STUDIES ON SOME POTENTIAL NON-WOOD FIBROUS PLANTS FOR PULP & PAPER MAKING

A THESIS

Submitted in fulfilment of the requirements
for the award of the degree
of
DOCTOR OF PHILOSOPHY

BY

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To My Father–

His Encouragement and
Confidence in me had
Been Constant and
Unconditional

CANDIDATE'S DECLARATION

I hereby certify that the work, which is being presented in the thesis entitled *"Studies on some potential non-wood fibrous plants for pulp & paper making"* in fulfilment of the requirements for the award of the degree of Doctor of Philosophy, submitted in the *Institute of paper technology, University of Roorkee*, is an authentic record of my own work carried out during a period from January, *1984* to *January, 1987* under the supervision of *Dr. N.J. Rao, Professor (Chemical Engineering) & Director and Dr. J.S. Upadhyaya, Sr. Instructor (Pulp & Paper), Institute of Paper Technology (University of Roorkee), Saharanpur.*

The matter embodied in this thesis has not been submitted by me for the award of any other degree.

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Candidate's Signature

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

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ABSTRACT

The paper industry in India has met the various challanges by adopting itself to the changed conditions. The country has an installed capacity of about 26.0 lakh tonnes producing a large variety of papers from a variety of raw materials. The target set for a paper capacity by the year 2000 A.D. are 42.5 lakh tonnes for paper and 12.9 lakh tonnes of newsprint.

It is a well known fact that present forest resources can not meet the demand of raw material even for the existing units leaving aside the additional requirement for the future growth of this industry. The forest based raw materials are in tremendous short supply and can not meet the projected paper capacities. Even with fuller utilization of bagasse, wheat and rice straws, the supply position will be far from satisfactory for meeting the set target. Further the depleting forest cover and the thrust to conserve ecological balance will force the industry to look alternative fibrous raw materials other than wood and bamboo.

The subject matter of the thesis is broadly divided into six chapters. A summarised account of the results of above mentioned investigations are given as below:

The first chapter of the thesis is an account of the various fibrous raw materials viz., hardwood, bamboo, bagasse, wheat & rice straw and other unconventional raw materials, which are being used for pulp and paper making. On the basis of general criteria for choosing a fibrous raw material for pulp and paper making, the following three potential non-wood fibrous raw materials have been chosen for the present investigations:

1. Sesbania aculeata
2. Sesbania sesban
3. Cajanus cajan

All these non-wood fibrous raw materials belong to a group which is fast growing in nature and producing soft white wooded plants, having good

characteristics for pulping as well as for paper making.

Second chapter of the thesis is an account of the anatomical and chemical studies on S.sesban, S.aculeata and C.cajan non-wood fibrous plants. For morphological characteristics, all these non-wood fibrous plants have been analysed for their density, fibre length, fibre diameter, lumen diameter and cell wall thickness. The morphological characteristics of these non-wood fibrous plants clearly indicated that the plant of S.sesban consist of a large number of vessels, fibres having thick walled with narrow lumen and the plant of S.aculeata consist of less number of vessels and fibres having thin walled with wider lumen while the plant of C.cajan also consist of less number of vessels and fibres having thin walled with wide lumen.

The results of proximate chemicals analysis of these non-wood fibrous plants indicated that these are having a high percentage of carbohydrate fraction with low lignin content and the extractives are comparable with bamboo. On the basis of the anatomical and chemical studies, it was concluded that S.aculeata, C.cajan and S.sesban are quite suitable non-wood fibrous raw material for pulp and paper making.

Chapter third deals with the studies on carbohydrates of these non-wood fibrous plants. The holocellulose, alpha cellulose, cellulose(by nitration method) and hemicellulose were isolated from those plants. The holocellulose fractions were analysed for ash, Klason lignin, alpha cellulose, pentosan hemicellulose, acetyl content, methoxyl content and uronic anhydride. The alpha cellulose and cellulose were analysed and the results of analysis indicated that the alpha cellulose of these plant are having glucan, mannan, xylan alongwith arabinan, while the cellulose showed the complete absence of arabinan fraction. The cellulose (isolated by nitration method) seems to be more pure cellulose as compared to alpha cellulose, as it was having higher amount of glucan fraction.

The thin, longitudinal and transverse sections having thickness about 20 to 30 μ have been cut and these were further delignified and the hemicellulose were also removed from these delignified sections. The infrared spectrums of holocelluloses, alphacelluloses, celluloses, untreated sections, delignified sections and delignified sections after removing hemicellulose, were recorded. The X-ray diffractograms of alpha cellulose and cellulose were also recorded. The hemicelluloses were analysed by G.L.C. and it indicated the presence of various sugars in different proportion. The hemicelluloses(18% KOH fractions) were also analysed for their ash, pentosan, methoxyl content, acetyl content, and uronic acid content. On the basis of above studies it was concluded that the nature of carbohydrate fraction of these plants resembled some what to bamboo and tropical hardwood carbohydrates.

Chapter fourth deals with thestudies on lignins, isolated from these plants by different methods. The various types of lignins viz., Klason, Willstätter, organosolv and thiolignins were isolated. The Klason, Willstätter and organosolv lignins were further subjected to analysis for their molecular weight, C, H and CH_3O-content and their C_9- formulas were also calculated. The thiolignins were also analysed for their sulphur content, Klason lignin, methoxyl and C and H contents. All these lignins were further subjected to alkaline nitrobenzene oxidation to know the various building units of lignins which are present in these non-wood fibrous plants. The infrared and ultra violet spectra of all these lignins were recorded. The result of alkaline nitro benzene oxidations clearly indicated that the lignins of these plants are madeup of guaiacyl-, syringyl-, and p-hydroxyphenyl propane units. On the basis of above studies, it was concluded that the lignins of S.sesban, S.aculeata and C.cajan resembled with bamboo and other tropical hard wood lignins rather than soft wood lignins.

Chapter fifth deals with the varoius pulping studies on these non-wood fibrous plants. It is further divided into six sub sections as follows:

Section-A, deals with the soda and soda-AQ pulping studies on these plants. The optimization of pulping conditions was made. The results of soda pulping revealed that a temperature of 165°C and 18% active alkali doses for S.sesban, C.cajan and 16% active alkali doses for S.aculeata may be taken as optimum. In alkaline delignification of these non-wood fibrous plants, two distinct overall mechanisms with different rate constants, each of which resembled a first order reaction pattern are involved. The Arrhenius activation energy of bulk delignification during soda pulping of S.sesban and C.cajan were found to be 91.90 KJ/mole and 84.14 KJ/mole respectively, while in the case of S.aculeata it was 80.34 KJ/mole. The soda pulps were bleached with conventional CEHH bleaching sequence giving pulps of around 76%(Elrepho) brightness. On the basis of results of pulp evaluation it was concluded that both the bleached and unbleached soda pulps of these plants showed good strength characteristics. An optimum freeness level for these pulps may be considered around 42 ± 2 °SR. The addition of AQ has a favourable influence on both the pulp yields and all the strength properties determined except for brightness. The spent liquors of soda cooks were analysed for their solids, residual alkali, inorganics, organics, pH, viscosity, °TW and calorific values. The calorific value ranges from 11702 KJ/Kg. to 12017 KJ/kg.

Section-B, deals with thekraft and kraft-AQ pulping studies on these non-wood fibrous plants. The optimization of pulping condition have been done. On the basis of experiments, it was concluded that a temperature of 160°C and 20% sulphidity and 14 % active alkali charge for S.aculeata and 16% active alkali charge for S.sesban and C.cajan, may be taken as optimum for the kraft pulping of these non-wood fibrous species. These results also indicated that the chemical requirement is about 2-3% less than that required for the pulping of bamboo and other tropical hardwoods. Besides the pulping conditions are mild, the total pulp yield is around 44 to 51% in the Kappa no. range of 22-30. The Arrhenius activation energy of bulk delignification in kraft pulping of S.aculeata, S.sesban and C.cajan were found around 81.59, 86.69 and 90.79 KJ/mole respectively. These pulps showed good response towards bleaching and CEHH bleaching sequence was used to get pulps with a brightness levels of 76-80%(Elrepho). The pulps freeness in the range of 42±2°SR seems to be optimum for the development of strength properties. Both the unbleached and bleached kraft pulps of these non-wood fibrous plants showed good strength properties. The use of AQ in conjunction with kraft process to produce bleachable grade pulps from these non-wood fibrous plants is beneficial in increasing the rate of delignification and enhancing the pulp yields. The total solid contents of the kraft spent liquors of these non-wood fibrousplants are towards little higher side thereby increasing the calorific values. The silica contents were also found to be quite low. The less silica content and higher calorific values of the spent liquors are an advantageous factors towards the energy conservation in chemical recovery process.

Section-C, deals with the alkaline sulphite(AS) and AS-AQ pulping on these non-wood fibrous plants. The pulping studies were made using different percentage of sodium sulphite and sodium hydroxide, 10.35% sodium sulphite (as Na_2O) and 4.65% sodium hydroxide(as Na_2O) for S.aculeata, 10.8% sodium sulphite (as Na_2O) and 6.2% sodium hydroxide(as Na_2O) for S.sesban and C.cajan may be considered as optimum for alkaline sulphite pulping. With increased alkalinity the rate of delignification also increased and approached to that of kraft. The AS unbleached and bleached pulps of these plants showed good strength properties. The tearing strength is largely governed by the alkalinity of the cooking liquor and reaching maximum at a terminal pH of spent liquors in the range of 9-11. These AS pulps showed good response towards optical properties and are having decidedly superior values for both the brightness and opacity. The pulps with a brightness level of about 76-79%(Elrepho) were obtained as a result of CEHH bleaching sequence. The addition of a small amount of AQ during AS pulping showed a significant influence both on pulping characteristic and over all strength properties of these pulps. The AS-AQ pulps showed good response towards bleaching and produced more brighter pulps.

Section-D, deals with the semi alkaline sulphite(SAS) and SAS-AQ pulping studies on these non-wood fibrous plants. The pulping studies were made using different amounts of Na_2SO_3 and Na_2CO_3, in order to know the optimum alkali ratio. The cookings were also made at different time to know the effect of cooking time during the course of pulping. The results of SAS pulping clearly indicated that the alkali ratio should be in the range of 0.80 - 0.85 to achieve as low Kappa No. as possible. A temperature of 170°C and total alkali charge from 16-20% (as Na_2O) may be taken as optimum for the SAS pulping of these plants. The AQ has a considerable effect in SAS pulping in reducing both Kappa no. and time at temperature. The pulps with a brightness level of 65-70%(Elrepho) were obtained as a result of CEH bleaching sequence. The pulp brightness were further increased upto a level of 78%(Elrepho) by using CEHH bleaching sequence. Both the unbleached and bleached SAS pulps have good bonding ability and thereby showed good values for strength properties.

Section-E, deals with neutral sulphite semichemical(NSSC) pulping studies on these non-wood fibrous plants. The optimization of sulphite/carbonate ratio was done by varying the ratio of sulphite to carbonate on a molal basis with a constent Na_2O charge of 6% for S.aculeata and 8% for S.sesban and C.cajan. The cookings were made at a temperature of 160°C using different time at temperature ranging from 30-120 minutes. For high yield NSSC pulps of short cooking cycle a sulphite/carbonate ratio of (60:40) appeared to be acceptable. The pulps with higher brightness resulted from greater amount of sulphite. The maximum values for strength properties were obtained at sulphite to carbonate ratio of 70:30 and a freeness level of around 42 ± 2°SR. The pulps obtained during NSSC pulping of these plants showed satisfactory strength properties for packaging grades of papers.

Section-F, deals with the blending studies of kraft pulps of these plants with pine kraft pulp. The present studies revealed that the addition of small quantities of unbleached soft wood pulp(atleast 5 %) in a furnish base having kraft pulps of these non-wood fibrous plant caused a definite improvement in nearly all the strength properties of the paper in comparison with the properties of individual pulps of these plants. The blending studies were conducted by mixing these two pulps after beating them separately. The improvement in tear index was more than the burst and tensile.

Chapter six deals with the over all conclusions of the present studies.

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LIST OF PUBLICATIONS OF THE CANDIDATE

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2. Chromatographic studies on oxidation products of lignin from Cajanus cajan. Holzforschung und Holzverwertung. 38(1), 16, (1986).
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18. Kraft pulping studies on Sesbania aculeata-The overall reaction pattern. Research and Industry. (Communicated).
19. Soda pulping studies on Sesbania sesban-The overall reaction pattern. TAPPI. (Communicated).

CONTENTS

INTRODUCTION:

Paper consumption may be considered as a yard stick of economic development of a country. Statistics show that there is a very strong correlation between capita income and per capita consumption of all types of paper products. Per capita consumption in most developing countries is lower than 10Kg/year, while that of industrialised countries is about 200 Kg/year. The per capita consumption data of different countries are given in Table 1.1. With the increase in population and literacy, the planning commission has indicated that the capacity creation of paper and board will need to be increased to 42.5 lakh tonnes by 2000 A.D. against the 1986 installed capacity of 26 lakh tonnes in the country(67). Thus, resources have to be mobilised to create this additional capacity of about 16.5 lakh tonnes in the coming 14 years.

The requirement and shortfall of wood is shown in Table 1.2. The agricultural residue and waste paper are also utilised to manufacture paper and board. The forest raw materials like bamboo and wood still form the main source of supply, contributing almost 70% of the total production of paper and board in the country. With this additional capacity creation of 16.5 lakh tonnes in the next 14 years, the dependence on bamboo and wood is not going to be different. It is, therefore, of vital importance to evaluate the present availability and future demand of forest raw material for paper industry, more so, when the growing population is going to imposesvast demands of fuel wood, bamboo and commercial timber on the depleting forests.

In order to develop a suitable strategy to meet the planned growth of paper industry, it is necessary to examine the present trends of technology in use, identify the constraints. Paper industry is capital intensive and paper is made from number of scare resources. In view of this the following points should be taken into consideration.

i) Plant practices and capacities.

ii) Modernisation Vs. New units.

iii) Technological changes to be adopted.

iv) Raw material.

In general, the paper is manufactured by pulping suitable fibrous raw materials. The pulping is done by mechanical, semi-chemical and chemical pulping processes. The cooked pulp is washed and the liquors are sent for chemical recovery. The pulp is bleached if required. Then it goes to stock preparation section where it is beaten and chemicals and fillers are added. Beater are being replaced by refiners. Then the pulp is fed to wire through a head box. The sheet is dewatered on a wire mesh, pressed in several roll presses and by vacuum before being dried on steam heated dryers. The sheet is calendered and coated if required. The performance of Indian paper industry in terms of various inputs can be summarised as under:

Fibrous raw material (Chemical pulp)	2.2-3.0 tonnes fresh wood debark/tonnes paper
Caustic soda	39-141 Kg/tonne paper
Chlorine	33-150 Kg/tonne paper
Steam	11.6-16.9 tonnes/tonne paper
Power	1288-1985 KWh/tonne paper
Water	200-400 M^3/tonne paper.

The best figures are still far below the world standards. This gives us enough scope for improvement. The country plans to increase its installed capacity to 42.5 lakhs tonnes by 2000 A.D. This can come from modernisation and renovation of existing units, expansion of existing large, medium and small mills and creation of new mills of green field units based on wood/bamboo/bagasse/agri-residues. The profitability of existing units has come down significantly in recent years due to increase in cost of inputs, decreased utilisation and increase in production costs. The cost of large new green field units is about Rs. 25,000/- per tonne while in the case of small and medium sized units based on unconventional raw materials, viz., bagasse etc. is Rs. 17,000/- per tonne of finished product with chemical recovery and effluent treatment system. There is also the availability of excise concession for (a) mills using unconventional raw materials and (b) mills of capacity below 15,000 TPY etc. Hence it is more profitable to install new small units based on unconventional raw materials in comparision to big units based on wood. Out of the 668 lakh hectares (22%) of the land mass under foresting only 325 lakh hectares are well managed forests. These figures are dangerously far below the 33% cover required for healthy eco-balance. There is urgent need to launch well planned schemes to conserve forests, to create undisturbed forest to meet ecological needs. For the demands of 42.5 lakh tonnes paper and board and 12.93 lakh tonnes newsprint (34 lakh tonnes and 10.3 lakh tonne actual production) nearly 95 lakh tonnes of air dry forest raw material will be needed (1 tonne pulp $\approx$ 2.8 tonne raw material). Today the industry consumes only 2% of wood and 51% of bamboo for paper sector. The requirement of forest raw material is given in table 1.2. This can be achieved by rejuvenation of bamboo forests to increase yield by 30% and by man made captive plantation of forests. The captive plantations can come in the unproductive, fallow and scrub land amounting to 826 lakh hectares. This is needed to boost the present availability of bamboo and hardwoods from 17 lakh A.D. tonnes and 11.5 lakh A.D. tonnes to 20 lakh A.D. tonnes and 47 lakh A.D. tonnes respectively by year 2000. This short fall of raw material will get aggraveted with increasing demand for fuel wood and the forest conservation Act, 1985. Act is implemented in the right spirit, the forest play a vital role in balancing the ecosystem as follows:

i) Maintenance of environmental stability, through preserving and where necessary, restoring the ecological balance, that has been adversely disturbed, by an insufficient appreciation of the role of forests and consequently their rapid depletion.

ii) Checking denudation and soil erosion in the catchment areas of rivers, in the interest of soil and water conservation, prevention of floods, as well as drought and control of premature siltation of reservoirs built at substantial cost. Checking erosion along bank of rivers, in hot and cold deserts of Thar and Ladakh.

iii) Meeting the requirement of fuelwood, fodder, minor forest produce and small timber of the rural and tribal areas.

The short fall of raw material can also be met to some extent by adopting technological changes such as, biopulping, high yield pulping, oxygen bleaching, improvement in refining system and closed cycle operation etc.

By considering the above factors the forest based raw materials are in tremendous short supply and cannot meet the projected paper capacities.

1.1:AGRICULTURAL RESIDUES:

The short fall of raw material can also be solved by using agricultural residue and non-conventional raw materials. The major agricultural residues and non-conventional raw materials for paper making are:

1) Rice and wheat straws.
2) Bagasse.
3) Cotton linters, jute, hessian cuttings and rags.
4) Waste paper.

It is possible to develop a capacity of atleast 1.5 million tonne based on straws and 0.75 million tonne based on bagasse by 2000 A.D. Such units must have a minimum of 50/80 TPD capacity be economically viable alongwith co-generation of power. At present 0.74 million tonnes capacity of paper and board i.e. 39% of total capacity is based on agri-residues.

Only 25% of straws will be available for industrial uses. The material being bulky, the transportation should be limited to 100 Km. from source. The portion released from bagasse for paper making will be limited to 0.75 to 1 million tonnes paper (about 10%). It is important to concentrate on these alternatives to give about 2.25 million tonnes production from these sectors.

Cotton linters, jute, hessian cuttings and rags are good raw materials for pulp and paper. However, their collection and storage pose some problems, their availability is also very limited. The annual collectable yields of various non-wood fibrous plants are given in Table 1.3.

Utilisation of waste paper has already started in a big way, though the waste paper is imported one. In many countries, this recycle contributes to 30% of total production while in developing countries it has not reached even 5% because most of the waste paper collected is used for packing purposes. The main source of waste papers are as follows:

1) Printing, converting and packing establishments.
2) Government offices and business houses.
3) Street sweepings.

As stated above, the major threat to the availability of this material for paper making comes from packaging demands and as a result, its availability to the paper industry depends on the industry's capacity to pay a price for recycling in stiff competition with those who have found alternative use for the material.

Taking into consideration various strategy including man made forest plantation, high yield pulping, fuller utilisation of bagasse, wheat and rice straw and other agricultural residues for pulping, utilisation of high filler quantity, the supply position will be far from satisfactory for meeting the set target. Hence it will force the industry to look to alternative fibrous raw material other than wood and bamboo. There is still wide scope for identifying some new potential non-wood fibrous plants for pulp and paper making.

1.2.NON-WOOD AS A PAPER MAKING RAW MATERIALS:

Improved techniques and better understanding of the behaviour of non-wood fibrous raw materials have made it possible to suitably design the stock preparation equipment as well as the paper machine dimensions to manufacture various grades of paper and boards. Due to their open structure and low lignin content, these fibrous raw materials can be pulped rapidly with milder cooking condition to yield easy bleachable pulps(43). The chemical grades pulps can be bleached to a higher brightness with less bleaching chemicals, due to low lignin content in pulps. Fibre dimensions, fibre length data and the unbeaten pulps freeness values provided ample evidence that most of the non-wood pulps do not need extensive refining to develop fibrillation, hydration and inter-fibre bonding properties(57,69). The washing of non-woodpulps are difficult due to the short fibre length, hence more washing steps and hydrofoils are required. A comparatively less quantity of rosin size and little higher amount of alum is required to produce paper, while using a good proportion of non-wood fibrous pulp. Due to slow drainage characteristics, the forming part of the wet end should be longer by 20-30% compared to the conventional wet end part of the paper machine. For uniform drainage, grooved table rolls, hydrofoils, vacuumfoils and wet suction boxes can be recoursed for achieving good sheet formation. Due to inherent water holding characteristics of non-wood pulp fibres, these provides a limitation in achieving high dryness of the paper web at the press part. Any attempt to achieve higher dryness by increasing the linear pressure has proved futile. Sheet crushing and felt marking are experienced, when the press loading is increased beyond a critical point. Paper produced out of non-wood pulps needs extended surface area and the drying has to be carried out at relatively low temperature. Due to high silica and pentosan content, weak black liquor(more washings) there is much more trouble in recovery plant. Hence ultimately increase the cost of recovery.

Paper making operation based on non-wood pulps is confined to a large extent among the developing nations. Most of the developing nations are facing foreign exchange shortage and therefore severe restrictions are imposed on pulp imports. This situation is likely to continue and paper industry in these countries has to depend increasingly on the locally available non-wood pulps. Mill will be obliged to use non-wood pulp as much as possible in their fibre furnish.

The main objective of the present investigation is to find out some suitable potential non-wood fibrous raw materials to supplement and to overcome the problem of raw material shortage to some extent experienced by the Indian pulp and paper industries. For the present investigation the following three non-wood fibrous raw materials have been chosen.

1) Sesbania aculeata.
2) Sesbania sesban.
3) Cajanus cajan.

All these non-wood fibrous raw materials belong to a group, which is fast growing in nature and producing soft white wooded plants having good characteristics for pulping as well as for paper making.

1.3:BOTANICAL DESCRIPTION OF S. aculeata, S. sesban AND C. cajan.

1.31:Sesbania aculeata(79).

The name of this plant is different in different Indian languages viz., Sanskrit-Jayanti, itakata; Hindi-Dhunchi; Marathi-Ramshevari; Gujrati-Sasiika, ikad; Telgu-Errajilugu, ettaienga; Tamil-Mullagathi, mulsaembai; Kannada-Mullujeerangi, dhaincha; Malayalam-Kitannu; Oriya-Dhaincha; Punjabi-Jayanti; Asami-Dhaincha. The photograph of Sesbania aculeata crop is given in annexure on page159.

It is shrubby, annual native to Australia and cultivated during rainy season almost throughout India upto an altitude of 1220 M., also occasionally found in marshes and swamps. Daincha is a monsoon season crop and adapts itself to varying soil conditions. It grows well in loamy, clayey, black and sandy soil and is highly resistant to drought, although it does well in regions receiving rainfall ranging from 55 to 110 cms. It also withstands with water logging and salinity. Daincha is propagated by seeds. Seeds are sown usually in June-July at the onset of monsoon, although daincha sowing continue in several regions from March through August. Seeds are sown either broadcast or drilled in, when broadcast, 90-110 kg. of seeds are used per hectare. In drilling, seeds are drilled in rows 30cms. apart at the rate of 20-60 kg/ha. A higher seed rate gives a thicker stand resulting in tender plants which can be easily pulled out and ploughed. Dhaincha reaches a height of 15-22.5 cm. during the first three weeks and then the growth becomes very rapid. It attains a height of 3-6 M. after 5-6 months. Stem green, sparingly prickly, branched from the base, leaves abruptly pinnate with linear oblong, glabrous leaflets, flowers in 3-4 flowered racemes, 1.25 cm. long, pale yellow, unspotted or spotted red to black, pod 15-25 cms. long straight or slightly curved with slightly indented margins.

Dhaincha is attacked by cladosporium sp. but it is not seriously affected by fungi, in India. Among the insect pests, the borer, Azygophleps scalaris Fabr. cause damage by boring into the stem and roots, eating away the contents and leaving only the epidermis. Caterpillars of Thyposidra Successaria Wlk. and Amsacta moorei butl, cause damage to dhaincha plants. Dhaincha is also reported to be attacked by several beetles and bugs. These can be checked by spraying 0.1 % BHC or 0.1 % Dieldrin. Irrigated dhaincha crop usually gives three cuttings, one each in May, July and September respectively. When grown during monsoons, it gives only one cutting within 6-8 weeks time. The annual plant yield ranges from 11.3-13.8 tonnes of green matter/ha. The dhaincha is a light weight material with a packing density of 120-135 kgs/m^3. Dhaincha is an ideal green manure crop as it is quick growing, succulent, easily decomposable with low moisture requirements and produces maximum amount of organic matter and nitrogen, like all legumes, dhaincha also fixes atmospheric nitrogen with its root nodules. About 18,175 tonnes of dhaincha ploughed in one hectare yield about 77kg. of nitrogen.

Dhaincha is grown in Bengal mostly for its fibre used in making fishing nets and ropes, as it is considered to be very durable under water. The fibre have fully retted, they are dried and the fibre removed. About 9% yield of fibre is obtained from stalks after retting and drying. Dhaincha is valued as a fodder for cattles. It can be cultivated mixed with non-leguminous Kharif fodder and can also be made into silage. It is reported to increase meat and milk production in cattle.

Dhaincha seeds are reported to contain (on dry wt. basis) crude protein, 32.67%, fibre 10.69%, ether extr. 2.94%, N-free extr. 48.75%, ash 4.93%, calcium 0.37% and phosphorous 0.59%. Seeds from Pakistan have been found to yield 28% of a gum having properties similar to those of guar gum and the gum is said to have possible applications in several industrial process. Seed meal, which contains about 53.46% protein on dry wt. basis, has been found to be a suitable substitute for groundnut meal in the preparation of culture medium for the growth of penicillium. Colloidal substance similar to those obtained from marine algae, locust been gum, guar gum and gum tragacanth are reported to occur in the seeds.

1.3.2:Sesbania sesban(S. aegyptica)(79).

The name of this plant is different in different Indian languages viz., Sanskrit-Jayanti; Hindi-Jainti, Jait, rawasan; Bengali-Jainti, jayant; Marathi-Shewarie, jarjan; Gujrati-Jayati, raishingin; Telgu-Samintha, Suiminta; Tamil-Chithagathi, Champai; Kannada-Arisina, jeenangi; Malayalam-Sempa, nellithalai; Oriya-Thaitimul, joyontri; Punjabi-Jaint, jait; Assami-Jintri, Jayantri. S. sesban is a soft wooded, quick growing short lived shrub 1.8-6M high, cultivated throughout the plains of India upto an altitude of 1,200 M. The photograph of Sesbania sesban crop is given in annexure on page160.

S. sesban can grow under widely different conditions and can provide large quantities of green manure. However, it is recommended for cultivation in regions liable to periodic innudation. It can also be grown under water logged condition and acid soils. It withstands salt concentration of 0.4-1% in seedling stage and 0.9-1.4% towards maturity. The leaves and pods dry up as a result of frost. Sesban is propagated through seeds. When grown as a shade plant in orchards, it is sown parallel to the row of young orchard plants about a foot from their periphery. It grows to about 4.5-6m on rich alluvial soil in one season. Leaves 7.5-15 cm. long, paripinnate, leaflets 8-20 pairs, linear oblong, glabrous, entire mucronate to acuminate, 6.0-25mm X 2.5-6.0mm flowers yellow or yellow spotted red to purple or with standard petals coloured purple or brown from out side, in 8-10 flowered, lax, axillary racemes, 2.5-14.0cm. long pods 12.5-22.5 cm. X 0.25-0.37 cm. pendulous, weak, distinctly torulose, twisted, sharply beaked 20-30 seeded and septate.

As the plant is quick growing, it is valued as a temporary hedge in North India. If left unclipped, it forms a low windbreak. Sesban is used on borders of nursery beds so as to protect young seedlings from cold or hot winds. Sesban is grown as support to betal, papper and grape vines and cucurbitaceous plants and also to support sugarcane. S. sesban is grown as a perinnial manure crop. The plant stands lopping well and produces regrowths very quickly. Excellent green manure is obtained when the plants are 60cm. high, lopped leaves can be used for compost in a corner of the field. A compost pit of 280cm X 180cm X 90cm. in any field is sufficient to produce basic requirements of manure for an acre of land. The plant is especially rich in nitrogen(4%) and exceeds the minimum of 2% over which organic nitrogenous materials render nitrogen available for plant growth. It nutrifies soil easily and used as green manure. The leaves are reported to improve the productivity and physical condition of saline soils significantly, manuring consecutively for three years is reported to increase the humus content of soil by 33% and decrease the salt content to a similar extent. Sesban is classed under famine foods because of its seeds, which are rich in protein. In Bihar, the flowers are eaten as vegetable. The leaves on analysis show that these contains(on dry wt. basis) protein 26.6%, phosphorus 0.34%. These datas clearly show that the leaves of S. sesban are a good source of protein, calcium and phosphorus.

Pigments isolated from the flowers include a complex of cyanidin and delphindin glycoside acylated with gallic and an unidentified acid. Atleast six flavonols, magnesium and traces of iron are present. The seeds contain protein 33.7%, fat 4.8%, N-free extr. 18.2%, cellulose 28.3%, ash 4.2% and vitamin-C .0894%. Sesban seed protein is of poor quality because of the presence of canavanine, which is a competitive inhibitor or arginine. The occurrence of canavanine in the seeds of this species distinguishes it from others. Untreated seeds from formosa are reported to be highly toxic and cannot be used as feed or protein supplement for live stock.

Bark is the source of a fibre used for making ropes. The plant yields about 56 tonnes of green matter per hectare. The bulk density of the chips is about 230- 245 kgs/m^3. Charcoal obtained from the plant is used for gun powder. Sesban plant is used as a fuel in jaggery industry. Sesban is grown in Deccan to furnish poles as a substitute for bamboo and for roofing huts. The plant is used as a nurse in forest plantations. The wooden toys are made from its wood in Burma. In Africa the stems are used for arrows and pipes. Sesban is a common cottage ornament. The leaves and flowers are used in religious offerings. The plant yields an insecticide and is also used in making ink.

Among the pests, prodenia litura, the tobacco caterpillar feeds on leaves and practically defoliates the plants. Azygophleps scalaris causes severe damage to sesban in South India and Bengal. Its larvae funnel through the main stem and practically eat away the contents of the stem leaving the epidermis only. It is controlled by uprooting the stems immediately after harvesting and burning them. DDT(0.05%) and BHC dust(5%) are cheap and effective, while product 1250 and parathion are also effective against the pests.

The plant is credited with galactogogue properties. The seeds are stimulant, emmenagogue and astringent and useful in checking diarrhoea and reducing enlargement of the spleen. In the form of ointment, the seeds are used to cure itches and various other skin eruptions.

1.33:Cajanus cajan(80).

An important leguminous crop, widely distributed in the tropics and cultivated extensively for its edible seeds. The name of this crop is different in different languages viz., Red gram, Pigeon Pea, Congo Pea; Sanskrit:Adhaki, tuvari, tuvarika; Hindi, Bengali & Marathi:Arhar, tur, tuver; Tamil:Thovaray; Telgu:Kandulu; Kannad:Togare; Malayalam:Thuvara; Oriya:Harade. It is an annual or perennial shrub, 1 - 3M. high, cultivated nearly throughout India as a pulse crop. It is often grown for green manure or for cover on plantations. Its deep and penetrating root system makes it specially valuable as a renovating and contour hedge crop for checking soil erosion. In America and Hawaii, cajanus is cultivated for fodder. The plant is probably a native of Africa and it is now grown in almost all the tropical countries of the world, including Africa, America, India, Australia, Hawaii, East and West Indies. In India, it is mainly grown in U.P., M.P., Bihar, Maharashtra and Tamil Nadu. Numerous types of Cajanus are known, differing in height, habit, time of maturity, colour, size and shape of pods and seeds. These types can be grouped broadly under two varieties. Arhar(C. cajanus var. bicolor D.C.) and tur(C. cajan var. flavus D.C.). The former includes most of the perennial types and comprises generally the late maturing, large, bushy plants, bearing purple streaked, yellow flowers and dark coloured pods, each having 4-5 seeds. The tur variety comprises early maturing, smaller plants, bearing yellow flowers and plain pods, each containing 2-3 seeds. Tur varieties are commonly cultivated in peninsular region and the late maturing arhar types are cultivated in U.P., Bihar, Bengal and Assam. Both varieties are cultivated in central provinces. The photograph of Cajanus cajan crop is given in annexure on page 161.

Cajanus is grown mainly as a mixed crop, the soil on which it is grown varies according to the requirements of the associated crop. It can be grown on almost all types of soil, not deficient in lime, but it prefers a medium moist soil, with good drainage. In north India, it is grown on the alluvial soils of the Indo-Gangetic plain, while in Bombay and Central India, it is grown on heavy black cotton soil. It is drought resistant and it suffers by water logging and is susceptible to frost. It is highly adaptable with respect to climate and grown both in dry and moist tropics. Under dry condition, it tends to mature quickly, while under humid conditions, it develops a luxuriant vegetable growth and ripens late. It is grown mostly as a Kharif crop in India i.e. sown about the commencement of the monsoon (June or July) and harvested in February or March. Occasionally, it is grown as a Rabi crop i.e. sown in October and harvested in March or April. It is generally sown between rows of the associated crops, one row for every 3 to 5 rows of the main crop. The distance between the rows varies from 1.5-7.5M. depending upon the nature and amount of admixture. When sown pure, the distance between the rows varies from 35 to 40 cms. in Central India and 45 to 90 cms. in Bihar and U.P. The amount of seed required varies from 1.12 kg. to 5.6 kg. per hectare, when sown mixed with other crops and 13.45 kg to 55.32 kg. per hectare, when sown pure. The plants sown in June or July, start flowering towards the end of September or beginning of October. The early maturing tur varities usually flower, month or two earlier than the late maturing arhar types. The flowers are mostly self pollinated but cross pollination also takes place. The first harvesting is usually done by hand picking. At the final harvest, the plants are cut as near the ground as possible, tied into bundles, when the leaves and pods are nearly dry. The pods are separated by vigorously shaking the plants or by beating with a wooden flail. The fallen material is beaten or trampled upon the bullocks and the seeds and chaff separated by winnowing.

In India, the average production of Cajanus cajanplant ranges from 14.58 million tonnes to 15.3 million tonnes (B.D.) during 1981 to 1986.

The bulk density of C. cajan chips is about 180-190 kgs/m^3. The seeds are split into dhal before marketing. Analysis of dhal without husk gave the following values, moisture 15.2%, protein 22.3%, fat (ether extract) 1.7%, mineral matter 3.6%, carbohydrate 57.2%, calcium 9.14% and phosphorus 0.26%, carotene evaluated as vitamin A 220 I.U. and vitamin B 150 I.U. per 100g.

The husk of pods and seeds obtained during threshing constitutes a valuable cattle feed. Mixed with broken bits of dhal, the husk is sold under the name chuni for feeding milch cattle. The dried stalks obtained after threshing are generally used for fuel or for thatching.

The most common pest of cajanus is the gram caterpillar, Heliothis obsoleta and gram pod fly (Agromyza obtusa M.) which bore into seeds and pods and cause considerable damage to the crop. The most common disease of cajanus is wilt caused by the fungus, Fusarium Udum Butl. The fungus, which is present in the soil, attacks the roots, stem or branches and the entire plant withers. The disease is common in the Indo-Gangetic plain and no direct method of control is known. The use of wilt resistent strains, pusa 51 and 80 and C.P.38 are recommended.

For the present investigation the following studies have been done:

1. Anatomical and chemical studies viz., proximate chemical analysis, anatomical studies and morphological studies.

2. Studies on lignins viz., Isolation of different types of lignins, Alkaline nitrobenzene oxidation studies, Infrared and ultravoilet spectroscopic studies.

3. Studies on carbohydrates viz., Isolation of holocellulose, cellulose and alphacellulose, Infrared spectroscopic studies and G.L.C. studies of hemicelluloses.

4. Studies on pulping and paper making viz., Soda and soda-AQ pulping, Kraft and Kraft-AQ pulping, Alkaline sulphite and Alkaline sulphite-AQ pulping,

Semi-alkaline sulphite and Semi-alkaline sulphite-AQ pulping and Neutral sulphite semi-chemical pulping studies.

Table-1.1: Per Capita Consumption of Different Countries During 1985(2)

Sl.No.	Countries	Per Capita kg.	Sl.No.	Countries	Per Capita kg.
1.	U.S.A.	284	13.	Hong-kong	162
2.	Sweden	235	14.	Australia	142
3.	Canada	202	15.	United Kingdom	139
4.	Finland	189	16.	Austria	130
5.	Newzealand	182	17.	France	119
6.	Denmark	180	18.	Singapore	116
7.	Switzerland	179	19.	Iceland	108
8.	Germany, fed. Rep.	174	20.	Taiwan	107
9.	Netharlands	171	21.	China, people's Rep.	9.3
10.	Japan	168	22.	Pakistan	3.6
11.	Belgium	168	23.	India	2.5
12.	Luxemburg	164	24.	Afghanistan	0.1

Table-1.2:Requirement of Forest Raw Materials For Paper & Board. (All figures in lakh tonnes)

Year	Installed capacity Requirement	Production with 80% capacity Utilisation	Requirement of raw material for 70% dependence forest raw material @ 2.8 air dry T $\approxeq$ 1 T of paper (Lakh air dry T)			Forest raw material available (Lakh air dry T)			Shortfall in forest raw material (Lakh air dry T)		
			Bamboo	Wood	Total	Bamboo	Wood	Total	Bamboo	Wood	Total
1991	28.0	22.4	22.0 (50%)	22.0 (50%)	44.0	17.0	11.5	28.5	5.0	10.5	15.5
1996	35.0	28.0	22.0 (40%)	33.0 (60%)	55.0	17.0	11.5	28.5	5.0	21.5	26.5
2000	42.5	34.0	20.0 (30%)	47.0 (70%)	67.0	17.0	11.5	28.5	3.0	35.5	38.5

T = Tonnes;

Source - Report of the raw materials committee of development council for paper, pulp and allied industries, Government of India - July 1983.

Table-1.3: Estimated Annual Collectable Yields of Various Non-Wood Plant Fibrous Raw Materials Per Hectare.

Sl.No.	Raw Materials	Estimated Collectable Fibrous Raw Material (BDMT/HA.)
1.	Sugar cane bagasse	5.0 to 12.4
2.	Wheat straw	2.2 to 3.0
3.	Rice straw	1.4 to 2.0
4.	Barley straw	1.4 to 1.5
5.	Bamboo, Natural growth	1.5 to 2.0
6.	Bamboo, cultivated	2.5 to 5.0
7.	Corn stalks	5.5 to 7.0
8.	Sorghum stalks	5.5 to 7.0
9.	Cotton stalks	1.5 to 2.0
10.	Sesbania-aculeata(79)	3.3 to 3.9
11.	Sesbania-sesban(79)	15.0 to 18.0
12.	Cajanus cajan (80)	3.29 to 3.40

For Sl. No 1 to 9, Reference NO. 3.

ANATOMICAL AND CHEMICAL STUDIES

Pulp and paper can be made from many different plants, but whether or not a plant is well suited for this purpose depends largely on the shape of its cells. Cells are hollow structural units that compose plants, each cell consisting typically of a cell wall enclosing a cavity. In early stages of growth the cell cavities contain protoplasm, but soon after the cell wall is fully formed, this disappears from the cells that are of value for paper making, leaving only the hollow tubular or quill-shaped type of structure known as fibre. All plant fibre cells have a primary wall and secondary wall layers. The outermost secondary layer is S_1, which is followed ontogenetically by S_2 and S_3. Bamboo fibres tend to have five or more secondary wall layers. The Primary(P) wall and S_1, S_2, S_3 layers mainly contain cellulose, hemicellulose and lignin. The cellulose, hemicellulose and lignin may be distributed in different layer of wood fibre cells as follows:

Table-2.1:General Cell Wall Chamical Composition of Coniferous Fibres (50).

Wall Designation	Approximate Chemical Composition,(%)		
	Cellulose	Hemicellulose and pectins	Lignin
P	10	20	70
S_1	35	25	40
S_2	55	30	15
S_3	55	40	05
Middle lamella (Exists between the P walls of contiguous fibres)	00	10	90

Substances such as pectic materials, waxes, fats, starches, resin, gums, organic crystals and other extractives and proteins are usually not regular components of the space or unit volumes of fibres but exist in specific location.

Except for the proteins and certain of the extractives, they are typically found only in the fibre lumens or on the fibre surface.

The bamboo fibres are uniformly thick to thin walled, with gradually tapering pointed ends, smooth walls, narrow to wide lumen and very sparse slit like pits. They are often bent, curved or folded and invariably show compressed, somewhat buckled areas with transverse markings, which stand out rather prominently in thick walled fibres. The parenchyma cells are fairly abundent. They are squarish to rectangular in shape. Vessel elements with numerous pits are usually present. They may be short and discoid or barrel shaped or long and cylindrical with truncated or tailed ends and simple or scalari formperforation.

Bagasse fibres are thick to thin walled, usually with straight, pointed ends and relatively more numerous slit, like or lenticular pits than in bamboo. Transverse markings similar to those of bamboo are quite common. Parenchyma cells are very abundent usually appreciably larger than those of bamboo. Vessels are similar to bamboo.

Searching for possible new crops of non-woody plant material involves the examination of a large number of plant samples. To check the suitability of a particular raw material in question for pulp & paper making, the initial tests involves consideration of anatomical characteristics, chemical composition, yield of fibrous constituents and a qualitative, physical and visual appraisal of the plants.Considerable amount of work(4,13) have been done to study the effect of anatomical characteristics and chemical properties of wood fibres on the nature and quality of pulp. The combined effect of physical characteristics of the raw material thus determine the ultimate properties of the pulp and paper as follows:

Table-2.2:Strength Table For Morphological Factors (33).

Sl.No.	Trend	Tensile and bursting Strength	Tearing Strength	Folding Strength	Sheet Density
1.	Fibre length rising	0 to +	+ +	0 to +	0 to -
2.	Cell wall thickness Late(summer) wood fraction(Tube structure) Rising	-	0 to +	- -	- -
3.	Cell wall thickness early(Spring)wood fraction(Ribbon structure) Rising	+	0 to -	+ +	+ +
4.	Fibre length to width (L/D)ratio Rising			+	
5.	Curling of fibres rising	- -	+	+	-

0	No influence or no distinct influence
+	marked positive influence
++	decisive positive influence
-	marked negative influence
--	decisive negative influence

The chemical composition of non-wood fibrous plants varies somewhat but on an average non-wood plants contains around 40% cellulose, 20-25% lignin, a few percent of so called extractives and the rest made up of a mixture of polymer non-glucose carbohydrates, so called hemicellulose.

Water solubility provides a measure of tannins, gums, sugars, colouring matter and starches in wood and pulp. The water solubles affect the pulp yield to some extent.

The one percent sodium hydroxide solubility of wood could indicate the degree of fungus decay or degradation by heat and light. As the wood decays or degrades, the percentage of the alkalisoluble material increases. It is often desirable to ascertain to what extent a low cellulose value is due to attack by fungi, because, in general, the greater such attack the lower the yield.

Alcohol-benzene solubility of wood is a measure of such substances as waxes, fats, resins, gums and phytosterols. The extractives influence both the pulping process and the quality of the resulting pulp. Extractives show up as deposits on critical machinery in the pulp mill and even more so in the paper mill. High content of extractives, means a higher tendency for so called pitch troubles and also for inhomogeneities in the paper caused by resin particles. The resin, when they are present in relatively large quantities and distributed over the fibre surfaces, will make them hydrophobic. This means that paper made from such fibres show a slow water absorbance. The percentage of lignin in the wood is related with the time required for chemical pulping, the higher the lignin content the longer the cooking time required for cooking. The residual lignin present in the pulp influences paper properties and particularly so the stiffness, the more the lignin the higher the stiffness.

In chemical pulping the cellulose is the main component to survive the cook, and variations in the cellulose content of the wood is therefore directly reflected by variations in pulp yield. This is not only of the greatest importance for the economy in pulp production but the yield level is also reflected strongly in the properties, the higher the cellulose content of the pulp the higher the load bearing capacity of the individual fibre in the pulp.

Hemicelluloses are composed of hexosans(e.g. glucose) and pentosans (e.g. xylose) respectively. The hemicellulose has a much lower molecular weight than the cellulose and is also amorphous in nature. It will consequently to a large extent be dissolved during chemical pulping. However, the fairly low quantities of hemicellulose associated with the pulp will have a great influence on quality, particularly on the swelling behaviour of the fibres. The higher the hemicellulose content the more rapid the swelling during beating which favourably influences the beatability of the pulp and also results in somewhat higher tensile breaking load in the paper.

The ash content gives an estimation of the content of mineral salts and other inorganic matters. Silica impairs the burning and sedimentation operations in the recovery process. When the wood contains large quantities of silica, it may show damaging effect on the processability of the wood or on the paper quality. The wood must be rejected on account of this or it must be sufficiently well cleaned before use.

It should be pointed out that it is extremly difficult, to seprate the influence of one factor from that of another, because of the complexity of the pulping process. In all commercial pulping process, delignification, hemicellulose dissolution, cellulose depolymerisation and fiber attack, take place simultaneously. It is impossible to eliminate any one of these effects completely, it is only possible to some extent to vary their respective intensity.

In the present investigations, the anatomical studies of (i) Sesbania sesban, (ii) Sesbania aculeata and (iii) Cajanus cajan have been done. The aim of the present study is to assess the suitability of these non-wood fibrous plants for pulp and paper making and to know the effect of fiber dimensions on the formation and structure of paper.

2.1. EXPERIMENTAL PROCEDURES.

2.1.1. SAMPLING AND PROXIMATE CHEMICAL ANALYSIS OF PLANT MATERIALS:

The plant samples were collected from the nearby region of Saharanpur. On receipt at the laboratory, these samples were further air dried, and then stored in a dry location until removed for analysis. Samples for chemical analysis and measurement of cellular dimensions were obtained by random selection of about 1 kg. of whole plant stalk excluding seeds, leaves and roots.

For chemical analysis, the stalks of S. sesban, S. aculeata and C. cajan were chipped. The chips were air dried and disintegrated in a Weverk laboratory disintegrator. The -40+60(-0.381+0.25)B.S.S. mesh wood meals were collected for chemical analysis. The proximate chemical analysis viz., Cold and Hot water solubility(73); 1% Sodium hydroxide solubility(73); Alcohol-benzene solubility (1:2V/V)(73); Lignin(73); Pentosan(73); Holocellulose(82); Alpha, beta and gamma cellulose(73); Ash(73); Silica(73); Acetyl content(74,81) and Methoxyl content(73) have been performed, to check the suitability of these non-wood fibrous raw materials in question for pulp and paper making. The results of proximate chemical analysis are reported in Table 2.3 alongwith the results of proximate chemical analysis of bamboo and bagasse.

2.12.MACERATION AND CELLULAR ELEMENTS MEASUREMENT:

Transverse sections(T.S.) and longitudinal sections(L.S.) of 20 to 30 μ thickness of these non-wood fibrous plants were cut on Lietz base sladge microtome 1300. For morphological study the samples were subjected to a chemical-physical maceration to separate the individual cellular elements from each other without damage. It involves the use of a hot aqueous acetic acid, sodium chlorite solution to remove most of the lignin and other binding materials without appreciable degradation of the cellulosic tissues. The microscope slides of cellular material were prepared according to IS method 5285-1969. Microscope slides were projected at a magnification of 40X and the fibres length were measured, while the fiber width and cell wall thickness were obtained by measuring the projected images at a magnification of 160X. The photomicrographsNos. 1,2,7,8,13,14are shown in annexure on page162-64, represent the L.S. and T.S. of these non-wood fibrous plants. The frequency percentage curves of fibre length, fibre diameter, lumen diameter and cell wall thickness are represented in figures 2.01 to 2.05 respectively. The values of density, fibre length, fibre diameter, lumen diameter, cell wall thickness and different ratios of the above dimensions are reported in able 2.4.

2.2.RESULTS AND DISCUSSIONS:

The results of proximate chemical analysis as given in table 2.3 indicated that the water solubles in these non-wood fibrous plants ranges from 3.32 to 6.30% as compared to 8.5% and 7.85% in bamboo and bagasse respectively. The S. aculeata is having minimum water solubles(3.32%), while the water solubles in C. cajan is 5.10% and S. sesban 6.30%, which is maximum. The alcohol-benzene solublesin these non-wood fibrous plantsranges from 3.28 to 4.45% as compared to 3.40% and 6.30% in bamboo and bagasse respectively. The alcohol-benzene solubles come under the catagory of extractives and these are totallyundesirable for pulp and paper making. The water solubles and alcohol-benzene solubles affected the pulp yields. As indicated by the results of proximate chemical analysis that these plants are having moderate quantities of extractives, so these will create lesser pitch troubles and also more homogeneities in the paper sheets. The 1% sodium hydroxide solubles in these plants ranges from 19.66% to 24.70% as compare to 26.8% and 33.6% in bamboo and bagasse respectively. The C. cajan is having the minimum 1% sodium hydroxide solubles(19.66%) among these non-wood fibrous plants. The lignin in these plants ranges from 17.65 to 19.79% as compared to 20.30% and 24.30% in bagasse and bamboo respectively. The S. sesban is having minimum lignin content (17.65%) and S. aculeata is having maximum lignin content (19.79%) among these non-wood fibrous plants. As indicated, these non-wood fibrous plants are having low lignin content, so these will require comparatively less cooking chemicals and shorter cooking cycle with improved tensile, burst, tear, fold and sheet density. These plants are having higher holocellulose ranges from 71.86 to 74.85% as comparedto 71.5% in bamboo and 70.6% in bagasse. The alpha cellulose contents in these plantsranges from 45.24% to 48.0% as compared to 42.0% in bagasse and 43.5% in bamboo. As indicated, these plants are having moderate quantities of alphacelluloses. The hemicellulose content in these plants ranges 25.24% to 27.8%

as comparedto 27.6% in bamboo and 28.45% in bagasse. The pentosan content in these plants ranges from 15.97 to 19.0% as compared to 18.3% in bamboo and 23.86% in bagasse. As indicated these plants are having low pentosan content, therefore these will give better pulp yield. The ash and silica contents in these plants ranges from 1.4 to 1.78% and 0.38 to 0.56% as compared to 3.8% and 2.1% in bagasse and 2.1% and 1.4% in bamboo. As indicated these plants are having quite low ash and silica content so these will show less damaging effect on the processability of the wood and will require less cleaning before use. The relults of proximate chemical analysis of S. aculeata are quite comparable with the values reported by Sadawarte etal(62).

All these non-wood fibrous plants consist of polygonal sclerenchyma cells and the thickening of cells is due to the deposition of lignin. The microscopic study of T.S. and L.S. of S. sesban, S. aculeata and C. cajan revealed that the S. sesban have a large number of vessels arranged in a scattered manner and they form diffuse porous wood. The vessels of S. aculeata have wide lumen but less in number than S. sesban and they are arranged in a ring, and form ring porous wood. The vessels of C. cajan either present in group or in isolated form, but less in number. The vessels of S. sesban are small having oblique septa. The S. aculeata vessels are longer in size having oblique septa. The vessels of C. cajan are round with large lumen and transverse septa. The vessels of these plants are short, barrel shaped having numerous pits. The L.S. of S. sesban and L.S. of S. aculeata having unicerate medullary rays. The L.S. of C. cajan showed the presence of both bicerate and unicerate medullary rays. The fibres of S. sesban are thickwalled, with gradually tapering pointed ends, smooth walls, narrow lumen and very sparse slit like pits. The fibres of S. aculeata and C. cajan are thin walled elongated with pointed ends, smooth walls, with wide lumen. The fibre of S. aculeata have more sparse slit like pits.

On the basis of the above discussions, a correlation between anatomical characteristics and properties of pulp and paper for S. sesban, S. aculeata and C. cajan have been elucidated and may be as follows, in the descending orderof merit.

TENSIL AND BURST STRENGTH(13,68).

Density	Ss	Cc	Sa
Cell wall thickness	Ss	Cc	Sa
Mühlesteph ratio	Ss	Cc	Sa
Ratio of lumen to fibre diameter	Sa	Cc	Ss
Over all	Sa	Cc	Ss

FOLD(21)

Density	Ss	Cc	Sa
Cell wall thickness	Ss	Cc	Sa
Ratio of lumen to fibre width	Sa	Cc	Ss
Fibre length	Ss	Sa	Cc
kel ratio	Ss	Cc	Sa
	Sa	Cc	Ss

RENT DENSITY(27,33).

Density	Ss	Cc	Sa
Cell wall thickness	Ss	Cc	Sa
Ratio of wall thickness to lumen diameter	Ss	Cc	Sa
Over all	Sa	Cc	Ss

TEAR(4).

Fibre length	Ss	Sa	Cc
Cell wall thickness	Ss	Cc	Sa
Over all	Ss	Sa	Cc

YIELD(16,58).

Density	Ss	Cc	Sa
Alpha cellulose	Sa	Cc	Ss
Over all	Cc $\gg$	Sa	Ss.

Ss = S. sesban; Sa = S. aculeata and Cc = C. cajan.

2.3.CONCLUSION:

The results of proximate chemical analysis showed that these plants have moderate quantities of solubles thereby creating lesser pitch troubles with improved homogenities in the paper sheet. These plants have low lignin and high alpha cellulose content, thereby require less cooking chemicals with shorter cooking cycle and gives comparatively higher pulp yields.

The knowledge of the fibre structures is very useful for determining the various properties of pulp & paper. The fibre length of S. sesban is more in comparison to S. aculeata and C. cajan, hence S. sesban is likely to possess the maximum value for tear. The S. aculeata and C. cajan will give higher pulp yields with better values for tensile, burst and fold than S. sesban, since all these properties are dependent on fibre width, wood density, cell wall thickness, cellulose and lignin content. The S. sesban wood consists of a large number of vessels, fibres having thick walled with narrow lumen and the wood of S. aculeata consists of less number of vessels, fibres having thin walled with wider lumen. While the wood of C. cajan also consists of less number of vessels, fibres having thin walled with wider lumen. The S. aculeata and C. cajan are somewhat better non-wood fibrous plants than S. sesban. On the basis of anatomical and chemical studies, it was concluded that S. aculeata, C. cajan and S. sesban are quite suitable non-wood fibrous raw material for pulp and paper making.

Table2.3: Proximate Chemical Analysis of S. sesban, S. aculeata, C. cajan, Bagasse and Bamboo.

Sl.No.	Particulars	S. sesban (%)	S. aculeata (%)	C. cajan (%)	Bagasse (6) (%)	Bamboo (52) (%)	S. aculeata (62) (%)
1.	Cold water solubility	2.37	2.64	3.42	5.91	7.6	2.89
2.	Hot water solubility	6.30	3.32	5.10	7.85	8.5	3.08
3.	Alcohol-benzene solubility (1:2V/V)	4.45	3.28	4.14	6.30	3.4	3.20
4.	1 % Sodium hydroxide solubility	24.70	22.40	19.66	33.6	26.8	20.30
5.	Lignin	17.65	19.79	18.72	20.30	24.30	21.10
6.	Pentosan	19.00	17.56	15.97	23.86	18.30	19.00
7.	Holocellulose	73.23	74.85	72.86	70.60	71.50	77.20
8.	Hemicellulose	27.80	26.40	25.24	28.45	27.60	---
9.	Alpha cellulose	45.24	48.00	47.31	42.00	43.50	---
10.	Beta cellulose	11.12	12.75	11.56	---	13.40	---
11.	Gamma cellulose	16.42	13.40	13.50	---	14.00	---
12.	Ash	1.40	1.78	1.72	3.80	2.10	1.84
13.	Silica	0.38	0.50	0.56	2.10	1.40	---
14.	Acetyl content	2.61	2.40	2.18	---	2.50	---
15.	Methoxyl content	3.70	4.17	3.35	---	3.10	---

Table 2.4:Morphological Characteristics of Sesbania sesban, Sesbania aculeata, Cajanus cajan And Bamboo.

Sl.No.	Particulars	S. sesban	S. aculeata	C. cajan	Bamboo(42)	S.aculeata(62)
1.	Colour	Light Brown	Light White	LightBrown	Light Green	Light Brown
2.	Density, gm/c.c.	0.498	0.360	0.485	0.521	0.30
3.	Fibre length,(L)mm average	0.914	0.843	0.765	1.7	0.72
	Variation	0.410-1.12	0.356-0.956	0.312-0.910	1.5-4.4	----
4.	Fibre width,(D) μ average	19.174	21.576	22.122	23.60	22.00
	Variation	10.355- 28.120	10.836- 31.240	10.870- 32.760	---	----
5.	Lumen width,(d) μ average	8.714	14.82	15.05	9.5	15.4
	Variation	3.450-9.784	4.02-22.120	4.10-22.642	---	---
6.	Cell wall thickness,(W) μ average	5.235	3.38	3.54	7.0	3.3
	Variation	2.60-9.756	1.657-5.120	1.620-5.442	---	---
7.	Flexibility coefficient(d/D)X100	45.44	68.68	68.03	40.5	70.0
8.	Ratio twice cell wall thickness to fibre width,(2W/D)	0.546	0.313	0.320	0.593	0.30
9.	Runkel ratio,(2W/d)	1.20	0.456	0.470	1.47	0.43
10.	Ratio of cell wall area to total cross sectional area %,(Mühlesteph ratio)	81.3	58.5	61.5	---	---
11.	Ratio of length to width,(L/D)	47.66	39.07	34.6	72.0	32.7
12.	Ratio of cell wall thickness to lumen width,(W/d)	0.60	0.22	0.23	0.74	0.21

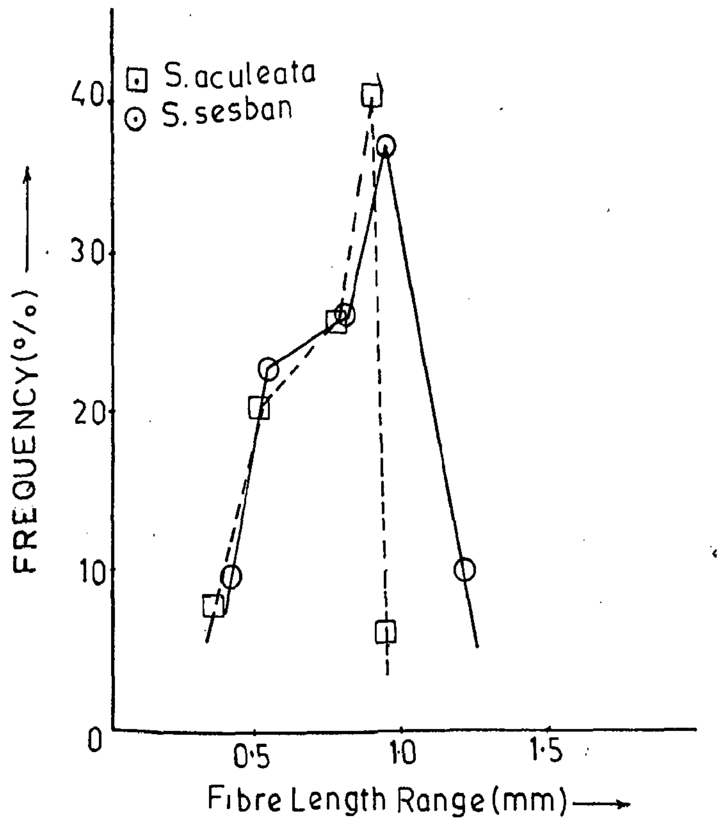


Fig. 2·01: PLOTS OF FIBER LENGTH RANGE (mm) VERSUS FREQUENCY (%) FOR S.sesban AND S.aculeata.

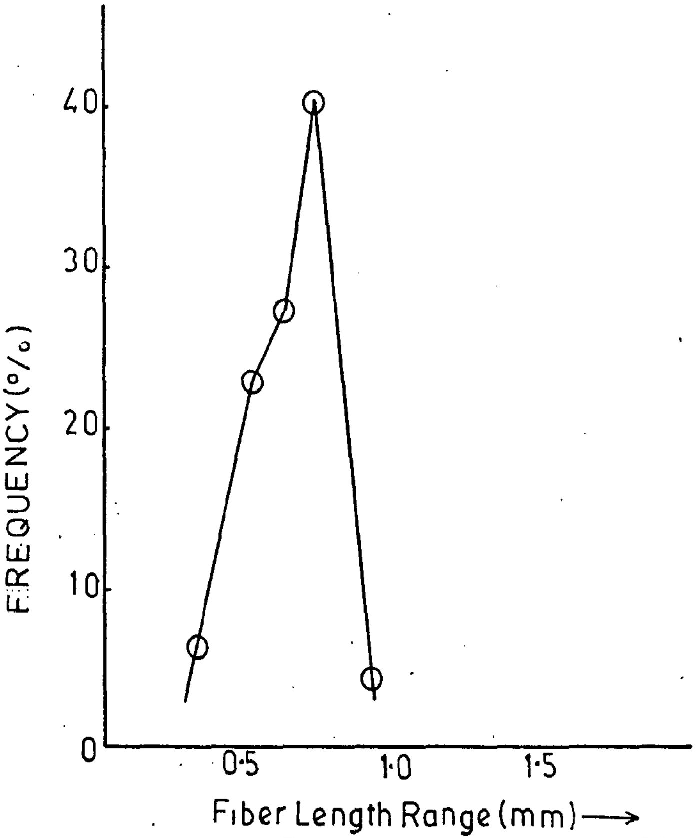


Fig. 2·02 PLOTS OF FIBRE LENGTH RANGE(mm) VERSUS FREQUENCY (%) FOR C.cajan.

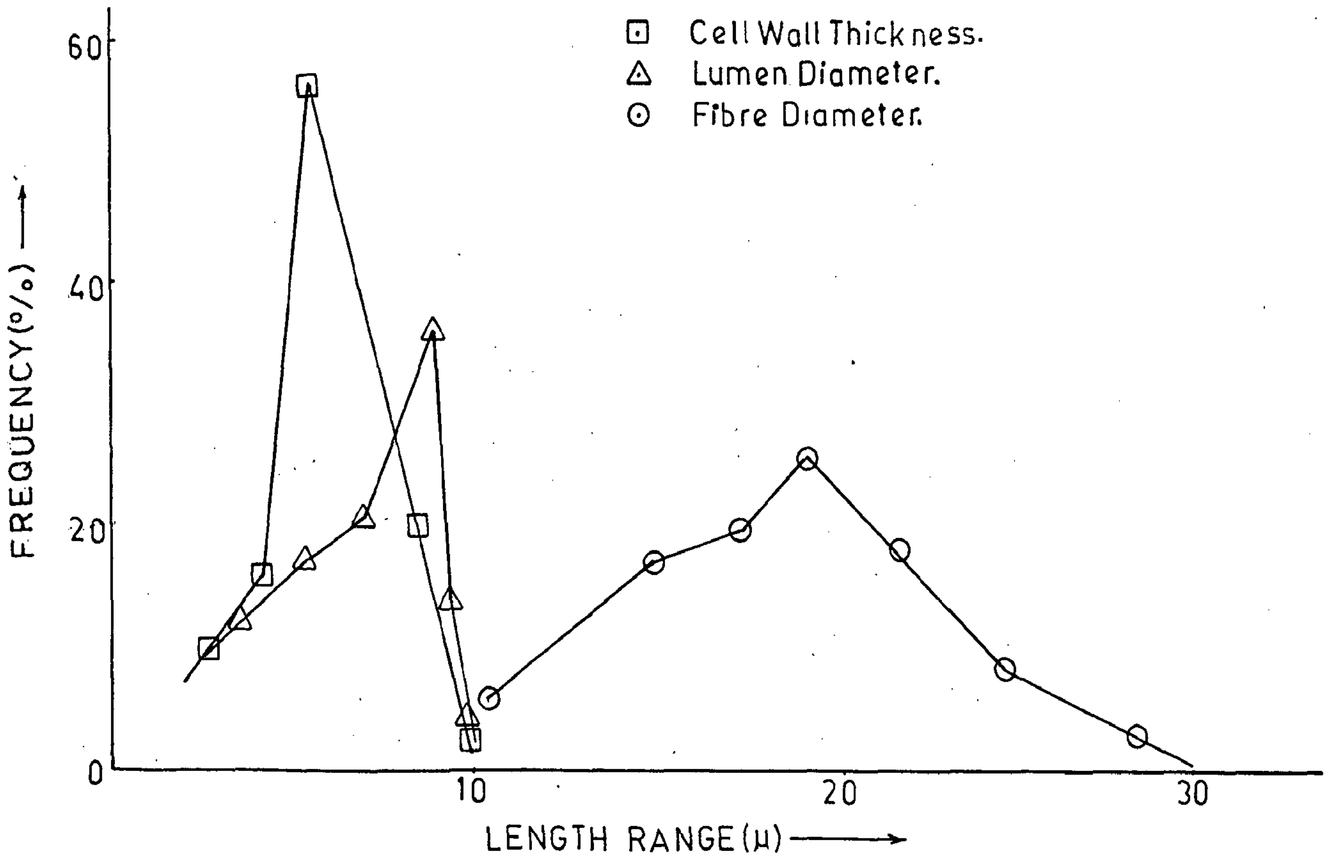


Fig. 2·03: PLOTS OF LENGTH RANGE(μ) OF CELL WALL THICKNESS, LUMEN DIAMETER AND FIBRE DIAMETER VERSUS FREQUENCY (%) FOR S.sesban.

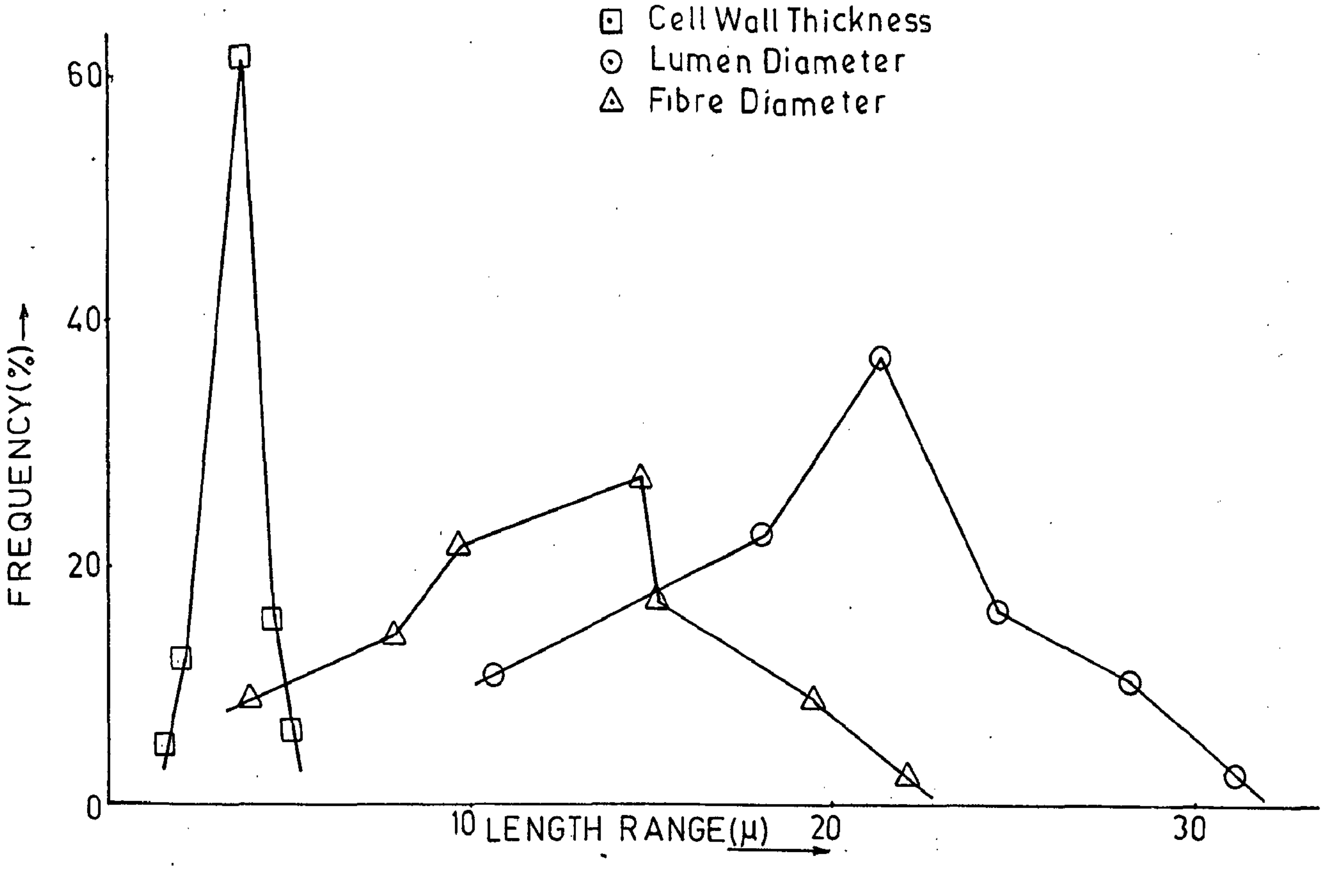


Fig. 2·04: PLOTS OF LENGTH RANGE(μ) OF CELL WALL THICKNESS, LUMEN DIAMETER AND FIBRE DIAMETER VERSUS FREQUENCY FOR *S. aculeata*.

