CHAPTER 1
CHAPTER - 1

INTRODUCTION AND LITERATURE SURVEY

1 Introduction :
1.1 State of art of ramie fiber :

Natural cellulosic fibers have occupied very important place as textiles since the mankind developed on the earth. Next to cotton, ramie has gained high potential in this category. The ramie bearing plant belongs to the Urtiaceae, the nettle family and was classified by Linnacus in 1937 as Urtica Nivea. Later on ramie plant family was named Boehmeria by gaudichand in honour of George Rudolph Boehmer. Different designations used for ramie fiber in various parts of the world are (1):

China: Tchou-ma, Chu-ma, Ch’utus, Dzi.
India: Rhea, Pooah, Kunkhoora, Kunchoor, Kurkunda.
Malaya and Indonesia: Rami, Calooe.
Indochina: Pan, Gooni.
Philippines: amarai.
Japan: Karamushi, Karora, Mao, Tsjo.
United States and Europe: China grass, Crude Fiber, Grass linen, Grass cloths.

The approximate total annual production of ramie was reported about 120 thousand tons, contrasting with cotton of 16 million tons in 1988. The People’s Republic of China (PRC) is by far the world’s leading producer of ramie, contributing about 70% share of the world total production. Other notable producers are Brazil and the Philippines, with small amounts being produced in several Asiatic Countries, Africa, USSR, and the West Indies. Ramie products
have an age-old history in Japan, where fabrics such as Chijini (crepe) have been 
woven for centuries.

Ramie production in India is very low in comparison to world production. Exact 
data of the production is also not available due to the lack of importance given to 
this fiber. It grows extensively as a wild plant in many parts of India, particularly 
in Northern - Eastern States, Kangara Valley and Nilgiri Hills. Although ramie, is 
fairly distributed in the country, it is cultivated to a small extent in the states like 
Assam, Meghalaya and Tripura and Sub Himalayan West Bengal. On the basis of 
data available at the Ramie Research Station, Sorbhog (Assam), the area of ramie 
crop in India is between 500-1000 hectors with a production capacity of 12-18 
quintal per hector of dry decorticated fiber. Central Research Institute for Jute and 
Allied Fibers (CRIJAF), Ramie Research Station (Sorbhog), The Jute 
Technological Research Laboratory (at present NIRJAF), Calcutta under Indian 
Council of Agricultural University and Assam Textile Institute and other 
technocrats will have to go a long way to develop a potential for this fiber in 
establishing the rural economy of the Northern-Eastern States (2-6).

Data published in Compendium of Textile Statistics of the bast fiber production in 
last five years (126) (table-1). Production and consumption figures of bast fibers 
are compared among India, developing countries and developed countries (table-
2). The data shows that India has the significant production and consumption of 
bast fibers (chart-1). Further the detail production data of various bast fibers 
(table-3) illustrate that ramie tends third after jute and flax. The average values of 
these data are expressed with the help of pie chart (chart-2). The total quantity of 
ramie that India produces utilizes mainly in tapestry and other low valued fabrics.
PRODUCTION DURING 1995-2000 in '000 tonns/year

<table>
<thead>
<tr>
<th>Type</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Developed</td>
<td>1466.3</td>
</tr>
<tr>
<td>India</td>
<td>1635.4</td>
</tr>
<tr>
<td>Others</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Chart - 1: Average production and consumption of bast fibres

CONSUMPTION DURING 1993-1997 in '000 tonns/year

<table>
<thead>
<tr>
<th>Type</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Developed</td>
<td>1245.4</td>
</tr>
<tr>
<td>India</td>
<td>1376.6</td>
</tr>
<tr>
<td>Others</td>
<td>500</td>
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Chart - 1: Average production and consumption of bast fibres
Table - 1

Countrywise production of bast fibers ‘000 tons

<table>
<thead>
<tr>
<th>Year -----→</th>
<th>95-96</th>
<th>96-97</th>
<th>97-98</th>
<th>98-99</th>
<th>99-2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>World</td>
<td>2714.5</td>
<td>3495.4</td>
<td>3842.3</td>
<td>2949</td>
<td>2545.8</td>
</tr>
<tr>
<td>Developing countries</td>
<td>2707.1</td>
<td>3488</td>
<td>3834</td>
<td>2941</td>
<td>2538.4</td>
</tr>
<tr>
<td>Developed countries</td>
<td>7.4</td>
<td>7.4</td>
<td>8.3</td>
<td>8</td>
<td>7.4</td>
</tr>
<tr>
<td>India</td>
<td>1458</td>
<td>1836</td>
<td>1953</td>
<td>1530</td>
<td>1400</td>
</tr>
</tbody>
</table>

Table - 2

Countrywise consumption of bast fibers ‘000 tons

<table>
<thead>
<tr>
<th>Year -----→</th>
<th>91-93</th>
<th>94</th>
<th>95</th>
<th>96</th>
<th>97</th>
</tr>
</thead>
<tbody>
<tr>
<td>World</td>
<td>3286</td>
<td>3050</td>
<td>2997</td>
<td>3029</td>
<td>3248</td>
</tr>
<tr>
<td>Developing countries</td>
<td>2735</td>
<td>2500</td>
<td>2486</td>
<td>2581</td>
<td>2808</td>
</tr>
<tr>
<td>Developed countries</td>
<td>551</td>
<td>550</td>
<td>511</td>
<td>448</td>
<td>440</td>
</tr>
<tr>
<td>India</td>
<td>1302</td>
<td>1343</td>
<td>1314</td>
<td>1411</td>
<td>1513</td>
</tr>
</tbody>
</table>

Very little information is available related to the processing and utilization of this fiber in high potential areas. Developments in the processing technique of ramie fiber may open up the application as value added products of this fiber, which will ultimately uplift the socio-economical status of the farmers and others (7-12).
Table - 3
World production of different bast fibers (in Mn.Kg)

<table>
<thead>
<tr>
<th>Year</th>
<th>Ramie</th>
<th>Flax</th>
<th>Hemp</th>
<th>Jute</th>
</tr>
</thead>
<tbody>
<tr>
<td>1988</td>
<td>346</td>
<td>919</td>
<td>152</td>
<td>3323</td>
</tr>
<tr>
<td>1989</td>
<td>201</td>
<td>803</td>
<td>108</td>
<td>3443</td>
</tr>
<tr>
<td>1990</td>
<td>106</td>
<td>688</td>
<td>84</td>
<td>3668</td>
</tr>
<tr>
<td>1991</td>
<td>71</td>
<td>731</td>
<td>66</td>
<td>3705</td>
</tr>
<tr>
<td>1992</td>
<td>72</td>
<td>591</td>
<td>76</td>
<td>3574</td>
</tr>
<tr>
<td>1993</td>
<td>79</td>
<td>530</td>
<td>64</td>
<td>3457</td>
</tr>
<tr>
<td>1994</td>
<td>124</td>
<td>590</td>
<td>52</td>
<td>3329</td>
</tr>
<tr>
<td>1995</td>
<td>154</td>
<td>7312</td>
<td>56</td>
<td>3037</td>
</tr>
<tr>
<td>1996</td>
<td>149</td>
<td>562</td>
<td>58</td>
<td>3609</td>
</tr>
<tr>
<td>1997</td>
<td>157</td>
<td>626</td>
<td>69</td>
<td>3373</td>
</tr>
<tr>
<td>1998</td>
<td>172</td>
<td>636</td>
<td>73</td>
<td>3396</td>
</tr>
<tr>
<td>Avg.of 11 Years</td>
<td>148.27</td>
<td>673.36</td>
<td>78</td>
<td>3446.72</td>
</tr>
</tbody>
</table>


Chart - 2 : Production of bast fibres
1.2 Classification of textile fibers (13-15):
Textile technologies have defined textile fiber as a "fine strand of sufficient length, pliability and strength to be spun into yarn and woven into cloth". The oldest fiber used as a raw material for clothing by historic man was obtained from natural resources either vegetable based or animal based. Various ways have been used to classify the textile fibers. According to Olney with the exception of asbestos and metallic wires, all natural or synthetic fibers are organic in composition and classified as in chart-3.

![Chart-3: Classification of organic fibers](image)

Natural cellulosic fibers are obtained from plants where the fibers can be readily and economically separated from the rest of the plant. They may be classified according to the portion of the plant from which they are removed. The most systematic way to classify the natural textile fibers is based on their origin and illustrated in chart-4.
**Chart - 4 : Classification of natural textile fibers**

1.3 Chemical compositions of cellulosic fibers (16-26):

The nature and chemical compositions of all vegetable fibers i.e. natural cellulosic fibers vary widely. The main responsible factors are the generic characteristics of the plant, conditions of growth, types of soil, age, part of the plant from which the sample originates, mode of cultivation and atmospheric conditions to which the fibers are directly exposed. Heterogeneity in both chemical and structural composition has a direct bearing on the fiber properties and surface morphology of fibers. The chemical compositions of important vegetable fibers are illustrated in table-4 (% on dry weight). Like cotton the main constituent of ramie fiber is cellulose. Ramie is unicellular in structure similar to cotton. Fiber strands of ramie are bound together by cementing material called gums. The largest constituent of gummy material is hemicellulose, followed by pectin, lignin, fats and waxes.

**Cellulose**

Cellulose is the most abundant of all naturally occurring organic compounds and probably makes up at least a third of all the vegetable matter in the world. It is the main constituents of the cell walls of the higher plants, having received its name for this reason. Cellulose is a polysaccharide or polymeric sugar that can be represented by simple formula \((\text{C}_6\text{H}_{10}\text{O}_5)_n\) (formula-1) When cellulose is completely hydrolyzed in dilute acid solutions, it produces the simple sugar glucose, which has the molecular formula \(\text{C}_6\text{H}_{12}\text{O}_6\). On comparison of two
formulas it was found that the repeat unit in cellulose is anhydro glucose molecule. Cellulose is a highly crystalline material, which forms no discrete crystals like those of glucose, from which it is derived. Native cellulose fibers consist of crystalline fibrils varying in complexity and length. This fibrilar structure is interspersed with material in same molecule may participate in both crystalline and less crystalline material along different portions of its length. Native cellulose contains very little genuine non-crystalline material. Five allomorphic forms of cellulose have been identified, but only cellulose 1 and cellulose 2 are important in textile processing (figure-1).

