

DEVELOPMENT OF MODIFIED TANNIN ADHESIVE
USING FORMALDEHYDE
*PHYSICO-CHEMICAL AND MECHANO-CHEMICAL
PROPERTIES*

A RESEARCH PROJECT

BY

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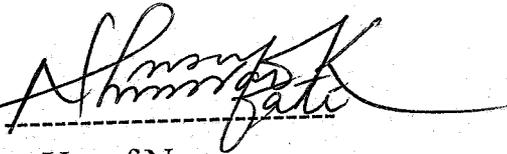
In partial fulfillment of the requirements for the Degree of
Bachelor of Engineering (Chemical Engineering).

Department of Chemical Engineering, School of Engineering
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DECEMBER, 2000

DECLARATION

I, Yusuf Nura, declare that this research project is solely the result of my work and has never been submitted anywhere for any degree . All literature cited have been duly acknowledged in the reference.



Yusuf Nura



Date

CERTIFICATION

This research project entitled *DEVELOPMENT OF MODIFIED TANNIN ADHESIVE USING FORMALDEHYDE. PHYSICO-CHEMICAL AND MECHANO-CHEMICAL PROPERTIES* by YUSUF NURA meets the regulations governing the award of the degree of Bachelor of Engineering (Chemical Engineering) of Federal University of Technology, and approved for its contribution to knowledge and literacy presentation.

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DEDICATION

This research project is dedicated to my dear late grand parents Mallam Mohammed Sani Auta and Mallam Lantana Umba Sani. May Allah forgive them and reward them with "Aljannah Firdausi" Amin. It is also dedicated to my dear Junior brother Yound Sagir Yusuf for he will by the grace of Allah grow to challenge this research project.

ACKNOWLEDGEMENT

All praise and gratitude are due to Allah the sustainer, the retainer and the maintainer of the heavens and earth who has made this work possible and for giving me the strength, the courage, the patience and perseverance, the strong will and the determination for completing my course successfully.

I must register my sincere appreciation to my parents, Alhaji Yusuf Halidu Wushishi Dallatun Kagara and Hajiya Fatima Yusuf Wushishi for their love, care, and support right from my childhood up to date. May Allah reward them abundantly - Amin.

I must also place on record my profound gratitude to my able supervisor Dr. M. O. Edoga who created time out of his tight schedule to see me through. Whose comments, corrections, and criticisms gave this project a sense of direction.

Words alone cannot express how grateful I am to my benefactors; Mallam Ahmed Yusuf and Mallam Bashir Yusuf for their untiring support towards my academic pursuit.

Worthy of mention also are some of my friends (course mates); Abdulkarim Bala Isah, Sue Attahiru Bobi and Maikano Hauwa. I will also like to acknowledge the kind gesture shown to me by the entire members of Alhaji Yusuf Wushishi family. As well as my entire course mates during our stay. In fact it was a wonderful time.

Finally, this project would have been incomplete if I fail to acknowledge the kind assistance rendered to me by the entire staff of Chemical Engineering Department, most especially Mallam Mohammed Sidi and Late Engr.

Akinwale AbdulwasIU Akinbode who died in ghastly motor accident along Ogbomosho – Ibadan road on the 2nd of November, 2000. May Allah forgive him and reward him with paradise. Adieu AbdulwasIU, Adiue till we meet in paradise where we will part no more “Insha Allah”. I will also never forget my grand parents late Mallam Mohammed Lawal and late Mallama Lantana Umba Lawal, may Allah reward them with “Aljannah firdausi” Amin. I will also register my profound gratitude to my friends; Aminu Isiya, Bala Bara’u, Bawa Yusuf (Barry), Mohammed Danjuma, Hadiza Mohammed Inga (Mrs), Rabiya Mohammed, Salihu Y. Mohammed and Zubairu Dan’asabe. And all others that are too numerous to mention.

ABSTRACT

Tannin extracted from mangrove bark by two different extractive methods; direct and indirect leaching was developed into wood adhesive.

Subsequently, formaldehyde was added to modify the tannin extract. The physico-chemical and mechano-chemical properties of the adhesive and bonded products were determined, respectively. The results show that the modified tannin adhesive using formaldehyde possesses some inferior properties such as brittleness, poor wet strength and long curing time.

Furthermore, it has been confirmed that tannin adhesive obtained at low temperature had higher bonding strength than the ones obtained at higher temperature. The shear strength of the adhesive ranges from 640 000N/m² to 1104 000N/m². On the other hand, the adhesive has a viscosity of 28.6cp, specific gravity of 1.013, and 1.34 refractive index.

Overall, extracting tannin at higher temperature resulted in denaturing the tannin composition present in the mangrove bark and hence may not be the best alternative means of developing a fast-setting tannin based wood adhesive.

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ABBREVIATIONS

ρ_w	=	Density of water
ρ_s	=	Density of the sample
μ	=	Viscosity
ν	=	Kinetic viscosity
C	=	Viscosity constant
t	=	Time taken for the sample to flow through the capillary of the viscometer.
F	=	Force required to shear the wood bonded by the adhesive.
P	=	Equivalent pressure required to shear the wood bonded by the adhesive.

CHAPTER ONE

1.0 INTRODUCTION

Adhesive is a non-metallic material that is capable of joining bodies together by surface tension and internal strength (adhesion and cohesion) without the structure of the bodies undergoing significant changes^[10]. Adhesives are required in small volume compared to metals, rubber, glass, paper, wood, plastic and fibers that they join together but just as enzymes, hormones and vitamins are required for individual well being.^[4]

In view of this, a great variety of polymers can be used in adhesive applications. The selection of adhesives depends upon the adherent and the end use. Consideration must be given to factors like porosity or impermeability of the adherent, its polarity and its modulus of rigidity. The adhesive film must not be stiffer than the adherent else, flexing will cause stresses to concentrate in the adhesive layer and bring about failure. Cost and availability are major considerations in the selection of products such as adhesive.^[1]

Mangrove bark tannin which is phenolic in nature is a renewable source used in formulating tannin adhesive by polycondensation reaction of the tannin extract with formaldehyde.

Although, researchers like Dalton 1950, 1953, Heritage 1951, 1952 have made efforts during the last five decades to develop adhesives for wood products from natural renewable and cheaper raw materials such as tannin, lignins and furan. However, their efforts was geared towards replacing the

most widely used aminoplastic and polyphenol derived largely from petroleum which is a finite natural resources.^[8]

1.1 Objective of study

To develop a modified tannin adhesive with improved working properties, performance and strength.

1.2 Approach

This study covers:

- (i) Extraction of tannin from mangrove bark.
- (ii) Development of tannin adhesive.
- (iii) Analyses of the physico-chemical properties of the adhesive formulated and
- (iv) Analysing the mechano-chemical properties of the tannin adhesive applied on woods.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 HISTORICAL BACKGROUND

Adhesives were utilized in a sophisticated manner even in the ancient times. The Egyptians used gum Arabics, and animal glue (all of natural origin) for various equipment including furniture. Apparently, the art of glueing stopped during the dark ages, but by the 16th century animal glue was again used in furniture. [8]

World war I saw a great increase in demand for adhesives both for boat and aircraft constructions and so; plywood bonded with casein and blood – albumen glue became important. The war periods saw the development of synthetic organic adhesives and the steady expansion of their applications.