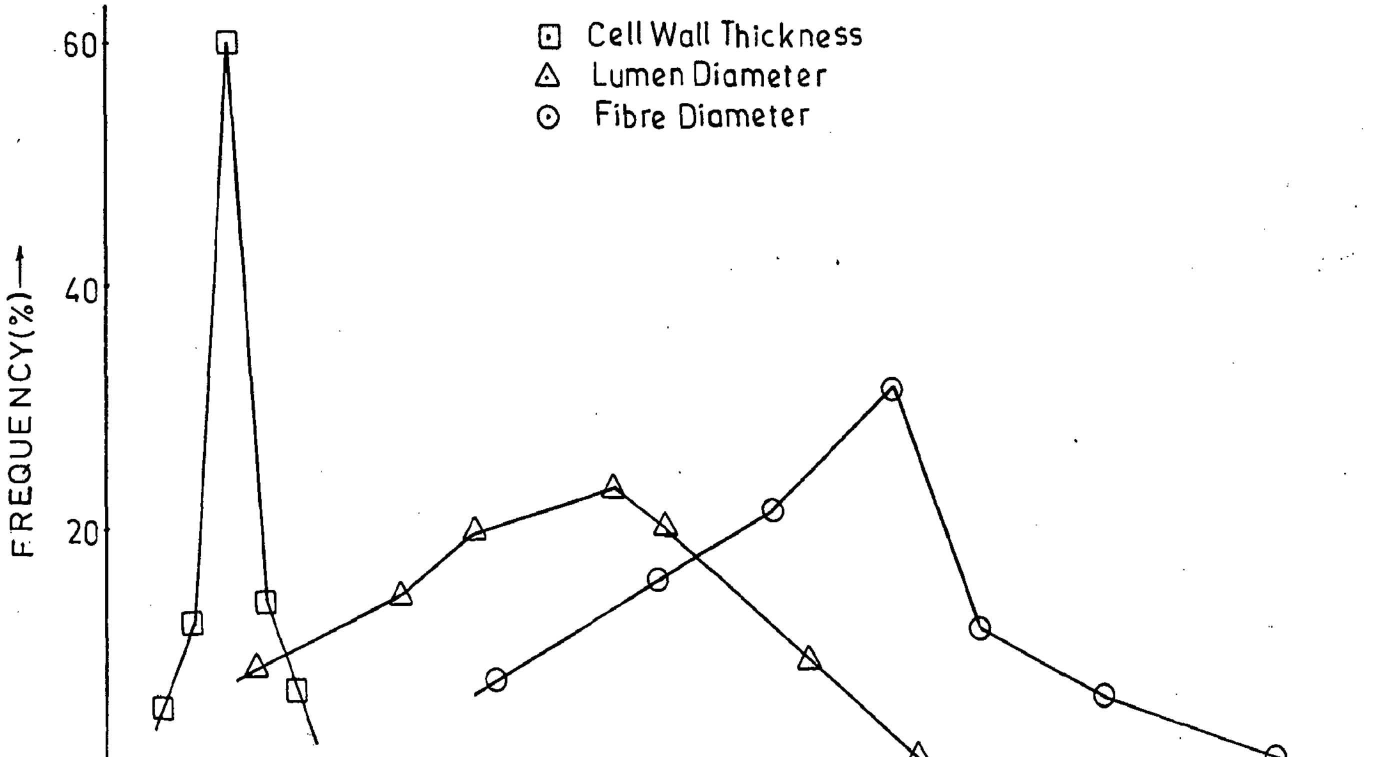
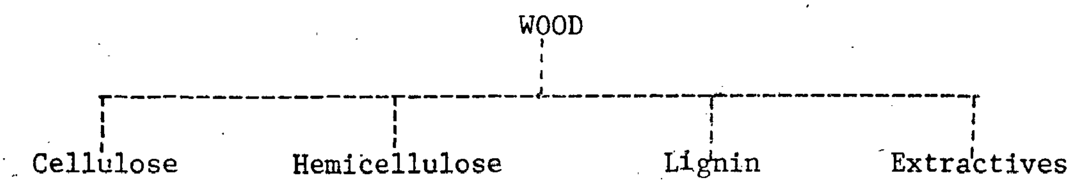


Fig. 2·05: PLOTS OF LENGTH RANGE (μ) OF CELL WALL THICKNESS, LUMEN DIAMETER AND FIBRE DIAMETER VERSUS FREQUENCY FOR *C. cajan*.

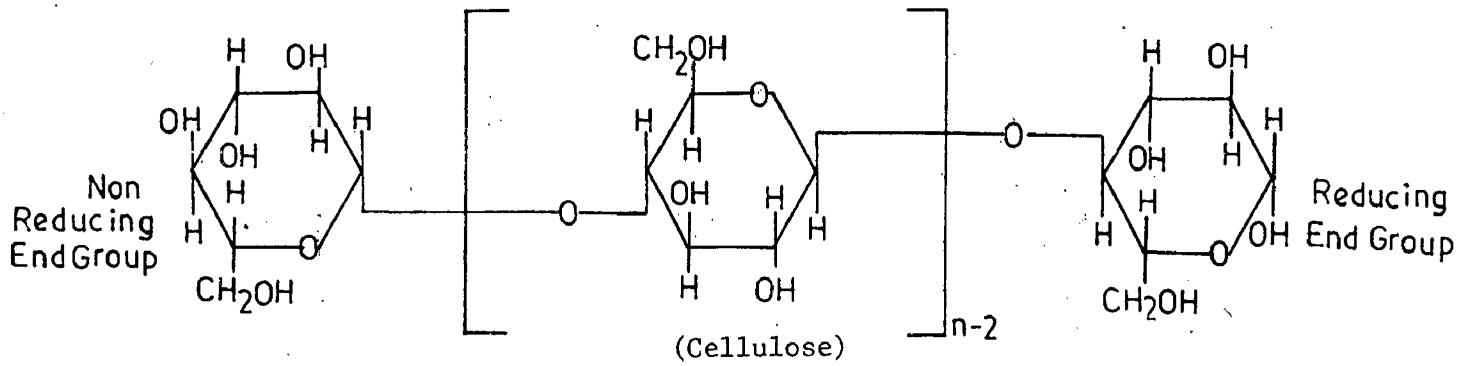
STUDIES ON CARBOHYDRATES

Wood is exceedingly difficult to define chemically, because it is a complex heterogeneous product of nature made up of interpenetrating components largely of high molecular weight. The principal components are generally classified as follows:



3.1.CELLULOSE:

Of all the naturally occuring compounds of Carbon, cellulose appears to be the most abundant polysaccharide in the world, and is the major constituent of the plant materials. It is created in enormous amounts annually as a result of photosynthesis and is also the principal component of cellwalls of all woods, straw, grasses, bast fibres and seed hairs etc. Cellulose is a high molecular weight, stereoregular linear polymer of repeating β-D glucopyranose units. Cellulose could be described as a polymer of D-glucose units involving 1:4-β-glucosidic linkage.



(Cellulose)

Generally cellulose is written as $(C_6H_{10}O_5)_n$, where 'n' is the degree of polymerisation (D.P.) ranging between 1000 to 5000, and the molecular weight

3.2.HEMICELLULOSE:

Hemicellulose refers to the mixtures of low molecular weight polysaccharides which are closely associated in plant tissue with cellulose. Hemicellulose are generally considered to be located in the middle lamella and throughout the bulk of the wood fibre, with some evidence for concentration towards the outer regions of the fibres. The ray and parenchyma cells of wood contain a greater percentage of hemicelluloses than do the fibre elements. The hemicelluloses are generally considered to be non crystalline. Hemicellulose polymers are composed of the following major saccharide units viz., D-xylose, D-mannose, D-glucose, L-arabinose, D-galactose, D-glucuronic acid and D-galacturonic acid. Table-3.1 gives a qualitative summary of the polymer composition of hemicelluloses from hardwoods and softwoods. It is evident that hardwood hemicelluloses are rich in xylan polymers with small amounts of glucomannan, whereas softwood hemicelluloses are rich in galactoglucomannan polymers and contain, as well as, significant quantities of xylan polymers.

Table-3.1:Major Carbohydrate Polymer Components of Hardwood And Softwood Hemicelluloses.

Polymer	Relative Amount	
	Softwood	Hardwood
4-0-methylglucuronoxylan	Small or none	Very large
4-0-methylglucuronoarabinoxylan	Medium	Trace
Glucomannan	NIL	Small
Galactoglucomannan	Very large	NIL
Arabinogalactan	Large	NIL

The infrared spectroscopy has uniquely served to provide answers to difficult problems and foremost among these is the identity of a given plant material. The only successful approach to this problem thus far has been the comparison of the spectrum of an isolated lignin and carbohydrate with the spectrum of the original and a delignified wood section. The X-ray diffraction analysis method is very useful for differentiating non-cellulosic carbohydrates from cellulose. Earlier applications of infrared absorption spectroscopy of cellulose were confined to the studies of cellulose molecule, investigations of physical, optical, and crystalline properties of more or less pure celluloses. The major use of infrared spectroscopy, as a tool of analytical chemistry, has been derived from the ability of this branch of spectroscopy to detect, to identify, and quantitative measurement of the specific organic functional groups.

3.3.EXPERIMENTAL PROCEDURES:

3.3.1.PREPARATION OF THE SAMPLES:

Transverse section (T.S.) and longitudinal sections(L.S.) or 20 to 30 μ thickness of these non-wood fibrous plants were cut on Lietz base sladge microtome 1300 (photomicrographs 1 to 24 are shown in Annexure on page 162 to 165).

Delignification of the sections were carried out according to well-known procedure(82). Hemicellulose were removed from the wood sections using 20% KOH solution, according to the method reported in literature(61). Holocelluloses were prepared accroding to the method of wise and co-workers. The results of holocellulose yields and holocellulose analysis are tabulated in Table 3.2. The alpha cellulose samples were prepared as per TAPPI standard method T:203 OS-74. Cellulose samples were prepared according to the nitration method reported in literature(75).

3.3.2.SUGAR ANALYSIS:

The alpha cellulose and denitrated cellulose nitrate were analysed to their corresponding sugars according to the method of Saeman and coworkers(70). The results of these analysis are reported in Tables 3.3 and 3.4.

3.3.3.EXTRACTION AND PURIFICATION OF HEMICELLULOSE FRACTIONS FROM HOLOCELLULOSE:

The hemicelluloses were extracted from holocelluloses according to the method reported in literature(82), by using different concentration of KOH viz., 5%, 18% and 20% potassium hydroxide + 4% boric acid. The hemicelluloses were purified accroding to the method of Timell and Tyminski(76). The crude and purified yield of hemicellulose fractions are tabulated intable 3.5, while the results of hemicellulose analysis(18% KOH fraction) are given inTable 3.6.

3.3.4.DETERMINATION OF NEUTRAL SUGARS BY GAS-LIQUID CHROMATOGRAPHY:

The G.L.C. of hemicelluloses have been performed accordingto TAPPI standard method T:249 Pm75 and the corresponding chromatograms of S. sesban, S. aculeata and C. cajan are represented in figures 3.11 to 3.13 respectively. The percentage of sugars(8) were also calculated and reported in Table 3.7.

3.3.5.INFRARED SPECTROSCOPIC STUDIES:

The infrared spectrums of wood dust, treated and untreated wood sections and holocellulose, alpha cellulose and cellulose of S. sesban, S. aculeata and C. cajan were recorded within the range of 4000 to 600 cm^{-1} using Perkin-Elmer infracord spectrophotometer.

3.3.6.X-RAY DIFFRACTION ANALYSIS:

The diffraction diagrams were obtained by Geiger countex X-ray diffractometer with copper radiation, monocromatized and focused by reflection on a bent quartz crystal, $\lambda=1.5387A^{o}$. Fig. 3.09and 3.10 showed the diffractograms of the cellulose and alpha cellulose, isolated from S.sesban, S.aculeata and C. cajan, which were characterised by a number of selective reflections. The angles of diffraction maxima and interplanar spacings are given in Table 3.8.

3.4.RESULTS AND DISCUSSIONS:

The infrared spectrums of cellulose and alpha cellulose Fig.3.01 and 3.02,isolated from S. sesban, S. aculeata and C. cajan were nearly the same.

There were little difference in band intensities. These spectrums showed the presence of bands at 3440 to 3400 $cm.^{-1}$;1650 to 1640 $cm.^{-1}$; 1170 to 1165 $cm.^{-1}$ and 895 to 890 $cm.^{-1}$. The bands of very weak intensities were also observed at the frequencies 1430, 1355, 1315, 1235, 1030 and 1090 $cm.^{-1}$ in infrared spectra of cellulose and alphacellulose. The holocellulose spectrums(Fig. 3.03) have the absorption bands at 3400, 2900, 1460, 1430, 1360, 1320, 1260, 1220 and 1160 $cm.^{-1}$. The band at 900 $cm.^{-1}$ and shoulder at 860 $cm.^{-1}$ were also present in the spectrum of holocellulose. It was observed that the few bands have either been broadened or flattened as a result of alphacellulose formation, suggesting that some of the fine structural characteristics of cellulose are reduced or lost. The most important spectral changes occured at bands 1450 $cm.^{-1}$ and 895 $cm.^{-1}$. The sensitivity of these two bands were such that the intensity of the 1450 $cm.^{-1}$ band decreased as the crystallinity was decreased, while the intensity of the band at 895 $cm.^{-1}$ increased as the cellulose was decrystallized. The change in the intensities of bands at about 1450 $cm.^{-1}$ and 900 $cm.^{-1}$ were very small, but they were in opposite directions(59). The band at 1335 $cm.^{-1}$ was due to the $C-CH_3$ deformation and a C-O stretching band at 1240-1235 $cm.^{-1}$, while the bands at 1030 $cm.^{-1}$ and 1090 $cm.^{-1}$ were assigned to C-H and C-O deformation.

The infrared spectrums of wood powder and untreated wood sections of S. sesban, S. aculeata and C. cajan in potassium bromide disks are shown in Fig.3.04 and 3.05 respectively. Figures 3.06 and 3.07 showed the spectra of delignified wood sections and treated sections after the removal of hemicellulose. To assist in identifying the bands in the spectra of wood sections, it was compared with the spectra of cellulose, Klason lignin, native xylan and ivory nut cross section(46)(mostly mannan) and these are shown in figures 3.01, 4.01 and 3.08 respectively.

The broad hydrogen bonded-OH stretching band near 3400 $cm.^{-1}$ and the CH stretching band near 2900 $cm.^{-1}$ in the spectra of wood sections were due to carbohydrate and lignin. The band near 1730 $cm.^{-1}$ in the wood sections was due to the C=O stretching of the -COOH and -$COOCH_3$ group in 4-O-methylglucuronoacetylxylan. When the sections were treated for hemicellulose removal, the band at 1730 cm^{-1} was weakened. The band at 1730 cm^{-1} was completely eliminated when the section were treated with 20% KOH. The band near 1650 cm^{-1} was observed in the spectra of pure cellulose, xylan and mannan. In pure cellulose, it was found that the intensity of the 1650 cm^{-1} band decreased with an increase in sample crystallinity(47). The lignin bands near 1595 and 1510 cm^{-1} in the spectra of wood sections were due to stretching modes of the benzene ring. When the samples were treated to effect delignification, the bands at 1595 cm^{-1} and 1510 cm^{-1} disappeared. The band near 1460 cm^{-1} was due to the CH_3 deformation in the lignin and xylan as well as the CH_2 bending of xylan. Small contributions to the intensity of the band were also from cellulose and hemicellulose -OH in plane bending modes. The band near 1430 cm^{-1} was primarily due to the -CH_2 scissor motion in cellulose. The band near 1365 cm^{-1} was due to CH bending in cellulose and hemicellulose. The band at 1320 cm^{-1} was due to the -CH_2 wagging mode in cellulose(8), and probably also in hemicellulose. The bands or group of bands with maxima at 1230 and 1270 cm^{-1} in the spectra of wood sections arise from all of its four major chemical constituents. In cellulose(45) a band at 1282 cm^{-1} was assigned to a CH bending frequency and a band at 1205 cm^{-1} was assigned to an-OH in plane bending frequency. In xylan a strong band was observed near 1240 cm^{-1} and this band was connected with the C-O stretching mode in the O=C-O group. The two bands at 1270 and 1220 cm^{-1} in Klason lignin and a band at 1240 cm^{-1} in mannan were not clear, and these were probably due to CH and OH bending frequencies. In these spectra a band near 1230 cm^{-1} was more intense like in hard-wood, which indicates that there was more xylan in these non-wood. The band near 1160 cm^{-1} in the spectra of wood sections was due to cellulose and this band has been interpreted as asymmetric C-O-C bridge stretching frequency. The band near 900 cm^{-1} in the spectra of wood sections was due to cellulose and other polysaccharides ring stretching frequencies in mannan.

It was observed that the relative intensities of the bands near 3400, 1430 and 1160 $cm.^{-1}$ were weaker in the spectra of transverse sections than in the spectra of longitudinal sections. The relative intensities of the bands at 1320 $cm.^{-1}$(cellulose) and 1730 $cm.^{-1}$(xylan) were stronger in the spectra of transverse sections than in the spectra of longitudinal sections. The spectra of transverse sections (T.S.) and longitudinal sections(L.S.) were slightly differ in the spectral region near 1000 $cm.^{-1}$. Two absorption bands at 900 $cm.^{-1}$ and 830 $cm.^{-1}$ were appeared in the spectrum of both the sections i.e. T.S. and L.S. The intensities of these bands were more in spectra of T.S. than L.S. A broad band near 1045 $cm.^{-1}$ was found in T.S., which was at the same position in the spectrum of L.S.

The X-ray diffraction diagram of cellulose and alphacellulose(Fig.3.09 & 3.10) were more diffuse than those of pure crystals, but still indicating definite crystalline regions. From X-ray investigations, it was concluded that alphacellulose and cellulose has about the same lattice as cellulose-II(66). The cellulose of S. sesban, S. aculeata and C. cajan showed nearly the same diffraction patterns and the angles of diffraction as reported by other workers(28). The similar effects were also observed for alphacellulose. The alpha cellulose showed slightly higher degree of order than cellulose, because reflections increase in sharpness in alphacellulose due to greater crystallite size or greater crystalline order. The X-ray diffraction of Sesbania aculeata cellulose showed that it has more crystalline order than Sesbania sesban and Cajanus cajan cellulose.

The Table 3.7 indicated that the hemicelluloses of these non-wood fibrous plants are made up of five basic sugars; three hexoses, glucose, mannose and galactose, and two pentoses, xylose and arabinose. All of these sugars exist in six membered pyranose ring form, except arabinose, which is more commonly found in the form of the five membered furanose ring. Therefore, only xylose does not have a free $-CH_2OH$ group on the number 5 carbon atom in the ring. Two uronic acids, i.e. glucuronic and galacturonic acids are made up of, what is frequently termed the uronic anhydride content of plant materials. In these sugar acids, the terminal -CH_2OH group exists as a carboxyl group. They both occur as side chain units of many of the hemicelluloses present in minor amounts in plant materials, but galacturonic acid is also present as a polymer(polyuronide) known commonly as pectin. The two types of derivative groups present in plant material hemicelluloses are the methoxyl and acetyl. The methoxyl group is linked as an ether group on the 4th position of glucuronic acid and as the methyl ester of the carboxyl group in pectin. The acetyl group is substituted on certain sugars in some hemicelluloses as an acetic acid ester.

3.5.CONCLUSION:

The results of these investigations indicated the presence of the two groups of bands, one near 3400 $cm.^{-1}$ and other between 1160 and 1040 $cm.^{-1}$, showed parallel polarisation in the spectrum of cellulose crystallites. The relative intensities of these two groups of bands appeared to be weakened in the spectra of wood cross sections, as would be expected if the cellulose chains in wood cross-sections were oriented nearly parallel to the section normal. In these spectrums the absorption maxima in the C-O stretching region were observed at the same or only slightly lowered frequencies than in the spectra of their longitudinal sections. The higher intensity of 1730 $cm.^{-1}$ band indicated that slightly higher content of xylan were present. The higher intensity of $1600cm.^{-1}$ band than 1500 and 1220 $cm.^{-1}$ bands indicated that the nature of these non-wood fibrous plants are somewhat similar to bamboo and hardwoods. The holocellulose of all these non-wood plants consist more xylan as in the case of hardwoods. The X-ray diffraction spectrograms of alphacellulose showed slightly more crystallinity than cellulose. The structure of cellulose and alphacellulose of these plants are similar to cellulose(II).

The results of GLC analysis of hemicelluloses showed that the main high. It was further confirmed by the isolation of large amounts of xylose from the acid hydrolysate of hemicellulose. The basic skeleton of the xylans found in the stalk or supporting tissue of these non-wood fibrous plants contains a linear (or singly branched) backbone of 1 → 4 linked anhydro-β-D-xylopyranose units, that are made up of completely anhydroxylose units, as also found in hardwoods. The nature of hemicelluloses in these non-wood fibrous plants resembled to those of hard wood and bamboo hemicelluloses.

Table-3.2:Yield And Analyses of Holocellulose Prepared From S. sesban, S. aculeata And C. cajan (% based on oven dry weight of holocellulose).

Sl.No.	Particulars	Sesbania sesban	Sesbania aculeata	Cajanus cajan	Bamboo aurndiacea(19)
1.	Yield*	73.23	74.85	71.86	67.5
2.	Ash content	1.30	1.42	1.35	2.5
3.	Klason lignin content	1.64	1.51	1.42	2.1
4.	Alphacellulose	61.80	64.12	64.40	58.8
5.	Pentosan content	15.72	15.20	13.44	23.1
6.	Acetyl~~e~~ content	1.08	1.10	1.02	2.9
7.	Methoxyl content	2.92	3.28	3.14	0.7
8.	Uronic anhydride	3.46	3.87	3.62	5.2
9.	Hemicellulose	37.95	35.25	35.12	21.5

* (% based on the oven dry weight of original material).

Table-3.3:Various Chemical Constituents of S. sesban, S. aculeata And C. cajan Non-Wood Fibrous Plants(% based on extractive free oven dry material).

Sl.No.	Name of Plant species	Alpha Cellulose	Lignin	Pentosan	Uronic anhydride	Cellulose (By Nitration method)
1.	S. sesban	45.24	17.65	19.00	4.12	41.8
2.	S. aculeata	48.00	19.79	17.56	3.95	45.6
3.	C. cajan	47.31	18.72	15.96	3.60	44.2

Table-3.4:Composition of Alpha-Cellulose And Cellulose
(% Based on extractive free oven dry material)

Sl.No.	Name of Plant Species	Alpha-Cellulose			Cellulose(By nitration)		
		Glucan	Mannan	Xylan + Araban	Glucan	Mannan	Xylan
1.	S. sesban	91.8	1.6	6.6	96.8	2.7	0.5
2.	S. aculeata	94.1	4.0	1.8	98.6	1.2	0.2
3.	C. cajan	92.5	3.8	3.7	98.2	1.5	0.3

Table-3.5:Yield of Hemicellulose Fraction From Holocellulose
(% Based on oven dry weight of wood meal).

Sl.No.	Plant Species	Extraction	Crude Yield (%)	Purified Yield (%)
1.	Sesbania sesban	A. 5% potassium hydroxide	13.4	10.2
		B. 18% potassium hydroxide	9.2	6.3
		C. 20% potassium hydroxide + 4% boric acid.	6.5	5.6
2.	Sesbania aculeata	A. 5% potassium hydroxide	14.1	10.8
		B. 18% potassium hydroxide	8.6	6.1
		C. 20% potassium hydroxide + 4% boric acid.	5.9	4.2
3.	Cajanus cajan	A. 5% potassium hydroxide	13.7	10.4
		B. 18% potassium hydroxide	8.5	5.8
		C. 20% potassium hydroxide + 4% boric acid.	5.2	4.4

Table-3.6:Analysis of Hemicellulose Fraction.(18% KOH Fraction).
(% Based on oven dry weight of Hemicellulose).

Sl.No.	Particulars	Sesbania sesban	Sesbania aculeata	Cajanus cajan	Bamboo aurndiacea(19).
1.	Ash content	2.20	2.12	2.17	--
2.	Pentosans	61.50	60.20	59.16	88.60
3.	Methoxyl content	0.98	1.02	0.99	1.00
4.	Acetyl content	Nil	Nil	Nil	Nil
5.	Uronic acid	20.60	20.80 2	20.20	--

Table-3.7:Relative Amounts of Sugars By GLC Present In Hemicelluloses.

Sl.No.	Sugars	Sesbania sesban (%)	Sesbania aculeata (%)	Cajanus cajan (%)	Bamboo aurndiacea(19). (%)
1.	Rhamanose	4.06	4.22	4.28	Nil
2.	Arabinose	5.16	5.10	5.04	11.6
3.	Xylose	76.90	76.20	75.70	78.8
4.	Mannose	5.30	5.60	5.90	Nil
5.	Galactose	6.15	6.37	6.70	1.8
6.	Glucose	2.38	2.50	2.36	Traces.

Table-3.8:X-Ray Diffraction Analysis Data of Cellulose And Alphacellulose.

Sl.No.	Plant Species	Maxima	Relative Intensity	Angle of Diffraction (2 θ)	Inter planar spacing d(A°)	Unit Cell dimensions Parameter	A°
CELLULOSE:							
1.	Sesbania sesban	R_1	W	12.00°	d(101)7.35	a	8.10
		R_2	S	20.14°	d(10$\bar{1}$)4.41	b	10.28
		R_3	S	21.84°	d(002)4.01	c	9.10
						β	61.80°
2.	Sesbania aculeata	R_1	W	12.18°	d(101)7.25	a	7.90
		R_2	S	20.04°	d(10$\bar{1}$)4.42	b	10.30
		R_3	S	21.80°	d(002)4.07	c	9.14
						β	63.00°
3.	Cajanus cajan	R_1	W	12.40°	d(101)7.12	a	7.90
		R_2	S	20.09°	d(10$\bar{1}$)4.41	b	10.29
		R_3	S	22.06°	d(002)4.02	c	9.00
						β	63.20°
ALPHACELLULOSE:							
1.	Sesbania sesban	R_1	S	12.18°	d(101)7.25	a	8.00
		R_2	S	19.91°	d(10$\bar{1}$)4.45	b	10.28
		R_3	VS	21.80°	d(002)4.07	c	9.16
						β	62.80°
2.	Sesbania aculeata	R_1	S	12.30°	d(101)7.18	a	7.90
		R_2	S	20.00°	d(10$\bar{1}$)4.43	b	10.30
		~~R_3~~	~~VS~~	~~21.80°~~	~~d(002)4.07~~	~~c~~	~~9.14~~
						β	63.00°
3.	Cajanus cajan	R_1	S	11.95°	d(101)7.39	a	8.20
		R_2	S	19.77°	d(10$\bar{1}$)4.48	b	10.30
		R_3	VS	22.00°	d(002)4.03	c	9.10
						β	62.40°

W=Weak, S=Strong and VS=Very Strong.

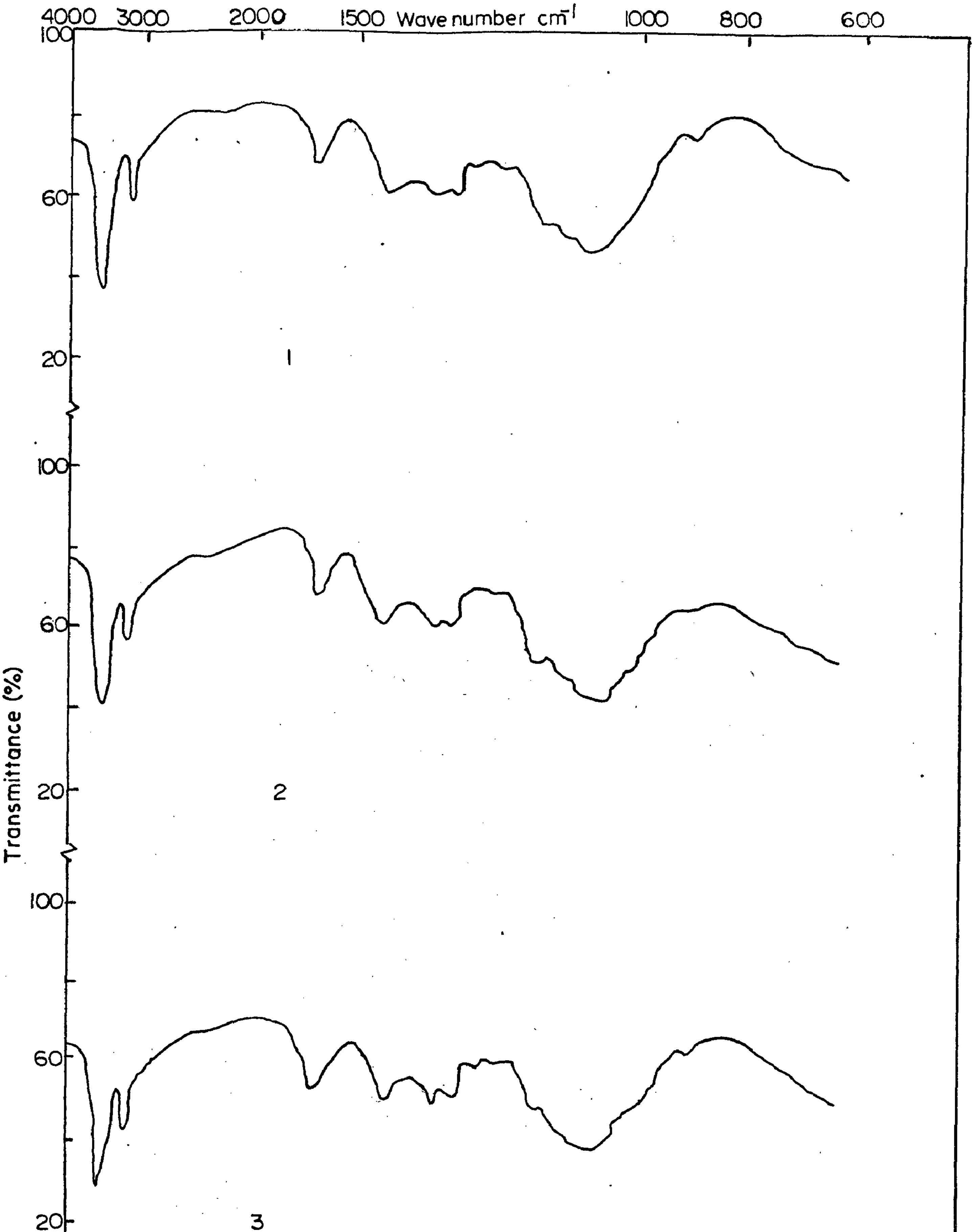


FIG. 3.01 :INFRARED ABSORPTION SPECTRUM OF CELLULOSE OF I. SESBANIA sesban 2. SESBANIA aculeata 3. CAJANUS cajan.

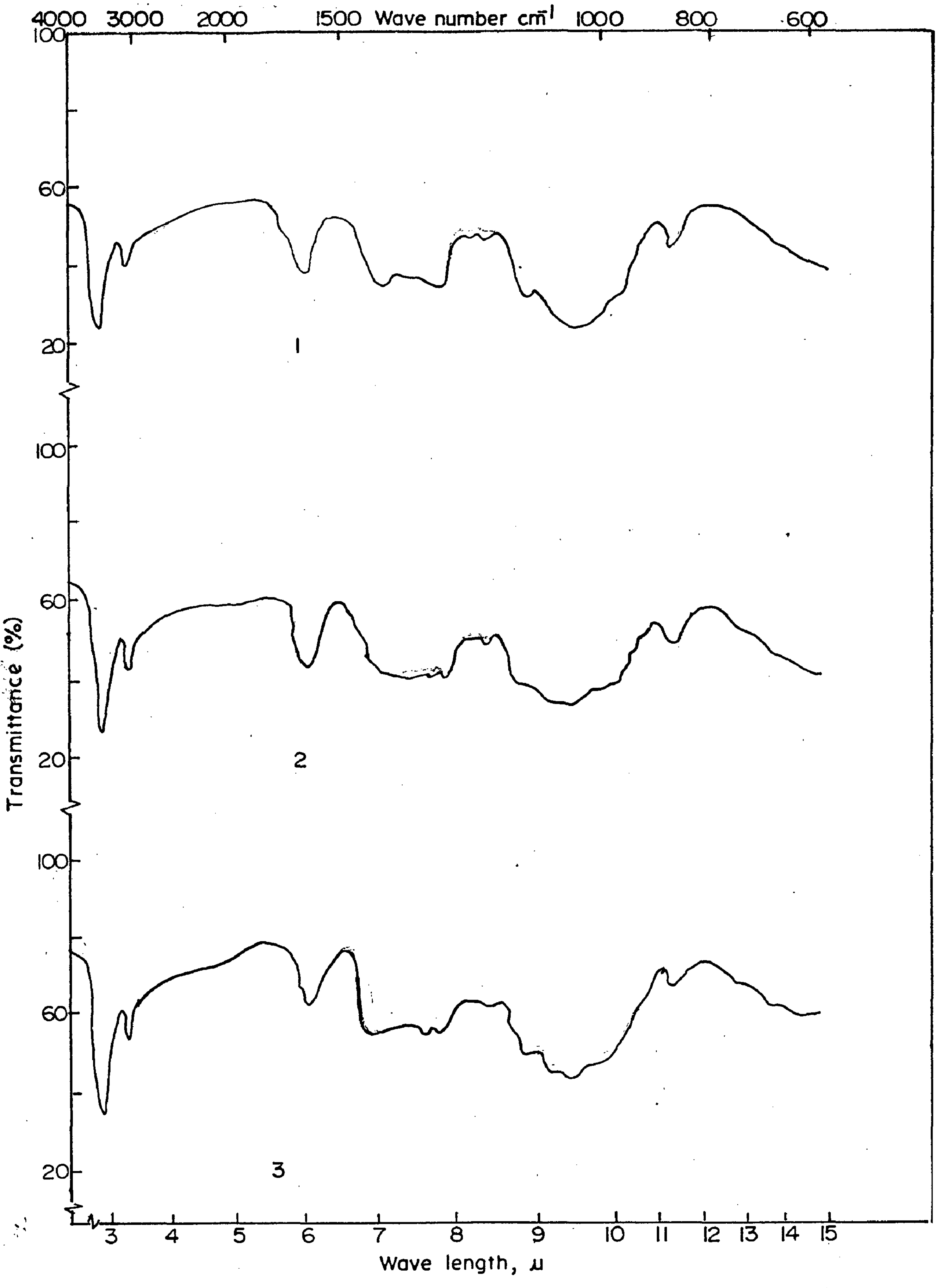


FIG.3.02: INFRARED ABSORPTION SPECTRUM OF ALPHA CELLULOSE OF.
1. SESBANIA sesban 2. SESBANIA aculeata 3. CAJANUS cajan.

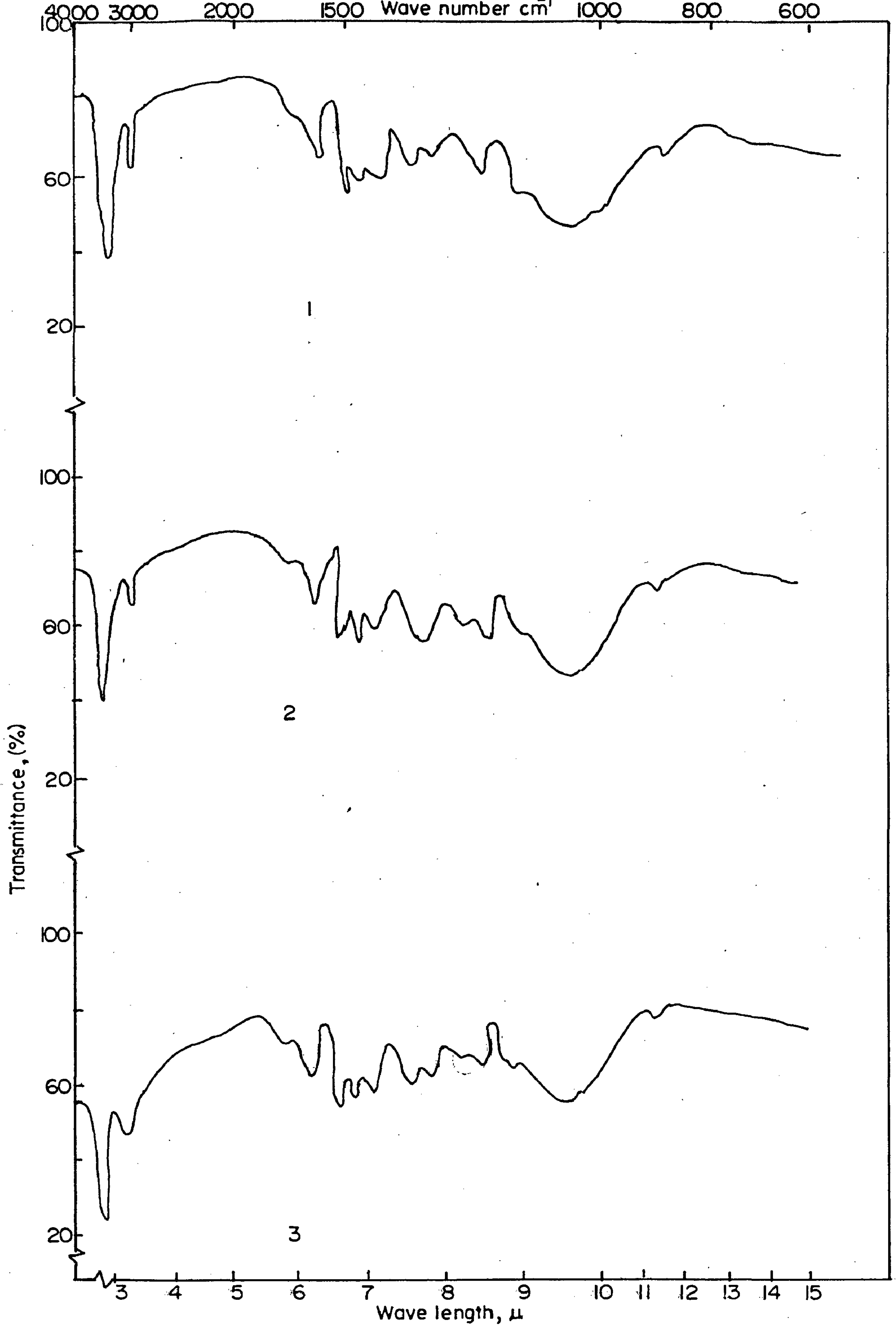


FIG.3.03: INFRARED ABSORPTION SPECTRUM OF HOLOCELLULOSE OF 1. SESBANIA sesban 2. SESBANIA aculeata 3 CAJANUS cajan.

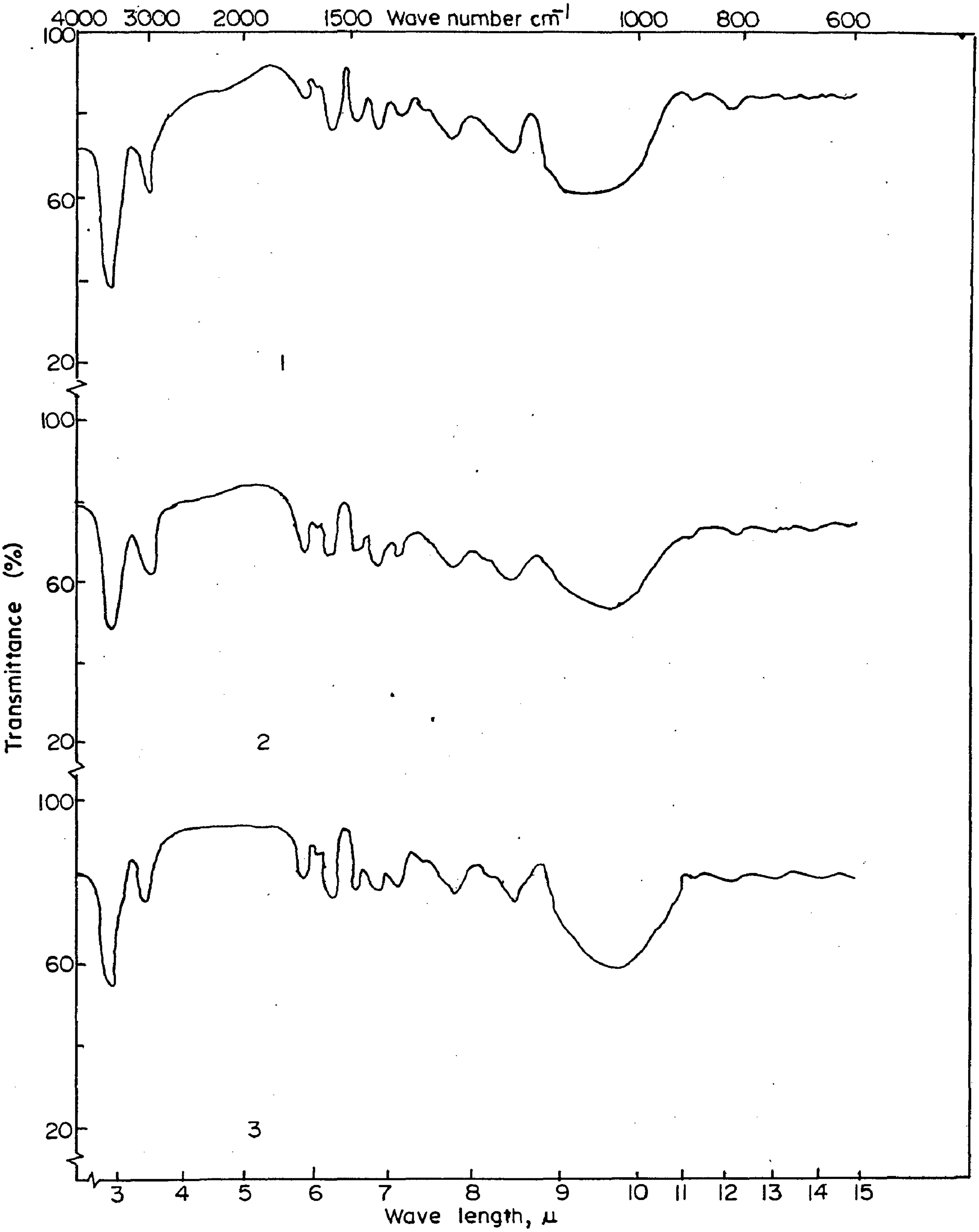


FIG.3.04:INFRARED SPECTRUM OF WOOD POWDER FROM 1. SESBANIA sesban 2. SESBANIA aculeata 3. CAJANUS cajan.

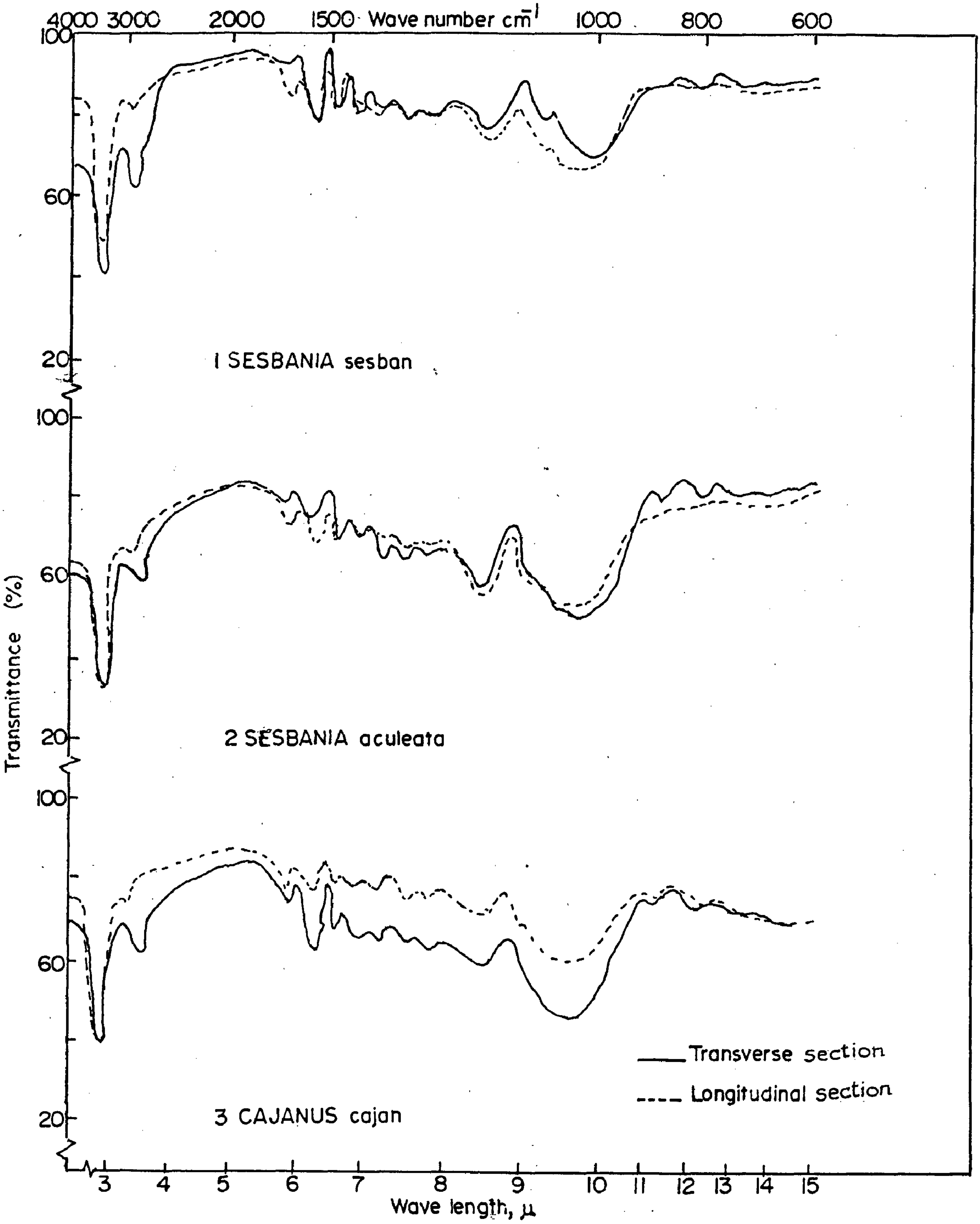


FIG.3.05: INFRARED SPECTRUM OF WOOD SECTION.

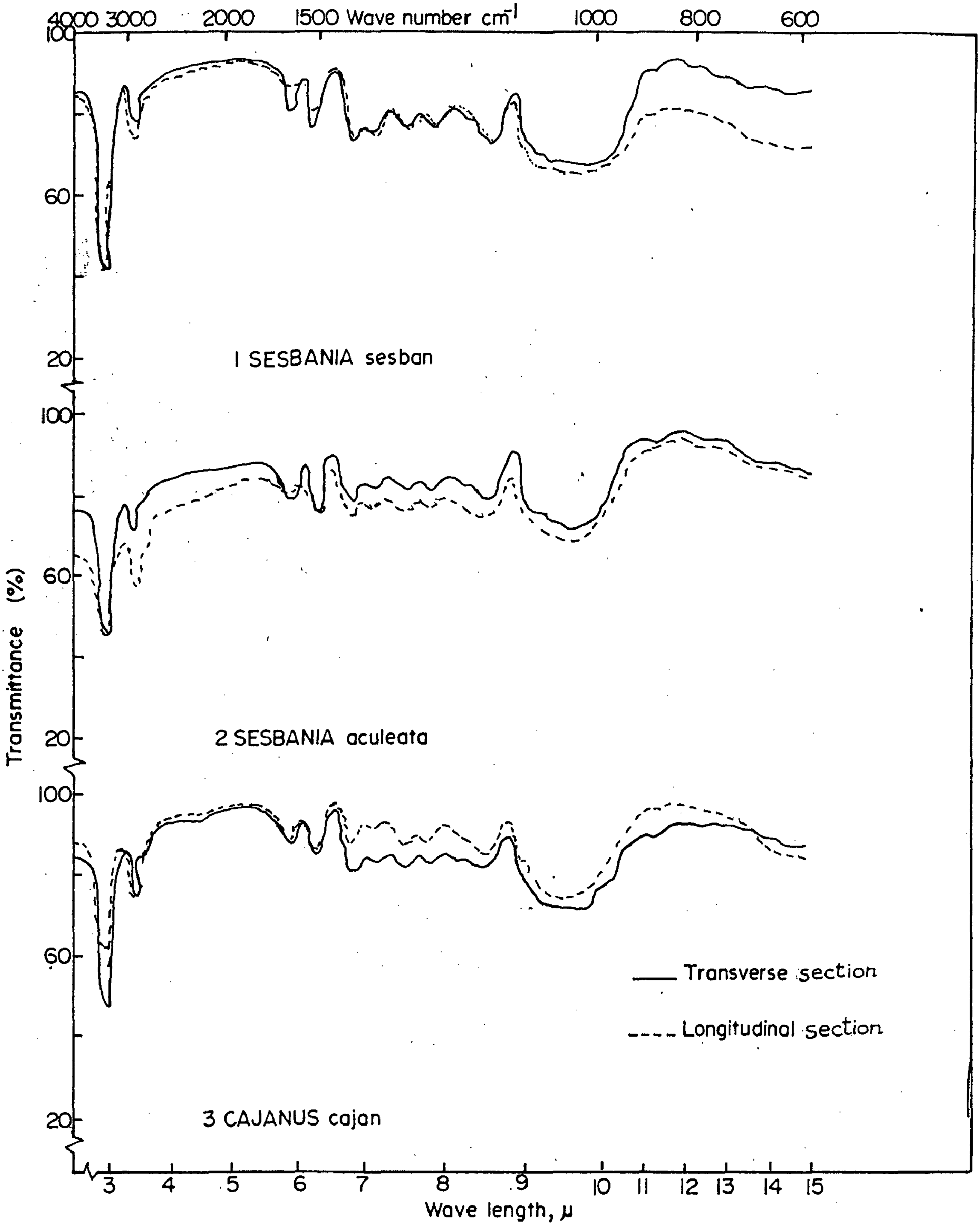


FIG.3.06 :INFRARED SPECTRUM OF DELIGNIFIED WOOD SECTION.

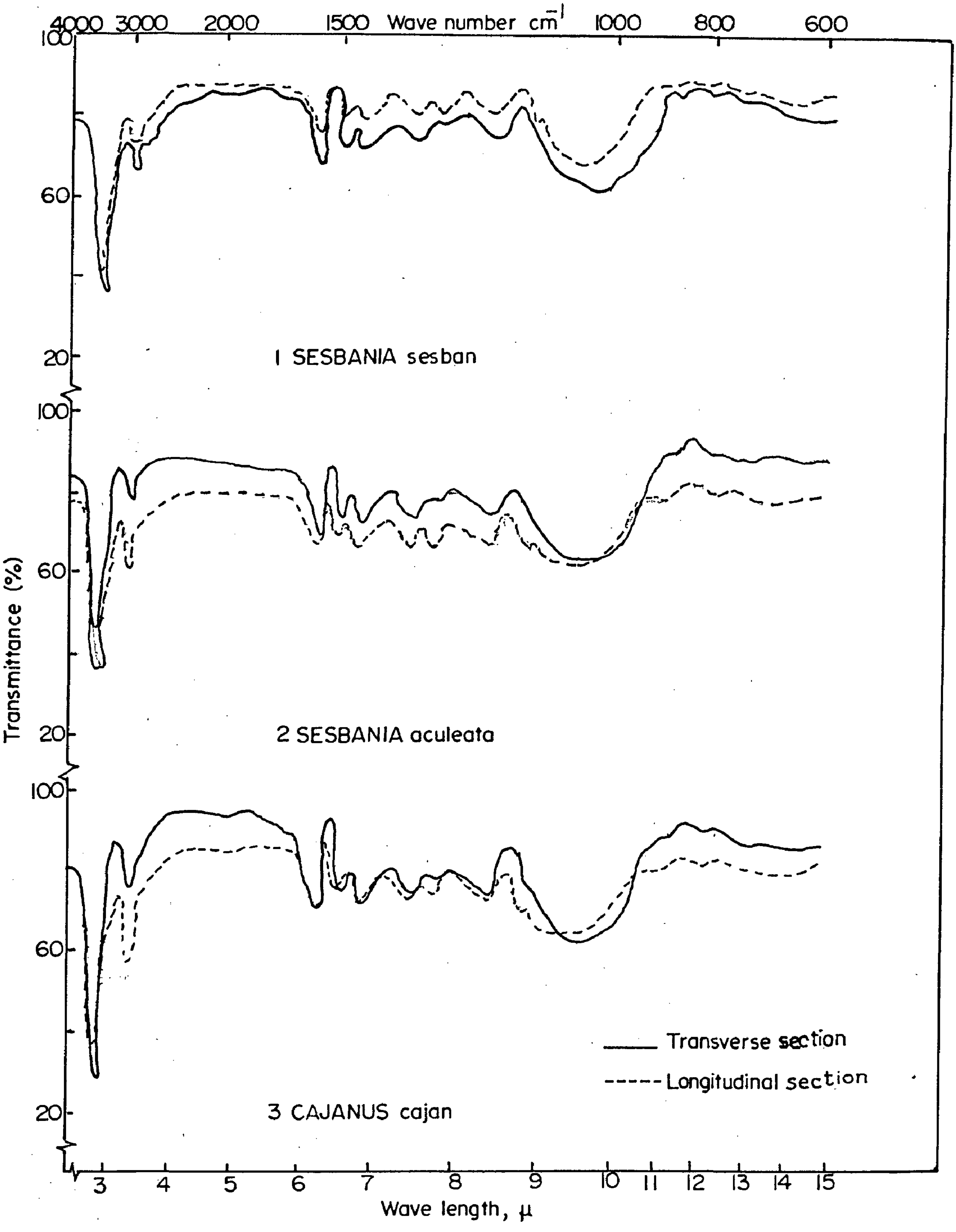


FIG.3.07:INFRARED SPECTRUM OF WOOD SECTION TREATED FOR REMOVAL OF HEMICELLULOSE.

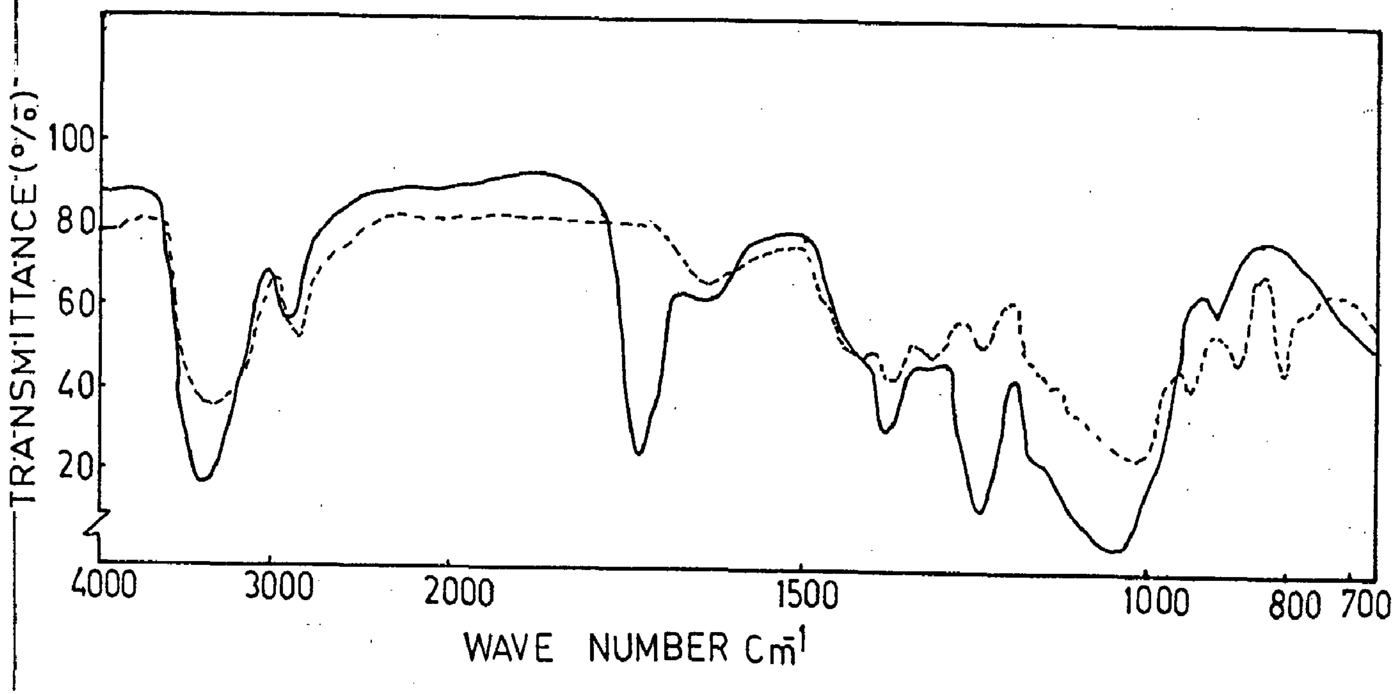


Fig.3.08: INFRARED SPECTRA OF 4-O-METHYLGLUCURONOACETYL XYLAN FROM WHITE BIRCH (SOLID CURVE) AND IVORY NUT SECTION (MANNAN) (BROKEN CURVE)

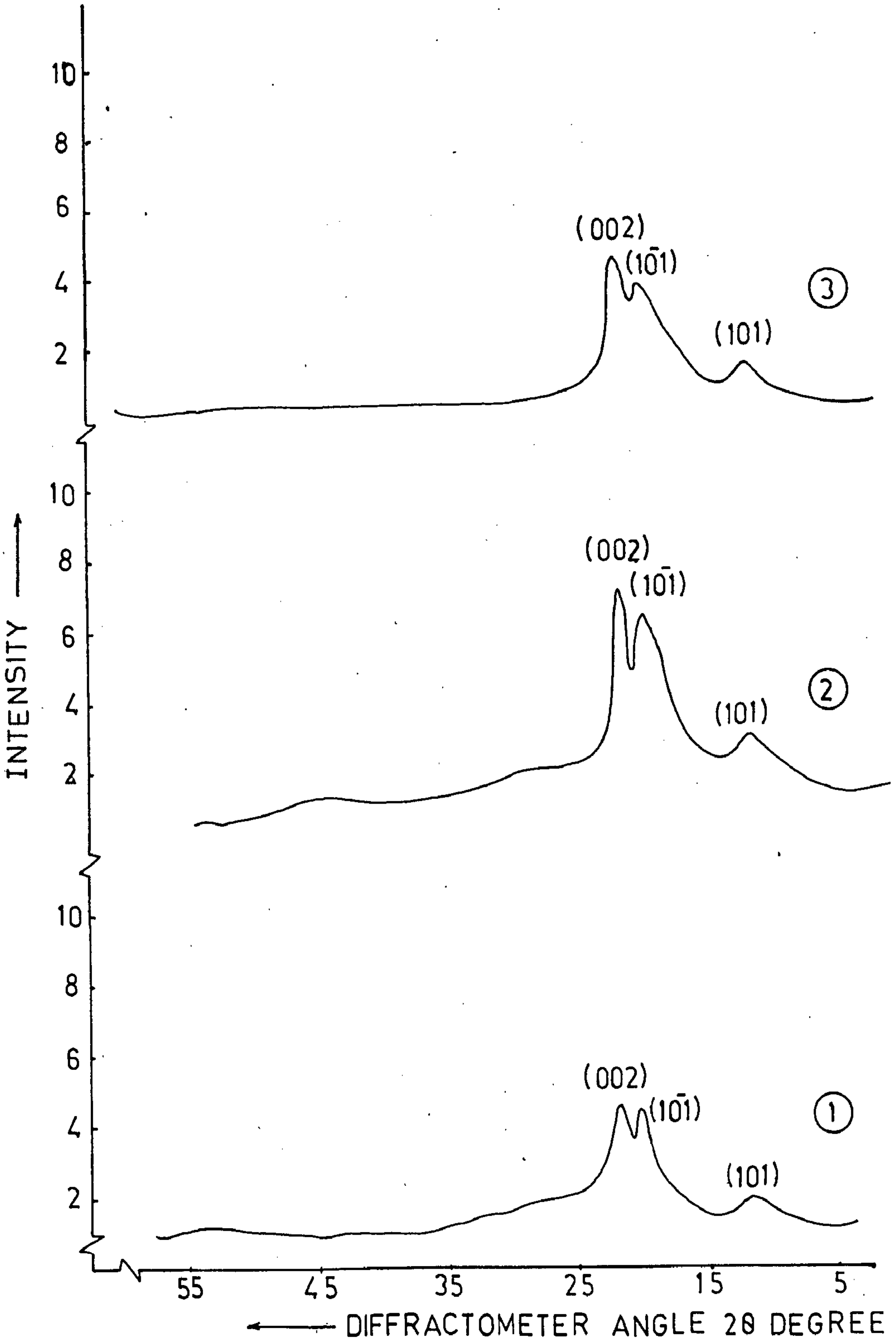


Fig.3·09: X-RAY DIFFRACTOGRAMS OF CELLULOSE OF ① S. sesban ② S aculeata AND ③ C cajan.

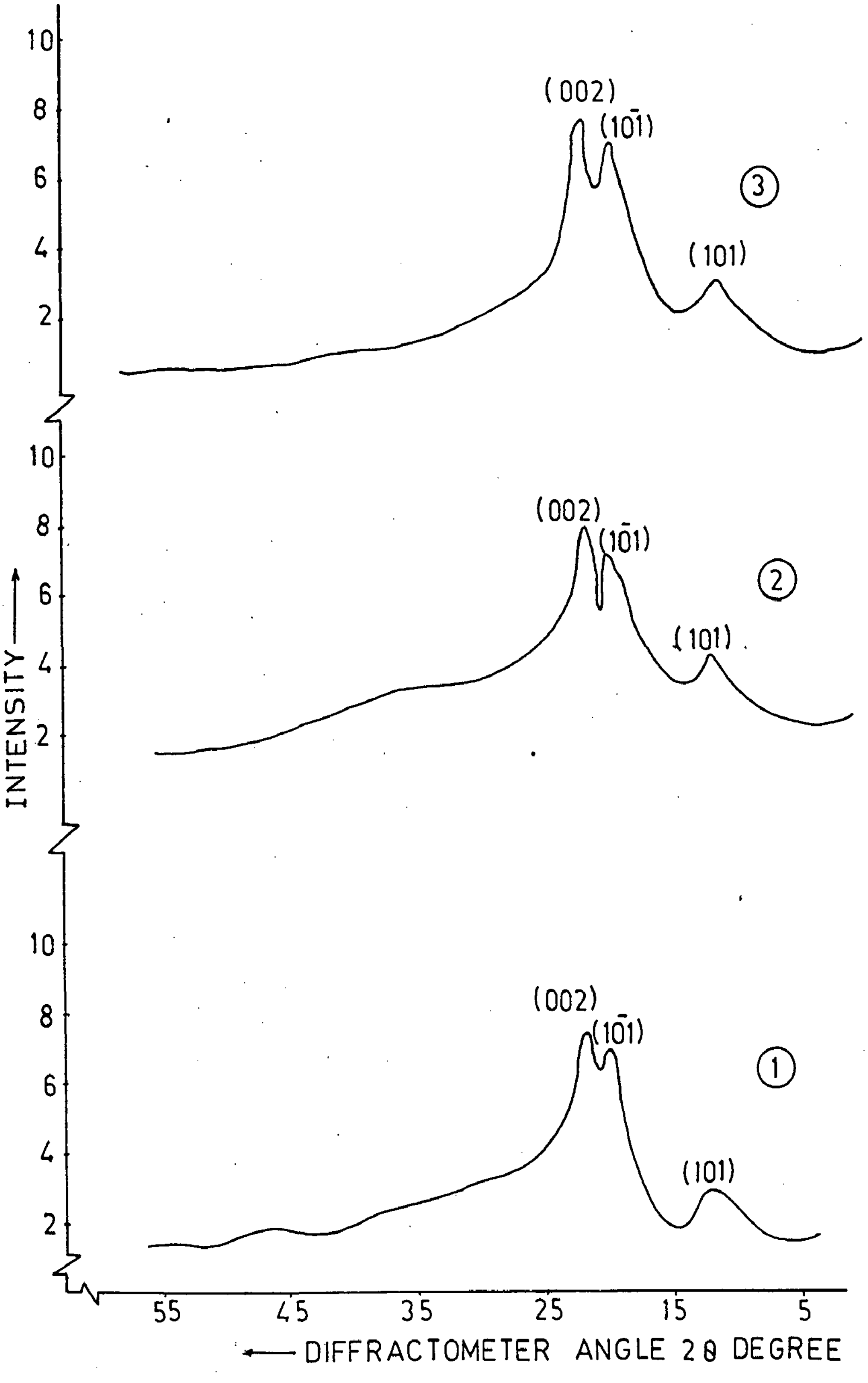


Fig.310: X-RAY DIFFRACTOGRAMS OF ALPHA CELLULOSE OF ① S.sesban ② S.aculeata ③ C cajan.

