The depletion of petroleum resources, along with the current concerns about the warming of the planet that can be attributed to human activities, make it urgent to shift dependence away from fossil resources to renewable biomass resources. In pursuing the dual goal of producing bio-power and biomaterials while enhancing the management of greenhouse emission, the concept of bio-refinery has emerged. The bio-refinery parallels the petroleum refinery, in the imbalance between transportation fuels and chemical needs. It operates on an abundant renewable raw materials (ligno-cellulosic, polysaccharides,...) which are fractionated through a series of processes, and further converted into commodity chemical molecules and transportation fuels. For the bio-refinery to be effective the contribution of plant biologists, carbohydrate chemists, structural biologists and process engineers is likely to be essential. To this end, researching dealing with the following items should be undertaken: (i) Biomass formation and modification: Identification of genes that contribute to biomass production and cell wall synthesis. (ii) Feedstock production: How to modify cell wall composition for optimal fuel production and extraction of high-value chemicals, (iii) Biomass deconstruction and conversion: Developing the science and technology needed to breakdown lignocellulosic materials into usable monomers, and improve bioconversion using enzymes and microbes. The prerequisite for achieving such goals implies a comprehensive characterization of: (i) the different individual bio-macromolecules that constitute the biomass resources; (ii) the intricate complexity of their associations.

Polysaccharides are the major components of the biomass; and among them, cellulose, hemicelluloses, starch,... They are produced by highly complex biosynthetic machineries that result in a concomitant polymerization and in situ structural architectures which encompass several level of structural organization. The structural elucidation of these bio-macromolecular assemblies escapes from the conventional and well-established methods developed for elucidating protein and virus three-dimensional structures. The most important method for the structure determination of crystalline polysaccharides is X-ray fibre diffraction. It has been observed that linear polysaccharides prefer to exist as long helices rather than more convoluted structures. A fibril sample may be a more relevant environment for biological macromolecules, as it can accommodate, without loss of order, changes in polymer structure and conformational flexibility that would destroy order in a single crystal. Besides, the native organisations of several polysaccharides occur in a fibril form and it is therefore relevant to investigate the structural results of concomitant biosynthesis and crystallization. In contrast to other macromolecules, the diffraction data that can be obtained from polysaccharides are not sufficient to permit crystal structure determination based on the data alone. Molecular modelling techniques must be used which allow for the calculation of diffraction intensities from various models of comparison with the observed intensities. The joint use of molecular modelling and diffraction techniques has been invaluable in the quantitative elucidation of three dimensional structures and architectures of assemblies involving polysaccharides components.

The presentation will exemplify on such macromolecular systems as cellulose and starch. It will illustrate how experimental data derived from synchrotron radiations diffraction and imaging, along with neutron diffraction and molecular modeling, have contributed to unravel the 3 dimensional features over several level of structural organizations, thereby providing ad hoc information to deconstruct and convert these naturally occurring materials into useful components without neglecting the unique architectures that are derived by bio-synthetic pathways and that are not attainable throughout thermodynamically driven processes.