Table-4  
Chemical compositions of important vegetable fibers

<table>
<thead>
<tr>
<th>Type of Fiber</th>
<th>Cellulose</th>
<th>Hemicellulose</th>
<th>Pectins</th>
<th>Lignin</th>
<th>Water soluble component</th>
<th>Fats and waxes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ramie</td>
<td>76.2</td>
<td>14.6</td>
<td>2.1</td>
<td>0.7</td>
<td>6.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Jute</td>
<td>71.5</td>
<td>13.4</td>
<td>0.2</td>
<td>13.1</td>
<td>1.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Flax</td>
<td>71.2</td>
<td>18.6</td>
<td>2.0</td>
<td>2.2</td>
<td>4.3</td>
<td>1.7</td>
</tr>
<tr>
<td>Hemp</td>
<td>74.4</td>
<td>17.9</td>
<td>0.9</td>
<td>3.7</td>
<td>2.3</td>
<td>0.8</td>
</tr>
<tr>
<td>Sisal</td>
<td>73.1</td>
<td>13.3</td>
<td>0.9</td>
<td>11.0</td>
<td>1.4</td>
<td>0.3</td>
</tr>
<tr>
<td>Cotton</td>
<td>91.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8.2</td>
</tr>
</tbody>
</table>

Formula - 1 : Structure of cellulose
Cellulose 1 is the form found in nature while cellulose 2 is the thermodynamically stable form produced when cellulose is regenerated from solution or subjected in the solid state to the process of mercerization. Crystalline orientation of cellulose is determined by X-ray diffraction methods. Extensive studies using infrared spectroscopy have reported that deuterium of monoclinic cell are approximately: $a = 0.835$, $b = 1.03$ (fiber axis), $c = 0.79\text{nm}$ and $\beta = 84^\circ$ in the case of cellulose 1. The unit cell of cellulose 2 is also monoclinic, with average dimensions of $a = 0.814$, $b = 1.03$, $c = 0.914\text{nm}$ and $\beta = 62^\circ$. 

Figure - 1: Structure of cellulose-1 and cellulose-2.
Hemicellulose:
Hemicellulose is a complex polysaccharide, branched or straight chain generally found with lignin. The major components of hemicellulose being xylose, galactose, arabinofuranose and glucoronic acid residues with some esterification and cross-linking components. It has been reported that the chain lengths of hemicellulose are much shorter than that of cellulose and that they generally make little direct contribution to the strength. They usually consist of amorphous polyuronides. They are insoluble in hot water and primarily hydrogen-bonded to cellulose. The hydrogen bonding to cellulose fibril is considerably stable, so that even with alkaline extraction a certain amount of hemicellulose residues can be expected to remain in the structure. Complete removal of lignin from the bast fiber facilitates the dissolution of the hemicellulose in caustic soda solutions. It is not possible to extract all the hemicellulose from the raw ramie by means of caustic soda solution, hot or cold. The polysaccharide hemicellulose may be wholly or in the part, molecularly combined and oriented with the cellulose molecules themselves. The hemicellulose commonly found in bast fiber is xylan (formula 2). The polyuronide hemicellulose is an encrusting substance, amorphous, and non-oriented, confined to the amorphous parts of the cell wall. The name, hemicellulose was coined by Schulze in 1891 to designate those substances in the cell wall that were less resistance to acids and alkalis than the main part of the cell wall. As the severity of alkaline treatment increases the amount of hemicellulose that is extracted from ramie i.e. bast fiber also increases, until all of it, comprising about 13 to 18 percent of the weight of the fiber, is finally removed.
Pectin:

Pectins are hetero polysaccharides made of a 1,4-linked galacturonic acid unit, sugar units of various compositions, such as arabinose, galactose, rhamnose and the respective methyl esters. Pectin comprises pectic acids and pectic salts in such forms as calcium, magnesium and iron salts. The walls of the soft cells surrounding the fiber bundles in stem and the walls of the fiber themselves in bast fiber contain appreciable amount of pectin substances which serve to bind the cells together. The pectic material in the ramie plant is not a homogeneous in nature, exists in a number of different forms. In very young plants the greater part of the pectic substance occurs is mainly water soluble form, but this disappears rapidly at the flowering stage and in the matured plant the pectic substance exists mainly as a pectin complex which contains calcium in combination and is insoluble in water. The different forms of pectin are all short-chain polyuronides with a general formula as shown in formula 3. Pectic substances can be removed from the fiber by boiling with alkalis and it is on this reaction several attempts have been made to study the structural behaviors of ramie. The solubility of pectin increases with an increase in the degree of esterfication and with decrease of molecular weight.
Lignin:
Lignin is a macromolecule with molecular weight of about 6,000 to 10,000 having much more complex polymeric structure than any other natural materials. Biosynthesis of lignin consists the combination of medium and high molecular weight polymer units (Oligo- and Poly-lignols). These poly lignols arise from the polymerization of three fundamental monomeric units, which differ from each other and each has many oxidative polymerization centers. Lignin is not a polysaccharide but found to contain the highest percentage of methoxy groups present in wood and is much difficult to extract than the other cellulosic associates. During the growth of woody tissues, the cells are initially enriched with carbohydrates some of which are successively transformed into lignin through a long series of reactions called the ‘lignification’. As a result, the spaces in the polysaccharide fibers of the cell walls are gradually filled with lignin. The cellulose fibers become cemented together and protected against physical and chemical damage. Lignin is the encrusting substance gluing the fiber cell walls. It can be found in the middle lamella and the secondary layer of the fibrils. Exact structure of lignin does not still known by scientists. Lignin differs from all other biopolymers in that it seems random three-dimensional structure does not have repetitive linkages between the monomeric building blocks. On hydrolysis of this compound different types of monomeric substances of formulas-4 & 5 were found. In lignin all these substances are joined together differently and give various complex structures.
Lignin is found mainly in the woody core, to which it gives rigidity, but also in the epidermal and cortical cells, and often in the walls of the ultimate cells comprising the fiber strands. Most plant tissues, in addition to carbohydrates and extractable material, contain amorphous polymeric materials called lignin. The role of this material together with cellulose and other carbohydrates of the cell walls are to provide strength and durability to the fiber. Lignifications in the walls of cell are more pronounced when the stem is over matured. Lignified tissues are tougher, show considerable resistance to degumming and tend to prevent separation of the fiber strands to which they are attached. Fragments of the woody core and of the epidermal and colored cortical cells frequently remain attached to the fiber after scotching. Herzog determined the lignin in fibers from different parts of the plant. He found that fibers from the root contained 3.8%, from the middle of the stem 2.36% and from the tip of the stem 1.65%. Lignin is insoluble in most of the organic solvents and undergoes chemical changes under relatively mild conditions. Lignin can be oxidized, solubilized in hot alkalis and condensed easily with phenols and thiols.

**Fats and waxes:**

Fats and wax content of ramie is approximate about 0.3%, which can be extracted from the fiber by benzene or ether. The wax, which varies in color, has an
unpleasant odor. Its melting point is about 61°C and its specific gravity is about 0.9083. According to Hoffmeister, fiber wax consists of 81.32% of unsaponifiable material and 18.68% saponifiable oils. The oil-wax constituent, in ramie fiber plays an important part in the spinning of this fiber.

**Coloring matter:**
These are present in very small quantities and situated in the cortical cells, beneath the epidermils, fragments of which remain attached to the fiber bundles after scutching. Chemically coloring materials are chlorophyll, xanthophylls and carotene together with modification of these substances. The coloring materials are usually associated with the complex compounds such as tannin.

1.4 **Properties of ramie fiber** (27-34):
Ramie is a vegetable fiber and depending on the soil, crop and other factors its properties varying considerably. Ramie fiber has naturally good whiteness and doesn’t change color on exposure to sunlight. It has good luster and has an exceptionally high resistance to the effects of bacteria and fungi including mildew. Yarns and fabrics made from ramie are highly absorbent and dry quickly. One series of experiments with yarn showed that when ramie yarn immersed totally in water, it absorbed 100% of water by its own weight within 10 minutes and 195% water in 72 hours. Fabrics made from ramie also show such absorbency depending on its construction and finish. Specific gravity of the fiber ranges from 1.54 to 1.56 and average of 1.51. The fiber denier ranges from 4.5 to 10.5 with an average value of 6 to 7 for fiber from the middle portions of the stalk. Fiber at the butt end of the stalk is about 45 to 50 percent heavier and the tip end is about 25 to 30 percent lighter than the fiber from the middle section. The tensile strength is very high ranging from 27 to 55 gm with an average of 30 to 40 gm. Tenacity i.e. breaking strength in grams per denier, ranges from 3 to 9 with an average of 6 to 7. Wet strength is 140 to 160 percent of dry strength. Elongation at break ranges from 2 to 10 percent with an average of 3 to 4 percent. The low elasticity of ramie contributes to its poor hand and feel and poor resistance to abrasion, pilling and
wringling. These problems, limit the use of ramie in knitting. However, its special characteristics are durability and strength. Ramie has a somewhat harsher feel and being slightly stiffer, has in fact the greatest cooling effects of all natural cellulosic fibers. The physical properties of ramie in comparison of cotton and flax are reported in table-5. Ranking of various bast fibers on the basis of some important physical properties are reported in table-6.

Behavior of ramie to chemical action is similar to cotton and other cellulosic fibers. Ramie remains unaffected in dilute caustic soda, while concentrated solution of caustic soda, at severe conditions, swell the fiber. Dilute mineral acids have little effect while concentrated solution of mineral acids dissolves the fiber completely even in cold. Fabrics of ramie are easily laundered, requiring no special care, and showing only little strength loss after repeated washings. The fibers of ramie can be dyed easily with those dyes used for other cellulosic fibers, although care must be taken to ensure complete penetration and leveling.

Some of the advantages and disadvantages of ramie fiber can be summarized as:

**Advantages:**

- Ramie is one of the strongest vegetable fibers in textile strength.
- Breaking strength of wet ramie yarn is as high as 160% of dry yarn.
- Ramie is remarkable for its wetting and drying, less soiling and hence ease of washing.
- Ramie is preferable for shirtings, suitings when blended with cotton and synthetic fibers.
- Unlike linen, durability of ramie to laundering, is practically unlimited and it can thus be good substitute for flax which is not grown in India.
- Ramie has a very high resistance to rotting, mildew and other organisms.
- Ramie has a silk like luster
### Table-5

<table>
<thead>
<tr>
<th>Physical properties</th>
<th>Ramie</th>
<th>Flax</th>
<th>Cotton</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Matured) Cell length - (mm)</td>
<td>150 – 300</td>
<td>25 – 65</td>
<td>15 – 60</td>
</tr>
<tr>
<td>Breadth – (10^3 mm)</td>
<td>15 – 80</td>
<td>10 – 35</td>
<td>15 – 20</td>
</tr>
<tr>
<td>Filaments gravemetric fineness (tex)</td>
<td>0.45 – 0.70</td>
<td>2.5 – 6</td>
<td>0.1 – 0.3</td>
</tr>
<tr>
<td>Tenacity (g/tex)</td>
<td>6 – 7</td>
<td>4.5 – 5.5</td>
<td>2 – 4.5</td>
</tr>
<tr>
<td>Extension at break (%)</td>
<td>3.5 – 4.5</td>
<td>2.5 – 3.5</td>
<td>6.5 – 7.5</td>
</tr>
<tr>
<td>Modulus of tortional rigidity</td>
<td>0.7 – 1.8</td>
<td>0.8 – 1</td>
<td>0.8 – 1.2</td>
</tr>
<tr>
<td>(x10^10 dynes/cm^2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural rigidity (dynes/cm^2)</td>
<td>0.8 – 1.2</td>
<td>1.83 – 2.5</td>
<td>0.3 – 1.0</td>
</tr>
<tr>
<td>Transverse swelling in H2O (%)</td>
<td>12 – 15</td>
<td>20 – 24</td>
<td>20 – 22</td>
</tr>
<tr>
<td>Moisture regain (%)</td>
<td>6.5</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Density (g/cc)</td>
<td>1.54 – 1.56</td>
<td>1.53 – 1.55</td>
<td>1.54 – 1.55</td>
</tr>
<tr>
<td>Refractive index η∥</td>
<td>1.595</td>
<td>1.960</td>
<td>1.575</td>
</tr>
<tr>
<td>η⊥</td>
<td>1.531</td>
<td>1.529</td>
<td>1.500</td>
</tr>
<tr>
<td>Comparative degree of crystallinity (X-ray diffraction) (%)</td>
<td>74</td>
<td>76</td>
<td>75</td>
</tr>
<tr>
<td>Angle of orientation</td>
<td>7° – 8°</td>
<td>6° – 7°</td>
<td>25° – 38°</td>
</tr>
<tr>
<td>Degree of polymerization</td>
<td>2660</td>
<td>2190 – 2420</td>
<td>&gt; 1000</td>
</tr>
</tbody>
</table>
### Table-6
**Ranking of various bast fibers according to properties**