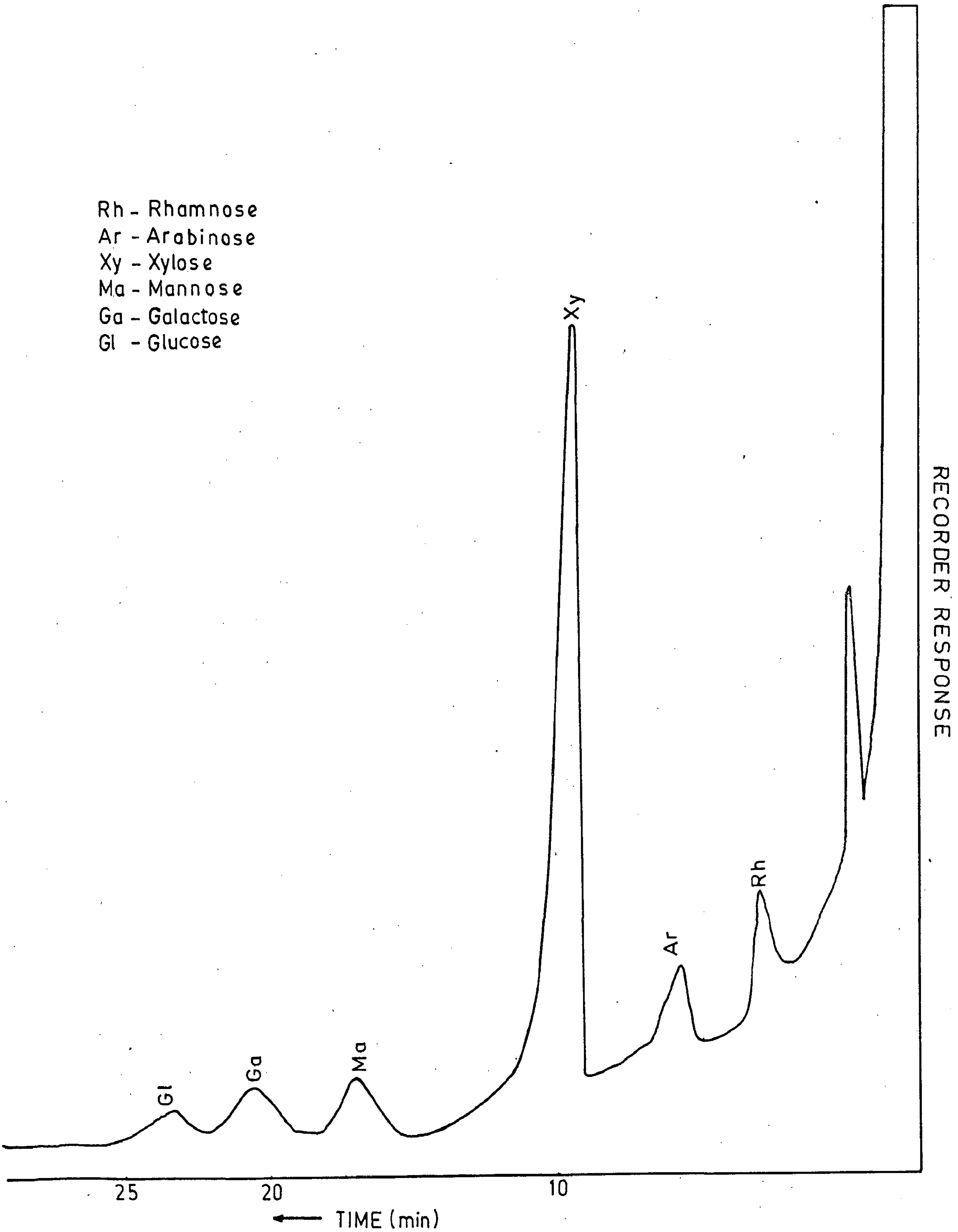


Fig. 3·11:- CHROMATOGRAM (Hemicellulose) OF S. sesban

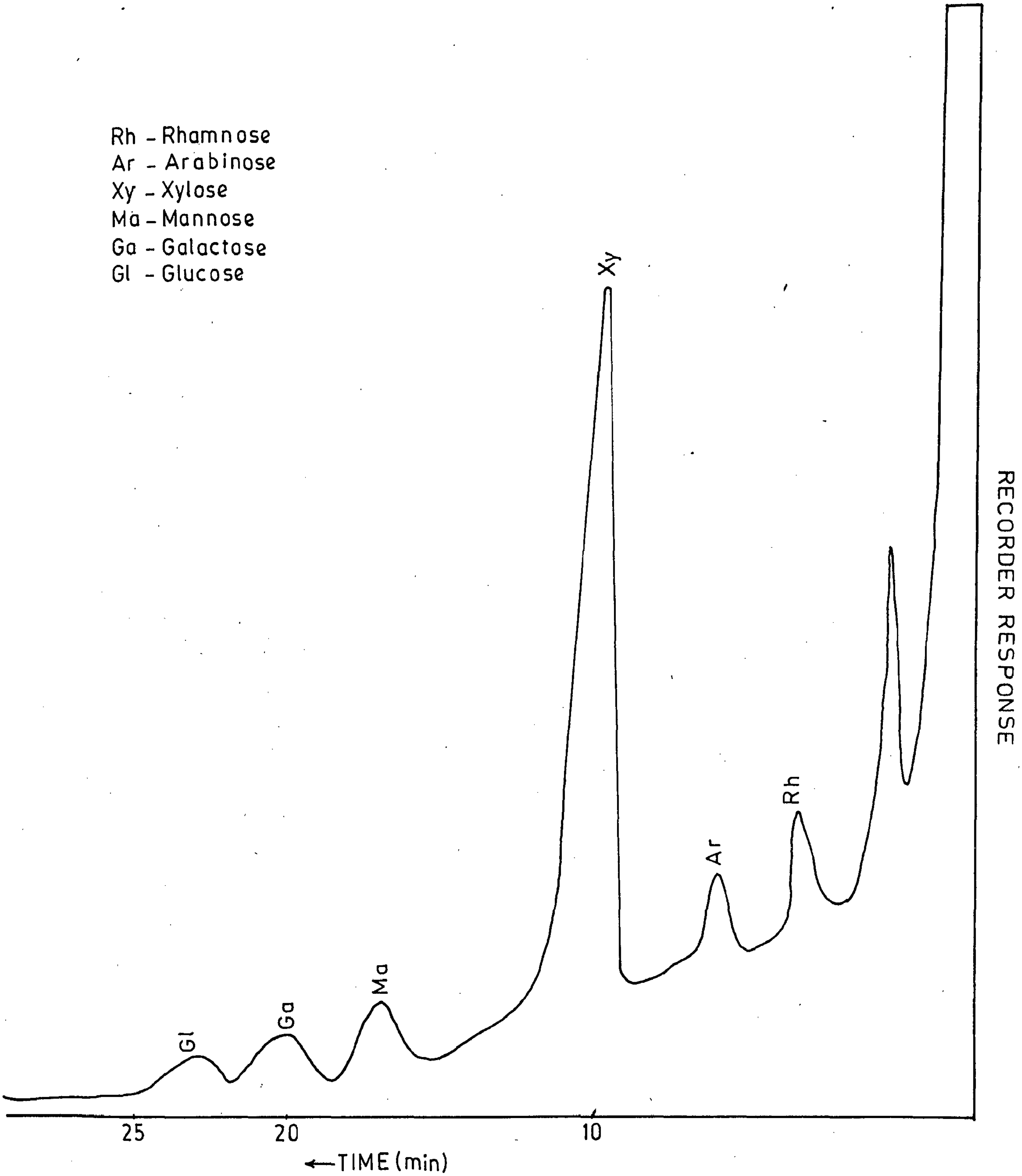


Fig. 3·12: CHROMATOGRAM (Hemicellulose) OF S. aculeata

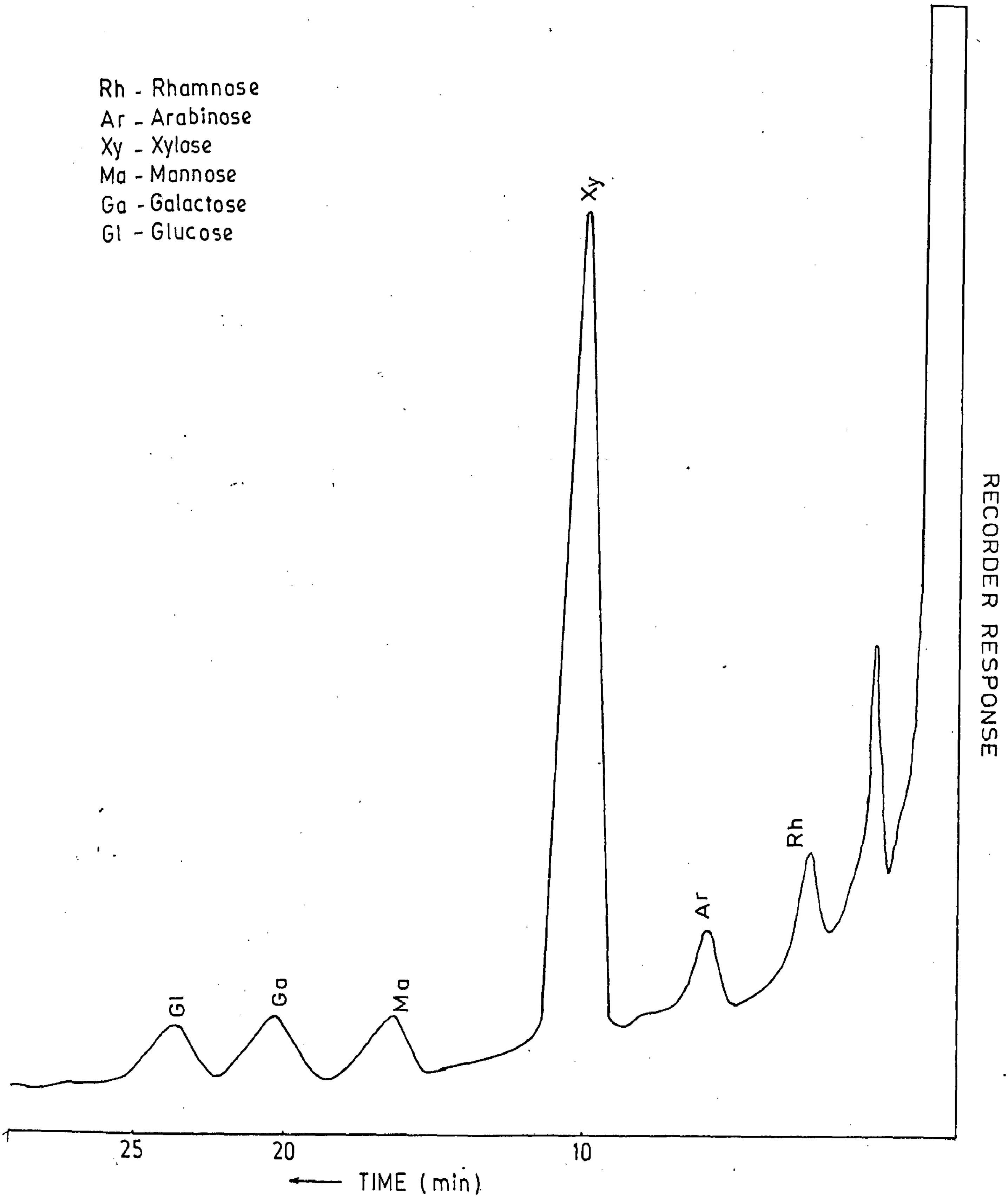


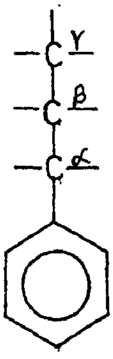
Fig. 3·13: CHROMATOGRAM (Hemicellulose) OF C.cajan.

CHAPTER IV

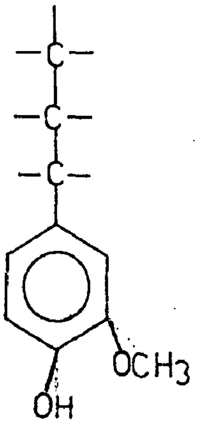
STUDIES ON LIGNINS

Mostly, plant tissues contain, in addition to carbohydrates and extractives, an amorphous polymeric material called lignin, varies between 18 to 38%. Lignin is also present in varying amounts in grasses and ferns. The biological role of lignin in living plants is to form, together with cellulose and other carbohydrates of the cell wall, a tissue of excellent strength and durability. Here, it functions chiefly as filler or cementing substance to impart rigidity to wood tissue. Plant lignin is concentrated mainly in the space between the cells (middle lamella) where it is deposited during the lignification of plant tissue. The completion of the lignification process usually coincides with stoppage of the living function of the cells. Wood lignins, for instance, are predominantly aromatic in nature and almost totally insoluble in known solvents, not hydrolysable to monomeric units, and devoid of the highly regular structure cocharacteristics of other natural polymers. Plant lignin can be divided into three broad classes that are commonly called, softwood(gymnosperm) lignin, hardwood(angiosperm)lignin and grass lignin. Lignin may be separated from associated wood components either by preferentially dissolving lignin or by preferentially dissolving non lignin components.

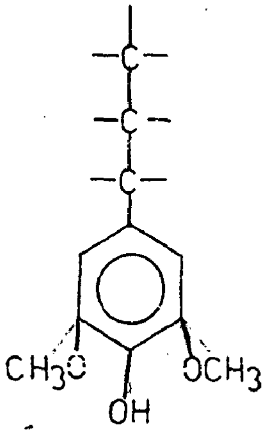
Most of the isolated lignins are non-crystalline brown amorphous powders. The average molecular weight of milled wood lignin (MWL) is found to be approximately 11,000. There is evidence that the average molecular weight of basic structural unit in the lignin polymer is about 184, on this basis the average D.P. is about 60. The molecular weight of different types of lignin range from about 1000 to 12,000. Lignin molecule is made up of a number of structural units. These units, which are identified, are similar in configuration and can be regarded as having a common skeleton, which is a phenylpropane unit (C_6-C_3)or C_9(I) type. Gymnosperm lignins generally are considered to represent polymers containing exclusively guaiacylpropane units(II). Hardwood(angiosperm) lignin contain both guaiacyl and syringylpropane units(III), as a minor component, many plant lignins may contain p-hydroxyphenyl propane units(IV). Grass lignins yield substantial amounts of p-hydroxybenzaldehyde on alkaline hydrolysis. However, with the exception p-hydroxycinnamic acid which exists in bagasse lignin in ester like combination.



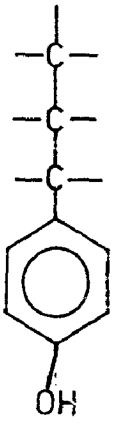
(I)
Phenylpropane
unit



(II)
Guaiacylpropane
unit



(III)
Syringylpropane
unit



(IV)
p-hydroxyphenylpropane
unit

The infrared spectroscopic studies were used to study the mechanism of various delignification processes of practical interest, which may take place in the lignin and polysaccharides during the process of digestion and the nature of the lignin-carbohydrate linkage in wood. Further the knowledge of the chemistry of lignin will be of much use in formulating rational approaches to the development of new improved delignification process.

To know the type of lignin associated with the plant tissues of these non-wood fibrous plants in question, it was very much desirable to isolate the various types of lignins viz., Klason, Willstättar, ethanal, methonal and thiolignins. These isolated lignin samples were further analysed for C,H,S and CH_3O content to know the elemental composition of the lignin. These lignins were also subjected to alkaline nitrobenzene oxidation and the various oxidation products were identified to know the nature of various basic building units of these lignins. To support the data these lignins were further subjected to infrared and ultraviolet spectroscopic studies and the spectrum were characterised. In contrast to the polysaccharides of the cell wall, which are transparent in visible and near ultraviolet light, lignin owing to its aromatic nature, absorb strongly in the ultraviolet range of the spectrum. The absorption spectrophotometry refers to the measurement of the absorption or transmission of electro-magnetic radiation of a specified wavelength or frequency. The main problem in lignin spectroscopy, as well as in lignin chemistry in general, is the impossibility of dissolving atleast the main part of the very reactive material without simultaneously changing its structure in some unknown way. The another difficulty arises from the polydispersity of the soluble lignin derivatives.

4.1.EXPERIMENTAL PROCEDURES:

4.1.1.RAW MATERIAL:

The stalks of S. sesban, S. aculeata and C. cajan were procured from nearby regions of Saharanpur and converted into chips. The chips were then disintegrated into wood mealB.S.S., (-40+60 mesh,-0.381+0.251 mm) in the laboratory disintegrator. The wood meals were extracted with a mixture of ethanol and benzene(1:2 V/V). The extracted wood meals were washed with hot water, and these pre extracted wood meals were further utilized for the isolation of lignins.

4.1.2.ISOLATION OF LIGNINS:

The Klason and Willstätter lignins were isolated by TAPPI Standard Method T222 OS-78 and Brook & Brauns methods(11) respectively and the results are tabulated in Table-4.1.

250 gms. 'of pre extracted wood meals of S. sesban, S. aculeata and Cajanus cajan were taken seperately in a 5 liter round bottom flask fitted with reflux condenser. Ethanol(3 liters) containing hydrochloric acid to give a solution of required acid concentration(o.2N) was added to the flask. It was refluxed for 5 hours at $100^{o}C$. The insoluble residues were filtered off and washed with ethanol. The filtrate and washings were concentrated to about

1 liter, neutralized with sodium bicarbonate, filtered, and the filtrate was added dropwise to large quantities of distilled water. The crude ethanol lignins were filtered, washed with water, and dried in a vacuum desiccator. The lignins were pruified from acetone-water mixture. In a similar fashion, the ethanol lignins from these non-wood fibrous plants were also isolated at different acid concentrations(0.2N, 0.4N, 0.6N, 0.8N and 1.2N) and the results are tabulated in Table-4.2.

26 gms. of pre extracted wood meals of S. sesban, S. aculeata and C. cajan were heated seperately in a small stainless steel bombs(capacity 200ml.) with 150 ml. absolute methanol containing 2% hydrochloric acid (o.2N) at 150 ± 1°C for 40 hours with occassional shaking. As the reaction was over, the bombs were cooled. The insoluble residues were filtered and washed with methanol. The methanol filtrate was concentrated to about 20 ml. and then distilled water (400 ml) and sodium hydroxide solution (10 ml., 0.5N) were added, and the mixture was boiled for 1 hr. The pH was adjusted to 1.0 by the addition of hydrochloric acid (5N) and the precipitated lignin was filtered off, washed with distilled water, and dried in a vacuum desiccator. In a similar way, methanol lignins from these non-wood fibrous plants were also isolated at different acid concentrations(0.2N, o.4N, 0.6N, 0.8N and 1.2N) and the results are recorded in Table-4.3.

The spent liquors of the sulphate cooks of S. sesban, S. aculeata and C. cajan were filtered on a muslin cloth and taken into glass beakers. The filtered liquors were heated to about 80°C and then acidify by adding hydrochloric acid to a pH level of aobut 3, to precipitate out the thiolignins. These residues dissolved in alkali, filtered and reprecipitated by the addition of hydrochloric acid, and subjected to thorough washing into sintered glass crucible till free of chloride ions. These isolated lignins were purified by dissolving them in dioxane and precipitating out in petroleum ether. Similarly, other thiolignins from these non-wood fibrous raw materials processed at different temperatures and different sulphidity levels were isolated and the results are reported in Table-4.4 and 4.5.

4.1.3.ALKALINE NITROBENZENE OXIDATION OF LIGNINS:

The Klason lignin, Willstätter lignin, organosolv lignins isolated at 0.2N hydrochloric acid concentration, and thiolignins isolated at 20% sulphidity were subjected to alkaline nitrobenzene oxidation according to the method of Stone and Blundell(72), and the results are reported in Table-4.6.

4.1.4.ANALYSIS OF LIGNINS:

The Klason lignin, Willstätter lignin, organosolv lignins and thiolignins were analysed for their C, H, S and methoxyl content(1,7).). The methoxyl content of lignins were determined according to TAPPI standard method T209Sü-72. The molecular weight were determined by means of osmotic pressure measurements method(18,25). The results are recorded in Tables-4.1 to 4.5.

4.1.5.INFRARED SPECTROSCOPY OF LIGNINS:

The infrared spectra of chemical substances are graphic records of the inter atomic and skeletal vibration of the molecules, with the frequency of vibration recorded along the x-axis and transmittance along the y-axis. The thiolignin isolated at 20 percent sulphidity and the organasolv lignins isolated at 0.2N acid concentration were taken for the spectroscopic studies. The spectrum of Klason lignins, (Fig. 4.01) Willstätter lignins(Fig.4.02), ethanol lignins(Fig4.03) methanol lignins(Fig.4.04) and thiolignins(Fig.4.05) of S.sesban, S. aculeata and C. cajan were recorded using perkin-Elmer infracord spectrophotometer in the range of 4000 to 600 cm.$^{-1}$.

4.1.6.ULTRAVIOLET ABSORPTION SPECTROSCOPY OF LIGNINS:

Solutions of the carefully purified material to be used for absorption spectrum determination were prepared in concentration of 0.1 gm. per liter. The solvents used were a mixture of 90 parts by volume of purified dioxane and

10 parts of distilled water. In making the absorption spectrum determinations, a thin cell, giving a solution thickness of about 1 mm. was used for the 90% dioxane sulutions. Dioxane has a high ultraviolet absorption and had to be used in thin layers if it was to pass any considerable quantity of ultraviolet light and hence the thin cell was used.

The spectra were measured with the help of spectrophotometer(Perkin-Elmer model) within the wavelength range of 220 to 350 mu. The solvent cell was placed in a reference beam and the solution cell was placed in other beam. From the values for transmittance, thickness of the layer of solution through which the light passed, and concentration of the solution, values for $\log_{10}$ K were calculated accroging to Bear and Lambert combined laws:

$$T = e^{-clk}$$

Where T = Transmittance of solution(as compared with solvent)

e = base of natural logarithms.

c = concentration of solute in grams per liter.

l = thickness of solution through which light passed in cm.

and k = absorption coefficient.

The value of absorption band with maxima and extinction coefficients for different lignins were calculated as follows and tabulated in Table-4.7.

$$D = \log_{10} \frac{I0}{Ix} = Ecx$$

Where D = Optical density

I0 = Intensity of incident light.

Ix = Intensity of transmitted light at the thickness x of absorbing layer

E = Extinction coefficient per unit concentration.

c = concentration of absorbent (mg. per ml.)

and x = thickness of the absorbing layer (mm.).

Log_{10} K plotted against wavelength gave the absorption curve of the solute. Thr graphs are shown in Fig. 4.06, 4.07 and 4.08.

4.2.RESULTS AND DISCUSSIONS:

As indicated in Table-4.1, the C, H & CH_3O percentage in Klason & Willstatter lignins of these non-wood fibrous plants are almost same. The organosolv lignins of S. sesban, S. aculeata and C. cajan isolated by extraction from dust with increasing concentration of hydrochloric acid in alcohols showed that the percentage of carbon and yield of lignin increased whereas the percentage of hydrogen and methoxyl content decreased with increasing concentration of acid (Tables-4.2 & 4.3). The low yield of ethanol and methanol lignins indicated that almost 50% of the dissolved lignin remained in the aqueous alcoholic mother liquor. The values of methoxyl content of methanol lignin were higher than the ethanol lignin , because new methoxyl groups were introduced into the lignin building units in case of methanol lignins.

Table-4.4 indicated that the alkaline pulping of these non-wood fibrous material in presence of sodium sulphite introduces sulphur into the lignin molecule. Higher concentration of sodium sulphite resulted in an increased amount of sulphur in the isolated lignin. The Klason lignin content of the isolated thiolignin remained practically the same while the Klason lignin content of pulp decreased. It was also observed that the maximum amount of lignin was delignified from the original raw materials at a level of 20% sulphidity. The methoxyl content of all the isolated thiolignins were in indirect proportion with the sulphidity i.e. as the sulphidity increased the amount of methoxyl content in thiolignins decreased.

Table-4.5 showed that as the temperature increased, the lignin recovery from the spent liquors also increased, but the carbon content decreased, while on the other hand the hydrogen and methoxyl content remained practically almost the same. The sulphur content in the isolated thiolignins increased with an increase in temperature and practically remained the same after a temperature of 140°C.

The alkaline nitrobenzene oxidation of all these lignins gave vanillin, syringaldehyde and p-hydroxybenzaldehyde as major products in varying proportion, indicated the pressence of syringyl-, guaiacyl- and p-hydroxyphenyl propane building units. The yields of syringaldehyde was higher as compared to that of vanillin. This suggested that these lignins contained more syringyl-repeating units than guaiacyl-repeating units. The yield of syringaldehyde in methanol lignin was higher, and it was due to the higher methoxyl value. The syringaldehyde to vanillin(S/V) ratios remained practically the same. The p-hydroxybenaldehyde to vanillin(H/V) ratios also remained practically the same. But (S/V)values were roughly two times higher than the (H/V)values, indicated the more efficient conversion of syringylpropane units to syringaldehyde in nitrobenzene oxidation.

In infrared spectrums of lignins, a band at 3400 $cm.^{-1}$ was common to almost all types of lignins and was due to hydroxyl group O-H stretching frequencies both phenolic and alcoholic(5). The band was broadened due to hydrogen bonding. The intensity of this band was more in ethanol lignin than methanol lignin. The absorption band at 3100 to 2900 $cm.^{-1}$ represented various types of C-H bonds. The shoulder at 2850-2800 $cm.^{-1}$ was assigned to methoxyl group(9) and the band at 1735-1700 $cm.^{-1}$ was due to carbonyl groups. In thiolignin, there was no band at 1735-1700 $cm.^{-1}$ region which represented that the principle change occured in C=0 region of thiolignin, similar findings have been reported by Marton in the case of pine milled wood lignin and kraft lignin(54). The frequencies observed at 1605-1595 $cm.^{-1}$, 1515-1505$cm.^{-1}$ and 1460-1420 $cm.^{-1}$ can be assigned as skeletal band of guaiacyl- and syringyl-type compounds. The two bands at 1600 $cm.^{-1}$ and 1500 $cm.^{-1}$ were characteristic of aromatic compounds and are due to the C=C vibration of benzene ring. In soft wood lignins the intensity of 1600 $cm.^{-1}$ band is lower than 1500 $cm.^{-1}$ band, while in hardwood, the intensity of these two bands are approximately equal or the intensity of 1600 $cm.^{-1}$ band is greater than 1500 $cm.^{-1}$ band. The band at 1430-1425 cm.$^{-1}$ was considered to be ring stretching modes strongly coupled by C-H in plane deformation. The band at 1460 cm.$^{-1}$ was due to C-H bonds including methoxyl groups. The band in the region of 1360-1350 cm.$^{-1}$ was due to the bending vibration of O-H bonds.

Although the bands are appeared at 1330 cm.$^{-1}$, 1220 cm.$^{-1}$, 1160 cm.$^{-1}$, 1120 cm.$^{-1}$, 1090 cm.$^{-1}$ and 1030 cm.$^{-1}$ in the I.R. spectrum, but the origin of these bands were less clear (There may be slight error due to shift in calibration) The bands at 1260, 1220 and 1120 cm.$^{-1}$ were due to guaiacyl- and 1330 and 1220cm.$^{-1}$ due to syringyl-derivatives were assignable to ring breathing with C-O stretching, guaiacylic band at 1120 and 1030 cm.$^{-1}$ were assigned to aromatic C-H in plane deformation. The band at 1160 cm.$^{-1}$ was assigned to both the modes described above. A general method to distinguish hardwood lignins from softwood lignins is, the presence of bands at 1270 cm.$^{-1}$ and at 1230 cm.$^{-1}$, but the intensity of band at 1270 cm.$^{-1}$, is more than the intensity of band at 1230 cm.$^{-1}$; the band at 1030 cm.$^{-1}$ is having equal or greater intensity than the 1135-1120 cm.$^{-1}$ band in softwoods. The reverse is true for hardwood lignins. The infrared absorption bands were also visible below 1000 cm.$^{-1}$ regions. The absorption bands at 900 cm.$^{-1}$ and 830 cm.$^{-1}$, which vary in wavelength depend upon the electro negativity of the side chain. These bands are characteristic of syringyl-compounds and are mostly found in tropical hardwoods lignin.

The ultraviolet absorption spectroscopic studies of lignin showed that all the UV spectrums showed a decrease from 220 mμ to a shallow minima near 260 mμ, with a pronounced shoulder near 230 mμ and a characteristic absorption maxima near 280 mμ(Fig.4.06, 4.07 and 4.08). These bands persists in spite of such alterations in the lignin molecule as are caused by methylation, acetylation treatment with methanol, ethanol, acids, sodium hydroxide or sodium hydrogen sulphide. This fact suggested that a band at about 280 mμ was due to some configuration of atoms in the lignin molecule which was not disturbed by ordinary substitution reactions and which, in its absorption of radiant energy, was not influenced by the state or action of other portions of molecule.

Lignin contained an oxygen ring and the oxygen ring was responsible for the characteristic absorption band of lignin at 280 mμ, and the oxygen ring was unaffected by substitutions in the lignin molecules and was relatively insensitive to ordinary chemical agents. The values of absorption maxima are reported in Table-4.7. These high values could be due to either some change in the structure of the molecules which enabled that group responsible for the absorption band at 280 mμ to absorb more strongly or the presence of a substituent which also had a relatively high absorption coefficient at 280 mμ. Methanol lignin, Willstätter lignin, Klason lignin and thiolignins showed the high value of maxima. The low value in case of ethanol lignin was due to the ethoxyl group being split off with the methoxyl in the analysis. The high value for thiolignin and in fact, the high$\overset{K}{/}$value at 280 mμ for thiolignin were possible due to changes in the lignin molecule brought about by the alkaline cooking conditions. A possible explanation would be that, under the strong acid conditions in the cooking process, water split off from the lignin molecule, giving rise to double bonds in conjugation with the benzene rings. In any case, it was evident that atleast the isolated lignin derivatives contain some kind of larger chromophores(17,63) than optically insulated benzene rings, though the proportion of these large chromophores must be small, since the absorption coefficient at about 320 mμ was relatively low. Hence the double bonds conjugated with the benzene rings were excluded in the lignin. Thus, with the exceptions just noted, it appeared that the absorption coefficients at 280 mμ of the lignins studied, were directly proportional to their native lignin contents. It was found that bamboo bagasse and grasses lignins resembled to some extent with hardwood lignins(14,26,59) showed absorption maxima at 281-283 mμ) isolated by means of alcohol, hydrochloric acid and sulfuric acid. The spectrum of Sesbania sesban , Sesbania aculeata and Cajanus cajan lignins showed absorption maxima in the range of 280-283 mμ.

4.3. CONCLUSION:

On the bases of above studies it was concluded that:

1. The Klason and Willstätter lignins have nearly the same percentage of C,H and methoxyl groups, while the methanol lignin have high methoxyl content than ethanol lignin.

2. The alkaline mitrobenzene oxidation products of these lignins indicated that these are composed of guaiacyl, syringyl-and p-hydroxy phenyl propane units.

3. The lignins of S. sesban, S. aculeata and C. cajan contains both phenolic and aliphatic hydroxyl groups which appeared to be strongly hydrogen bonded.

4. The presence of 1730-1700 cm.$^{-1}$ band in I.R spectrum show the presence of carbonyl group in Klason, Willstätter, ethanol and methanol lignin. The absence of this band in spectrum of thiolignin indicated the absence of carbonyl group in thiolignin.

5. The absorption bands in I.R spectrums at 1600, 1500, 1460, 1420&1360 cm.$^{-1}$ further confirmed the presence of guaiacyl and syringyl-, groups. Greater intensity of 1600 cm.$^{-1}$ band as compared to that of 1500 cm.$^{-1}$ supported the presence of p-hydroxyphenyl propane units.

6. Absorption band at 830cm.$^{-1}$ accompanied by a weak band at 900 cm.$^{-1}$ is characteristics of hardwood lignins.

7. Greater intensity of 1120 cm.$^{-1}$ band than that of 1030 cm^{-1} band indicated that these lignins have similarities to hard wood lignin.

The ultraviolet absorption spectrum study of lignins leads to fact that the reaction of lignin with methonal of alkline pulping agents increased its absorption coefficient. The two characteristic bands in the UV spectrums of lignins at 200 to 230 mμ and 280 to 283 mμ were specifically attributable to the oxygen substituted benzene nucleus in lignin.

The high absorption in the 300 to 350 mμ range indicated the presence of other chromophoric groups in lignin viz., carbonyl groups or double bonds conjugated with the benzene rings.

From the above studies, it was concluded that the lignin of S.sesban, S.aculeata and C. cajan resembled with hardwood and bamboo lignin rather than soft wood lignins.

Table-4.1:Elementary Composition of Lignins Isolated From Sesbania sesban, Sesbania aculeata And Cajanus cajan.

Sl.No.	Name of Plant species	Types of lignin	Molecular Weight	Carbon content (%)	Hydrogen content (%)	Methoxyl content (%)	C_9 formula
1.	Sesbania sesban	Klason	1585	61.40	5.5	14.80	$C_9H_{8.12}O_{3.16}(OCH_3)_{0.96}$
2.	Sesbania aculeata	--do--	1850	60.30	5.9	15.30	$C_9H_{8.86}O_{3.20}(OCH_3)_{0.98}$
3.	Cajanus cajan	--do--	1828	62.10	5.5	15.50	$C_9H_{8.00}O_{3.05}(OCH_3)_{0.96}$
4.	Sesbania sesban	Willstätter	1570	60.80	6.0	14.30	$C_9H_{9.24}O_{3.22}(OCH_3)_{0.92}$
5.	Sesbania aculeata	--do--	1842	61.00	5.7	15.40	$C_9H_{8.46}O_{3.18}(OCH_3)_{0.98}$
6.	Cajanus cajan	--do--	1810	61.60	5.5	15.00	$C_9H_{8.12}O_{3.14}(OCH_3)_{0.96}$

Table-4.2:Yield And Elementary Composition of Ethanol Lignin Isolated From Sesbania sesban, Sesbania aculeata and Cajanus cajan Wood Meal at Different Acid Concentration.

Sl. No.	Name of plant species	Hydrochloric acid concentration in ethanol (N)	Molecular weight	Yield of ethanol lignin(On O.D. wood meal basis) (%)	Methoxyl content (%)	Carbon content (%)	Hydrogen content (%)	C_9 formula
1.	Sesbania sesban	0.2	1540	7.20	17.78	58.66	6.35	$C_9H_{8.04}O_{2.99}(OCH_3)_{1.32}$
2.	-----do-----	0.4	----	7.80	17.60	59.00	6.10	$C_9H_{7.87}O_{2.97}(OCH_3)_{1.29}$
3.	-----do-----	0.6	----	8.34	17.00	60.80	5.86	$C_9H_{7.93}O_{2.93}(OCH_3)_{1.25}$
4.	-----do-----	0.8	----	8.92	16.50	61.62	5.80	$C_9H_{7.90}O_{2.84}(OCH_3)_{1.22}$
5.	-----do-----	1.2	----	9.48	16.10	62.10	5.73	$C_9H_{7.76}O_{2.81}(OCH_3)_{1.18}$
6.	Sesbania aculeata	0.2	1824	8.90	17.35	58.90	6.20	$C_9H_{7.70}O_{2.93}(OCH_3)_{1.35}$
7.	-----do-----	0.4	----	9.26	17.10	59.60	5.85	$C_9H_{7.58}O_{2.83}(OCH_3)_{1.34}$
8.	-----do-----	0.6	----	10.00	16.84	60.83	5.80	$C_9H_{7.41}O_{2.76}(OCH_3)_{1.29}$
9.	-----do-----	0.8	----	10.30	16.70	62.00	5.62	$C_9H_{7.46}O_{2.70}(OCH_3)_{1.26}$
10.	-----do-----	1.2	----	10.85	16.55	62.25	5.45	$C_9H_{7.44}O_{2.67}(OCH_3)_{1.23}$
11.	Cajanus cajan	0.2	1800	8.25	17.80	58.82	6.28	$C_9H_{8.33}O_{2.98}(OCH_3)_{1.29}$
12.	-----do-----	0.4	----	8.79	17.35	59.75	6.00	$C_9H_{8.22}O_{2.97}(OCH_3)_{1.26}$
13.	-----do-----	0.6	----	9.60	17.10	60.36	5.85	$C_9H_{7.94}O_{2.83}(OCH_3)_{1.22}$
14.	-----do-----	0.8	----	10.06	16.92	61.64	5.72	$C_9H_{7.90}O_{2.78}(OCH_3)_{1.17}$
15.	-----do-----	1.2	----	10.54	16.64	62.10	5.50	$C_9H_{7.72}O_{2.79}(OCH_3)_{1.16}$
16.	Eucalyptus grandis(36)	0.2	----	7.30	19.70	60.02	6.20	----

Table-4.3:Yield And Elementary Composition of Methanol Lignin Isolated From Sesbania sesban, Sesbania aculeata and Cajanus cajan Wood Meal at Different Acid Concentration.

Sl. No.	Name of plant species	Hydrochloric acid concentration in methanol (N)	Molecular wieght	Yield of methanol lignin(On O.D. wood meal basis) (%)	Methoxyl content (%)	Carbon content (%)	Hydrogen content (%)	C_9 formula
1.	Sesbania sesban	0.2	1685	4.60	20.50	59.50	6.00	$C_9H_{9.28}O_{3.23}(OCH_3)_{1.14}$
2.	-----do-----	0.4	----	4.68	20.00	60.00	5.87	$C_9H_{8.84}O_{3.24}(OCH_3)_{1.13}$
3.	-----do-----	0.6	----	5.00	19.40	60.67	5.84	$C_9H_{8.42}O_{3.06}(OCH_3)_{1.09}$
4.	-----do-----	0.8	----	6.10	18.96	61.75	5.78	$C_9H_{8.48}O_{3.01}(OCH_3)_{1.06}$
5.	-----do-----	1.2	----	6.75	18.35	62.40	5.65	$C_9H_{8.40}O_{2.98}(OCH_3)_{1.04}$
6.	Sesbania aculeata	0.2	1977	5.26	21.00	60.00	5.86	$C_9H_{9.04}O_{3.24}(OCH_3)_{1.12}$
7.	-----co------	0.4	----	5.50	20.70	60.86	5.80	$C_9H_{8.40}O_{3.22}(OCH_3)_{1.10}$
8.	-----do------	0.6	----	6.00	20.00	61.95	5.64	$C_9H_{8.36}O_{3.09}(OCH_3)_{1.08}$
9.	-----do-----	0.8	----	6.45	19.60	62.70	5.62	$C_9H_{8.03}O_{2.97}(OCH_3)_{1.07}$
10.	-----do-----	1.2	----	7.10	19.10	63.12	5.58	$C_9H_{7.92}O_{2.97}(OCH_3)_{1.06}$
11.	Cajanus cajan	0.2	1930	5.00	20.00	59.70	6.10	$C_9H_{9.12}O_{3.21}(OCH_3)_{1.15}$
12.	-----do-----	0.4	----	5.35	19.50	60.20	6.00	$C_9H_{8.64}O_{3.16}(OCH_3)_{1.12}$
13.	-----do-----	0.6	----	5.87	19.00	61.82	5.80	$C_9H_{8.40}O_{3.12}(OCH_3)_{1.10}$
14.	-----do-----	0.8	----	6.20	18.20	62.60	5.72	$C_9H_{8.17}O_{2.99}(OCH_3)_{1.09}$
15.	-----do-----	1.2	----	6.66	18.00	62.78	5.60	$C_9H_{7.78}O_{2.97}(OCH_3)_{1.07}$

Table-4.4:Process Conditions And Characteristics of Thiolignin Isolated From S. sesban, S. aculeata And C. cajan

COOKING CONDITIONS

Active alkali (as Na_2O)% = 16 (S.sesban and C. cajan)
= 14 (S.aculeata)

Liquor to wood ratio = 3.0:1 (S.sesban and C.cajan)
= 3.5:1 (S.aculeata)

Time from 30°C to 105°C = 45 minutes.

Time from 105°C to 160°C = 45 minutes.

Time at 160°C = 120 minutes.

Sl. No.	Plant species	Sulphidity (%)	Unbleached pulp yield (%)	Klason lignin in thiolignin (%)	Sulphur in thiolignin (%)	Klason lignin in pulp (%)	Methoxyl (%)	Carbon (%)	Hydrogen (%)
1.	Sesbania sesban	15	53.2	75.4	1.60	13.00	14.7	61.60	5.70
		18	50.6	74.5	1.73	7.70	14.3	60.50	5.65
		20	47.0	74.0	1.80	4.36	14.0	58.30	5.62
		25	44.5	74.2	1.89	4.24	13.5	58.40	5.59
2.	Sesbania aculeata	15	53.6	75.0	1.55	7.92	15.3	60.80	5.79
		18	51.5	74.8	1.75	6.79	14.8	59.38	5.74
		20	47.5	75.2	1.87	4.21	14.3	58.90	5.65
		25	43.0	74.8	1.98	4.18	13.9	58.60	5.58
3.	Cajanus cajan	15	54.0	75.6	1.57	9.25	15.4	61.30	5.74
		18	52.0	76.2	1.78	7.19	15.2	60.82	5.70
		20	50.2	75.0	1.82	4.18	14.4	58.65	5.64
		25	47.5	74.5	1.88	4.10	14.0	58.58	5.60
4.	Eucalyptus grandis (35)	25	53.9	80.7	1.85	4.10	15.9	60.59	5.96

Table-4.5: Elementary Composition of Thiolignins of S. sesban, S. aculeata And C. cajan Isolated at 20% Sulphidity And At Different Temperature.

Sl. No.	Plant species	Temperature (°C)	Yield of lignin (%)	Klason lignin in thiolignin (%)	Sulphur in thiolignin (%)	Methoxyl content (%)	Carbon content (%)	Hydrogen content (%)	C_9 formula
1.	Sesbania sesban	130	4.00	76.4	1.60	14.6	61.42	5.75	$C_9H_{8.68}O_{3.16}S_{0.104}(OCH_3)_{0.94}$
		140	5.80	75.2	1.72	14.3	60.10	5.70	$C_9H_{8.64}O_{3.34}S_{0.108}(OCH_3)_{0.92}$
		150	6.12	74.3	1.78	14.2	58.92	5.66	$C_9H_{8.58}O_{3.50}S_{0.110}(OCH_3)_{0.91}$
		160	6.65	74.0	1.80	14.0	58.30	5.62	$C_9H_{8.54}O_{3.60}S_{0.112}(OCH_3)_{0.90}$
2.	Sesbania aculeata	130	3.80	77.2	1.65	15.1	61.80	5.80	$C_9H_{8.68}O_{3.06}S_{0.102}(OCH_3)_{0.97}$
		140	6.00	76.0	1.82	14.7	60.62	5.72	$C_9H_{8.62}O_{3.26}S_{0.112}(OCH_3)_{0.94}$
		150	6.60	75.6	1.86	14.5	58.90	5.69	$C_9H_{8.58}O_{3.48}S_{0.116}(OCH_3)_{0.93}$
		160	7.20	75.2	1.87	14.3	58.60	5.65	$C_9H_{8.54}O_{3.54}S_{0.116}(OCH_3)_{0.92}$
3.	Cajanus cajan	130	4.10	77.6	1.58	15.2	62.06	5.78	$C_9H_{8.62}O_{3.04}S_{0.098}(OCH_3)_{0.98}$
		140	6.20	76.4	1.74	14.9	61.25	5.72	$C_9H_{8.56}O_{3.16}S_{0.108}(OCH_3)_{0.96}$
		150	6.50	75.3	1.80	14.6	59.10	5.68	$C_9H_{8.54}O_{3.46}S_{0.112}(OCH_3)_{0.94}$
		160	7.12	75.0	1.82	14.4	58.65	5.64	$C_9H_{8.52}O_{3.54}S_{0.114}(OCH_3)_{0.92}$
4.	Eucalyptus grandis (35)	150	6.90	74.0	4.12	14.1	48.03	4.86	

Table-4.6:Alkaline Nitrobenzene Oxidation Products of Lignin Isolated From Sesbania sesban, Sesbania aculeata And Cajanus cajan.

Sl. No.	Plant species	Types of lignin	Lignin Oxidation Products (%)			Mol-ratios	
			Vanillin (V)	Syringaldehyde (S)	p-hydroxybenzaldehyde (H)	S/V	H/V
1.	Sesbania sesban	Klason	5.9	12.00	5.3	2.03:1	0.89:1
2.	Sesbania aculeata	--do--	6.2	12.20	5.8	1.96:1	0.93:1
3.	Cajanus cajan	--do--	6.0	12.30	5.0	2.05:1	0.83:1
4.	Sesbania sesban	Willstätter	5.6	11.62	5.1	2.03:1	0.91:1
5.	Sesbania aculeata	----do----	6.1	11.90	5.4	1.95:1	0.88:1
6.	Cajanus cajan	----do----	6.0	12.10	4.8	2.01:1	0.80:1
7.	Sesbania sesban	Ethanol	5.4	10.64	5.2	1.97:1	0.96:1
8.	Sesbania aculeata	---do---	6.0	12.25	5.9	2.04:1	0.98:1
9.	Cajanus cajan	---do---	5.7	11.30	5.4	1.98:1	0.95:1
10.	Sesbania sesban	Methanol	5.5	11.61	5.1	2.10:1	0.92:1
11.	Sesbania aculeata	---do---	5.9	12.48	5.3	2.10:1	0.89:1
12.	Cajanus cajan	---do---	5.8	11.80	5.6	2.03:1	0.96:1
13.	Sesbania sesban	Thiolignin	5.4	10.42	4.7	1.92:1	0.87:1
14.	Sesbania aculeata	----do----	6.2	12.30	5.9	2.05:1	0.98:1
15.	Cajanus cajan	----do----	5.8	11.50	5.4	1.98:1	0.93:1
16.	Bamboo (Dendrocalamus strictus) (15)	----do----	5.1	6.50	1.5	1.27:1	0.29:1
17.	Eucalyptus grandis (36)	Ethanol	5.5	11.16	---	2.10:1	---
18.	Eucalyptus grandis (35)	Thiolignin	3.9	6.90	---	1.76:1	---

Table-4.7:Ultraviolet Absorption Maxima And Extinction Coefficients Of Lignin Isolated From Non-wood Fibrous Plants.

Sl. No.	Plant species	Types of lignin	Solvent	Maximum m μ	Extinction coefficient Log E
1.	Sesbania sesban	Ethanol	90% dioxane	280.5	3.18
		Methanol	----do----	283.0	3.23
		Willstätter	----do----	282.5	3.21
		Klason	----do----	282.0	3.24
		Thiolignin	----do----	284.0	3.25
2.	Sesbania aculeata	Ethanol	----do----	281.0	3.20
		Methanol	----do----	282.0	3.21
		Willstätter	----do----	280.0	3.21
		Klason	----do----	282.0	3.23
		Thiolignin	----do----	283.5	3.25
3.	Cajanus cajan	Ethanol	----do----	280.5	3.15
		Methanol	----do----	283.0	3.22
		Willstätter	----do----	282.0	3.17
		Klason	----do----	282.3	3.25
		Thiolignin	----do----	282.5	3.26

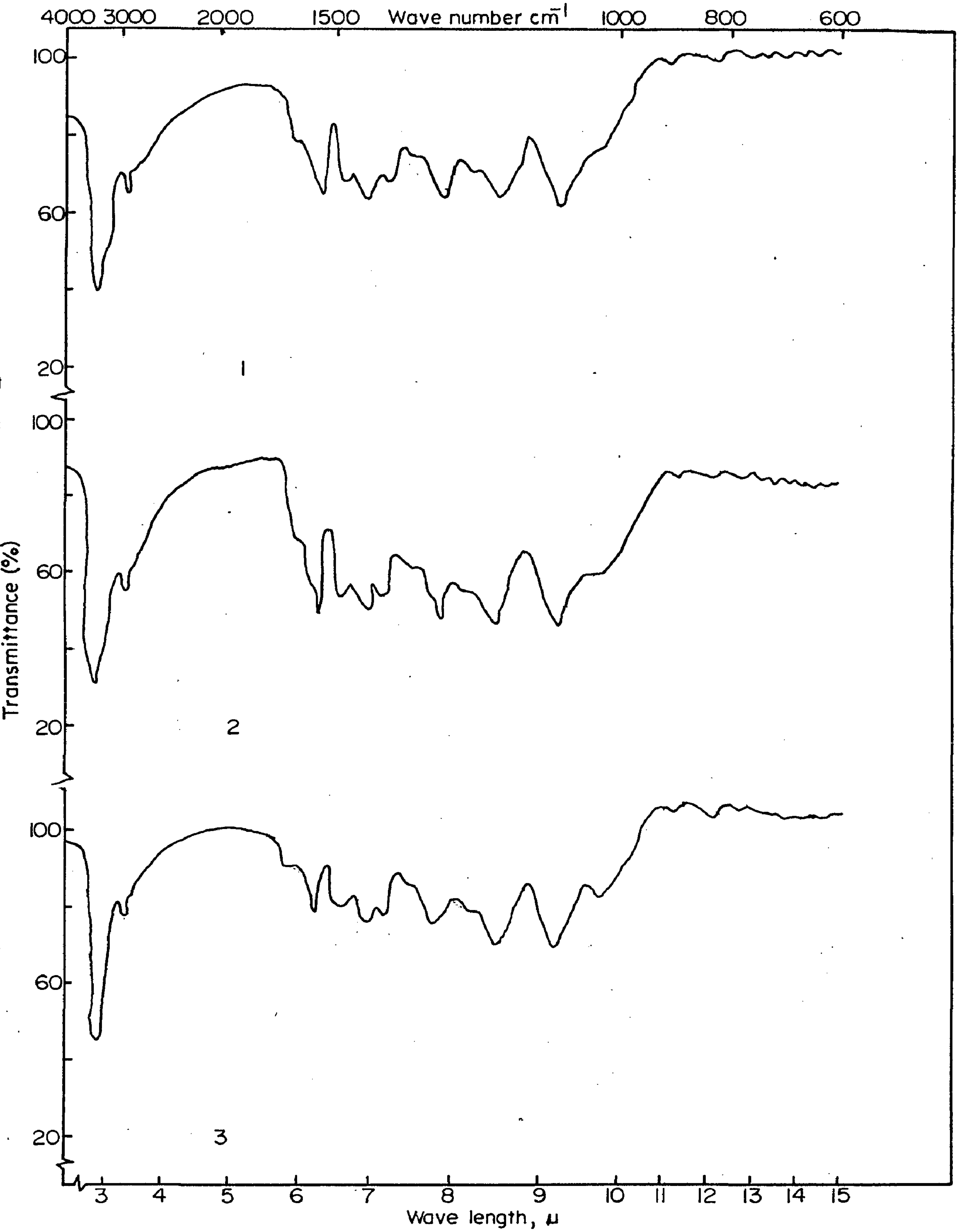


FIG.4.01: INFRARED ABSORPTION OF KLASON LIGNIN OF 1.SESBANIA sesban 2.SESBANIA aculeata 3. CAJANUS cajan.

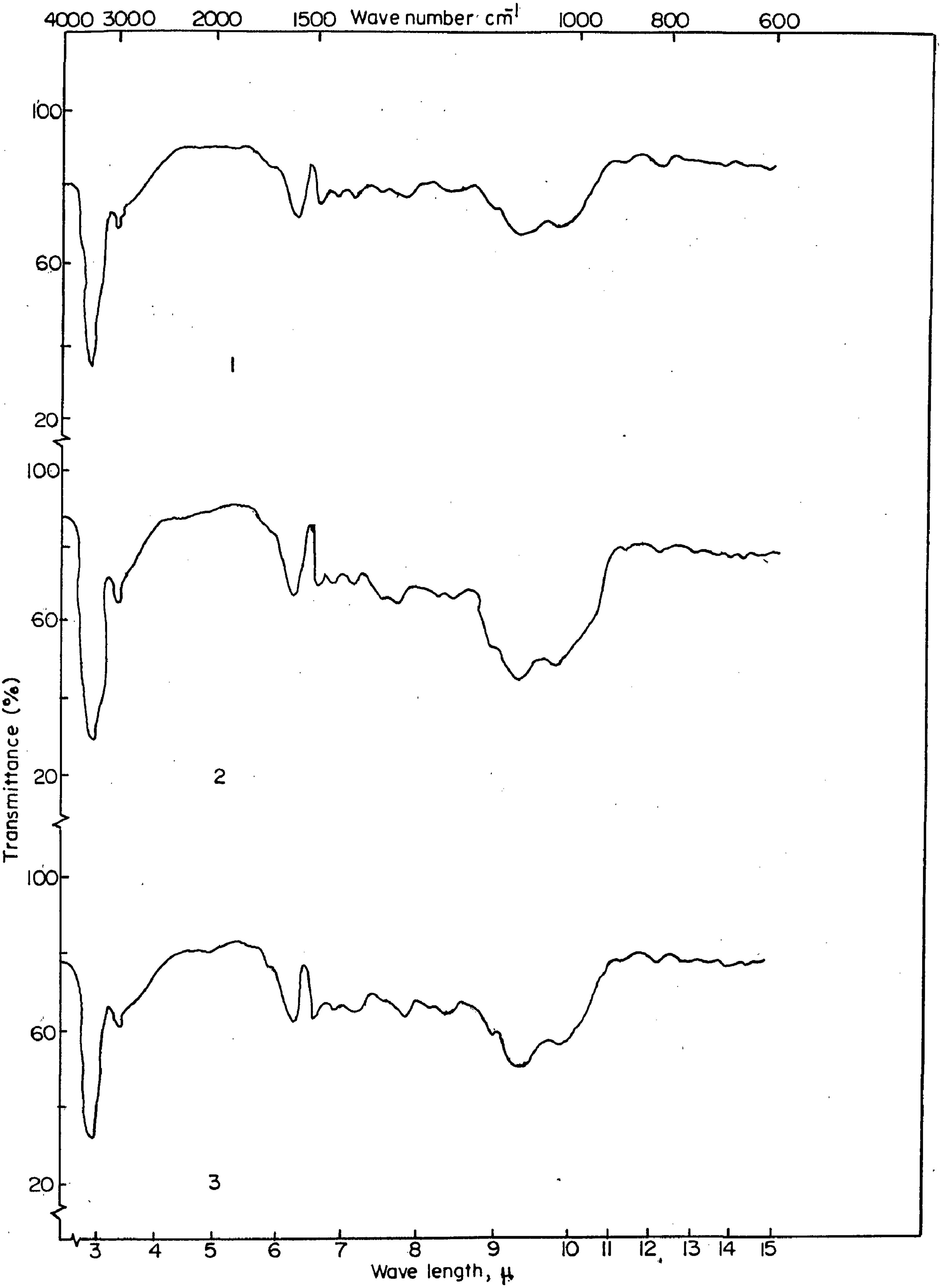


FIG.4.02:INFRARED ABSORPTION SPECTRUM OF WILLSTATTER LIGNIN OF 1. SESBANIA sesban 2. SESBANIA aculeata 3. CAJANUS cajan.

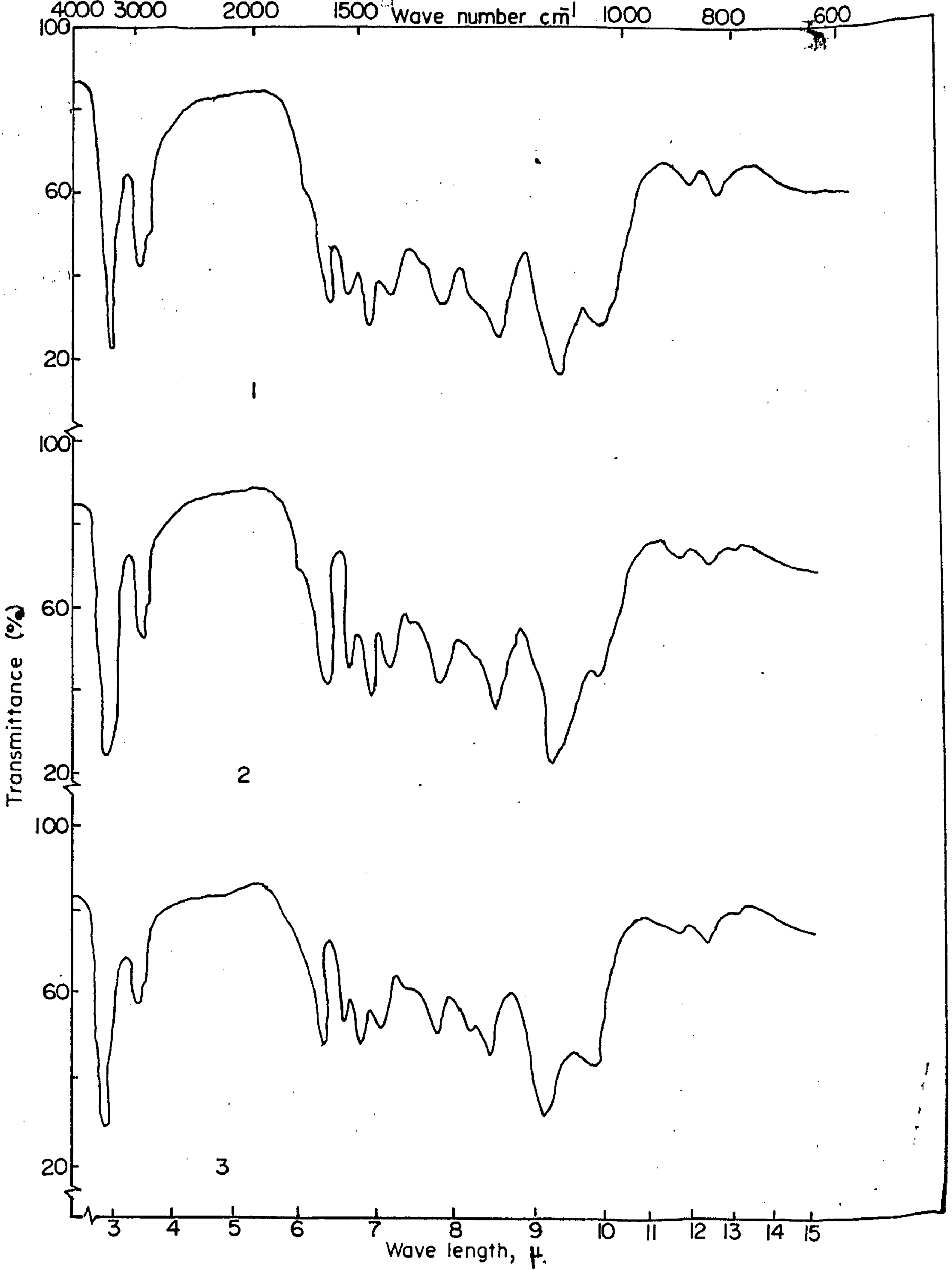


FIG.4.03:INFRARED ABSORPTION SPECTRUM OF ETHANOL LIGNIN OF 1.SESBANIA sesban 2. SESBANIA aculeata 3. CAJANUS cajan.

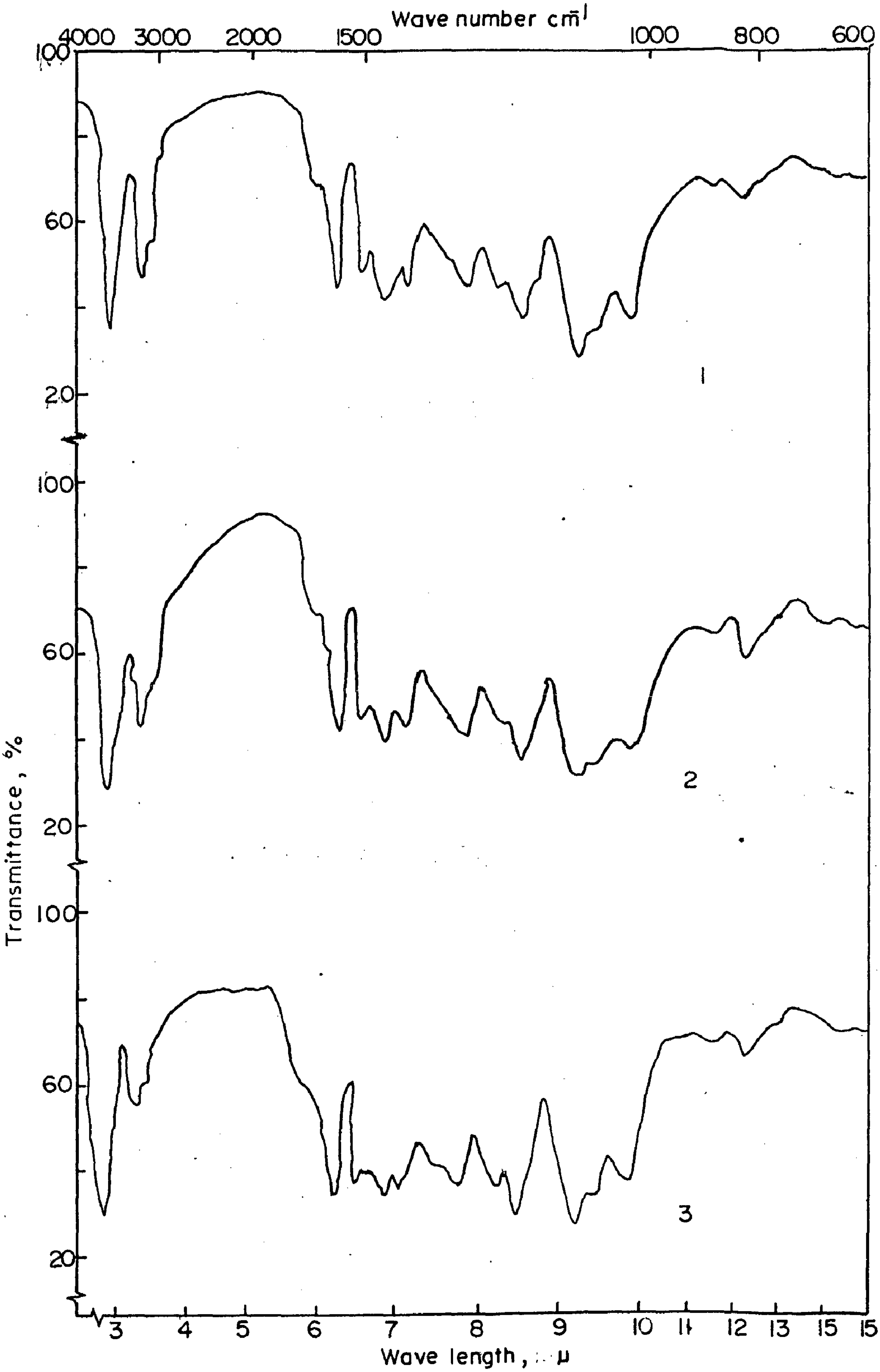
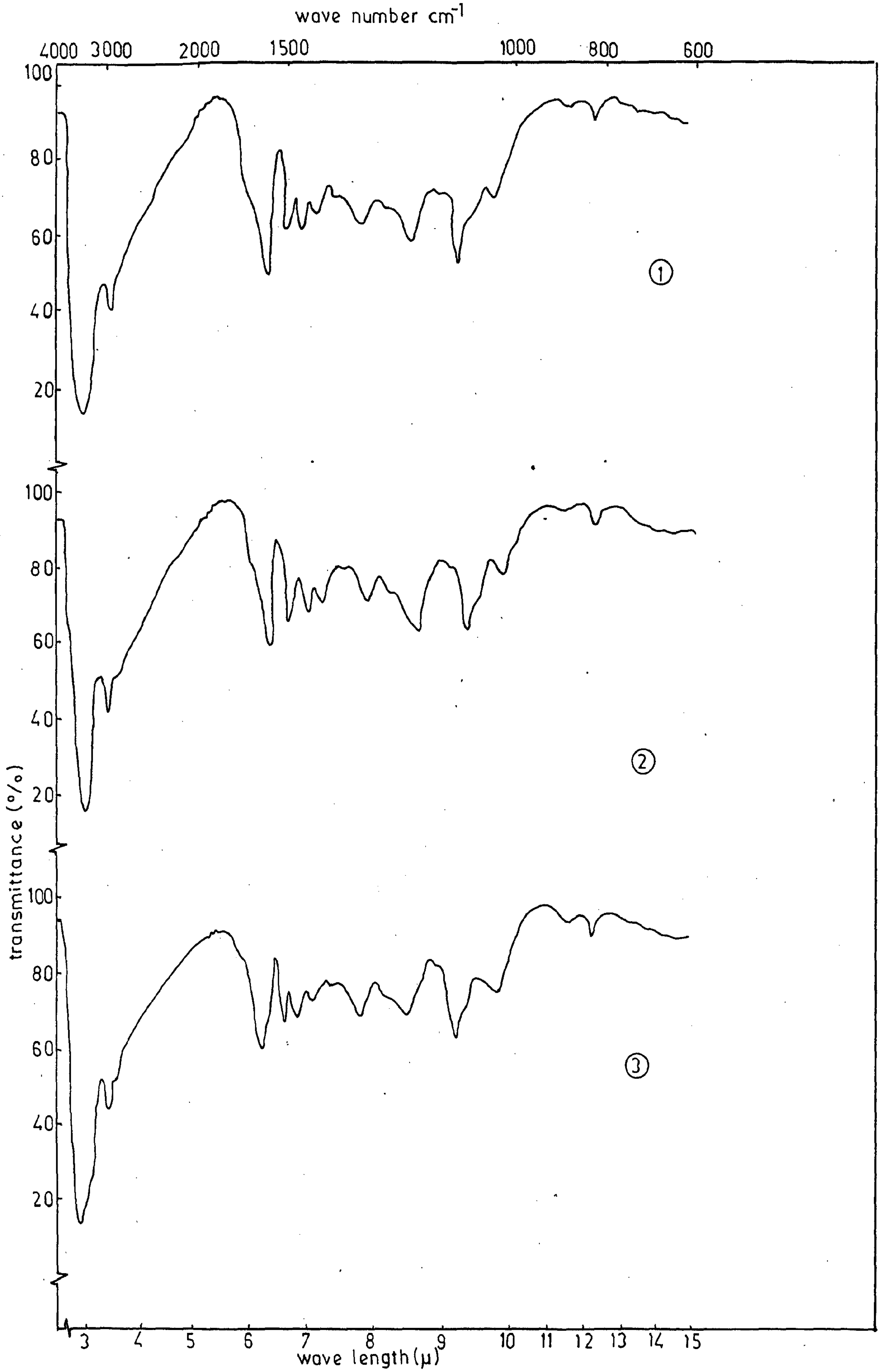


FIG.4.04: INFRARED ABSORPTION SPECTRUM OF METHANOL LIGNIN OF 1. SESBANIA *sesban* 2. SESBANIA *aculeata* 3. CAJANUS *cajan*



G.4.05: INFRARED ABSORPTION SPECTRUM OF THIOLIGNIN (20% SULPHIDITY) OF

① S. sesban ② S. aculeata ③ C. cajan

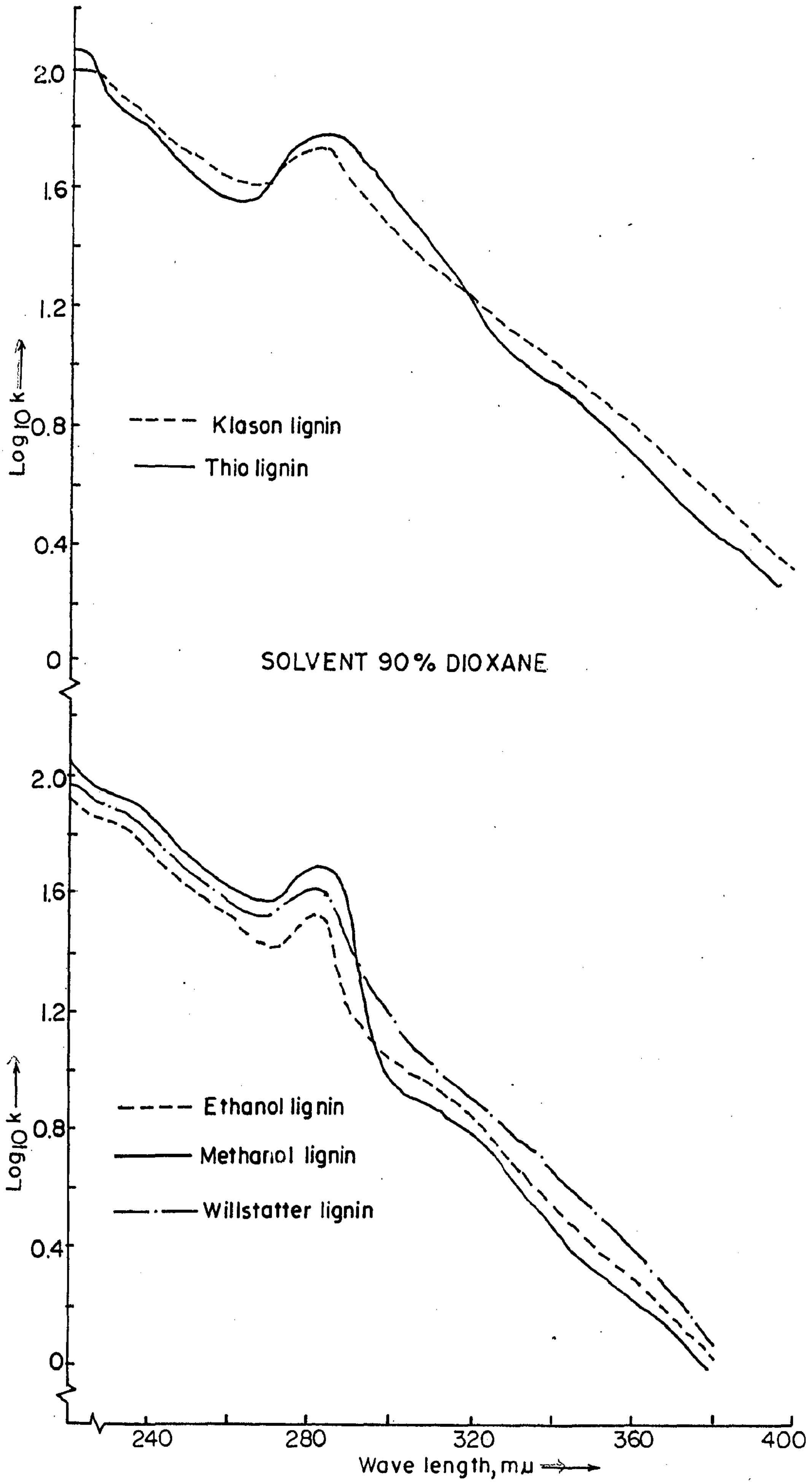


FIG.4.06:ABSORPTION SPECTRA OF SESBANIA *sesban*. LIGNIN

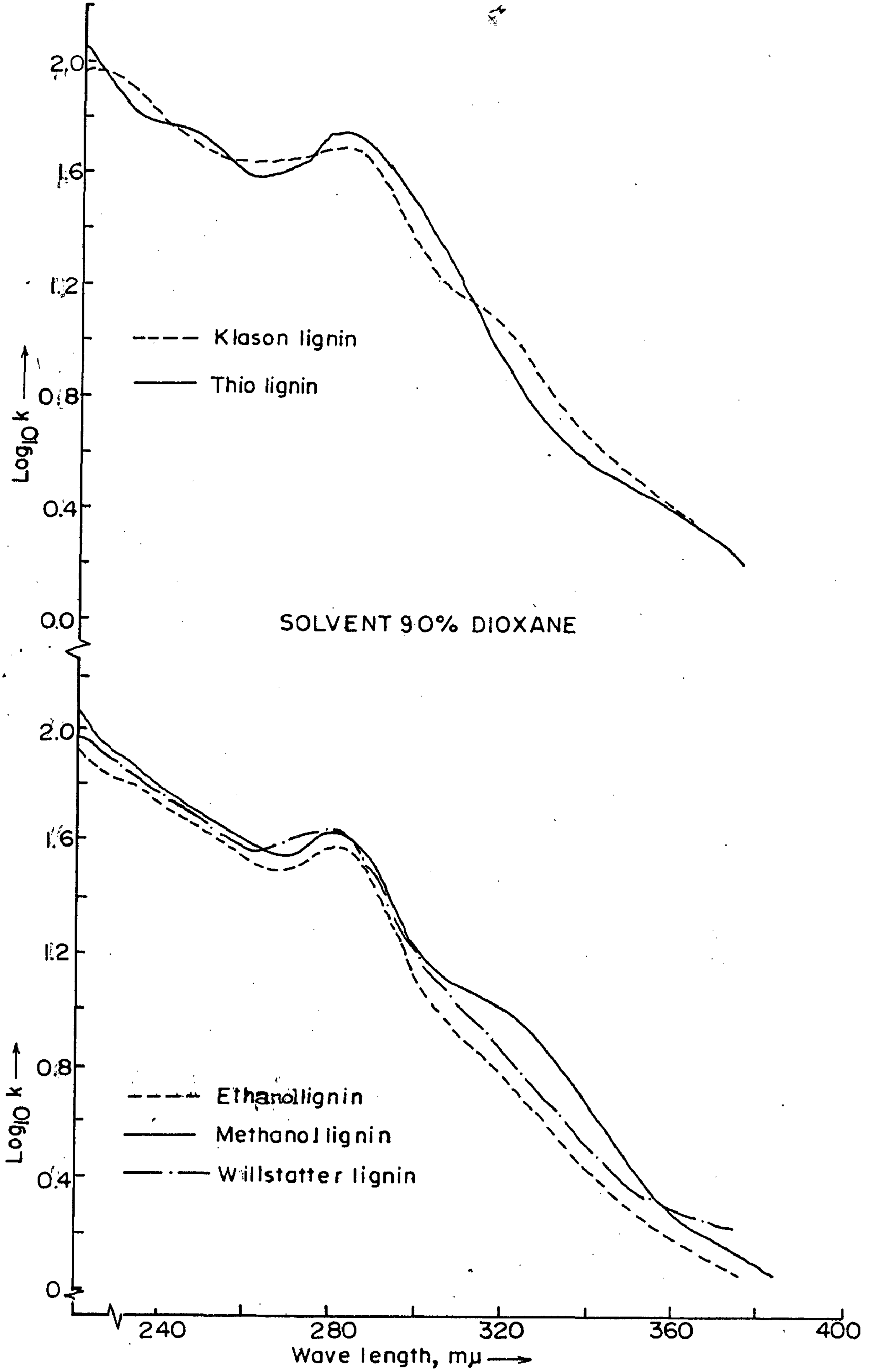


FIG.4.07:ABSORPTION SPECTRA OF SESBANIA *aculeata* LIGNIN.

