CHAPTER II

SISAL: A POTENTIAL PAPERMAKING FIBRE
2.1 Introduction

Sisal has been an important leaf fibre, which is a potential and prospective material for paper making in the present study. It has been grouped under the broad heading of “hard fibres” among which it is placed second to Manila in durability and strength [1]. The fibre has been usually obtained from the leaves of the monocotyledonous herbaceous plant of *Agave Sisalana* (Fig. 2.1). The word sisal means cold water which has come from a harbor town in Yucatan, Maya, Mexico [2] in Central America. Sisal had been exported for the first time from Mexico to Tanzania via Hamburg in 1893. Agave plants had been grown by the Maya Indians before the arrival of the Europeans. A little later, sisal bulbils sent from Kew Gardens were planted in Kenya. After a difficult start sisal production in East Africa prospered and by the 1960's Tanzania had alone totalled some 2,30,000 tons. In comparison to other plant fibres, sisal has many advantages like it can thrive in wastelands and has the capacity to yield superior quality fibres continuously for 6-8 years, with least management input.

Henequen, which resembles sisal is also indigenous to Mexico and had been in fact, regarded as sisal. The Maya Indians, who have been preparing the fibres by hand had mostly used it for ropes, carpets and clothing. Since, some clothes used to be known as “nequen” by the Mexicans, the name “henequen” has perhaps originated from that. In Mexico henequen production (largely in the Yucatan peninsula) has fallen from a peak of about 160,000 tons in the 1960's to about less than 10,000 tons today, all of which has been converted into local products. Both China and Mexico have now become the major importers of sisal fibre, than growers. Today Brazil is the main world producer of sisal with around 1,25,000 tons [3]. However, the first commercial plantings in Brazil had not been done until the late 1930's and the first sisal fibre exports from there were made in 1948. It had been only after the 1960's that Brazilian production gained momentum and the first of many spinning mills, largely devoted to the manufacture of agricultural twines got established there. Sisal has provided about 2% of the 65% of plant fibres produced in the world and has thus, occupied 6th place among the fibre plants [4]. Sisal has been one of the most extensively cultivated hard fibre and had accounted for half the total production of textile fibres in the world [5, 6].
In India, sisal had been introduced by the Portuguese in the fifteenth century and now those can be found throughout the country. Sisal has been a xerophytic plant which can survive on poor soils in drought prone tropical regions. Thus, it has mainly grown and has been found in the arid and semi-arid regions of Andhra Pradesh, Bihar, Jharkhand, Odisha, Karnataka, Maharashtra and West Bengal. Particularly in Odisha, it has been abundantly available and randomly distributed throughout the State but highly concentrated in its central and western belts especially, in the Bamra region of the State. But considering its huge potential, it has remained an underutilized resource except for a few of its traditional uses not only in this State (Odisha) but in the country as a whole. The plant has been locally known by different names like “Murbaa” and “Hathibaara (which means fence for elephants in the regional language)”, depending on its use in varying geographical locations of the State. So, the later name has also indicated the traditional use of the sisal plants for fencing or hedging purpose. Even today, many plantations of sisal can be seen on the roadside as well as on the borders of the fields in various parts of the country, probably to preserve soil erosion and protect the farmlands from grazing animals and many other unwanted elements (Figure 2.1).

![Figure 2.1 Sisal Plants as Fence](image)

Development of synthetic fibres has eroded the traditional sisal markets but new avenues have opened up in this technological era for its diverse applications. The use of sisal as reinforcement fibre in cement or concrete [2, 7-15], mortar based composites [16,
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17, 18, 19, composite resins [20-27], polymer matrix [28-45], bitumen and plasterboard has also been explored and exploited in the recent past. Several researchers have also reported the use of sisal fibres in thermoplastic composites [46, 47, 48, 49, 50], wood panels [51] and rubber (synthetic as well as natural) based composites [52-57]. Bio-based composites [58], benzoxazine/epoxy composites [59] and nano composites [60] have also been reported to have been produced with the employment of sisal fibres. Most of them have observed an improvement in the bonding at the fibre-polymer interfaces, which is suggested to have taken place due to chemical treatments of the fibre. Specifically, treatments using chemicals such as sodium hydroxide, isocyanate, permanganate and peroxide have been found to improve the bonding at the fibre-polymer matrix interface, which results in a considerable enhancement in the tensile and other physical properties of the composites to varying degrees.

Recently, research has also progressed towards the development of fabric by using chemically-treated sisal fibres [61] and the major findings of the research have revealed that sisal fibres treated with NaOH could be successfully spun into yarns with the aid of a binding agent and the resulting yarns exhibited finer, weaker and highly absorbent characteristics. However, the chemically treated sisal fibres produced a fabric with lower flexural rigidity and showed insignificant effect of fabric softeners on them. Being a comparatively stiff fibre, it has been suggested that the pliability of sisal fibres may be enhanced by chemical treatments [62, 63], after which the fibres may be suitably employed in the textile or in the craft industry.

The present work has been especially intended to interpret and determine the potential of the locally available sisal fibre not only as a paper-making raw material, but also to explore the ability and effectiveness of this fibre as a supplementary fibre when blended with the other types of pulp fibres particularly, the weak and recycled ones, which happen to be the chief raw materials in the hand-made paper manufacturing units as well as many other small to medium scale paper/paperboard manufacturing industries based on the recycling technology.
2.2 Nomenclature, Plant Description and Fibre Extraction

2.2.1 Botanical Classification

Sisal is a herbaceous monocotyledonous plant which can be botanically classified in the following manner and aptly given the name *agave sisalana perrine*.