<table>
<thead>
<tr>
<th>Properties</th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Durability</td>
<td>Ramie</td>
<td>Flax</td>
<td>Hemp</td>
<td>Jute</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>Ramie</td>
<td>Hemp</td>
<td>Flax</td>
<td>Jute</td>
</tr>
<tr>
<td>Length of fiber cells</td>
<td>Ramie</td>
<td>Flax</td>
<td>Hemp</td>
<td>Jute</td>
</tr>
<tr>
<td>Cohesiveness</td>
<td>Flax</td>
<td>Hemp</td>
<td>Jute</td>
<td>Ramie</td>
</tr>
<tr>
<td>Fineness</td>
<td>Ramie</td>
<td>Flax</td>
<td>Hemp</td>
<td>Jute</td>
</tr>
<tr>
<td>Uniformity</td>
<td>Flax</td>
<td>Ramie</td>
<td>Hemp</td>
<td>Jute</td>
</tr>
<tr>
<td>Pliability</td>
<td>Flax</td>
<td>Ramie</td>
<td>Jute</td>
<td>Hemp</td>
</tr>
<tr>
<td>Colour</td>
<td>Ramie</td>
<td>Flax</td>
<td>Hemp</td>
<td>Jute</td>
</tr>
<tr>
<td>Cellulose in raw fiber</td>
<td>Ramie</td>
<td>Hemp</td>
<td>Jute</td>
<td>Flax</td>
</tr>
</tbody>
</table>

**Disadvantages:**
- Ramie is stiff and low in resiliency hence it wrinkles very easily.
- Ramie has a high crystalline molecular structure, which make it difficult to dye.
- Ramie is low in elasticity, brittle and breaks if folded repeatedly in the same place.
- Ramie is more difficult to spin then other natural fibers.

### 1.5 Morphological constitution of ramie fiber (35-37):

The ramie plant grows 1 – 2.5 mt high with broad, heart shaped leaves on a nearly branched stem. The fibers are located in the cortex layer covered by a thick woody layer of the stem surrounded by the soft, pithy core, which constituents about one-third of the diameter of the stem. The structure of the ramie stem is similar to that of flax and other bast fiber plant stems. The individual cells of ramie are unusually...
long, ranging from 0.5 to 20 inch with an average of 5 to 6 inch. Width of fiber ranges from 25 to 75 micron, averaging 30 to 50 micron. The shape of the matured cell is approximately cylindrical with an almost no twist. In ramie the cellulose chains run almost longitudinal and it has been observed that the fiber extends lengthwise about 1 to 2 percent when wetted. The surface is characterized by small node like ridges and striations, which sometimes result in polygonal cross-sections of the fiber (figure-2). The cell walls are thick and the lumina is well defined. Immature fiber is ribbon like, varying from a rather flat to an elliptical shape, and has a small amount of twist. Cell walls are thin and lumina is flat and undeveloped, extending across the long width of the fiber. The fibers end in a rounded point, the cell walls being thickened and lumen almost disappearing. The crystalline nature of ramie is responsible for its marked birefringence i.e. difference of refractive index along and across the fiber axis.

Figure – 2 : Longitudinal view and cross sectional view of ramie fiber
1.6 Production of ramie fiber (38-39):

Climatic conditions:
The climatic requirements for ramie cultivation are warm (25 to 31°C), moist, tropical or subtropical with an annual rainfall of 150-250 cm evenly distributed throughout the year. Any excess of rainfall over the normal requirements of the crop are neither particularly helpful nor harmful, provided there is proper drainage and the plant roots are never water logged. Ramie is extremely sensitive to water logging and field of ramie covered with water for a period of 36 to 48 hrs will be eradicated. The relative humidity should be between 25 to 80 %. Strong wind (speed > 30 km/hr) is not suitable for ramie, as it damage the fiber by rubbing of stalks with each other.

Soils:
Ramie fiber requires a high fertile soil with high organic matter contents. Sandy loam type of soil with sufficient amount of organic matter is the best suited. It can be raised in clay or sandy soil with application of heavy dose of organic matter. Ramie cannot tolerate longer period of water stagnation, so poorly drained soil should be avoided. Ramie cannot be grown in alkaline soils. It can be grown in slightly acidic soils. The growth of ramie required optimum pH of 5.5-6.4 for mineral soils and pH range of 5-5.6 for organic soils. Ramie required heavy amount of calcium. Highly acidic soils required application of lime. Soils having poor depth are unsuitable. Fertilization for better yield depends upon the compositions of the soil and the quantity of crop required. The necessity for heavy fertilization increases with each growing year. Considering the specific eydophoclimatic requirements of ramie, the Sub-Himalayan, W. Bengal, Assam and Northern - Eastern States like Meghalaya, Nagaland, Tripura, Mizoram, Arunachal Pradesh and Manipur are the most suitable for ramie cultivation in India.
Propagation:

Ramie may be propagated in the following steps, listed in the order of their importance and merit.

1. Rhizome cutting
2. Division of parent rootstock
3. Layering and
4. Stem cutting

Propagation means cutting from the rhizomes. The strong, well established plants are uprooted, the rhizomes are immediately cut into 12-15 cm lengths and 1.2-1.5 cm diameters, and are planted as soon as possible after cutting in trenches 10-12 cm deep. In some areas, where hand labors are used for plantation, the cut pieces of rhizomes are sprouted before being planted to insure viability. Freshly dug rhizomes should be kept in the shade and watered at intervals or covered with gummy bags to prevent drying. Other means of propagation like stem cuttings and layering can also be exploited after standardizing the methods by thorough investigation and extensive field trials. Ramie is also grown from the seeds but it requires more labor and seldom breeds true and is used chiefly in experimental work for developing new varieties. New emerging trends in botanical research, like ‘tissue culture’, have an ample scope to develop suitable method of propagation for ramie. The land is to be ploughed and laddered repeatedly and weeds removed by raking, if necessary by employing manual labor. Row to row spacing of 60 cm and rhizome to rhizome spacing within a row of 30 cm will give better yield. It was observed in Ramie Research Station that planting of ramie in the month of May-June is suitable for sustaining higher fiber production for longer period. Ramie is a perennial crop and once planted, it continues even up to 8 to 9 years but after 5 to 6 years the yield decline rapidly.

Methods of cultivation vary in relation to local customs, labor cost and degree of mechanization available in an area. In the United States, on large plantations, agricultural machineries are used for almost every cultivating operation. Ramie,
being a perennial crop, periodic wedding is required according to its growth and time of harvest. Weeding may be done manually but it involves the labor cost. Ramie is a heavy feeder and consumes large amounts of plant nutrients. A liberal application of organic materials, supplemented by NPK fertilizers is essential for raising a good crop (table-7). Burnt ashes of dried leaves, straws, water hyacinth, etc. are also considered as effective manures for ramie. From the results obtained, application of NPK @ 30: 15: 25 Kg / ha for each of the four cuttings of the year appears optimum. The plants are quick growing during the cropping season and therefore fertilizer application should not be delayed. The fertilizers are applied in between rows and worked into the soil by wheel hoeing but when the inter-spaces are covered up in older plantation; they may be broad cast over the field. In view of the heavy withdrawal of plant nutrients by ramie, it is essential that all the leaves and decortication waste of the crop is returned to the soil after each harvest. Since 60 tones of ramie plant removes about 300 Kg of calcium per year per hectare, so lime should be added frequently, more so if the soil is acidic. About 2 tones of lime are added during preparation of land. Periodical addition of macro and micronutrients are also essential for proper growth and development of ramie plant. Micronutrient materials such as CuSO₄, MnSO₄, and ZnSO₄ @ 50 Kg / ha each may be applied to the soil before planting. Much is not known about the requirements of minor elements. This is also to be determined, if possible by crop often gives clue to deficiencies.

Incidence of disease in ramie is quite low. Only moderate infestation of hairy caterpillar and leaf roller had been observed. This infestation can be controlled by spraying any contact insecticide like Endo-Sulfan (0.04 %). Candorot diseases caused by Sclerotium rolfsii may cause plant lodging in case of severe attack. The leaf spot disease of ramie appears rusty brown spot with a gray center surrounded by concentric circles on the leaves. Clean cultivation, application of balanced fertilizers and if necessary spraying of bordeaux mixture can control the leaf spot. Recently it has been observed that, root knot nematode causing economic losses to
the crop. Removal of the whole affected plant, crop rotation and clean cultivation may be practiced to avoid the nematodes. Ramie, so far observed in India, doesn’t suffer from any serious diseases. The only malady is chlorosis, mostly confined to highly acidic soils. Liming coupled with application of nitrogen invariably restored normalcy. Application of large quantities of compost or farm yard manure also removed chlorotic condition. In countries like Philippines, Japan and Florida, reports on incidence of some other diseases and pests have been published, but these are not reported in India.

Table 7
Annual nutrients uptake by ramie (60 tones of green matter from 4 cuttings)

<table>
<thead>
<tr>
<th>Element</th>
<th>Kg / ha / annual</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>205.75</td>
</tr>
<tr>
<td>P</td>
<td>24.40</td>
</tr>
<tr>
<td>K</td>
<td>104.60</td>
</tr>
<tr>
<td>Ca</td>
<td>284.10</td>
</tr>
<tr>
<td>Mg</td>
<td>53.45</td>
</tr>
</tbody>
</table>

Harvesting:
Once the root system was properly established in the soil, four crops may be harvested in a year in the order of 50 – 45 – 45 – 50 days crop age. Harvesting is done by cutting the stalks close enough to the ground to insure maximum stalk length and prevent stumps from sprouting but high enough above ground to prevent damage to the new stalks.

Symptoms of maturity of canes can be used for harvesting of ramie for higher yield and quality fibers. The symptoms are:

1. Lower portion of the stalks turn light brown or coppery colour.
2. Lower leaves turn yellowish and begin to shade.
Apical part of the plant shows bending tendency.

New sprouts just begin to appear above the ground.

The bark of the stem can be petted easily from the stick.

For obtaining fine and soft fibers, roots must be cut before they mature and begin to flowering. Harvesting is done by hand with a short curved knife. Mechanization of harvesting is difficult because of possible damage to the new stalks. At first two harvests the stems are about 6.5 ft. high and about 5.5 ft. at the third. Production of crude fibers per acre varies considerably in relation to climate and soil, skill of cultivation and efficiency of fiber removed from the stalk. The average yield of crude fiber is about 1,250 lb., 1,500 lb., and 800 lb for the first, second and third harvest respectively. Total annual yield of green stalks and leaves per acre range from 25,000 to 50,000 lb in climates where three crops a year are harvested and 50,000 to 1,00,000 lb in climates where five crops a year are harvested. The photograph of ramie fiber plants in the field is shown in figure-3.