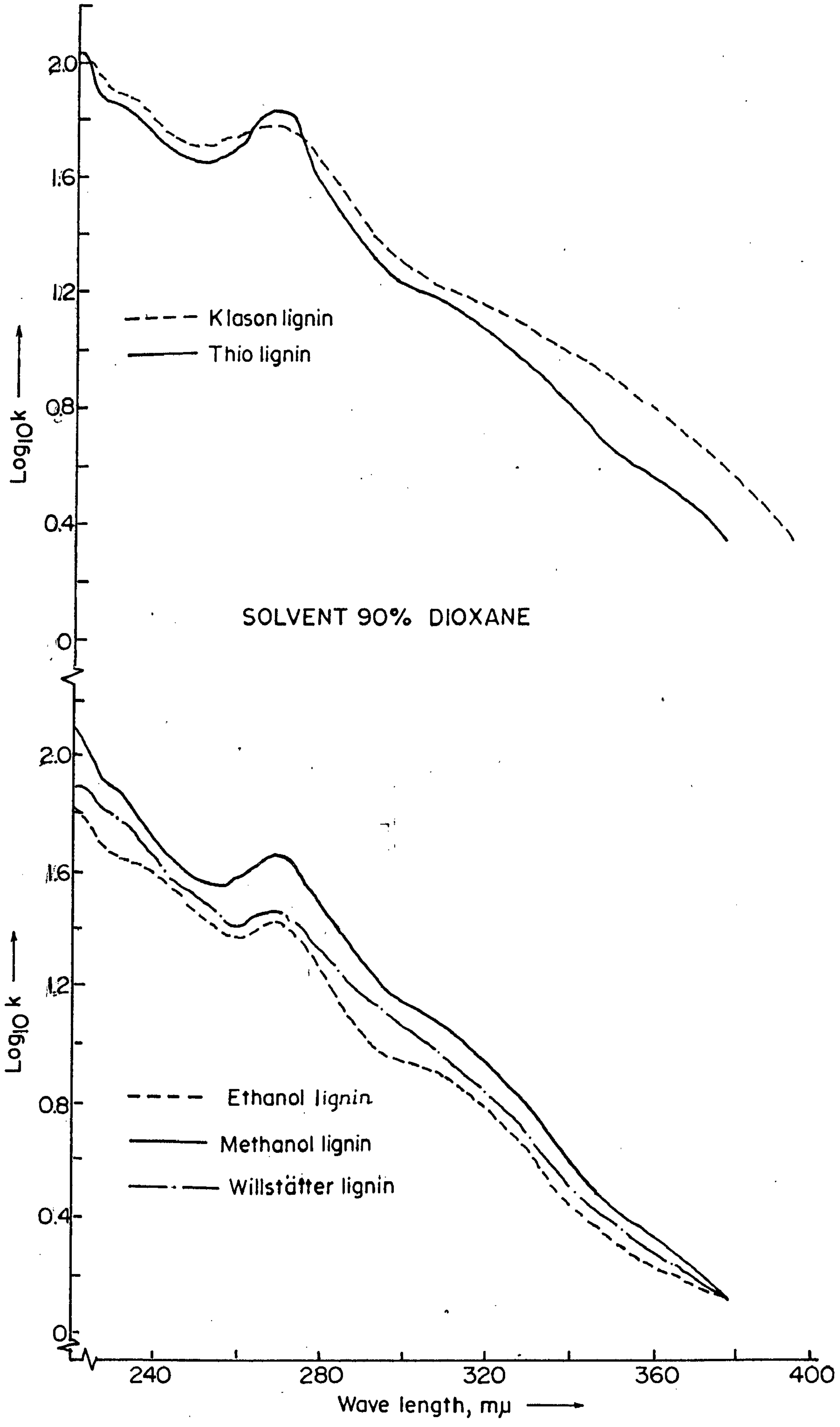


FIG.4.08: ABSORPTION SPECTRA OF CAJANUS *cajan* LIGNIN.

PULPING STUDIES

SODA PULPING STUDIES:

The soda process is particularly applicable to hardwoods alongwith agricultural residues, where the advantages of sulfidity are of a lower magnitude than for softwoods and where the generation of odorous sulphur compounds is also more pronounced than with softwoods. In addition, hardwoods are often used in paper grades where pulp strength requirements are not demanding and can be supplied by the softwood kraft component of the furnish. If care is taken to avoid overcooking, soda pulp may be adequate for the hardwood component of a mixed furnish. Even though caustic is used as the chamical makeup in the soda process, it is difficult to maintain the system completely free of sulfide since sulphur introduced with the wood, water and fuel oil accumulates in the system and is converted to sulfide in the recovery furnace.

5.1.EXPERIMENTAL PROCEDURES:

5.1.1.RAW MATERIAL AND ITS PREPARATION:

The stalks of S. sesban, S. aculeata and C. cajan were collected from nearby regions of Saharanpur. The stalks of all these plants were chipped and screened. The chips those passing through 12.7 mm screen but retained on a 6.35 mm screen were collected. The accepted chips were air dried under atmospheric conditions. The moisture content of fresh(green) chips vary from 55 to 60%, while that of air dry chips vary from 8-12 %.

5.1.2.PROXIMATE CHEMICAL ANALYSIS:

The proximate chemical analyses of S. sesban, S. aculeata and C. cajan are given in table-2.3 on page 29.

5.1.3.PULPING STUDIES:

5.1.3.1.OPTIMIZATION OF PULPING CONDITIONS:

All the cooks were made in a laboratory WEVERK tumbling electrically heated digester (0.02 M^3 capacity). For optimization of pulping conditions, the cookings were made in stainless steel bombs, containing 100 gm. of O.D. cellulosic raw material. The cooking liquor, was then charged to the bombs at atmospheric conditions. For cooking of S. sesban and C. cajan the liquor to wood ratio was maintained at 3.5:1, while in the case of S. aculeata it was maintained at a level of 4:1. The bombs were sealed and placed in a glycol bath controlled at 60° C in which the bombs were rotated at 4 r.p.m., temperature equilibrium was reached within 2 min., after which it was raised to maximum temperature in 90 min. At the end of the cooks the bombs were cooled rapidly. The pulp obtained from each bomb was washed, defibered, screened and evaluated.

5.1.3.2.INFLUENCE OF TEMPERATURE:

In this series of experiments, the soda pulping of S. sesban, S. aculeata and C. cajan were studied at different temperatures ranging from 145° C to 175° C. The residual lignin contents associated with the pulp (on wood basis)were determined and these were plotted versus cooking time (at temperature) of reaction (Fig.5.01A) and the results are reported in Table-5.1A.

In figure 5.01A, all the curves could be approximated by two straight lines at each temperature investigated. The steeper slope is related with the rapid solubilization of bulk of the lignin (bulk delignification) and the more gentle to the slow solubilization of the residual lignin (residual delignification), and are having different velocity constants. The bulk delignification corresponds to the removal of easily assessible lignin present in the middle lamella and the residual delignification corresponds to the removal of lignin present in primary wall, secondary wall and the central interconnections cavity etc. The delignification of wood in alkaline pulping is also associated with the solubilization of significant amounts of hemicelluloses(40). These plots clearly indicate that when the temperatures were decreased from 175°C to 145°C, the cooking time to reach transition from bulk to residual delignification and the pulp lignin content corresponding to this transition point both increased. In other words, at the transition point, a lower pulp lignin contents were obtained at 175°C than at 145°C.

The yield drop of pulps were studied at 165°C with decreasing amounts of the undissolved lignin. In figure 5.03A straight lines of distinct slopes were found for bulk and residual delignification with a sharp bend in the range of transition. During bulk delignification of pulps, the ratio of lignin to carbohydrates solubilized was about 1:0.84, 1:0.75 and 1:0.68 for S.sesban, C.cajan and S.aculeata respectively, whereas during residual delignification this ratio was about 1:7.8, 1:6.7 and 1:6.2 for S.sesban, C.cajan and S.aculeata respectively, i.e. about nine times greater. The high loss of carbohydrates relative to the dissolved lignin found in the residual delignification(40) suggested that commercial soda pulping should be limited to the range of bulk delignification only.

The degree of delignifications was determined as follows:

Degree of delignification (DD),%=1-(L/Lo)X100

Where L = Residual lignin

Lo= Initial lignin content in raw material.

Figure 5.01A clearly indicated that at lower temperature range, the residual lignin content decreased sharply and at higher temperature range, the magnitude of decrease in the amount of residual lignin contents have not much effect and remains practically constant. Moreover it is achieved at the cost of increasing the temperature and at higher temperature the degradation of carbohydrate fraction also increased. The nature of the curves after transition point is almost horizontal straight line, this clearly indicated that the bulk delignification phase is over upto this transition point and it is not economical to continue pulping reaction beyond this particular temperature. It is not advisable to go for higher temperature beyond 165°C, hence this particular temperature must be considered as optimum temperature for soda pulping of these plants.

To estimate Arrhenius activation energy of the bulk delignification in soda pulping of Sesbania sesban, Cajanus cajan and Sesbania aculeata, the logarithms of the velocity constants (per second) found at temperature investigated were plotted versus reciprocal of the corresponding absolute temperature (Fig. 5.05A), and approximately straight lines were observed. The slope values multiplied by the gas constant gives the activation energy of the over-all reaction (Table-5.3A). The Arrhenius activation energy(45) of bulk delignification in soda pulping of S.sesban and C.cajan were found to be about 91.90 KJ/mole and 84.14 KJ/mole respectively, while in the case of S.aculeata, it was found to be 80.34 KJ/mole, which is very low in comparison to soft woods(78), whereas that of residual delignification was only about two thirds of this value in spite of the fact that lignin solubilisation during residual delignification is more difficult than during bulk delignification. This indicated, either the existence of an association between lignin and carbohydrates in the wood(49) or the formation of bonds during pulping (39,41).

5.1.3.3. INFLUENCE OF ACTIVE ALKALI CHARGE:

The influence of active alkali charge during bulk delignification was investigated at 165°C using 12, 14, 16, 18 and 20% active alkali(as NaOH) doses, and the results are reported in Table-5.2A and illustrated in figure 5.02A. This figure clearly indicated that all the curves could be approximated by two straight lines at each alkali doses investigated. The steeper slope is related to rapid solubilization of bulk of the lignin (bulk delignification) and the more gentle to the slow solubilization of the residual lignin(residual delignification) and are having different valocity constants. The nature of the curves clearly indicated that when the concentration of active alkali decreased the cooking time to reach transition from bulk to residual delignification and pulp lignin content corresponding to this transition point, both increased. In other words, at the transition point, a lower pulp lignin contents were obtained at higher alkali doses than at lower alkali doses.

Fig.5.02A also clearly indicated that the magnitude of decrease in pulp lignin content is high at lower active alkali doses than at higher active alkali doses. The degree of delignification was calculated after 3 hrs. at 12, 14, 16, 18 and 20% active alkali doses and these were found to be 41.92, 56.37, 64.87, 87.36 and 91.33% respectively in case of S.sesban, while in case of C.cajan these were found to be 41.24, 53.52, 67.95, 87.98 and 90.32%. The degree of delignification was also calculated for S.aculeata at 12, 14, 16 & 18% active alkali doses and these were found to be 49.46, 69.17, 88.88 and 92.42% respectively. It seems that the degree of delignifications remain practically constant beyond 18% active alkali dose in case of S.sesban and C.cajan, while in case of S.aculeata, the degree of delignifications remain practically constant beyond 16% alkali dose.

The plots of active alkali versus Kappa number and pulp yield(Fig.5.04A) indicated that the Kappa number decreased linearly with a result of an increase in active alkali. An optimum Kappa number around 30 is achieved at 18% active alkali dose in case of S.sesban and C.cajan, while in case of S.aculeata this particular value is achieved at 16% active alkali dose. Moreover, the pulp yields also decreased linearly with a result of an increase in active alkali doses upto a limit of 18% in case of S.sesban and C.cajan and 16% in case of S.aculeata, and afterwards the magnitude of decrease in pulp yield is higher, hence 18% and 16% active alkali may be considered as optimum alkali doses for the soda pulping of S.sesban, C.cajan and S.aculeata respectively.

5.1.4. SODA PULPING OF S.sesban, C.cajan AND S.aculeata:

Further for detailed study, the cookings were made in laboratory digester. The cooking of S.sesban and C.cajan were made with 18% active alkali (as NaOH), while the cooking of S.aculeata was made at 16% active alkali (as NaOH) charge; using the same process condition as used in bomb cooking, The time required to reach the maximum temperature of 165°C was 90 min., and time at temperature was 180 minutes. After completion of cookings the pulps were taken out from the digester, washed on a flat stationary screen having 100 mesh wire bottom for the removal of residual cooking chemicals, and further disintegrated in laboratory disintegrator. The disintegrated pulps were screened through a vibratory flat WEVERK screen with 0.15 mm. slits. The screened pulps were further analysed and the results of over-all pulpings are reported in Tables 5.1A and 5.2A.

5.1.5. SODA-ANTHRAQUINONE PULPING:

Many different additives have been used to improve the yield and quality of soda pulp. Among the additives can be mentioned, sodium borohydride, hydrosulphide and a number of cyclic quinone compounds of which anthraquinone(AQ) has given quite encouraging results. The influence of AQ as an additive in the soda pulping was studied by adding 0.1% AQ on dry wood basis. The cooking conditions, pulp yield and physical strength properties are reported in Table 5.6A.

5.1.6. BLEACHING STUDIES:

The unbleached pulp of S.sesban, C.cajan and S.aculeata were bleached by the use of CEHH bleaching sequences. The bleaching conditions alongwith their results are tabulated in Table-5.4A.

5.1.7. FIBRE CLASSIFICATION STUDIES:

The fibre classification studies of S.sesban, C.cajan and S.aculeata soda pulps were made with the help of Bauer-McNett fibre classifier with mesh screen numbers 20, 60, 80 and 120. The results are reported in Table 5.9A. The photomicrographs of unbleached and bleached, unbeaten and beaten pulps fibres of these plants are shown in annexure on page 166 to 171.

5.1.8. PULP EVALUATION STUDIES:

The unbleached and bleached pulps were separately beaten in PFI(73) mill to different freeness levels. Standard sheets of 60 g/m^2 were made on British sheet forming machine; pressed and dried as per IS method(32). These sheets were conditioned at a temperature of 25-26°C and 60-65% relative humidity and evaluated for various physical strength properties(32). The results of pulp evaluation of unbleached and bleached pulps both are reported in Tables-5.5A to 5.8A respectively.

5.1.9.SPENT LIQUOR CHARACTERISTICS:

The spent liquors obtained as a result of soda pulping of S.sesban, C.cajan and S.aculeata were analysed for total solids, residual active alkali, organics, inorganics and calorific value as per TAPPI standard methods and the results are reported in Table 5.10A.

5.2.RESULTS AND DISCUSSIONS:

The unbleached S.sesban, C.cajan and S.aculeata pulps showed excellent response to bleaching by CEHH bleaching sequence for obtaining a high degree of brightness. The unbleached pulps brightness were 35-37%(Elrepho). In these bleaching studies about 25% chlorine of the Kappa number was applied. During chlorination stage, 60-70% chlorine of the total chlorine was used, which was almost totally consumed. The alkali requirements were about 1.5% in the extraction stage. The application of about 2% chlorine as calcium hypochlorite in the hypochlorite first stage(H_1) gave pulps of around 72% (Elrepho) brightness. To get pulps of better brightness, CEHH sequence was applied. In hypochlorite second stage (H_2) about 1% chlorine(as calcium hypochlorite) was used, which gave pulps of 76% brightness (Elrepho)/ The bleached pulps viscosity values are quite comparable to that of bamboo and other tropical hardwoods.

The results of unbleached and bleached S.sesban, C.cajan and S.aculeata pulps evaluation are shown in Tables-5.5A to 5.8A. These results indicated that the initial freeness and drainage time of both the pulps were found to be higher in comparison to that of bamboo pulp at the same freeness level. The freeness of unbeaten pulps were found to be around 14-16°SR. The sheets formed from unbeaten pulps were having apparent density around 0.60-0.63 g/cm^3.

The plots of pulps freeness versus apparent density, tear, tensile, burst indexes, folding endureance and porosity of S.sesban, C.cajan and S.aculeata unbleached pulps at various levels of freeness have shown in fig. 5.06A, while the same plots for bleached S.sesban, C.cajan and S.aculeata pulps have shown in fig.5.07A. These plots clearly indicated that the apparent density, burst index, folding endurance, tensile index are in direct proportion with the freeness of the pulps i.e. all these properties showed an improving trend with a result of an increase in freeness upto a certain level of freeness, while the tear index of both the unbleached and bleached pulps of S.sesban, C.cajan and S.aculeata first showed a little enhancement and than sharp decline continuously. The porosity is in indirect proportion with the freeness of pulps i.e. porosity showed a continuous decreasing trend as the freeness increases as a result of beating. The bleached pulps showed a good value for opacity. On the basis of these results it can be concluded that both the unbleached and bleached S.sesban, C.cajan and S.aculeata pulps showed good strength characteristics except for tear. An optimum freeness level for S.sesban, C.cajan and S.aculeata pulp may be considered around $42\pm2^{\circ}$SR and beyond this the beating should not be continued.

The comparison of the total pulp yields of soda pulp to that of soda-AQ pulps at same Kappa number showed that the yield increased with the addition of small amounts of AQ during pulping. Addition of 0.1% AQ raised the yield by approximately 3% units compared with the cooks without AQ. In bleaching, the total chlorine consumption is nearly the same in both the cases. The viscosity of bleached soda-AQ pulps are slightly higher than the bleached soda pulp. The physical strength properties of soda-AQ pulps showed somewhat improvement over the soda pulps at the same Kappa no. The brightness of soda-AQ pulps are lower than the soda pulps.

The results of spent liquors analysis obtained after soda pulping of S.sesban, C.cajan and S.aculeata under the optimum conditions are given in table 5.10A. The total solid contents in spent liquors were towards little higher side and

and these are due to the shorter fiber length of S.sesban, C.cajan and S.aculeata.fibre The calorific values of spent liquors were little higher than bamboo soda spent liquor and these are due to the presence of high solid contents. The silica contents in the spent liquors were found to be very low. The lower silica contents and higher calorific values of S.sesban, C.cajan and S.aculeata spent liquors are advantageous factors towards the energy conservation in the chemical recovery system.

5.3.CONCLUSION:

At each temperatures level studied, the undissolved lignin plotted versus cooking times showed approximate linearity, but the rate constants of the two mechanism were different. The mechanism of alkaline delignification with greater rates constant was found to be related with bulk delignification, and the other to residual delignification. The Arrhenius activation energy of bulk delignification in soda pulping of S.sesban,C.cajan and S.aculeata were about 91.90, 84.14 and 80.34 KJ/mole, respectively. During residual delignification at 165 ^{o}C in soda pulping, the carbohydrates loss per unit weight of lignin solubilised was about nine times greater than that in the bulk delignification. This indicated either the existance of an association between lignin and carbohydrates in wood or the formation of bonds during pulping. The pulp showed good bleach response. The CEHH bleaching sequence was used to get a bleached pulps with a brightness level of 76-80%(Elrepho). Both bleached and unbleached pulps showed good strength properties.

The soda-AQ pulping gave positive results for the possiblities of improving the soda pulping method to one that is fully commensurate with kraft cooking. It can be concluded that the addition of AQ has a favourable influence on both the pulp yields and all the quality properties determined except for brightness.

Table-5.1A: Effect of Temperature (145°C to 175°C) at 18% Active Alkali (as NaOH) For S.sesban And C.cajan & 16% For S.aculeata During Soda Pulping.

Temperature (°C)	Time at temperature (Hr.)	S.sesban Yield (%)	S.sesban Lignin (%)	C. cajan Yield (%)	C. cajan Lignin (%)	S. aculeata Yield (%)	S. aculeata Lignin (%)
145	1.0	62.7	15.25	63.2	15.50	62.5	15.10
	1.5	61.1	13.50	61.3	13.80	60.0	13.50
	2.0	59.4	12.20	60.0	12.50	57.4	12.20
	2.5	56.0	10.75	56.4	11.00	54.7	10.60
	3.0	54.6	9.60	55.7	9.78	51.8	9.30
	3.5	52.7	8.32	52.8	8.12	50.0	7.76
	4.0	51.3	7.50	50.4	6.50	48.7	6.25
	5.0	48.2	6.00	48.5	6.30	48.0	6.20
155	1.0	61.2	14.13	61.9	13.75	58.6	13.72
	1.5	56.8	12.00	59.1	11.70	56.2	11.88
	2.0	53.5	9.75	56.4	10.00	54.5	9.98
	2.5	49.0	7.91	54.6	8.00	53.7	7.60
	3.0	47.5	6.30	52.0	6.20	51.9	5.00
	3.5	46.0	4.70	48.8	4.72	51.0	4.50
	4.0	45.8	4.12	45.2	4.00	49.2	4.20
	5.0	44.6	3.48	44.5	3.20	47.0	3.60
165	1.0	55.8	12.90	57.4	12.20	56.4	12.50
	1.5	53.1	10.50	55.6	9.65	54.2	10.00
	2.0	50.2	7.40	53.0	7.00	52.5	7.50
	2.5	47.8	5.10	51.5	4.98	50.6	4.95
	3.0	45.7	2.23	49.0	2.25	48.5	2.20
	3.5	42.8	2.10	46.0	2.20	45.2	2.08
	4.0	41.5	1.90	44.5	2.00	41.8	2.00
	5.0	38.6	1.56	44.7	1.80	41.0	1.82
175	1.0	53.9	12.20	54.5	11.50	55.0	11.80
	1.5	51.5	9.00	52.1	8.80	52.8	9.00
	2.0	47.9	6.50	50.2	6.40	51.4	6.25
	2.5	44.7	3.40	48.4	3.90	47.8	3.70
	3.0	40.2	1.80	44.8	1.80	41.0	1.30
	3.5	36.4	1.50	41.2	1.78	35.6	1.27
	4.0	35.2	1.27	38.6	1.56	33.0	1.00
	5.0	34.3	1.12	36.5	1.30	31.5	0.80

Time from 30°C to 105°C = 30 minutes

From 105°C to maximum temperature = 60 min.

Wood to liquor ratio = 1 : 35. For S.sesban and C.cajan
= 1:4 for S. aculeata.

Table-5.2A:Effect of Alkali Charge (12 to 20% Active Alkali Doses) At 165 °C Temperature During Soda Pulping Of S. sesban, C. cajan and S. aculeata.

Active alkali doses (as NaOH) (%)	Time at 165°C (Hrs.)	S. sesban Lignin (%)	S. sesban Kappa (no.)	S. sesban Yield (%)	C. cajan Lignin (%)	C. cajan Kappa (no.)	C. cajan Yield (%)	S. aculeata Lignin (%)	S. aculeata Kappa (no.)	S. aculeata Yield (%)
12	1	15.60	----	----	15.70	----	----	15.10	----	----
	2	13.00	----	----	13.25	----	----	12.30	----	----
	3	10.25	45.0	53.2	11.00	48.7	56.4	10.00	44.0	54.8
	4	7.87	----	----	8.20	----	----	7.50	----	-----
	5	7.80	----	----	7.50	----	----	6.00	----	-----
14	1	14.80	----	----	15.10	----	----	14.50	----	-----
	2	11.50	----	----	11.80	----	----	10.40	----	-----
	3	7.70	40.5	51.0	8.70	42.3	53.7	6.10	37.4	52.4
	4	6.00	----	----	6.50	----	----	5.14	----	----
	5	5.62	----	----	5.50	----	----	5.00	----	----
16	1	13.80	----	----	14.34	----	----	12.50	----	----
	2	9.50	----	----	10.20	----	----	7.50	----	----
	3	6.20	37.0	48.3	6.00	36.5	51.2	2.20	31.0	48.5
	4	4.38	----	----	4.50	----	----	2.00	----	----
	5	3.80	----	----	3.75	----	----	1.82	----	----
18	1	12.80	----	----	12.20	----	----	11.30	----	----
	2	8.00	----	----	7.00	----	----	6.20	----	----
	3	2.23	30.0	45.7	2.25	31.0	49.0	1.50	27.6	45.2
	4	1.90	----	----	2.00	----	----	1.46	----	----
	5	1.56	----	----	1.80	----	----	1.30	----	----
20	1	11.00	----	----	11.20	----	----			
	2	6.00	----	----	6.25	----	----			
	3	1.53	25.4	42.0	1.81	27.0	44.6			
	4	1.00	----	----	1.46	----	----			
	5	0.65	----	----	1.25	----	----			

Time from 30 °C to 105 °C = 30 minutes, From 105 °C to 165 °C = 60 minutes;

Wood to liquor ratio = 1:3.5 for S.sesban and C. cajan, 1:4 for S. aculeata.

Table-5.3A:First Order Rate Constant For Bulk Delignification In Soda Pulping Of S.sesban, C.cajan And S.aculeata.

Sl.No.	Temperature °C	Rate constant KS^{-1}		
		S.sesban	C. cajan	S.aculeata
1	145	0.6461×10^{-4}	0.6397×10^{-4}	0.7676×10^{-4}
2	155	1.1195×10^{-4}	1.1200×10^{-4}	1.4714×10^{-4}
3	165	2.3509×10^{-4}	2.3949×10^{-4}	2.5588×10^{-4}
4	175	3.4986×10^{-4}	3.6464×10^{-4}	3.9023×10^{-4}
5	Activation energy	21.96 Kcal/mole 91.90 KJ/mole	20.13 Kcal/mole 84.14 KJ/mole	19.22 Kcal/mole 80.34 KJ/mole

Table-5.4A:Bleaching Conditions And Results Of Soda And Soda-AQ Pulp Of S.sesban, C.cajan And S.aculeata.

Sl. No.	Particulars	S.sesban		C.cajan		S.aculeata	
		Soda	Soda-AQ	Soda	Soda-AQ	Soda	Soda-AQ
1.	Unbleached pulp Kappa No.	30.00	32.00	31.00	32.00	29.20	31.40
2.	Chlorination stage (C)						
	Amount of Cl_2 added on pulp %	4.70	5.00	4.85	5.00	4.27	4.90
	Amount of Cl_2 consumed on pulp %	4.68	4.99	4.84	4.98	4.25	4.89
	Amount of Cl_2 consumed on Cl_2 basis %	99.57	99.80	99.79	99.60	99.50	99.80
	Final pH	1.98	1.95	2.10	2.04	1.90	1.97
3.	Alkali extraction stage(E)						
	NaOH added on pulp %	1.50	1.50	1.40	1.50	1.60	1.50
	Initial pH	11.60	11.57	11.50	11.46	11.61	11.52
	Final pH	10.42	10.38	10.30	10.21	10.32	10.18
4.	Hypochlorite Ist Stage(H_1)						
	Hypo added as avail. Cl_2 on pulp%	1.82	1.92	1.90	1.90	1.85	1.88
	Hypo consumed as available Cl_2 on pulp %	1.70	1.85	1.86	1.87	1.80	1.82
	Hypo consumed on Cl_2 basis %	93.40	96.30	97.89	98.42	97.29	96.80
	Final pH	7.98	7.80	8.21	7.86	7.95	7.90
5.	Hypochlorite IInd Stage(H_2)						
	Hypo added as avail. Cl_2 on pulp%	0.92	0.80	0.77	0.80	0.70	0.76
	Hypo consumed as available Cl_2 on pulp %	0.83	0.74	0.72	0.77	0.63	0.70
	Hypo consumed on Cl_2 basis %	90.00	92.50	93.40	96.30	89.60	92.10
	Final pH	7.70	7.40	7.80	7.50	7.70	7.60
6.	Total Cl_2 added on pulp %	7.44	7.72	7.52	7.70	6.82	7.54
7.	Total Cl_2 consumed on pulp %	7.21	7.58	7.42	7.62	6.68	7.41
8.	Bleaching losses %	9.57	9.80	10.40	10.10	9.80	10.20
9.	Bleached pulp yield %	40.80	41.90	43.00	43.98	42.90	43.30
10.	Pulp brightness (Elrepho) %	75.40	75.00	76.00	75.20	75.70	74.80
11.	Viscosity, C.E.D.(0.5%)cp	9.80	10.00	10.20	10.40	10.00	10.30

Bleaching Conditions:	C	E	H_1	H_2
Consistency (%)	2.8	10	9	9
Temperature (°C)	27±2	55±2	45±2	45±2
Time (Minute)	30	120	60	120

Table-5.5A:Strength Properties of S.sesban, C.cajan And S.aculeata Unbleached Soda Pulps.

Plant species	PFI Revolution (No)	Freeness (^{o}SR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index (mNm^2/g)	Burst index (KPa.m^2/g)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min.)	Folding endurance Köhler Molin
Sesbania	0	14	3.8	0.60	2.40	0.65	10.43	1560	14
sesban	1200	34	13.4	0.67	4.32	2.98	45.65	680	151
	1730	40	16.2	0.70	4.86	3.60	55.00	400	196
	2000	43	17.4	0.71	4.22	4.13	56.65	240	224
Cajanus	0	14	4.3	0.62	3.74	0.81	17.64	1450	12
cajan	1000	35	16.4	0.71	4.60	3.89	48.64	770	160
	1500	44	19.0	0.76	4.10	4.44	57.70	325	210
	1900	48	21.5	0.77	3.22	4.82	60.71	210	226
Sesbania	0	15	4.3	0.60	3.40	0.76	22.18	1400	10
aculeata	950	30	14.3	0.71	5.30	3.65	55.60	525	205
	1300	38	17.0	0.75	6.20	4.30	68.82	210	265
	1600	44	19.3	0.76	4.65	4.95	70.71	160	290

Table-5.6A:Cooking Condition And Strength Properties of Soda-AQ Pulping of S.sesban, C.cajan And S.aculeata.

Active alkali as (NaOH) % = 18 (for S.sesban and C.cajan)
= 16 (for S.aculeata)

Liquor to wood ratio = 3.5:1 (for S.sesban and C.cajan)
= 4.0:1 (for S.aculeata)

Time from 30 °C to 105 °C = 30 minutes, 105 to 165 °C = 60 minutes.

At 165 °C = 120 minutes.

Pulp yield % = 46.4(S.sesban), 49.2(C.cajan) & 48.2(S.aculeata).
Kappa No. = 32.0(S.sesban), 32.0(C.cajan) & 31.4(S.aculeata).

Plant species	PFI Revolution (No.)	Freeness (°SR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index ($mN.m^2/g$)	Burst index ($KPa.m^2/g$)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min.)	Folding endurance Köhler Molin
Sesbania sesban	0	15	4.1	0.60	2.60	0.80	18.42	1500	12
	1100	30	10.5	0.68	5.14	2.62	44.75	800	121
	1500	35	14.0	0.72	4.30	3.10	49.74	380	189
	1900	43	17.4	0.75	3.85	4.20	58.65	230	220
Cajanus cajan	0	15	4.4	0.61	3.99	0.85	17.13	1300	11
	940	30	12.1	0.74	4.68	3.22	47.95	700	124
	1200	36	17.0	0.79	4.14	3.90	49.49	350	156
	1600	45	19.4	0.82	3.78	4.38	58.20	310	212
Sesbania aculeata	0	16	4.5	0.67	4.54	0.98	20.23	1270	12
	940	30	13.3	0.72	5.60	4.06	59.88	650	210
	1400	40	18.0	0.77	6.05	4.62	67.85	200	242
	1800	45	19.5	0.78	4.42	4.92	71.00	180	255

Table-5.7A:Strength Properties of S.sesban, C.cajan And S.aculeata Bleached Soda Pulps.

Plant species	PFI Revolution (No.)	Freeness (^oSR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear Index ($mN.m^2/g$)	Burst Index ($KPa. m^2/g$)	Tensile Index (Nm/g)	Porosity Bendtsen (ml/min.)	Folding endurance Köhler Molin	Brightness (Elrepho) (%)	Opacity (%)
Sesbania	0	16	4.3	0.63	2.70	0.85	15.61	1050	16	74.2	90.4
sesban	1200	39	17.2	0.75	4.05	3.20	46.46	165	108	69.6	85.2
	1400	46	20.0	0.77	3.60	3.90	51.20	110	125	68.0	81.6
	1600	52	24.5	0.78	3.10	4.10	52.24	80	142	66.3	79.5
Cajanus	0	17	4.5	0.76	2.93	0.98	24.45	825	10	75.2	90.0
cajan	850	36	17.4	0.84	4.15	3.10	46.52	150	94	72.0	84.2
	1000	42	19.4	0.86	3.55	4.06	53.70	75	130	69.2	81.0
	1400	50	24.2	0.89	2.52	4.25	55.24	60	145	66.7	76.3
Sesbania	0	16	4.5	0.65	2.30	0.86	28.63	700	15	76.0	89.3
aculeata	800	35	16.7	0.79	4.72	3.80	51.00	85	112	72.4	86.0
	960	40	18.5	0.81	4.32	4.00	57.09	75	140	70.0	84.1
	1200 2	44	20.8	0.82	3.60	4.12	59.00	50	154	68.8	82.0

Table-5.8A: Strength Properties of Bleached Soda-AQ Pulps of S.sesban, C.cajan And S.aculeata.

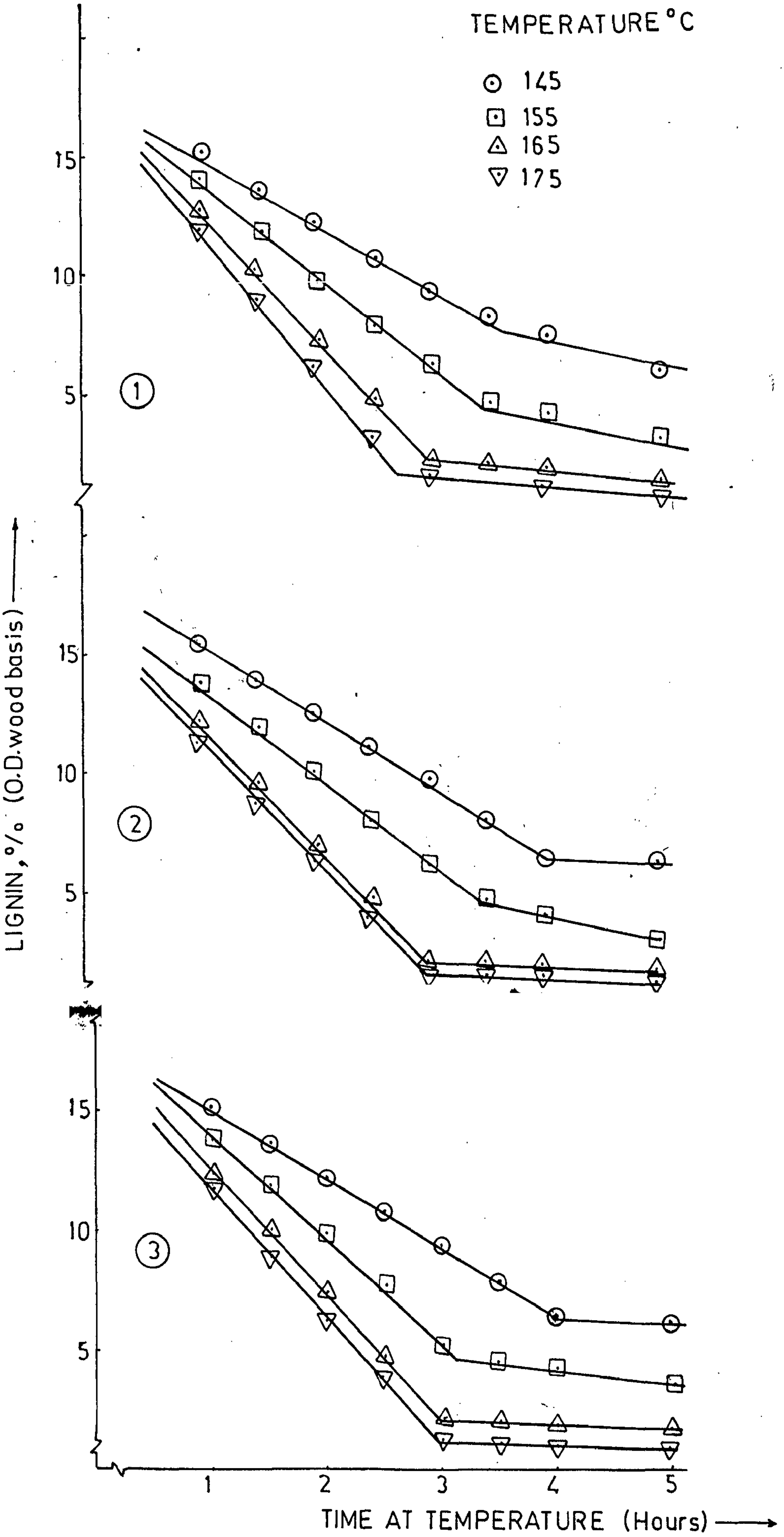
Plant species	PFI Revolution (No.)	Freeness (^{o}SR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index (mN.m^2/g)	Burst index (KPa.m^2/g)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min.)	Folding endurance Köhler Molin	Brightness (Elrepho) (%)	Opacity (%)
Sesbania	0	17	4.4	0.60	2.58	0.90	17.00	1020	15	73.8	90.0
sesban	1000	33	11.0	0.72	4.41	2.45	42.49	260	98	69.7	86.3
	1300	45	19.2	0.74	3.54	3.96	51.50	140	114	67.8	82.0
	1700	52	21.4	0.80	3.00	4.19	52.00	90	130	65.4	81.2
Cajanus	0	17	4.5	0.65	2.80	0.90	22.59	900	16	74.6	91.2
cajan	800	32	13.6	0.76	4.13	3.19	44.20	450	89	72.0	86.0
	950	39	18.2	0.81	3.64	3.50	50.40	170	110	69.9	82.5
	1250	44	20.0	0.84	3.48	4.10	53.10	105	122	68.7	82.0
Sesbania	0	16	4.5	0.69	3.20	1.18	22.79	950	17	74.9	89.6
aculeata	650	24	9.2	0.72	3.80	3.29	48.57	450	80	72.0	86.4
	950	39	18.0	0.77	4.64	3.84	57.49	110	135	70.2	82.6
	1000	42	19.1	0.87	3.65	4.10	59.20	80	140	69.0	82.0

Table-5.9A:Bauer- McNett Fibre Classification Of Soda Pulps.

Sl.No.	Mesh size	S. sesban		C. cajan		S. aculeata	
		Unbleached (%) 14(°SR) Kappa no.30	Bleached (%)16(°SR)	Unbleached (%)14(°SR) Kappa no.31	Bleached (%)17(°SR)	Unbleached (%)15(°SR) Kappa no.29.5	Bleached (%)16(°SR)
1.	+20	15.0	2.0	13.0	1.9	13.6	2.2
2.	-20+60	46.7	34.4	47.0	36.7	49.0	38.0
3.	-60+80	20.0	29.0	21.6	26.9	19.5	27.0
4.	-80+120	8.0	14.0	7.5	15.0	5.2	13.8
5.	-120	10.3	20.6	10.9	19.5	12.7	19.0

Table-5.10A:Soda Spent Liquor Characteristics Of S.sesban, C.cajan & S.aculeata.

Sl.No.	Particulars	VALUES			
		S. sesban	C. cajan	S. aculeata	Bagasse(44)
1.	Black liquor solids %	24.54	22.85	28.64	24.70
2.	Residual active alkali, g.p.l.	3.70	3.90	3.50	---
3.	Inorganic as NaOH %	24.78	25.26	31.41	42.70
4.	Organic %	75.22	74.74	72.59	57.30
5.	Silica %	2.96	3.08	3.20	---
6.	Calorific value KJ/kg.	11702	11863	12017	---
7.	Brookfield viscosity at 30°C, Lv spindle No.1 cp.	13.90	13.60	13.80	14.45
8.	pH of liquor at 30°C	10.13	10.40	10.40	---
9.	°Tw at 30 °C	17.00	18.80	20.50	---



1A: PLOTS OF RESIDUAL LIGNINS(%)VS.TIME OF REACTION AT 18(%)A

ALKALI FOR ①S.sesban ②C.cajan AND 16% AA FOR ③S.acule

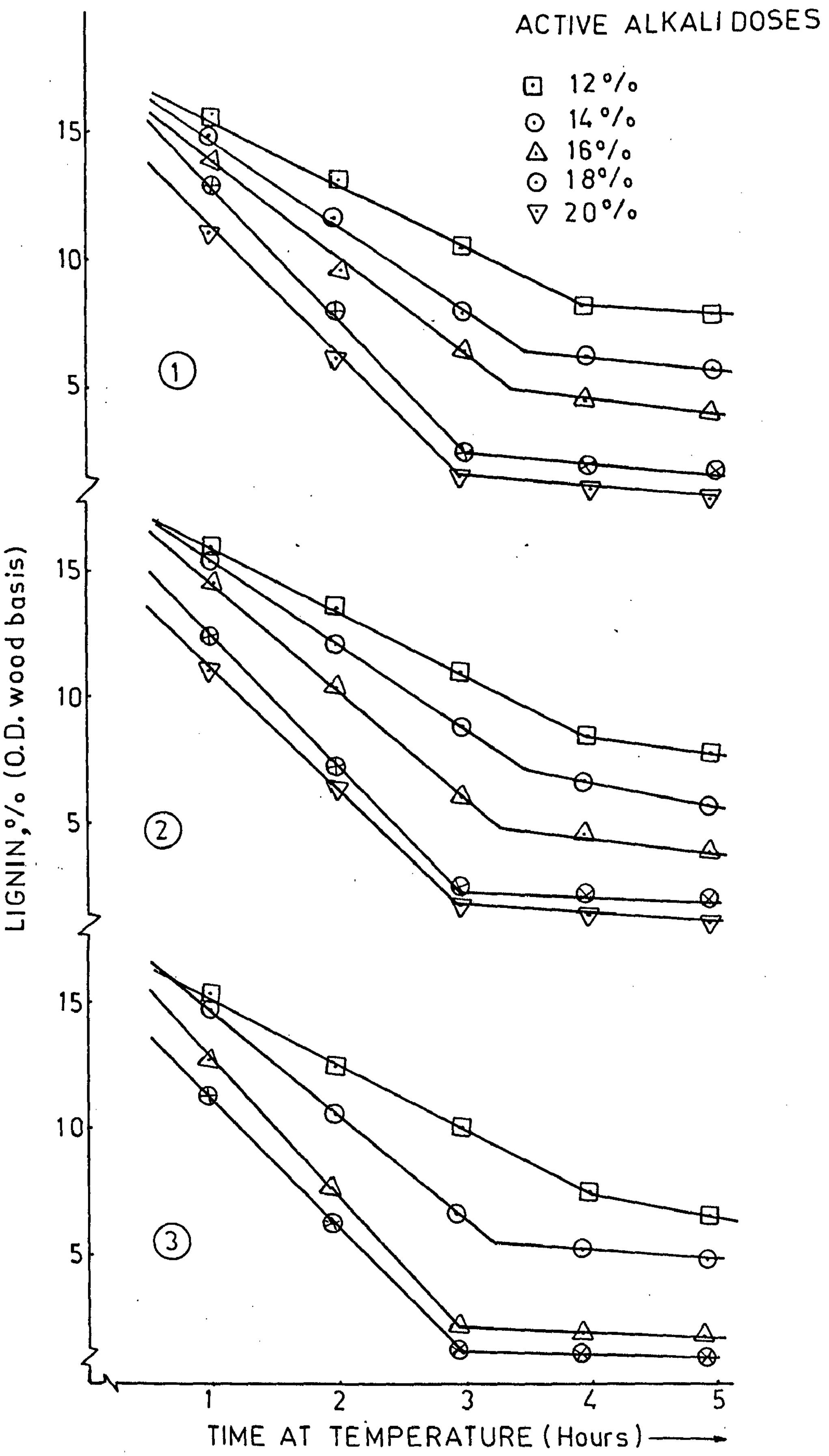


Fig.5·02 A: PLOTS OF RESIDUAL LIGNINS(%)VS. TIME OF REACTION AT 165 °C AT DIFFERENT LEVELS OF ACTIVE ALKALI DURING SODA PULPING OF ① S.sesban ② C.cajan ③ S. aculeata

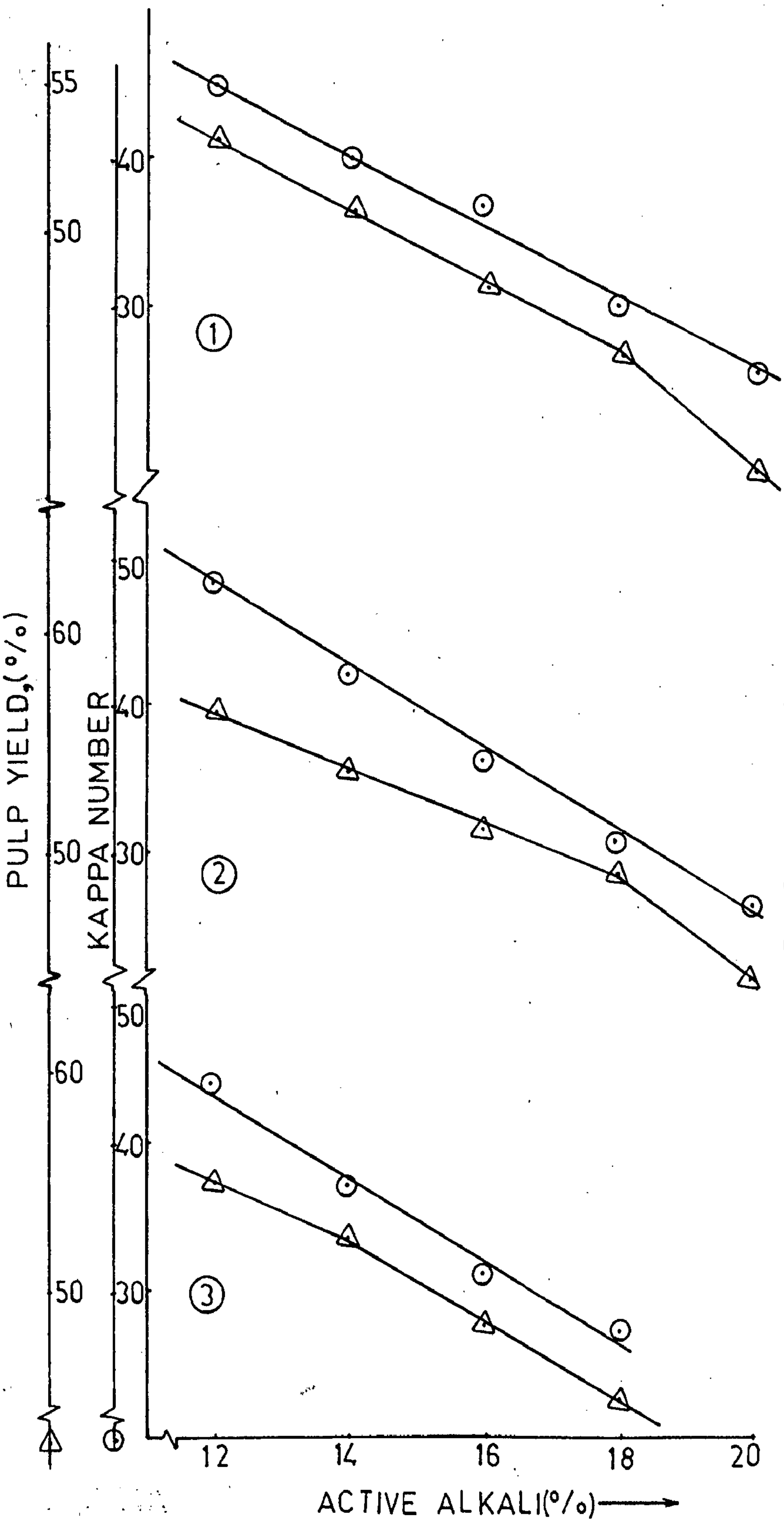


Fig. 5·04 A: PLOTS OF ACTIVE ALKALI(°/o) VS. KAPPA NUMBER AND PULP YIELDS DURING SODA PULPING OF ① S.sesban ② C.cajan AND ③ S, aculeata.

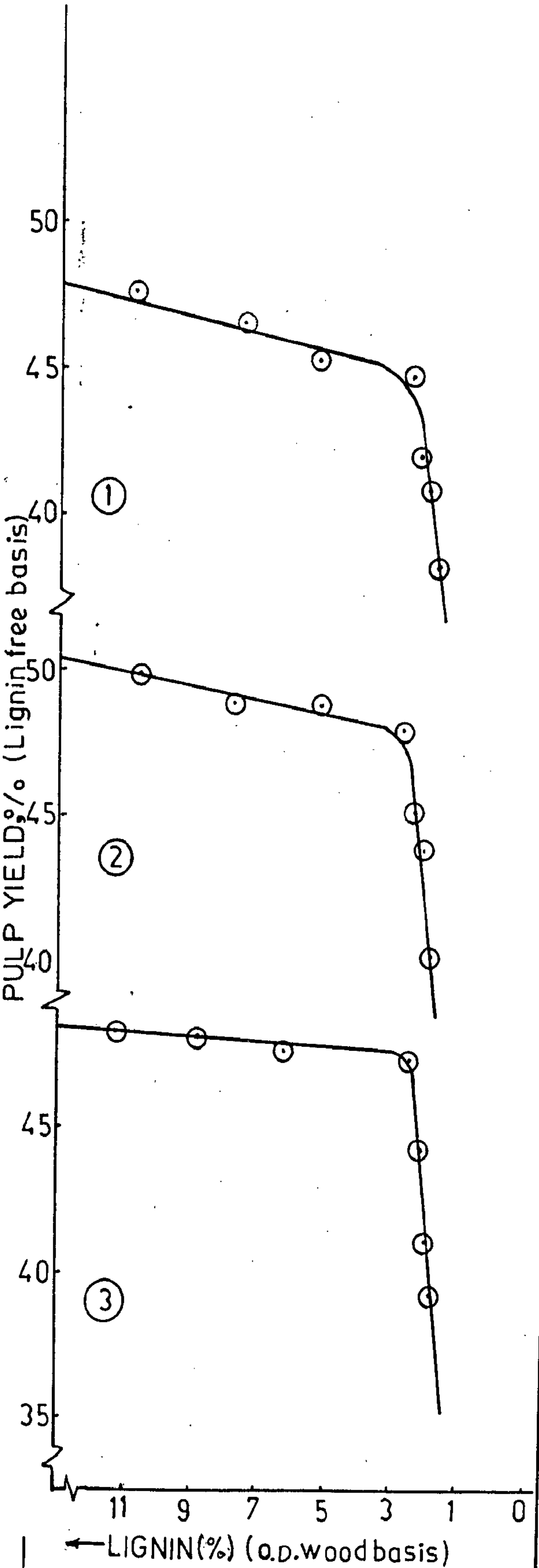


Fig. 5·03A: PLOTS OF LIGNIN(°/o) VS. PULP YIELD(°/o) DURING SODA PULPING OF ① S.sesban ② C. cajan AND ③ S aculeata

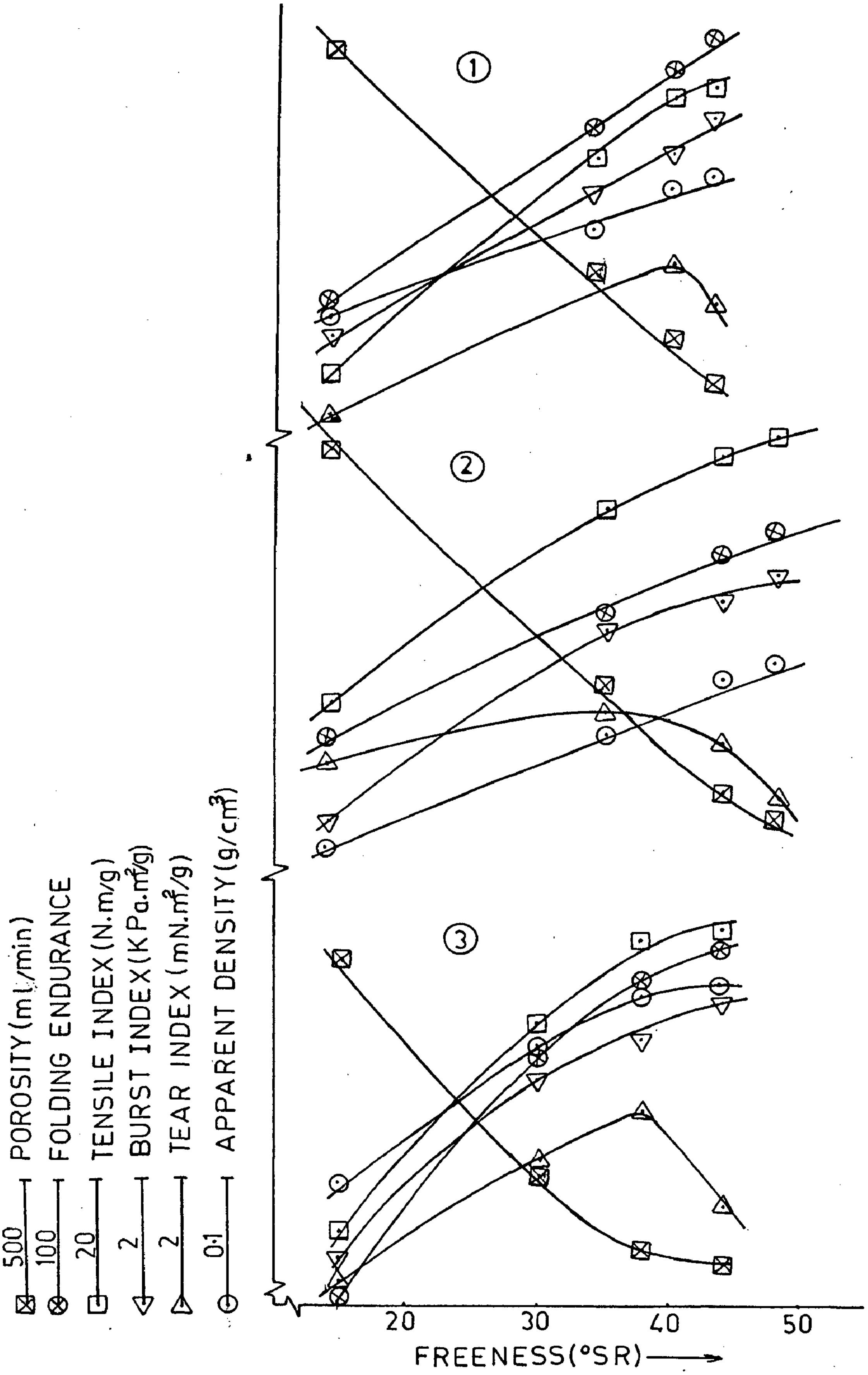


Fig. 5 06A: PLOTS OF PULP FREENESS (°SR) VS. STRENGTH PROPERTIES OF ① S.sesban ② C.cajan AND ③ S.aculeata SODA UNBLEACHED PULPS

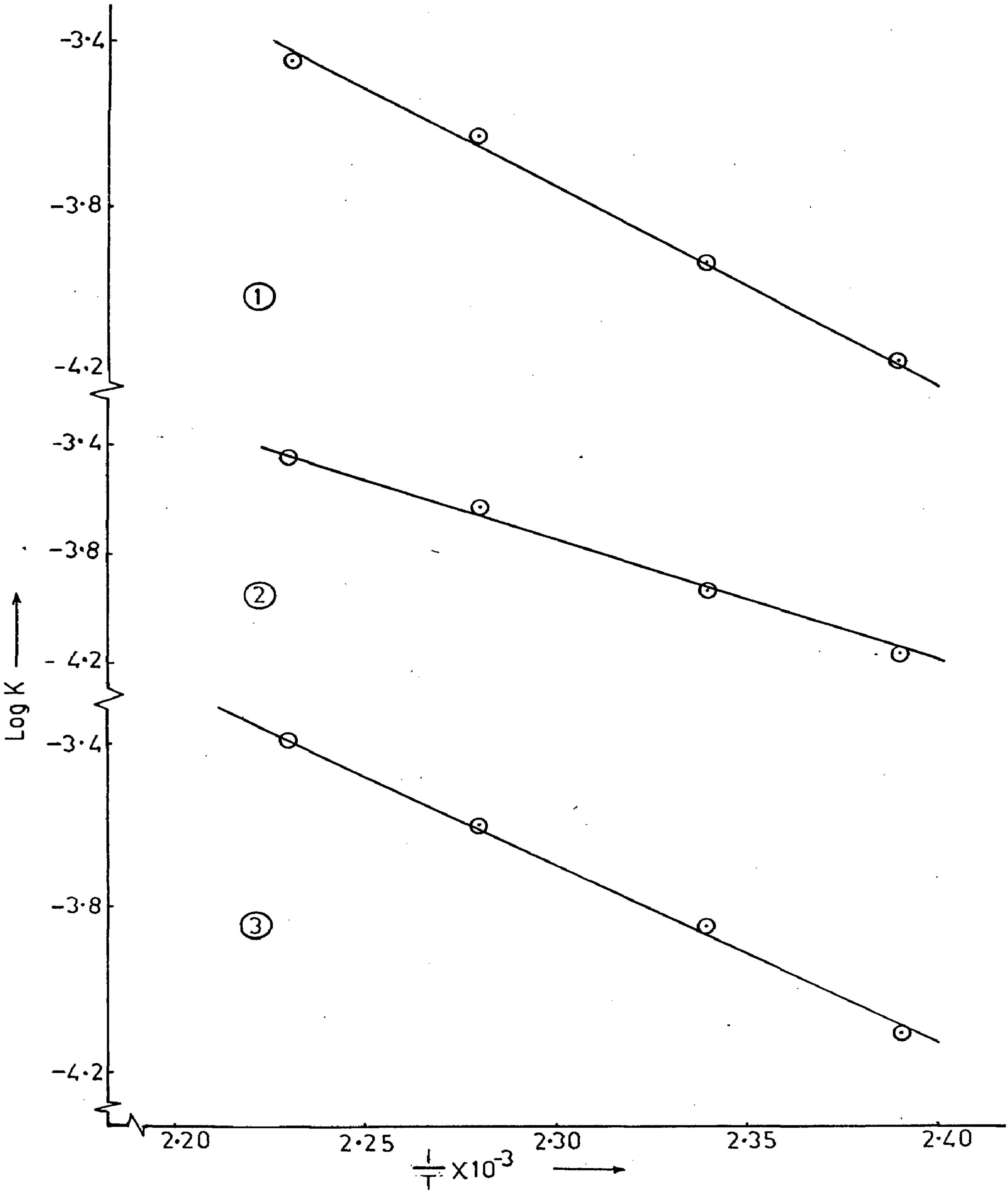


Fig. 5·05A: PLOTS OF LOG RATE CONSTANT (K) VS. RECIPROCAL OF THE ABSOLUTE TEMPERATURE DURING BULK DELIGNIFICATION OF ① S. sesban ② C. cajan AND ③ S. aculeata

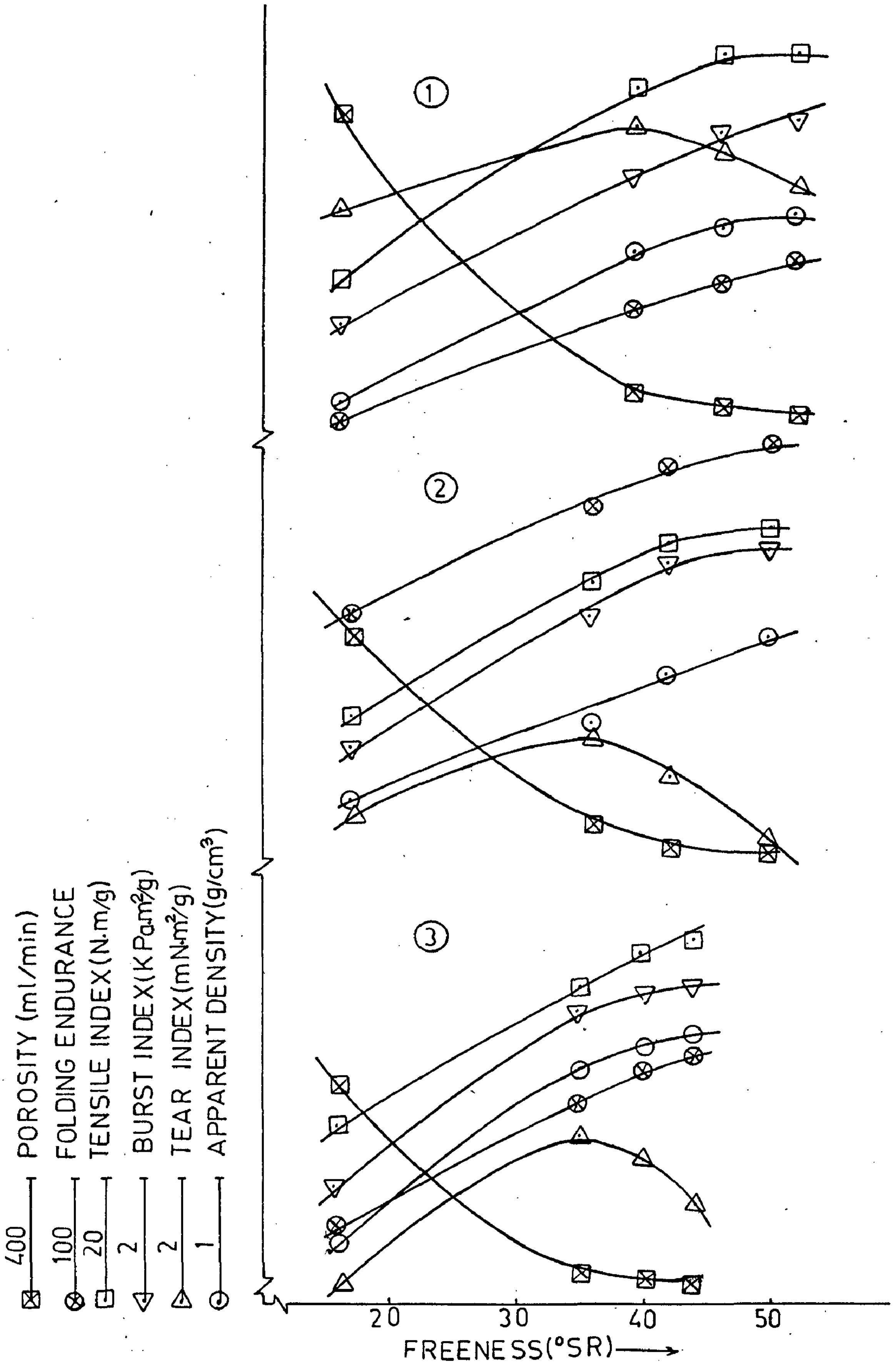


Fig.5 07A: PLOTS OF PULP FREENESS(°SR)VS. STRENGTH PROPERTIES OF ① S.sesban ② C.cajan AND ③ S.aculeata SODA BLEACHED PULPS.

KRAFT PULPING STUDIES:

Pulping converts wood chips into separate fibres, by the chemical reaction between lignin and the active chemical in the cooking liquor, NaOH and Na_2S. The reactions that occur between wood and alkaline cooking liquors are extremely complex and incompletely understood. The solubilisation of lignin obviously requires reduction of polymer size and the formation of hydrophilic groups. Lignin derivatives precipitated from black liquor by acid contain more acidic hydroxyl groups than does native lignin. It appears that the formation of additional hydroxyl groups occurs during cooking possibly from the hydrolysis of methoxyl, from the furan or pyran ring opening or from the breaking of a linkage between lignin and carbohydrate.

At elevated temperatures (over 160 ^{o}C), aqueous alkali hydrolyses many β-0-4 linkages of native lignin, cleaving the polymer chains and contributing to solubility. During alkaline cooking, chemical attack upon hemicellulose and lignin occurs more or less simultaneously, as it does in all commercial cooking processes. Carbohydrates in the spent liquor occur as sodium salts and are degraded in molecular weight such that these residues are not precipitated by acid. The pulping process takes place in a three phase system: (i) the solid phase, consisting of the wood chips:(ii) the liquid phase where moisture is inside the chips, and the chemical solution, or cooking liquor, is outside the chips (early in the cook, at least, these are actually two separate liquid phases): and (iii) the gas phase which is made up, in the case of kraft pulping, of gases located in the lumens of the fibres. Such a system includes not only actual chemical reactions, but also several physical phenomena such as sub division of the solid phase, flow of fluids, diffusional processes, flow of heat, etc.

The addition of the sulfide ion accelerates the rate of delignification, with less damage to the cellulose and hemicellulose. The generally accepted theory postulates that the sulfide brings about episulfide in the propane chains connecting the phenolic groups in lignin molecule. Further, reaction brings about a breaking of the lignin molecule into smaller segments, whose sodium salts are soluble in the cooking liquor. The Na_2S has a further advantage in that it hydrolyses to NaHS and NaOH. As NaOH is consumed in the reaction, more NaOH is made available by this hydrolysis, thus avoiding excessively high concentrations of NaOH in the liquor supplied to the cook.

5.1.EXPERIMENTAL PROCEDURES:

5.1.1.PULPING STUDIES:

5.1.1.1.OPTIMIZATION OF PULPING CONDITIONS:

The methods of raw material preparation are given on page 63. The pulping studies were made in a laboratory WEVERK electrically heated tumbling digester. The cookings for the optimization of kraft pulping conditions were made in small stainless steel bombs containing 100 gms. of oven dried cellulosic raw material. The cooking of S.sesban, S.aculeata and C.cajan were made by maintaining the proper liquor to wood ratio, and with different doses of active alkali(12-20%), different sulphidity levels(10-25%) and at different temperatures (140-170°C). These pulps were then washed, defibred, screened and evaluated.

5.1.1.2.INFLUENCE OF TEMPERATURE:

In the present investigation, the kraft pulping of S.aculeata, S.sesban and C.cajan at 20% sulphidity and at different temperatures ranging from 140-170°C were studied. The S.aculeata was cooked at 14% active alkali dose, while the S.sesban and C.cajan were cooked at 16% active alkali doses. The residual lignin content associated with the pulp(on wood basis) were determined(Table-5.1B) and these were plotted against the cooking time of reaction as shown in fig.5.01B. These curves clearly indicated that the curves could be approximated by two straight line at each temperature investigated. The curves with steeper slopes are related with the rapid solubilisation of bulk of the lignin(bulk delignification) and the curves with more gentle slopes are related with the slow solubilisation of the residual lignin(residual delignification).

Both parts of these curves are having different velocity contants. These plots also clearly indicated that as the temperatures were decreased from 170 -140 °C, the cooking times to reach transition from bulk to residual delignification and the pulp lignin contents corresponding to this transition both increased. The degree of delifnifications were calculated as in the case of soda pulping. These figures (5.06B) also indicated that at lower temperature range the residual lignin contents decreased sharply, while at higher temperature range, the magnitude of decrease in the amount of residual lignin contents were not so pronounced. Moreover at higher temperatures the degradation of carbohydrates fraction also increased and it is not advisable to go for higher temperature beyond 160°C. The nature of the curves after the transition points are almost horizontal straight lines clearly indicating that the bulk delignification phases are over upto these transition points and it is not economical to continue the cooking beyond this optimum temperature. The Arrhenius activation energy of the bulk delignification in kraft pulping of S.aculeata, S.sesban and C.cajan were calculated and reported in Table-5.3B.

5.1.1.3.INFLUENCE OF ALKALI CHARGE:

As indicated above, the kraft pulping of S.aculeata, S.sesban and C.cajan should be terminated at the transition point (i.e. 160 °C) between bulk and residual delignification phases. In rapid kraft pulping, the consumption of active alkali was found to be constant over a wide range of alkali charge(48). Further more it was found that the excessive active alkali charge which remains unconsumed during the course of pulping, adversly decreases the pulp viscosity. The plots of pulp yields Vs. active alkali doses (fig.5.04B) also indicated that in case of kraft pulping of S.aculeata, an active alkali charge beyond 14%, while in case S.sesban and C.cajan, an active alkali dose beyond 16% degrades the carbohydrates fraction quite severely, thereby decreasing the pulp yields. The plots of Kappa numbers Vs. active alkali doses (Fig. 5.04B) also indicated the degree of delignification during the course of kraft pulping

The yield drop of the pulps (calculated free of lignin) were studied at 160 °C using 14% active alkali charge for S.aculeata, and 16% for S.sesban and C.cajan at 20% sulphidity. The results of this series of experiments are shown in fig. 5.03B. At these reaction conditions, all points approximate the same line consisting of two straight line portions with distinct slopes connected by a sharp bending in the range of transition from bulk to residual delignification. During bulk delignification of pulps, the ratio of lignin to carbohydrates solubilised was about 1:0.63, 1:0.60 and 1:0.67 for S. aculeata, S. sesban and C. cajan respectively, whereas during residual delignification this ratio was about 1:6.8, 1:6.4 and 1:7.2 for S. aculeata, S. sesban and C. cajan respectively, i.e. about eleven times greater.

In accordance with fig. 5.03B, the cooking temperature had relatively little influence upon the ratio of lignin to carbohydrates solubilised during the course of bulk delignification. This supported the suggestion that in the alkaline delignification of wood there is a definite relationship between the solubilisation of lignin and cellulosic portions (40). The high loss of carbohydrates relative to the dissolved lignin found in the residual delignification suggested that commercial kraft pulping should be limited to the range of bulk delignification only.

The graphs were also plotted between sulphidity and Kappa number(Fig.5.05B). These curves clearly indicated that there is a sharp decrease in Kappa number upto a sulphidity levels of 20% and beyond this level of sulphidity, the effect of lowering in Kappa number is not so much pronounced as in the case of lower level of sulphidity. It can be said that beyond this particular level of sulphidity, the effect of using high sulphidity is almost diminished.

5.1.2.KRAFT PULPING OF S.aculeata, S.sesban AND C.cajan:

The kraft pulping of S. aculeata, S. sesban and C. cajan were made in laboratory WEVERK electrically heated tumbling digester. The cooking of S.aculeata was done at 14% active alkali dose (as Na_2O), while the cooking of S.sesban and of S.aculeata, S.sesban and C.cajan. An optimum kappa number around 30 was achieved at an active alkali charge of 14% in case of S. aculeata, while in case of S.sesban and C.cajan, this particular level was achieved at an active alkali charge of 16%.