<table>
<thead>
<tr>
<th>Kingdom</th>
<th>Plant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Division</td>
<td>Magnoliophyta</td>
</tr>
<tr>
<td>Class</td>
<td>Liliopsida</td>
</tr>
<tr>
<td>Order</td>
<td>Asparagales</td>
</tr>
<tr>
<td>Family</td>
<td>Agavaceae</td>
</tr>
<tr>
<td>Genus</td>
<td>Agave</td>
</tr>
<tr>
<td>Species</td>
<td>Sisalana</td>
</tr>
<tr>
<td>Binomial Name</td>
<td><em>Agave sisalana perrine</em></td>
</tr>
</tbody>
</table>

2.2.2 Plant Description

Sisal plant has a stalk on which the succulent leaves grow out spirally. The lance-shaped leaves are fleshy and rigid having a dark green color. Sisal has been a stoloniferous plant, which produces shoots from the stolons, known as suckers or bulbils, which can be used for propagation. The suckers / bulbils are grown in nurseries until they are about 50 to 70 cm high and then planted in the main field [64]. The sisal plant looks like an overgrown pineapple with a pineapple-like bole (a short, stocky trunk) from which the leaves extend (Figure 2.2). For a mature plant, the bole is about 50cm in height and about 20cm in diameter. The leaves attain lengths of up to 2m, but are usually about 1.0–1.2m long. The leaves which can be as wide as 12cm, usually terminate with a sharp, highly lignified spine about 1.0-1.5cm long. The outside of the sisal leaf consists of a well-developed epidermis with a waxy surface. This epidermis contains cutin, waxes and carbohydrates. At various stages of growth, it has 100-150 dark-to-pale green leaves formed in a dense rosette on the trunk. The mature leaves covered with a waxy-bloom, resemble a two-edged sword having thickness of about 6 mm at the centre. Initially, all leaves grow vertically on the plant. But with age, they fan out gradually to an angle of about 45°. The mature leaves have been those which lie closest to the ground and contain the coarsest and the longest fibres. Cutting of the leaves has been found to commence after 2½ yrs when the plant has about 100 leaves. The plant produces approximately 200-
250 leaves throughout its productive period and the life span of this plant has been estimated to be about 7-10 years.

![A matured sisal plant](image1.png) ![Locally growing sisal plants](image2.png)

**Figure 2.2(a) A matured sisal plant**  **Figure 2.2(b) Locally growing sisal plants**

### 2.2.3 Extraction of Pulping Fibres from Sisal Plant

Fibres from the sisal leaf can be extracted by a process commonly known as decortication by different methods like retting, scraping, retting followed by scraping or by mechanical means using decorticators or fibre raspadors. Though the extraction of sisal fibre from the leaves is largely done by the retting process, the extraction on respador machine yields superior quality fibres in comparison to those obtained from the retting process. Moreover, the fibres extracted by the use of raspador machines are economically more viable. A normal sisal leaf weighing about 600g has been found to yield about 3% by weight of fibres with each leaf containing about 1000 fibres [65]. Although, the leaf fibre bundles extracted for cordage are very long (70-130cm), the ultimate pulping fibre length ranges from 1.5-4 mm with an average of about 3 mm. The decorticated sisal leaf fibre bundles have been highlighted in **Figure 2.3(a)**. The decorticated and uniformly cut sisal fibres, as used for various investigations have also been shown in **Figure 2.3(b)**.
The ultimate pulp fibres from boles have been found to be weaker than those from the leaves. The bole fibres have not been observed to be in the form of fibre bundles like that of the leaf fibres except in the leaf butt ends attached to the boles. The base of the bole is woody and fibrous, but the ultimate pulp fibres have been found to be shorter with low fibre content. The upper portion has been observed to become increasingly pithy containing almost no fibrous material towards the growing tip. The bole has been observed to be covered with a highly lignified cortical layer to which the leaves are attached. The bases of the leaves which remain attached to the bole when leaves are cut contain leaf fibre. So, the bole fibre has been less desirable for pulping because of the lower fibre content, lower fibre strength, highly lignified cortical layer and dirt trapped between the leaf butts and the bole. Pulping studies have however indicated that a good quality pulp can be produced if leaves and boles are pulped together provided the amount of boles does not exceed 23% of the total green weight of leaves and boles. But for getting the highest quality of sisal pulp, fibres can be obtained from the leaves only [66].

A good sisal plant has the capacity to yield about 200-250 commercially useable leaves throughout its productive period with each leaf having a mass composition of 4% fibre, 0.75% cuticle, 8% other dry matter and 87.25% moisture. Average composition of the sisal plant as selected for pulping purpose has been provided in the following table (Table 2.1) [Personal communications: From the users of sisal fibres for rope making].
Table 2.1 Average composition of sisal plant at 40 months

<table>
<thead>
<tr>
<th></th>
<th>Leaves</th>
<th>Boles</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green Weight (kg)</td>
<td>27</td>
<td>8</td>
<td>35</td>
</tr>
<tr>
<td>Fiber Content (%)</td>
<td>6.0</td>
<td>4.8</td>
<td>5.7</td>
</tr>
<tr>
<td>Pith (%)</td>
<td>6.1</td>
<td>8.7</td>
<td>6.7</td>
</tr>
<tr>
<td>Epidermal &amp; Cortical material (%)</td>
<td>2.2</td>
<td>3.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Solubles (%)</td>
<td>2.5</td>
<td>7.3</td>
<td>3.6</td>
</tr>
<tr>
<td>Total Solids (%)</td>
<td>16.8</td>
<td>23.8</td>
<td>18.4</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>83.2</td>
<td>76.2</td>
<td>81.6</td>
</tr>
</tbody>
</table>

Notes: 1. Leaves include "spike" leaves.
2. Flowering poles excluded.