World war II gave considerable impetus to the development and application of these adhesives in term of increasing structural significance particularly in the plywood industry.

It was the energy crisis and consequent high cost of phenolic material that called for researchers to search for substitute phenols, and hence the development of tannin – based adhesives by Pizzy.^[11]

2.2 DEVELOPMENT OF TANNIN/FORMALDEHYDE ADHESIVES

Research on tannin/formaldehyde adhesive started in the early 1950s with work of Daltan (1950) who reported extensively on the adhesive properties of extracts from six plant species namely wattle (*Acaci mearnsii*)

2.3 TANNIN

Tannin is a generic term for a widely occurring group of substances of vegetable origin, capable of rendering raw hides into leather.

Tannins are also substances present in plants and are amorphous in nature with astringent taste, giving blue-green colour with iron salts and are precipitated from water solution and alkaloids.

It can also be defined as the polymerization product of phenolic compound with molecular formula $C_{76}H_{52}O_{46}$.^[11]

TABLE 2.1: SOURCES OF CONDENSED TANNIN

<i>S/NO</i>	<i>FAMILY</i>	<i>PLANT MATERIAL</i>	<i>YIELD %</i>
1.	Myrtaceae	Eucalyptus astringen bark Eucalyptus wandoo (bark and heartwood)	40 – 50 12 – 15
2.	Leguminosae	Acacia catechu (heartwood) Acacia Malisima (bark) Robinia Psendacacia (bark)	15 35 – 40 7
3.	Anacardiaceae	Schinopsis larentzii (heartwood) Schinopsis balansae (heartwood)	16 – 7 20 – 25
4.	Rhizophoraceae	Rhizophora candelaria (bark) Rhizophora Mangle (bark)	25 – 30 20 – 30
5.	Fagaceae	Castanea satira (bark) Quercus robur (bark)	8 – 14 12 – 16
6.	Pinaceae	Picea abies (bark) Pinus sylvestris (bark)	5 – 20 16

Routine estimations of tannin concentrations in commercial extracts such as those shown in Table 2.1 are normally performed by a weight difference method. An aqueous infusion is prepared and the total solids determined by evaporation of an aliquot.^[2]

2.4 CHEMISTRY OF TANNIN

Although, the natural tannins may differ in chemical constitution and reactions, all have the common property of precipitating gelation from solution and all dissolve in water to give solutions that range in colour from light straw to dark-red to brown indicating that each tannin has its own characteristics colouring matter, which explains their uses in tanning industries.

2.4.1 CLASSIFICATION OF TANNINS

Tannins may be classified into two groups namely; the CONDENSED TANNINS and the HYDROLYSABLE TANNINS. The latter (Hydrolysable) are esters of gallic acid; hexa-hydroxydiphenic acid or similar substances with glucose or other saccharides. On the other hand, the former (condensed) on treatment with hot mineral acids do not give rise to any hydrolytic product but form insoluble substances.

2.4.2 CONDENSED TANNIN

The condensed tannins are our concern because they are chemically and commercially important than the hydrolysable tannins for use in the development of modified tannin adhesive using formaldehyde.

Condensed tannin constitute more than 90% of the total world production of commercial tannins (Pizzi).^[8]

This class of tannin yields insoluble brick red precipitate on treatment with hot dilute mineral acids condensed and their flavonoids. Falvan-3-ol also known as leucoanthocyanadins are know for their widely distribution.

Tannin poly flavonoid essentially consist of several mono flavonoid units, about five to eleven. Among the groups of mono flavonoids known, only flavon-3, 4 – diols and certain flavon-3-ol are used in tannin formation. The two phenolic rings (A) and (B) present in a tannin molecule one joined by a heterocyclic ring.

2.4.3 STRUCTURE OF A TANNIN MOLECULE

There are four possible combination of resorcinol andphloroglucinol (A) ring with catechol and pyrogallol (B) rings. The main polyphenolic pattern is that of resorcinol (A ring) withpyrogallol (B ring). They constitute about 70% of the total tannin available.

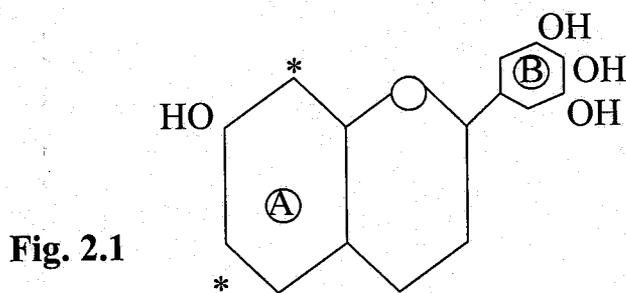


Fig. 2.1

Fig. 2.1: Phloroglucinol 'A' ring with pyrogallol 'B' ring.

The secondary but parallel pattern is based on resorcinol (A rings) and catechol (B ring). These tannins represent about 25% of the total faction of bark tannin.

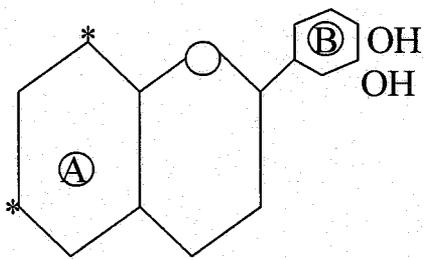


Fig. 2.2: Resorcinol 'A' ring with catechol 'B' ring.

Tannin molecule can also form an oligomeric compound possible through hydrogen bonding as shown in fig. 2.3 below. In this study, lumps of coagulate gelly-like materials formed in the extracted solution. The lumps are suspected to be the product of fungal attack on the carbohydrates, particularly, the sugars. Extensive hydrogen bonding between the molecules say, tannin – carbohydrates, tannin – tannin and tannin – gums (resins) could lead to the formation of insoluble materials (oligomers) which would precipitate from the solution in the form of particles or gels. Example of hydrogen – bonded tannin oligomer is shown below.