5.1.1.4.INFLUENCE OF SULPHIDITY:

In order to know the influence of sulphidity during the course of kraft pulping of S.aculeata, S. sesban and C. cajan, the cookings were done at 160 °C with 14% active alkali charge in case of S. aculeata, while in case of S.sesban and C. cajan, 16% active alkali charge using different levels of sulphidity viz., 10%, 15%, 20% and 25%, and the results of these experiments (Table-5.2B) have been plotted in fig. 5.02B. The curves follows the same pattern as in the case of influence of temperatures. The steeper slope of the curves represented the rapid solubilisation of bulk of the lignin and the other part of the curve represented the residual delignification.

These curves clearly indicated that at lower sulphidity levels, the variation in the amount of residual lignin contents is too much in comparison to variation at higher sulphidity levels. There were practically no variation in the amount of residual lignin contents beyond 20% sulphidity level, therefore 20% sulphidity may be considered as optimum level of sulphidity, as there is practically no gain of using higher doses of sulphidity.

The degree of delignifications were calculated at transition points. These were calculated after 1.5 hrs. for S.aculeata and after 2 hrs. for S. sesban and C.cajan at 10, 15, 20 and 25% sulphidity levels. The corresponding values of degree of delignifications at these particular levels of sulphidity are 46.44, 62.76, 89.19 and 90.30 for S.aculeata, and 46.18, 60.68, 87.65 and 89.58 for S.sesban, and 53.26, 73.29, 88.78 and 89.58 for C.cajan respectively. The degree of delignification increased with an increase in sulphidity levels and it seems that there were practically no difference in the degree of delignification at 20% and 25% sulphidity levels. Hence it is not advisable to use sulphidity beyond 20% for kraft pulping S.aculeata, S.sesban and C.cajan.

C.cajan were made at 16% active alkali dose (as Na_2O). The liquor to wood ratio of 3.5:1 was maintained for S.aculeata and 3:1 for S. sesban and C. cajan. These studies were conducted at a temperature of 160 °C using 20% sulphidity. After completion of the cooking, the pulps were washed on a laboratory flat stationary screen having 100 mesh wire bottom for the removal of residual cooking chemicals, and further disintigrated in the laboratory disintigrator. The disintigrated pulps were screened through a vibratory flat WEVERK screen with 0.15 mm slits. The screened pulps were further evaluated and the results of over-all pulpings are reported in Table-5.4B.

5.1.3.KRAFT-ANTHRAQUINONE PULPING:

The use of anthroquinone (AQ)as an additive for kraft pulping to increase pulping efficiency and pulp yield is now well known. Its effectiveness however is considerably species dependent and for this reason a study was initiated to evaluate its potential as an additive for kraft pulping of these non-wood fibrous plants. The kraft-AQ pulping studies on S. aculeata, S. sesban and C. cajan have been done by adding a small amount of AQ(0.1%) on O.D. wood basis. The pulping conditions and results of kraft-AQ pulping are tabulated in Tables-5.3B& 5.7B.

5.1.4.BLEACHING STUDIES:

The kraft and kraft-AQ unbleached pulps of S. aculeata, S. sesban and C. cajan were bleached using CEHH bleaching sequence. The pulp bleaching conditions alongwith their results are tabulated in Table-5.5B.

5.1.5.FIBRE CLASSIFICATION:

The fibre classification studies of S. sesban, C. cajan and S. aculeata kraft pulps were made with the help of Bauer- McNett fibre classifier with mesh screen numbers 20, 60, 80 and 120. The results are reported in table 5.10B. The photomicrographs of unbleached and bleached, unbeaten and beaten pulps fibres of these plants are shown in annexure on page166. to 171.

5.1.6.PULP EVALUATION STUDIES:

The unbleached and bleached pulps were separately beaten in PFI(73) mill to different freeness levels. Standard sheets of 60 g/m^2 were made on British sheet forming machine; and evaluated for various physical strength properties as per IS method(32) The results of pulp evaluation of unbleached and bleached pulps both are reported in Tables-5.6B to 5.9B.

5.1.7.SPENT LIQUOR CHARACTERISTICS:

The spent liquors obtained as a result of kraft pulping of S. aculeata, S. sesban and C. cajan were analysed for its total solid contents, residual alkali, organic and inorganics and calorific value as per TAPPI standard method and the results are recorded in Table 5.11B.

5.2.RESULTS AND DISCUSSIONS:

The results of pulping experiment as indicated in table 5.3B revealed that the chemical requirements are 14% to 16% (as Na_2O) for S. aculeata and 16%to 18% (as Na_2O) for S. sesban and C. cajan were required to get pulps with 30-22 Kappa number at a 'H' factor values of about 750 in case of S. aculeata and for the S. sesban and C. cajan the 'H' factor value is 947. The results of these experiments clearly suggested that the chemical requirements are about 2-3% less than that required for the pulping of bamboo and many other tropical hardwood, incase of S. aculeata. Besides the pulping conditions were mild, the total pulp yield was around 46-50% in the Kappa number range of 22-30, quite comparable to that of bamboo and many tropical hardwoods.

The unbleached S. aculeata, S. sesban and C. cajan pulps showed excellent response to bleaching by CEHH sequence for obtaining a high degree of brightness. In these bleaching studies about 25% chlorine of the kappa number was applied, during chlorination stage, 60 to 70% chlorine of the total chlorine demand was used, which was almost totally consumed. The alkali requirements in the extraction stage were about 1.5%. The application of about 1.5 to 2% chlorine as calcium hypochlorite in the first hypochlorite stage(H_1) gave pulps of around 75%(Elrepho) brightness. To get pulps of better brightness, CEHH sequence was applied. In hypochlorite second stage(H_2) about 1% chlorine (as calcium hypochlorite) was used, which gave pulps of 78 to 80%(Elrepho) brightness. It is quite certain that about 1.0 to 1.5% less chlorine as calcium hypochlorite was required in the hypochlorite stages than that required for bamboo or tropical hardwood pulps for bleaching upto the same degree of brightness. The pulps viscosity values are quite comparable to that of bamboo and other tropical hardwoods.

The results of pulp evaluation as indicated in Tables-5.6B to 5.9B revealed that the pulps of these non-wood fibrous plants beat easily. The initial freeness and drainage time of both the unbleached and bleached pulps are found to be higher, when compared to that of bamboo or hardwood pulps. The freeness of unbeaten pulps were found to be around 12-15 ^{o}SR. The sheets formed were of higher density and even the hand sheets of unbeaten pulps were having apparent sheet density around 0.62 to 0.70 gm/cm^3, which is the value obtained around 32 ^{o}SR freeness in the case of bamboo pulps.

The plots of pulp freeness versus apparent density, tear, tensile, burst, folding endurance and porosity of S. aculeata, S. sesban and C. cajan unbleached pulps at various levels of freeness have shown in fig.5.07B, while the same plots for bleached S. aculeata, S. sesban and C. cajan pulps have been shown in fig.5.08B. These plots clearly indicated that the apparent density, burst index, folding endurance, tensile index are in direct proportion with the freeness of the pulps i.e. all these properties showed an improving trend with a result of an increase in freeness upto a certain level of freeness, while the tear index of both the unbleached and bleached pulps of S. aculeata, S. sesban and C. cajan first showed a little enhancement and then continously decreased. The porosity is in indirect proportion with the freeness of pulps i.e. porosity showed a continuous decreasing trend as a result of an increase in freeness level. On the basis of these plöts; it can be concluded that both the unbleached S. aculeata, S. sesban and C. cajan pulps showed good strength characteristics except tear, upto a certain level of freeness and beyond this the trend reverse. An optimum freeness level for S. aculeata, S. sesban and C. cajan pulps may be considered around 42 ± 2 °SR and beyond this the beating should not be continued.

A major factor in determining the profitability of kraft-AQ pulping is the magnitude of the yield increase obtained with AQ at a given Kappa number, as this estra pulp is obtained at no extra cost apart from the cost of the AQ. To obtain the same Kappa number in kraft-AQ pulping, less cooking time is required in comparison with kraft pulping. The bleached kraft-AQ pulps have low value of brightness than the kraft pulps. The S. aculeata, S. sesban and C. cajan kraft-AQ pulps showed a slightly improvement in all the strength properties except tearing strength.

The results of kraft spent liquors analysis obtained as a result of the kraft pulping of S. aculeata, S. sesban and C. cajan under the above optimum conditions are given in Table-5.11B. The calorific values of these spent liquors are little higher than bamboo kraft spent liquor due to the presence of high solid contents. The silica contents in the spent liquors was found to be very low in comparison to bamboo kraft spent liquor. The less silica contents and higher calorific values of these spent liquors are an advantageous factor towards the energy conservation in chemical recovery process.

5.3.CONCLUSION:

In alkaline delignification of these non-wood fibrous raw materials, two distinct overall mechanisms are involved and each of which resembled a first order reaction pattern. The mechanism with greater rate constants was found to be related to bulk delignification and the other to residual delignification. The Arrhenius activation energy of bulk delignification in kraft pulping of S. aculeata, S. sesban and C. cajan were found around 81.59, 90.79 and 86.69 KJ/mole respectively, these values are quite low in comparison to softwoods and hardwoods.

The pulps showed good response towards bleaching and the chemical consumption during bleachings were low. The CEHH bleaching sequence was used to get pulps with higher brightness.

The S. aculeata pulp beat fast in comparison to S. sesban and C. cajan pulps and these pulps should not be beaten for a long time or to a very high degree of freeness in order to preserve tear and opacity. The pulps freeness in the range of 42 ± 2 ^{o}SR seems to be optimum for the development of strength properties, thereby showing a net saving of substantial amount of energy during beating operation. Both the unbleached and bleached kraft pulps of S. aculeata, S. sesban and C. cajan showed good strength properties except tear. The use of AQ in conjunction with the kraft process to produce bleachable grade pulps from these non-wood fibrous plants is beneficial in increasing the rate of delignification and enhancing the yield of pulps. The addition of small amounts of AQ(0.1%) showed the pulp yield gain about 2%. There were no significant differences between the strength properties of the kraft-AQ pulps and kraft pulps. The only difference was a slight decrease in tearing strength.

The total solid contents in the kraft spent liquors of these non-wood fibrous plants are towards little higher side thereby increasing the calorific values. The silica contents were also found to be quite low. The less silica contents and higher calorific values of these spent liquors are an advantageous factor towards the energy conservation in chemical recovery processes.

Table-5.1B:Effect Of Temperature(140°C to 170°C) at 20% Sulphidity And 16% Active Alkali For S.sesban And C.cajan, 14% Active Alkali For S.aculeata During Kraft Pulping.

Sl. No.	Time at Temp. (Hrs)	TEMPERATURES °C														
		140			150			160						170		
		Residual lignin(%)			Residual lignin(%)			Residual lignin(%) and yield(%)						Residual lignin(%)		
		Sesbania sesban	Cajanus cajan	Sesbania aculeata	Sesbania sesban	Cajanus cajan	Sesbania aculeata	S.sesban		C.cajan		S.aculeata		Sesbania sesban	Cajanus cajan	Sesbania aculeata
								(R)	(Y)	(R)	(Y)	(R)	(Y)			
1.	0.5	---	---	17.20	---	---	15.70	--	--	--	--	13.70	--	---	---	11.25
2.	1.0	13.76	13.50	13.50	12.24	12.00	12.00	9.50	55.4	9.28	57.0	8.20	56.0	8.76	8.50	6.64
3.	1.5	12.00	11.73	10.00	9.25	9.00	7.25	6.70	52.5	6.62	54.8	2.14	49.8	5.14	5.00	1.85
4.	2.0	10.52	10.20	6.75	7.25	7.00	4.30	2.18	47.0	2.10	50.2	2.00	47.5	1.70	1.82	1.68
5.	2.5	8.60	8.12	6.50	4.95	4.50	3.80	2.00	44.6	1.84	47.5	1.86	44.0	1.65	1.60	1.46
6.	3.0	6.87	6.50	6.20	3.75	3.50	3.70	1.75	41.8	1.78	44.0	1.80	42.9	1.58	1.48	1.28
7.	4.0	6.35	6.14	5.75	3.70	3.38	3.50	1.60	40.0	1.67	40.8	1.65	39.6	1.41	1.20	1.16
8.	5.0	6.00	5.89	5.38	3.50	3.10	3.20	1.48	37.0	1.51	38.7	1.40	37.2	1.24	0.98	1.00

R = Residual lignin & Y = Pulp yield.

Liquor to wood ratio = 3:1 for S.sesban and C.cajan & 1:3.5 for S.aculeata

Time from 30 °C to 105°C = 45 minutes

Time at 105°C = 45 minutes

Time from 105°C to maximum temperature = 45 minutes.

Table-5.2B:Effect of Sulphidity (10% to 25%) At 16% Active Alkali (As Na_2O) For S. sesban and C. cajan, 14% Active Alkali for S. aculeata During Kraft Pulping.

Sulphidity (%)	Time at 160 °C (Hrs.)	Sesbania sesban		Cajanus cajan		Sesbania aculeata	
		Residual lignin(%)	Kappa no.	Residual lignin(%)	Kappa no.	Residual lignin(%)	Kappa no.
10	0.5	---	---	---	---	16.20	---
	1.0	13.20	---	13.40	---	13.50	---
	1.5	11.50	---	11.20	---	10.60	48.5
	2.0	9.50	44.2	8.75	46.0	8.50	---
	2.5	7.30	---	6.80	---	6.00	---
	3.0	5.50	---	6.20	---	5.80	---
	4.0	5.20	---	5.70	---	5.38	---
	5.0	5.00	---	5.20	---	5.00	---
15	0.5	---	---	---	---	15.40	---
	1.0	12.00	---	11.96	---	11.86	---
	1.5	9.47	---	8.75	---	7.37	39.0
	2.0	6.94	38.0	5.00	36.5	4.25	---
	2.5	4.38	---	4.50	---	3.70	---
	3.0	4.00	---	4.20	---	3.50	---
	4.0	3.85	---	3.70	---	3.38	---
	5.0	3.50	---	3.25	---	3.12	---
20	0.5	---	---	---	---	13.70	---
	1.0	9.50	---	9.28	---	8.20	---
	1.5	6.70	---	6.62	---	2.14	30.4
	2.0	2.18	31.0	2.10	29.8	2.00	---
	2.5	2.00	---	1.84	---	1.86	---
	3.0	1.75	---	1.78	---	1.80	---
	4.0	1.60	---	1.67	---	1.65	---
	5.0	1.48	---	1.61	---	1.40	---
25	0.5	---	---	---	---	12.00	---
	1.0	8.15	---	8.10	---	7.51	---
	1.5	4.75	---	4.91	---	1.92	27.4
	2.0	1.89	28.7	1.95	26.9	1.80	---
	2.5	1.84	---	1.72	---	1.67	---
	3.0	1.67	---	1.70	---	1.61	---
	4.0	1.55	---	1.54	---	1.43	---
	5.0	1.10	---	1.15	---	0.97	---

Time from 30 °C to 105 °C = 45 minutes, time at 105 °C = 45 minutes.
Time from 105°C to 160 °C = 45 minutes.

Liquor to wood ratio = 3:1 for S. sesban and C. cajan
=3.5:1 for S. aculeata.

Table-5.3B:Kraft And Kraft-AQ Pulping Conditions Of S. sesban, C. cajan And S. aculeata.

Sl. No.	Particulars	Kraft Pulping					Kraft-AQ
1.	Sulphidity %	20	20	20	20	20	20
2.	Active alkali as Na_2O %	12	14	16	18	20	14* 16
3.	Bath ratio	1:3 1:3.5*	1:3 1:3.5*	1:3 1:3.5*	1:3 1:3.5*	1:3 1:3.5*	1:3 1:3.5*
4.	Initial pH	13.30	13.40	13.40	13.42	13.42	13.40
5.	Cooking schedules						
	30 °C to 105 °C,min.	45	45	45	45	45	45
	at 105 °C,min.	45	45	45	45	45	45
	105 °C to 160 °C, min.	45* 60	45* 60	45	45	45	45
	at 160 °C, min.	90* 120	90* 120	90* 120	90* 120	90* 120	60* 90
6.	Results						
	S. sesban						
	Unscreened pulp yield %	54.2	52.5	48.4	45.0	38.9	48.2
	Screened pulp yield %	51.6	49.4	47.0	43.8	38.2	47.9
	Kappa no.	40.0	35.0	31.0	22.3	17.5	32.4
7.	C. cajan						
	Unscreened pulp yield %	55.7	54.2	51.0	48.9	40.8	52.0
	Screened pulp yield %	52.9	51.6	50.2	47.7	40.0	51.3
	Kappa no.	41.0	36.0	29.5	23.0	18.4	30.0
8.	S. aculeata						
	Unscreened pulp yield %	56.4	51.2	46.5	42.0	---	51.4
	Screened pulp yield %	52.0	49.8	45.7	41.9	---	50.7
	Kappa no.	38.2	30.4	24.2	20.0	---	31.0

* For Sesbania aculeata.

Table-5.4B:First Order Rate Constant For Bulk Delignification in Kraft Pulping Of S. sesban, C. cajan And S. aculeata.

Sl.No.	Temperature °C	KS^{-1}		
		S. sesban	C. cajan	S. aculeata
1.	140	0.8676×10^{-4}	0.8956×10^{-4}	1.3653×10^{-4}
2.	150	1.6632×10^{-4}	1.5993×10^{-4}	2.1750×10^{-4}
3.	160	3.5620×10^{-4}	3.6439×10^{-4}	4.5698×10^{-4}
4.	170	4.8618×10^{-4}	4.7979×10^{-4}	5.5016×10^{-4}
5.	Activation energy	21.72 Kcal/mole 90.79 KJ/mole	20.74Kcal/mole 86.69 KJ/mole	19.52 Kcal/mole 81.59 KJ/mole

Table-5.5B:Bleaching Conditions And Results of S.sesban, C.cajan And S.aculeata Kraft And Kraft-AQ Pulps.

Sl. No.	Particulars	S. sesban		C. cajan		S. aculeata	
		Kraft	Kraft-AQ	Kraft	Kraft-AQ	Kraft	Kraft-AQ
1.	Unbleached pulp Kappa no.	31.00	32.20	29.50	30.00	30.40	31.00
2.	Chlorination stage(C)						
	Amount of Cl_2 added on pulp %	4.60	5.12	4.65	4.70	4.85	4.60
	Amount of Cl_2 consumed on pulp %	4.59	5.10	4.63	4.68	4.82	4.58
	Amount of Cl_2 consumed on Cl_2 basis %	99.78	99.60	99.00	99.50	99.28	99.56
	Final pH	1.95	1.90	1.84	1.92	1.74	1.90
3.	Alkali extraction stage(E)						
	NaOH added on pulp %	1.60	1.50	1.50	1.50	1.50	1.50
	Initial pH	11.46	11.40	11.30	11.39	11.36	11.40
	Final pH	10.20	10.26	10.00	10.12	10.20	10.14
4.	Hypochlorite Ist Stage(H_1)						
	Hypo added as available Cl_2 on pulp %	1.78	1.90	1.80	1.80	1.40	1.85
	Hypo consumed as available Cl_2 on pulp %	1.75	1.84	1.74	1.76	1.38	1.77
	Hypo consumed on Cl_2 basis%	98.00	96.80	96.60	97.77	98.50	98.00
	Final pH	8.10	7.90	7.80	7.90	7.70	8.00
5.	Hypochlorite 2nd Stage(H_2)						
	Hypo added as available Cl_2 on pulp %	0.70	0.77	0.70	0.70	0.90	0.75
	Hypo consumed as available Cl_2 on pulp %	0.68	0.71	0.64	0.65	0.82	0.71
	Hypo consumed on Cl_2 basis%	97.00	92.20	90.00	92.80	91.00	94.66
	Final pH	8.00	7.80	7.80	8.00	7.80	7.90
6.	Total Cl_2 added on pulp%	7.08	7.79	7.15	7.20	7.15	7.20
7.	Total Cl_2 consumed on pulp %	7.02	7.65	7.01	7.09	7.02	7.06
8.	Bleaching losses %	9.60	9.80	9.20	9.60	9.00	9.30
9.	Bleached pulp yield %	42.50	43.20	45.60	46.38	45.26	46.00
10.	Pulp brightness(Elrepho)%	76.80	76.00	79.80	78.00	78.70	77.90
11.	Viscosity, C.E.D.(0.5%)cp	11.30	11.50	11.60	11.80	12.40	12.50

Bleaching conditions	C	E	H_1	H_2
Consistency %	3	10	9	9
Temperature °C	27±2	55±2	45±2	45±2
Time(minute)	25	120	60	120

Table-5.6B:Strength Properties Of S.sesban, C.cajan And S.aculeata Kraft Unbleached Pulps.

Plant species	PFI Revolution (No.)	Freeness (^oSR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index ($mN.m^2/g$)	Burst index ($KPa.m^2/g$)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min.)	Folding endurance Köhler Molin
Sesbania	0	13	3.8	0.58	2.87	0.82	20.15	1400	15
sesban	1000	28	10.2	0.67	4.50	3.95	41.46	620	233
	1700	39	16.0	0.74	5.64	4.70	54.45	220	307
	2300	46	18.5	0.77	4.85	5.14	60.58	105	352
Cajanus	0	15	4.4	0.65	3.40	0.88	30.58	950	15
cajan	1200	30	14.3	0.79	4.91	4.87	52.54	300	262
	1700	38	17.6	0.82	5.62	5.49	62.83	190	320
	2200	48	21.5	0.85	4.70	5.40	59.98	80	350
Sesbania	0	14	4.2	0.63	4.35	1.93	37.38	815	16
aculeata	1400	34	16.1	0.78	5.78	6.12	76.51	230	524
	1650	38	17.4	0.82	6.20	6.71	78.68	120	620
	2000	45	19.8	0.86	5.30	6.90	81.00	60	662
		250 CSF(62)	18.0	0.85	7.01	6.82	8.00km	0	1413 (MIT)

Table-5.7B:Strength Properties Of S.sesban, C.cajan And S.aculeata Kraft-AQ Unbleached Pulps.

Plant species	PFI Revolution (No.)	Freeness (^oSR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index ($mN.m^2/g$)	Burst index ($KPa.m^2/g$)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min.)	Folding endurance Köhler Molin
Sesbania	0	15	4.0	0.66	2.94	0.98	19.91	1600	12
sesban	1000	30	12.4	0.73	4.48	4.10	46.70	700	224
	1650	35	14.5	0.78	5.14	4.77	53.36	260	280
	2100	44	17.0	0.79	4.52	5.26	61.23	120	320
Cajanus	0	15	4.4	0.67	3.88	1.29	33.42	700	18
cajan	1300	30	14.4	0.72	4.12	4.65	55.42	510	267
	1600	36	17.0	0.78	4.90	5.13	62.07	170	280
	1850	42	19.0	0.80	4.48	5.59	66.18	90	345
Sesbania	0	15	4.3	0.64	4.65	1.42	33.39	650	12
aculeata	1400	34	16.1	0.77	4.96	6.20	77.12	260	478
	1700	40	18.0	0.83	5.92	6.83	81.20	110	598
	2050	46	20.1	0.87	4.80	6.98	82.70	65	670

Table-5.8B:Strength Properties Of S.sesban, C.cajan And S.aculeata Kraft Bleached Pulps.

Plant species	PFI Revol-ution (No.)	Free-ness (^{o}SR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index (mN.m^2/g)	Burst index (KPa.m^2/g)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min)	Folding endurance Köhler Molin	Brightness (Elrepho) (%)	Opacity (%)
Sesbania sesban	0	14	4.0	0.60	2.75	1.06	20.87	900	15	76.2	90.1
	800	30	13.2	0.73	4.27	3.39	46.30	225	96	73.2	88.3
	1200	35	15.4	0.76	5.21	4.20	51.36	150	118	71.5	84.7
	1450	45	19.6	0.78	4.20	4.48	55.50	110	135	69.7	82.0
Cajanus cajan	0	17	4.6	0.66	2.59	1.25	31.42	800	16	79.5	92.0
	800	35	17.0	0.80	4.40	3.80	47.23	220	150	73.8	88.1
	1000	40	19.2	0.83	4.50	4.24	52.00	160	190	72.5	85.3
	1200	45	21.6	0.86	4.20	4.75	57.10	80	187	70.6	82.2
Sesbania aculeata	0	15	4.2	0.66	4.10	1.79	37.59	530	18	78.6	89.6
	950	39	18.4	0.79	4.78	5.15	63.60	75	282	74.4	86.2
	1150	45	21.0	0.84	4.40	5.82	70.45	60	330	71.0	82.4
	1400	60	52.1	0.89	3.60	5.75	68.16	55	310	65.2	76.5
		250 CSF(62)	19.0	0.90	6.08	6.12	5.50 km	68	891 (MIT)	---	68.0

Table-5.9B:Strength Properties Of S.sesban, C.cajan And S.aculeata Kraft-AQ Bleached Pulps.

Plant species	PFI Revolution (No.)	Freeness (°SR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index (mN.m^2/g)	Burst index (KPa.m^2/g)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min.)	Folding endurance Köhler Molin	Brightness (Elrepho) (%)	Opacity (%)
Sesbania	0	16	4.1	0.68	2.57	1.10	22.34	1150	10	75.3	90.4
sesban	900	32	13.0	0.75	3.50	3.42	46.94	600	85	72.4	86.2
	1500	42	17.6	0.76	4.70	4.30	50.75	230	110	69.4	83.6
	1700	46	20.4	0.80	4.06	4.56	55.82	120	122	68.8	82.4
Cajanus	0	17	4.6	0.72	2.42	1.52	34.30	650	14	78.0	91.6
cajan	800	34	16.8	0.80	3.90	3.72	51.20	480	92	74.6	89.0
	1100	43	20.6	0.84	4.28	4.35	57.51	190	165	71.8	85.4
	1200	46	21.7	0.86	4.10	4.82	58.94	110	176	69.6	82.0
Sesbania	0	17	4.6	0.65	4.50	1.65	34.00	600	16	78.0	89.0
aculeata	700	33	16.5	0.76	4.98	4.41	58.40	140	194	75.2	85.7
	900	39	18.4	0.80	4.67	4.87	65.60	90	278	72.6	84.0
	1150	46	21.3	0.86	4.25	5.90	72.25	60	320	70.2	83.0

Table-5.10B:Bauer- McNett Fibre Classification Of Kraft Pulps.

Sl.No.	Mesh size	S. sesban Un-bleached (%) $13^{o}SR$ Kappa no. 31	S. sesban Bleached (%) $14^{o}SR$	C.cajan Un-bleached (%) $15^{o}SR$ Kappa no. 29.5	C.cajan Bleached (%) $17^{o}SR$	S. aculeata Un-bleached (%) $14^{o}SR$ Kappa no. 30.4	S. aculeata Bleached (%) $15^{o}SR$
1.	+20	16.4	3.2	13.5	2.5	14.8	2.9
2.	-20+60	44.5	37.1	46.4	36.8	47.3	39.0
3.	-60+80	21.2	26.0	21.0	28.4	22.5	27.6
4.	-80+120	7.2	13.5	6.6	13.0	8.0	12.1
5.	-120	10.7	20.2	12.5	19.3	9.4	18.4

Table-5.11B:Kraft Spent Liquor Characteristics Of S.sesban, C.cajan And S.aculeata.

Sl. No.	PARTICULARS	VALUES S.sesban	C. cajan	S.aculeata	S.aculeata (62)	Bamboo (34)
1.	Black liquor solids %	27.10	25.50	28.37	19.40	18.80
2.	Residual active alkali gpl	3.50	3.60	3.60	4.00	4.20
3.	Inorganic as NaOH %	29.26	36.45	35.20	34.40	35.00
4.	Organic %	70.74	63.55	64.80	65.60	65.00
5.	Silica %	3.06	3.16	3.32	---	---
6.	Calorific value KJ/kg.	14567	14538	14692	12218	13961
7.	Brook field viscosity at 30 °C Lv spindle no.1 cp	14.50	14.00	14.20	13.00	14.80
8.	pH of liquor at 30 °C	10.20	10.30	10.15	10.30	10.40
9.	°Tw at 30 °C	21.47	22.40	25.00	20.00	---

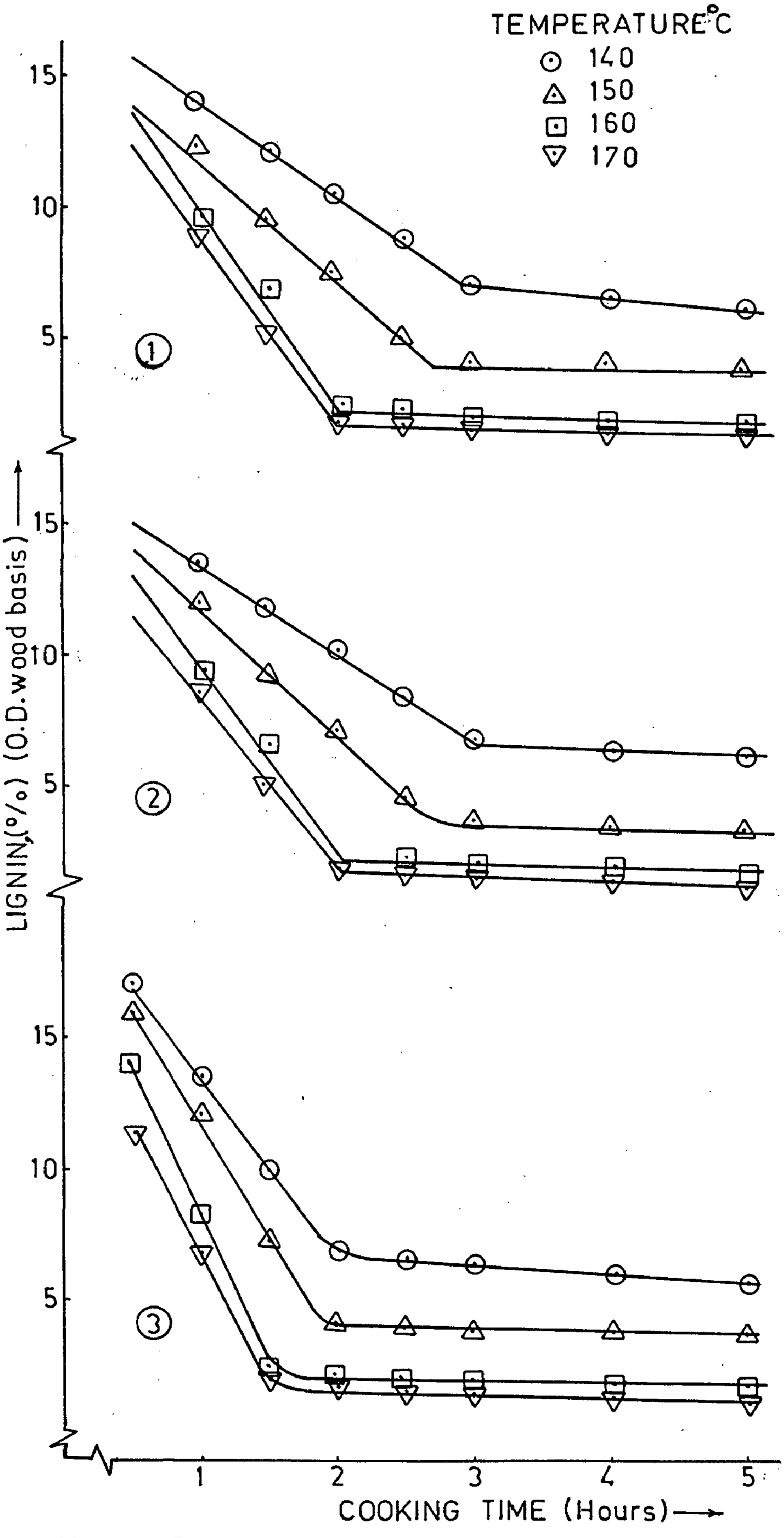


Fig.5·01B: PLOTS OF RESIDUAL LIGNIN VS. TIME OF REACTION AT 16 % AA FOR ① S.sesban ② C.cajan AND 14 % AA FOR ③ S.aculeata AND 20 % SULPHIDITY DURING KRAFT PULPING.

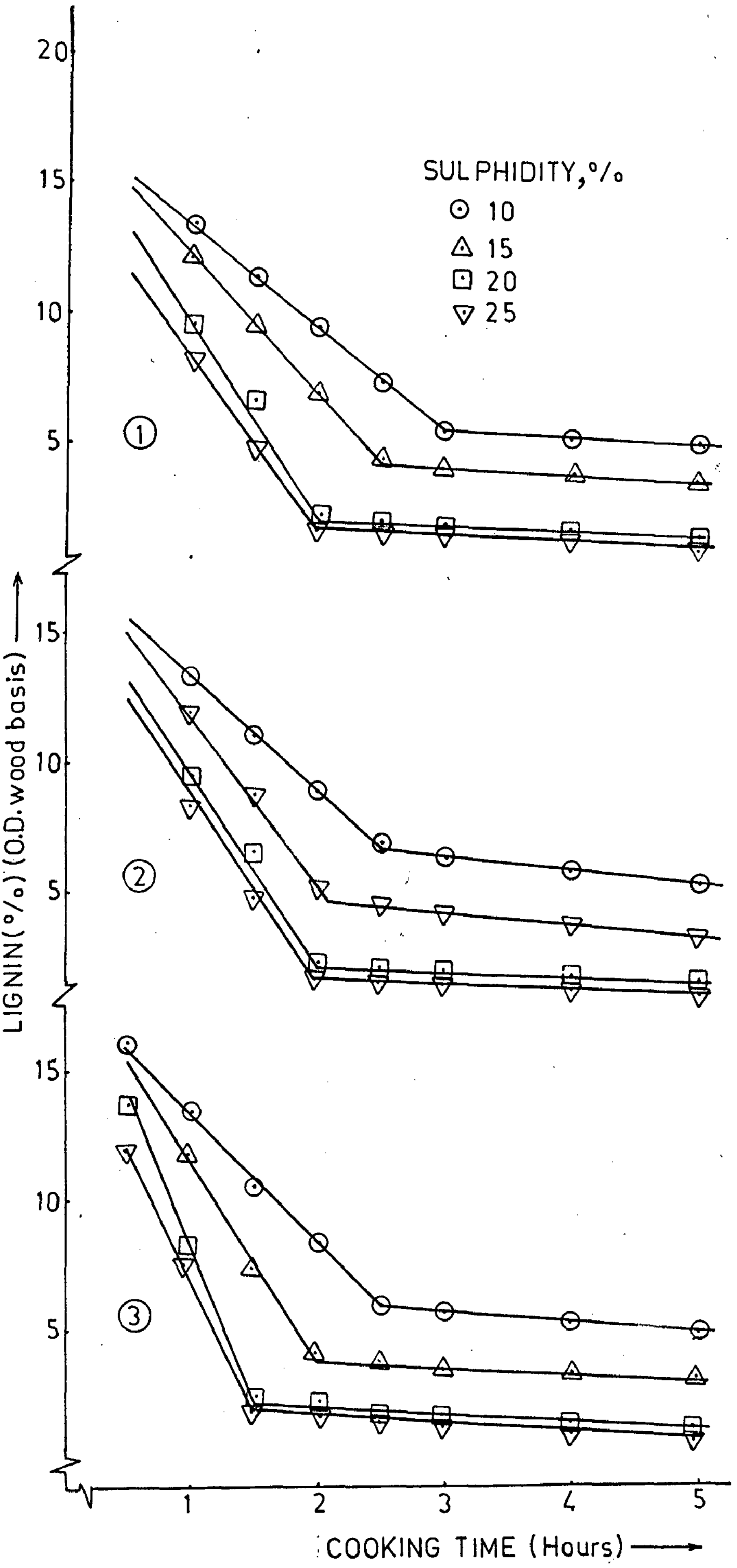


Fig. 5·02 B: PLOTS OF RESIDUAL LIGNIN VS. TIME OF REACTION AT 160°C WITH 16% AA FOR ① S. sesban ② C. cajan AND 14% AA FOR ③ S. aculeata USING DIFFERENT LEVELS OF SULPHIDITIES.

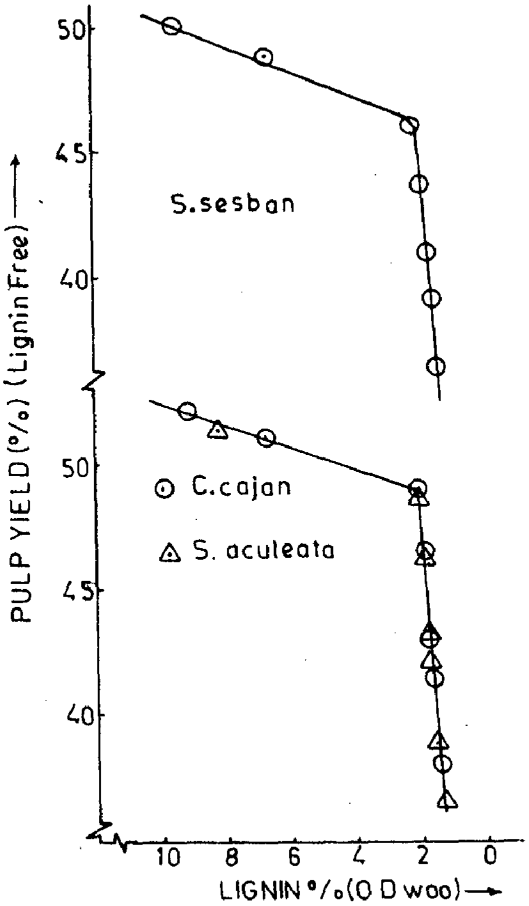


Fig.5·03B: PLOTS OF LIGNIN°/o VS.YIELD°/o DURING THE KRAFT PULPING OF S.sesban, C.cajan AND S.aculeata.

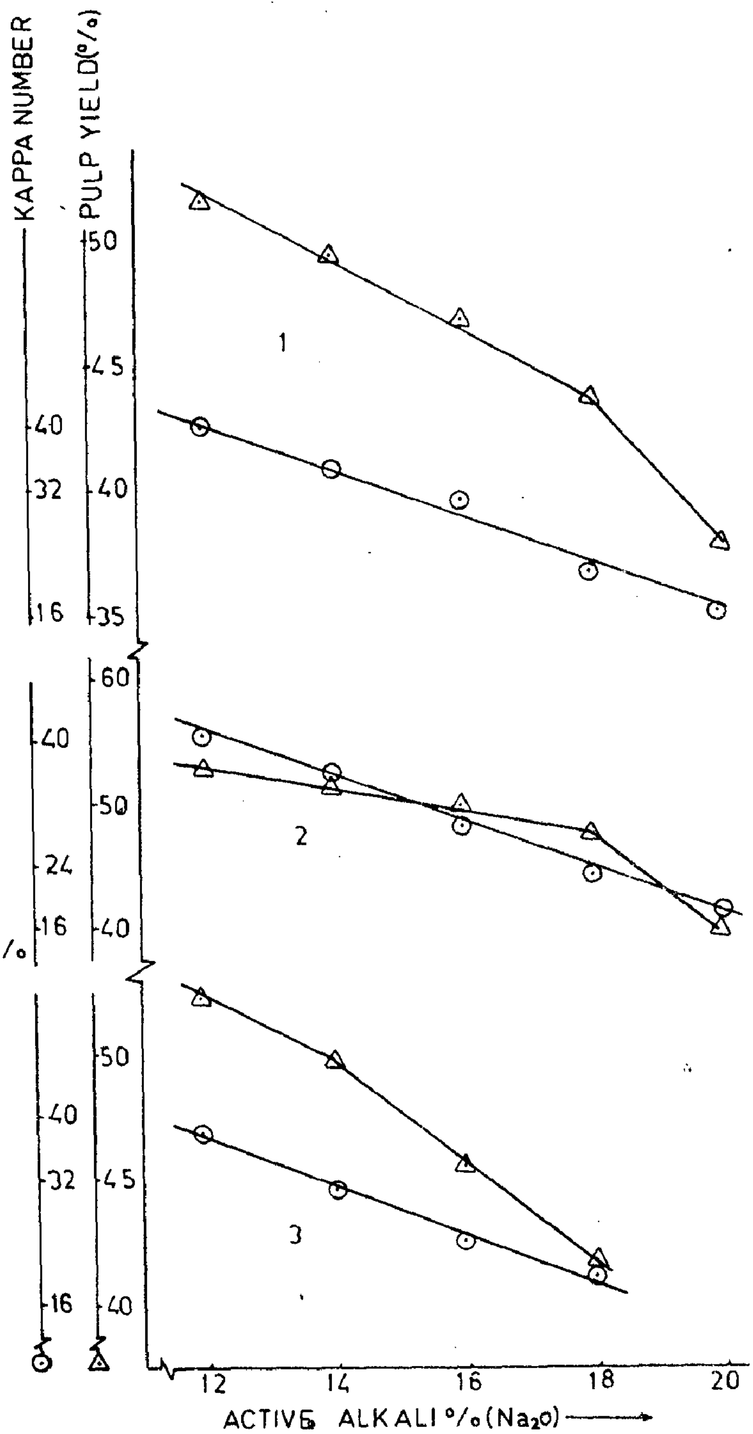


Fig.5.40 B: PLOTS OF ACTIVE ALKALI °/o VS. PULP YIELD AND KAPPA NUMBER DURING KRAFT PULPING OF ① S.sesban ② C. cajan AND ③ S. aculeata.

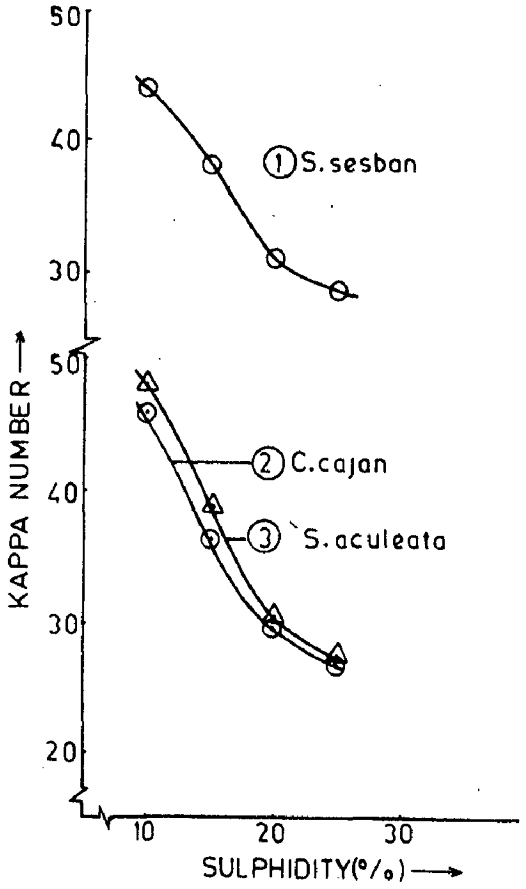


Fig.5·05B: PLOTS OF KAPPA NUMBER VS. SULPHIDITY AT 160°C WITH 16% A.A FOR ①S.sesban ②C.cajan AND 14% A.A FOR ③S.aculeata

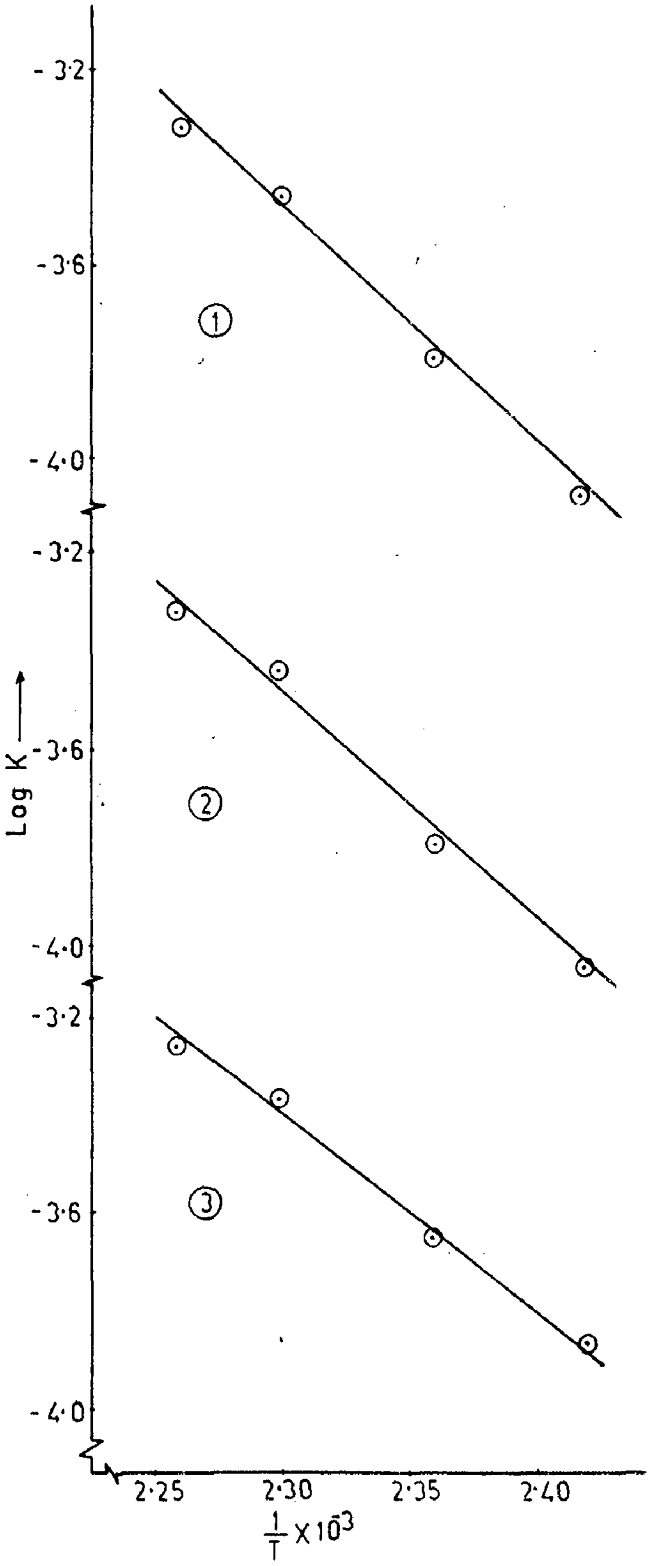


Fig.5·06B: PLOTS OF THE Log RATE CONSTANT VS. RECIPROCAL OF THE ABSOLUTE TEMPERATURE OF ①S.sesban ②C.cajan AND ③S.aculeata KRAFT PULPING.

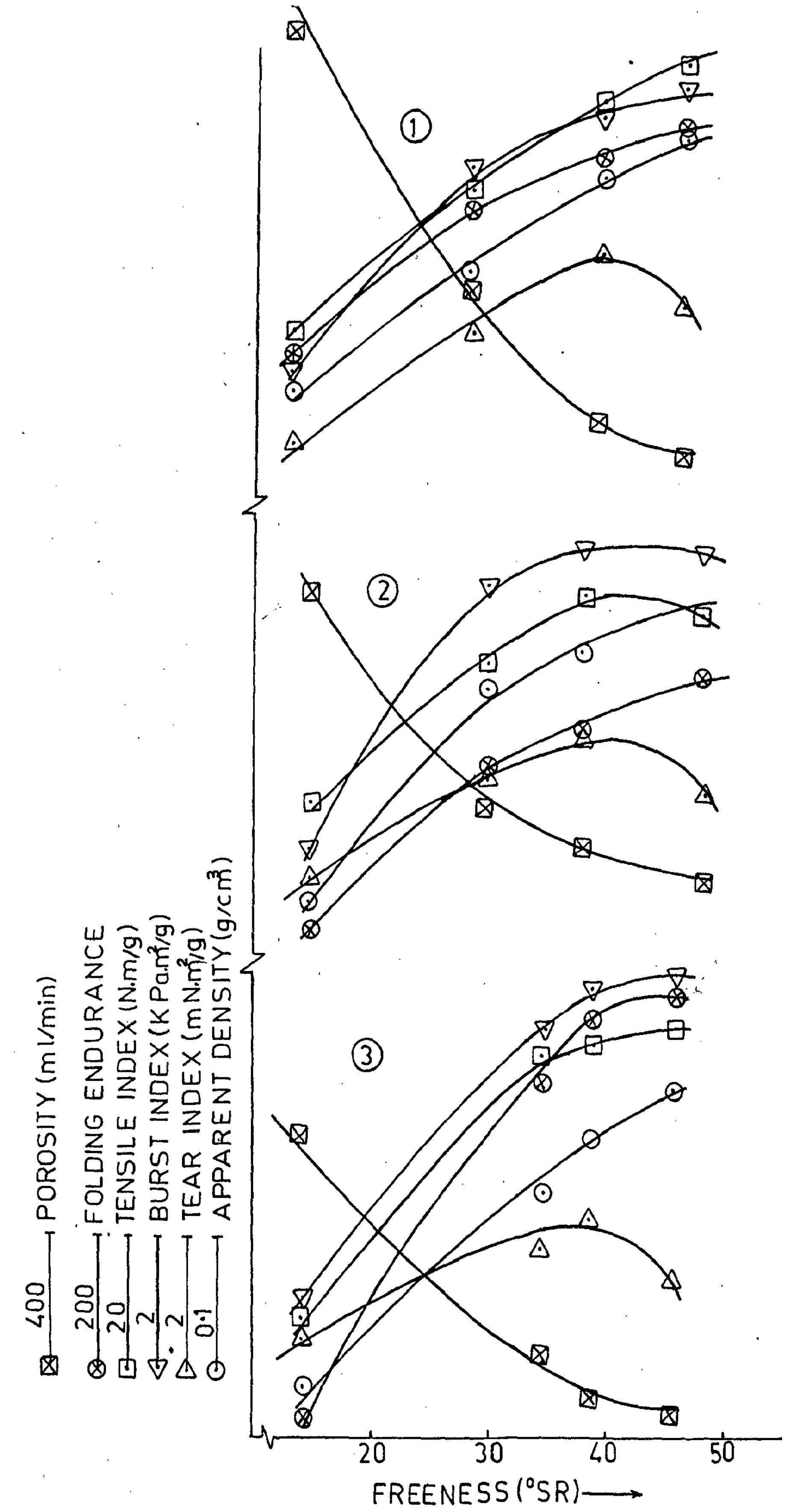


FIG. 5.07B: PLOTS OF PULP FREENESS(°SR) VS. STRENGTH PROPERTIES OF ①S.sesban ②C.cajan AND ③S. aculeata KRAFT UNBLEACHED PULPS.

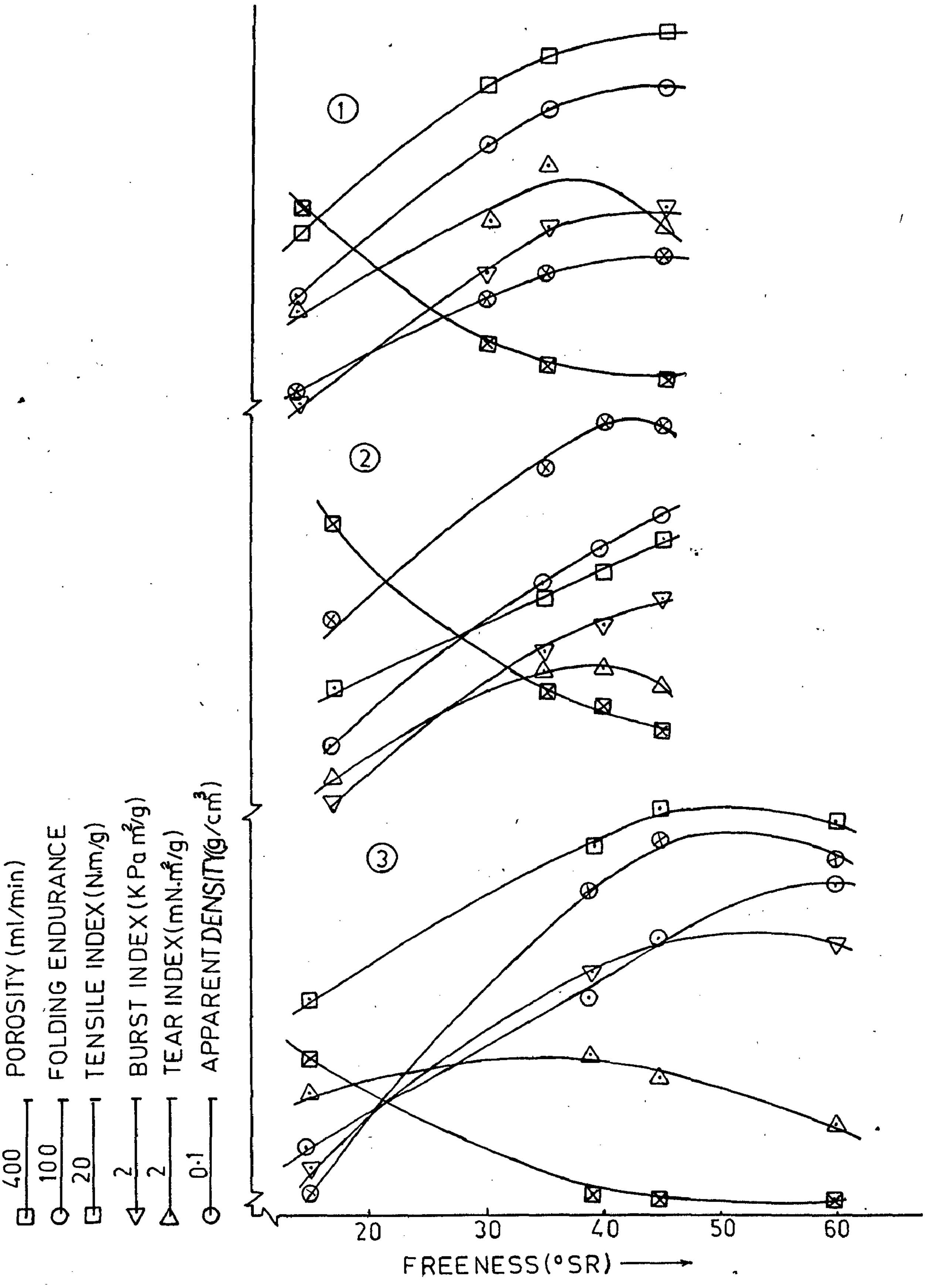


Fig. 5.08B: PLOT OF PULP FREENESS (°SR) VS. STRENGTH PROPERTIES OF ① S. sesban ② C. cajan AND ③ S. aculeata KRAFT BLEACHED PULPS.

SECTION (C)

ALKALINE SULPHITE PULPING STUDIES:

Over the past dacades, high yield sulphite pulping of hard woods has been investigated as a means of making a low cost pulp for the production of newsprint, printing papers, and tissue papers. Different combinations of pulping variables viz., presteaming/liquor impregnation procedure, cooking liquor pH, sodium sulphite/sodium bisulphite content, cooking temperature, time and liquor to wood ratio etc., have been tried.

In the late 60s, the alkaline sulphite (AS) pulping process was developed as an alternative to kraft pulping. By 1973, the AS pulping process had been tested in pilot plant and mill trials(29,64). Although its immediate advantage is the elimination of the foul odour of kraft mill, while maintaing pulp strength. Although excellent properties of fully cooked coniferous sulphite pulps prepared under mildly alkaline conditions have been described by many investigators(10,56), but the industrial acceptance did not come forth at that time. The main reasons includes-the doubts concerning the cost, reliability of existing sodium sulphite recovery system, yield lower than that of kraft at a given kappa number and air quality regulations less severe than those of the present.

The emergence of this sulphite process at moderate alkalinity with anthraquinone(AQ) as its essential additive offers the industry, a pulp of kraft like strength at higher yield and better bleachability than conventional kraft, while substantially reducing the air pollution problem. In parallel with these developments, three sulphite recovery systems have come into commercial use, thus removing the major obstackle to the expansion of modern sulphite technology(31). The comparison, of the process economics of the moderately alkaline sulphite-AQ with that of kraft process are reported in literature(55,71). In India there is no mill, which is using alkaline sulphite pulping process. The preliminary conclusions of these studies indicated that this process is very interesting from the point of view of both economy and quality, but is still in the development stage.

5.1.EXPERIMENTAL PROCEDURES:

5.1.1.PULPING STUDIES:

The methods of raw material preparation are given on page no.63 . For the optimisation of pulping conditions, the S.sesban, S.aculeata and C.cajan chips were cooked in laboratory WEVERK rotary tumbling electrically heated digester(0.02 M^3 capacity), having bombs of 1 litre capacity, furnishing sufficient pulps for evaluation as well as for conducting bleaching experiments. During these studies, the technical grade chemicals were used except that of sodium sulphite, which was of analytical grade. During the course of pulping, the liquor to wood ratios of 4:1 for S.aculeata and 3.5:1 for S.sesban and C.cajan were maintained using the following time schedule for heating the digester.

From room temperature to 105 ^{o}C = 45 minutes.

From 105 ^{o}C to maximum temperature of cooking = 30 minutes.

The pulping studies were made using different ratios of sodium shlphite to sodium hydroxide in order to know the optimum ratio of these cooking chemicals. The cookings were also made at different time to know the effect of cooking time during the course of pulping. During cooking the digester pressure was reduced to zero by gas relief at 105^{o}C. At the end of cooking cycle, the cooked chips and liquor were blown from the digester and the cooked chips were passed through a Bauer refiner with a plate clearance of 0.1 mm. These pulps were screened through a laboratory flat WEVERK screen with 0.15 mm slits and the screened pulps were washed, pressed and crumbled. The yields and Kappa numbers were determined. The spent liquors were analysed for residual sulphurdioxide and its pH were also determined. The results of these studies are reported in Tables 5.1C and 5.2C.

5.1.2.ALKALINE SULPHITE-ANTHRAQUINONE PULPING:

The AS-AQ pulping studies on S.sesban, S.aculeata and C.cajan have been done using the same process conditions, with the addition of small amounts of AQ(0.1%) and the results of these studies are reported in Table-5.8C.

5.1.3.BLEACHING STUDIES:

Since the alkaline sulphite process in its original form is found to be less selective than the kraft process with respect to delignification in the bleachable range, one would expect that the cost of bleach chemicals would be correspondingly higher, this however, is not the case in actual practice. The S.sesban, S.aculeata and C.cajan alkaline sulphite pulps are somewhat easier to bleach, have higher brightness ceiling, and suffer considerably less brightness reversion. A four stage, (CEHH) bleaching sequence was applied to selected pulps. The bleaching conditions and results are given in Table-5.6C.

5.1.4.FIBRE CLASSIFICATION:

The fibre classification studies of S.sesban, S.aculeata and C.cajan alkaline sulphite pulps were made with the help of Bauer- McNett fibre classifier using screens with mesh number, 20, 60, 80 and 120. The results are reported in Table-5.11C. The photomicrographs of unbleached, bleached, unbeaten and beaten pulps fibres of these plants are shown in annexure on page 166 to 171.

5.1.5.PULP EVALUATION:

The alkaline sulphite pulps were beaten in a PFI mill(73) and laboratory handsheets of 60 gms/m^2 were made on laboratory British sheet forming machine. The pulp evaluations were made according to IS method(32) and the results are reported in Tables-5.7C to 5.10C.

5.2.RESULTS AND DISCUSSIONS:

The amount of sodium sulphite charged had a considerable influence on the rate of cooking. The results of a series of S.sesban, S.aculeata and C.cajan bomb scale digestions, cooked for constant temperature and time with the addition of sufficient sodium sulphite to give a spent liquor pH close to 10(Table-5.1C) are plotted in fig.5.01C. The amount of residual lignin decreased from 10% of the original wood to less than 2% as the sodium sulphite charge was increased from 6.8 to 12.8%(as Na_2O). The second series of cooking at increased time showed that the increased time had a little influence on the amount of lignin removed and may possibly even have caused redeposition where the digestions were made with small amounts of sulphite. From the cooking results, an optimum sulphite charge of about 10.35%(as Na_2O) for S.aculeata and 10.80%(as Na_2O) for S.sesban and C.cajan were indicated. Increasing the amount of sodium sulphite also improved the selectivity of cooking. Fig.5.02C provides a comparison of Kappa numbers at equal yields indicated that as Kappa numbers increased, the yields also increased. In fig.5.03C, the residual lignins(Kappa no.X.0.15) are plotted against cooking time. A high initial rate of delignification was shown which decreased steadily, with an appreciable amount of the lignin being quite resistant. The initial high rate of delignification, which is common to a varying degree to nearly all delignification process, is undoubtedly partly due to high initial alkaline concentration in the cooking liquor. It may also correspond to easily assessible and less condensed lignin where its high rate of dissolution coincides with that of wood polyoses. The interaction of lignin and hemicelluloses in the wood was probably one of the major factor affecting the rate and selectivity of the delignification during the later stages, whether this involves a primary of secondary valence bond or both.

The plots between Kappa Numbers and caustic doses charged fig.5.04C, during alkaline sulphite pulping of S.sesban, S.aculeata and C.cajan clearly indicated that the rate of cooking was faster at higher alkalinity doses. The pH of the cooking liquor was increased by adding additional amounts of caustic, keeping the amount of sodium sulphite constant(Table-5.2C). As the caustic charge increased from 0.78 to 8.52%(as Na_2O), the Kappa number decreased from 95 to 19, due to higher rate of delifnification at higher alkalinity. The decrease in Kappa number was very sharp at lower doses of alkali(below 4.65% as Na_2O), but the cooking rate was greatly influenced beyond a caustic dose above4.65 to 6.20%(as Na_2O) and Kappa no. was continuously decreased as the amount of caustic increased. As increase in the terminal pH, reduced the cooking time at maximum temperature by approximately 70%.

The tearing of the S.sesban, S.aculeata and C.cajan pulps decreased regularly with increasing Kappa number, other conditions being constant, while burst and tensile index held constant within narrow limits of Kappa number (upto 80). Burst and tensile index tends to decrease more uniformly with increasing Kappa number(Tables-5.3C to 5.5C) and further decreased at a very low Kappa number. The prolonged digestion or high chemicals are required for obtaining low Kappa number pulps, using caustic soda undoubtedly results in the loss of fibre strength.

The S.sesban, S.aculeata and C.cajan alkaline sulphite pulps showed good response towards optical properties and are having decidedly superior values for both the brightness and opacity. The pulps with a brightness level of about 76-79%(Elrepho) were obtained as a result of four stage (CEHH) bleaching sequence, because the unbleached pulps also possessed a good level of brightness. Due to the high initial brightness, the total chlorine consumption is low during bleaching of S.sesban, S.aculeata and C.cajan alkaline sulphite pulps.

The pulps of selected cooks were beaten to different °SR levels. The physical strength properties of unbleached and bleached S.sesban, S.aculeata and C.cajan alkaline sulphite pulps are reported in Tables-5.7C to 5.10C. The initial freeness and drainage time of both the unbleached and bleached pulps were found high. The freeness of unbeaten pulps were 15-16 °SR. The plots of pulps freeness levels versus various physical strength properties of S.sesban, S. aculeata and C.cajan unbleached and bleached alkaline sulphite pulps are shown in Figures 5.05C & 5.06C, respectively. These clearly indicated that the apparent density is almost directly proportional to the freeness of pulps. The unbeaten, bleached pulps have a higher initial apparent sheet density. These plots also indicated that both the tear index and porosity are in indirect porportional to the freeness level i.e. both of these decreased with a result of an increase in freeness levels. The apparent density, burst index, tensile index, folding endurance are in direct proportion with freeness i.e. all these increased as a result of an increase in freeness. The strength properties increased upto a certain °SR after that the strength properties showeda decline trend as a result of over beating or higher freeness values. It is obvious from these results that these pulps should not be beaten to a freeness range beyond 42 ± 2 °SR.

The addition of a small amount of AQ(0.1%) during alkaline sulphite pulping of S.sesban, S.aculeata and C.cajan showed a significant influence both on pulping characteristics and the overall strength porperties of these pulps. A same level of Kappa number is achieved in alkaline sulphite anthraquinone pulping of these plants at the same temperature and same chemical charge with a substantial reduction in time at temperature. The AS-AQ pulps showed good response towards bleaching and produced more brighter pulps than alkaline sulphite pulps. Good values of tensile, tear and burst are achieved in AS-AQ pulping(30,51).

5.3.CONCLUSION:

The long digestion time required for alkaline sulphite pulping of S.sesban, S.aculeata and C.cajan pulps can be reduced by increasing the alkalinity of cooking liquors to a pH level of 10 or above and still produce pulp superior to kraft. The biggest drawbacks to AS pulping is the slow rate of delignification. With increased alkalinity, the rate of delignification also increased and approached to that of kraft. The selectivity at moderate alkalinity was slightly superior to, and at high alkalinity was the same as kraft. The proportion of sodium hydroxide greatly influenced the rate of delignification during alkaline sulphite pulping of S.sesban, S.aculeata and C.cajan. The alkaline sulphite unbleached and bleached pulps of these plants showed good strength properties, especially burst and tensile. The strength of the pulps, especially the tear, is largely govened by the alkalinity of the cooking liquor, and reaching a maximum at a terminal pH of 9 to 11.

The alkaline sulphiteanthraquinone pulping process at intermediate alkalinity was characterised by unique maxima of delignification, pulp yield and viscosity which were produced when the cooking liquor contains 75 to 90% sodium sulphite, the remainder consisting of sodium hydroxide(as Na_2O). The resulting pulps were as strong or even stronger than conventional kraft pulps and bleached much more easily. Bleached grade AS and AS-AQ pulps delignify much more readily than kraft pulps with conventional bleach sequences. Because of their high viscosity and easy bleaching characteristics, they also have great potential for use in chlorine free bleach sequences. Application of anthraquinone to AS cooks results in greater gains in selectivity of delignification, pulp yield, strength and bleachability than its application to soda and kraft cooks.

Table-5.1C:Pulping Conditions And Characteristics Of Bomb-Scale Digestion, Effect Of Amount Of Sodium Sulphite And Cooking Time During Alkaline Sulphite Pulping Of S.sesban, C.cajan And S.aculeata.

Sl.	S.sesban & C.cajan Chemical charge %on O.D. wood		S. aculeata Chemical charge %on O.D. wood		S. sesban				C. cajan				S. aculeata			
No.	Na_2SO_3	NaOH	Na_2SO_3	NaOH	Spent Liquor SO_2	Spent Liquor pH	Yield	Kappa	Spent liquor SO_2	Spent liquor pH	Yield	Kappa	Spent liquor SO_2	Spent liquor pH	Yield	Kappa
	(As Na_2O)		(As Na_2O)		(gpl)		(%)	(no.)	(gpl)		(%)	(no.)	(gpl)		(%)	(no.)
1.	6.8	6.2	6.35	4.65	6.5	9.0	61.7	81	6.7	8.8	63.4	79	6.4	8.9	61.8	82
2.	7.8	6.2	7.35	4.65	7.0	9.2	57.6	70	7.2	9.1	58.7	68	7.0	9.0	58.0	73
3.	8.8	6.2	8.35	4.65	7.6	9.3	56.0	55	7.5	9.2	55.5	53	7.7	9.1	53.5	51
4.	9.8	6.2	9.35	4.65	7.7	9.6	52.5	42	8.2	9.2	54.0	41	8.0	10.2	52.0	39
5.	10.8	6.2	10.35	4.65	8.1	10.2	49.8	34	8.4	10.1	52.6	32	8.5	10.2	51.0	33
6.	11.8	6.2	11.35	4.65	8.8	10.5	47.5	30	9.0	10.4	50.2	29	9.0	10.3	49.9	30
7.	12.8	6.2	12.35	4.65	9.2	10.6	46.7	28	9.1	10.4	48.9	27	9.1	10.3	48.7	26
8.	6.8	6.2	6.35	4.65	6.2	8.9	62.0	83	6.0	9.0	62.5	84	6.6	9.0	61.7	91
9.	7.8	6.2	7.35	4.65	7.2	9.2	57.0	69	6.8	9.3	57.4	70	6.8	9.5	56.8	78
10.	8.8	6.2	8.35	4.65	8.1	9.4	53.4	52	8.0	9.2	53.0	50	8.2	10.0	52.1	48
11.	9.8	6.2	9.35	4.65	8.0	10.1	50.5	38	8.1	9.8	50.3	31	8.3	10.1	49.5	32
12.	10.8	6.2	10.35	4.65	8.7	10.3	48.0	32	8.3	10.4	49.2	29	8.6	10.2	49.0	29
13.	11.8	6.2	11.35	4.65	8.9	10.2	46.2	27	8.6	10.2	48.0	26	9.5	10.1	48.0	25
14.	12.8	6.2	12.35	4.65	9.4	10.2	45.2	25	8.4	10.1	46.2	24	9.4	10.3	47.2	23
EFFECT OF COOKING TIME																
15.	10.8	6.2	10.35	4.65	10.0	10.4	62.5	85	9.8	10.3	62.0	81	9.1	11.1	60.9	92
16.	10.8	6.2	10.35	4.65	9.7	10.1	58.4	72	9.4	10.2	57.8	74	9.8	10.8	55.5	62
17.	10.8	6.2	10.35	4.65	9.5	10.2	54.7	50	8.6	10.4	56.5	54	9.6	10.6	54.1	54
18.	10.8	6.2	10.35	4.65	9.3	10.0	53.2	46	8.5	10.2	55.0	48	9.2	10.2	52.0	47
19.	10.8	6.2	---	---	9.2	10.1	50.4	37	8.2	10.2	53.7	39	---	---	---	--

Liquor to wood ratio = 3.5:1 (For S.sesban & C.cajan)
= 4:1 (For S.aculeata)
Time from 30 °C to 105°C = 45 minutes.
Time from 105°C to 175°C = 30 minutes.

Time at 175 °C for Sl.No. 1 to 7 = 3hrs. for S.sesban&C.cajan
= 2hrs.45 min. for S.aculeata
Time at 175 °C for Sl.No. 8 to 14= 3hrs.30 min. for All three
Time at 175 °C for Sl.No.15 to 18= 30, 60, 90 & 120 min.
Time at 175 °C for Sl.No. 19 = 150 minutes.

Table-5.2C:Pulping Conditions And Characteristics Of Bomb-Scale Digestion, Effect Of Amount Of Sodium Hydroxide And Cooking Time, During Alkaline Sulphite Pulping Of S.sesban, C.cajan And S.aculeata.

