

LIGNOCELLULOSIC BIOMASS - NEW RESOURCES FOR BIOPOLYMERS PRODUCTION

Lăcrimioara ȘENILĂ^{1,*}, Eniko KOVACS¹, Daniela SCURTU¹, Lucian DORDAI¹,
Cecilia ROMAN¹

¹ INCDO-INOE 2000, Research Institute for Analytical Instrumentation ICIA Cluj-Napoca

* lacri.senila@icia.ro

Abstract: Lignocellulosic biomass is a renewable and abundant material that can be used as raw material to obtain biopolymers. In this paper, the production of carbohydrates from lignocellulosic biomass was investigated in order to obtain raw materials for biopolymer production. A technological methodology for polylactic acid (PLA) and polyhydroxyalkanoate (PHA) production from lignocellulosic biomass was proposed. The autohydrolysis pretreatment of peach orchards leads to carbohydrates separation at high temperatures (160, 180, and 200°C) and pressure (80 bar). The effect of pretreatment methods for carbohydrate production was evaluated. The structural characterization of lignocellulosic biomass, before and after pretreatment, was carried out by reflected light microscopy.

Keywords: Lignocellulosic biomass, biopolymers, pretreatment

1. Introduction

Considering the availability of fossil fuels and their impact on the atmosphere, i.e., the greenhouse effect, developing alternative renewable energy becomes imperative for sustainable development. Therefore, biomass becomes the major source of “green energy”. Lignocellulosic biomass is an abundant source, affordable, renewable, and available in large quantities, which received considerable attention as a promising alternative to fossil fuels [1]. Lignocellulosic biomass comes from the following sources: crop residues, wood, herbaceous biomass, agro-industrial residues, and vegetable waste. In recent years, biofuels and bioenergy production from lignocellulosic raw materials was considerably developed. In contrast, the production of chemicals and biomaterials from renewable raw materials remains limited [2,3]. The major components of lignocellulosic biomass, namely cellulose and hemicellulose, can be converted into bioethanol and bioplastics, whereas lignin can be converted into polymers. Cellulose is a complex consisting of 3000 or more glucose units, whereas hemicellulose is formed from pentoses (xylose and arabinose), hexoses (mannose, glucose, and galactose) and uronic acids. Lignin is a complex polymer consisting of three types of precursor alcohols: p-coumaric, coniferyl and p-synapic alcohols [4].

White biotechnology is an industrial biotechnology for durability, in which microorganisms or enzymes are used to produce fuels and chemicals from renewable resources. Biopolymers are biodegradable and non-biodegradable (fossil fuel). Biodegradable polymers are cellulose, hemicelluloses, polylactic acid, poly succinic acid, polyhydroxyalkanoates, gluten, and algal biopolymers [5].

The main components of lignocellulosic biomass (cellulose and hemicelluloses) need to be extracted and subjected to pretreatment and hydrolysis to obtain biopolymers.

Over the last few years, many pretreatment, hydrolysis, and fermentation methods have been developed, but each presents advantages and disadvantages. Most plastics start out as hydrocarbons derived from crude oil, the global plastic production extending every year. The growing production of petroleum-based plastics has a negative impact on the environment. Therefore, bioplastic innovation and research activities, which provide alternatives to conventional plastics are needed. In recent years, global innovative biopolymers such as polyhydroxyalkanoates (PHA), polyhydroxy butyrate (PHB) and polylactic acid (PLA) have been the most used alternatives. The production of biopolymers from lignocellulosic waste consists of four steps:

2.2. Sample description

The lignocellulosic biomass samples were purchased from the Research Station of the University of Agricultural Sciences “Ion Ionescu de la Brad” from Iași, farm no. 3 „Vasile Adamachi” (Romania). The samples were collected immediately after the cutting operations of peach trees, dried and shredded to a diameter of 0.2 mm.