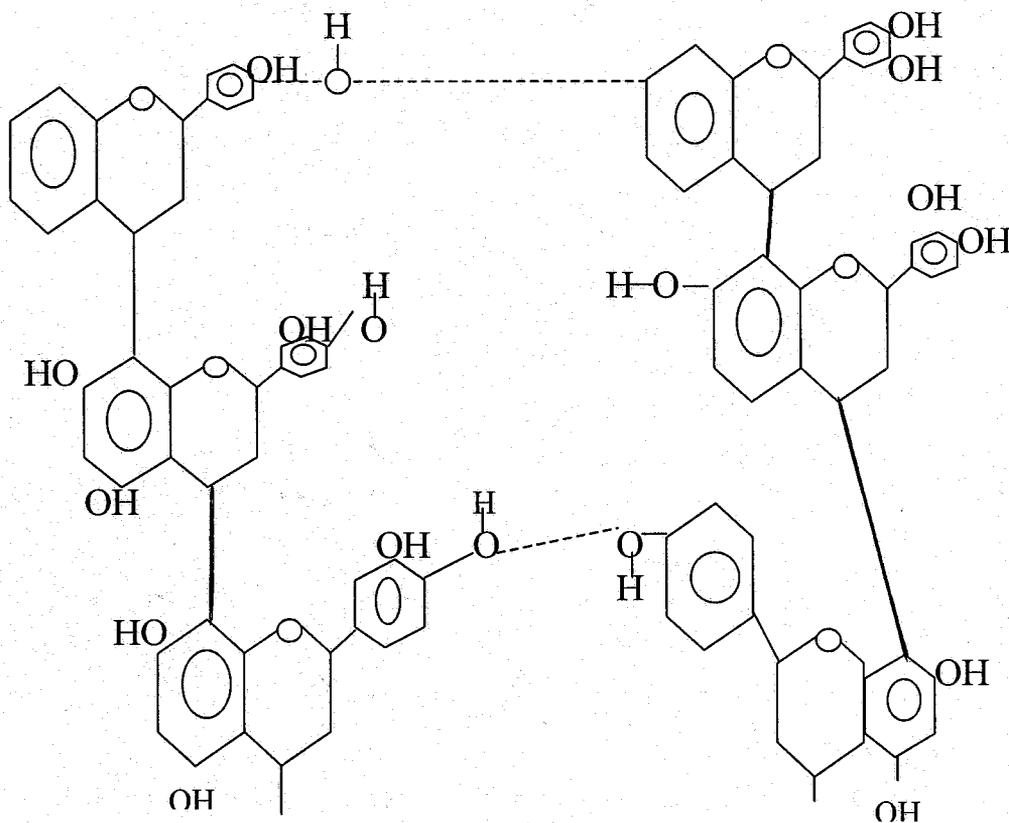


Fig 2.3: Hydrogen bonded tannin oligomer

2.4.5 REACTIVITY OF TANNIN

Due to their macromolecular nature, condensed tannins exhibit unique reaction normally expected of flavon-3-ols some of the nuclei in condensed tannins have the ability to form cross links with aldehyde. Because of their sizes and shape (imposing stereo hindrances) tannin molecules become immobile at a low level of condensation with formaldehyde. This causes the available reactive site to be too far apart from further methylene bridge formation and thus leads to incomplete polymerization and cross linking and therefore weakness.

2.4.6 PURIFICATION OF TANNINS

Tannins, especially those extracted from raw materials with the aid of acids are purified by conversion by the action of bases or basic compound into insoluble or difficult soluble salts which are free from impurities by washing the water or organic solvents and then decomposed by acids or in some cases by salts, the tannin solution is finally evaporated. For the decomposition of the tannin compounds, acids or salts that give insoluble compounds with the base or bases are preferably used. The crude tannins may be previously treated with reducing agents such as sulphuric acid, hydrosulphuric acid or other acids of sulphur but preferably with volatile reducing acids.^[8]

2.5 USES OF TANNIN

Tannin has found wide range of applications after the Second World War, when its traditional market (leather tanning) declined progressively coupled with increased price and decrease availability of synthetic phenolic

materials due to the advent of energy crisis. Some of the uses of tannin are discussed below;^[10]

1. Manufacture of Adhesive

Condensed tannins are phenolic raw materials that can be used for the manufacture of synthetic resins, in contrast to hydrolysable tannins, which readily react with formaldehyde. The ability to undergo formaldehyde condensation is a reliable diagnostic test for condensed tannins.

2. Leather Tanning

Leather tanning forms the traditional use of tanning in ancient times. It turns the gelatin of hides into insoluble non-putrefying element.

3. Protection of Metals

Recent archaeological excavation have revealed that tannins in the soils preserve iron objects by exerting bacteriostatic action against the sulphate – reducing vibro, *V desulfuricans*. Mild oxidation increases the toxicity of tannins towards sulphate – reducing bacteria and mangrove tannins should be highly effective and economical for the underground protection of iron pipes and tubes.^[10]

2.6 REQUIREMENTS FOR TANNIN ADHESIVE

Generally requirements of organic adhesives are that, they must;

- (1) Be based on high polymers or materials which convert to high polymers
- (2) Be capable of being applied in some manner as a liquid e.g. high polymer dissolves in solvent, a liquid lower molecular

(2) SOLVENT (THINNER)

Solvents are needed in adhesive design depending on the type of adhesives materials, to disperse the adhesive to a spreadable liquid form.

(3) EXTENDERS

Extenders are substances that generally have adhesive action. They are added to an adhesive to reduce the amount of primary binder required per unit area and thus reduce the cost of the actual joint. For urea – formaldehyde adhesive formulation, cereal flour are commonly used as extenders, and are often used to reduce costs in hardwood plywood manufacture.

(4) MODIFIERS (FORTIFIERS)

These are materials that are added to adhesive raw material primarily to improve the performance of the resultant bond. A typical example is the addition of resorcinol along with paraformaldehyde to a tannin adhesive to improve the resistance of the joints to weathering or exposure to other severe conditions.^[7]

(5) CURING AGENTS (POSITIVE CATALYST) AND HARDENERS

Curing agents are substances that markedly speed up the cure of adhesive materials when added in minor amounts as compared to the amounts of the primary reactants. They are usually chosen to increase the rate of a specific chemical reactions of curing adhesive.

(6) FILLERS

Fillers are relatively substances added to primary adhesive materials to improve its working properties, performance, strength, as well as reduce cost and surface tacking. Walnutshell flour or Pecan shell flour, metallic and inorganic fillers such as aluminium powder, alumina or china clay are often

added to adhesives as fillers to improve viscosity and spreadability of the adhesive.

(7) BUFFER

Buffer is a substance usually added to the polymer to resist a change of pH on addition of acid or alkali. Due to the fluctuation in pH of many polymeric system during synthesis, it is pertinent that a suitable buffer solutions be added so as to maintain a constant pH.

(8) PLASTICIZERS

Plasticizers are liquid or solid substances added to synthetic or natural resins to modify their flow properties and invariably prevent brittleness of the dried/cured materials.

(9) STABILIZER (NEGATIVE CATALYST)

These are substances usually added to prevent chemical decomposition of a substance. For instance, the presence of chlorine atoms in PVC causes the molecular chain to be polarized and there are in consequence, dipolar attractive forces between adjacent molecules.

(10) PIGMENTS

Aside from their decorative functions, pigments also are used in stabilization by screening out ultraviolet light. Both organic or inorganic pigments may be used. Titanium dioxide, cadmium reds, chrome, oranges and yellows, phthalocyanine greens and blues are examples.

CHAPTER THREE

3.0 EXPERIMENTAL PROCEDURES

3.1 MATERIALS AND EQUIPMENT

The materials used in formulating the adhesive are given below.

3.1.1 MANGROVE BARK

The mangrove bark was obtained from Warri, Delta state. The fresh bark was obtained from mangrove tree. The inner part of the fresh bark was white but later turned reddish brown upon drying at atmospheric condition.

The bark was used to extract the tannin using ethanol, acetone and water as solvents.