2.3. Proximate Analysis

Due to the geographical variation of the natural fibres, sisal fibres have been collected from two different locations approximately 100kms apart, one with irrigation facilities and the other is a rain-fed area. Some of the characteristics of the fibres viz., chemical constituents (cellulose, pentosan, lignin, pectin, ash & silica) and solubilities in various solvents viz. water, ethanol, benzene, acetone and different concentrations of alkali, from both of these sources have been investigated and the results tabulated (Table 2.2) for comparison. Decorticated fibres were procured from Bamra (rain-fed area), in Sambalpur district (Sisal-1) and the other type (Sisal-2) were procured from Nildungri (irrigated area), also in the Sambalpur district of Odisha.

The sisal fibres were thoroughly cleaned by removing the residual pithy materials attached to the fibres after decortication (extraction of fibres from the leaves), washed with water and air-dried. The fibres were then cut to uniform length of approximately 2-4 cm with the help of a pair of scissors for using them in various laboratory-scale investigations. Results of a few preliminary investigations carried-out upon the sisal fibres procured from two different locations as mentioned above, have been summarized in Table 2.2. Moisture percentage of the fibres was calculated by weighing the oven-dried (5-6 hr at 90°C) fibres three to four times and taking the average of all the readings.
The density of sisal fibre was determined by obtaining the fibre width [67], with the help of a compound microscope at 40x resolution and liquid pycnometry technique [68].

Chemical analysis has been performed according to TAPPI standard methods [69] as follows: T 223 CM-84-pentosan, T 222 OM-88-lignin (acid insoluble), T 207 OM-88 for hot and cold water solubilities, T 212 OM-88 for 1% alkali solubility. Solubility was also determined for varying concentrations of the alkali viz. 3%, 5% and 7%. The holocellulose content was evaluated with the method adopted by Wise et al, [70]. The α-cellulose was determined according to the modified method of Sarkar et al, [71] and the pectin content was estimated with 0.5% ammonium oxalate solution [72]. The ash and silica contents were determined gravimetrically as mentioned below. The results of the various physical and chemical analysis has been summarized in Table 2.2.

2.3.1 Solubilities of Sisal Fibre

The solubility of the sisal fibres have been studied by keeping 1 gm of fibres in 50 ml of solvents for 48 hours at room temperature. The solvents were removed and the rest undissolved fibres were dried and weighed till three concordant readings. The difference in the weight after and before the dissolution was considered as the weight of dissolved substance. The results obtained from above experiments are given in Table 2.2

2.3.2 Determination of Ash Content in Sisal Fibre

The ash content of the fibre was determined gravimetrically by weighing the incinerated sisal fibres in a previously weighed porcelain basin. The difference in weight of the basin containing sisal fibres before incineration and after incineration indicated the ash content. The weights of the basin with the contents (grayish amorphous powder of ash) were taken only after complete cooling of the basin.

For the sake of accuracy, the ash content was determined by repeating the procedure for different weights of sisal fibres (viz. 2, 4, 6 etc.). The percentage of ash content determined for sisal fibres collected from two locations has been summarized in Table-2.2.
2.3.3 Determination of Silica

Silica content in the sisal fibres has been determined using the hydrochloric acid method by dissolving the cut, depithed and properly cleaned 4 g of fibres in 20 ml of the conc. HCl solution, which was evaporated to dryness on a hot plate. On cooling, 5 ml of conc. HCl was added and the mixture was diluted with milipore water to about 100 ml and warmed. After warming the mixture solution, it was filtered through an ashless filter paper. The precipitate was washed properly till the filtrate does not contain any trace of chloride. On proper agitation and washings, complete removal of chloride could be achieved as confirmed by the AgNO₃ test.

The paper with the precipitate was ignited on a previously weighed ignition crucible and on cooling the crucible was again weighed and let the weight be 'X' gram. Weighing the crucible after addition of a few drops of concentrated sulfuric acid and 2-3 ml of 48% hydrofluoric acid to the weighed precipitate and careful evaporation and cooling of the contents gave the value Y gram. Addition of HF volatilize the contents as silicon tetrafluoride. The difference in weights (X-Y) indicates the silica content in the sisal fibres. The processes of heating, cooling and weighing were repeated till constant weight was obtained.

The above process for determining the silica content in sisal fibres was repeated two more times by taking 4g of the fibres in each case. Finally, the silica percent was calculated by taking the average of the results obtained in the three experiments. Similarly, the silica content in the fibres obtained from a different source (sisal-2) was determined and the results obtained have been summarized in Table 2.2.

2.3.4 Determination of Lignin (Acid-Insoluble)

To 1g of cut sisal fibres kept in a 100ml beaker in a water bath to maintain the reaction at room temperature, 20 ml of the previously prepared 72% H₂SO₄ was added and kept the beaker standing at room temperature for nearly 2 hr, covered with a watch glass. The solution was transferred to a 1-litre round bottomed flask. The volume was made to 500 ml with milipore water (to maintain the acid concentration to be 3%). The solution was refluxed on a hot plate for 4 hr and was kept overnight to allow the lignin to settle. The lignin was filtered with the help of a previously weighed G-4 crucible (w₁), by
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using a suction pump. The precipitate (i.e., the acid insoluble lignin) was washed with hot water to make it acid-free. The G-4 crucible with the lignin was put in an electric oven for drying and on complete drying, it was cooled to room temperature and its weight was taken. The process of drying, cooling and weighing was repeated till a constant weight was obtained. Let this weight be \( W_2 \). The difference in both the weights \((W_2 - W_1)\) gave the weight of acid insoluble lignin, \( A \). The percentage of acid insoluble lignin was calculated by applying the following formula:

\[
\text{Lignin } \% = \frac{(A \times 100)}{W}
\]

Where, \( A = \) weight of lignin in g \((W_2 - W_1)\)

\( W = \) Oven-dry weight of the sisal fibre

The above mentioned procedure has been followed for the determination of the acid insoluble lignin by taking 1g and 2g of sisal fibres from both of the sources (i.e., sisal-1 and sisal-2) and for each case at least three experiments have been performed to confirm the results. The average of the results obtained in each case has been calculated to finally get the acid-insoluble lignin in sisal fibres. Observations and the data obtained from various calculations have been summarized in Table 2.2.