![Figure - 3 : Field of ramie fiber plants](image-url)
The leaves of the harvested canes are to be defoliated manually by sickle or chemically by Pentachlorophenol or Endothal sprayed several days before harvesting (figure-4). Nutrients removed by green plant may be returned to the soil partly by defoliation in the field. The leaves are also highly valued feed for the cattles.

![Figure - 4: Ramie fiber plant](image)

**Decortication:**

Decortication means separation of fibers in the form of fiber strands (the continuous filaments which are made up of bundles of individual fibers) by removing the bark and woody part of the stalks (shive) and of a portion of the gums. Decortication process affects the quality and the quantity of crude fiber obtained. Decorticated fiber strands are generally termed “Crude Ramie Fiber”. In earlier days, decortication was carried out manually. Still in certain areas and in China this operation is performed manually. The manual decortication process consists of either peeling or beating the bark, with the fiber adhering to it, from the stalk when freshly cut or after drying. The stalk may or may not be soaked before the bark is removed. The fiber is then freed from the bark by alternate soaking and scraping. Before decortication, leaves are removed from the stalks, either by hand.
or by running long bamboo poles up and down the stalks before cutting. Fresh or salt, still or running and cold or hot water is used, depending upon the local custom. Beating is done by flailing stalk or bark against wooden or rock surface or by pounding with wooden paddles or mallets. Drying of fiber is by sun or air. In some areas, mainly in Southeast Asia and Indonesia, bark is scraped from the length of the stalk, leaving the fiber adhering to the stalk, which is then washed and dried. After drying, fiber is peeled from the stalk in the form of strands. To prevent damage to the fiber during the scraping operation, plant is allowed to mature botanically i.e. to flower and seed, so that the bark may be thick and firm. The resulting fiber is coarse, and in areas where this method of fiber removal is used, fiber is generally used for twine and not for weaving fabrics.

Thousands of machines for decortication have been developed in various countries since 1800 when ramie began to arouse interest for commercial use. In the United States alone, more than 2000 patents have been issued. The first fairly successful machine, was a small portable type, patented in France in 1896. The basic principle of decortication machine consists of first crushing the stalk and then holding it by mechanical means against the scraping action of blades, set at intervals in the outer circumference of a rotating wheel. The tip end of the stalk, is inserted and the fiber freed for about half its length when the stalk, is pulled from the machine. The butt end is then fed into the machine until the remaining length of fiber is freed, when it is pulled from the machine and hung up to dry. A large stationary machine, patented in Germany in 1933, primarily for decorticating Sisal fiber was readily adopted for ramie fiber. A small portable machine now in wide use was patented in Japan in 1947, and utilizes the basic of the early machine, freeing the full length of the fiber in a continuous operation with one set of rotating blades and eliminating the need for defoliation. A companion machine, intend to be used with the decortication for brushing the fiber after decortication and drying, was patented at the same time. Several machines have been developed in the United States since 1940, and are in use in various areas. These machines
also utilize the basic principle of the early machines and include both the small portable or semi portable type as well as the large stationary type. Experimental work is being done in the development of harvester-decorticators. Some of the decortication machines with their suppliers are listed in table-8. The efficiency of the machine decortication varies considerably. Quantity of crude fiber yield from the larger machines ranges from 2.5 to 3.5 percent on the basis of total weight of green stalks and leaves, and from the smaller machines 2.5 to 6 percent. The decortication fiber consists about 19 to 30 percent of non-cellulosic materials called gummy material or impurities.

Table-8
Name of the decortication machines and their suppliers

<table>
<thead>
<tr>
<th>Decortication machine</th>
<th>Suppliers</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Large Machines</strong></td>
<td></td>
</tr>
<tr>
<td>Henschel Corona iii :</td>
<td></td>
</tr>
<tr>
<td>Commands: 1000 Hectares</td>
<td>Stulcken Maschinen Hamburg</td>
</tr>
<tr>
<td></td>
<td>W. Germany</td>
</tr>
<tr>
<td><strong>Small Machines</strong></td>
<td></td>
</tr>
<tr>
<td>Mejora 100-26</td>
<td>A.Faure &amp; CIE 21, Place du Champ-de.Foire</td>
</tr>
<tr>
<td></td>
<td>Limoges, France</td>
</tr>
<tr>
<td>S- 50 Decorticator</td>
<td>Kawahara Gikon Sangyo Co.Ltd. 421- 1, Motomachi</td>
</tr>
<tr>
<td>OR Type 101 N</td>
<td>Fuchi—Shi,Hiroshima, Japan</td>
</tr>
<tr>
<td>Hand Decorticator</td>
<td>Chuo Boeki Goshi Kaisha, Central Commercial Co.,</td>
</tr>
<tr>
<td>OR Type 101 N</td>
<td>Ibaraki, Osaka, Japan</td>
</tr>
<tr>
<td>LASIS Decorticator</td>
<td>Central Sales Agency, 12- A Netaji Subhas</td>
</tr>
<tr>
<td></td>
<td>Road,Calcutta, India</td>
</tr>
</tbody>
</table>

26
2 Literature survey:

2.1 Degumming of ramie fiber (40-43):

Raw fiber called decorticated fiber contains hydrophobic non-cellulosic surface materials that make them nonwettable in water. For effective chemical processing (dyeing and finishing) and maintaining (cleaning) of ramie assemblies involving aqueous media, improved and uniform water wetting properties are essential. Therefore, the first step of ramie fiber processing to make it usable for textile purposes is degumming process. The Decorticated fiber contains 19 to 30 % gum as encrusting material, and this should be brought down to 2 to 6 % for good spinnability. Degumming means the removal of the gums, waxes and pectins remaining on the crude fiber after decortication. Proper degumming separates the individual fiber and leaves them in a soft, clean state with their strength and other characteristics intact. Maintenance of production of degummed fiber of a uniformly good quality requires considerable skill because the crude fiber varies in quality from area to area and season to season. The successful accomplishment of the degumming operation, like decortication, was formerly a major barrier to commercial use of ramie fiber. In areas of the world where the fiber is processed by hand, degumming is accomplished by repeatedly soaking, scraping, washing and sun drying the fibers. In some areas, lye, made from ashes or lime used in the soaking water. Degumming on commercial scale is done by the mills, which spun the fiber. Degumming may be carried out on the undried or dried fiber, the later being preferable. The important physical and chemical properties of properly degummed ramie can be summarized as follow:

- Enhanced wet strength (160 % of dry) achieved
- Luster improved
- Microbial resistance increased
- Increased dyeability to various cellulosic dyes was obtained
- Easy drying characteristics achieved
There are two basic methods used on commercial scale for degumming of decorticated ramie fiber.

1. Chemical Degumming
2. Microbial Degumming

2.2 Chemical degumming of decorticated ramie fiber (44-47):
The chemical process of degumming consists of boiling the fiber in a chemical solution, usually made with caustic soda. The amount of chemical used depends largely upon the quality of the crude fiber, the quantity of barks, shives and gum on it. In one of the process, for crude fiber with a 30% residual gum content, caustic soda, approximately 5 to 6 percent of the dry weight of fiber is added to enough water to make a solution with a liquor ratio of 1:5 to 1:6. A reducing agent, usually sodium sulphite, is also added to the solution. A wetting agent, is added to the degumming solution or the fiber is soaked in water for 24 hours before boiling. Cooking i.e. boiling in open vats, varies in relation to equipment and method, the more usual time being somewhat between 1 to 4 hours. After cooking, the fiber is rinsed, neutralized, washed and centrifuged several times, then oiled and dried. Chemical degumming can be done with pressure kiers, but the equipment is not used extensively. Different degumming technologies use different auxiliaries to improve the efficiency of the operation.

Dasgupta and Co-workers have degummed ramie fiber with caustic soda solution in different concentrations (1 to 5% owf) at various temperatures ranging from 90 to 125° C for 1 h. After degumming, samples were washed, soured with acetic acid, washed and dried. They have reported that on progressive degumming, tenacity of fiber increases while fineness decreases. Addition of sodium sulphite to the extent of 0.5% owf in the degumming solution improves the tenacity of the fiber by reducing the degradative action of oxygen on cellulose in presence of hot alkali. Ramie fiber degummed to 3.3% and below was resistance to fungal attack.
The fiber with 6.9% gum had some resistance but those with higher gum content were attacked by fungus very quickly (48).

In one of the experiments B. Luniak, has added soap in the caustic soda degumming solution or pretreated with aluminum sulphate or zinc sulphate. However, such process did not improve the degumming efficiency or the properties of the fiber. In certain cases the fiber was more smooth by the above treatments but smoother fiber creates more difficulty in processing (49).

Misra and co-workers have recorded small angle X-ray scattering data of degummed ramie fibers. An increase in the concentration of sodium hydroxide solution resulted in an increase in swelling of macromolecules present in the fiber (50).

Degumming under pressure removes most of the gum while the open cooking method removes a lesser amount. Allison advocated an open cooking system which brings about a loss of 10 to 12% of the gummy material. However, Allison admitted that the partially degummed fiber was coarser than produced by pressure cooking.

Pan and Co-workers have degummed ramie fiber with caustic soda (2°Tw) and non-ionic surfactant (2% owf) at 95°C for 2 hr. They have reported that sodium, potassium, calcium, silicon and copper present in decorticated fiber reduced on degumming and these would facilitate the subsequent processing and improve the drapability of fiber (table-9) (52).

Wong has reported that sodium pyrophosphate is better than sodium phosphate in washing, after boiling-off using caustic soda. He has reported that sodium pyrophosphate can also used as an auxiliary during the boiling-off procedure because of its stability in hot water (53).
Table-9
Element present in decorticated and degummed ramie fiber

<table>
<thead>
<tr>
<th>Name of the element</th>
<th>Element present (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Decorticated fiber</td>
</tr>
<tr>
<td>Sodium</td>
<td>12.0</td>
</tr>
<tr>
<td>Potassium</td>
<td>34.7</td>
</tr>
<tr>
<td>Calcium</td>
<td>175.0</td>
</tr>
<tr>
<td>Silicon</td>
<td>115.0</td>
</tr>
<tr>
<td>Copper</td>
<td>0.8</td>
</tr>
</tbody>
</table>

In one of the degumming process, Y.Zheng and Co-workers have used sodium pyrophosphate, sodium meta silicate and sodium sulfite as a washing auxiliaries for caustic soda degumming. They have observed that such process (washing process) reduces the costs, duration and amount of pollution. Although, sodium pyrophosphate is very permeable, diffusible and expensive, sodium meta silicate is more preferable.