3.1.2 EQUIPMENT

The equipment used during the experiment include:

1. Weighing balance
2. Beaker
3. Round bottom flasks
4. Glass reactor
5. Thermometer
6. Extraction thimble
7. Soxhlet apparatus
8. Electric stirrer
9. Retort stand
10. Grinding machine
11. Water bath
12. Viscometer

13. Stop watch
14. Refractometer
15. Density bottle
16. Magnetic stirrer
17. Shear stress machine
18. Density bottle

3.2 Collection And Treatment Of Mangrove Bark

Fresh bark of mangrove tree was obtained from Warri, Delta state. The sample was dried using sunlight until a constant weight was obtained. The constant weight indicated that the bark was moisture free. The choice of the sunlight as the drying medium was attributed to the fact that very high temperature usually resulted to the denaturing of tannin composition present in the bark.

The sample was then ground with a grinding machine to a very fine powder. No sieving was done as all the particles were used in the extraction.

3.3 Extraction By Direct Leaching

10 grams of ground bark was measured into three different beakers. And 200ml of distilled water was added into the three different beakers to obtain the solutions. The three different solutions were placed on hot plates with an inbuilt magnetic stirrer for the tannin to leach out for about 2 hours at different temperatures of 70°C, 80°C and 90°C. At the end of the extraction time the solutions were filtered using filter paper. The extracts were collected and the solvent (distilled water) was evaporated. The same procedure was repeated using ethanol and acetone as solvents under the same conditions of time and volume of solvent (200ml).

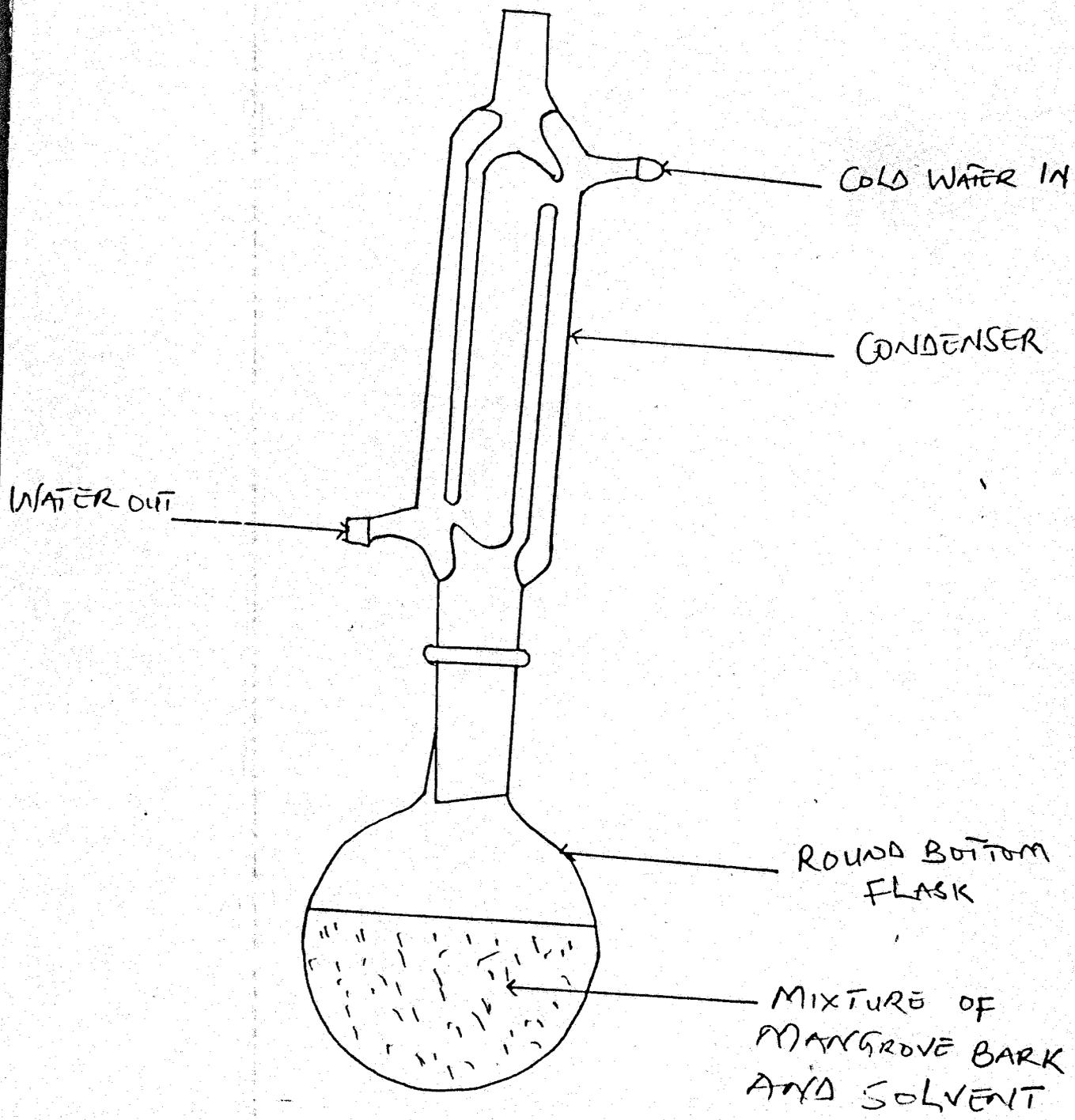


Fig 3.1: Direct Leaching Set-up Apparatus

3.4 Extraction Using Indirect Leaching(Soxhlet Apparatus)

10 grams of ground mangrove bark was measured and put into three different thimbles and subsequently placed in the soxhlet apparatus. Then 200ml of ethanol was measured and poured into three different round bottom flasks for extracting the desired tannin at different temperatures of 60°C, 70°C and 80°C for about 2 hours each. The three different solutions obtained were mixtures of the desired tannin and the solvent used for the extraction (ethanol). In order to obtain the desired tannin the solvent was evaporated. This procedure was repeated using acetone as solvent.