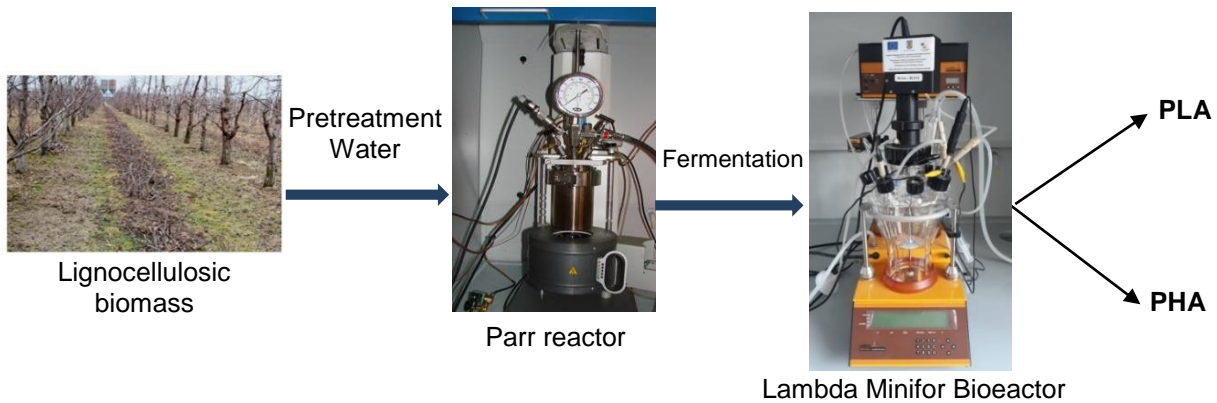


Fig. 2. Schematic representation of the technological approach of this paper

2.3 Pretreatment of lignocellulosic biomass

The pretreatment method was carried out according to our recent publication [4]. Carbohydrates were extracted at three different temperatures (160, 180, and 300°C) for 15, 30, and 45 min. At the end of the experiments, the solids and liquid samples were collected and separated by filtration. Cellulose, lignin, and hemicellulose content was determined according to the reference [12].

2.4 Structural characterization of lignocellulosic biomass by using reflected light microscopy

The lignocellulosic biomass, before and after pretreatment, was characterized by a reflected light microscope (Kern OKN-1, Germany). The microscope is an infinity optical system and has a 50 W halogen incident illumination unit. The samples were analyzed by a light microscope at up to 40 x magnification.

3. Results and discussion

The chemical composition of lignocellulosic biomass (peach orchards) used in this study is presented in Table 1. Cellulose is the most abundant component of lignocellulosic biomass (30.8 ± 0.8%). The moisture content was 10%. The high content of holocellulose (57.1%) recommends the peach orchard biomass as raw material for bioplastic production.

Table 1: Chemical composition of lignocellulosic biomass (peach orchards)

Component	Amount (% w/w)
Cellulose	30.8 ± 0.8
Hemicelluloses	26.3 ± 0.4
Lignin	29.5 ± 0.3
Ash	2.5 ± 0.01
Extractables	1.3 ± 0.01

When synthesizing biopolymers such as PHA and PLA from lignocellulosic biomass, the first step is to obtain carbohydrates. The use of autohydrolysis pretreatment for the separation of cellulose from lignocellulosic biomass led to hemicellulose solubilized in liquid fraction and cellulose and lignin separated in the solid fraction. The separation of biomass components depends on the pretreatment method used.

Pretreatment with water at high temperatures and pressure is an ecological pretreatment that uses as solvent only water. The efficiency of the pretreatment depends on temperature, time, and pressure. The mechanism involves the formation of hydrogen ions that act as Lewis acids. Humidity can generate carbonic acid, which improves the hydrolysis of hemicelluloses in the liquid phase [8]. The experiments were carried out at different temperatures (160, 180, and 200°C), reaction times (15, 30 and 45 min), and the same pressure (80 bar). The chemical composition of the solid fractions resulted after the pretreatment are presented in Figure 3 (a-c).