2.3.5 Isolation of Lignin from Sisal Fibres by Acid-Hydrolysis

The uniformly cut sisal fibres (2-3 cm in length) were thoroughly washed with milipore water and air-dried. On complete drying, 20 g of the air-dried fibres were kept in a solution of acetone for 24 hr. The fibres were then filtered off from the acetone solution and washed with milipore water. After thorough washing, the fibres were spread on a clean filter paper in the open air. Then the air-dried fibres were subjected to the following extraction method with the help of a soxhlet apparatus.

The air-dried fibres (20 g) were taken in a round-bottomed flask and an azeotropic mixture of 225 ml p-dioxane and 25 ml of 0.1N HCl in H\(_2\)O was added to it. The mixture was refluxed in the round-bottom flask for about 4 hrs and then the contents were transferred to the soxhlet apparatus and reflux continued for another 6 hr. The contents were then cooled and filtered through a coarse-sintered glass Buchner funnel covered with filter paper to avoid plugging. The resulting filtrate consisting of lignin/ water/ dioxane mixture was then neutralized with an aqueous saturated solution of sodium
bicarbonate to approximately 5.0-5.5 pH value. This filtrate solution was then concentrated at approximately 35°C and at the atmospheric pressure to about 10% of the original volume. Milipore water (300ml) was added to the reduced volume and the solution was concentrated again to remove the last traces of dioxane. The resulting solution (aqueous lignin) was transferred to a 1-litre beaker and diluted with milipore water to a volume of approximately 700 ml, acidified to a pH of 2.0 - 2.5 and freeze-dried for 3 – 5 days when the lignin coalesced.

Weight of this freeze-dried lignin was found to be 1.840 g

& \% Yield = 1.840/20 \times 100 = 9.2\%.

2.3.6 Isolation of Holocellulose

The holocellulose was isolated by the sodium chlorite method as used for jute by Chattopadhyay and Sarkar (1946). The same procedure was adopted in this case. Uniformly cut sisal fibres were extracted with acetone in a Soxhlet apparatus for 8 hr to remove the extractives (which consist of compounds such as fatty acids, fatty alcohols, free sterols, alkanes, steroid hydrocarbons etc.). 4 g (w_1) of the defatted sisal fibres were then treated with 0.7% sodium chlorite (liquor ratio 1: 50) for 2 hrs at the boiling water bath. The pH was maintained between 4.5 to 5 using acetic acid and sodium acetate buffer. It was then filtered and washed thoroughly with distilled water. After thorough washing the residual fibres were air dried and their weight was taken which gave the weight of holocellulose (w_2).

The loss in weight (w_1 – w_2) was also recorded which approximately corresponds to the value of lignin content in the fibre (Table-2.1). The above mentioned procedure was followed to determine the holocellulose in both the sisal fibres (obtained from the two different geographical locations).

2.3.7 Estimation of α-Cellulose

The α-celluloses were obtained by treating the holocelluloses of sisal-1 and sisal-2 with 17.5% caustic soda solution. The insoluble portions in the alkali solution were filtered off and dried. The oven-dry weight of these insoluble fractions were taken,
which gave the \(\alpha\)-cellulose content in both the types of fibres. The percentages of hlocelulose and \(\alpha\)-cellulose in the sisal fibres are presented in Table 2.2.

2.3.8 Estimation of Pentosan (T 223 CM-84)

To 1g (OD weight) of ethanol-benzene extracted sisal fibres contained in a 500 ml distillation flask, 100 ml of 12% HCl (prepared by diluting 307 ml of conc. HCl to 1 litre with distilled water), was added. On heating the flask attached to a dropping funnel containing 300 ml of HCl, the distillate was collected in a receiver placed in ice-bath. The distillation was carried-out @ 50 ml/ 15 min. till 300 ml of the distillate was collected. The stop clock of the funnel was adjusted during distillation to maintain 100 ml acid level in the flask.

On completion, the condensate was transferred to 1 litre flask to which 50 ml of distilled water was added and the condensate cooled to 0° C by the addition of ice. 20 ml of bromate-bromide solution prepared by taking 5.57 g KBr\(_O_3\), 50 g KBr and 1 g Na\(_2\)CO\(_3\) diluted to 1 litre, was added to the ice cooled condensate and allowed to stand for 5 min. 10 ml of 10% KI solution was added to it and the resulting solution was titrated with 0.1N Na\(_2\)S\(_2\)O\(_3\) solution using starch indicator. The volume of thiosulphate consumed gave the volume \(V_1\). A blank titration was carried-out by the above mentioned procedure by taking 350 ml of the distillate. The volume of thiosulphate consumed was noted as \(V_2\). The \(V_1\) values were obtained for each type of sisal fibres (Sisal Type 1 and Sisal Type 2). The percentage of pentosan was then determined by applying the following formula:

\[
\text{Pentosan (\%) = } \frac{7.5xNz(V_2 - V_1)}{W} - 1.0
\]

Where,
- \(N\) = Normality of thiosulphate solution (0.1N)
- \(V_1\) = Volume of thio consumed for the sample
- \(V_2\) = Volume of thio consumed for the blank titration
- \(W\) = OD weight of sample (sisal fibres)

2.3.9 Summary of Physico-Chemical Analysis

The summary of the various physico-chemical analysis performed on the sisal fibres (sisal type-1 and sisal type-2) by the above mentioned procedures have been provided in a tabulation form (Table 2.2) as shown in the next page.
Table 2.2 Proximate physico-chemical analysis of sisal fibres

