8. SUMMARY & CONCLUSIONS

The present investigation entitled “Studies on solvolytic structural transformation and degradation of cellulose” was carried out at Chemistry of Forest Products Division, Forest Research Institute, Dehradun (Uttarakhand). The study focuses on the structural transformation of cellulose and its simultaneous degradation carried out during various alkali, acidic and physical treatments. Cotton fibers were chosen as raw material because cotton contains the highest percentage of cellulose among natural fibers. The effect of different treatments on cellulose was analyzed by crystallinity index of the treated cellulose fibers examined by wide-angle X-ray diffraction (WAXD) technique and by the estimation of total reducing sugar.

Cellulose is a homo-polysaccharide, composed of D-glucose units linked together by β-1,4-glucosidic bonds. Cellulose is intimately associated with hemicellulose and densely packed by the layers of lignin, which protect it against the further hydrolysis. Cellulose is a material that does not melt at the temperature lower than its degradation temperature. Strong intra- and inter-molecular hydrogen bonds in cellulose prevent its molecules from dissolution in most common solvents. Although it is well documented in the literature that there are a number of approaches for the pretreatment of the cellulose, such as physical, chemical, and biological methods and their combinations. Pretreatment aims to decrease the crystallinity of the cellulose, increases the biomass surface area, removes hemicellulose and breaks the lignin seal.

The present study deals with the alkaline treatment of cellulose with different chemicals such as sodium hydroxide, urea, ammonia, and in combination with respect to treatment time, treatment temperature and concentrations of the chemicals. Result of the present investigation reveals that reaction of cellulose with sodium hydroxide (≤15wt%) results in the swelling of the cellulose molecule and transforms parallel cellulose I present in native cellulose to antiparallel cellulose II by the process of mercerization. During the process of mercerization, entire fibers are converted into a swollen state and the assembly and the orientation of microfibrils are completely
disrupted. The original parallel-chain crystal structure of cellulose I changes to anti-parallel chains of cellulose II, resulting in the decrease in the crystallinity. Mercerization mainly depends on the type and concentration of the alkali used, treatment temperature and treatment time.

Interaction of cellulose with urea results in the slight decrease in the crystallinity of cellulose I. This is due to the fact that urea does not contribute towards dissociation of hydrogen bonds and swelling of cellulose microfibrils and thus no structural transformation from cellulose I to cellulose II polymorph takes place. However, cellulose interaction with liquid ammonia results in the formation of an addition compound of a reduced crystallinity. The cellulose regenerated after the treatment results in the formation of a fairly disordered cellulose with the lattice type of cellulose I.

The study carried out with sodium hydroxide in combination with urea reveals that the crystallinity of cellulose was further decreased as compared to sodium hydroxide alone. This can be explained by the fact that urea opposed the requisite swelling and spacing needed for the transformation from cellulose I polymorph to cellulose II polymorph through urea–NH₃⁺…O⁻–cellulose interaction and prevents the reassociation of cellulose molecules, which further leads to the reduction in the crystallinity. Furthermore, the study carried out with sodium hydroxide in combination with ammonia leads to the decline in the crystallinity of the cellulose. The aqueous sodium hydroxide and anhydrous liquid ammonia treatments alter the crystalline structure of cellulose with reduced crystallinity.

Acidic treatment of cellulose results in the degradation of the cellulose molecule which increases with the increase in concentration of the acid, treatment time and treatment temperature analyzed by the estimation of total reducing sugar. An important aspect of the treatment was that it leads to an increase in the crystallinity of the cellulose without any structural transformation. This can be explained by the preferential degradation of amorphous cellulose present in native cellulose, leading to a minor increase in the crystallinity of the cellulose molecule.
Apart from alkaline treatment and acidic treatment, a study of physical parameters such as microwave, ultrasonication, photolysis and thermal aging of cellulose was also carried out to assess the structural transformation and degradation of the cellulose molecule. The present study of microwave treatment of cellulose was performed as microwave energy can easily penetrate to particle inside and all particles can be heated simultaneously, thus reducing heat transfer problems. Microwave heating has been used to disrupt the recalcitrant structures of lignocellulose. In the study, effect of microwave treatment on the cellulose was discussed. The results show a decrease in the crystallinity index compared to the untreated cotton linters. Structural transformation from cellulose I to cellulose II polymorph was not observed. This can be explained due to the fact that microwave being a physical parameter alone was not able to dissociate hydrogen bonds available in cellulose I polymorph.

The study on the treatment of cellulose with ultrasonic waves was also carried out. A liquid sample when irradiated with ultrasonic (>20 kHz) waves results in agitation of the molecule. Sound waves that propagate into the liquid media result in alternating high-pressure (compression) and low-pressure (rarefaction) cycles. During rarefaction, high-intensity sonic waves create small vacuum bubbles or voids in the liquid, which then collapse violently (cavitation) during compression, creating very high local temperatures. The effect of ultrasonication on cellulose results in the decrease in the crystallinity compared to untreated cotton linters. Structural transformation from cellulose I to cellulose II polymorph was not observed. This can be explained by the fact that ultrasonication was not able to dissociate hydrogen bonds available in cellulose I polymorph as ultrasonication being a physical parameter.

Treatment studies with photolysis and thermal aging was further performed for the structural transformation and degradation of the cellulose. Photolysis occurs by the activation of the polymer macromolecule caused by the absorption of light energy by the polymer where as the main process responsible for natural cellulose aging is the random hydrolysis of the glycosidic linkages between the glucose residues in the macromolecule of cellulose. The data obtained after the photolytic treatement and thermal aging of cellulose reveals that the decrease in the crystallinity as compared to
untreated cotton linters. Furthermore, structural transformation from cellulose I to cellulose II polymorph was not observed in both the cases. This can be explained due to the fact that photolysis and thermal aging being a physical parameter alone were not able to dissociate hydrogen bonds available in cellulose I polymorph for the transformation to cellulose II.

Thus in nut shell the overall treatment studies carried out for the structural transformation and degradation of cellulose can be summarized as follows:

- Treatment of cellulose with sodium hydroxide (≤15wt%) results in the swelling of the cellulose molecule and transforms parallel cellulose I to antiparallel cellulose II by the process of mercerization, which results in the decrease in the crystallinity of the cellulose molecule.
- Treatment of cellulose with urea results in the minor decrease in the crystallinity of the cellulose molecule while leading to no change in the structure.
- Treatment of cellulose with ammonia results in an excessive swelling and a change in the lattice dimensions and formation of disordered form of cellulose of low crystallinity as compared to untreated cotton linters.
- Treatment of cellulose with sulphuric acid at variable concentration, reaction time and temperature resulted in the degradation of the cellulose molecule and leading to an increase in the crystallinity index due to the preferential degradation of amorphous cellulose.
- Treatment of cellulose with physical parameters such as microwave, ultrasonication, photolysis, thermal ageing resulted in the slight decrease in the crystallinity index with a minor change in TRS concentration.