Kundu and Co-workers have pretreated decorticated fiber with 0.2 % aluminium sulphate for 6 to 8 h at room temperature. Degumming was then carried out with sodium hydroxide (1 % w/v) in presence of sodium chloride, sodium sulphite and EDTA at 94 to 96°C for 2h. It was observed that all the degumming treatments successfully reduced gum content to below 6 % owf. Combination of sodium hydroxide and sodium sulphite is the most efficient as it removes about 90 % gums from the decorticated fiber. The tensile strength of decorticated ramie was observed higher than that of alkali treated fiber. They have also studied the IR spectral data and reported that the characteristics peaks corresponding to gum in ramie were absent in degummed fiber (54).
Various methods of chemical degumming are reported in the literatures for the removal of gum from crude fiber, but none is entirely satisfactory for achieving perfect and uniform degumming. Most of the processes are covered by patents, giving very little information about methods adopted. In most of the works physico-mechanical properties were studied. Kinetics of alkaline degumming reactions, role of various constituents of gummy material, extent of removal of various components etc. have not been well defined in any literatures.

2.3 Microbial degumming of decorticated ramie fiber:
The potential for enzyme application in the textile processing is very high. Enzymes have been used for many years in breweries, wineries and food processing units. For many long time textile chemists and technologists have searched enzyme application in the primary textile industries. The first exposure to enzyme involved in desizing of cotton fabric with amylase. From the copious amounts of research and development work that is being done, it appears that the use of enzymes in textile processing will increase significantly.

2.3.1 Enzymes (56-58):
Enzymes are protein, which catalyze the specific chemical reactions and are known as biocatalyst. “An enzyme can be defined as a polypeptide(s) that catalyses a reaction with a certain degree of specificity”. The building blocks that produce enzymes are various amino acids, and can be written in the following general formula:

\[ \text{[NH} - R\text{CONH} - R\text{CO} \ldots]_n \]

As the polymeric chain length increases, more and more, ionic and other interactions, eventually cause the complex molecule to assume certain three dimensional configurations. When this orientation happens, the inter wind polymeric mass becomes a protein, and some of these proteins function as enzymes. There are a number of factors that may distinguish one enzyme from
another, and these include the particular amino acid present, the order in which they are linked together and the presence or absence of metal ions. Most important is the conformation or shape of the protein structure. Enzymes are present in all living organisms, where they serve to promote the reactions which are essential for life. Protein molecules that function as enzymes are biological catalyst. They do not eat anything i.e. these components do not cause a reaction to occur. These components only accelerate reaction at substrate surface that would naturally occur at much slower rates in absence of enzymes. As shown in figure-5, for a given reactions to occur, there is an associated energy level, but the activation energy for a specific reaction can be lowered by the use of catalyst. Biological catalysts accelerate reaction, but unlike the high-temperature reactions that occurred in resin finishing, enzymes accelerate reaction at much slower temperatures. In addition to the relatively low temperature at which enzyme function, these material also are effective at environmentally benign pH's and pressure.

**Figure - 5 : Activation energy of enzymatic reaction**
2.3.2 Enzyme reaction (59-62):
Enzymes are not living organism, but are protein structure of varying complexity, based on chains of amino acids linked by peptide linkages. All enzymes are water soluble products. The amino acid chains are coiled in such way that the hydrophobic proteins are oriented inwards, allowing maximum hydrogen bonding intra molecularly with water or other molecules. Water is an essential medium for the proper functioning of all enzymes.

Enzymes are enormously effective catalysts which permit reactions that under normal condition would simply not occur, to proceed and at greatly accelerated rate. They are true catalysts that are not consumed in the reaction, but provide a low energy path for the reaction to proceed and can then catalyze further reactions, as shown in the equation-1.

\[
E + S \rightarrow ES \rightarrow E + P
\]
\[\text{(Enzyme)} \quad \text{(Substrat)} \quad \text{(Enzyme-Substrate Complex)} \quad \text{(Product)}\]

------- Equation - 1

Enzymes are highly specific and will catalyze only one reaction, without having any effect on the other components of a system. The molecule, on which enzyme acts, is known as substrate. The efficiency of an enzyme-catalyzed reaction depends upon the following factors:

- Enzyme concentration
- Temperature of reaction
- pH of system
- Presence of activators and
- Presence of inhibitors.
At optimum conditions of temperature and pH, over all reaction depends on the
time required to form an enzyme substrate complex and the time required to form
the product. To facilitate quicker formation of an enzyme substrate complex,
足够的酶应该可用和产物在酶的附近浓度应该更高。太高浓度的产物，
adversely affect enzyme action. Low enzyme dosage are selected for long reaction
time. Higher dosages of enzyme can reduce the over all reaction time, however it
should not be exceedingly high.

Enzymes are proteins and their proton accepting property depends on the extent of
ionization of their reactive groups. Hence, different enzymes exhibit maximum
reactivity at different pH. Any change of pH lowers the reaction rate.

The effects of temperature on enzyme activity are complex and are also inter­
related to other variables. With increase in temperature, the activity increases due
to increased possibilities of enzyme coming closer to the substrate molecule, at the
same time due to heat of denaturizing, enzyme proteins also gets accelerated.
Hence enzymes are observed to exhibit maximum activity in a narrow temperature
ranges.

Thermal stability of alpha amylases improves by incorporation of calcium in the
form of calcium chloride. Calcium is an essential stabilizer for such enzymes.
Only those commercial products which do not disturb the pH of the system, should
be selected. Thus non-ionic wetting agents are preferable.

Certain chemicals, such as alkalis, antiseptic and acid liberating salts tend to
inhibit enzyme activity. This could either reversible or irreversible. For successful
development of a commercial process, enough care has to be exercised to avoid
such inhibition. In case of textile processing, inactivation of the enzymes, after the
treatment is completed is an important. Residual activity must be avoided.

Enzymes can be inactivated by, for example, lowering the pH and or raising the
temperature of system. The inactivation condition depends upon the enzyme types.
For example, Pullulanse enzyme can be deactivated in solution at 80°C and at pH
of 3.0 within 15 minutes. In many processes where the step following the enzyme treatment is carried out under conditions critical for the enzyme, inactivation occurs as a natural part of the process.

Enzyme molecule contains specific groups for effective catalysis, carrying amino acid side chains capable of accepting or donating protons or such groups that act as nucleophiles. Ordinarily chemical reaction in a test tube can be accelerated by changing the pH because increased $\text{H}^+$ or $\text{OH}^-$ ions facilitate the reactions. The amino acid side chains in the enzyme molecule could be acidic or basic, which are capable of bringing about strong reactions. Certain enzymes are known to show electrophillic attack on substrate with the help of metallic ions as co-factors.

The effectiveness of enzyme is due to the specific binding and location of specific groups at the active site which also responsible for its specificity. Till date about 1200 different enzymes have been isolated and studied, and each one of them has been found to possess a range of specificities. It is generally believed that the functional groups at the active site are fixed points of attachment with the substrate. Emil Fischer postulates a lock and key hypothesis to explain this interaction between the enzyme molecule and the substrate (Figure-6). Since enzymes are catalysts, they themselves are not changed by the reaction that the substrate undergoes. After the reaction has been completed, enzyme will reabsorbed on the other part of the substrate or on the other substrate. The process continues until the enzyme is 'poisoned' by a chemical bogie or inactivated by extremes of temperature, pH or by other negative conditions in the processing environment.
Enzyme-substrate interaction can be studied with the help of figure-7, where substrate concentration has been shown on the X-axis and velocity of reaction on Y-axis. When the enzyme-catalyzed reaction is studied at various substrate concentration, a hyperbolic curve is obtained. Three points, mainly A, B and C can be examined on a curve, which represent three situations. At point A, substrate concentration (S) is very low and the rate of reaction is directly proportional to substrate concentration. As the substrate concentration is gradually increased, the velocity of reaction also increases reaching a maximum by point B. At high substrate concentration the rate of reaction becomes independent of its concentration, and the enzyme appears to be fully saturated with the substrate.

For all enzymes, the rate at which they carry out their catalytic effect increases with an increase in substrate concentration, under favorable conditions. The maximum rate of activity, which can vary from enzyme to enzyme, is achieved when all the active sites of an enzyme are saturated with substrate. This saturation effect was noticed by Leonor Michalis and Maud Menten, who presented their equation to describe the basic kinetic action of enzymes involving a single substrate and product. The equation is defined as follow:
Where,

\[ V = \text{Velocity of reaction} \]
\[ V_{\text{max}} = \text{Maximum velocity of reaction} \]
\[ f_{\text{ES}} = \text{Fraction of sites filled} \]
\[ [S] = \text{Substrate concentration} \]
\[ K_m = \text{Michaelis Constant} \]

The Michaelis -- Menten equation is sufficient to describe the most of the enzymes catalyzed reactions. It can be utilized to determine \( K_m \) at various substrate concentrations and the values can be used in predicting the rate limiting steps. Therefore \( V_{\text{max}} \) and \( K_m \) should be carefully determined.
2.3.3 Significance of enzyme application (63):

A detailed study on enzyme application in textiles, show that it can provide several advantages over conventional methods.

- Conventional chemical processes are generally severe and fiber damage may occur. However, enzymes are characterized by their ability to operate under very mild conditions. As a result processes may take place without additional harm to fiber.
- Enzymes are readily biodegradable and therefore potentially harmless to the environment.
- Enzymatic processes are considered as economical, because it utilized less steam energy and avoid use of other auxiliaries.
- Catalytic biodegradation of enzyme eliminates use of harmful or pollution generating chemicals in various textile wet processing. Thus, it further reduces the effluent load of textile industries.
- Enzymatic actions are specific. For example, amylase type of enzyme acts only on starch without affecting the fiber. Thus, substrate quality will not be affected.
- Enzymes are catalytic systems and after reaction it can be generated as it is and reused again.
- Enzymatic biofinishing reduces pills and surface hairiness. It provides soft handle, luster and smoothness.

2.3.4 Limitations of enzyme application (63):

The important limitations of enzyme applications can be summarized as follow:

- Enzymatic technology is possible on living organs i.e. it is applied only on natural fibers such as cotton, wool, silk and bast fibers. This technology can not be utilized for man-made and synthetic fibers. However, new enzymes and technology can be developed to get advantage on synthetic fibers.
- Enzymatic action is slow process. It requires long reaction time hence production rate is also very low.
- Technology with respect to enzyme application in textile processing has not been developed. At present, enzymes are used at industrial levels only in desizing of starch and biofinishing or stonewash finishing application.
- Proper control of reaction is essential, otherwise severely damage the fabric by hydrolysis reaction.

2.3.5 Enzyme classes for textile uses (64):
Some of the most common enzymes that are used in textile and related areas in processing are listed in table 10 and briefly discussed below.