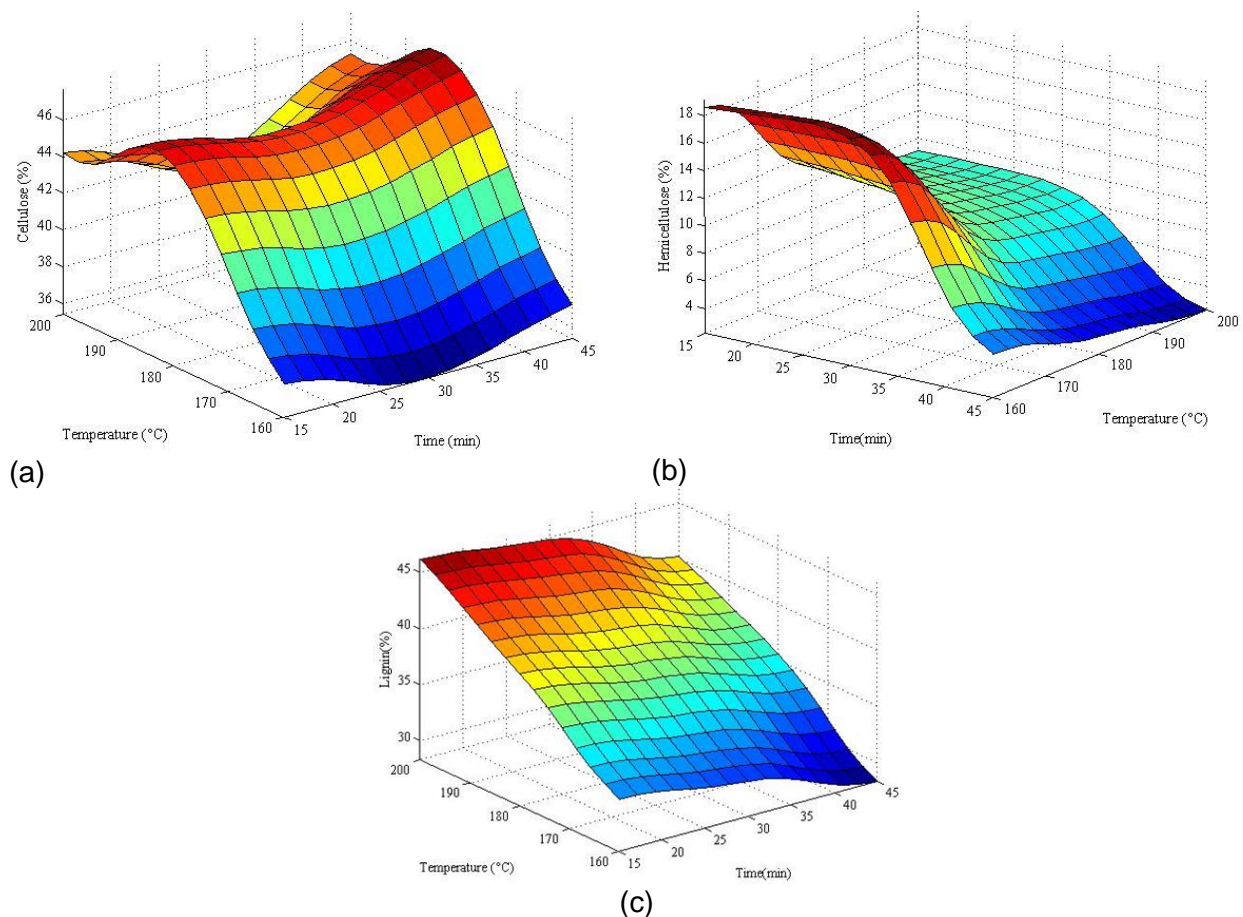


Fig. 3. (a) Content of cellulose, (b) hemicelluloses and (c) lignin in solid fraction separated after pretreatment, at different conditions