Sl.	S.sesban & C.cajan Chemical charge % on O.D. wood		S. aculeata Chemical charge %on O.D. wood		S. sesban				C. cajan				S. aculeata			
No.	Na_2SO_3	NaOH	Na_2SO_3	NaOH	Spent Liquor SO_2	Spent Liquor pH	Yield	Kappa	Spent liquor SO_2	Spent liquor pH	yield	kappa	Spent liquor SO_2	Spent liquor pH	yield	kappa
	(As Na_2O)		(As Na_2O)		(gpl)		(%)	(no.)	(gpl)		(%)	(no.)	(gpl)		(%)	(no.)
1.	10.8	0.78	10.35	0.78	6.3	7.4	63.3	91	6.5	7.2	63.2	87	6.7	7.4	62.0	95
2.	10.8	1.55	10.35	1.55	6.7	8.0	60.0	82	6.8	8.1	59.8	78	6.9	8.1	58.2	87
3.	10.8	3.10	10.35	2.32	6.6	8.9	57.5	78	7.0	8.7	58.2	74	7.4	8.6	56.4	79
4.	10.8	3.88	10.35	3.10	7.5	9.4	56.0	70	7.6	9.1	57.5	72	8.2	9.2	55.7	68
5.	10.8	4.65	10.35	3.88	7.9	9.7	55.2	56	7.8	9.5	56.4	64	8.1	9.7	52.4	46
6.	10.8	5.42	10.35	4.65	8.0	10.0	51.0	39	8.1	9.8	54.0	53	8.5	10.1	51.0	32
7.	10.8	6.20	10.35	6.20	8.1	10.2	49.8	34	8.4	10.1	52.6	32	9.0	10.7	48.7	28
8.	10.8	6.98	10.35	6.98	8.6	11.2	46.4	28	8.5	11.0	49.5	28	9.4	11.3	47.5	24
9.	10.8	7.75	10.35	7.75	9.1	11.6	42.7	26	9.2	11.8	45.0	25	9.2	11.6	43.0	22
10.	10.8	8.52	10.35	8.52	9.3	12.0	39.5	22	9.6	12.1	41.6	21	9.3	12.0	39.0	19

Liquor to wood ratio = 3.5:1 (for S.sesban & C.cajan);
= 4:1 (for S.aculeata)
Time from 30 °C to 105°C = 45 minutes.
Time from 105°C to 175°C = 30 minutes.
Time at 175°C for S.sesban & C.cajan
Sl. No. 1 and 2 = 4 Hrs.
Sl. No. 3 to 5 = 3 Hrs. 30 minutes.
Sl. No. 6 and 7 = 3 Hrs.
Sl. No. 8 = 2 Hrs. 45 minutes.
Sl. No. 9 = 2 Hrs.
Sl. No.10 = 1 Hr. 30 minutes.

Time at 175°C for S.aculeata-
Sl. No. 1 to 3 = 4 Hrs.
Sl. No. 4 = 3 Hrs. 30 minutes.
Sl. No. 5 = 3 Hrs.
Sl. No. 6 & 7 = 2 Hrs. 45 minutes.
Sl. No. 8 = 2 Hrs. 30 minutes.
Sl. No. 9 = 2 Hrs.
Sl. No.10 = 1 Hr. 30 minutes.

Table-5.3C:Pulping Conditions And Pulp Characteristics Of S.sesban alkaline sulphite pulps.

Cook No.	Chemical charge % on O.D. wood		Time at 175°C Hr.Min.	Spent liquor		Pulp yield (%)	Kappa (no.)	Freeness (°SR)	Burst index (Kpa. m^2/g)	Tear index ($mN.m^2/g$)	Tensile index (N.m/g)	Folding endurance Köhler Molin
	Na_2SO_3	NaOH (as Na_2O)		So_2gpl	pH							
					TERMINAL pH 8-12							
S_1	7.8	6.2	3:30	7.2	9.1	56.2	66	40	2.96	3.54	42.40	82
S_2	8.8	6.2	3:30	7.6	9.3	53.6	52	41	3.12	3.95	45.16	95
S_3	9.8	6.2	3:00	8.0	9.6	50.0	40	40	3.85	4.16	47.82	102
S_4	10.8	6.2	3:00	8.2	10.1	49.0	32	42	4.20	4.50	51.40	138
S_5	11.8	6.2	2:30	8.1	9.8	47.7	31	39	4.25	4.66	52.00	140
S_6	10.8	6.2	3:30	9.2	10.0	50.0	36	40	4.10	4.60	51.75	135
S_7	11.8	6.2	3:30	8.1	10.3	47.2	30	42	3.90	4.28	50.20	130
					TERMINAL pH 12-13							
S_8	10.8	7.75	2:00	9.2	11.6	42.2	25	40	3.47	4.10	42.85	85
S_9	10.8	8.52	1:30	9.4	11.9	39.0	20	41	3.38	4.25	43.20	91
S_{10}	10.8	9.30	1:00	9.7	12.1	37.4	18	41	3.35	4.28	41.76	80

Liquor to wood ratio = 3.5:1, Time from 30 °C to 105°C = 45 minutes, time from 105 °C to 175°C=30 min.

Table-5.4C:Pulping Conditions And Pulp Characteristics Of C.cajan Alkaline Sulphite Pulps.

Cook No.	Chemical charge % on O.D. wood		Time at 175 °C	Spent liquor		pulp yield	Kappa (no.)	Freeness	Burst index	Tear index	Tensile index	Folding endurance
	Na_2SO_3	NaOH (as Na_2O)	Hr.Min.	So_2gpl	pH	(%)		(°SR)	(Kpa. m^2/g)	$(mN.m^2/g)$	(N.m/g)	Köhler Molin
					TERMINAL pH 8-12							
C_1	7.8	6.2	3:30	7.0	8.9	57.0	67	42	3.06	5.15	46.39	94
C_2	8.8	6.2	3:30	7.7	9.0	53.0	49	40	3.30	5.20	47.65	97
C_3	9.8	6.2	3:00	8.3	9.6	52.7	39	41	3.62	5.50	49.76	106
C_4	10.8	6.2	3:00	8.5	10.2	51.4	31	40	4.84	6.09	55.88	131
C_5	11.8	6.2	2:30	8.2	9.5	50.8	30	42	4.90	6.14	56.20	134
C_6	10.8	6.2	3:30	9.0	10.0	50.0	30	44	4.80	5.90	54.39	112
C_7	11.8	6.2	3:30	8.2	10.2	49.4	28	41	4.20	5.67	51.92	110
					TERMINAL pH 12-13							
C_8	10.8	7.75	2:00	9.8	11.4	45.0	25	40	3.74	5.10	46.96	91
C_9	10.8	8.52	1:30	9.2	11.7	41.4	21	40	3.48	5.42	49.85	102
C_{10}	10.8	9.30	1:00	9.4	12.2	39.8	19	42	3.80	5.35	48.12	98

Liquor to wood ratio = 3.5:1

Time from 30 °C to 105°C = 45 minutes, time from 105 °C to 175 °C = 30 minutes.

Table-5.5C:Pulping Conditions And Pulp Characteristics Of S.aculeata Alkaline Sulphite Pulps.

Cook No.	Chemical charge % on O.D. wood		Time at 175 °C	Spent liquor		Pulp yield	Kappa (no.)	Freeness	Burst index	Tear index	Tensile index	Folding endurance
	Na_2SO_3 (as Na_2O)	NaOH	Hr.Min.	So_2 gpl	pH	(%)		(°SR)	(Kpa.m^2/g)	(mN.m^2/g)	(N.m/g)	Köhler Molin
						TERMINAL pH 8-12						
A_1	7.35	4.65	2:45	7.0	8.8	57.6	71	40	3.04	4.52	40.99	176
A_2	8.35	4.65	2:45	7.4	9.0	53.2	51	41	4.20	5.30	58.13	262
A_3	9.35	4.65	3:00	8.0	10.0	51.5	38	40	4.70	5.65	65.40	290
A_4	10.35	4.65	3:00	8.4	10.3	50.8	32	40	4.86	6.10	68.73	315
A_5	11.35	4.65	2:45	9.0	10.4	49.4	29	42	4.65	5.90	66.96	300
A_6	6.35	4.65	3:30	7.2	9.3	61.0	98	39	3.45	4.90	37.65	150
A_7	10.35	4.65	3:30	8.6	10.3	48.7	28	40	4.50	6.07	67.50	335
A_8	11.35	4.65	3:30	8.7	10.5	47.2	22	42	4.10	4.60	54.50	220
						TERMINAL pH 12-13						
A_9	10.35	6.98	2:30	9.2	11.4	47.5	24	40	3.75	5.10	59.69	240
A_{10}	10.35	7.75	1:30	9.4	11.7	43.0	22	40	3.50	4.58	50.76	190
A_{11}	10.35	8.52	1:00	9.6	12.0	40.4	20	41	3.90	5.65	52.45	210

Liquor to wood ratio = 4:1, Time from 30 °C to 105 °C = 45 min., Time from 105 °C to 175 °C=30 min.

Table-5.6C:AS And AS-AQ Bleaching Conditions And Results Of S.aculeata, S. sesban And C. cajan.

Sl. No	Particulars	S.aculeata		S.sesban		C. cajan	
		AS	AS-AQ	AS	AS-AQ	AS	AS-AQ
1.	Unbleached pulp kappa number	32	31	32	30	31	30
2.	Chlorination stage(C)						
	Chlorine applied as available Cl_2 on pulp %	4.80	4.68	4.78	4.52	4.62	4.70
	Chlorine consumed as available Cl_2 on pulp %	4.78	4.67	4.76	4.50	4.60	4.69
	Final pH	1.97	1.98	1.90	1.94	1.92	
3.	Extraction stage (E)						
	NaOH applied on pulp %	2.00	2.00	2.00	2.00	2.00	2.00
	Initial pH	11.20	11.34	11.30	11.36	11.40	11.38
	Final pH	10.20	10.40	9.90	10.20	10.10	10.22
4.	Hypochlorite Ist stage (H_1)						
	Hypo applied as available Cl_2 on pulp %	1.75	1.80	1.80	1.74	1.78	1.80
	Hypo consumed as available Cl_2 on pulp %	1.70	1.74	1.76	1.70	1.72	1.75
	Final pH	7.90	7.80	8.00	7.90	8.10	8.20
5.	Hypochlorite IInd stage (H_2)						
	Hypo applied as available Cl_2 on pulp %	0.77	0.72	0.74	0.70	0.70	0.75
	Hypo consumed as available Cl_2 on pulp %	0.72	0.68	0.70	0.66	0.67	0.70
	Final pH	7.60	7.60	7.80	7.80	7.70	7.80
6.	Total Cl_2 applied on pulp %	7.32	7.20	7.32	6.96	7.10	7.25
7.	Total Cl_2 consumed on pulp %	7.20	7.09	7.22	6.86	6.99	7.14
8.	Bleaching losses	10.60	10.40	10.30	10.10	10.50	10.40
9.	Yield	45.40	45.90	43.90	44.34	46.00	46.30
10.	Brightness (Elrepho) %	79.20	80.00	76.00	77.10	79.60	80.20
11.	Viscosity CED(0.5%) cp	12.00	12.10	11.00	11.20	11.40	11.70

Bleaching conditions	C	E	H_1	H_2
Consistency %	3	10	9	10
Temperature °C	27±2	58±2	45±2	42±2
Time(minute)	30	120	60	120

Table-5.7C:Strength Properties Of S.sesban(cook no.S_4), C.cajan(cook no.C_4) And S.aculeata(cook no.A_4) Unbleached Alkaline Sulphite Pulps.

Plant species	PFI Revolution (No.)	Freeness (°SR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index (mN.m^2/g)	Burst index (KPa.m^2/g)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min.)	Folding endurance Köhler Molin
Sesbania	0	14	3.8	0.64	2.56	0.92	14.41	1250	10
sesban	1300	30	10.5	0.70	5.20	3.52	43.46	310	170
	1600	35	13.5	0.72	5.80	4.04	48.85	195	220
	2400	47	19.0	0.75	4.37	4.74	56.37	95	242
Cajanus	0	15	4.4	0.62	2.92	0.95	15.74	1200	10
cajan	1200	30	14.3	0.74	5.40	4.12	46.56	280	196
	1600	36	16.5	0.79	6.14	4.60	54.10	160	235
	2000	45	20.0	0.84	5.60	5.10	62.62	80	242
Sesbania	0	15	4.4	0.64	3.80	0.96	28.08	850	14
aculeata	1550	35	16.5	0.76	6.27	4.86	62.40	170	320
	1950	44	19.2	0.83	5.76	5.60	76.56	90	380
	2400	50	40.24	0.85	4.72	5.48	72.40	60	412

Table-5.8C:Cooking Conditions And Strength Properties Of S.sesban, C.cajan And S.aculeata Alkaline Sulphite-AQ Pulps.

Particulars	S. sesban	C. cajan	S. aculeata
Na_2So_3(asNa_2O,O.D. wood basis) %	10.8	10.8	10.35
NaOH(asNa_2O, O.D. wood basis) %	6.2	6.2	4.65
AQ (O.D. wood basis) %	0.1	0.1	0.10
Liquor to wood ratio	3.5:1	3.5:1	4:1
Time from 30°C to 105°C(min.)	45	45	45
Time from 105°C to 170°C(min)	30	30	30
Time at 170°C(min.)	135	135	120
Screened pulp yield %	49.5	51.7	51.2
Kappa number	29.0	30	31

Plant species	PFI Revolution (No.)	Freeness (°SR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index ($mN.m^2/g$)	Burst index ($KPa.m^2/g$)	Tensile index (Nm/g)	Porosity Bendtsen (ml.min.)	Folding endurance Köhler Molin
Sesbania sesban	0	15	4.1	0.61	2.92	0.90	18.74	1300	12
	1300	30	10.5	0.69	5.65	3.50	44.52	320	196
	1800	38	15.0	0.73	6.19	4.10	52.39	175	234
	2300	44	18.2	0.75	4.56	4.70	58.90	110	258
Cajanus cajan	0	15	4.4	0.61	2.31	0.95	17.64	1300	12
	1200	30	14.3	0.72	5.33	4.17	48.92	260	220
	1700	38	17.0	0.78	6.07	4.90	55.25	150	245
	2000	44	19.4	0.81	5.40	5.30	62.72	140	272
Sesbania aculeata	0	15	4.4	0.63	3.39	0.98	25.34	830	12
	1200	30	14.2	0.75	6.20	4.50	56.12	325	290
	1750	40	17.6	0.82	5.90	4.92	64.40	110	385
	2050	46	21.2	0.84	5.80	5.85	73.20	80	452

Table-5.9C: Strength of Properties Of S.sesban(cook No.S_4), C.cajan(cook No.C_4) And S.aculeata(cook No.A_4) Bleached Alkaline Sulphite Pulps.

Plant species	PFI Revolution (No.)	Freeness (°SR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index ($mN.m^2/g$)	Burst index ($KPa.m^2/g$)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min.)	Folding endurance Köhler Molin	Brightness (Elrepho) (%)	Opacity (%)
Sesbania	0	16	4.3	0.65	1.92	0.98	15.65	1060	10	75.7	89.0
sesban	1100	32	13.0	0.73	4.61	3.10	40.50	240	81	73.2	86.4
	1300	40	17.1	0.77	4.95	3.81	46.12	160	95	71.4	84.3
	1500	45	19.5	0.78	3.90	4.12	51.24	80	110	69.5	82.0
Cajanus	0	17	4.5	0.63	2.08	1.12	17.26	940	12	77.2	89.6
cajan	900	35	17.0	0.78	4.85	3.40	44.32	130	110	75.6	85.1
	1100	40	19.3	0.82	5.10	3.80	47.37	90	155	73.0	83.4
	1250	46	21.8	0.85	4.20	4.60	55.65	75	162	72.0	81.0
Sesbania	0	16	4.5	0.67	3.45	1.16	26.19	850	12	79.0	89.0
aculeata	800	32	13.7	0.80	5.20	3.74	56.31	120	186	75.0	85.0
	1200	45	21.1	0.86	4.28	4.85	67.50	45	245	72.6	81.6
	1600	60	52.4	0.92	3.30	3.35	58.10	35	160	66.2	76.0

Table-5.10C:Strength Properties Of S.sesban, C.cajan And S.aculeata Bleached Alkaline Sulphite-AQ Pulps.

Plant species	PFI Revolution (No.)	Freeness (^{o}SR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index (mN.m^2/g)	Burst index (KPa.m^2/g)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min)	Folding endurance Köhler Molin	Brightness (Elrepho) (%)	Opacity (%)
Sesbania	0	16	4.3	0.67	2.76	0.95	19.64	1100	14	76.2	89.2
sesban	1200	36	14.5	0.75	4.50	3.42	41.16	250	96	72.4	85.4
	1350	42	18.2	0.80	4.80	3.62	47.22	150	114	70.3	83.2
	1600	46	20.0	0.81	3.82	3.92	52.52	85	122	69.7	81.0
Cajanus	0	16	4.4	0.66	2.52	1.10	20.63	900	14	80.3	89.0
cajan	1000	36	17.5	0.71	4.16	3.42	44.40	120	90	76.3	84.6
	1100	40	19.4	0.82	4.80	3.90	48.31	85	168	75.0	82.0
	1250	45	21.0	0.85	4.10	4.85	56.00	75	184	73.2	79.4
Sesbania	0	17	4.5	0.66	3.20	1.12	25.80	770	14	79.6	90.3
aculeata	800	30	12.5	0.78	5.12	3.70	53.60	130	228	76.0	89.2
	1100	42	19.1	0.84	4.70	4.20	62.36	70	310	74.2	84.4
	1250	45	21.2	0.86	4.36	4.90	69.50	50	347	73.5	79.6

Table-5.11C:Bauer--McNett Fibre Classification of Alkaline Sulphite Pulps.

Sl.No.	Mesh size	Sesbania sesban		Cajanus cajan		Sesbania aculeata	
		Unbleached(%) 14 ^{o}SR Kappa no.32	Bleached(%) 16 ^{o}SR	Unbleached(%) 15 ^{o}SR Kappa no.31	Bleached(%) 16 ^{o}SR	Unbleached(%) 15 ^{o}SR Kappa no.32	Bleached(%) 16 ^{o}SR
1.	+ 20	17.00	3.40	13.80	2.60	15.20	3.00
2.	- 20 + 60	42.00	35.80	45.20	37.00	46.20	38.20
3.	- 60 + 80	20.50	26.50	19.10	24.50	19.40	27.60
4.	- 80 + 120	6.00	14.00	5.50	15.40	5.80	13.20
5.	- 120	14.50	20.40	16.40	22.50	13.60	18.00

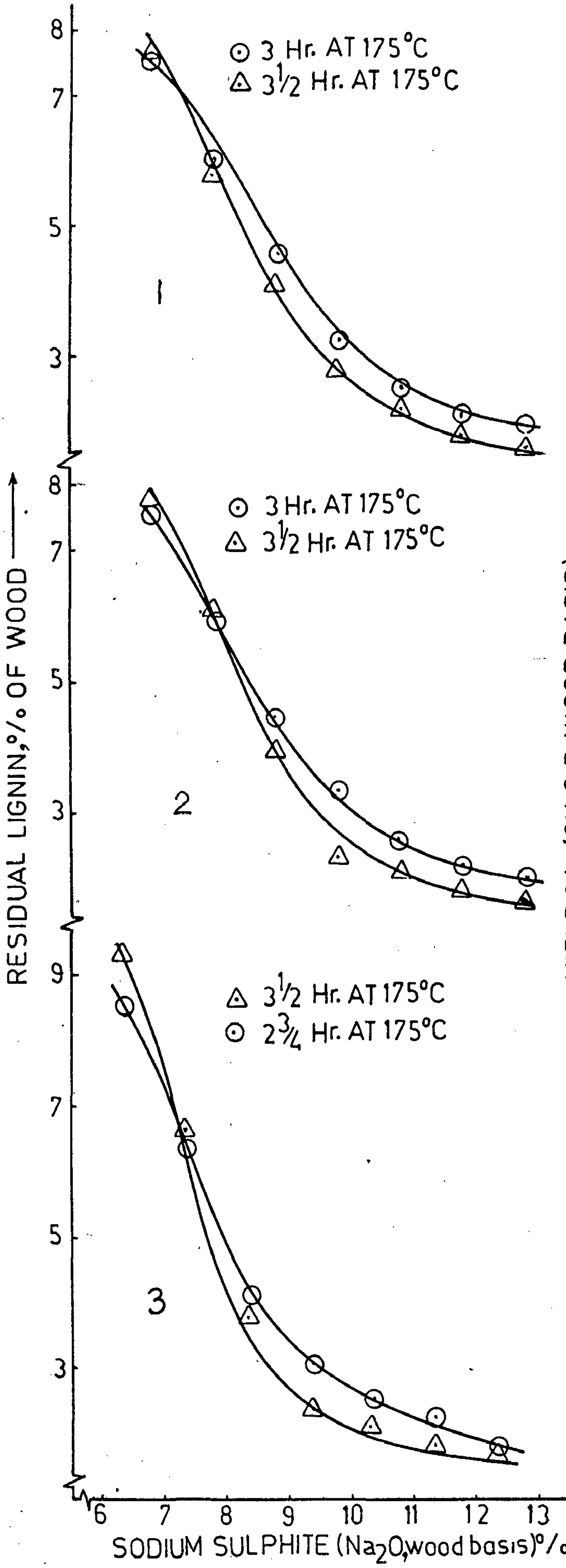


FIG 5.01C: RELATION BETWEEN AMOUNT OF SODIUM SULPHITE (Na_2O)% VS. RESIDUAL LIGNIN (0·15×KAPPA NO.) REMOVAL DURING ALKALINE SULPHITE PULPING OF ① S. sesban ② C. cajan AND ③ S. aculeata

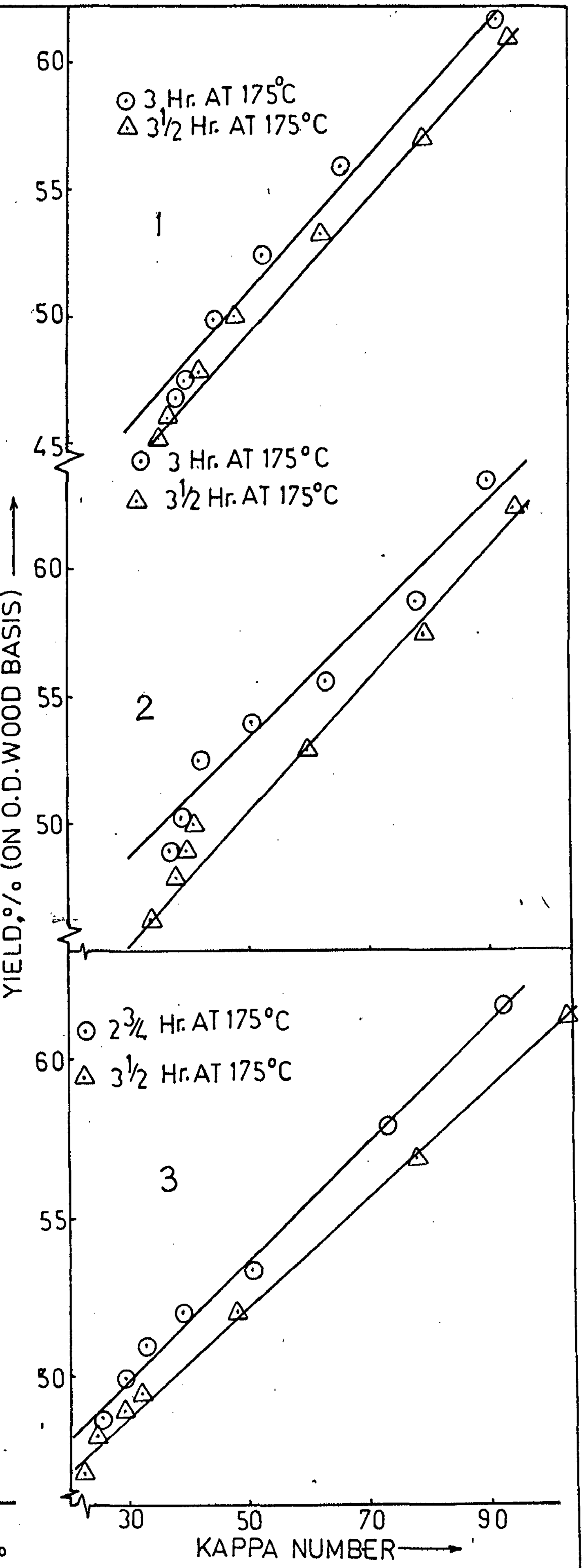


FIG. 5.02C: PLOTS OF KAPPA NUMBER VS. PULP YIELD(%) OF ① S. sesban ② C. cajan AND ③ S. aculeata ALKALINE SULPHITE PULPING AT DIFFERENT COOKING TIME.

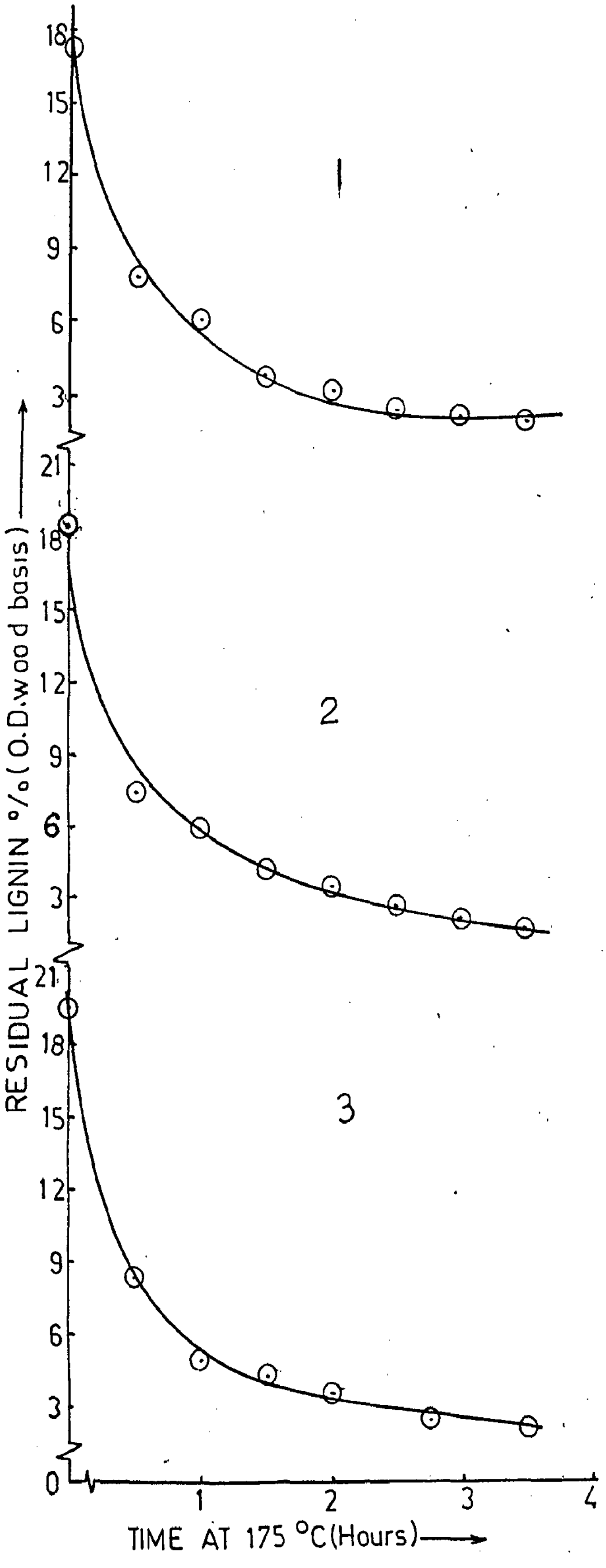


FIG.5.03C: RELATION BETWEEN COOKING TIME AND DEGREE OF LIGNIN (0·15XKappa NO.) REMOVAL DURING ALKALINE SULPHITE PULPING OF ① S.sesban ② C.cajan AND ③ S.aculeata

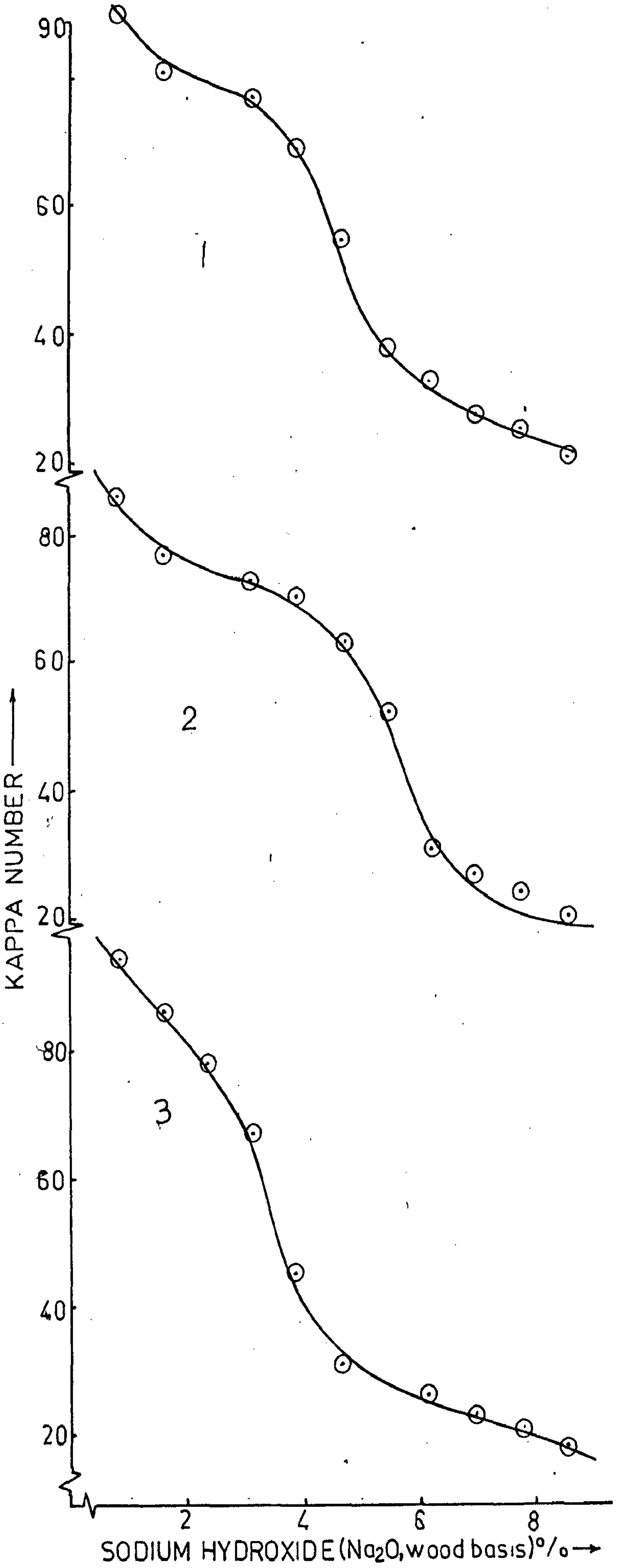


FIG.5.04C: PLOTS OF SODIUM HYDROXIDE CHARGE VS.KAPPA NUMBER DURING ALKALINE SULPHITE PULPING OF ① S.sesban ② C.cajan AND ③ S.aculeata.

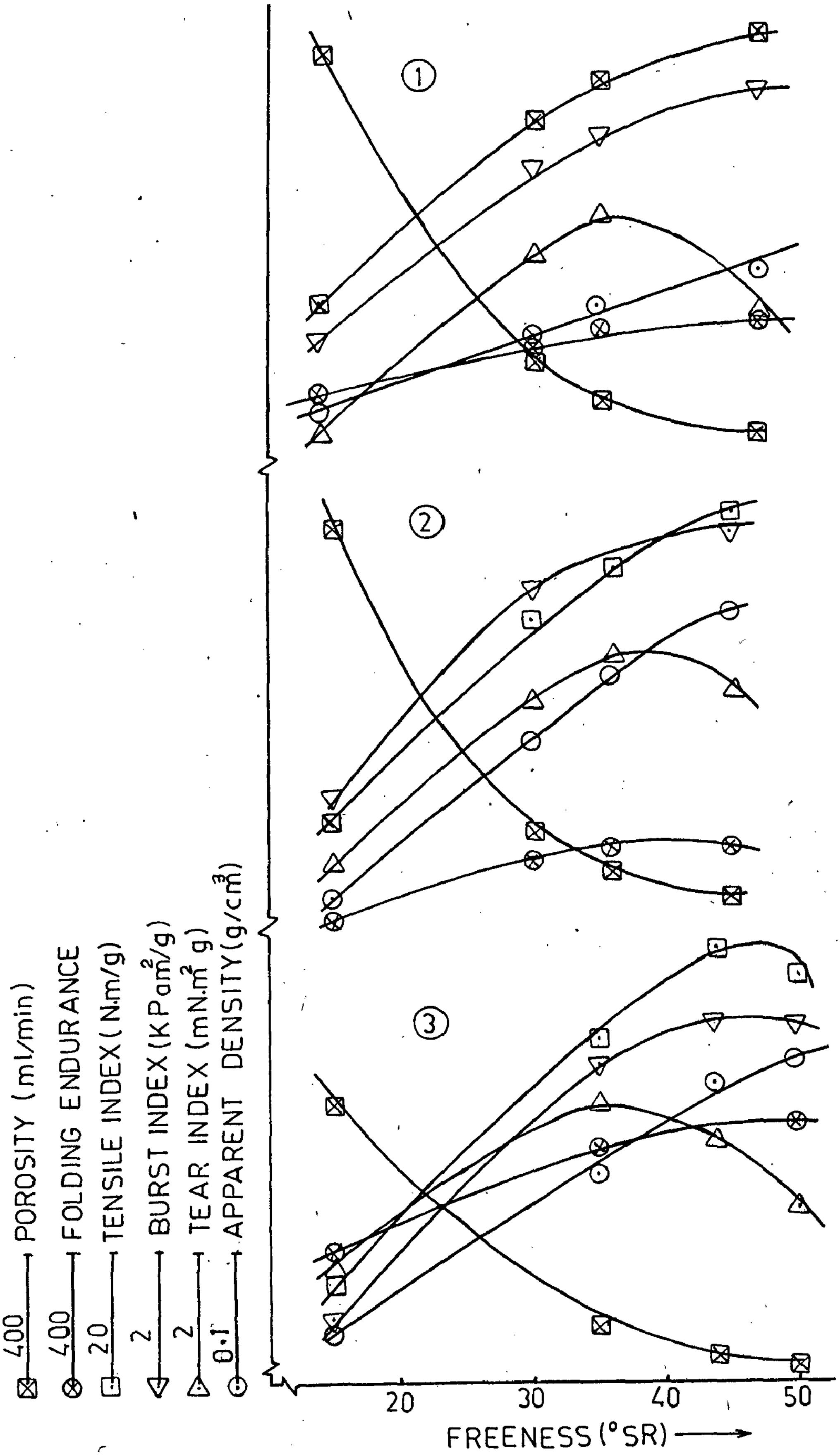


FIG.5.05C: PLOTS OF PULPSFREENESS(°SR) VS. STRENGTH PROPERTIES (Table 5·7D) OF ① S.sesban ② C. cajan AND ③ S. aculeata UNBLEACHED ALKALINE SULPHITE PULPS.

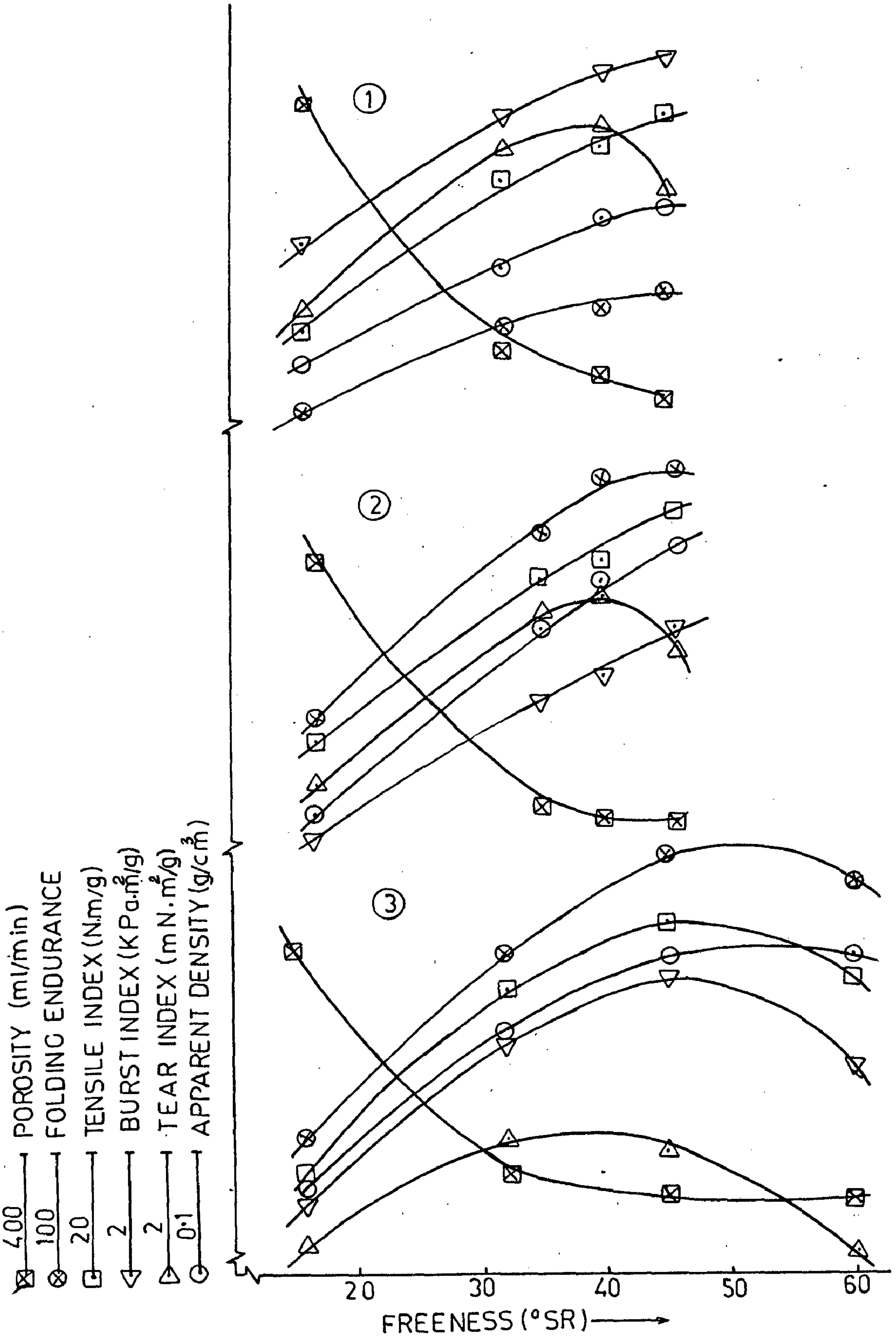


FIG. 5 06C: PLOTS OF PULP FREENESS (°SR) VS. STRENGTH PROPERTIES (Table 5.9D) OF ① S. sesban ② C. cajan AND ③ S. aculeata BLEACHED ALKALINE SULPHITE PULPS.

SEMI-ALKALINE SULPHITE(SAS) OR NEUTRAL SULPHITE PULPING STUDIES:

A new and potentially very important development in sulphite pulping is the moderately alkaline sulphite, semialkaline sulphite, or neutral sulphite-anthraquinone(AQ) process, all terms used to describe the same new process. Traditionally neutral sulphite pulping has been used, for producing coarse pulps in high yield, mainly from hard woods. There is no other single pulping process that is as varsatile as sulphite. It can produce well defined marketable pulp products over a range of 30-90% yield and over a pH range of 1-13. Conventional sulphite is characterised, among other things, by its high unbleached brightness and moderate physical strengths. Its high initial brightness and subsequent ease of bleaching are of insignificant economic importance.

Perhaps the most promising development in the past few years for the production of kraft like sulphite pulp has been the discovery of neutral sulphite pulping with anthraquinone(AQ) addition, producing pulps that are very close in physical strength to conventional kraft pulps, but at a significantly higher yield. According to Ingruber(30) alkaline sulphite (AS) cooking corresponds to a cold cooking pH of 10-13.5 with the cooking liquor containing mainly Na_2SO_3 and NaOH. Neutral or semialkaline sulphite (NS or SAS) corresponds to a cold cooking pH of <12.5 with the cooking liquor containing mainly Na_2SO_3 and Na_2CO_3. Such pulps, both unbleached and bleached have now been in commercial production for many years. Normally these pulps are mixed in the furnish for the production of printing papers such as newsprint, magazine paper and base paper for coating(24,52). The preliminary conclusions of these studies indicated that this process is very interesting from the point of view of both economy and quality, but is still in the development stage. The most promising initial applications of the process seem to be in production of packaging grades of papers and news reinforcement. With such views in mind it was considered worth while to expose these non-wood fibrous raw material to semi-alkaline sulphite pulping process for producing high yield pulps.

5.1.EXPERIMANTAL PROCEDURES:

5.1.1.PULPING STUDIES:

The methods of raw material preparation are given on page 63. For the optimization of pulping conditions, 100 gms. O.D. chips of S.sesban, S.aculeata and C.cajan were cooked in laboratory WEVERK tumbling electrically heated digester(0.02 M^3 capacity) having stainless steel bombs of 1 litre capacity. During these studies, technical grades chemicals were used except that of sodium sulphite which was of analytical grade. All dilutions were made with tap water. The cooking of S.sesban, S.aculeata and C.cajan chips were made at the following conditions.

Total alkali (as Na_2O) S.aculeata = 12 - 18 %
S.sesban & C.cajan = 14 - 20 %

Alkali ratio (Na_2SO_3:total alkali) = 0.60 - 0.95

Wood to liquor ratio S.aculeata = 1:4
S.sesban and C.cajan = 1:3.5

Time to maximum temperature = 90 minutes.

Time at maximum temperature = 180-210 minutes.

The pulping studies were made using different amounts of sodium sulphite and sodium carbonate in order to know the optimum alkali ratio of these pulping chemicals. The cookings were also made at different time to know the effect of cooking time during the course of pulping. During cooking the digester pressure was reduced to zero by gas relief at 105 °C. At the end of the cooking cycle, the cooked chips and liquor were blown fromthe digester and the cooked chips were defibred through a Bauer laboratory refiner with a plate clearance of 0.5mm, followed by a second pass at 0.1 mm. plate clearance. The pulps were washed and screened through a laboratory vibratory flat WEVERK screen with 0.15mm. slits and the screened pulps were washed, pressed and crumbled. The pulps were analysed for yield, rejects and Kappa number. The spent liquors were also analysed for its pH value. The results of these studies are reported in Tables-5.1D to 5.5D.

5.1.2.SEMI-ALKALINE SULPHITE-ANTHRAQUINONE PULPING:

SAS-AQ pulping have been done by adding a small amount of AQ(0.1%, on O.D. wood basis) using the same process conditions as used in case of plane SAS pulping. The results of these studies are reported in Table-5.8D.

5.1.3.BLEACHING STUDIES:

The bleaching studies on S.sesban, S.aculeata and C.cajan semi-alkaline sulphite and SAS-AQ pulps were done with the CEHH bleaching sequence. The bleaching conditions alongwith their results are tabulated in Tables-5.9D to 5.13D.

5.1.4.FIBRE CLASSIFICATION:

The fibre classification studies of S.sesban, S.aculeata and C.cajan SAS pulps were made with the help of Bauer- McNett fibre classifier using screens with mesh numbers, 20,60, 80 and 120. The results of fibre classification studies are reported in Table-5.14D. The photomicrograph of unbleached, bleached, unbeaten and beaten pulps fibres of these plants are shown in annexure on page 166 to 171.

5.1.5.PULP EVALUATION:

These pulps were beaten in a PFI mill(73) for different freeness levels and laboratory hand sheets of 60 g/m^2 were made on laboratory British sheet forming machine, to evaluate these pulps samples. The strength properties were determined by IS method(32) and the results are reported in Tables5.6D, 5.7D and 5.12D.

5.2.RESULTS AND DISCUSSIONS:

The most important factors influencing the result of SAS cooking were found to be the total alkali charge, the alkali ratio (Na_2SO_3:total alkali, both as Na_2O). Especially when the aim is to produce fully defibred pulps, the impregnation of cooking liquor into the chips is necessary. The influence of the total alkali charge and the alkali ratio during the course of S.sesban, S.aculeata and C.cajan pulping are shown in figures 5.01D and 5.02D. These figures clearly indicated that the alkali ratio should be in the range of 0.80-0.85 to achieve pulp with as low a kappa number as possible. An increase in the total alkali charge accelerates the delignification. It was also found that the Na_2SO_3 charge has a greater influence on delignification than the total alkali charge. Figures 5.03D and 5.04D showed that the pulp yields and rejects both decreased as the amount of sodium sulphite or alkali ratio increased upto a level of 0.80- 0.85 and beyond that the pulp yield showed an increasing trend and it is due to the fact that pH of the cooking liquor decreased as the amount of Na_2SO_3 increased in the total alkali. Although in SAS pulping Na_2SO_3 is the main delignifying agent but at lower pH level it is comparatively less effective than at higher pH level i.e. the rate of delignification increased at higher pH level, the more the pH of SAS cooking liquor the higher will be the rate of delignification and shorter will be the cooking cycle. The increase in yield beyond 0.85 alkali ratio is due to fact that beyond this alkali ratio the pH of the cooking liquor showed a decreasing trend thereby reducing the rate of delignification and the cookings were made for a particular time, during this cooking time the complete delignification could not be achieved. The delignification stops at a Kappa number level of around 50. With an increase in the Na_2SO_3 charge and cooking time, a lower Kappa number may possibly be achieved. The retarded delignification in SAS cooking may be due to the rapid decrease in the cold pH already in the early stages of cooking. Most of the chemicals of the cooking liquor charged consumed till the digester temperature raised upto the maximum temperature. This is why, the cooking method has been called neutral suphite (NS) or semi-alkaline sulphite(SAS) cooking. The most interesting aspects of the SAS pulping process are comparatively brighter pulps with high yields. The total hemicellulose contents of SAS pulps are high, and the high yields of SAS pulps are partly due to stabilization of hemicelluloses(Xylan and glucomannan) and partly due to the mild alkaline cooking conditions, which preserve the hemicellulose in pulp (29.30 & 31).

The AQ has a considerable effect in semi-alkaline sulphite pulping(22,77). The pulps of low Kappa numbers are obtained by adding 0.1% AQ at a alkali ratio of 0.85, total alkali charge of 18%(as Na_2O) for S.sesban and C.cajan and 16% for S.aculeata; and less cooking time at temperature is required.

The laboratory experiments showed that chemically defibred pulps with a Kappa number of about 50 can easily be produced under varying cooking conditions. The optimum bleaching conditions for these pulps were not determined and only some indicative bleaching experiments were carried out. The brightness of unbleached pulps varies between 41-44%(Elrepho). Because of the rather high Kappa number, the chlorine consumption is slightly higher. The pulps with brightness levels of about 65-70%(Elrepho) were obtained as a result of CEH bleaching sequence. For high brightness levels CEHH bleaching sequences were also applied giving the pulps with a brightness level of about 78%(Elrepho). The effect of bleaching on the papermaking properties are shown in Tables-5.12D and 5.13D.

SAS-AQ pulps have low Kappa numbers thereby showed good response towards CEHH bleaching sequence and gave bleached pulps with higher brightness.

The bleached and unbleached pulps are beaten in PFI mill. The SAS and SAS-AQ pulps are more easily beaten upto a desired level of freeness. It means a shorter time is required to beat SAS and SAS-AQ pulps thereby requiring less energy during beating and refining. Tables-5.6D, 5.7D and 5.12D showed the strength properties of unbleached and bleached pulps. Bleaching does not markedly change the papermaking properties of SAS pulps. The strength propertiesof a certain unbleached pulp type can be visualized by plotting the graph between Kappa numbers and strength properties(Fig.5.05D) of unbleached pulp and apparent density versus strength properties of bleached pulps(Fig.5.06D). SAS pulps of S. aculeata and C.cajan have good bonding ability thereby showed comparatively higher values of strength properties. Tear index of SAS pulps are relatively high and it is probably caused by the properties of the fibre, i.e. stiffness combined with good bonding ability.

Bleaching seems to have only a minor effect on strength properties. The strength properties slightly decline as a result of bleaching. In addition to brightness, opacity is an important property of many grades of paper. SAS pulps have high scattering coefficient. This is because the fibres are stiff and uncollapsed which provides a large optically active area, but have good bonding ability due to high local plasticity and good bonding strength.

5.3.CONCLUSION:

The semi-alkaline sulphite process offers many advantages including the high pulp yield. The yield of SAS S.sesban,S.aculeata and C.cajan pulps decreased as a result of an increase in cooking time as well as total chemicals. The Kappa number decreased both with an increase in cooking time and chemicals. The production of SAS pulps is quite economic in comparison to other pulping processes. The SAS process is free from foul odour of liquor and condensates. Inspite of several advantages, the SAS process bears with many draw-backs which includes the longer cooking time for getting pulps with low Kappa number.

The most notable feature of SAS-AQ pulping is the high yield for bleachable grade of pulps from S.sesban, S.aculeata and C.cajan which are still higher than that obtained with the kraft process. Inspite of their high hemicellulose content, unbleached SAS-AQ pulps have a light scattering coefficient equal to or higher than that of kraft pulps. The physical properties of SAS-AQ pulps are good, which makes them suitable for many grades of paper.

Table-5.1D:Pulping Conditions And Characteristics Of S.aculeata Semi-Alkaline Sulphite Pulps Of 12% Total Alakli (As Na_2O).

PARTICULARS	I SERIES					II SERIES				
Sodium sulphite(O.D. wood as Na_2O) %	7.20	8.40	9.60	10.80	11.40	7.20	8.40	9.60	10.80	11.40
Sodium carbonate(O.D. wood as Na_2O)%	4.80	3.60	2.40	1.20	0.60	4.80	3.60	2.40	1.20	0.60
Alkali ratio	0.60	0.70	0.80	0.90	0.95	0.60	0.70	0.80	0.90	0.95
White liquor pH	11.20	10.70	10.50	10.00	9.50	11.20	10.70	10.50	10.00	9.50
Unscreened pulp yield %	78.71	75.26	70.93	70.00	71.48	77.70	72.49	69.24	68.04	71.13
Screened pulp yield %	75.40	71.80	68.40	67.70	68.80	74.60	69.70	66.90	66.00	68.60
Rejects %	4.40	4.10	3.70	3.40	3.90	4.20	4.00	3.50	3.10	3.70
Kappa no.	96.00	80.60	72.20	65.60	73.10	88.90	75.40	62.70	62.00	72.77
Spent liquor pH	8.20	8.10	8.00	7.90	7.50	8.20	8.00	7.90	7.80	7.40

Cooking conditions:

Wood chips = 100 gms(O.D)

Liquor to wood ratio = 4:1

Time from 30 °C to 170 °C = 90 minutes

Time at 170 °C (I Series) = 180 minutes

Time at 170 °C (II Series) = 210 minutes.

Table-5.2D:Pulping Conditions And Characteristics Of Bomb Cooking Of S.sesban, C.cajan And S.aculeata Semi-Alkaline Sulphite Pulps At 14% Alkali (as Na_2O)

PARTICULARS	I SERIES					II SERIES				
Sodium sulphite (O.D. wood as Na_2O) %	8.40	9.80	11.20	12.60	13.30	8.40	9.80	11.20	12.60	13.30
Sodium carbonate(O.D. wood as Na_2O) %	5.60	4.20	2.80	1.40	0.70	5.60	4.20	2.80	1.40	0.70
Alkali ratio	0.60	0.70	0.80	0.90	0.95	0.60	0.70	0.80	0.90	0.95
White liquor pH	11.20	10.85	10.50	10.00	9.56	11.20	10.85	10.50	10.00	9.56
Sesbania sesban										
Unscreened pulp yield %	75.60	71.00	67.14	67.50	70.50	72.00	68.90	65.20	66.00	68.60
Screened pulp yield %	72.42	68.16	64.68	65.00	67.92	69.12	66.28	63.00	63.89	66.10
Rejects %	4.20	4.00	3.80	3.60	3.90	4.00	3.80	3.50	3.20	3.70
Kappa no.	89.4	75.00	68.00	66.40	72.00	87.20	73.00	65.60	62.50	69.40
Spent liquor pH	8.30	8.20	8.10	7.80	7.40	8.20	8.10	8.00	7.70	7.50
Cajanus cajan										
Unscreened pulp yield %	78.20	74.00	70.30	69.50	72.00	76.80	72.50	69.00	68.20	71.00
Screened pulp yield %	74.68	70.90	67.84	67.00	69.12	73.65	69.60	66.65	66.16	68.44
Rejects %	4.50	4.20	3.60	3.50	4.00	4.10	4.00	3.40	3.00	3.60
Kappa no.	95.00	79.40	71.50	69.00	73.80	88.00	74.60	64.50	63.70	71.50
Spent liquor pH	8.20	8.20	8.00	7.70	7.40	8.30	8.20	8.10	7.80	7.40
Sesbania aculeata										
Unscreened pulp yield %	76.29	70.55	67.84	68.94	69.90	75.71	69.08	66.20	66.00	68.13
Screened pulp yield %	74.00	69.50	66.50	67.20	68.00	72.00	67.60	65.00	64.60	66.60
Rejects %	3.10	3.00	2.00	2.60	2.80	3.00	2.80	1.80	2.20	2.00
Kappa no.	87.30	74.20	61.40	61.00	71.20	81.40	70.00	59.30	59.00	62.50
Spent liquor pH	8.10	8.10	8.00	7.70	7.40	8.10	8.00	7.80	7.60	7.30

Cooking conditions for S.sesban and C.cajan

Wood chips = 100 gms(O.D)
Liquor to wood ratio = 3.5:1
Time from 30°C to 170°C = 90 minutes

Time at 170°C(I series) = 180 minutes
Time at 170 °C(II series) = 210 minutes

Table-5.3D: Pulping Conditions And Characteristics of Bomb Cooking Of S.sesban, C.cajan And S.aculeata Semi-Alkaline Sulphite Pulps At 16% Total Alkali (as Na_2O).

PARTICULARS	I SERIES						II SERIES			
Sodium sulphite (O.D. wood as Na_2O) %	9.60	11.20	12.80	14.40	15.20	9.60	11.20	12.80	14.40	15.20
Sodium carbonate(O.D. wood as Na_2O) %	6.40	4.80	3.20	1.60	0.80	6.40	4.80	3.20	1.60	0.80
Alkali ratio	0.60	0.70	0.80	0.90	0.95	0.60	0.70	0.80	0.90	0.95
White liquor pH	11.30	10.90	10.54	10.10	9.60	11.30	10.90	10.54	10.10	9.60
<u>Sesbania sesban</u>										
Unscreened pulp yield %	73.60	68.20	64.50	65.70	67.40	70.20	66.50	62.60	63.00	66.40
Screened pulp yield %	71.45	66.30	63.00	64.13	65.58	68.24	64.70	61.37	61.62	63.74
Rejects %	3.00	2.80	2.20	2.40	2.70	2.80	2.70	2.00	2.20	2.50
Kappa nao.	83.60	71.40	63.80	63.00	70.00	80.00	68.40	60.70	58.40	62.00
Spent liquor pH	8.30	8.30	8.00	7.80	7.50	8.20	8.10	8.00	7.70	7.40
<u>Cajanus cajan</u>										
Unscreened pulp yield %	76.00	71.40	68.00	68.20	70.50	74.80	70.00	66.50	67.20	68.60
Screened pulp yield %	73.56	69.26	66.50	66.70	68.46	72.56	67.97	65.17	65.90	66.82
Rejects %	3.20	3.00	2.30	2.20	2.90	3.00	2.90	2.00	1.70	2.60
Kappa no.	86.80	75.00	62.30	62.70	71.00	81.00	69.00	59.50	59.00	64.00
Spent liquor pH	8.20	8.10	7.90	7.60	7.40	8.20	8.00	8.00	7.70	7.40
<u>Sesbania aculeata</u>										
Unscreened pulp yield %	75.00	69.97	65.47	66.48	69.10	70.79	68.54	62.82	63.95	68.10
Screened pulp yield %	73.00	68.20	64.70	65.30	67.60	69.60	66.30	62.30	63.00	65.70
Rejects %	2.80	2.60	1.20	1.80	2.20	2.60	2.30	1.00	1.50	2.10
Kappa no.	81.00	64.30	57.80	59.20	63.70	74.50	62.60	55.20	56.80	61.00
Spent liquor pH	8.30	8.10	7.90	7.50	7.50	8.30	8.20	8.10	7.70	7.60

Table-5.4D:Pulping Conditions And Characteristics of Bomb Cooking Of S.sesban, C.cajan And S.aculeata Semi-Alkaline Sulphite Pulps At 18% Total Alkali (as Na_2O).

PARTICULARS	I SERIES					II SERIES				
Sodium sulphite (O.D. wood as Na_2O) %	10.80	12.60	14.40	16.20	17.10	10.80	12.60	14.40	16.20	17.10
Sodium carbonate(O.D. wood as Na_2O) %	7.20	5.40	3.60	1.80	0.90	7.20	5.40	3.60	1.80	0.90
Alkali ratio	0.60	0.70	0.80	0.90	0.95	0.60	0.70	0.80	0.90	0.95
White liquor pH	11.44	10.90	10.58	10.13	9.64	11.40	10.90	10.58	10.13	9.64
Sesbania sesban										
Unscreened pulp yield %	71.70	65.42	62.57	63.17	65.82	68.40	63.90	60.42	61.00	64.20
Screened pulp yield %	69.76	63.42	61.65	62.18	64.40	66.63	62.50	59.70	60.20	63.12
Rejects %	2.80	2.50	1.50	1.60	1.90	2.60	2.20	1.20	1.30	1.70
Kappa no.	78.00	66.50	57.20	53.40	62.80	70.50	64.00	54.00	55.70	58.60
Spent liquor pH	8.40	8.30	8.10	7.90	7.60	8.30	8.20	8.10	8.00	7.70
Cajanus cajan										
Unscreened pulp yield %	75.50	70.00	66.40	67.00	69.00	71.60	68.14	64.00	64.84	67.80
Screened pulp yield %	73.24	68.00	65.47	65.86	67.62	69.66	66.54	63.25	64.00	66.58
Rejects %	3.00	2.80	1.40	1.70	2.00	2.70	2.40	1.10	1.30	1.80
Kappa no.	82.00	66.20	58.40	60.00	62.00	74.00	63.40	54.50	55.20	60.00
Spent liquor pH	8.30	8.30	8.20	8.00	8.10	8.20	8.10	8.00	7.80	7.90
Sesbania aculeata										
Unscreened pulp yield %	72.60	68.60	63.30	64.51	66.98	68.48	66.61	61.55	62.00	64.40
Screened pulp yield %	70.90	66.50	62.70	63.50	65.80	68.40	64.70	61.00	61.20	63.42
Rejects %	2.40	2.10	1.00	1.60	1.80	2.20	2.00	0.90	1.40	1.60
Kappa no.	72.20	62.10	55.30	56.30	62.00	70.00	59.60	52.00	52.50	56.40
Spent liquor pH	8.40	8.20	8.10	7.80	7.60	8.30	8.20	8.00	7.70	7.50

Table-5.5D: Pulping Conditions And Characteristics Of Bomb Cooking Of S.sesban & C.cajan Semi-Alkaline Sulphite At 20% Total Alkali (as Na_2O).

PARTICULARS	I SERIES					II SERIES				
Sodium Sulphite (O.D. wood as Na_2O) %	12.00	14.00	16.00	18.00	19.00	12.00	14.00	16.00	18.00	19.00
Sodium Carbonate(O.D. wood as Na_2O) %	8.00	6.00	4.00	2.00	1.00	8.00	6.00	4.00	2.00	1.00
Alkali ratio	0.60	0.70	0.80	0.90	0.95	0.60	0.70	0.80	0.90	0.95
White liquor pH	11.50	10.92	10.60	10.16	9.64	11.50	10.92	10.60	10.16	9.64
Sesbania sesban										
Unscreened pulp yield %	69.30	63.18	60.78	62.20	64.50	66.70	61.20	58.74	59.70	63.00
Screened pulp yield %	67.55	62.00	60.26	61.32	63.41	65.30	60.10	58.20	59.00	62.12
Rejects %	2.60	1.90	1.20	1.40	1.70	2.10	1.70	0.92	1.20	1.40
Kappa no.	76.40	62.30	53.00	58.40	61.00	66.70	58.30	49.20	51.40	55.60
Spent liquor pH	8.30	8.20	8.10	7.90	7.60	8.30	8.20	8.20	7.80	7.50
Cajanus cajan										
Unscreened pulp yield %	73.00	68.20	64.00	65.30	67.80	70.20	66.00	62.80	63.50	65.60
Screened pulp yield %	71.17	67.00	63.23	64.45	66.72	68.80	64.82	62.18	62.74	64.62
Rejects %	2.50	1.90	1.20	1.40	1.60	2.00	1.80	1.00	1.20	1.50
Kappa no.	77.00	61.00	54.60	55.00	60.20	68.00	57.00	51.00	52.40	58.80
Spent liquor pH	8.30	8.20	8.00	7.80	7.50	8.30	8.20	8.00	7.90	7.50

Table-5.6D:Pulping Conditions, Characteristics And Results Of Pulp Evaluation Of S.sesban, C.cajan And S.aculeata Semi-Alkaline Sulphite(SAS) Pulps At Different Total Alkali Charge.

Sl. No.	PARTICULARS	Total Alkali 16 % (Na_2O) S.aculeata		TOTAL ALKALI 18% AS(Na_2O) S.sesban		C. cajan		S.aculeata		TOTAL ALKALI 20% AS(Na_2O) S.sesban		C. cajan	
1.	Sodium sulphite (O.D. wood) %	12.80	13.60	14.40	15.30	14.40	15.30	14.40	15.30	16.00	17.00	16.00	17.00
2.	Sodium carbonate(O.D. wood) %	3.20	2.40	3.60	2.70	3.60	2.70	3.60	2.70	4.00	3.00	4.00	3.00
3.	Alkali ratio	0.80	0.85	0.80	0.85	0.80	0.85	0.80	0.85	0.80	0.85	0.80	0.85
4.	White liquor pH	10.54	10.50	10.58	10.52	10.58	10.52	10.58	10.54	10.60	10.61	10.60	10.61
5.	Screened pulp yield %	62.00	60.90	59.00	58.20	63.00	62.20	60.80	59.20	57.40	56.00	61.00	60.00
6.	Kappa number	54.40	53.20	53.60	52.80	54.00	52.50	51.60	50.40	49.00	48.20	50.60	49.50
7.	Spent liquor pH	8.10	8.00	8.00	7.90	8.00	7.80	8.00	7.90	8.10	7.90	8.10	8.00
8.	Apparent sulphite (as Na_2SO_3) gpl	6.80	6.70	6.40	6.20	6.70	6.50	6.50	6.30	6.10	5.80	6.40	6.30
9.	PFI Revolution (No.)	1700	1750	2000	2040	1900	2050	1850	1900	1960	2100	1900	1850
10.	Freeness (°SR)	43	44	41	43	44	47	44	45	42	45	45	44
11.	Drainage time (Sec)	18.70	19.00	17.00	17.50	19.20	21.10	19.10	19.40	16.70	17.80	19.40	19.20
12.	Apparent density$_2$(g/cm^3)	0.72	0.74	0.70	0.74	0.72	0.75	0.77	0.79	0.73	0.77	0.74	0.76
13.	Tear index ($mN.m^2/g$)	6.10	5.90	5.21	5.11	5.35	5.12	5.70	5.46	4.82	4.75	5.10	4.92
14.	Burst index ($KPa.m^2/g$)	5.06	5.30	4.86	4.90	4.80	4.92	5.72	5.95	5.05	5.12	5.10	5.20
15.	Tensile index (N.m/g)	68.12	68.70	52.34	53.53	57.00	57.76	71.45	72.42	53.00	55.67	58.65	60.20
16.	Folding endurance (Köhler Molin)	310	326	220	226	240	248	355	370	230	247	306	310
17.	Porosity(Bendtsen)ml/min	110	105	150	140	150	130	95	80	140	110	120	105
18.	Brightness (Elrepho) %	41.00	42.00	38.60	39.00	38.70	41.00	42.00	44.00	38.50	40.20	40.30	40.40

Cooking variables:

Liquor to wood ratio = 3.5:1(for S.sesban and C.cajan)
= 4:1(for S.aculeata)

Time from 30°C to 170°C = 90 minutes.
Time at 170°C =210 minutes.

Table-5.7D:Cooking Conditions And Strength Properties Of S.sesban, C.cajan And S.aculeata Semi-Alkaline Sulphite-AQ Pulps.

PARTICULARS	S. sesban	C. cajan	S. aculeata
Alkali charge(O.D. wood) %	18	18	16
Alkali ratio	0.85	0.85	0.85
AQ (O.D. wood) %	0.10	0.10	0.10
Liquor to wood ratio	3.5:1	3.5:1	4:1
Time from 30 °C to 165°C (Minutes)	90	90	90
Time at 165 °C (Minutes)	180	180	180
Pulp yield %	57.8	61.6	60.2
Kappa number	42.6	40.6	41.2

Plant species	PFI Revolution	Freeness (^{o}SR)	Drainage Time (Sec)	Apparent density (g/cm^3)	Tear index ($mN.m^2/g$)	Burst index ($KPa.m^2/g$)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min)	Folding endurance Köhler Molin
Sesbania sesban	0	14	3.8	0.62	4.26	1.30	25.89	1400	11
	1200	30	10.4	0.67	6.00	4.19	54.70	650	170
	1600	36	13.6	0.73	5.42	4.52	56.12	140	186
	2100	45	17.8	0.74	4.80	4.95	62.00	130	214
Cajanus cajan	0	14	4.2	0.62	4.61	1.29	24.91	850	14
	1050	30	14.2	0.70	5.80	4.62	47.30	460	171
	1650	42	18.5	0.76	5.20	5.30	62.08	110	231
	2100	50	42.5	0.79	4.15	5.44	63.28	95	240
Sesbania aculeata	0	14	4.2	0.67	5.88	1.18	30.15	800	16
	1100	32	15.1	0.74	6.49	4.72	54.63	400	285
	1600	41	19.3	0.76	5.90	5.35	73.00	115	320
	2000	47	22.1	0.81	4.90	6.10	79.10	70	441

Table-5.8D: Bleaching Conditions And Characteristics Of S.sesban Semi-Alkaline Sulphite(SAS) And SAS-AQ Pulps.

Sl.No.	PARTICULARS	PULP NUMBERS				
		1	2	3	4	SAS-AQ
1.	Unbleached pulp Kappa no.	53.60	52.80	49.00	48.20	42.60
2.	Chlorination stage (C)					
	Chlorine applied as available Cl_2 on pulp %	8.00	7.89	7.30	7.12	7.20
	Chlorine consumed as available Cl_2 on pulp %	7.90	7.86	7.29	7.10	7.18
	Final pH	1.80	1.70	1.90	1.80	1.90
3.	Alkali Extraction (E)					
	NaOH applied on pulp %	1.80	1.80	1.80	1.80	1.80
	Initial pH	11.30	11.20	11.40	11.20	11.40
	Final pH	10.00	10.20	9.70	9.90	10.10
4.	Hypochlorite Ist stage (H_1)					
	Hypo applied as available Cl_2 on pulp %	2.80	3.00	2.80	2.70	2.50
	Hypo consumed as available Cl_2 on pulp %	2.76	2.94	2.75	2.68	2.45
	Final pH	7.80	7.90	7.80	7.70	7.90
5.	Hypochlorite 2nd stage (H_2)					
	Hypo applied as available Cl_2 on pulp %	1.10	1.20	1.00	0.90	1.00
	Hypo consumed as available Cl_2 on pulp %	1.02	1.13	0.98	0.86	0.92
	Final pH	7.70	7.70	7.80	7.70	7.90
6.	Total Cl_2 added on pulp %	11.90	12.09	11.10	10.72	10.70
7.	Total Cl_2 consumed on pulp %	11.68	11.93	11.02	10.64	10.55
8.	Bleaching losses %	10.60	10.20	9.80	9.30	9.00
9.	Bleached pulp yield %	52.75	52.26	51.78	50.80	52.60
10.	Viscosity CED (0.5%) cp.	11.40	11.30	11.00	11.20	11.40
11.	Brightness (Elrepho) %	76.00	76.40	76.80	76.60	77.00

PROCESS VARIABLES		C	E	H_1	H_2
1.	Consistency %	3	10	10	10
2.	Temperature °C	25 ± 2	60 ± 2	45 ± 2	45 ± 2
3.	Time (Minutes)	30	90	60	120

Table-5.9D:Bleaching Conditions And Characteristics Of C.cajan Semi-Alkaline Sulphite(SAS) And SAS-AQ Pulps.