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Properties</th>
<th>Sisal Type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SISAL-1</td>
</tr>
<tr>
<td>1.</td>
<td>Moisture (%)</td>
<td>10.11</td>
</tr>
<tr>
<td>2.</td>
<td>Width (mm)</td>
<td>0.3</td>
</tr>
<tr>
<td>3.</td>
<td>Density (Pycnometer method)</td>
<td>1.453</td>
</tr>
<tr>
<td></td>
<td>(width method)</td>
<td>1.645</td>
</tr>
<tr>
<td>4.</td>
<td>Tensile strength, B.L. (km)</td>
<td>6.1</td>
</tr>
<tr>
<td>5.</td>
<td>Solubility in alkali</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1% NaOH</td>
<td>22.7%</td>
</tr>
<tr>
<td></td>
<td>3% NaOH</td>
<td>23.8%</td>
</tr>
<tr>
<td></td>
<td>5% NaOH</td>
<td>30.0%</td>
</tr>
<tr>
<td></td>
<td>7% NaOH</td>
<td>32.55%</td>
</tr>
<tr>
<td></td>
<td>in organic solvents</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ethanol cold</td>
<td>0.65%</td>
</tr>
<tr>
<td></td>
<td>Ethanol hot</td>
<td>0.8%</td>
</tr>
<tr>
<td></td>
<td>Benzene cold</td>
<td>1.15%</td>
</tr>
<tr>
<td></td>
<td>Benzene hot</td>
<td>3.79%</td>
</tr>
<tr>
<td></td>
<td>Ethanol-Benzene (1:1) cold</td>
<td>0.88%</td>
</tr>
<tr>
<td></td>
<td>Ethanol-Benzene (1:1) hot</td>
<td>1.75%</td>
</tr>
<tr>
<td></td>
<td>Water cold</td>
<td>0.25%</td>
</tr>
<tr>
<td></td>
<td>Water hot</td>
<td>0.54%</td>
</tr>
<tr>
<td>6.</td>
<td>Acetone Extractives (%)</td>
<td>4.79</td>
</tr>
<tr>
<td>7.</td>
<td>Holocellulose (%)</td>
<td>87.05</td>
</tr>
<tr>
<td>8.</td>
<td>α-Cellulose (%)</td>
<td>61.76</td>
</tr>
<tr>
<td>9.</td>
<td>Lignin % (Acid insoluble)</td>
<td>11.7</td>
</tr>
<tr>
<td>10.</td>
<td>Ash (%)</td>
<td>1.128</td>
</tr>
<tr>
<td>11.</td>
<td>Silica (%)</td>
<td>0.33</td>
</tr>
<tr>
<td>12.</td>
<td>Pentosan (%)</td>
<td>22.34</td>
</tr>
<tr>
<td>13.</td>
<td>Pectin (%)</td>
<td>1.2</td>
</tr>
</tbody>
</table>

All the experiments were repeated more than three times and the values were averaged within an error of 6%.
2.4 Microscopic Observations

Photographs (2.4a-l) of the unmodified sisal fibre and the fibres with various treatments and modifications have been taken with the help of a compound microscope at 40x magnification to study the morphological characteristics of the fibre and also to analyze the effects of various chemicals, physical modifications as well as dyes on the fibre surface. Some valuable conclusions have been drawn from the photo-analysis, which not only throws some light on the structural and morphological aspects of the fibre but also renders support towards the suitability of these fibres as a paper-making raw-material.

a. Sisal fibres

b. Fibres treated with 7% NaOH
c. Dilute hydrochloric acid treated fibre
d. Dioxane treated fibre
e. Surfactant (SDS) treated fibre
f. Fibre scratched with a blade
g. Fibres beaten in a mortar and pestle (2-3 hr)

h. Fibres beaten in a beater (1.30 hr)

i. SDS treated fibres beaten (4-5 hr) in a mortar

j. Alkali (7%) treated sisal fibre soaked in a dye solution

k. Untreated fibre soaked in a dye solution

l. Alkali treated (7%) sisal fibre (Vertical direction)

Figure 2.4 Microscopic photographs of modified/unmodified sisal fibres

2.5 Paper making from Sisal Fibres

2.5.1 Pulping and paper making

The sisal fibres collected from Nildungrī, near Sambalpur (Type-2) were selected for the pulping due to the proximity of this area to the research field. The fibres cut into uniform size of approximately 2-4 cm in length with the help of a hand operated straw cutter were thoroughly cleaned to remove the residual pithy materials attached to the fibres after decortication (separation/extraction of fibres from the leaves). The pithy
materials which mainly consist of the parenchyma cells obstruct the beating process and may also affect the properties of the paper sheets prepared from these fibers. Hand sheets were prepared by both mechanical as well as semi chemi-mechanical processes of varying basis-weight and were evaluated for their physical properties especially, the burst strength and the corresponding pulp yields. The 1-min cob values of sized and unsized sheets were also determined and the results presented in Table-2.3.

Table 2.3 Properties of Sheets at different stages of beating

<table>
<thead>
<tr>
<th>Beating time, min</th>
<th>60</th>
<th>75</th>
<th>90</th>
<th>105</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freeness, °SR</td>
<td>10-11</td>
<td>12-14</td>
<td>15-17</td>
<td>18-20</td>
<td>24-25</td>
</tr>
<tr>
<td>Unscreened pulp yield, %</td>
<td>≥ 90</td>
<td>≥ 87</td>
<td>≥ 85</td>
<td>≥82</td>
<td>≥ 79</td>
</tr>
<tr>
<td>Burst Factor, gfcm$^2$/g</td>
<td>8.12</td>
<td>9.75</td>
<td>10.37</td>
<td>12.56</td>
<td>12.89</td>
</tr>
<tr>
<td>Breaking Length, m</td>
<td>1187</td>
<td>1400</td>
<td>1691</td>
<td>1854</td>
<td>1753</td>
</tr>
<tr>
<td>Tear Factor, gfm$^2$/g</td>
<td>122</td>
<td>147</td>
<td>124</td>
<td>114</td>
<td>136</td>
</tr>
<tr>
<td>Double Fold (M.I.T)</td>
<td>0</td>
<td>3</td>
<td>4</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>