The solid yield of the fraction recovered after pretreatment varied between 55.2 -70.1%. It decreased with the temperature increase and reaction time. This is caused by the solubilization of the hemicellulose in the liquid fraction. The solid fraction composition was analyzed after each experiment to determine the cellulose, hemicellulose, and lignin content. The cellulose content ranged from 32.0 to 45.1/100 g of pretreated biomass, while the lignin content ranged from 35.0 to 48.1/100 g of pretreated biomass. The hemicellulose content decreases with the temperature increase and reaction time from 15 min to 45 min. Autohydrolysis pretreatment can separate cellulose from lignocellulosic waste, which can be used as a raw material in the production of bioplastics. For a maximum efficiency of cellulose, the separation is recommended as a pretreatment of lignocellulosic biomass, at a temperature of 180°C for 30 minutes.

Structural characterization of lignocellulosic biomass by using reflected light micrographs

Autohydrolysed biomass has a different texture than untreated biomass. The structure of the untreated biomass shows resistance, while the autohydrolysed structure indicates degraded biomass after the pretreatment. Untreated biomass structure is rigid and has longitudinal sections and a fibrous structure, whereas the treated biomass shows crystalline form. Reflected light microscopy confirms the efficiency of the autohydrolysis pretreatment.

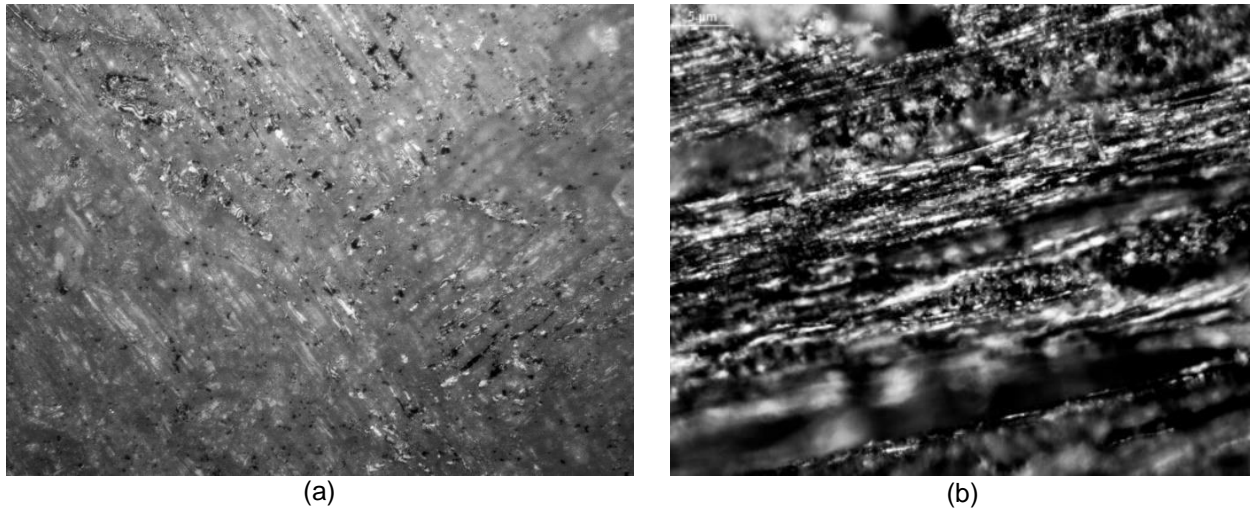


Fig. 4. Reflected light micrographs of the: (a) untreated (b) pretreated biomass (180°C, 30 min)

Technological approach proposed

The obtained cellulose could be further used for PLA and PHA production. The technology of obtaining PLA from cellulose will contain the following main steps: (i) enzymatic hydrolysis of cellulose and simultaneous fermentation with specific bacteria for the production of lactic acid; (ii) purification and separation of lactic acid from the fermentation medium; (iii) lactic acid polycondensation with the PLA obtainment and (iv) separation and characterization of the obtained PLA bioplastic (Figure 5).