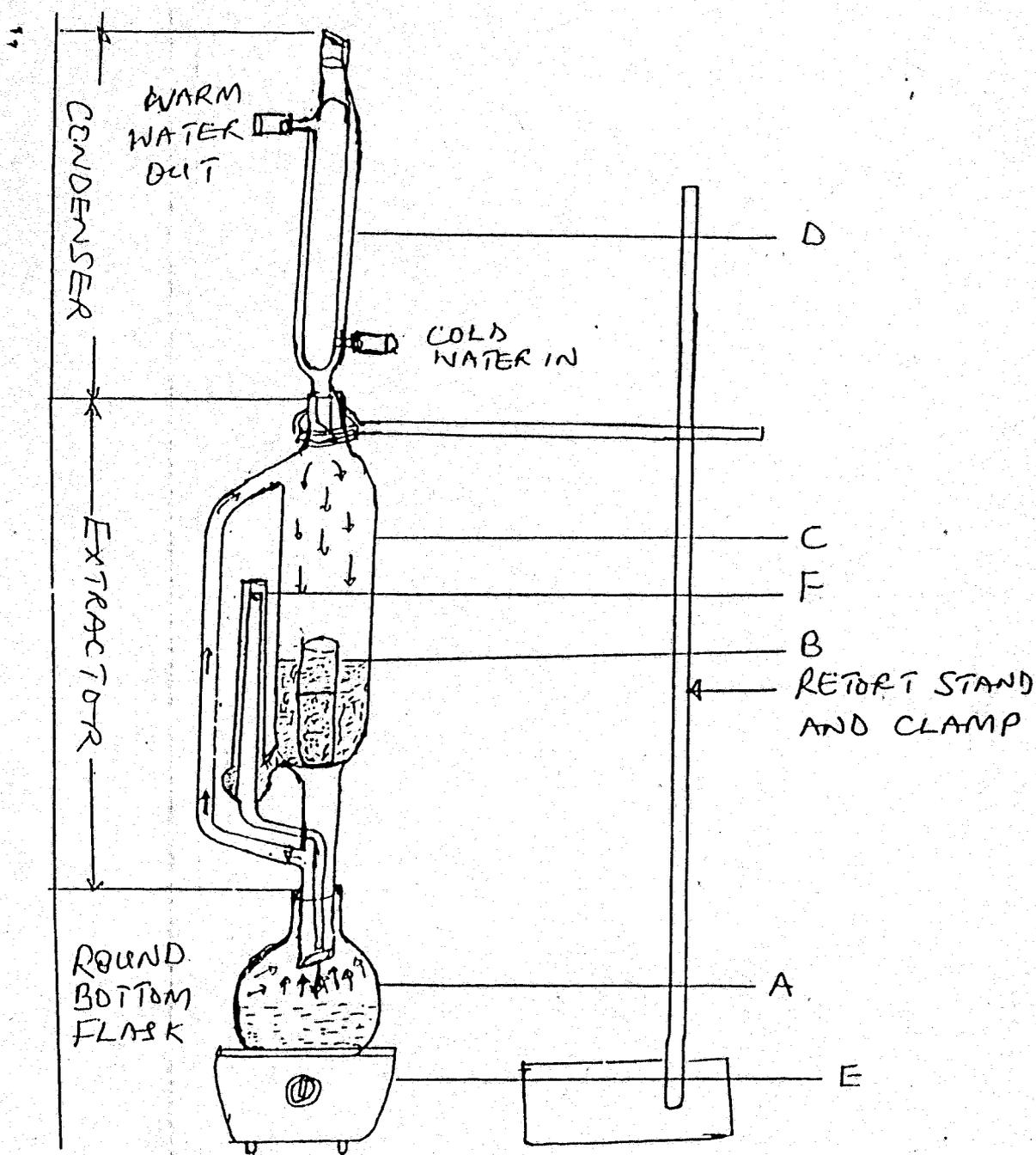


Fig 3.2: Soxhlet Apparatus

3.5 Development of Modified Tannin Adhesive

In developing the modified tannin adhesive, formaldehyde was first charged into the reactor after stabilizing the pH at about 8.5 with caustic soda (NaOH). The whole system was clamped with a retort stand placed on a magnetic stirrer. Water bath supplied hot water which heated the reaction mixture to the required temperature of 100°C. The tannin pH (6.5) was intermittently charged into the reactor to avoid gelling of the mixture. The reaction was allowed to proceed for 3 hours. At the end of the reaction the resin obtained was concentrated in an oven for sometime at 40°C to enable the viscosity to build up.

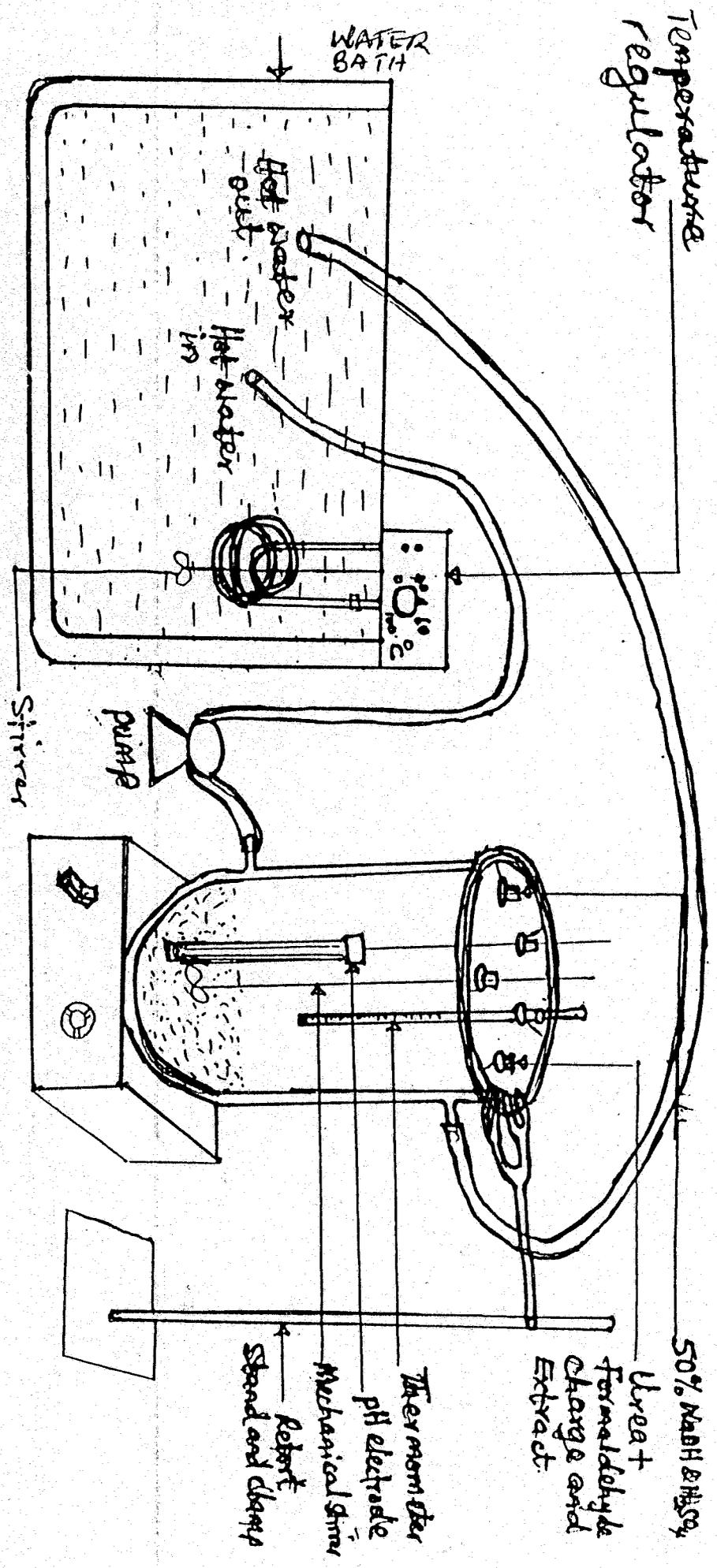


Fig 3.3: Set-up for Development of Modified Tannin Adhesive

3.6 PHYSICO-CHEMICAL PROPERTIES

3.6.1 Specific Gravity

A cleaned density bottle was accurately weighed and the reading was recorded. The density bottle was then filled with tannin and weighed again. The tannin was then poured and allowed to dry. The cleaned, dried bottle was again accurately weighed. The bottle was then filled with distilled water and weighed again. Since the volume of the empty density bottle was the same in both cases, the density of the sample and that of the water were calculated i.e., after the volumes of water and tannin are measured.

Finally, the specific gravity of the tannin was calculated as the ratio of the density of the sample to the density of equal volume of water at 4°C.