<table>
<thead>
<tr>
<th>Name of enzyme</th>
<th>Origin</th>
<th>Substrate</th>
<th>Reaction in which it involved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulase</td>
<td>Aspergillus Niger</td>
<td>Cellulose</td>
<td>Cellulose hydrolysis</td>
</tr>
<tr>
<td>Hemicellulase</td>
<td>Rhizopus, Oruaze</td>
<td>Hemicellulose</td>
<td>Hydrolysis of hemicellulose</td>
</tr>
<tr>
<td>Pectinase</td>
<td>Penicillium Fuiculosm</td>
<td>Pectin</td>
<td>Degradation of Pectin</td>
</tr>
<tr>
<td>Lipase</td>
<td>Plant, Gastric Juice</td>
<td>Fats &amp; waxes</td>
<td>Removal of fat &amp; waxes</td>
</tr>
<tr>
<td>Protease</td>
<td>Aspergillus Niger</td>
<td>Protein</td>
<td>Protein Degration</td>
</tr>
<tr>
<td>Amylase</td>
<td>Bacillus Subtilis</td>
<td>Amylose, Amylo</td>
<td>Removal of size</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pectin &amp; Starch</td>
<td></td>
</tr>
<tr>
<td>Laccase</td>
<td>Aspergillus Niger</td>
<td>Indigo dye</td>
<td>Improvement in the dyeing</td>
</tr>
<tr>
<td></td>
<td>Penicilium</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

39
Cellulase (65-67):
The treatment of cotton with cellulase is a well known way of gaining fiber surface modification. Controlled cellulase hydrolysis allowed to obtain clean fiber surface from microfibrils. This improves the appearance and the hand of used garments. If selected cellulases activities are used, microfibrils at the surface can be raised and fabrics with an aged look can be obtained. This fiber surface modification leads to dramatic changes in the hand and to the related low stress mechanical properties.

Cellulase is multi component system commonly produced by soil-dwelling fungi and bacteria. This fungi and bacteria produce cellulase to reduce cellulose to glucose, which is then used as a nutrient. The first postulates, concerning the nature of the mechanism of enzymatic hydrolysis was revealed by Reess, etal. It proposes two steps processes. A component termed as C1 was thought to initiate hydrolysis by preliminary activation or disaggregation of the cellulose chains. Subsequently, Cx the second component was responsible for the depolymerisation to soluble cello-oligo saccharides.

The cellulase enzyme consists mainly three types of activity,

1: Endoglucanases or β-1,4-Glucan Glucanohydrolase:
It hydrolyses cellulose polymers randomly along the chains, preferentially attacking on amorphous region. It acts on the interior of the polymer to generate new ends.

\[
\begin{align*}
C_x \\
\mid \\
G\longrightarrow G\longrightarrow G\longrightarrow G\longrightarrow G\longrightarrow G\longrightarrow G\longrightarrow G
\end{align*}
\]

2: Exoglucanases or β-1,4 Glucan Cellobiohydrolase:
It acts on the non-reducing ends of the polymer chains to release cellobiose

\[
\begin{align*}
C_1 \\
\mid \\
G\longrightarrow G\longrightarrow G\longrightarrow G\longrightarrow G\longrightarrow G\longrightarrow G
\end{align*}
\]
3: β-Glucosidase:
It hydrolyses cellobiose into glucose

\[ \text{B} \longrightarrow \text{G} \]

\[ \text{B} \cdots \cdots \text{G} \]

The three types of cellulase components act synergistically in degrading cellulose to glucose (figure-8).

![Figure 8: Synergistic action of enzymes on cellulose](image)

**Figure – 8: Synergistic action of enzymes on cellulose**

A mechanism and rate analysis of the enzymatic hydrolysis of the cellulosic material shows that the rate of hydrolysis reaction depends on:

- Physical structure of the substrate
- The nature of the cellulase complex and
- Inhibitory effects of both substrate and product.

The rate of enzyme catalysed hydrolysis changes as the acidity of the reaction medium changes. If one plots the rate of hydrolysis against the pH of the solution,
a bell shaped curve is obtained. The rate is fastest at about pH of 7.4 and slowest in either acidic or more alkaline solution. The kinetics of enzymatic hydrolysis of cellulose have received relatively little attentions probably due to the difficulties arising from dealing with an insoluble substrate, complex enzyme systems etc. Enzymatic hydrolysis of fibrous cellulose has some similarities with other reactions of fibrous cellulose. For e.g. the same modification that increases the sensitivity of cellulose to the reaction by mineral acid also are effective in increasing sensitivity of cellulose to enzyme attack. However, for the most part it is stressed that the enzyme is much larger in molecular size than the mineral acid that the attack by the former is much slower and reduction in molecular weight of cellulose molecule by the former is much smaller. Similar evident confounded by the fact that reaction of an enzyme with a soluble substrate is neither simple nor fully understood, that the problem is more complicated when an insoluble substrate is involved, hence there is certain confusion regarding the knowledge of cellulase – cellulose reaction.

The simple mechanism of cellulase enzyme on cellulosic fiber can be understood as follow:

The oxygen bridge between β- glucose residues, known as 1, 4 – glucoside linkage, is formed by glucose condensation with the elimination of water molecule in cellulosic fiber. Cellulase enzyme, which is capable of degrading cellulose, perform specific catalytic action on the 1, 4 – linkage of the glucose residues of the cellulose molecules. The hydrolysis of this linkage breaks the long cellulose chains into smaller ones, which may further reduced to glucose. The chemical reaction can be represented as in figure-9.
Hemicellulose (68):

Hemicellulase, a brand group of enzymes are xylan degrading enzymes, because xylan is the most abundant hemicellulose, ranking second only to cellulose. Xylan consists of a homopolymeric backbone of 1, 4-β-D-Xylopyranose units. Depending on its origin the backbone may be substituted. In ramie, hemicellulose also carries L-arabinofuranose units, usually linked to position 3 of D-Xylose. Glucoronic acid residues or its 4-O-Methylether are also present in smaller amounts. Ferulic acid was found esterified to C-5 of arabinose residues in arabino xylan from sugarcane bagasse.

Hemicellulase enzyme complex, so far reported, contains heterogeneity of activites of type endo- and exo acting xylanases namely, 1, 4-β-D-Xylanases, B-Xyldiases, A-Arabinosidases, A-Glucuronidases, Acetyl Xylan Esterases and Ferulic acid esterase. Endo- enzyme attacks the xylan in random manner, giving a decrease in degree of polymerization of the substrate and liberates shorter oligomers, xylobiose and even xylose.
B-xylosidases are exo-glucosidases and hydrolyze xylo-oligosaccharides to xylose. B-xylosidase activity is present in the most microbial hemicellulotic systems and has been purified from fungi and bacteria. Generally, B-xylosidases does not show activity towards xylan. In the case of Bacillus (Pumilus xylosidase, xylobiose is the best substrate in the series of) xylo-oligomers up to degree of polymerization (Van Doorslar et al., 1985). A-L-Arabinosidases hydrolyse non-reducing A-L-arabino furanosyl groups of arabinosidases, arabinoxylanases and arabino galactans (Kagi; 1984). A-D- Glucuronidases are required to cleave the terminal 4-O-Methylglucuronic acid side chains.

Esterase removes ester groups from the C-2 and C-3 positions of xylose residues in xylo-oligomers. The presence of acetyl xylan esterase activity is of major importance for the efficient hydrolysis of acetylated xylons.

**Pectinase (69):**

Pectinases are enzymes that catalyse the hydrolysis of pectins. In cotton, pectins are associated with the outer zone of the fibre known as the cuticle and may account for 1% of the weight of dry raw cotton. In ramie fibre pectins are associated in multicellular structure and amount is about 4 to 5% on dry weight of raw ramie fibre. Enzymatic removal of pectin is an alternative to conventional alkaline boiling for making cotton and ramie absorbent.

**Lipase (70):**

Lipases are enzymes that catalyze the hydrolysis of fats. Common fats are esters of glycerol and fatty acids. Lipases attack the ester bonds in these fats regenerating water insoluble glycerol and water insoluble fatty acids, which are converted into water soluble salts by addition of alkali as shown in reaction (figure-10). Fats often are included in sizing formulations to promote lubricity of the sized warp yarns, but these fats can be difficult to remove by lipase enzymes in amylase formulation, results in effective removal of both starches and fatty lubricants.
Lignin degrading enzyme (61):

Biodegradation of lignin is unusual because

- Lignin biopolymer is having random three-dimensional structure which have repetitive linkages between the monomeric building block.
- Despite of its potentially high energy content, does not used as sole energy source by any known living organism.
- The organisms and the mechanisms by which lignin macromolecule is degraded are exceptional.

In 1913 it was reported that fungal peroxidases degrade lignin. Recently, lignin degradation by bacteria has received increasing attention. Bacteria, however, decompose lignin slowly and incompletely compared with that by white-rot-fungi. Fungous solublise lignin to high molecular weight carbohydrate complexes. Lignin degrading enzyme in white-rot-fungus Phanerochate Chrysosporium was discovered in 1983. It degrades lignin by cleavage of Cx-Cb bond in a dimeric lignin as shown in figure-11. The enzyme was identified as a peroxidase and brings about degradation of lignin by oxidation.
After oxidation by lignin peroxidase, the reduction of several of the resultant products with the exception of ring cleavage compounds take place. Once the lactones are formed they are very slowly degraded to CO₂ by P-Chrysosporium while the quinines are degraded initially at rate similar to that of veratyl alcohol itself. The scheme of lignin degradation in P-Chrysosporium is shown in figure-12.

Figure – 12: The scheme of lignin degradation in p-chrysosporium
2.4 Application of enzymes in degumming of ramie fiber (39, 71, 72):
The bacteriological process of degumming has received much attention, but so far no standard process has been developed on a commercial scale using microorganisms for degumming of ramie.

Kundu and Roy reported that a strain of Bacillus Substilis in sterilized water at 31°C to 32°C partially degummed ramie ribbons in 6 to 7 days without any degradation to the fiber (73).

Clostridium Corallium was reported to be effective in wetting and degumming without damage to the fiber. Studie on microbial degumming of ramie, carried out at JTRL, Calcutta, revealed that mixed bacterial cultures, freshly isolated from the Rhizospheres on Sunn hemp fiber (Crotoleria Juncea) were found to be effective in bringing down the gum content to 15 % at an incubation period of 7 to 10 days by utilizing the gums of ramie as source of carbon and energy. The better fiber strength and fineness signified that the encrusting gummy materials were removed to a great extent with out any cellulotypic activity by the cultures. A combination of microbial and chemical methods was attempted by the initial treatment with the culture isolated from the sunn hemp fiber Rhizospheres, followed by mild alkali boiling. The gum removed by the combined treatment was more effective than that of the chemical treatment alone (74).

Pal and Bhattacharya have isolated different mixed bacterial cultures capable of utilizing the gum of ramie fibers as a sole source of carbon and energy. Four of them showed promising results. Each of the mixed cultures contained several bacterial species, which grew in association with one another. An attempt to separate an individual organism for isolation and identification failed, since it did not grow separately, probably owing to its dependence on the metabolic products of other organisms in the mixed culture for nutrition and growth. The bacterial cultures, which were found to be highly pectinolytic were adapted to grow in and were maintained in a suitable selective medium developed in the laboratory and containing ramie gum as the sole source of carbon. A fiber sample was incubated
at 30°C for a particular time (7 to 10 days), washed and dried. Similar to chemical degumming, microbial degumming also affect on the fineness and tenacity of fiber. They also reported the effect of combined systems on the gum content and properties of fiber. The mixed degumming method is simple and economical in that less alkali is required, the treatment is less drastic and fiber properties such as softness, feel and luster are improved (75).

S.Roy and et al., have degummed ramie fiber with fungal culture, which was collected from Microbiological Laboratory, Assam at room temperature for different time periods (1, 3, 5, 7, 9 and 11 days). They have reported that gum, lignin and pectin contents decrease gradually with the increase in treatment period. The best results obtained after 5 and 7 days incubation and considered as recommended standards (76).

Work upon the enzymatic degradation of lignin on ramie and other fibers has also been reported by Basu and Ghose (77).

