)	Phenolic group (g/l)	Particle size (nm)
1	D1	15	15	45	2.57	0.578	1337
2	D2	25	25	25	1.91	0.377	233.6
3	D3	15	5	45	2.69	0.618	1547
4	D4	25	25	65	1.71	0.315	174.1
5	D5	25	15	45	1.6	0.268	169
6	D6	15	15	45	2.48	0.554	878.1
7	D7	15	15	45	2.53	0.567	955.4
8	D8	25	5	65	2.01	0.407	293.6
9	D9	25	5	25	2.06	0.4217	437.6
10	D10	15	25	45	3.17	0.7647	1987
11	D11	5	5	25	3.14	0.7562	1857
12	D12	15	15	65	2.26	0.4835	520
13	D13	5	5	65	3.19	0.771	2034
14	D14	15	15	45	2.47	0.549	611.4
15	D15	5	25	25	4.37	1.135	3325
16	D16	15	15	45	2.63	0.599	1360
17	D17	15	15	45	2.74	0.631	1733

18	D18	5	15	45	3.71	0.929	2194
19	D19	5	25	65	4.04	1.029	2836
20	D20	15	15	25	2.88	0.675	1779

Annex-2 tanning recipe

ARTICLE ;GOAT PICKLED				BATCH NO ;		
COLOUR ;				NO.OF PCS ; 5		
THICKNESS ;				SQ.FT ;		
GRADE ;				SHAVED WEIGHT ; -		
WEIGHT ;- PICKLED WEIGHT *1.5 % =						
S.NO	PROCESS	NAME OF THE CHEMICAL	%	RUNTIME	PH/RE MARK	PROPERTY AND PURPOSE OF THE CHEMICAL
1	DEPICKLE	H ₂ O@30 ⁰ C	100			
		NaCl - SALT	10	5*		Check Be ⁰ 6 to 7
		SODIUM BI CARBON	1.0			
		Wetting agent	0.5	15*		
		LOAD PICKLE SKIN		30*	5.8/6	
2	PICKLING	COLD WATER	60			
		NaCl - SALT	6.0	15*		Check Be ⁰ 6 to 7
		FORMIC ACID (1;10) (HCOOH)	0.4	2 *10+20*		
		SULPHURIC ACID (1:10) – H ₂ SO ₄	0.9	3 *10+30	2.8/3.0	
3	CHROME TANNING	PICKLE WATER	60			
		BCSD	4.0	30*		
		BCS	4.0	60*		
CHECK CHROME PENETRATION AT THE CUT CROSS SECTION.						
4	BASIFICAT IN	SODIUM FORMATE	1.5	3*5+20		
		SODIUM BI CARBON	1.0	3*15+20		
CHECK CHROME EXHAUSTION & WASHED WELL, PILE WITHOUT FOLDING FOR 48 HOURS.						

Annex-3 tensile strength and tear load-double edge tear

Measurement of tear load-double edge tear

Sample	Maximum load (N)	Tear strength (N/mm)	Thickness (mm)	Direction
SS1	100.639	74.961	1.3417	Along
	117.311	85.075	1.38	Across
	108.975	80.078	1.360851	Average
SS2	96.471	70.7591	1.3633	Along
	120.7843	85.7512	1.39915	Across
	108.6278	78.2711	1.3812	Average
SS3	75.9783	65.0431	1.16916	Along
	103.0703	87.3423	1.18	Across
	89.5243	76.1927	1.1746	Average
SF1	79.4517	50.449	1.5767	Along
	85.3563	61.3262	1.3917	Across
	82.404	55.8876	1.4842	Average
SF2	84.3143	61.0271	1.3828	Along
	86.7457	58.9774	1.47083	Across
	85.53	59.9508	1.42667	Average
SF3	65.9057	61.4047	1.0733	Along
	80.8410	69.8893	1.1567	Across
	79.278	65.647	1.115	Average
C	76.3257	66.1506	1.1542	Along
	95.7763	86.9350	1.1017	Across
	86.051	74.2897	1.12795	Average
D	89.8717	74.442	1.2075	Along
	96.1237	79.1142	1.215	Across
	92.9977	76.7781	1.21125	Average

Tensile strength

Sample	Force breaks (N)	Tensile strength (N/mm ²)	Thickness (mm)	Direction
SS1		29.7348	1.461	Along
		44.801	1.317	Across
		36.878	1.389	Average
SS2	598.368	43.36	1.38	Along

	492.083	37.242	1.321	Across
	545.573	40.383	1.351	Average
SS3	501.609	43.297	1.159	Along
	276.737	25.067	1.104	Across
	389.273	34.403	1.1315	Average
SF1	395.522	27.505	1.438	Along
	301.745	19.969	1.511	Across
	348.635	23.636	1.475	Average
SF2	444.857	33.256	1.292	Along
	305.913	23.071	1.326	Across
	375.385	28.677	1.309	Average
SF3	364.96	33.867	1.077	Along
	221.511	21.975	1.008	Across
	293.234	28.114	1.043	Average
C	487.095	48.371	1.007	Along
	262.496	25.289	1.038	Across
	373.643	36.542	1.0215	Average
D	416.365	38.481	1.082	Along
	206.23	19.292	1.069	Across
	311.29	28.944	1.0755	Average

Declaration

I, the under signed, declare that this thesis is my own work and that all sources of material used for the thesis have been accordingly acknowledged.

Tewodros kassa

Date

This is to certify that the above declaration made by the candidate is correct to the best of my Knowledge.

Advisor, J.Raghava Rao (DR)