Sl.No.	PARTICULARS	PULP NUMBERS				
		1	2	3	4	SAS-AQ
1.	Unbleached pulp Kappa no.	54.00	52.50	50.60	49.50	40.60
2.	Chlorination stage (C)					
	Chlorine applied as available Cl_2 on pulp %	8.10	7.89	7.56	7.40	6.35
	Chlorine consumed as available Cl_2 on pulp %	8.07	7.87	7.55	7.38	6.34
	Final pH	1.90	1.80	1.80	1.90	1.90
3.	Alkali Extraction (E)					
	NaOH added on pulp %	2.00	2.00	2.00	2.00	2.00
	Initial pH	11.40	11.30	11.20	11.40	11.30
	Final pH	10.10	10.00	9.80	9.60	10.10
4.	Hypochlorite Ist stage (H_1)					
	Hypo added as available Cl_2 on pulp %	3.10	3.00	2.90	2.84	2.40
	Hypo consumed as available Cl_2 on pulp %	3.04	2.95	2.86	2.80	2.36
	Final pH	7.80	7.60	7.80	7.90	8.00
5.	Hypochlorite 2nd stage (H_2)					
	Hypo added as available Cl_2 on pulp %	1.15	1.10	1.10	1.00	0.98
	Hypo consumed as available Cl_2 on pulp %	1.10	1.07	1.06	0.98	0.92
	Final pH	7.60	7.50	7.70	7.80	7.80
6.	Total chlorine added on pulp %	12.35	11.99	11.56	11.24	9.73
7.	Total Cl_2 consumed on pulp %	12.21	11.89	11.47	11.16	9.62
8.	Bleaching losses %	11.00	10.40	10.50	10.70	10.50
9.	Bleached pulp yield %	57.40	56.18	55.76	53.58	55.13
10.	Viscosity CED(0.5%) cp.	11.60	11.40	11.00	11.10	11.30
11.	Brightness (Elrepho) %	77.40	77.50	77.20	77.00	77.70

PROCESS VARIABLES:		C	E	H_1	H_2
1.	Consistency %	3	10	9	9
2.	Temperature °C	25±2	60±2	45±2	45±2
3.	Time (Minutes)	30	90	60	120

Table-5.10D: Bleaching Conditions And Characteristics Of Sesbania aculeata Semi-Alkaline Sulphite(SAS) And SAS-AQ Pulps.

Sl.No.	PARTICULARS	PULPS NUMBERS				
		1	2	3	4	SAS-AQ
1.	Unbleached pulp Kappa no.	54.40	53.20	51.60	50.40	41.20
2.	<u>Chlorination stage</u> (C)					
	Chlorine applied as available Cl$_2$ on pulp %	8.84	8.60	8.38	8.10	6.92
	Chlorine consumed as available Cl$_2$ on pulp %	8.81	8.59	8.36	8.08	6.90
	Final pH	1.80	1.80	1.90	1.70	1.90
3.	<u>Alkali extraction stage</u>(E)					
	NaOH added on pulp %	2.00	2.00	2.00	2.00	2.00
	Initial pH	11.20	11.20	11.10	11.00	11.30
	Final pH	10.10	10.20	10.10	9.50	9.80
4.	<u>Hypochlorite 1st stage</u>(H$_1$)					
	Hypo added as available Cl$_2$ on pulp %	2.30	2.25	2.25	2.00	1.98
	Hypo consumed as available Cl$_2$ on pulp %	2.26	2.23	2.21	1.99	1.93
	Final pH	7.70	7.80	7.60	7.90	7.80
5.	<u>Hypochlorite 2nd stage</u>(H$_2$)					
	Hypo added as available Cl$_2$ on pulp %	1.25	1.10	0.90	0.90	1.00
	Hypo consumed as available Cl$_2$ on pulp %	1.17	1.02	0.81	0.84	0.92
	Final pH	7.60	7.70	7.50	7.60	7.70
6.	Total Cl$_2$ added on pulp %	12.39	11.95	11.53	11.00	9.90
7.	Total Cl$_2$ consumed on pulp %	12.24	11.84	11.38	10.91	9.75
8.	Bleaching losses %	11.20	10.60	10.40	11.00	10.60
9.	Bleached pulp yield %	55.00	53.90	54.00	52.30	53.80
10.	Pulp brightness(Elrepho)%	79.30	78.00	78.20	78.70	80.00
11.	Viscosity CED(0.5%) cp.	11.80	11.70	11.40	11.00	11.30

PROCESS VARIABLES:		C	E	H$_1$	H$_2$
1.	Consistency %	3	10	10	10
2.	Temperature °C	25±2	60±2	45±2	45±2
3.	Time (Minutes)	30	90	60	120

Table-5.11D:Strength Properties Of S.sesban, C.cajan And S.aculeata Semi-Alkaline Sulphite Bleached Pulps.

Sl.No.	PARTICULARS	S.sesban Pulps Number				C.cajan Pulps Number				S.aculeata Pulp Number			
		1	2	3	4	1	2	3	4	1	2	3	4
1.	PFI Revolution (No.)	1400	1450	1400	1500	950	1000	1200	1100	900	980	1150	1200
2.	Freeness (^{o}SR)	44	45	44	46	42	44	45	42	41	44	45	46
3.	Drainage time(Sec)	19.00	19.20	19.00	19.40	19.60	21.20	21.50	19.40	19.00	19.80	21.20	21.50
4.	Apparent density(g/cm^{3})	0.80	0.83	0.84	0.86	0.83	0.84	0.86	0.88	0.80	0.82	0.83	0.86
5.	Tear index (mN.M^{2}/g)	4.22	4.16	3.83	3.76	4.55	4.40	4.30	4.27	5.15	5.08	4.98	4.80
6.	Burst index (KPa.m^{2}/g)	3.50	3.76	4.10	4.35	3.97	4.10	4.50	4.66	4.10	4.30	4.80	5.04
7.	Tensile index (N.m/g)	42.60	45.47	47.10	48.80	49.30	51.67	53.40	55.75	61.65	63.16	64.20	66.65
8.	Folding endurance (Köhler Molin)	109	113	118	122	152	156	167	170	254	257	262	268
9.	Porosity Bendtsen (ml/min)	110	105	95	90	105	95	85	80	90	80	75	60
10.	Brightness(Elrepho) %	71.40	71.00	70.80	70.20	72.70	72.30	72.00	72.80	74.60	74.30	74.00	74.40
11.	Opacity(%)	84.20	83.00	83.60	81.00	86.40	84.00	81.00	79.00	84.00	82.00	81.40	82.00

Table-5.12D:Strength Properties Of S.sesban, C.cajan And S.aculeata Semi-Alkaline Sulphite-AQ Bleached Pulps.

Plant species	PFI Revolution (No.)	Freeness (^oSR)	Drainage time (Sec)	Apparent density (g/cm^3)	Tear index ($mN.m^2/g$)	Burst index ($KPa.m^2/g$)	Tensile index (N.m/g)	Porosity Bendtsen (ml./min)	Folding endurance Köhler Molin	Brightness (Elrepho) (%)	Opacity (%)
Sesbania	0	16	4.3	0.65	3.30	1.40	29.20	800	17	76.4	90.5
sesban	1050	32	13.0	0.74	4.26	3.20	44.26	370	90	74.0	88.2
	1200	37	16.3	0.79	4.10	3.40	50.38	110	115	72.8	86.7
	1500	46	19.3	0.82	3.98	4.30	54.97	80	150	71.2	81.6
Cajanus	0	16	4.5	0.69	3.92	1.40	30.66	600	18	79.2	90.0
cajan	800	36	16.5	0.76	5.10	3.60	48.25	160	94	76.2	86.8
	950	40	19.2	0.82	4.65	3.98	52.00	65	143	74.0	83.1
	1200	45	20.5	0.85	4.38	4.60	57.12	60	164	73.6	79.8
Sesbania	0	16	4.4	0.68	3.92	1.20	28.47	670	18	79.4	90.2
aculeata	800	35	16.2	0.73	5.48	3.59	48.32	310	162	76.3	86.2
	950	38	18.7	0.76	5.15	4.52	59.84	80	244	75.5	84.0
	1200	45	20.3	0.82	4.92	5.10	68.21	75	271	74.6	81.6

Table-5.13D:Bauer -Mc Nett Fibre Classification Of Semi-Alkaline Sulphite Pulps.

Sl.No.	Mesh Size	Sesbania sesban		Cajanus cajan		Sesbania aculeata	
		Unbleached (%) 15 °SR Kappa no. 52.8	Bleached (%) 17 °SR	Unbleached (%) 16 °SR Kappa no. 52.5	Bleached (%) 17 °SR	Unbleached (%) 14 °SR Kappa no. 53.2	Bleached (%) 16 °SR
1.	+20	16.8	3.4	14.0	2.5	15.0	2.9
2.	- 20+ 60	42.4	36.4	45.0	34.7	49.8	37.7
3.	- 60+ 80	19.6	25.2	20.2	26.2	19.0	28.0
4.	- 80+120	6.8	14.0	6.4	12.0	7.0	13.8
5.	-120	14.4	21.0	14.4	24.6	14.2	17.6

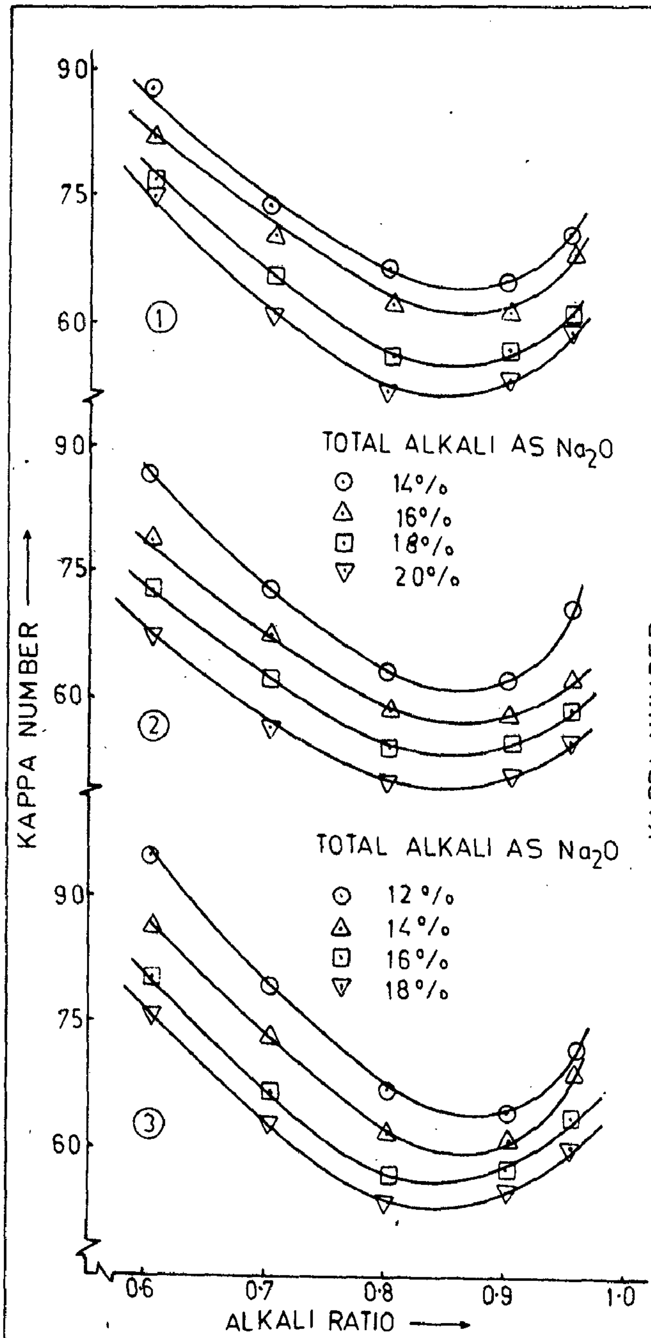


FIG.5.01D: PLOTS OF ALKALI RATIO VS. KAPPA NUMBER DURING SEMI-ALKALINE SULPHITE PULPING AT 170 °C (180 Min) OF ① S.sesban ② C.cajan AND ③ S.aculeata.

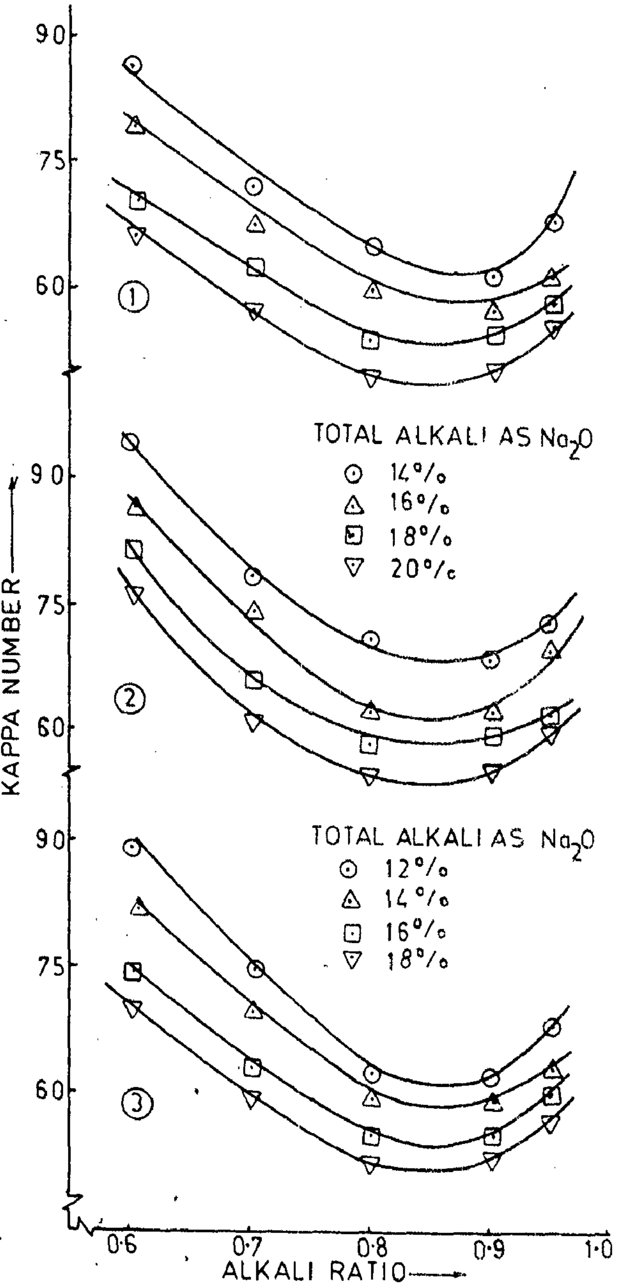


FIG. 5.02 D: PLOTS OF ALKALI RATIO VS. KAPPA NUMBER DURING SEMI-ALKALINE SULPHITE PULPING AT 170°C (210 Min) OF ① S. sesban ② C.cajan AND ③ S. aculeata.

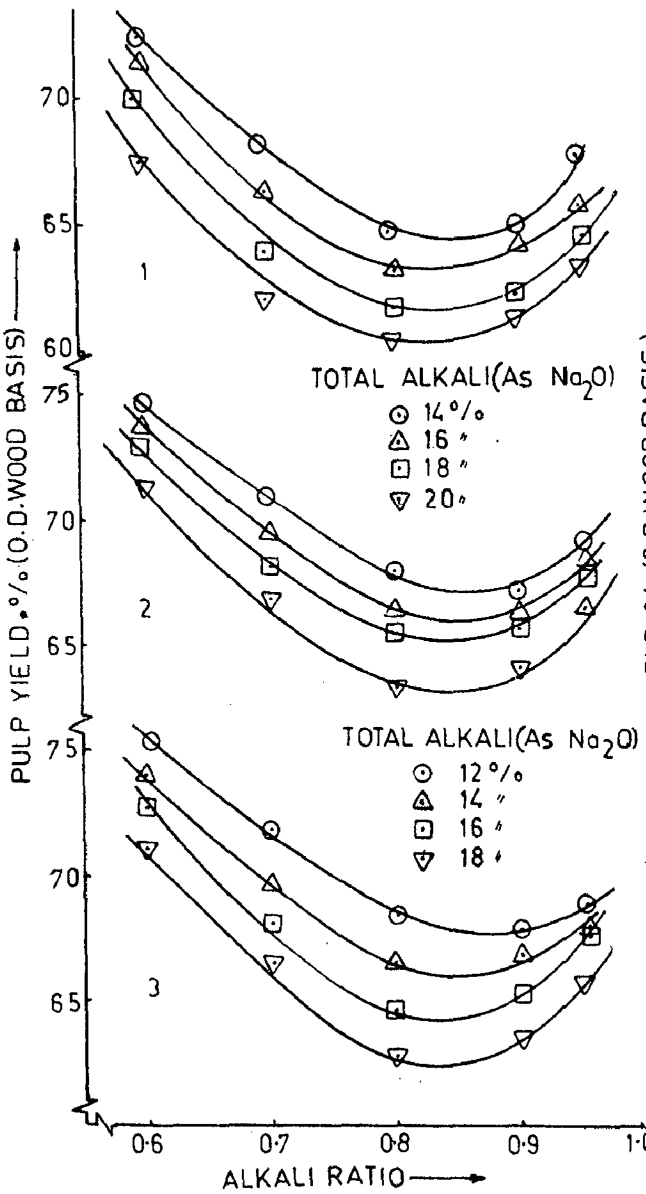


FIG.5·03D: PLOTS OF ALKALI RATIO VS. PULP YIELD DURING SEMI-ALKALINE SULPHITE PULPING AT 170°C (180 Min) OF ① S. sesban ② C. cajan AND ③ S. aculeata.

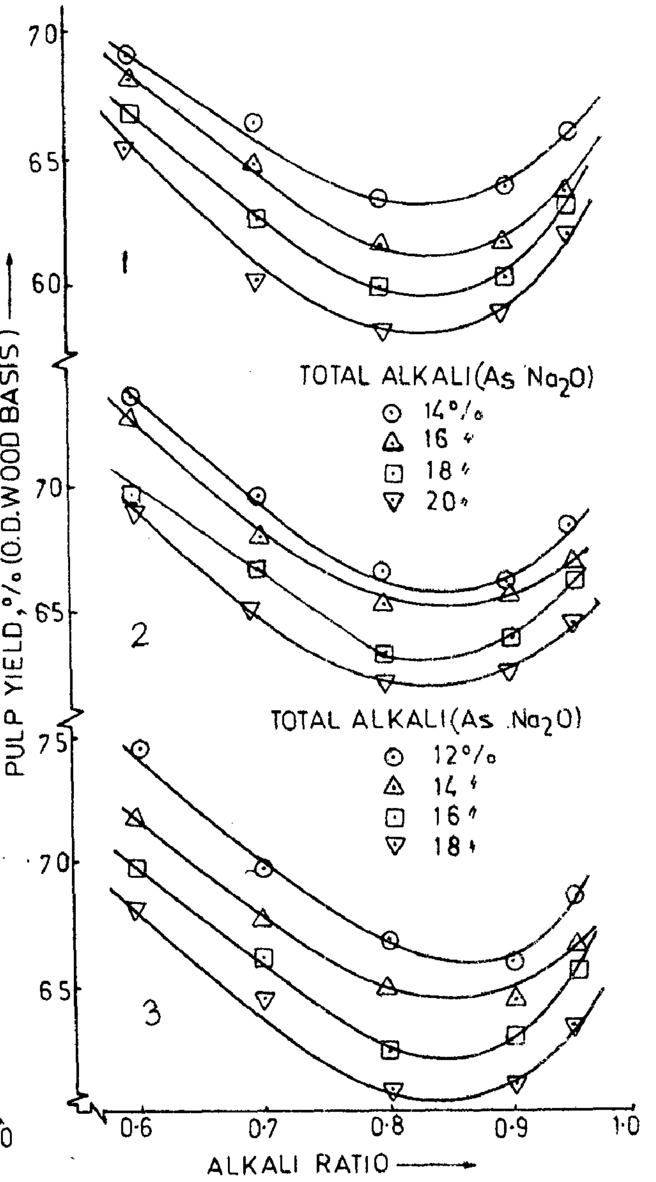


FIG.5·04D: PLOTS OF ALKALI RATIO VS. PULP YIELD DURING SEMI-ALKALINE SULPHITE PULPING AT 170°C (210 MIN) OF ① S. sesban ② C. cajan ③ S. aculeata.

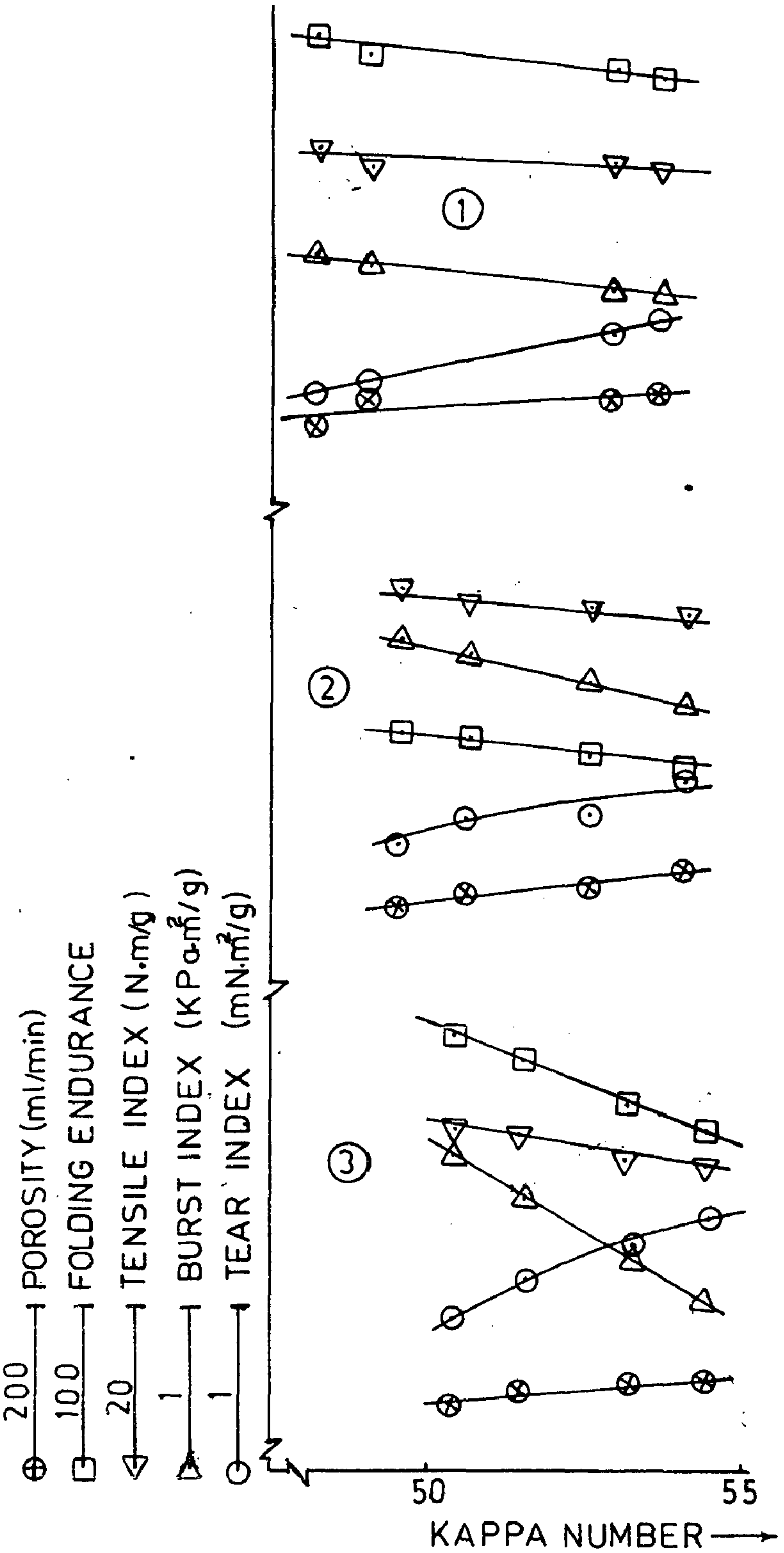


FIG.5.05D: PLOTS OF KAPPA NUMBER VS. STRENGTH PROPERTIES OF SEMI-ALKALINE SULPHITE UNBLEACHED PULPS OF ① S. sesban ② C. cajan AT 18 % AND 20 % TOTAL ALKALI (As Na_2O) ③ S aculeata AT 16 % AND 18 % TOTAL ALKALI (As Na_2O) WITH ALKALI RATIO 0·80 AND 0·85.

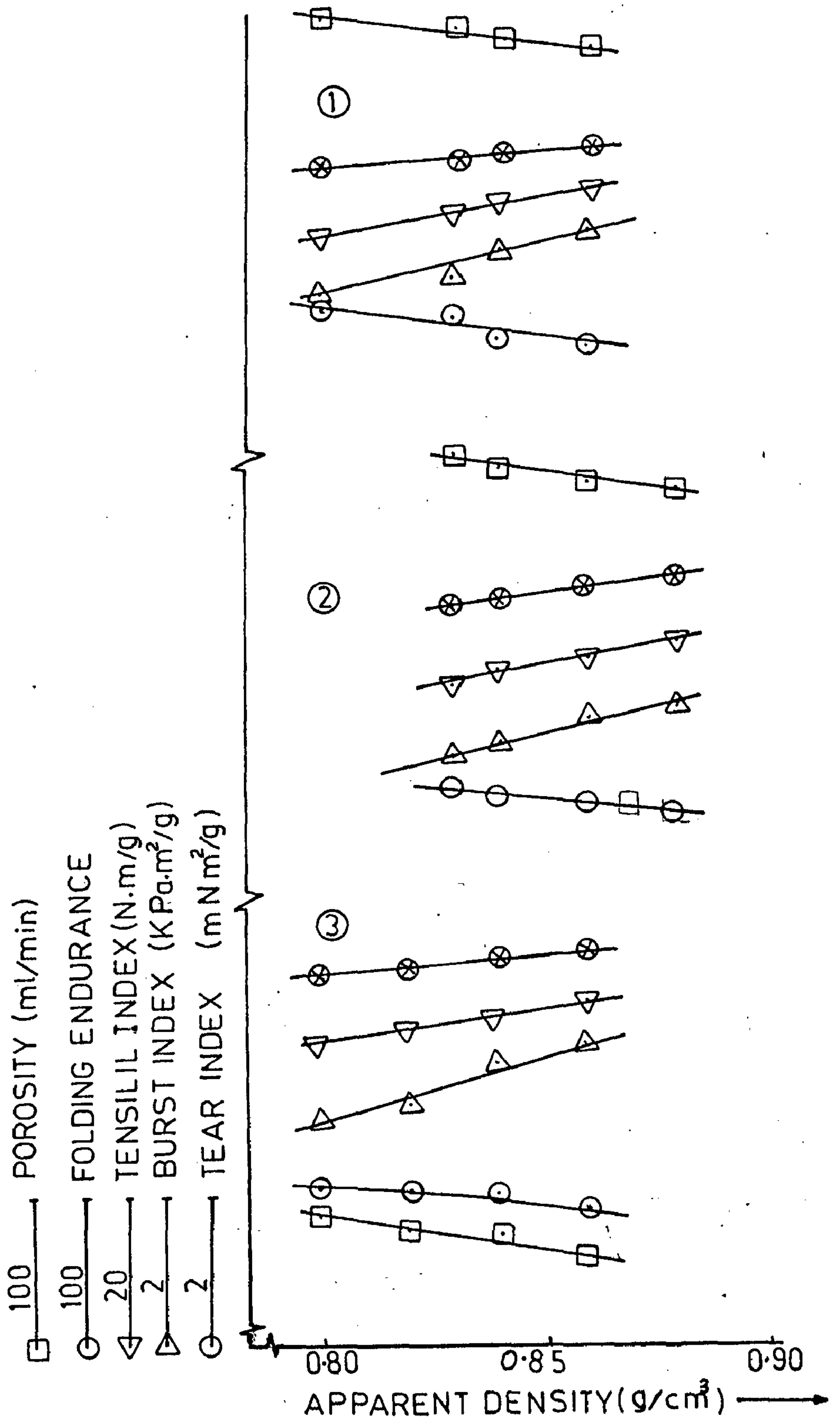


FIG. 5.06D: PLOTS OF APPARENT DENSITY VS. STRENGTH PROPERTIES OF SEMI-ALKALINE SULPHITE BLEACHED PULPSOF ① S. sesban ② C cajan AT 18°/o AND 20°/o TOTAL ALKALI (As Na_2O) ③ S. aculeata AT 16°/o AND 18°/o TOTAL ALKALI (As Na_2O) WITH ALKALI RATIO. 0·80 AND 0·85.

NEUTRAL SULPHITE SEMI-CHEMICAL PULPING STUDIES:

The traditional neutral sulphite semi-chemical (NSSC) process continues to hold its own for the production of coarse pulps in a yield range of 65%-85% for use in corrugating medium, linerboard, bag and wrapping papers. The process is largely restricted to hardwoods. Changes in the process have been minimal since the process was originally introduced and have been mainly in the type of equipment used and the introduction of instrumentation and control systems. Continuous digesters are being used for NSSC pulping. The neutral sulphite semi-chemical (NSSC) pulping is generally performed, by employing sodium sulphite as the active pulping agent alongwith sodium hydroxide or sodium carbonate or bicarbonate as a buffering chemical to neutralize wood acids, which are released during the course of pulping operation(37). The ratio of sulphite to buffering agent is considered to be of great importance. The buffering agent is used to control the corrosion of equipment and to stablize the carbohydrate during the course of pulping. By maintaining the pH of the cook in the alkaline range, severe corrosion conditions are avoided.

An advantage of the process is that the process is attractive economically due to relatively low consumption of chemicals and high yields attainable, it is not essential to recover the chemical and therefore a NSSC pulp mill leads itself to small units with a minimum of plant investment. The pulps obtained are more or less entirely used for the production of corrugating medium.

5.1.EXPERIMENTAL PROCEDURES:

5.1.1.PULPING STUDIES:

The methods of raw materials preparation are given on page 63. All the cooks were made in a laboratory WEVERK tumbling electrically heated digester (0.02 M^3 capacity) having stainless steel bombs, the bombs were rotated in a temperature controlled oil bath. The cooks were first made in bombs using 100gms. O.D. chips of S.sesban, S.aculeata and C.cajan to study the effect of different proportions of sodium sulphite and sodium carbonate at constant total sodium charge, on pulp yield(38). When a temperature of 100°C was reached, the digester pressure was momentarily relieved to zero psi. At the end of the cooks, digester pressure was relieved to atmosphere over a period of 15 min. and the spent liquor and cooked chips were taken out. The residual sulphite was determined iodimetrically in the presence of ice and the pH of these samples were also measured. The partially cooked chips were immediately defibred in a Bauer refiner. The chips were given two pass through the refiner at a clearance of 0.3mm between the plates and a consistency of slightly over 8.0%, and a second pass at 0.1mm with 10% consistency. The defibred pulps were screened through a vibratory flat WEVERK screen with 0.15 mm slits. The pulps were washed with cold water in a laboratory screen fitted with 100 mesh wire bottom. The pulp yields were determined and the recovered pulps were dewatered by centrifugation, to a dry matter content of about 25%. the pulp cakes were defibred and representative samples were removed for the determination of moisture contents. The pulps were evaluated as per the IS method(32). All the cooks were made in duplicate. Cooking conditions and pulp strength properties are shown in Tables-5.1E, 5.2E and 5.3E.

The optimization of sulphite to carbonate ratio was done by varying the ratio of sulphite/carbonate on a molal basis with a constant sodium charge of 6%(as Na_2O) for S.aculeata and 8%(as Na_2O) for S.sesban and C.cajan. Sulphite and carbonate were used in seven combinations to includes 100, 80, 60, 40, 30, 20 and 0% of total sodium oxide as carbonate with different time at temperature during the course of NSSC pulping of S.aculeata, S.sesban and C.cajan. The results are reported in Tables-5.1E and 5.2E.

5.1.2.PULP EVALUATION:

These pulps were beaten in a PFI mill to a freeness level of about 38±2 °SR and evaluated these pulps samples according to IS method(32). The pulps obtained at sulphite to carbonate ratio of 70:30 were beaten to different °SR and evaluated for the physical strength properties and the results are tabulated in Tables-5.2E and 5.3E.

5.2.RESULTS AND DISCUSSIONS:

The effect of different proportions of sodium sulphite and sodium carbonate (molal basis) on pulps yields and other characteristics at constant sodium charge were studied. Figure 5.01E illustrates the data from table 5.1E. The graphs were plotted between pulp yields(%) versus cooking time at a maximum temperature of 160°C. For the first half hour at that temperature, the lowest yields were obtained with combination of carbonate and sulphite rather than with 100% sulphite or 100% carbonate. For 2 hrs. at maximum temperature, the lowest yields were obtained with combinations of 70% sulphite + 30% carbonate and 60% sulphite + 40% carbonate. For a quick/short cook such as used for corrugating medium, maximum delignification was achieved at a combination of the two chemicals in the ratio of 60% sulphite and 40% carbonate. For cooks of longer duration maximum delignification was achieved at a combination with a little higher percentage of chemicals as sulphite (70% sulphite + 30% carbonate). The slopes of the curves in the figure5.01E represented the relative rates of pulping. As indicated by their steeper slopes, the pulping rates, after the first ½ hr., are shown to be greater for the liquors containing the major percentage of chemicals as sulphite. These results indicated that for corrugating medium short cooks of ½hr. duration at maximum temperature using a combination of 60% sulphite and 40% carbonate are recomended.

Figure 5.02E represented the data of table 5.1E. In this figure, the different cooking time interval curves are plotted between different liquor compositions and pulp yields. These curves showed the effect of liquor composition on the resulting pulp yields for each time interval. The ½ hr. and 1 hr. curves showed fairly well defined dips near the 60% sulphite point, again indicating this combinations of chemicals as an efficient pulping agent for short cooks. The 1½ hrs. and 2 hrs. curves both flatten near the 70% sulphite point, indicating that for longer cooks, a liquor of 70% sulphite and 30% carbonate might be utilised. The results of these studies indicated that after a maximum degree of delignification, the yields again increased irrespective of the time at temperature cookings, this phenomena of increasing the yields after maximum delignification can be explained on the basis that the rate of delignification decreased after the desired proportion of sulphite to carbonate in the liquor. It is observed that the rate of delignification decreased after 60% sulphite in the buffer for shorter cooks of ½ hr. and after 70% sulphite content in buffer for longer cooks of two hr. duration, thereby giving higher yields as the carbonate content decreased from the desired level. The pulps with same pulp characteristics, which were obtained at an optimum dose of sulphite to carbonate proportion can also be achieved with higher doses of sulphite, but it requires comparatively longer cooking times at maximum temperature to reach the same degree of delignification.

The mass cookings were made at a total chemical charge of 8% (asNa_2O) for S.sesban and C.cajan and 6% (as Na_2O) for S.aculeata using the proportion of sulphite to carbonate 60:40 for shorter cookings of ½ hr. duration. The longer cookings of 2 hrs. duration were made at the same total chemical charge using 100% carbonate, 100% sulphite and a combination of sulphite to carbonate in the ratio of 70:30 for the evaluation of pulps for enduses. The pulps of ½ hr. duration cooks were evaluated for strength properties. The S.aculeata pulps showed comparatively better strength properties than S.sesban and C.cajan. The pulps of longer cooking duration(2 hrs.) were also evaluated for their strength properties. The S.aculeata pulps showed better strength properties at all combination of chemicals studied. The pulps which were obtained at a sulphite to carbonate ratio 70:30 showed better values of strength properties in comparison to pulps obtained with 100% sulphite and 100% carbonate. The strength properties of pulps obtained at 100% sulphite dose showed better values of strength properties

than pulps obtained at 100% carbonate doses. The pulp and paper qualities obtained would, of course, be the decisive factor in justifying charges with higher percentage of carbonate doses.

The pulps (2 Hrs.) duration obtained at optimum proportions of sulphite to carbonate (70:30) were evaluated for strength properties after beating them upto different levels of freeness and the results are reported in Table 5.3E and plotted in figure 5.03E. The figures showed that the maximum values for strength properties were obtained at a freeness level of about 42±2°SR. Hence it is not advisable to beat these pulps beyond this particular level of freeness. The plots showed that, burst, tensile, apparent density, folding endurance increased as a result of an increase in the °SR, upto a certain limit, while the porosity, tear and brightness decreased as the freeness increased.

5.3.CONCLUSION:

In the NSSC pulping process, the carbonate component was found to have an appreciable pulping effect. This was true wheather it served as additional chemical or as partial replacement for the sulphite. The addition of sodium carbonate to sodium sulphite, shortened the cooking times and appreciably affecting the strength properties. With high yield pulps from rapid/short cooking cycles the highest strength values were reached with sulphite to carbonate ratio of 60:40. It also provides opportunities for saving in sulphur. For bleachable grade pulps of longer cooking duration, addition of carbonate to reach sulphite to carbonate ratio of 70:30 showed higher rates for degree of delignification. In addition to its corrosion inhibiting properties, sodium carbonate must be considered as an effective pulping agents when used in combination with sodium sulphite in the NSSC process.

Table-5.1E: Neutral Sulphite Semi-Chemical Pulping Of S.sesban, C.cajan And S.aculeata At Constant Total Sodium Charge.

Time at temperature (min)	Cooking liquors Na_2CO_3 (%)	Cooking liquors Na_2SO_3 (%)	Weight ratio of sulphite/ carbonate	S. sesban Screened pulp yield (%)	S. sesban Spent liquor (pH)	C. cajan Screened pulp yield (%)	C. cajan Spent liquor (pH)	S. aculeata Screened pulp yield (%)	S. aculeata Spent liquor (pH)
30	100	0	0.00	80.7	8.8	82.7	8.8	84.0	8.9
	80	20	0.30	79.0	8.7	81.0	8.6	81.7	8.7
	60	40	0.79	78.0	8.8	78.7	8.9	79.5	9.0
	40	60	1.78	77.0	8.6	78.2	8.7	79.2	8.9
	30	70	2.77	78.5	8.3	79.8	8.4	79.8	8.6
	20	80	4.75	79.5	8.1	81.2	8.0	81.0	8.1
	0	100	---	80.0	7.6	82.0	7.4	82.6	7.2
60	100	0	0.00	79.5	8.7	81.0	8.6	82.1	9.0
	80	20	0.30	78.0	8.5	80.0	8.4	80.0	8.9
	60	40	0.79	76.4	8.3	77.0	8.5	77.5	9.1
	40	60	1.78	75.2	8.0	76.2	8.2	76.0	8.8
	30	70	2.77	75.7	7.9	76.8	7.8	76.8	8.4
	20	80	4.75	76.8	7.6	78.5	7.7	78.2	8.1
	0	100	---	77.5	7.2	79.6	7.3	79.4	7.1
90	100	0	0.00	79.0	8.6	80.0	8.8	81.0	8.7
	80	20	0.30	76.3	8.5	78.1	8.6	78.4	8.8
	60	40	0.79	73.9	8.2	75.6	8.4	75.7	8.6
	40	60	1.78	72.1	8.0	74.3	8.1	73.5	8.2
	30	70	2.77	71.8	7.9	73.6	7.9	73.2	7.7
	20	80	4.75	73.2	7.5	75.0	7.4	74.8	7.3
	0	100	---	74.6	7.1	76.4	6.8	75.5	6.9
120	100	0	0.00	77.8	8.6	79.5	8.7	80.2	8.6
	80	20	0.30	74.0	8.4	76.0	8.5	77.2	8.4
	60	40	0.79	72.5	8.2	73.8	8.3	74.4	8.3
	40	60	1.78	70.8	7.9	71.7	7.9	72.0	8.1
	30	70	2.77	70.2	7.7	71.2	7.2	71.5	7.7
	20	80	4.75	71.2	7.1	72.2	7.0	72.5	7.1
	0	100	---	71.7	6.6	7.30	6.7	73.4	6.6

Cooking conditions are given on page no. 144.

Table-5.2E:Neutral Sulphite Semi-Chemical Pulping And Strength Properties Of S.sesban, C.cajan at Constant Sodium Charge (8% as Na_2O) And S. aculeata (6% as Na_2O).

Plant species	Cooking liquor Total Na_2O as Na_2CO_3		Weight ratio of Na_2SO_3/ Na_2CO_3	Time at 160°C	Spent liquor	Na_2SO_3	Screened pulp yield	Kappa	Free-ness	Apparent density	Burst index	Tear index	Tensile index	Bright-ness (Elrepho)	Concora* crush resistance
	Na_2CO_3	Na_2SO_3													
	(%)	(%)		(min)	(pH)	(gpl)	(%)	(no)	(°SR)	(g/cm^3)	(KPa. m^2/g)	(mN.m^2/ g)	(N.m/g)	(%)	(lb)
Sesbania sesban	100	0	0.00	120	8.6	0.0	77.6	136	40	0.66	2.23	4.10	31.82	21.4	49.8
	40	60	1.78	30	8.6	5.2	76.8	132	42	0.67	2.30	4.40	35.42	26.9	52.4
	30	70	2.77	120	7.7	5.7	70.0	108	40	0.65	3.36	5.17	42.23	32.3	69.7
	0	100	---	120	6.6	12.3	71.7	117	41	0.64	2.45	4.49	36.41	37.5	62.5
Cajanus cajan	100	0	0.00	120	8.7	0.0	79.2	144	42	0.68	2.34	4.18	34.60	23.0	51.4
	40	60	1.78	30	8.7	5.3	78.0	136	41	0.65	2.55	4.65	38.82	30.1	53.2
	30	70	2.77	120	7.2	6.0	70.9	112	40	0.65	3.62	5.22	46.22	35.4	71.8
	0	100	---	120	6.7	12.5	73.0	125	40	0.67	2.50	4.86	40.76	41.3	64.6
Sesbania aculeata	100	0	0.00	120	8.6	0.0	80.0	146	40	0.69	2.24	4.20	36.50	24.2	52.2
	40	60	1.78	30	8.9	5.4	79.2	142	42	0.70	2.62	4.90	40.36	32.5	55.0
	30	70	2.77	120	7.7	6.2	71.2	114	41	0.68	3.98	5.34	49.93	36.2	75.4
	0	100	---	120	6.6	12.6	73.2	121	41	0.67	2.70	4.96	44.42	42.1	66.5

* Concora tests are made by TAPPI standard T809 OS-71.

Cooking conditions of Table-5.1E & 5.2E.

Total Na_2O charge(O.D. wood) % = 8 for S.sesban & C.cajan
= 6 for S.aculeata.

Time from 30 °C to 105°C = 30 minutes.
Time from 105°C to 160°C = 60 minutes.

Liquor to wood ratio = 4.5:1 for S.sesban & C.cajan.
= 5:1 for S.aculeata.

Table-5.3E:Strength Properties Of S.sesban, C.cajan And S.aculeata, NSSC Pulps Cooked At Na_2CO_3:Na_2SO_3 (30:70)

Plant species	PFI Revol-ution (No)	Freeness (^oSR)	Drainage Time (Sec)	Apparent density (g/cm^3)	Tear index ($mN.m^2/g$)	Burst index ($KPa.m^2/g$)	Tensile index (Nm/g)	Porosity Bendtsen (ml/min)	Folding endurance Köhler Molin	Brightness (Elrepho) (%)
Sesbania sesban	0	16	4.1	0.60	3.86	1.10	21.56	1100	11	43.2
	1100	30	10.2	0.64	4.78	2.95	36.26	390	55	41.4
	1750	42	17.0	0.68	5.10	3.56	44.23	140	82	40.6
	2000	46	18.2	0.70	4.20	4.10	48.94	90	90	35.7
Cajanus cajan	0	15	4.3	0.58	3.55	1.60	23.55	1050	19	44.3
	1000	30	14.0	0.63	4.50	3.16	42.25	350	70	43.2
	1600	42	18.2	0.69	5.16	3.80	47.70	120	94	41.5
	1900	48	21.4	0.74	4.12	4.40	51.10	80	112	36.4
Sesbania aculeata	0	16	4.4	0.60	3.80	2.60	26.65	900	15	44.2
	1050	32	14.1	0.65	5.10	3.55	46.16	260	82	43.0
	1500	39	17.2	0.68	5.35	3.90	48.90	110	106	42.6
	1850	45	19.0	0.72	4.32	4.50	54.19	80	120	37.5

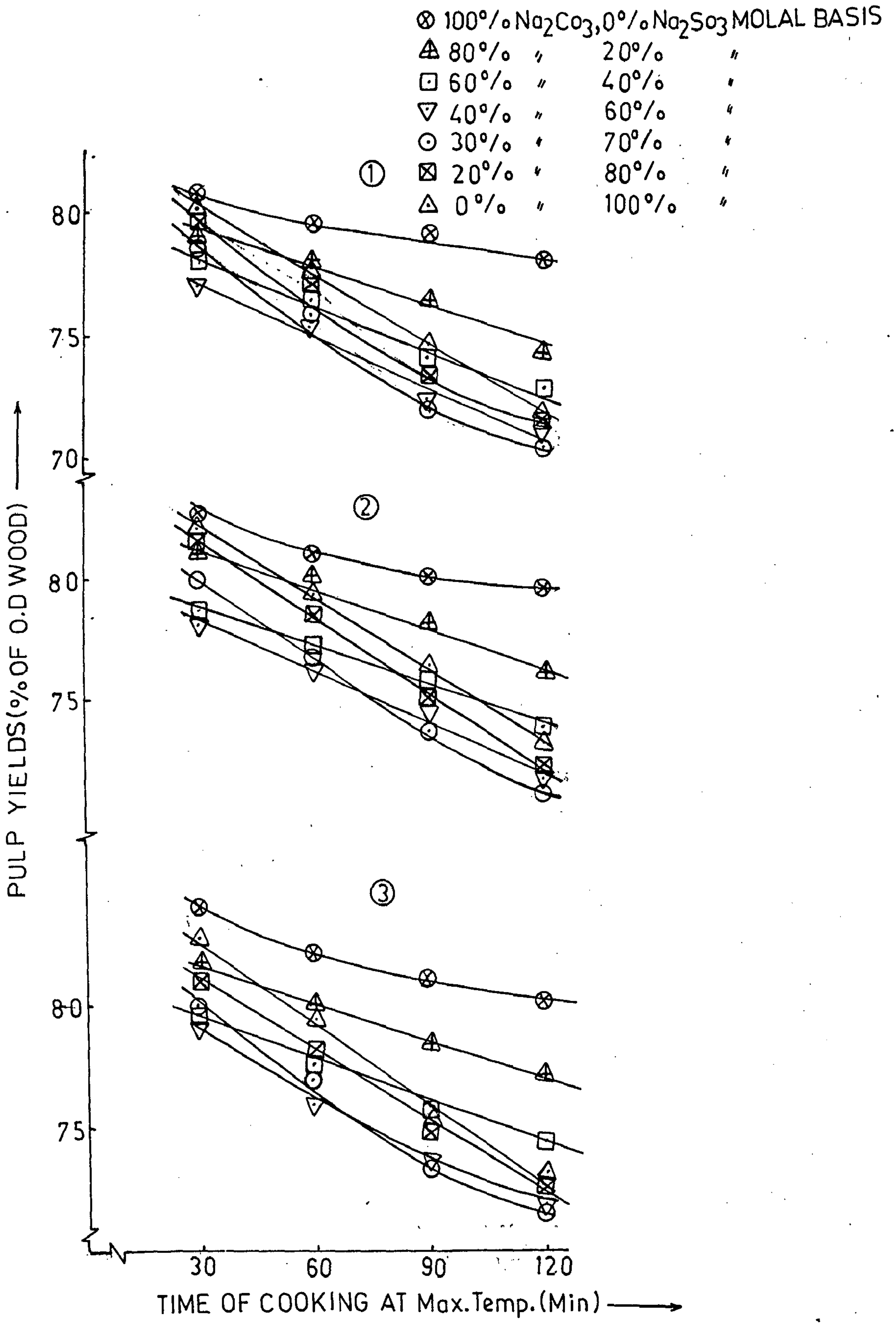


Fig. 5.01E:EFFECT ON PULP YIELDS DUE TO VARYING SULPHITE/CARBONATE RATIOS WHEN SODIUM CHARGES ARE CONSTANT DURING NSSC PULPING OF ① S.sesban ② C.cajan AND ③ S.aculeata

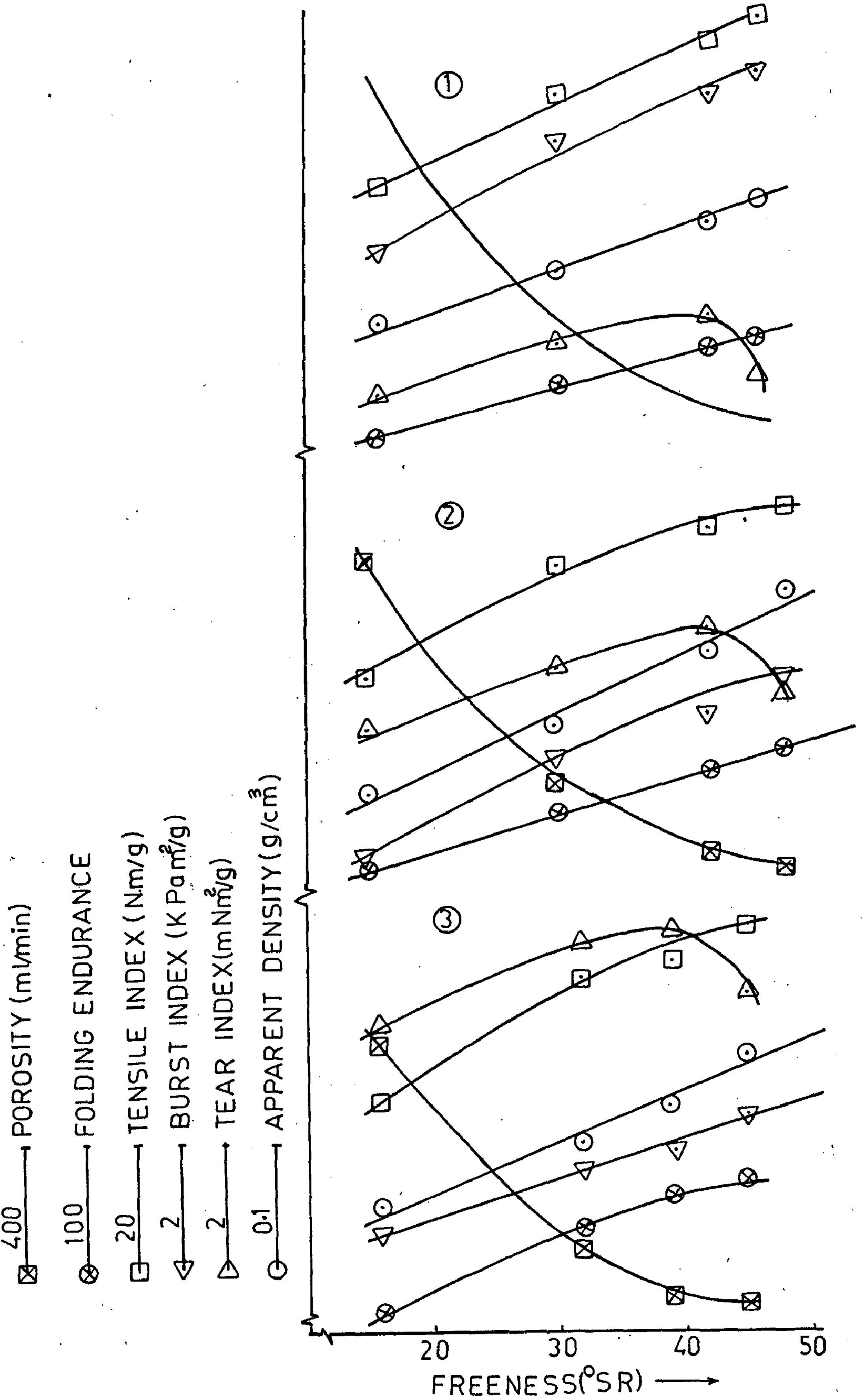


FIG 5.03E: PLOTS OF FREENESS (°SR) VS. STRENGTH PROPERTIES OF ① S. sesban ② C. cajan AND ③ S. aculeata DURING NSSC PULPING AT Na_2CO_3:Na_2SO_3 RATIO (30:70).

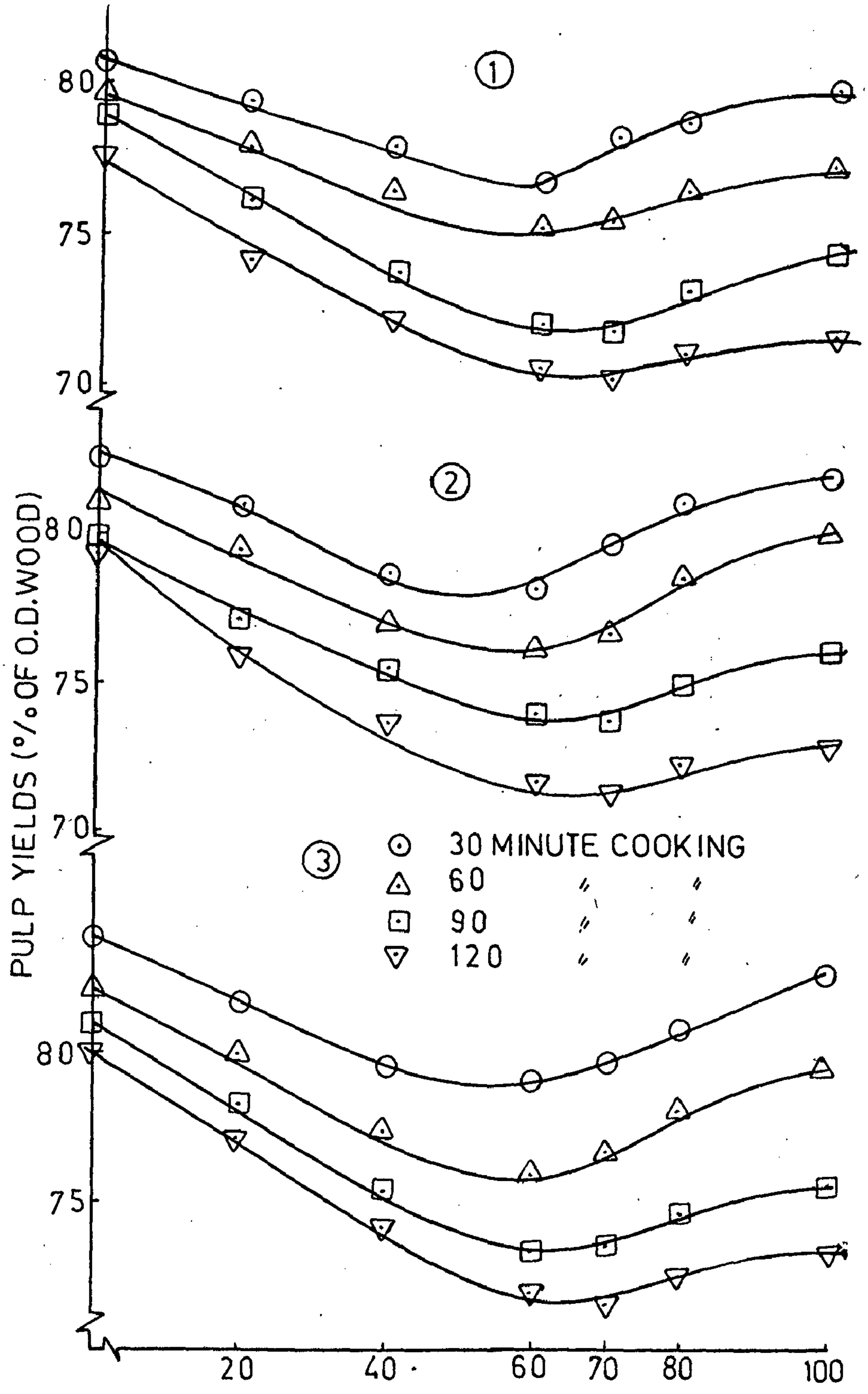


FIG. 5.02E: PLOTS OF PULP YIELDS VS. MOLE % SODIUM SULPHITE BASED ON CONSTANT SODIUM CHARGE DURING NSSC PULPING OF ① *S. sesban* ② *C. cajan* AND ③ *S. aculeata*.

BLENDING STUDIES:

Most commercially produced papers contain more than one fibrous component and many others also contain non-fibrous materials, e.g. clay and titanium oxide, to improve the properties given by the pulp furnish. The pulp blends are chosen such that the resultant pulp and paper properties are more acceptable when considered as a whole than those of the individual components. The overall assessment of the choice of material for a given furnish is influenced by such factors as the relative costs of the various pulps, their availability, their ease of beating and overall wet-end performance, e.g. runnability, and formation. Since the addition of fillers reduces the strength of the sheet while commensurately improving the opacity and brightness, the quantities that can be added in order to attain satisfactory optical properties are limited. Hence the final paper will often contain various pulps and fillers blended in such a way as to produce economically a sheet, which satisfies a customer's specifications.

5.1.BLENDING OF PULPS BEATEN SEPRATELY:

The pine kraft pulp was prepared in a WEVERK laboratory electricaly heated, tumbling digester. The cooking conditions and results are reported in Table-5.2F. The softwood kraft pulp was beaten to 40°SR, while the S.sesban, S.aculeata and C.cajan kraft pulps were beaten to 39°SR, 38°SR and 38°SR respectively. The beaten kraft softwood pulp was mixed with beaten S.aculeata S.sesban and C.cajan kraft pulps/in diffetent proportion and standard sheets of 60 gms/m^2 were made on laboratory British sheet forming machine. The sheets were tested for various strength properties as per the IS:1060. The results are recorded in Table-5.1F.

5.2.PROPERTIES OF BLENDED PULPS:

Table-5.1F as well as figure5.01F showed the strength properties of blends having S.sesban, S.aculeata and C.cajan pulps and softwood pulp.

The blends showed overall improvement in all the strength properties, but tear increases substantially in comparison to other properties. The blending of long fibred pulp upto the extent of atleast 5% of the total furnish improved the runnability of these short fibred pulps on paper machine. The improvement in strength properties is directly proportional to the amount of long fibred soft wood pulp, i.e. more the percentage of long fibre in the furnish, the more will be the improvement in strength properties. The magnitude of improvement in strength properties is quite substantial upto 30% long fibred pulp in blends and beyond this amount, the magnitude of improvement declined i.e. improvement in strength properties is not too much. The strength properties of blends having atleast 5% long fibred pulp are good and much more higher than the values required for different grades of paper.

5.3.CONCLUSION:

The present studies revealed that the addition of small quantities of unbleached soft wood pulp in a furnish base having kraft pulps of these non-wood fibrous plants caused a definite improvement in nearly all the strength properties of the paper in comparison with the properties of indivisual pulps of S. aculeata, S. sesban and C. cajan. As revealed from the literature this improvement was observed better when the furnish was prepared with these two pulps beaten seperately. As reported in literature(12,20), blending after beating the pulps separately showed improvement in strength properties as compared to mixed cooking and separate cooking and mixed beating. The improvement in tensile index and tear index was quite considerable while the improvement in burst index was not too much. It was concluded that the paper from blended pulps of S. aculeata, S. sesban and C. cajan mixed with atleast 5% softwood pulp can be manufactured without difficulty on a paper machine running at a high speed. The sheet thus obtained will have higher strength characteristics and a better formation of paper than pure kraft pulps of S.sesban, S.aculeata and C.cajan and it is quite suitable for production of different grades of paper.

Table-5.1F:Strength Properties Of Softwood Kraft Pulp And S.sesban, S.aculeata And C.cajan Kraft Pulps mixed after beating.

Proportion		Drainage time (Sec)	Apparent density (g/cm^3)	Tear index (mN.m^2/g)	Burst index (KPa.m^2/g)	Tensile index (N.m/g)	Folding endurance Köhler Molin
Soft wood (%)	S.sesban (%)						
0	100	16.0	0.74	5.64	4.70	54.45	307
2	98	15.9	0.73	5.72	4.95	56.50	312
5	95	15.6	0.74	6.10	5.28	62.95	340
10	90	15.4	0.72	6.40	5.36	65.07	358
15	85	15.1	0.71	6.80	5.67	71.37	370
20	80	14.6	0.72	7.12	5.95	73.04	396
30	70	14.4	0.70	7.35	6.26	75.60	440
40	60	13.4	0.69	7.62	6.18	75.10	435
50	50	11.5	0.67	7.85	6.02	74.00	450
	S.aculeata						
0	100	17.4	0.82	6.20	6.71	76.51	620
2	98	17.4	0.80	6.35	6.82	79.63	634
5	95	17.1	0.81	6.76	6.94	81.25	647
10	90	16.9	0.78	6.98	7.21	82.90	669
15	85	16.4	0.79	7.47	7.38	84.75	680
20	80	16.1	0.74	7.62	7.66	86.20	694
30	70	15.2	0.70	7.86	8.27	90.04	723
40	60	14.2	0.68	8.04	8.16	90.60	732
50	50	13.1	0.69	8.24	8.08	89.50	750
	C.cajan						
0	100	17.6	0.82	5.62	5.49	62.83	320
2	98	17.4	0.81	5.80	5.52	64.36	335
5	95	17.3	0.80	6.25	5.70	67.00	356
10	90	17.0	0.76	6.52	6.10	70.07	382
15	85	16.7	0.76	6.95	6.37	73.51	412
20	80	16.2	0.73	7.10	6.70	75.38	432
30	70	15.6	0.75	7.40	7.22	78.70	460
40	60	14.5	0.73	7.65	7.10	79.20	470
50	50	13.3	0.73	7.94	6.96	78.45	481

Table-5.2F: Strength Properties of Standard Pulp Sheets Of Different Raw Materials For Comparison.

Sl. No.	Raw Materials	Drainage Time (Sec)	Freeness (^oSR)	Total Chemicals as (Na_2O) (%)	Sulphidity (%)	Liquor to wood ratio	Time* at temp (Hr.)	Temp. (^oC)	Unbleached pulp yield (%)	Kappa (no)	Tear index ($mN.m^2/g$)	Tensile index (Nm/g)	Burst index ($KPam^2/g$)	Folding endurance
1.	Pine	7.2	40	18.0	25	3.5:1	4	170	45.2	33.5	10.96	110.00	9.10	1200
2.	Eucalyptus(20)	---	--	20.0	25	4:1	4	170	52.2	**20.8	9.90	82.30	5.38	404
3.	Bumbusa tulda (xx)	13.8	45	17.0	25	4:1	4	170	41.5	31.0	10.40	74.20	5.80	780
4.	Bagasse(20)	---	--	15.0	23	6:1	3	142	47.0	**10.2	6.47	70.63	5.45	390
5.	Wheat straw(xx)	19.2	40	12.0(b)	--	6:1	3	140	42.5	29.5	5.95	56.30	3.92	170
6.	Rice straw (65)	---	--	12.5(b)	--	6:1	2	140	39.0	--	6.86	55.23	5.19	500

(*) This includes one hour to reach to maximum temperature.

(xx) Unpublished work of Institute of Paper Technology, Saharanpur(India)

(**) Permanganate number

(b) Soda pulping.

CONCLUSIONS

The present investigations have been done on the non-wood fibrous raw materials viz., S.sesban, S.aculeata and C.cajan. The perhectare yield of fibrous material is highest in case of S.sesban among these three and other non-wood fibrous raw materials. The perhectare yield of fibrous raw materials of S.aculeata and C.cajan are higher than straws and comparable to bamboo. The results of proximate chemical analysis indicated that S.aculeata is having minimum water solubles among these three non-wood fibrous raw materials. The water solubles content of S.aculeata(3.32%) is quite low in comparison to water solubles content of bagasse and bamboo. The alcohol-benzene solubles of these non-wood fibrous raw materials are quite comparable to bamboo and bagasse. The S.aculeata is having little higher amount of lignin among these plants but it is quite comparable with lignin in bagasse and still quite low in comparison to the lignin content of bamboo. The S.sesban is having maximum pentosan content among these three raw materials, but this amount of pentosan is quite comparable with the pentosan content of bamboo and still quite low than the pentosan content of bagasse. The S.aculeata is having maximum holocellulose among these three raw materials and this amount of holocellulose is substantive higher than the holocellulose in bamboo and bagasse. S.sesban is having little higher amount of hemicellulose among these plants and it is quite comparable with the hemicellulose content in bamboo and comparatively low than bagasse hemicellulose. S.aculeata is having maximum amount of alpha cellulose amongst all including bamboo and bagasse. The S.aculeata and C.cajan are having little higher amounts of ash and silica than S.sesban, but these amount of ash and silica are substantive low than ash and silica content in bagasse and bamboo. The morphological studies revealed that all these three non-wood fibrous plants are having short fibres in comparison to bamboo and bagasse. The lumen diameter of S.aculeata and C.cajan are higher than the lumen diameter of S.sesban and bamboo. The cell wall thickness of S.aculeata and C.cajan is quite lower than

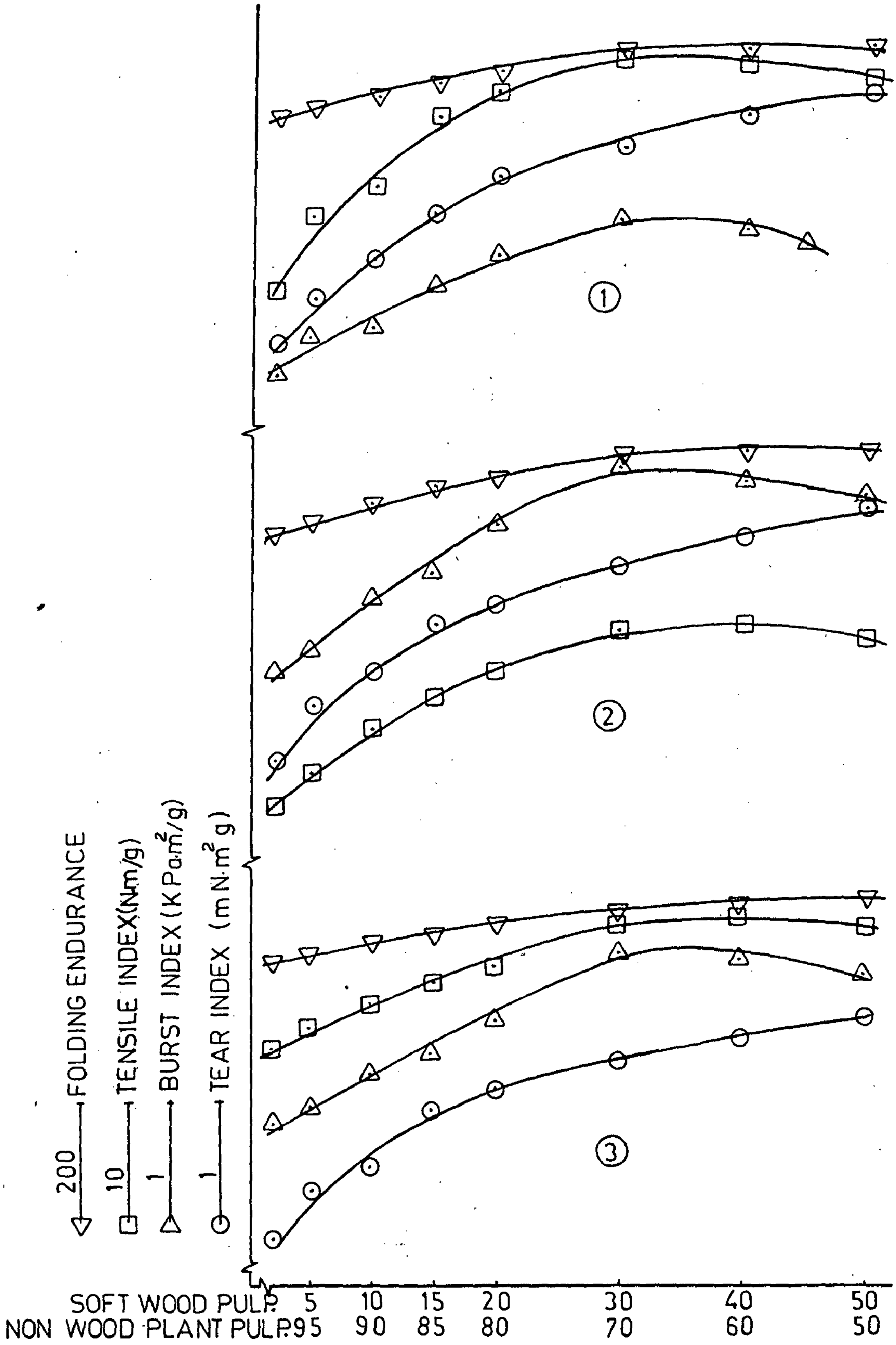


FIG. 5.01F: PLOTS BEWEEN DIFFERENT PROPORTION OF PULP BLENDS VS. STRENGTH PROPERTIES OF ① S.sesban ② C.cajan AND ③ S.aculeata

S.sesban and bamboo. On the basis of morphological and chemical studies it was concluded that S.aculeata is comparatively better non-wood fibrous raw material among all these plants. The infrared spectrum and G.L.C. studies on carbohydrates showed that these plants are having higher amount of xylan fraction indicating that the nature of carbohydrates resembled to those of bamboo and hardwoods carbohydrates. The infrared spectrum and alkaline nitrobenzene oxidation studies of lignins showed the presence of guaiacyl-, syringyl- and p-hydroxyphenylpropane units. These studies clearly indicated that the nature of lignins is somewhat similar to those of bamboo. The pulping studies on S.sesban, S.aculeata and C.cajan were done by soda, kraft, alkaline sulphite, semi-alkaline sulphite and NSSC processes. The effect of small doses of AQ(0.1%) was also studied in all process except NSSC pulping processes.As indicated earlier that these raw materials resembled with bamboo and tropical hardwoods in many respects rather than the typical agricultural residue like bagasse and straws. These pulping studies revealed that the total chemical requirement for pulping of these raw materials is comparatively low than that required for bamboo and hardwoods. These results also indicated that the total cooking cycle is also shortend, required milder cooking conditions and gave higher pulp yields than bagasse, straws and bamboo. The results of pulping studies revealed that the kraft pulping process is best suited for the pulping of these raw materials for making high strength papers as in case of bamboo and woods. For higher yields the alkaline sulphite and semi-alkaline sulphite pulping processes may also be recommended for getting papers with moderate strength properties. The brightness of alkaline sulphite and semi-alkaline sulphite pulps were far far better than soda and kraft pulps. The pulping studies with AQ revealed that the use of AQ shortens the cooking cycle to get the pulps with same kappa numbers. The results of bleaching studies indicated that the pulps of these raw materials are easily bleachable with low bleach chemicals requirement. The conventional CEH or CEHH bleaching sequences are quite suitable for making pulps with higher brightness level. Although on bleaching the alkaline sulphite and semi-alkaline sulphite pulps, the bleach chemical demand increased and it is due to little higher retention of lignin with unbleached pulps. Like other non-wood fibrous pulps, these pulps are also easily beatable thereby requiring low energy requirement during the process of beating and refining. The optimum freeness level was found to be around 42±2°SR for these pulps with moderate strength properties. The hand sheets evaluation data of these pulps indicated that the overall strength properties of kraft pulps were better than other pulps for making high strength papers (kraft and sack kraft). The tearing strength of alkaline sulphite pulps were found to be better than other pulps. The soda pulps may also be used for making various grades of paper which do not require high strength properties like kraft. The AS and SAS processes are also well suited to produce high yield pulps for making various grade of paper(writing & printing, packaging and strong coated base paper etc.). The NSSC pulps may be used for making corrugating medium, liner board, coated base paper and other grades of packaging papers. Although papers with moderate strength properties can be produced by utilizing centpercent pulps of these non-wood fibrous plants, but due to the shorter nature of fibres in these plants, created lots of problems during processing. These pulps require more surface area for washing purposes and producing papers with low tearing strength in comparison to bamboo and woods. Therefore it is very much desirable to use at least 5% long fibred pulps to enhance the rate of drainage and to improve those physical strength properties which depends on long fibred stock. The soda and kraft spent liquors studies revealed that they contained substantive low amount of silica than bamboo and bagasse spent liquors. The viscosity and calorific value of these spent liquors are quite comparable to those of bamboo spent liquor. The recovery of chemicals may be done from the spent liquors of these raw materials as in case of bamboo. A summarized account of optimized cooking conditions and phycial strength properties of soda, kraft, alkaline sulphite, semi-alkaline sulphite and neutral sulphite semi-chemical pulpings with(0.1% AQ) and without AQ for S.aculeata, C.cajan and S.sesban are given in Tables 6.1, 6.1A, 6.1B & 6.1C. On the basis of above investigations these plants can be categorised according to their relative order of merit in descending order as:

Sesbania aculeata > Cajanus cajan > Sesbania sesban

The various problems related with the utilization of these non-wood fibrous plants for pulp and paper making, can be minimised upto some extent by taking certain precautions during processing. For washing of the pulps of these non-wood fibrous plants the vacuum washers with multistage counter current washing system, can be used. For screening and cleaning of these pulps, it is desirable to do two stage screening and three stage centricleaning during processing. A comparatively less quantity of rosin size and little higher amount of alum will be required to produce paper while using a good proportion of these non-wood fibrous plants.Slow drainage characteristic, high fines, limitation to achieve high drynss value of the paper web at the press part, tendency to blistering and cockling due to rapid drying are some of the problems that should be encountered while using these non-wood fibrous pulps for paper making. The drainage problems can be minimized by using more vacuum foils or by increasing wire length by atleast 15 to 20% over that required for bamboo or wood pulps. Wet web strength can be increased by adding 2-5% long fibred pulps or by using closed draw system. The press part problems can be minimized by using a bi-nip or tri-nip press systems. The paper produced out of these non-wood fibrous pulps will need extended surface area for drying and it should be done at relatively low temperature. The drying section should be split into smaller groups to provide better draw controls and for improved over all evaporation rate.