2.5 Properties of degummed ramie fiber:

2.5.1 Physical properties of degummed fiber:

It has been reported that the removal of non-cellulosic components from the bast fibers decreases their moisture absorption capacity and increases tensile strength and fineness of fiber. Goswami and Mukherjee have treated raw linen with alkalis and reported that with the increase in weight loss of fiber, whiteness index and absorbency increases while yellowness index decreases (92). Macmillan and et al. have studied the effects of alkalis on jute fiber and found that with the removal of non-cellulosic impurities fiber strength decreases (93). Enzymatic degumming of flax fiber has been studied by Bhattacharya and Shah. They have found that on removal of gummy material, breaking load and yellowness index decrease while whiteness index and absorbency increase (94).

Similar behavior has been observed for ramie fiber also. Degumming of different varieties of ramie fiber were performed by Chakravarthy et al. using caustic soda in such way that the residual gum contents were approximately 15, 5 and 2 % of
the dry weight of fiber. It was observed that progressive degumming leads to gradual increase in the tenacity of the fiber. Stress-strain diagram indicates that degummed ramie would be able to absorb sudden increases in stress more efficiently than the fiber with larger amounts of gum in it. Thus the products from degummed ramie would be expected to be more durable to those made from ramie containing higher gum content. Moisture absorption ability of ramie decreases with the removal of gummy material from fiber. Further, it has been observed that the rates of evaporation gradually became slower as the gum content of fiber increases. Wearing apparels made from degummed ramie, because of its lower absorption and higher rate of evaporation of moisture would feel cooler and more comfortable in hot weather compared to products made from ramie with larger amounts of gum. They have also observed that on degumming, the fiber gradually separates into individual cells and the fiber to fiber friction becomes lower (51). A study was made on the physical and chemical properties of raw and degummed ramie fibers of varieties, R-1411, R-1412 and R-1415 by Thakur and Co-workers. It was reported that R-1411 had the highest breaking load and tensile strength having higher cellulose and gum contents than other two varieties (55). Kundu and et al. have studied alkaline degumming of matured and unmatured ramie fibers. In both the varities removal of gummy material decrease the tensile strength of fibers were observed (54). Degumming of different varities of ramie fibers have been analyzed by Das Gupta and et al. They have reported that with the decrease of residual gum content on degumed fibers, tenacity increases while fineness decreases (48).

2.5.2 Structural properties of degummed fiber:
Ramie fiber is characterized by high crystallinity. Ray et al. studying the influence of gum on the crystalline structure of ramie indicated that the gum in decorticated ramie resides mostly in the fibrous matter but does not take part in the crystalline structure of the cellulose in ramie. Removal of the gum enables the fiber to take more crystalline form (21). Hermans studied the crystallinity by X-ray method and
obtained a value for crystallinity in ramie of 70% in the native state and 50% in the mercerized state (95). Warwicker has also observed a decrease in the crystalline orientation of the fiber when treated with caustic soda (98). However, Viswanathan found no change in crystallinity in native and mercerized states of the fibers if a 'disorder function' was taken into consideration while calculating the crystalline parameters (96). On the other hand, Kulshreshtha et al. studying the axial order in ramie, reported evidence of paracrystallinity in the fiber (97). Chang et al. found in ramie that had been treated similar but under tension that, with increasing concentration of caustic soda, the crystallinity decreased, whereas in fibers treated without tension, the crystallinity at first decreased and then increased (106).

2.5.3 Surface behavior of ramie fiber:

The surface structure of fiber has a great influence on their behavior at every stage of the conversion of raw material into the products. Rahaman investigated the changes in surface morphology of jute fibers and the influence of lignin after progressive delignification (99). Guha Roy et al. studied the delignification and bleaching treatments (100). Das et al. also studied jute fibers at different stages of growth, as well as their fracture modes (101). The structural features and fracture morphology of raw and chemically treated pineapple leaf fiber have been studied using SEM by Saha and co-workers. They have reported that surface morphology progressively changes with gradual removal of non-cellulosic constituents like lignin and hemicellulose (102).

The surface phenomenon of various vegetable fiber has been examined by Ansari et al. The study revealed that all the fibers have a hollow lumen, the size of which varies from fiber to fiber and ramie sample shows a very ribbon-like structure (103). The surface feature of raw, degummed and bleached ramie fibers were studied by Kundu and co-workers. They observed that the undegummed fibrillar structure is covered with structural polysaccharide components and not clearly visible. The fibrillar alignment parallel and straight with no surface deposits has
been observed on removal of gummy material (54). Ray has also studied the surface topology of ramie and reported that as the fiber was degummed, the overlying patches on the surface became smaller in area and the distinct detail, consisting of longitudinal fibrillar elements was progressively revealed on the fiber surfaces (104). Osborne studied the molecular arrangement of the fiber with the polarizing microscope and observed striations on the surface of the fiber (105).

2.5.4 Infrared (IR) spectroscopy behavior of ramie fiber:

The IR spectra of all natural cellulosic fibers are essentially the same, except for some small differences, probably due to differences in impurity content, orientation and crystallinity. Ellis and Bath, using unpolarized and plane polarized light, first studied the IR spectra of ramie fibers in the near infra red region 10,000 – 4000 cm⁻¹ (111). The IR spectra of oriented ramie fibers in the region 3800 – 600 cm⁻¹ were reported by Tsuboi. He studied the effects of deuteration and interpreted the dichroism observed on the basis of the crystal structure of cellulose (112). Marrinan and Mann studied the IR spectra of bleached ramie fiber and other cellulosic samples and their crystalline modifications in the 3600 – 2800 cm⁻¹ region using a deuteration technique (113). Liang and Marchessaul studied the IR spectra of oriented films of ramie and other cellulose crystallites in the region 3600 – 2800 cm⁻¹ and in the frequency range 1700 – 640 cm⁻¹. They determined the polarization properties of bands and proposed a system of hydrogen bonding in the crystal structure of Cellulose-I (114, 115). They also studied the IR spectra of doubly oriented films of mercerized ramie and Fortisan crystallites over the frequency range 3600 – 650 cm⁻¹ (116). The physico-chemical nature of ramie at different stages of crop growth has been studied by IR spectra by Kundu and Co-workers (117). From IR study, they reported that the pectin has been found to be maximum or 40 days of old ramie whereas hemicellulose for 70 days old ramie. IR spectra of degummed ramie fibers (2.3 % gum content) in untreated and alkali treated conditions were observed over the frequency range of 4000 – 300 cm⁻¹ by Sao and et al. The sharp changes in the spectrum due to the transition from
Cellulose-I to Cellulose-II was observed in the concentration range 12 – 15 % (w/w) of alkali (47). An analysis of ramie-acrylic blends of different blend compositions has been reported by Dey and Co-workers using an IR spectral technique (118). Kundu and et al. have studied the effects of chemical deguming treatments on decorticated ramie fiber. IR spectral study revealed that the degummed and bleached ramie fibers comprised only cellulosic materials. They reported that the characteristic peak at 1740 cm$^{-1}$ of the carbonyl group of uronic acid (a constituent of hemicellulose) and at 925-920 cm$^{-1}$ of galactan (a constituent of pectin) were present in the spectrum of decorticated fiber but absent in degummed ramie. Only those peaks characteristic of cellulose viz. 3500 – 3000, 1375 – 1370 and 1060 cm$^{-1}$ were much prominent in the spectrum of processed ramie (54).

2.5.5 Thermal properties of ramie fiber:
Thermal degradation of natural cellulosic fibers are highly influenced by the temperature, time of heating, environmental atmosphere and non-cellulosic impurities. Thermal behavior of developing cotton fibers has been examined by Lawson and co-workers. They have reported that endothermic peaks at 77°C and 340°C were due to the evaporation of adsorbed water, wax etc., and decomposition of cellulose respectively while the additional thermal transitions indicate the presence of non-cellulosic components. They have also observed smaller endotherms around 140-150°C and 170-180°C, the lower temperature endotherms are close to the $T_m$ of anhydrous glucose, hemicellulose, as well as β-sitosterol and γ-sitosterol while the higher temperature endotherms are possibly related to the melting of hemicellulose and pectin (107). Thermal degradation of modern and ancient linen fabric was investigated by Ferrero and et al. using DSC. They have observed that a similar pattern to that for cotton degradation was found and the essential influences of impurities occurring naturally or occasionally have been observed (108). Calamari and et al. studied the thermal analysis to estimate the extents of cotton-weathering, since cotton fibers were found to follow very
different characteristics patterns of thermal degradation, depending on the amount of naturally occurring impurities (109). In the thermal study by Ansari and et al. on different types of flax fibers, they have also examined the ramie fiber. They have examined the thermal behavior of different varieties of flax, abaca, cotton and ramie and reported that ramie fiber is thermally the most stable, while flash hydrolyzed flax fiber is the least (110). An analogous investigation on ramie fibers has not been previously reported.

2.5.6 Chemical properties of degummed ramie fiber:
It has been observed that water absorption properties and wettability of ramie fiber was found to be improved on the progressive removal of gummy material (34, 48, 119). Further it was reported that the degummed ramie fiber dry rapidly compare to that of raw fiber. D. Das and et al. have reported that highly crystalline and highly oriented fine structure of ramie makes the required dyes and chemical diffusion difficult in comparision to that for cotton (84). Sen and Hermanns found that swelling of a bast fiber in water decreases with an increase in the number of ultimate in the cross section of the fiber. After delignification (i.e. removal of gummy material) the swelling was found to be increased (120).

2.5.7 Microbial resistivity of degummed ramie fiber:
Very few literatures pertaining to microbial phenomenon of ramie fiber has been available. Abrams in his work on degumming of bast fiber has reported increases of resistance to mildew. This he has suggested due to the loss of the amorphous region in the cellulose which are more susceptible to degrading influences than the crystalline portion (121). Resistance of degummed ramie to microbial damage has been examined by Das Gupta et al, The tenacity retained after incubation in soil was found to be increase with the decrease of residual gum content on fiber (48). Similar behavior has been observed by Bhattacharya and Das on ramie fiber after degumming using different amines (125). Chemical composition of the fibers influences on susceptibility of bast fiber to micro organisms growth has been reported by Searle. Lignin content offers protection from micro organisms (124).
Elkin showed that the resistance of flax to microbial decay increases with the severity of the alkaline boil, because the latter treatment removes more accessible non-cellulosic constituents (122). According to Basu and Ghose, hemicellulose is found to be highly susceptible to fungal attack (123).

2.6 Bleaching of ramie fiber (78-79):

The degummed ramie fiber is fairly white. For pure white fibers, bleaching is essential and was carried out either in fiber stage or in fabric level. Since bleaching results in a small loss of weight and fiber strength, it is recommended only at absolute necessity. As such bleaching of ramie materials can be carried out at different stages as per requirement of the end product. For milky white, fiber can be bleached in advance in stainless steel vat by treating the material with hypochlorite or peroxide as per the procedure followed for cotton. Luniak described a bleaching process in which the fiber is given a mild peroxide treatment with 0.2 to 0.3 vol. active oxygen per liter and stabilizer. The treatment is followed by a sodium hypochlorite treatment (2g active chlorine / liter). A bleaching process using sodium per borate in two stages is also reported. It is observed that combined degumming and bleaching for ramie using sodium per borate gives good results. Degumming and calcium hypochlorite bleaching containing 1% chlorine gives satisfactory results.