3.6.2 Viscosity

A known quantity of sample was poured into U – tube viscometer with capillary and then corked. The U – tube was suspended into the viscometer bath containing water and the temperature of the bath was 35°C. The cork was then removed and the time for the content to run up was noted using a stop-watch. Then the result of the viscosity of the tannin was calculated.

3.6.3 pH Measurement

A pH meter/electrode was used to measure the pH of the resin produced. This was done by inserting the pH meter into a beaker containing tannin adhesive. The value of the pH of the resin was then read from the instrument after a couple of minutes.

3.6.4 Refractive Index

The surface of the refractometer was cleaned with 95% ethanol and subsequently was dried. The liquid sample was then placed on the lower prism

so that the entire width of the prism plate was covered. This was done using dropper to come into direct contact with the prism as this might scratch the prism surface. The upper prism was then brought into contact with the lower prism so that the liquid forms an unbroken layer between the two. The control was manipulated to bring the light and dark fields into focus with the cross hairs in order to obtain the readings.

3.7 MECHANO-CHEMICAL PROPERTY

3.7.1 Shear Strength Test

The flat bottom test piece (wood) was placed on top of the shear jack fixture. While holding the test piece, the height of the jack was adjusted until the test piece just touched the base of the shear test fixture.

Load through jacking was gently and slowly applied. The load reading at the failure was noted and recorded.

WOOD TEST PIECE BEFORE APPLICATION OF ADHESIVE

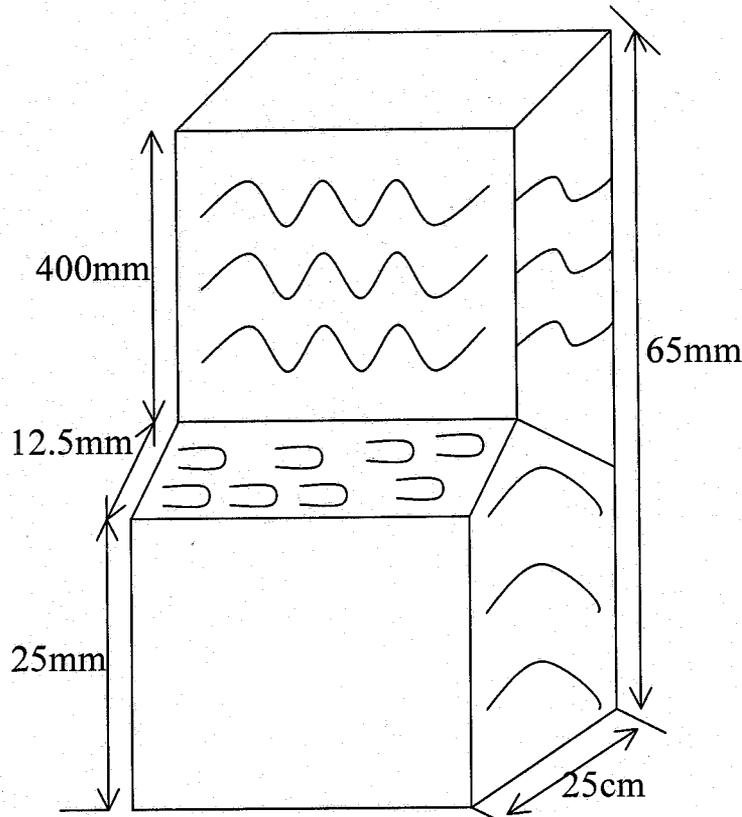


Fig. 3.4: Wood test piece before application of adhesive

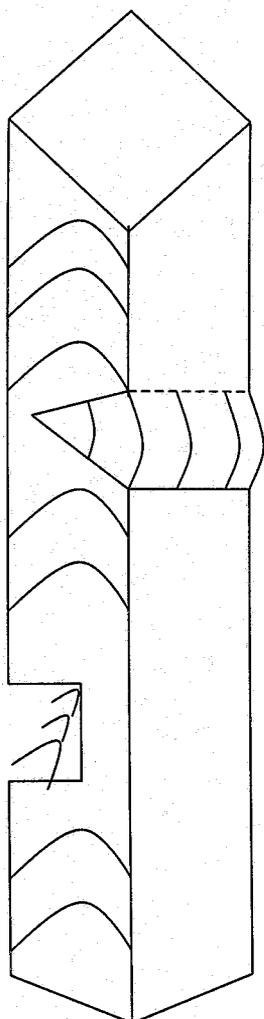


Fig. 3.5: Two Test Pieces Joined Together After Application Of The Prepared Tannin Adhesive.

CHAPTER FOUR

4.0 RESULTS AND DISCUSSION

4.1 EXPERIMENTAL RESULTS

4.1.1 Results Obtained From Direct Leaching

**Table 4.1 : Extraction of Tannin from Mangrove Bark
Using distilled Water (200ml/run)**

<i>Temp °C</i>	<i>Time(hr)</i>	<i>Mass of sample(g)</i>	<i>Extract(g)</i>	<i>Raffinate(g)</i>	<i>% Extract</i>
70	2	10	2.025	7.975	20.25
80	2	10	2.093	7.903	20.93
90	2	10	2.354	7.646	23.54

**Table 4.2 : Extraction of Tannin from Mangrove Bark
Using ethanol (200ml/run)**

<i>Temp °C</i>	<i>Time(hr)</i>	<i>Mass of sample(g)</i>	<i>Extract(g)</i>	<i>Raffinate(g)</i>	<i>% Extract</i>
60	2	10	2.171	7.829	21.71
70	2	10	2.257	7.743	22.57
80	2	10	2.396	7.604	23.96

**Table 4.3 : Extraction of Tannin from Mangrove Bark
Using acetone (200ml/run)**

<i>Temp °C</i>	<i>Time(hr)</i>	<i>Mass of sample(g)</i>	<i>Extract(g)</i>	<i>Raffinate(g)</i>	<i>% Extract</i>
50	2	10	2.245	7.755	22.45
60	2	10	2.323	7.677	23.23
70	2	10	2.419	7.581	24.19

**4.1.2 RESULTS OBTAINED USING INDIRECT LEACHING
(SOXHLET APPARATUS)**

**TABLE 4.4 : Extraction of Tannin from Mangrove Bark
Using ethanol (200ml/run)**

<i>Temp °C</i>	<i>Time(hr)</i>	<i>Mass of sample(g)</i>	<i>Extract(g)</i>	<i>Raffinate(g)</i>	<i>% Extract</i>
60	2	10	1.908	8.092	19.08
70	2	10	2.025	7.975	20.25
80	2	10	2.107	7.893	21.07

**TABLE 4.5 : Extraction of Tannin from Mangrove Bark
Using acetone (200ml/run)**

<i>Temp °C</i>	<i>Time(hr)</i>	<i>Mass of sample(g)</i>	<i>Extract(g)</i>	<i>Raffinate(g)</i>	<i>% Extract</i>
50	2	10	2.019	7.981	20.19
60	2	10	2.043	7.957	20.43
70	2	10	2.135	7.865	21.35

4.1.3 RESULTS OF PHYSICO-CHEMICAL PROPERTIES

TABLE 4.6 : Results of physico-chemical properties

<i>PROPERTIES</i>	<i>VALUES</i>	<i>STANDARD VALUES</i>
pH	6.52	6.5 - 7
Specific gravity	1.013 g/cm ³	
Refractive index	1.34	
Viscosity	28.6	

4.1.4 RESULTS OF MECHANO-CHEMICAL PROPERTY

TABLE 4.7 : Shear Strength Test

<i>Sample</i>	<i>Quantity of adhesive applied (g)</i>	<i>Load acquired at failure</i>	<i>Pressure in N/m²</i>
A	2	40	640 000
B	3	47	752 000
C	4	62	992 000
D	5	69	1104 000

Cross – sectional area of the wood covered with adhesive

$$= (25 \times 25)\text{mm}$$

$$= 25 \times 10^{-3} \times 25 \times 10^{-3}$$

$$= 6.25 \times 10^{-4}\text{m}^2$$

See appendix on how the pressure in N/m² and in PSi were calculated.

