**Romanian Academy** 

"Petru Poni" Institute of Macromolecular Chemistry

lasi, Romania

Habilitation thesis

Natural polymers as key elements of biorefinery value chains: conversion reactions and possible applications

Dr. Iuliana Spiridon

2016

## Table of contents

Abstract	5
Abstract-Ro	8

## Section I.

Chapter 1. Main components of biomass: Structure and Characterization	
2.1. Cellulose	12
2.2 Hemicelluloses	23
2.3. Lignin	30
Chapter 2. Biomass processing	
Major processes used to separate biomass components	45
2.1.1. Conventional processes	45
2.1.2. Non-conventional processes	48
2.1.2.1 Ionic liquids	48
2.1.2.2 Microwave heating	51
2.1.2.3 Biological agents	51

## Section II

re work61
-----------

References
------------

## Abstract

Biomass has come into the focus of many researchers as a raw material for the production of food, fibers and fuel. The concept of biomass biorefinery to produce biofuel, bioproducts, and chemicals has been around for 70 years. The growing interest it has attracted is due to the depletion of fossil resources and the environmental pollution caused by petroleum-based polymers, which determine increasing demands for renewable resources. These are biodegradable and have low environmental impact and safety risks. On the other hand, national security and geopolitical aspects also play a significant role in the search for alternative energy and the use of sustainable and domestic renewable sources.

Section I consists of two chapters that shows the main components of biomass, their structure and properties. Also, the main methods used for their separation are presented. The main components of lignocellulosic biomass are cellulose, hemicelluloses, and lignin. Biomass includes hardwood, softwood, grasses, agricultural and forest residues, domestic and municipal solid wastes, as well as food industry residues.

Natural fibers provide an excellent reinforcement effect for thermosets and thermoplastics materials. Biohybrids based on starch as a blend component with polyolefins and compostable polyesters have been developed, while carbohydrates, terpenes or proteins are chemically modified and used in different applications. Microfibrillated cellulose has been used as a component of polymer nanocomposites, including applications in medical implants. However, converting lignin and hemicelluloses to fuel with high efficiency remains a much greater challenge.

The technical feasibility of producing various types of biofuels (e.g., ethanol, butanol, and hydrocarbon fuels) from biomass carbohydrates, particularly cellulose, has been well demonstrated. The biorefinery concept integrates both transformation processes and equipments in order to produce power, fuels and chemicals from biomass. The implementation of this concept is challenging because of technological limitations.

The generation of energy and biofuels and the production of value added products from lignocellulose processing is the key aspect towards an economic sustainability of biorefineries. Thus, total valorization of vegetal or animal biomass may lead to an improvement in the overall economics and sustainability of an integrated biorefinery, while the development of an effective utilization process for lignin is the key to success in the future biorefinery research. Lignocellulose biorefining should be a success due to the renewable character of lignocellulose, and to the resulting conversion products. The latter have a great potential to replace traditional petrochemical products and gain a secure position on the future bio-based product market. It must be mentioned that, in order to improve the potential of biomass components to be converted into materials that would penetrate new markets, the performance of these biopolymers must first be increased. Thus, the chemical or enzymatic modification of these biomass components is the best way to solve this problem and it is discussed in Section II. Cellulose, hemicelluloses and lignin can be used as component of different blends, composites or fibers. These materials can replace current analogues to overcome the environmental issues associated with petroleum -based products. Their applicability is determined by their behavior under the circumstances they are being used. Therefore, their careful assessment under different ambient conditions, as well as the study of the miscibility–compatibility–property relationships between components, is imperative.

Cellulose and other polymeric materials can also be blended prior to the electrospinning process to create hybrid fibers with new suitable properties. By different derivatization techniques, materials suitable for various applications, such as enteric coatings, hydrophobic matrices, and semi-permeable membranes to be used in agriculture, the pharmaceutical and cosmetics industries etc., could be obtained.

The dissolution of biomass and polysaccharides/lignin derivatization in ionic liquids to obtain new materials by new processing technologies, including blends, composites, fibers and ion gels is a great challenge. These materials can replace current analogs to overcome the environmental issues associated with petroleum-based products. However, the chemical versatility of both biomass components and ionic liquids will allow new developments, leading to the next generation of biomass based materials, which are expected to be produced in the near future. Different selective modifications of lignin are suitable to transform it into a complex material with valuable potential applications in the medicinal and pharmaceutical fields, where lignin-derived substances could be used as building blocks for the fabrication of microcapsules.

In order to assess chemical modifications and their implications, numerous experimental techniques, such as optical spectroscopy, electron microscopy, surface scanning, light scattering, magnetic resonance, mass spectrometry, X-ray diffraction, zeta-potential measurements, as well as thermal techniques and chromatography, will be used.

Building a high performance research team, establishing collaborative relationships with colleagues from our institute and from other organizations (research institutes, universities, small and medium-sized companies), promoting innovative ideas and developing a new and competitive research area represent altogether the guarantee of implementing the research projects to be developed in the coming years.