There is no systematic data available regarding the availability of these plants, in literature. Collection of these non-wood fibrous raw materials is also one of the major problems, since no proper utilisation of these raw materials have been done so far. The bulk density of these raw materials are quite higher than the bulk density of straws and bagasse but still lower than bamboo and woods, therefore transportation is also one of the major problem for transporting them from one place to other for processing. The S.aculeata and C.cajan are seasonal crops, while the S.sesban is available round the year, hence S.aculeata and C.cajan should be stored for off season requirement of these plants. Due to the bulky nature, the space requirement for storage of these materials is more and proper care should be taken during storage as these are easily degradable by the attack of micro-organisms in comparison to woods. Prior to the utilization of these non-wood fibrous plants for pulp and papermaking on mill scale, it is desirable to carry out the extensive studies in certain areas, which are still untouched and important. The extensive studies viz., thermomechanical pulping(TMP), chemi thermomechanical pulping(CTMP), mechanochemical pulping, chemi-mechanical pulping(CMP), semi-chemical pulping, bio-pulping and oxygen bleaching etc., on these non-wood fibrous plants should be made.

Hence it was concluded that the S.aculeata, C.cajan and S.sesban are quite suitable non-wood fibrous raw materials for pulp & paper making. Due to the acute shortage of raw materials, these can be considered as a partial replacement of conventional raw materials for pulp & paper making.

Table-6.1:Optimized Cooking Conditions And Strength Properties Of Soda, Kraft, Alkaline Sulphite, Semialkaline Sulphite And Neutral Sulphite Semi-Chemical Pulpings With (0.1% AQ) And Without AQ For S.aculeata, C. cajan And S. sesban.

Soda And Soda-AQ

Active Alkali (as NaOH) % = 16
= 18*
Bath ratio = 1:4
= 1:3.5*
Time from 30°C to 105°C = 30 min#
105°C to 165°C = 60 min#
At 165°C (without AQ) = 180 min#
At 165°C (with AQ) = 120 min#

Kraft And Kraft-AQ

Active Alkali (as Na_2O)% = 14
= 16*
Bath ratio = 1:3.5
= 1:3*
Time from 30°C to 105°C = 45 min#
At 105°C = 45 min#
105°C to 160°C = 45 min#
At 160°C (without AQ) = 90 min.
= 120 min*
At 160°C (with AQ) = 60 min.
= 90 min*

Alkaline Sulphite And Alkaline Sulphite-AQ.

Sodium sulphite (as Na_2O)% = 10.35
= 10.8*
Sodium Hydroxide (as Na_2O)% = 4.65
= 6.2*
Bath ratio = 1:4
= 1:3.5*
Time from 30°C to 105°C = 45 min#
105°C to 175°C = 30 min#
At 175°C (without AQ) = 180 min#
At 175°C (with AQ) = 120 min.
= 135 min.*

Semi alkaline Sulphite And Semi alkaline Sulphite-AQ.

Total Alkali (as Na_2O) % = 16
= 18*
Alkali ratio = 0.85#
Bath ratio = 1:4
= 1:3.5*
Time from 30°C to 105°C = 30 min#
105°C to 170°C = 60 min#
At 170°C (without AQ) = 210 min#
At 170°C (with AQ) = 180 min#

Neutral Sulphite Semi chemical

Total Na_2O % = 6
= 8*
Na_2CO_3:Na_2SO_3 = 30:70#
Bath ratio = 1:5
= 1:4.5*
Time from 30°C to 105°C = 30 min.#
105°C to 160°C = 60 min.#
At 160°C = 120 min.#

* For S.sesban and C.cajan.
\# For S.aculeata, C.cajan and S.sesban.

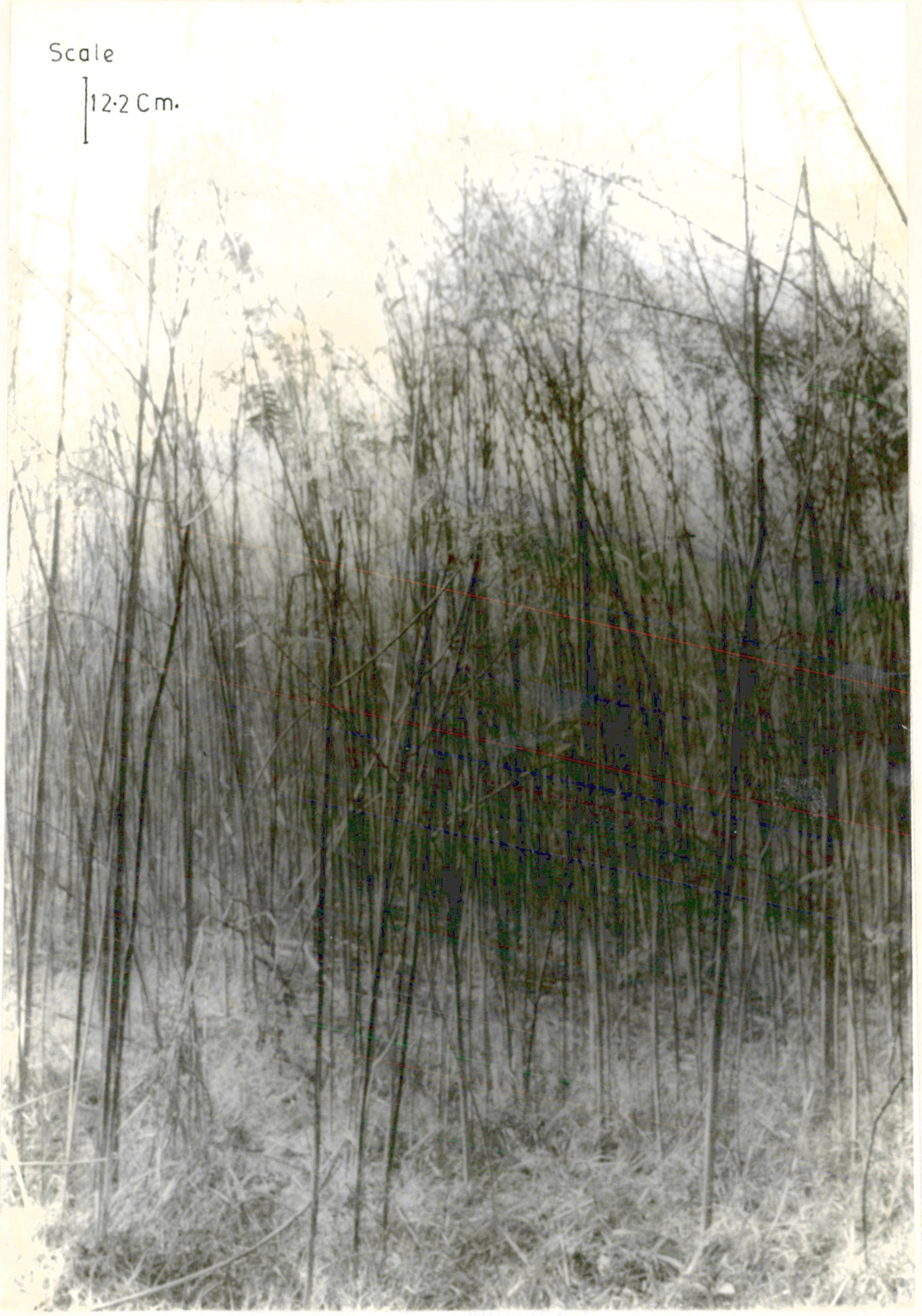
Table-6.1A:Optimized Strength Properties Of S. aculeata.

Types of pulping	UNBLEACHED PULP						BLEACHED PULP						
	Yield (%)	Kappa (No)	Free-ness (^{o}SR)	Burst index (KPa. m^2/g)	Tear index (mN.m^2/g)	Tensile index (Nm/g)	Yield (%)	Free-ness (^{o}SR)	Burst index (KPa. m^2/g)	Tear index (mN.m^2/g)	Tensile index (Nm/g)	Brightness (Elrepho) (%)	Opacity (%)
Soda	47.6	31.0	44	4.95	4.65	70.71	42.9	44	4.12	3.60	59.00	68.8	82.0
Soda-AQ	48.2	32.0	45	4.92	4.42	71.00	43.3	42	4.10	3.65	59.20	69.0	81.8
Kraft	49.8	30.4	45	6.90	5.30	81.00	45.3	45	5.82	4.40	70.45	71.0	82.4
Kraft-AQ	50.7	31.0	40	6.83	5.92	81.20	46.0	46	5.90	4.25	72.25	70.2	83.0
Alkaline sulphite	50.8	32.0	44	5.60	5.76	76.56	45.4	45	4.85	4.28	67.50	72.6	81.6
Alkaline sulphite-AQ	51.2	31.0	46	5.85	5.80	73.20	45.0	45	4.90	4.36	65.90	73.5	79.6
Semi alkaline sulphite	60.9	53.2	44	5.30	5.90	68.70	53.9	44	4.30	5.08	63.16	74.4	82.0
Semi alkaline sulphite-AQ	60.2	41.2	41	5.35	5.90	73.00	53.8	45	5.10	4.92	68.21	74.6	81.6
Neutral sulphite semi chemical	71.2	114.0	39	3.90	5.35	48.90							

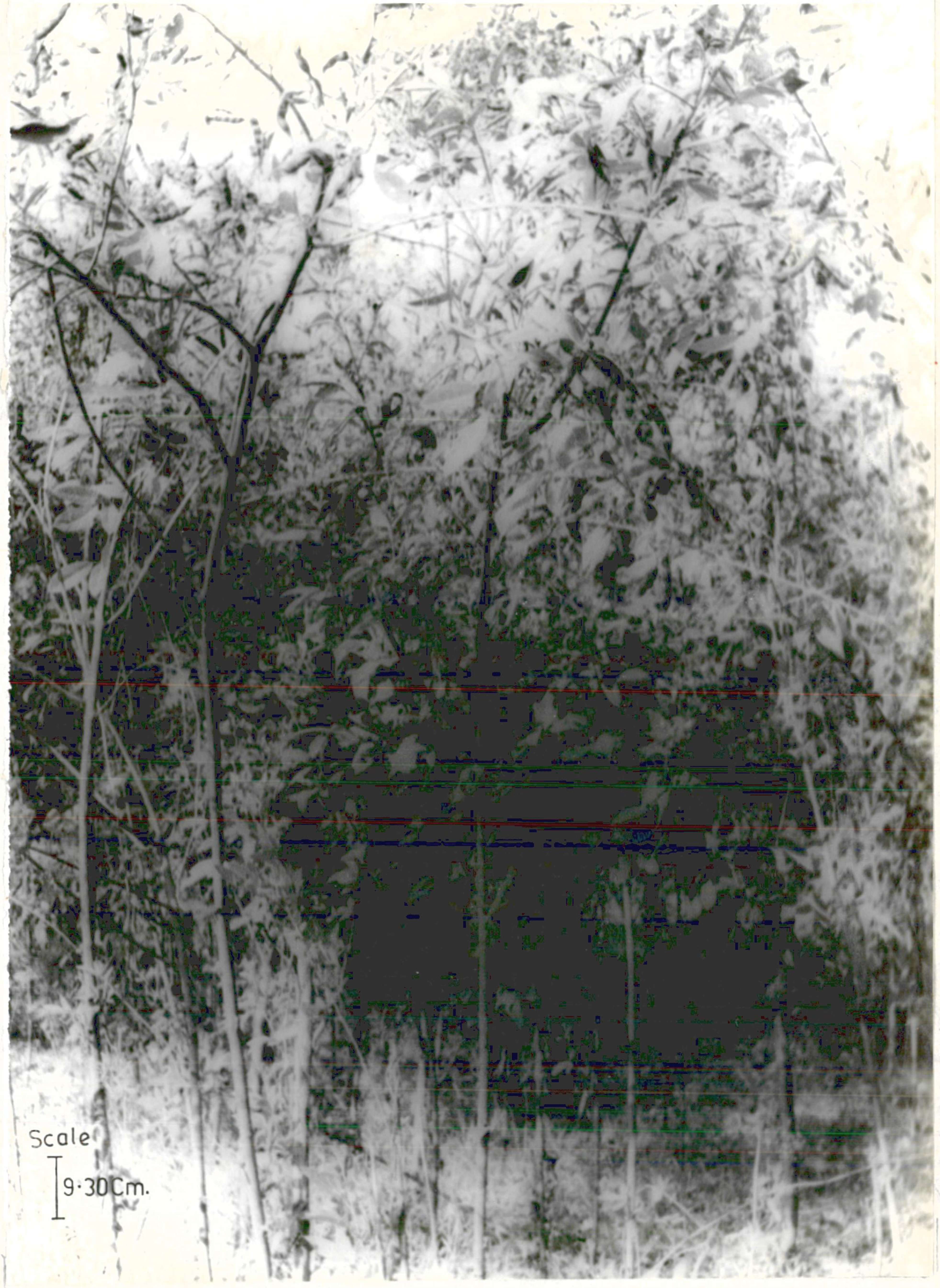
Table-6.1C:Optimized Strength Properties Of S.sesban.

Types of pulping	UNBLEACHED PULP						BLEACHED PULP						
	Yield (%)	Kappa (no)	Freeness (^{o}SR)	Burst index (KPa. m^2/g)	Tear index (mN.m^2/ g)	Tensile index (Nm/g)	Yield (%)	Freeness (^{o}SR)	Burst index (KPa. m^2/g)	Tear index (mN.m^2/ g)	Tensile index (Nm/g)	Brightness (Elrepho) (%)	Opacity (%)
Soda	45.7	30.0	43	4.13	4.22	56.65	40.8	39	3.20	4.05	46.46	69.6	85.2
Soda-AQ	46.4	32.0	43	4.20	3.85	58.65	41.9	45	3.96	3.54	51.50	67.80	82.0
Kraft	47.0	31.0	46	5.14	4.85	60.58	42.5	45	4.48	4.20	55.50	69.7	82.0
Kraft-AQ	47.9	32.0	44	5.26	4.52	61.23	43.2	42	4.30	4.70	50.75	69.4	83.6
Alkaline sulphite	49.0	32.0	47	4.74	4.37	56.37	43.9	45	4.12	3.90	51.24	69.5	82.0
Alkaline sulphite-AQ	49.5	29.0	44	4.70	4.56	58.90	44.30	46	3.82	3.92	52.52	69.7	81.0
Semi alkaline sulphite	58.2	52.8	43	4.90	5.11	53.53	52.26	45	3.76	4.16	45.47	71.0	83.0
Semi alkaline sulphite-AQ	57.8	42.6	45	4.95	4.80	62.00	52.60	46	4.30	3.98	54.97	71.2	81.6
Neutral sulphite semi chemical	70.0	108.0	42	3.56	5.10	44.23							

ANNEXURE



Photograph of Sesbania aculeata Plant

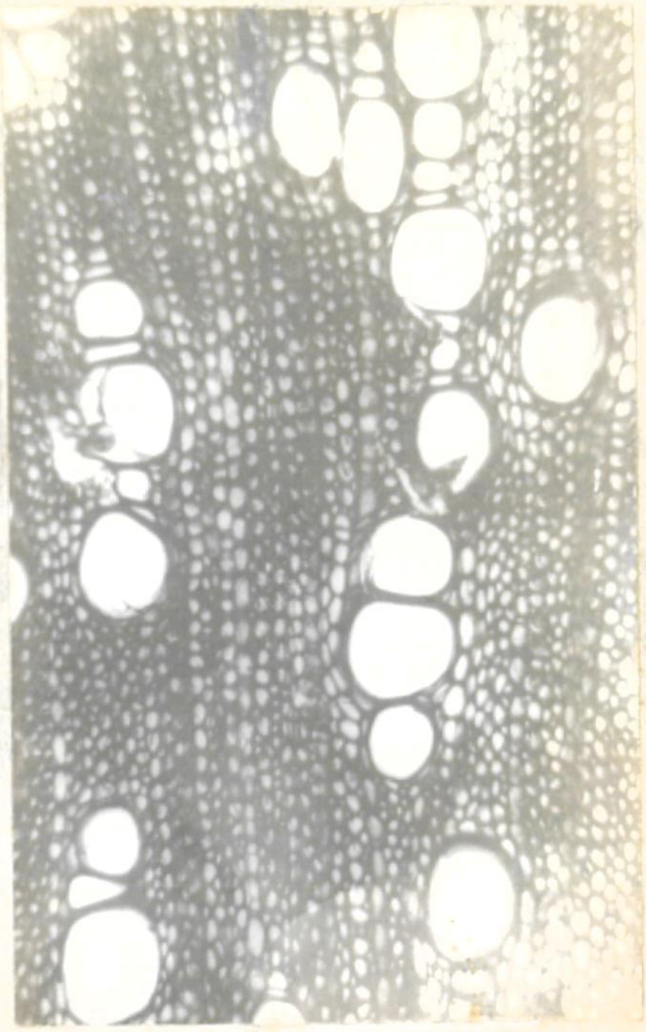


Photograph Of Cajanus Cajan Crop

PHOTOGRAPH OF SESBANIA sesban PLANT

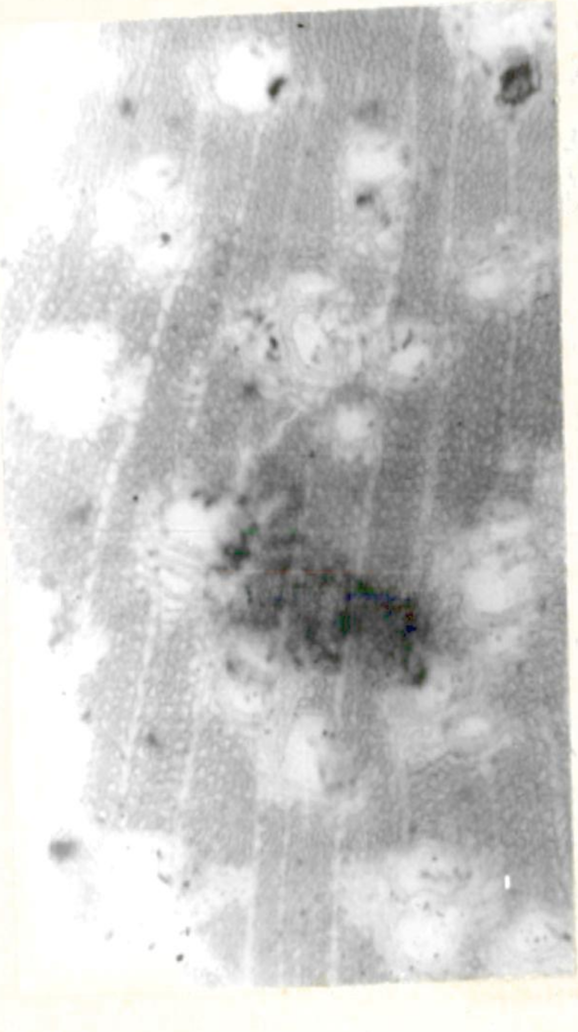
PHOTOMICROGRAPH-1
S. sesban; T.S. (40 X)

PHOTOMICROGRAPH-2
S. sesban, L.S.(40 X)



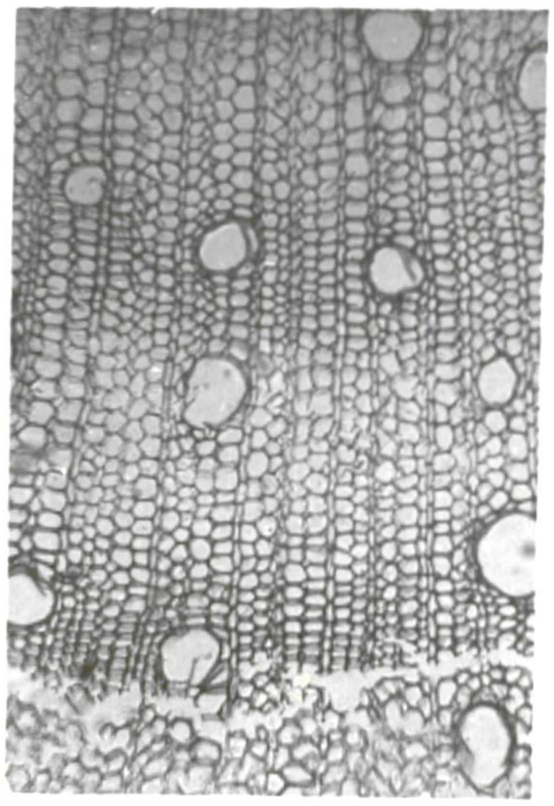
PHOTOMICROGRAPH-3
S. sesban, T.S.(40 X)
delignified

PHOTOMICROGRAPH-4
S.sesban, L.S.(40 X)
delignified

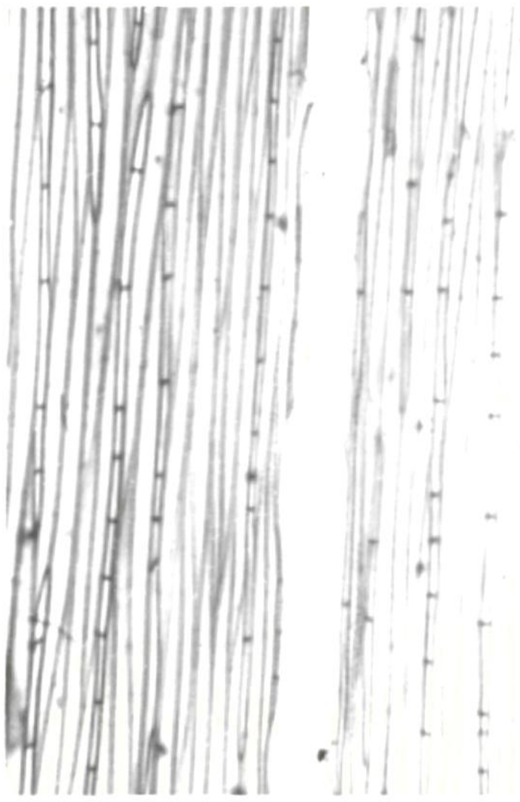


PHOTOMICROGRAPH-5
S.sesban, T.S.(40 X)
Hemicellulose
Free

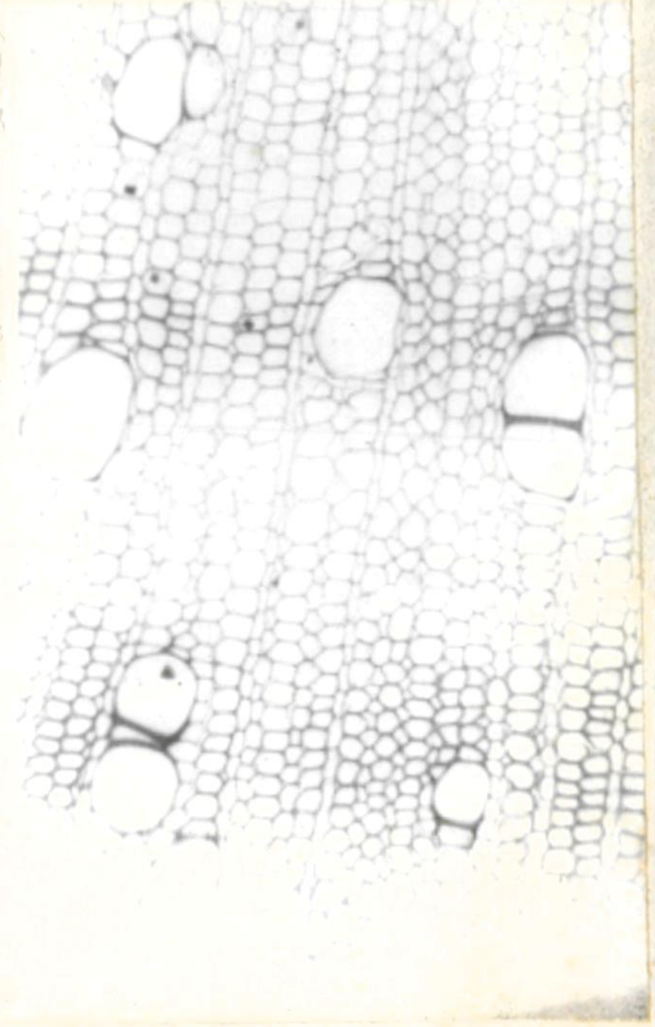
PHOTOMICROGRAPH-6
S.sesban, L.S.(40 X)
Hemicellulose
Free



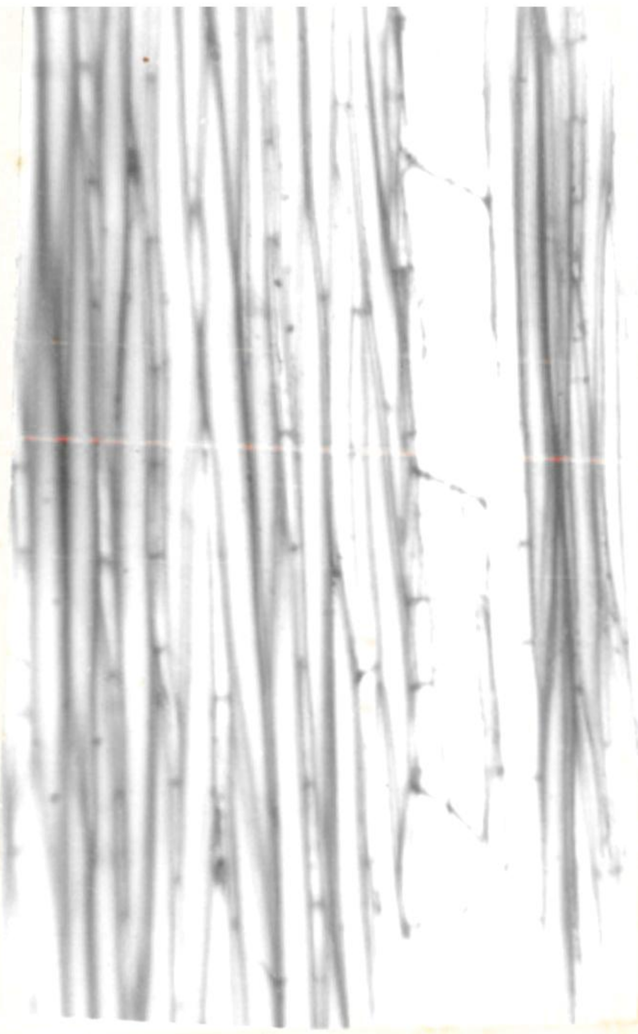
PHOTOMICROGRAPH - 7
S. aculeata, T.S. (40 X)



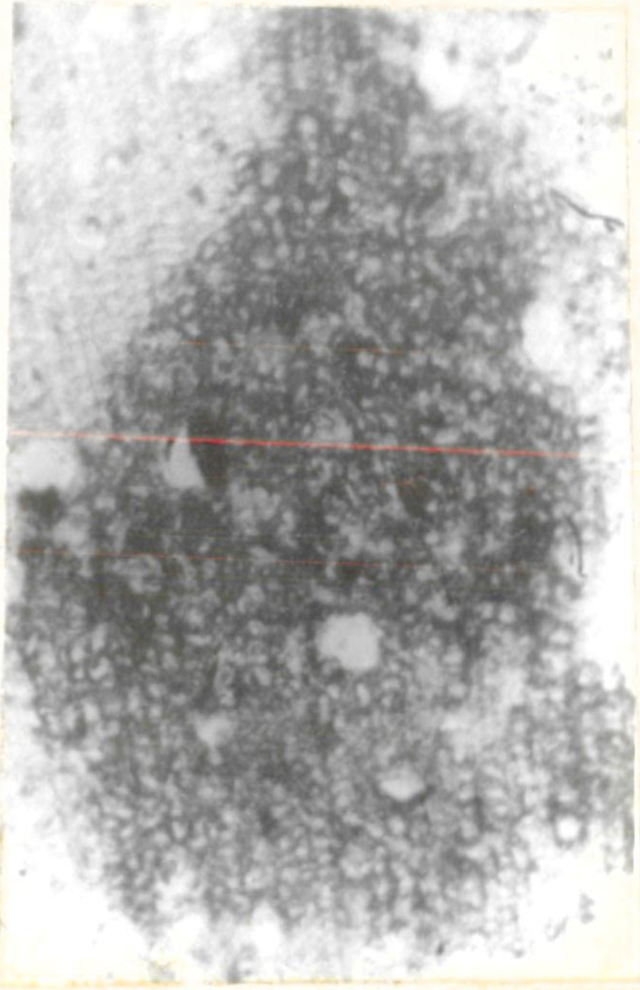
PHOTOMICROGRAPH - 8
S. aculeata, L.S. (40 X)



PHOTOMICROGRAPH - 9
S. aculeata, T.S. (40 X)
delignified



PHOTOMICROGRAPH - 10
S. aculeata, L.S. (40 X)
delignified



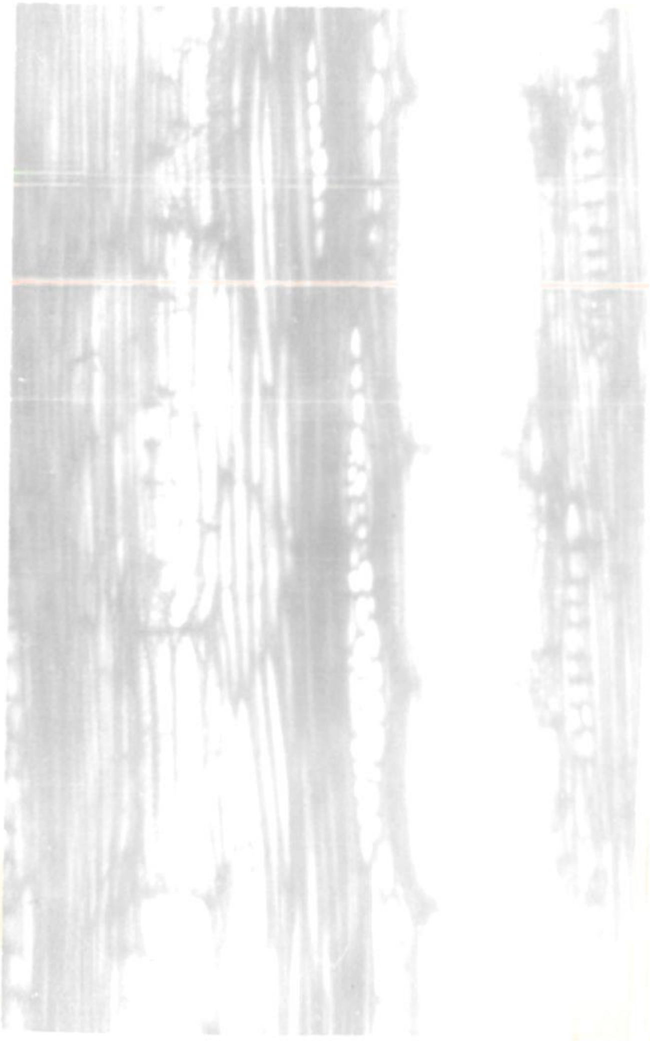
PHOTOMICROGRAPH - 11
S. aculeata, T.S. (40 X)
Hemicellulose Free

PHOTOMICROGRAPH - 12
S. aculeata, L.S. (40X)
Hemicellulose Free

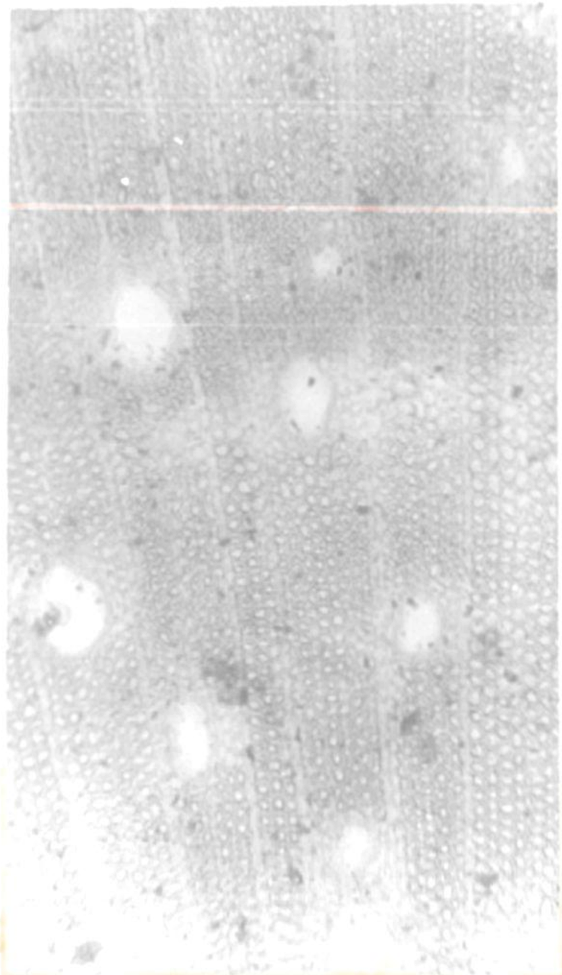
PHOTOMICROGRAPH -13
Cajanus cajan, T. S. (40X)

PHOTOMICROGRAPH -14
Cajanus cajan, L. S. (40X)

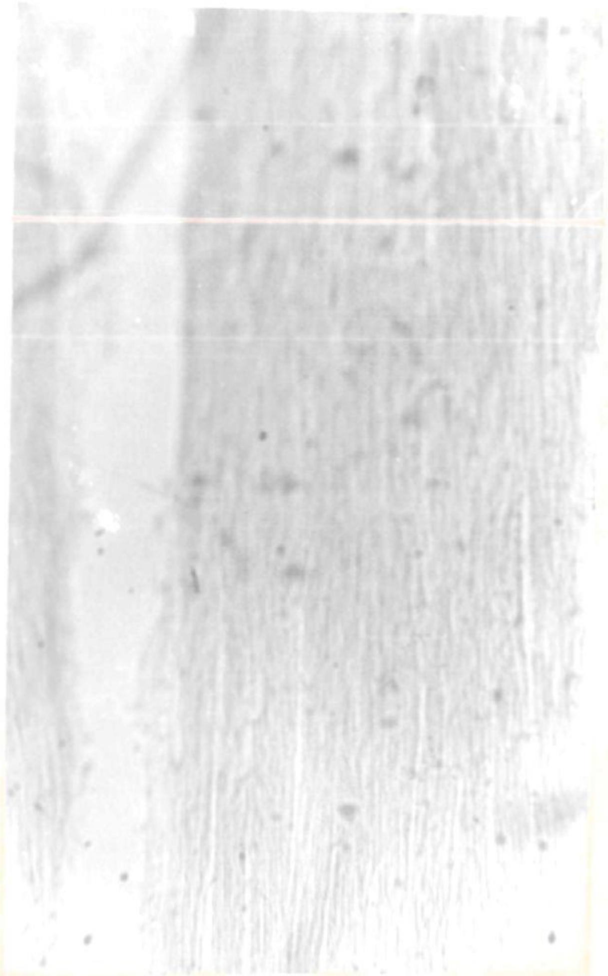
PHOTOMICROGRAPH -15
Cajanus cajan, T. S. (40X)
delignified



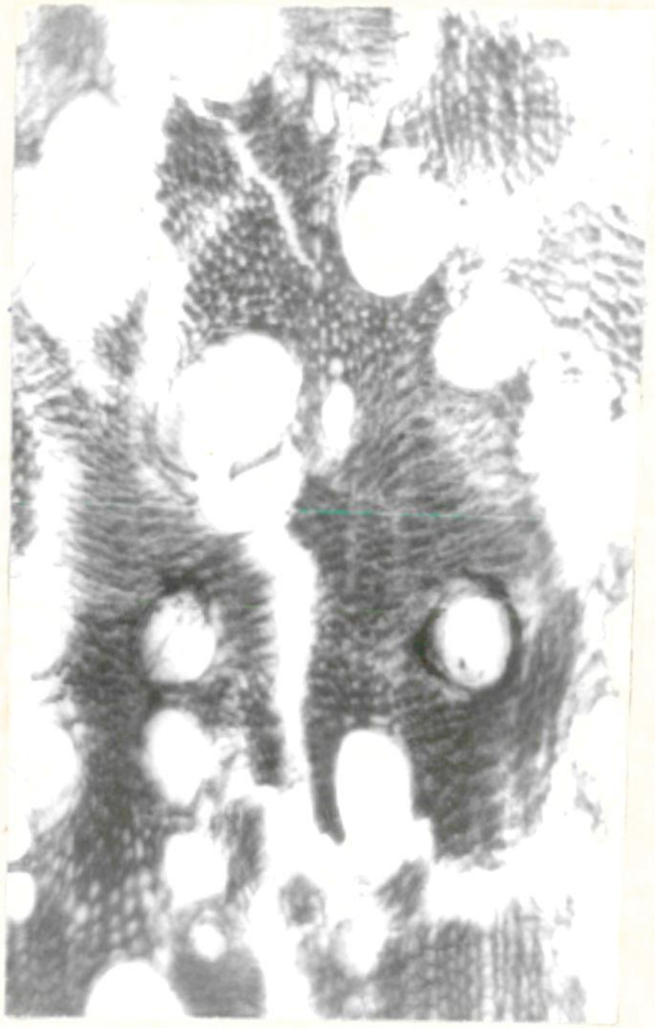
PHOTOMICROGRAPH -16
Cajanus cajan, L. S. (40X)
delignified



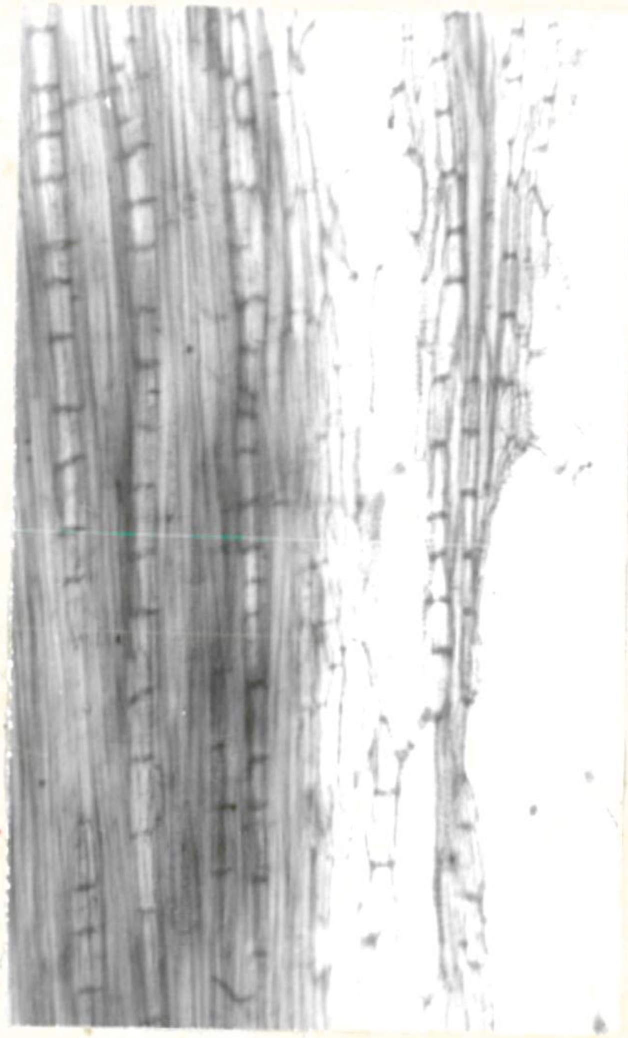
PHOTOMICROGRAPH -17
Cajanus cajan, T. S. (40X)
Hemicellulose Free



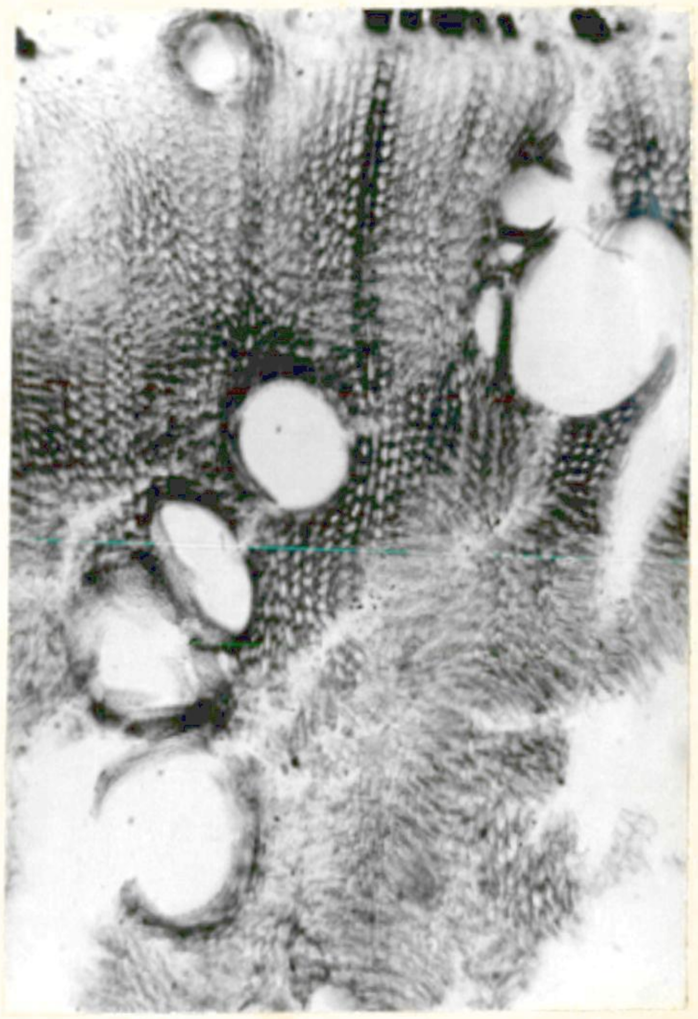
PHOTOMICROGRAPH -18
Cajanus cajan, L. S. (40X)
Hemicellulose Free



PHOTOMICROGRAPH-19
S.sesban, T.S.(40 X)
KBr disc



PHOTOMICROGRAPH-20
S.sesban,L.S.(40 X)
KBr disc

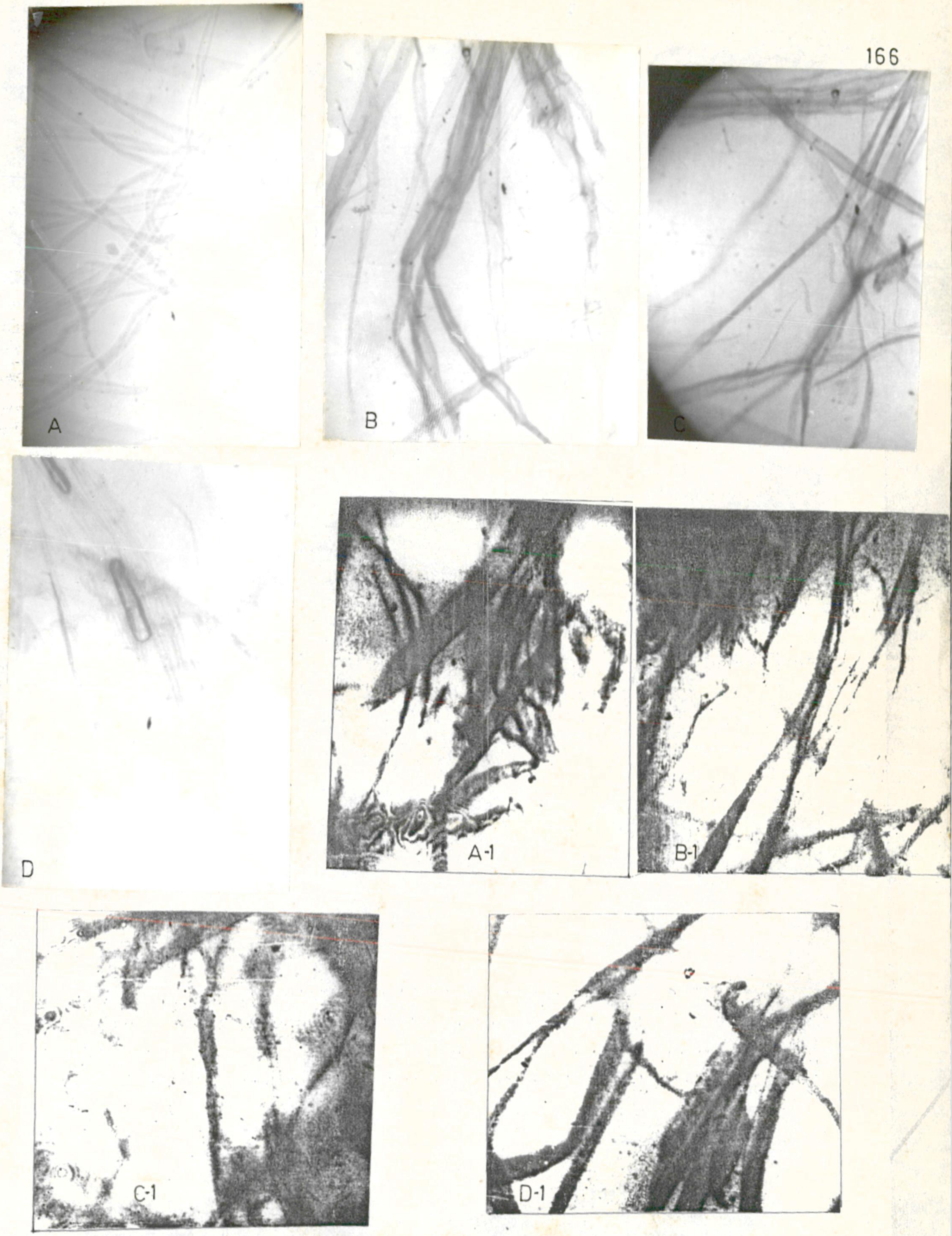


PHOTOMICROGRAPH-21
S.aculeata,T.S.(40X)
KBr disc

PHOTOMICROGRAPH-22
S.aculeata,L.S.(40X)
KBr disc

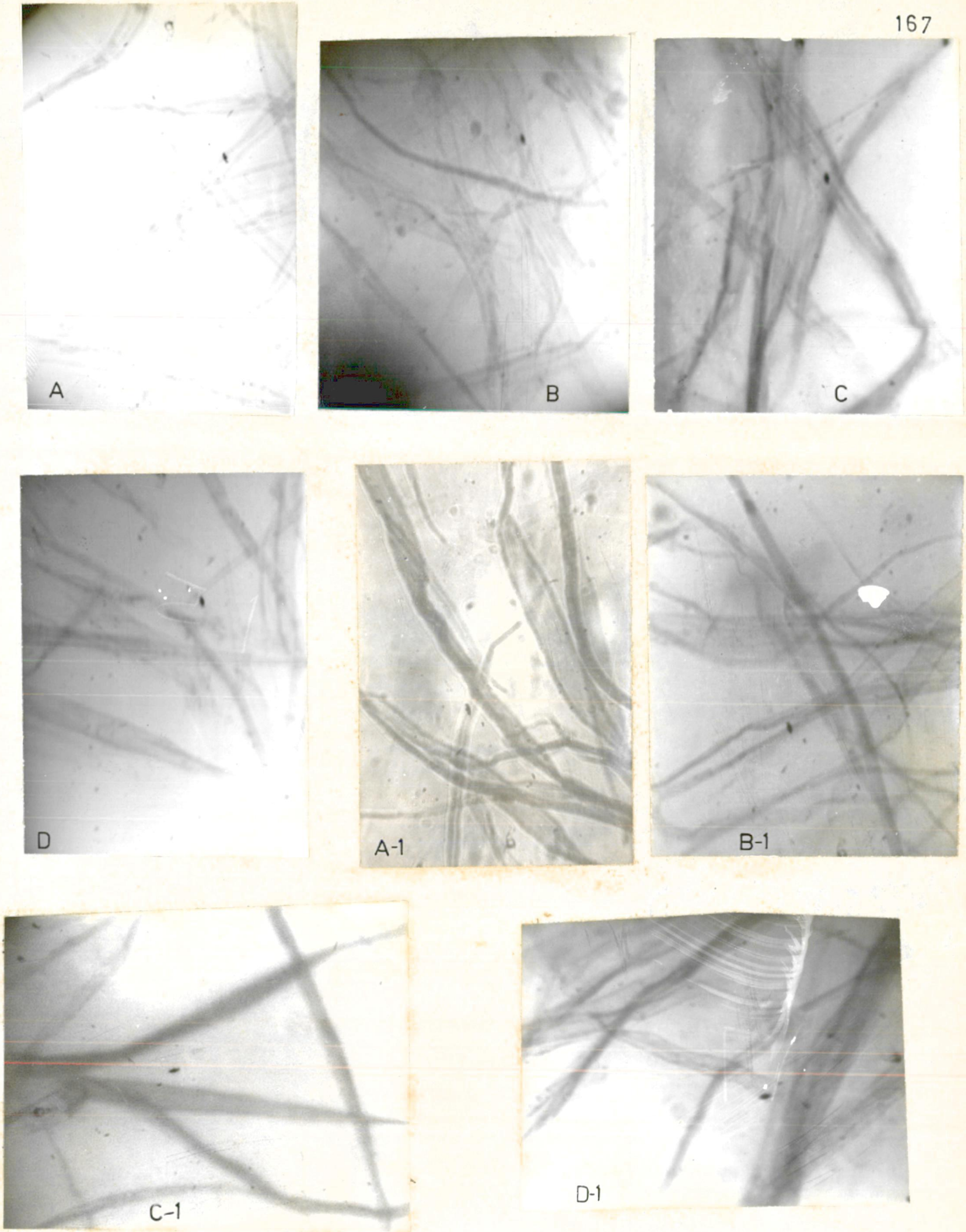
PHOTOMICROGRAPH-23
C. cajan, T.S. (40 X)
KBr disc

PHOTOMICROGRAPH-24
C.cajan, L.S. (40 X)
KBr disc



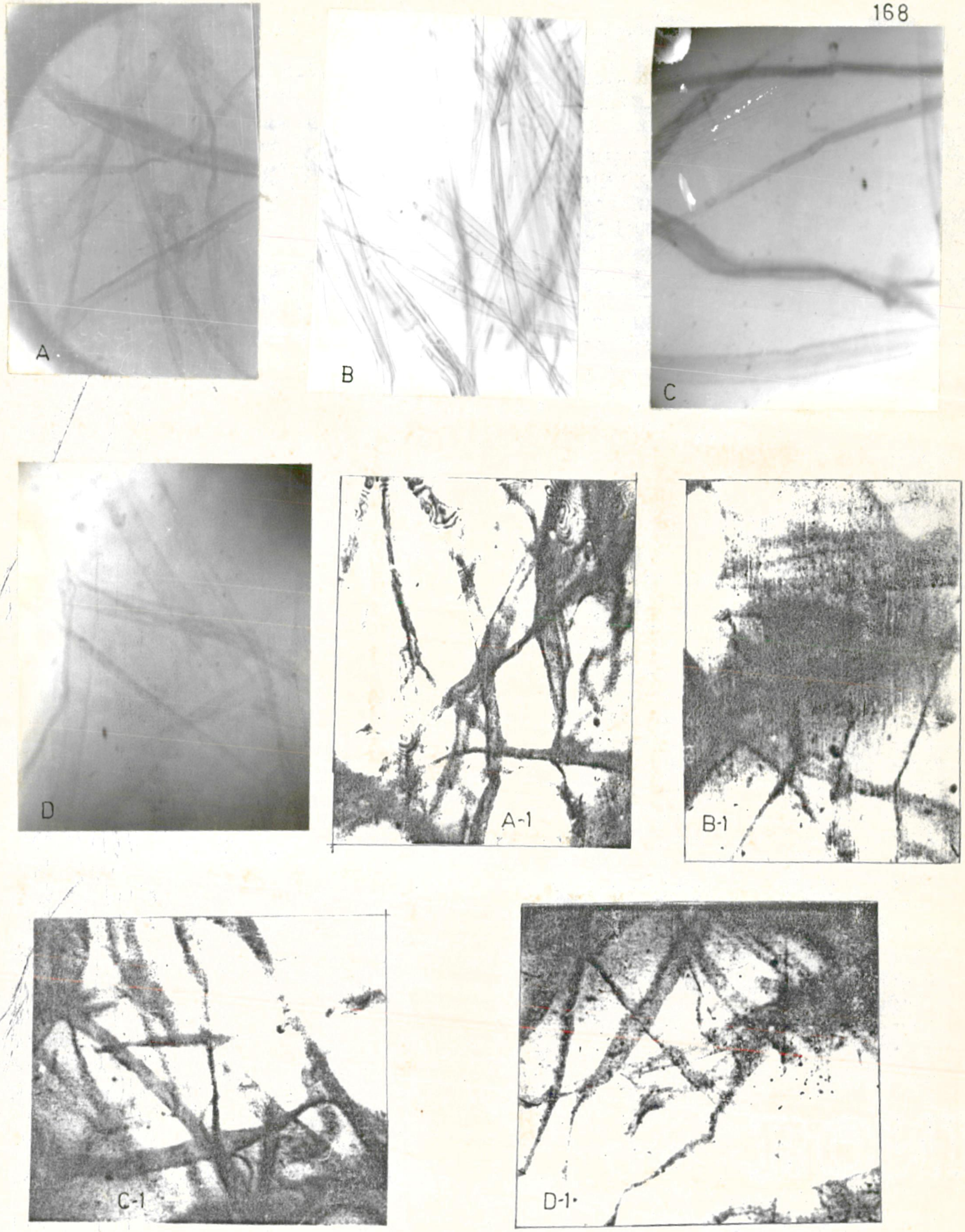
Photomicrograph of S. sesban unbeaten Pulp (Soda-A) (Kraft-B) (Alkaline Sulphite-C) (Semi Alkaline Sulphite-D)

Photomicrograph of S. sesban beaten Pulp (Soda-A-1) (Kraft-B-1) (Alkaline Sulphite-C-1) (Semi Alkaline Sulphite-D-1) (40×)



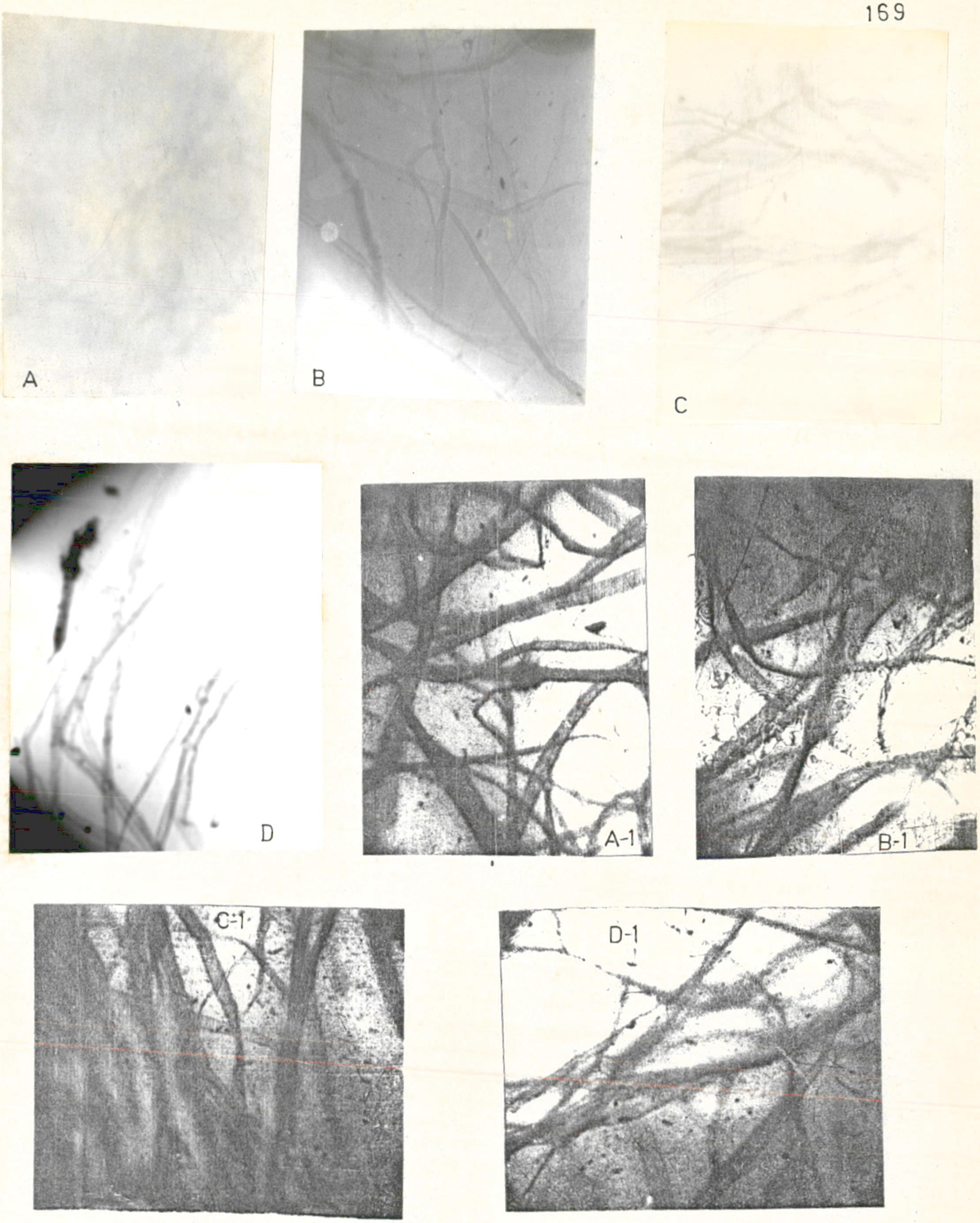
Photomicrograph of C.cajan unbeaten Pulp (Soda-A)(Kraft-B)
(Alkaline Sulphite-C) (Semi Alkaline Sulphite-D)

Photomicrograph of C.cajan beaten Pulp (Soda-A-1) (Kraft-B-1)
(Alkaline Sulphite-C-1) (Semi Alkaline Sulphite-D-1) (40X)



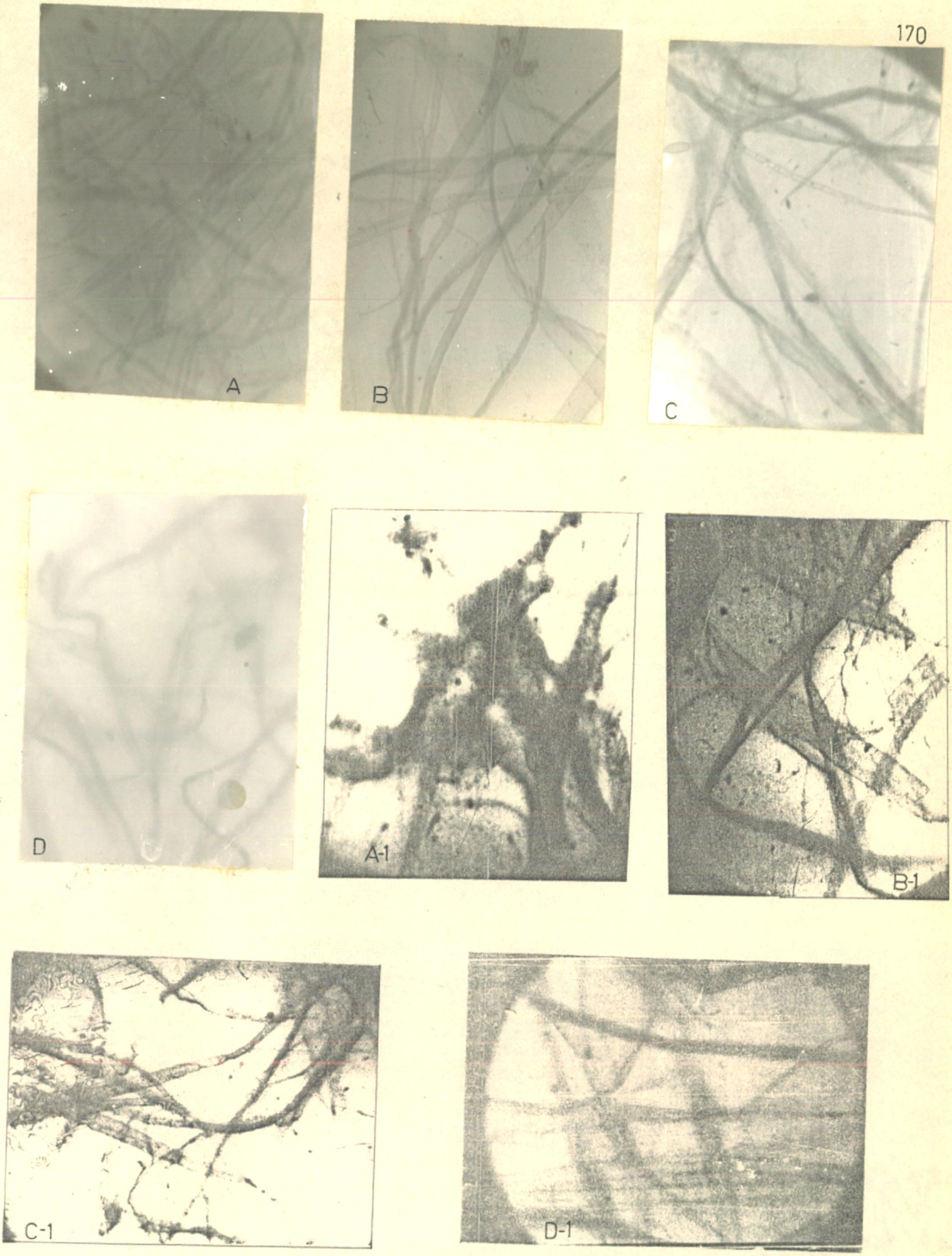
Photomicrograph of S. aculeata unbeaten Pulp (Soda-A)(Kraft-B) (Alkaline Sulphite-C) (Semi Alkaline Sulphite-D)

Photomicrograph of S. aculeata beaten Pulp (Soda-A-1)(Kraft-B-1) (Alkaline Sulphite-C-1) (Semi Alkaline Sulphite-D-1)(40X)



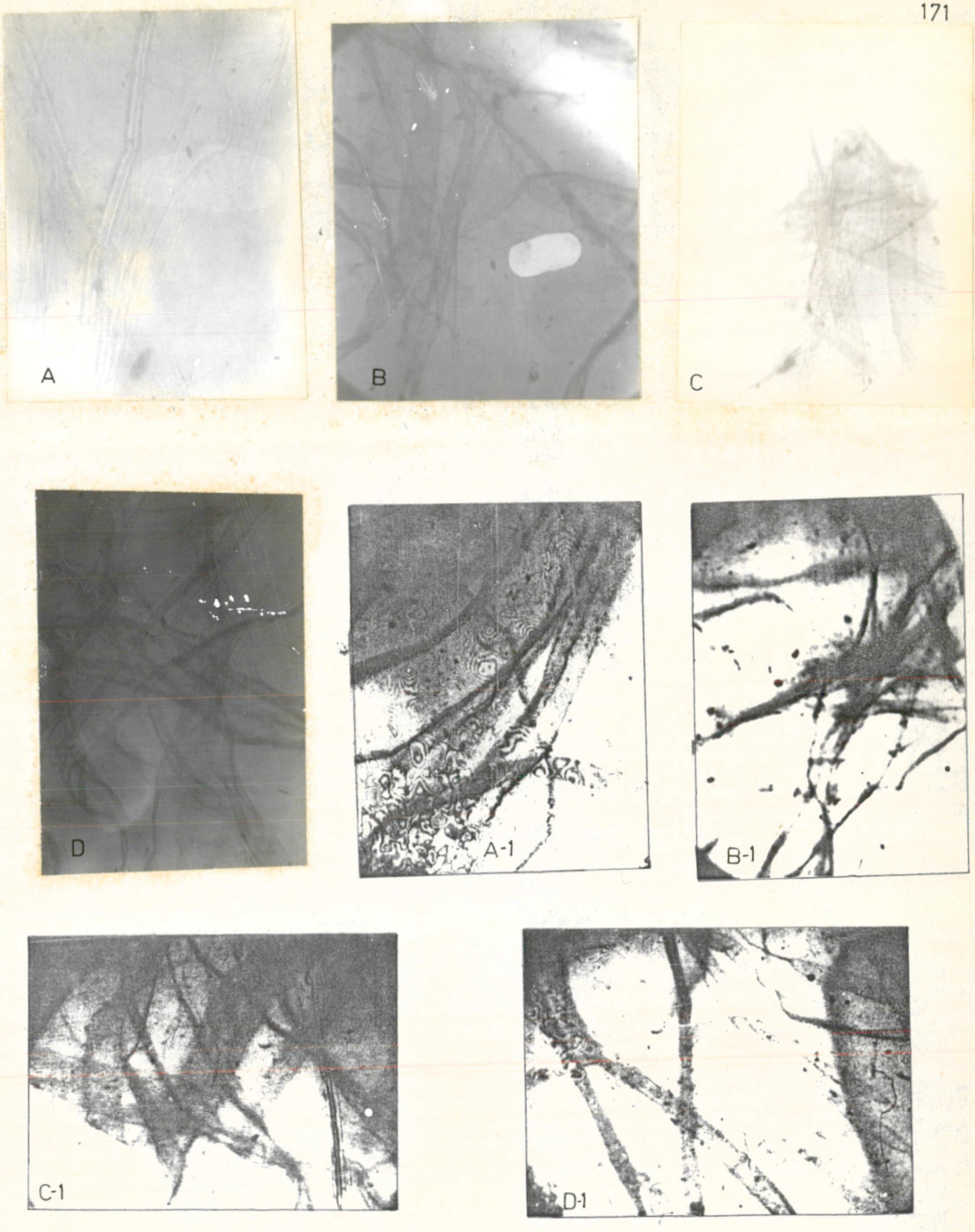
Photomicrograph of S. sesban Bleached unbeaten Pulp (Soda-A)(Kraft-B) (Alkaline Sulphite-C) (Semi Alkaline Sulphite-D)

Photomicrograph of S. sesban Bleached beaten Pulp (Soda-A-1)(Kraft-B-1) (Alkaline Sulphite-C-1) (Semi Alkaline Sulphite-D-1)(40X)



Photomicrograph of C.cajan Bleached unbeaten Pulp (Soda-A)(Kraft-B) (Alkaline Sulphite-C) (Semi Alkaline Sulphite-D)

Photomicrograph of C.cajan Bleached beaten Pulp (Soda-A-1)(Kraft-B-1) (Alkaline Sulphite-C-1)(Semi Alkaline Sulphite-D-1)(40X)



Photomicrograph of S. aculeata Bleached unbeaten Pulp (Soda-A)(Kraft-B) (Alkaline Sulphite-C) (Semi-alkaline sulphite-D)

Photomicrograph of S. aculeata Bleached beaten Pulp (Soda-A-1)(Kraft-B-1) (Alkaline Sulphite-C-1) (Semi-alkaline sulphite-D-1) (40×)

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