4.2 DISCUSSION

Table 4.1., 4.2 and 4.3 are results obtained from direct leaching using different solvents i.e distilled water, ethanol and acetone.

In Table 4.1, the highest yield obtained was 2.354g at a temperature of 90°C while in Table 4.2, the highest yield obtained was 2.396g at a temperature of 80°C and for Table 4.3 the highest yield obtained was 2.419g at a temperature of 70°C. This indicates that more yield was obtained at higher temperature.

Also Table 4.4. and 4.5 show results obtained from indirect leaching (soxhlet apparatus) and they also show that more yield was obtained at higher temperature. This is attributable to the fact that solubility increases with increase in temperature.

Comparing the two methods shows that more yield was obtained by direct leaching rather than indirect leaching. This was confirmed when the whole yields obtained in Table 4.2 (direct leaching) was compared with Table 4.4 i.e using ethanol at different temperatures. It was found that Table 4.3 gave more yield than Table 4.4. And when Table 4.3 (direct leaching) is compared with Table 4.5 (indirect leaching) i.e., using common solvent (acetone), it is seen that the yield obtained in Table 4.3 was more than the yield obtained in Table 4.5. This can be attributed to the fact that in direct leaching there was agitation using stirrer which must have increased the rate of leaching of the soluble portion from the solid.

Moreover, when the three solvents used were compared it is found that acetone gave better yield followed by ethanol and lastly distilled water. This is owing to the fact that acetone has a lower boiling point 58°C then followed by ethanol 78°C and then distilled water has the highest boiling point 100°C . Therefore since acetone has a lower boiling point, the rate of extraction will be higher because it easily boil and hence it extracts faster then followed by ethanol and lastly distilled water. This is true for the two different methods.

Physico-chemical properties carried out shows that the pH of the tannin extract was 6.52. Also the refractive index of the tannin extracted was 1.34 which is within the range available in the literature i.e., 1.3 - 1.6. The lower range i.e., 1.3 is for alcohols and ketones while the upper range i.e., 1.6 is for

heavy hydrocarbon liquid. Therefore since the refractive index was 1.34 this shows that it falls within the alcohol group. Moreover, specific gravity of the tannin was found to be 1.013. Lastly the viscosity of the tannin was also found to be 28.6Cp...

Finally mechano-chemical properties of the adhesive formulated was tested. Among the properties tested included shear strength test. The shear strength test showed that the load required to shear the test piece increased with increase in the quantity of adhesive applied for the same cross-sectional area. This is shown in Table 4.7. The poor bonding strength was as a result of brittleness, poor wet strength and long curing time of the adhesive formulated.

CHAPTER FIVE

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

From the experimental results obtained it is observed that at higher temperature, the mangrove bark gave higher yield of tannin than at lower temperature in the two different methods. Conclusion, therefore, can be made that the rate of extraction increased with increase in temperature. Though tannin extracted at low temperature gave adhesive with better bonding strength than the one obtained at high temperature. This may be attributed to the fact that at higher temperature tannin composition may be degraded.

Also two different methods used in this study showed that the extraction of tannin by direct leaching gave more yield than by indirect leaching. This advantage of the direct leaching over indirect leaching was as a result of the agitation that took place in the direct leaching method.

Finally, the low bonding strength of the adhesive is attributed to the brittleness of the adhesive formulated, poor strength and its long curing time.

5.2 RECOMMENDATIONS

Since the results obtained in this study show that tannin adhesive formulated at low temperature had better bonding strength than the one obtained at higher temperature even though it gives more yield, the following recommendations are made.

- (1) Since the reaction mixture has a higher tendency of gelling even at higher pH say 7 – 8, standard buffer solution should be investigated so as to stabilize the mixture to proceed to conclusion.
- (2) Tannin adhesive formulation at different temperature apart from the one tried should be investigated.
- (3) In characterizing the tannin adhesive physico-chemical properties like nuclear magnetic resonance (NMR), Infra-red (IR) and differential scanning calorimeter (DSC) should be carried out.
- (4) Tensile strength, compression strength, bending strength and impact strength of the adhesive applied on the wood should be investigated as part of the mechano-chemical properties.

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APPENDIX

CALCULATIONS ON EXTRACTS AND PERCENTAGE OF EXTRACTS FOR DIRECT LEACHING

TABLE 4.1

$$\text{Extract} = \text{Mass of the sample} - \text{Raffinate}$$

$$\text{At } 70^{\circ}\text{C} = 10 - 7.975$$

$$= \underline{\underline{2.025\text{g}}}$$

$$\% \text{ Extract at } 70^{\circ}\text{C} = \frac{10 - 7.975}{10} \times 100$$

$$= \underline{\underline{20.25\%}}$$

$$\text{Extract at } 80^{\circ}\text{C} = 10 - 7.903\text{g}$$

$$= \underline{\underline{2.093\text{g}}}$$

$$\% \text{ Extract at } 80^{\circ}\text{C} = \frac{10 - 7.903}{10} \times 100$$

$$= \underline{\underline{20.93\%}}$$

$$\text{Extract at } 90^{\circ}\text{C} = 10 - 7.646$$

$$= \underline{\underline{2.354\text{g}}}$$

$$\% \text{ Extract at } 90^{\circ}\text{C} = \frac{10 - 7.646}{10} \times 100$$

$$= \underline{\underline{23.54\%}}$$

The same procedure for table 4.1.2 and 4.1.3

FOR SOXHLET EXTRACTION METHOD

TABLE 4.4

$$\text{Extract} = \text{Mass of the sample} - \text{Raffinate}$$

$$\text{At } 60^{\circ}\text{C} = 10 - 8.092$$

$$= \underline{\underline{1.908\text{g}}}$$

$$\% \text{ Extract at } 60^{\circ}\text{C} = \frac{10 - 8.092}{10} \times 100$$

$$= \underline{\underline{19.08\%}}$$

$$\text{Extract at } 70^{\circ}\text{C} = 10 - 7.975\text{g}$$

$$= \underline{\underline{2.025\text{g}}}$$

$$\% \text{ Extract at } 70^{\circ}\text{C} = \frac{10 - 7.975}{10} \times 100$$

$$= \underline{\underline{20.25\%}}$$

$$\text{Extract at } 80^{\circ}\text{C} = 10 - 7.893$$

$$= \underline{\underline{2.107\text{g}}}$$

$$\% \text{ Extract at } 80^{\circ}\text{C} = \frac{10 - 7.893}{10} \times 100$$

$$= \underline{\underline{21.07\%}}$$

The same procedure is applicable to table 4.2.2.