2.5.2 Sheets Prepared by Mechanical Process

The cleaned fibres were subjected to the pulping and paper-making process. They were kept in water for nearly 1 hr prior to beating for softening the fibres to facilitate fibre swelling and hydration, which is one of the fundamental requirements and purpose of the beating process during pulping. The fibres were then beaten in an experimental beater (Hollander type of 251 capacity) as shown in Figure 2.5, for varying time intervals at 2-3% pulp consistency (initially in a high and then at medium load).
Freeness (which measures the extent of hydration in fibre by measuring the adsorbed water) of the pulps were examined with the help of a Schopper Reigler Freeness Tester at different stages of beating and the strength properties of the resulting sheets examined. Paper sheets were prepared by the handmade technique of lifting the uniformly distributed pulp from a vat containing pulp at a lower consistency, on a self fabricated mold of 30 mesh size followed by couching, pressing, drying in air and calendaring, with the help of a small power operated calendaring machine. The properly conditioned paper sheets were then subjected to various types of tests. All the tested samples were of same basis weight with variation of ±5 GSM.

2.5.3 Sheets prepared by Semi chemimechanical Process

Burst Factor and 1 min-cobb size values were also determined and are tabulated (Table-2.3), along with their basis weight (GSM) values for sheets, prepared by the mechanical process without any use of chemicals. Some samples were also tested for these properties, prepared by the semi chemimechanical pulping process. In the semi chemimechanical pulping method, cleaned and uniformly cut (4-5cm) sisal fibres were steam digested in a 5-l capacity pressure cooker for different intervals of time from 1-3 hr in 10% sodium hydroxide concentration on weight of oven dry fibres and 10 ml hydrogen peroxide. The material to liquor ratio was maintained at 1:5 (w/v) in all cases. The cooked fibres were washed free of liquor, and subjected to the beating process. It was found that the cooked fibres consumed less beating time than the uncooked fibres to reach the same degree of pulp freeness. Properties of the various sample sheets prepared by the semi chemimechanical process have been highlighted in Table 2.4.
Table-2.4 Properties of un-sized and sized paper sheets cooked at varying time intervals

<table>
<thead>
<tr>
<th>Cooking time (hr)</th>
<th>Unscreened Pulp yield (%)</th>
<th>Use of sizing chemicals/fillers</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>GSM</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>B.F. (g/m²)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1min Cob value (g/m²)</td>
</tr>
<tr>
<td>1.00</td>
<td>87</td>
<td>Rosin/starch</td>
<td>85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19.81</td>
</tr>
<tr>
<td>1.00</td>
<td>87</td>
<td>Rosin/starch</td>
<td>141</td>
</tr>
<tr>
<td>1.30</td>
<td>85</td>
<td>Rosin/starch</td>
<td>88</td>
</tr>
<tr>
<td>1.30</td>
<td>85</td>
<td>Rosin/starch</td>
<td>152</td>
</tr>
<tr>
<td>2.00</td>
<td>83</td>
<td>Rosin/starch</td>
<td>79</td>
</tr>
<tr>
<td>2.00</td>
<td>83</td>
<td>Rosin/starch</td>
<td>150</td>
</tr>
<tr>
<td>2.30</td>
<td>80</td>
<td>Rosin/starch</td>
<td>82</td>
</tr>
<tr>
<td>2.30</td>
<td>80</td>
<td>Rosin/starch</td>
<td>149</td>
</tr>
<tr>
<td>3.00</td>
<td>75</td>
<td>Rosin/starch</td>
<td>85</td>
</tr>
<tr>
<td>3.00</td>
<td>75</td>
<td>Rosin/starch</td>
<td>144</td>
</tr>
<tr>
<td>--</td>
<td>≥90</td>
<td>--</td>
<td>60</td>
</tr>
<tr>
<td>--</td>
<td>≥90</td>
<td>--</td>
<td>70</td>
</tr>
<tr>
<td>--</td>
<td>≥90</td>
<td>--</td>
<td>102</td>
</tr>
<tr>
<td>--</td>
<td>≥90</td>
<td>--</td>
<td>150</td>
</tr>
<tr>
<td>--</td>
<td>≥90</td>
<td>--</td>
<td>200</td>
</tr>
<tr>
<td>--</td>
<td>≥90</td>
<td>--</td>
<td>300</td>
</tr>
</tbody>
</table>

2.6 Comparison of Properties of Sisal and Rag Sheets

Various properties of the hand sheets prepared from sisal fibres as well as cotton rags (textile wastes), the conventionally used raw material in the hand made paper industries, have been tested and the results tabulated (Table 2.5) for the sake of comparison. Both the types of fibres were pulped by the mechanical pulping process to the same degree of Freeness at nearly the same pulp consistency. The paper sheets prepared from the unsized pulps were examined for various physical properties. It was observed during the beating of both types of fibre (experimental sisal and the conventional cotton textile wastes), that the sisal fibres consumed more beating time than the rag fibres, probably due to high stiffness and lignin content of the sisal fibres in comparison to the rag fibres.
Table 2.5 Comparison of physical properties of sheets prepared from sisal and rag pulps