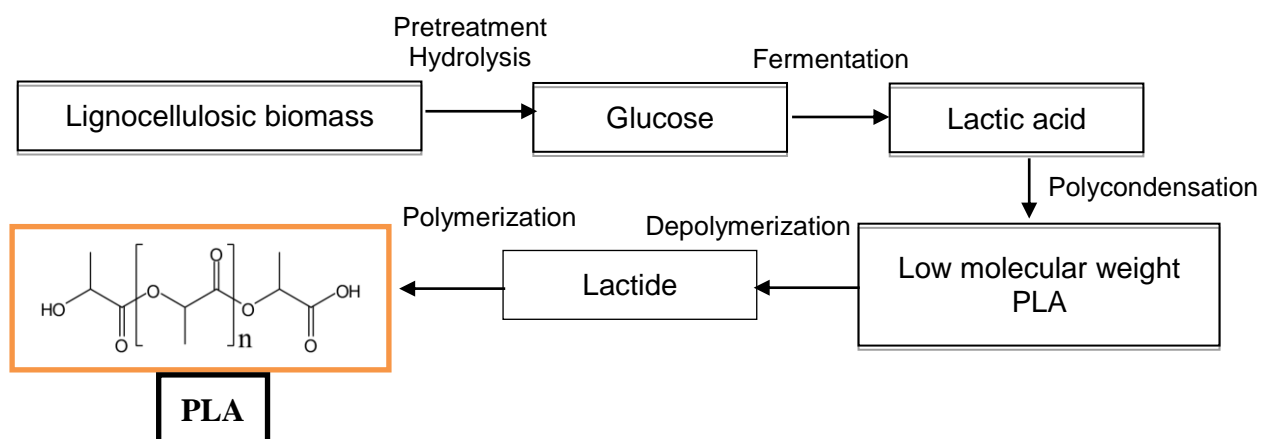


Fig. 5. Schematic representation of the biosynthetic pathway for the production of PLA from lignocellulosic biomass

The technology of PHA production from lignocellulosic biomass contains the following main stages: (i) fermentation with specific bacteria for direct production of PHA, (ii) purification and separation of PHA from the fermentation medium and (iii) characterization of the obtained PHA bioplastic.

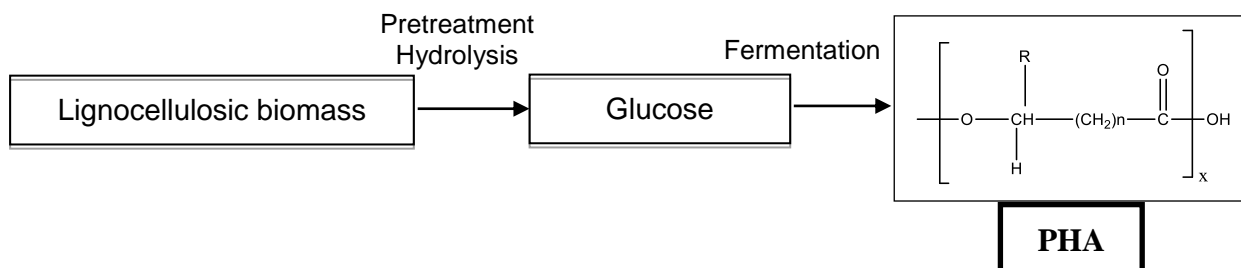


Fig. 6. Schematic representation of the biosynthetic pathway for the production of PHA from lignocellulosic biomass

4. Conclusions

Extraction of carbohydrates from lignocellulosic biomass was performed using an autohydrolysis pretreatment. The lignocellulosic biomass used in this study has a high content of cellulose and hemicelluloses, recommended as raw material for bioplastics production. Two new technologies for bioplastics (PLA and PHA) were proposed.

Acknowledgments

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