Hydrogen peroxide and sodium hypochlorite were used for bleaching both decorticated and degummed ramie at JTRL, Calcutta. The yarns and fabrics show loss of dry strength and gain in wet strength of bleached material over its original state. The loss was more in fiber stage and less in fabric stage. Hydrogen peroxide was found to be more effective bleaching agent for ramie.

In one of the experiments, N.C.Pan and Co-workers have reported that bleaching of degummed ramie can be carried out in a closed vessel for 1 h at 80°C with hydrogen peroxide (1 Vol.), trisodium phosphate (5 g/l), sodium hydroxide (1 g/l), sodium silicate (10 g/l) and ultravon JU (5 g/l). The results of bleaching were excellent.
2.7 Softening of ramie fiber (80):
Fiber separation to the desired extent cannot be achieved in case of degummed fiber. Softening treatment with a suitable chemical is therefore an essential, before spinning as the fiber is hard. The softening treatment consists of soaking of fiber in water and subsequent treatment with a cationic surfactant. Alternative method was an application of jute batching emulsion on the fiber after the moisture is reduced to the desired level. The fiber at a moisture content of 25 to 30 % was then passed through the conventional jute softener machine for kneading. Similar types of softening treatments were reported for ramie by Luniak. Some times sulfonated castor oil also used for this purpose.

2.8 Spinning of ramie fiber (81-83):
There is no specialized spinning system for ramie, but any system designed for cotton, wool or silk can be adopted. Spinning is a multi stage process that consists of three basic steps: carding, drawing and spinning. The main difficulty in spinning of ramie results from the combination of high tensile strength with longer fiber length and the breaker card cannot break the fiber into staple lengths suitable for subsequent spinning. It is usually necessary to pass fiber through a stapling system to obtain requisite staple lengths. For different spinning machines different staple lengths of the fiber are required and this can be achieved either by stapling as described above or by mechanical sorting into basic length groups. Yarn preparations for the longer fibers are usually done on adaptations of machinery designed for wool fibers and for shorter fibers cotton system is adopted in America. Machineries adopted for flax and spun silk fibers are in use in China and the far East. Few ramie products are illustrated in figure-13
Figure – 13: Important products of ramie fiber

The spinnability of indigenous ramie fiber was assessed in the different spinning system such as jute, cotton, wool, spun silk and flax system in collaboration with leading textile institutes.

(a) Jute system:
In jute system, both decorticated and degummed ramie (up to 9% gum content) were processed in spinning machinery with suitable techniques developed in the institute. Mechanical softening treatment was given to the fiber prior to processing. Yarn of counts 50 to 60 tex and up to 32 tex were spun from the decorticated and degummed ramie fiber respectively. The following equipment was used for this purpose; softener, breaker, card, finisher card, drawing frames, roving frames and spinning frames. The staple length of ramie required on jute machineries was found to be around 25 to 30 cm. Spinning of ramie on James Mackie and Sons Jute amchinerise resulted in yarns of counts 200 to 54 tex when spun directly from draw frames and yarns of 84 tex resulted when spun from roving frames.

(b) Cotton system:
Degumed ramie, after treatment with cationic softener in the form of sliver can be processed in cotton system effectively (CTRL, Bombay). Ramie was stapled to about 38 mm length and processed. Due to its coarseness (5 to 6 denier), ramie yarns were hairy and processing of the fiber alone possessed some problems which were over come by suitable chemical treatment. Kundu has reported that ramie has been successfully cottonised. It has been found that cottonised ramie can be spun
and woven in standard cotton machineries. Such cottonised ramie can easily be blended with cotton, wool, silk, rayon etc. It has claimed that both 100% cottonised ramie and of unions from 25 to 50% have been spun on cotton machines with out adjustment. The development of ramie fiber in India and cottonisation can met the shortage of long staple cotton in the country to a great extent.

(c) Woolen system:
Ramie sliver was stapled to 10 cm, passed through card, gilled, drawn and made into bobbins and then spun on worsted ring spinning frame.

(d) Spun silk system:
Degummed ramie fiber on treatment with 10% alkali gave better spinning performances. In the spun silk unit longer fiber length could be maintained resulting in better yarn properties. Yarns from 100% ramie was much stronger than from 50:50 ramie:silk blend.

(e) Flax system:
Twistless spinning process developed for flax at Verelinitstitut TNO in Delft was tried for ramie. It was found that ramie can be processed on the continuous green-flax processing system. Ramie and polyester blend spun on such system behave similar to that of flax and polyester yarn when subjected to the finishing process to give 'easy care' properties.

2.9 Dyeing of ramie fiber (84-91):
Degummed ramie fiber, in comparison to cotton is coarser, more heat resistance, rapidly dyeable, less extensible with highly crystalline and highly oriented fiber. Highly crystalline and highly oriented fiber structure of ramie makes the required dye diffusion difficult in comparison to that of cotton. In most of the cases, ring dyeing of ramie gives lower rub fastness. Very few reports were available on the rub fastness for cellulosics material but little information are available on ramie fiber.
Several reports on the preparation and processing of ramie fiber, including degumming and spinning developments were available but very few works reported on the preparation and dyeing of ramie yarns and fabrics and most of them were patented.

Direct dye can be applied on ramie fiber, similar to cotton, but the depth attained may differ considerably. In one of the report L.Cheek and et al., have studied the effects of caustic soda mercerization, either slack or with tension, on the direct dye up take and colour yield of ramie, linen and cotton fibers. Treated and untreated ramie exhibited lower dye bath exhaustion compare to that of cotton and linen, but for a given dye content the visual depth of the dyeing on ramie was higher.

Limited amounts of ramie are dyed with reactive dyes by methods similar to those for cotton. In one report of D.Das and et al., dyed ramie after treatment with swelling agents. They have reported that pretreatment with 20% NaOH or 20% Urea under slack condition shows appreciable amount of decrystallisation and considerable improvement in reactive dye up take with low to moderate strength loss, indicating practical importance for possible industrial application.

Vat dyes can also applied on ramie like other cellulosic fibers, however no reports were available on the performances of such dyeing.

Bast fibers, such as flax, hemp, jute and ramie contain impurities that interfere with the absorption of both naphthol and diazo components. Thus a significant proportion of insoluble azoic dye remains on the fiber surface and unless the impurities are not removed by appropriate pretreatment, dyeing of inadequate penetration and fastness are obtained. In order to achieve satisfactory penetration of naphthol, exhaustion should begin at 70°C or above, omitting the formaldehyde, and be completed in cooing bath at 25 to 30°C. Coupling was carried out similar to cotton, a more intensive after treatment is required to remove the greater proportion of loosely held azoic dye from the fiber surface.

In one of the research L.M.Zhou and Co-workers have studied the effect of cross linking agent on ramie fabric dyeability. Cross-linking with 1,2,3,4-
butanetetracarboxylic acid decreased the dyeability ramie fabric. The parameters related to the dyeing process, such as equilibrium adsorption, dyeing rate and maximum adsorption capacity were all reduced by the cross linking treatment. However, the activation energy of dyeing was increased. Mercerised fabrics show higher dyeability than non-mercerised ramie fabric.

3 Scope of the present work:
Ramie ranks as a classic fiber in that it has been grown and used in many countries since time immemorial. It can play a very important role as a textile material as it has excellent tenacity, enhanced wet strength, luster, excellent dyeing, easy drying, high moisture absorption and microbial resistivity. The reason for limited use of ramie is attributed to the difficulties encountered in the production, extraction and processing of this fiber. It has tremendous scope for commercial utilization as a substitute for flax and cotton especially for superior quality garment and other areas, which has to be explored.

Ramie is cultivated to a limited extent in Assam and N.Bengal in India. The report of National Commission on Agriculture indicates favorable signs for export prospects of Indian ramie to European countries, Canada and Japan. As per the report, ramie cultivation would be profitable in India and the envisaged estimated requirements of ramie around 10,000 ha might not be considered sufficient for ramie plantation. Ramie cultivation in India would prove remunerative provided the plantation and processing are done on technically sound lines and the textile industries maintain constant demand and ramie takes to blending with synthetic, wool, silk and similar fibers. This needs the encouragement through government policy as it is done recently with flax fiber.

In spite of extensive literature survey, no systematic scientific works on ramie fiber processing starting from its degumming alongwith their value added
applications are available. This envisages that enough scopes of scientific works are possible with this fiber. This concept encourages to take this work.

Various methods of degumming are reported in the literatures for the removal of gum from crude ramie fiber, but none is entirely satisfactory for achieving perfect and uniform degumming. The most of them are covered by patents, giving very little information about methods adopted and the properties of the degummed fiber thus obtained. Conventionally caustic soda is widely practiced as a degumming agent for ramie fiber. Different alkalis metal salts, other than caustic soda were tried for degumming of ramie under different process conditions. The applicability of combination of various metallic salts on degumming performance was also investigated. Environmental friendly process is demand of today's industrial development. Therefore, an eco-friendly degumming processes using enzymes and peracetic acid, were also developed. Various degumming systems were compared with conventional caustic soda process and optimization of degumming conditions was derived. A novel spectral analysis method was developed for the determination of constituents of gummy material (hemicellulose and pectin) in degummed liquor. A scientific approach of degumming process was also studied using kinetic parameters of degumming reaction mainly of alkalis and enzyme.

Physico- mechanical properties of degummed fibers of various systems were analyzed and compared against conventional caustic soda degummed sample. Chemical compositions of decorticated and degummed samples were also determined using standard prescribed method. A co-relation has been derived with the constituents of gummy material and its physical properties. Such co-relation is considered as a tool to describe the progress of degumming process.

In order to develop potential of ramie fiber in different areas, thermal behavior of degummed fibers were carried out. Various degummed fibers were thermally degraded along with parent sample at the wide range of temperatures to establish their thermal degradation. The results were co-related with the residual gum
content of fiber vis-a-vis constituents of gummy material and decomposition temperature.
The surface behavior of decorticated and degummed fibers, were also observed through image and SEM analysis. The results were co-related with the degumming systems and their chemical compositions. An attempt was also made to investigate the contribution of various chemical constituents in gummy material and their presence at different level of degumming process through IR spectral analysis. Similar study was made for degummed fibers of various systems. Such informations, throw a light of an inside of various degumming operation.
New era of application i.e. geo-textile and medical textile were also examined of the said fiber. Various analytical tests of degummed fiber samples having different residual gum content were carried out for this study. Properly degummed ramie has found very high scope in such areas of application. Such products of ramie, may develop its application as a value added fiber, which may increase the cultivation acres in India. With this respect it is possible to uplift on the large scale the socio-economic status of the farmers and others in the relevant areas.
To develop the potential of ramie in area of textile apparels and garments its dyeing behavior should also be considered. Dyeing performance of ramie fiber having different residual gum content was studied with structurally different direct dyes. Co-relation of dyeing with residual gum content and the individual constituent of gummy material were established. Fastness properties of dyed samples were also investigated with direct dyes. Such studies reveal that like other cellulosic fibers, ramie can be dyed effectively provided the gum content in the fiber is limited to certain extent.
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