<table>
<thead>
<tr>
<th>Tests</th>
<th>Sisal (200g)</th>
<th>Cotton rags (200g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis weight (GSM) ±5</td>
<td>80</td>
<td>120</td>
</tr>
<tr>
<td>Porosity (ml/min)</td>
<td>2000</td>
<td>3840</td>
</tr>
<tr>
<td>Stiffness (Taber)</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>Breaking Length, (mtr)</td>
<td>1400</td>
<td>1540</td>
</tr>
<tr>
<td>Tear Factor, 100gfm²/g</td>
<td>147</td>
<td>135</td>
</tr>
<tr>
<td>Double Fold, M.I.T</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Opacity, %</td>
<td>100.00</td>
<td>100.00</td>
</tr>
<tr>
<td>Burst Factor, gfcm²m²/g</td>
<td>3.0</td>
<td>10.178</td>
</tr>
</tbody>
</table>

2.7 Results and Discussion

2.7.1 Physico-Chemical Analysis

Physical characteristics and chemical composition of the two types of sisal fibres (sisal-1 and sisal-2) collected from two geographical locations approximately 100 kms apart are quite comparable and exhibit very little variations as visible from the data presented in Table-1. The density of the fibres obtained from the calculation by using the width of the fibres is found to be high when compared to pycnometer technique and are in the range of 1.365 – 1.630. In the liquid pycnometry technique, measuring the volume of fibres by liquid displacement method, was done by taking both water and hexane separately to avoid any swelling of the fibres in water through hydrogen bonding. However, the difference in the volumes of a fixed weight of material is within 6%. Comparison of the physical dimensions of sisal fibre (possessing average length of 3 mm and width of 20 μm) to that of some typical papermaking raw materials like depithed bagasse having length 1.13 mm and width 20 μm [73], cotton stalks with length 0.83 mm and width 19.60 μm [74], Aspen possessing length of 0.96 mm and diameter of 20.80 μm [75], wheat straw having length of 0.74 mm and diameter of 13.20 μm [76] and canola stalks possessing length 1.17 mm and width 23.02 μm [77] positively supports the dimensional suitability of sisal fibres and also justifies the possibility of employing them for the papermaking purpose.
To investigate on the lipophilic contents in the sisal fibre, acetone was used as an extractant. After ten hours of reflux in a soxhlet, 4-5% of the lipophilic materials could be extracted, which may be present mostly at the surface of the fibres. Low extractive content in the fibres is a good indication for pulping as it has been observed that the presence of extractives in the unbleached pulps negatively affect the bleaching process [78]. It has also been pointed out that presence of extractives in the fibre interfere with the lignin isolation process by the formation of condensation products with lignin during the pulping process [79]. On analyzing the solubilities of sisal fibres at various concentrations of alkali (viz. 1%, 3%, 5% and 7%), it may be concluded that more surface chemicals could be extracted with higher concentration of alkali.

2.7.2 Microscopic Photo Analysis

Photographs of the unmodified sisal fibre and the fibres with various treatments and modifications (Figures 2.4.1 – 2.4.12) have been taken with the help of a compound microscope at 40x magnification to study the morphological characteristics of the fibre and also to analyze the effects of various chemicals, physical modifications and dyes on the fibre surface. Some valuable conclusions have been drawn from the photo-analysis, which not only reveals the structural and morphological features of the fibre but also renders support towards the suitability and applicability of these fibres as a paper making raw-material.

Sisal fibres consist of micro-fibrils arranged parallel to each other along the fibre axis to form a bundle with gummy materials (or other substances) in the inter-fibrillar region as visible from Figure 2.4a.

When refluxed with alkali, the gummy and easily extractable materials are removed from fibres and so the fibrils seem to be more separated (Figure 2.4b). With acid, however, the removal of these materials are more prominent with scattered fibrils (Figure 2.4c).

To remove the organic soluble materials, the sisal fibres were refluxed in a soxhlet for 10 hours. No significant change in the microscopic picture (Figure 2.4d) is
noted indicating the presence of less amount of organic cementing materials for inter fibrillae binding.

Treatment of the fibre with sodium dodecyl sulphate (SDS), which is a surfactant, does not seem to delignify the fibre significantly, instead it appears to have formed a protective covering on the fibre surface as may be seen from Figure 2.4e. The formation of a protective layer on the fibre surface may also be gauged from the fact that even after macerating the SDS treated fibre with a mortar and pestle for about 4-5 hr, no significant change could be detected on the fibre morphology as evident by comparing Figures 2.4e and 2.4i. The interaction of SDS with sisal fibre surface is mostly due to the adsorption of the surfactant on the hydrophilic surface of the sisal fibre.

We could remove the sticky materials present with the fibrils by scratching the fibre with a sharp blade (Figure 2.4f), providing support to the mechanical (beating) process of defibrillation and delignification of the fibres, during pulping in papermaking. But most of these modifications appear to be taking place only at the peripheral region of the fibre surface rather than the core portion of the fibre.

On comparing Figure 2.4g (fibres beaten with a mortar and pestle for 2-3 hr) and Figure 2.4h (fibres beaten in an experimental beater), it may be concluded that the sisal fibres can be more effectively defibrillated or pulped in the beater than with the mortar and pestle.

The sisal fibre seems to possess good adsorption capacity towards dyes/colours as clearly visible from the photographs (Figure 2.4j and 2.4k). The fibre had been dissolved in an orange colour dye solution for an hour and then was washed with water for several times before taking the photograph. The dye appears to have adhered to the fibre surface firmly. Both the chemically treated fibres and the untreated fibres seems to have a good response towards the dye solutions as clearly visible from Figures 2.4j and 2.4k respectively.
The proximate chemical analyses were performed by using standard techniques and the results are tabulated in Table 2.2. High cellulose (61-68%) and low lignin (10-12%) contents in comparison to the conventional pulping fibers of hardwoods, which contain 38-49% cellulose and 23-30% lignin and the unconventional agro-residues of cereal straws, which contain 28-36% cellulose and 12-20% lignin [80], show a positive indication for employing the locally available sisal fibres as a paper-making raw material. Pentosan contents (19-23%) were also comparable or slightly less than the wood (19-26%) and non-wood fibres, (23-32% for the agro-residues), [80]. Low silica percentage in the sisal fibres is further a green signal for pulping, as it would cause less damage to the beating equipment. Low composition of ash and silica in the sisal fibres is conclusively pointing towards the existence of only trace amounts of inorganic mineral salts in the fibres which is a better symptom for producing good quality white and bright colored papers as the presence of a high concentration of the inorganic metallic ions like Fe²⁺, Co²⁺, Mn³⁺, Cr⁺¹ etc. (which are transition elements and usually known to form colored compounds) in the ensuing paper samples may give rise to undesirable color effects in the sheets. Presence of metals in the raw materials has also been observed to interfere with the pulping and bleaching chemicals, particularly where hydrogen peroxide is used [81-84].