CALCULATIONS ON VISCOSITY AND SPECIFIC GRAVITY

SPECIFIC GRAVITY

$$\text{Volume of the sample} = 10\text{cm}^3$$

$$\text{Equal volume of water} = 10\text{cm}^3$$

$$\text{Mass of the density bottle (M}_1) = 26.21\text{g}$$

$$\text{Mass of the density bottle (M}_1) + \text{sample (M}_2) = 36.34\text{g}$$

$$\text{Mass of the density bottle (M}_1) + \text{water (M}_3) = 36.21\text{g}$$

$$\text{Mass of the sample (M}_4) = M_2 - M_1$$

$$\begin{aligned} M_4 &= 36.34 - 26.21 \\ &= 10.13\text{g} \end{aligned}$$

$$\text{Mass of water (M}_5) = M_3 - M_1$$

$$\begin{aligned} \therefore M_5 &= 36.21 - 26.21 \\ &= \underline{10\text{g}} \end{aligned}$$

$$\therefore \text{The density of water at } 25^\circ\text{C} (\rho_w) = \frac{\text{Mass}}{\text{Volume}}$$

$$\rho_w = \rho_w \text{ at } 25^\circ\text{C} = \frac{10}{10} = \underline{\underline{1\text{g/cm}^3}}$$

$$\text{and the density of the sample } (\rho) = \frac{\text{mass}}{\text{volume}}$$

$$\rho_s = \rho = \frac{10.13}{10} = \underline{\underline{1.013\text{g}}}$$

$$\text{Specific gravity of the tannin (sample)} =$$

$$\rho_s = \frac{1.013}{1} = \underline{\underline{1.013}}$$

VISCOSITY

Viscosity (μ) = kinematic viscosity (ν) x density (ρ)

$$\mu = \nu \times \rho$$

but $\nu = C \times t$

where C = Viscosity constant = 0.0882

t = time taken for the sample to flow through the capillary of the viscometer.

i.e $\nu = 0.0882 \times 320\text{sec}$

$$= \underline{28.224\text{sec}}$$

$$\therefore \mu = \nu \times \rho$$

$$\mu = 28.224 \times 1.013$$

$$= \underline{28.6\text{cp}}$$

CALCULATION OF TABLE 4.7

SPECIMEN A

$$\text{Mass} = 40\text{kg}$$

$$\therefore F = mg \quad \text{where } g = 10\text{m/s}^2$$

$$\therefore F = 40 \times 10 = \underline{400\text{N}}$$

$$\text{hence } P = F/A$$

$$\text{but } A = 6.25 \times 10^{-4}\text{m}^2$$

$$\begin{aligned} \therefore P &= \frac{400}{6.25 \times 10^{-4}} \\ &= \underline{640000\text{N/m}^2} \end{aligned}$$

Converting to psi

$$\text{We have } 1\text{psi} \rightarrow 6895\text{N/m}^2$$

$$\therefore 1\text{N/m}^2 = \left(\frac{1}{6895} \right) \text{psi}$$

$$\text{hence } 640000\text{N/m}^2 = \quad \times \text{psi}$$

$$\rightarrow \frac{640000}{6895} = \underline{92.8\text{psi}}$$

SPECIMEN B

$$\text{Mass at failure} = 47\text{kg}$$

$$F = m \times g$$

$$= 47 \times 10 = \underline{470\text{N}}$$

$$\text{hence } P = F/A$$

$$P = \frac{470}{6.25 \times 10^{-4}}$$

$$P = 752000\text{N/m}^2$$

$$\rightarrow \frac{752000}{6895} \rightarrow \underline{109.1\text{psi}}$$

SPECIMEN C

$$\text{Mass at failure} = 62\text{kg}$$

$$F = m \times g$$

$$= 62 \times 10 = \underline{\underline{620\text{N}}}$$

hence $P = F/A$

$$P = \frac{620}{6.25 \times 10^{-4}}$$

$$P = 992\,000\text{N/m}^2$$

$$\rightarrow \frac{992000}{6895} \rightarrow \underline{\underline{143.9\text{psi}}}$$

SPECIMEN D

$$\text{Mass at failure} = 69\text{kg}$$

$$F = m \times g$$

$$= 69 \times 10 = \underline{\underline{690\text{N}}}$$

hence $P = F/A$

$$P = \frac{690}{6.25 \times 10^{-4}}$$

$$P = 1104\,000\text{N/m}^2$$

$$\rightarrow \frac{1104\,000}{6895} = \underline{\underline{160\text{psi}}}$$

weight polymer which can be polymerized further, a polymer that can be melted, softened or cooled.

- (3) Exhibit the required cohesive strength.
- (4) Exhibit the required adhesive strength.

NOTE

The last requirement will of course depend on the adhesive type and the nature of the surface to be bonded.

While the first three requirements are properties which may be satisfied by many polymers and materials which form high polymer and curing.

2.4.9 COMPOSITION OF TANNIN ADHESIVE

In designing or formulating adhesives for performance and processability a great number of variations are possible depending on the nature of adhesive.

Adhesive compositions are the constituent or ingredients or additives that make up the adhesive. An adhesive composition may consist of the following ingredients.

- (1) Resin powder or solution
- (2) Solvent (thinner)
- (3) Extenders
- (4) Modifiers (fortifiers)
- (5) Curing agent (accelerator) and hardener
- (6) filler
- (7) Buffer
- (8) Plasticizer
- (9) Stabilizer and
- (10) Pigment.

1. RESIN POWDER OR SOLUTION

The polymer (adhesive) for commercial use are provided in four common forms; dry, liquid, solution in a liquid and dispersion in a liquid, which are purely the product of the original reactants.

callitris calcarata, Pinus Radiata, Eucalyptus redunca, Eucalyptus crebra and Eucalyptus considemiana. All the tannins reacted with formaldehyde to form resins and four of them gave strong water resistant bonds when used as hot press adhesives.

Dalton (1953) carried out further work on viscosity control with wattle and pinus Radiata extracts. He reported that tannin solutions after heating with sulphite have lower viscosities and are suitable for the preparation of adhesive for use with mechanical roller spreader. The sulphited tannin solutions were tested as adhesives from plywood and all gave bonds which were water resistant to six hour immersion in boiling water through wood failures were low.

A number of investigations have examined the use of ground bark as a reactive extender to particularly replace phenol requirements in plywood adhesive.

Hartman (1977) was successful in the development of a 100% natural product-based plywood adhesive by combining a slurry of finely ground bark in sodium hydroxide with equal weight 50% wattle tannin solutions. Southern pine plywood glued with this formulation passed requirement for exterior sheathing grade plywood.

An important break-through when Pizzi's adhesive group (1980) applied Kreibich's "Honeymoon" concept to the use of wattle based cold-setting adhesive for finger joining lumber Pizzi (1980), not only showed that it was possible to replace 50% of phenol resorcinol formaldehyde resins, but that the tannin - based adhesives cured more rapidly than fast - cure resins formulated with expensive m - aminophenol. [1]