However, the existence of some useful metals in trace amounts is desirable since, they are known to assist in producing good quality papers. For instance, the addition of molybdenum metal in the form of Na₂MoO₄ to the oxygen delignified pulp has been discovered to have increased its brightness level by ~2% El and reduced the PC No. by ~3.5 [85]. A similar study carried out previously by Eckert et al., 1982 [86] with H₂O₂ in acid media using oxygen delignified softwood pulps further clarify the usefulness of some metals in papermaking. Even the role of trace amounts of many metallic elements like Ca, Fe, Cu, Mn, Mg and Si in the bleaching processes using peroxide has been found to be beneficial, as reported by several authors [87-90], mostly by imparting superior optical properties to the paper.

Lower lignin percentage is suggestive of an inexpensive pulping process (low consumption of cook chemicals and/or less beating time), which is an important
requirement for the economical viability of any ligno-cellulosic material particularly in the small scale paper industries. The measured lignin percentages (10.22-11.7) of the sisal fibres may be a little higher than the actual value as it is believed that high protein content interfere with Klasson lignin analysis (TAPPI Standard T-222) or the acid insoluble lignin, due to the insolubility of some proteins in acids that may also be present in the concerned fibres.

2.7.3 Analysis of the Physical Properties of the Sheets

In order to preserve the eco-friendly nature of the hand-made papermaking process as well as to minimize the influence of various chemicals on the properties of the final sample sheets, we have endeavored to prepare paper sheets without adding any chemical additives, and have studied and compared the physical characteristics of the paper sheets prepared with the addition of some common and essential additives like starch/rosin as well as with sheets produced from the chemically digested fibres prior to beating.

It is observed that with the increase in beating time, freeness values of the pulp increased. This is due to an increase in defibrillation of the microfibrillar bundles (of which the sisal fibre is structurally composed of) and thereby more adsorption of water on the fibre surface, resulting in higher swelling of the fibres. The improvement in the strength properties of the paper sheets prepared at higher stages of beating, as evident from values in Table-2.3, may be attributed to the better swelling of fibres leading to an enhancement in inter-fibrillar hydrogen-bonding within the final sample sheets.

A considerable improvement in the burst strength values of hand-sheets can be observed when the sheets were treated with mild chemicals viz. rosin (used for sizing) and starch (used as a filler). Remarkable enhancement in the strength property (burst factor) could be detected for the chemically digested (alkaline-peroxide) sisal fibres prior to beating. Moreover, the chemically cooked fibres were found to have reduced the beating time and lower the pulp yields significantly. Sizing chemicals and fillers tend to fill the voids or vacuum spaces present within the microfibrillar network, that gives rise to the paper web-structure. Optimum doses of some these substances (rosin/starch) helps to increase the number of hydrogen-bonds within the paper structure thereby, enhancing
its strength properties. Chemical digestion further accelerates the delignification that results in reduction of the beating time.

High cobb values for un-sized papers (Table 2.4) is indicative of large number of voids and empty spaces within the sheets, which may be responsible for the lesser amount of inter-fibre interactions thus ultimately resulting in the formation of a poor sheet structure and subsequently weakening the sheet strength.

On comparing the data obtained by several physical examinations of the sheets, prepared from the experimental sisal fibres as well as the conventionally used rag fibres in the handmade sector (Table 2.5), it can be concluded that sisal fibre is quite comparable and competitive with the rag fibre for paper manufacturing. In fact, slightly higher values of the strength properties (like burst, tear, tensile in terms of breaking length), observed in case of sisal paper as compared to the rag paper is directly suggestive of utilizing the sisal fibres also as a strength enhancing additive for weak and recycled pulps.

2.8 Conclusion

Hand made paper has its demand due to its eco-friendly characteristics and socio-economical significance through employment generation in rural or sub-urban areas in developing countries. The paper prepared by the hand made technique chiefly involves the mechanical pulping process and occasionally includes the semi-chemimechanical processes basically, to preserve its eco-friendly nature and make the end products cost effective. In the wake of this, compromise in some properties (especially, the strength and optical properties) of the ensuing paper sheets, as compared to the mill-made papers is a natural consequence. On analyzing the various physico-chemical characteristics of the sisal fibres, it may be concluded that sisal fibre has great paper making potentials. Microphoto analysis renders great support to the paper making abilities of the sisal fibre. Study on the pulping characteristics of sisal fibre showed that sisal fibre has good unscreened pulp yields (> 80-90%), high tear strength, moderate tensile and burst strengths at low degree of beating. The tensile and the burst strengths showed an improvement with the
increase of the beating time. Optimum doses of mild chemical additives also exhibited a positive influence on the paper sheet qualities.

Comparison of the various properties of the sheets produced from sisal pulp with the sheets from the conventionally used paper making fibres in the hand-made sector (cotton rags), further renders great support to the paper making potentials of the locally available and un-conventional sisal fibres. Good physical properties of the sisal fibres further suggests towards its applicability as a reinforcing additive in different grades of weaker pulp furnishes.
2.9 References


