Conference paper

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# Modern supercritical fluid technologies for the processing of plant biocomposites: theory and practice

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**Abstract:** The biochemical processes of synthesis and self-organization of the components of the lignin-carbohydrate matrix lead to the formation of a complex multi-component system considered as a nanobiocomposite, which is a thermodynamically limited ordered system of biopolymers in *quasi*-equilibrium. The concept of the thermodynamic state of the lignin–carbohydrate matrix and the possibility of regulating the areas of thermodynamic compatibility of components due to chemical and/or physical impact allow to consider the supercritical fluid technologies (SCFTs) as a tool for directing changes in the biocomposite's structure and properties at the molecular level and also as a way of creating essentially new technologies for the complex processing of plant raw materials.

**Keywords:** biopolymer; green chemistry; ICGC-7; nanobiocomposite; supercritical fluid technologies; wood matrix.

## Introduction

The priority trend of development of economic activities is an increasing demand for the involvement of renewable plant raw materials as one of the main types of natural resources. This is a result of the gradual depletion of mineral and hydrocarbon raw materials and the special chemical composition of biological objects, which are used as sources of valuable products with unique consumer properties. At the same time, one of the priorities of the European and Russian "Forest Technology Platform" (as part of the platform "BioTech 2030") [1] is the bio-refining of wood. This is the production of high-value-added products on the basis of complex deep processing of forest resources directly in the region of growth, including the combination of forest plantations (in particular plantations of accelerated growth) with agricultural production. In addition, it is necessary to take into account the fact that global processes related to climate change have led to a significant change in the species composition of the plant world, expressed in the predominance of higher deciduous wood species over conifers. As a result, there is an urgent need to create and implement modern environmentally friendly technological solutions [2] focused on the complex processing of various types of plant raw materials, such as coniferous and deciduous wood, wood greenery, bark, sawmill waste, and so on. In this case, the development of technological solutions must take into account the complexity

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of the macro- and microstructure of wood matrix formed during the biosynthesis of major components of biomass, the characteristic features of the chemical nature and properties of components and their distribution in wood substances, and the formation of intermolecular and intramolecular bonds and complexes [3].

## Overview of current state

When evaluating the current state of the chemical technologies of wood processing, it can be stated that the main solutions were developed nearly two centuries ago and were associated with the separation of biomass into components under high temperatures and aggressive chemical environments. Nowadays these technologies have undergone some changes, although not drastic ones. These changes were connected with increasing the ecological safety of production and the quality of pulp and paper products produced at the pulp and paper mills. At the same time, a breakthrough in this field is possible only with a new interdisciplinary approach to considering the structure and properties of wood substances as an object of fundamental (chemistry of natural compounds; biology and biochemistry; organic, physical, and analytical chemistry; polymer chemistry, etc.) and applied (engineering) sciences and the principles of “nature-like” technologies. This statement can be explained as follows. Historically, the wood matrix was considered as a “reinforced concrete”, that is, as a composite where the cellulose acts as reinforcement and the lignin–carbohydrate complex acts as a filler [4]. Subsequent studies have clearly shown that the important feature of the plant biomass is that its composition is made of not only two of the most common native polymers – cellulose and lignin – but also their unique complex. The formation of this complex takes place at the nanoscale during the process of radical dehydrogenative polymerization of monolignols under the action of plant enzymatic systems and obeys the laws of deterministic chaos.

The peculiar features of the biosynthesis of the main wood matrix biopolymers and the formation of their functional nature and structure determine the complex hierarchical organization of cell walls [5]. The plant cell walls are diverse in composition and structure: the cell wall polymers may differ in different parts of the same cell, the same organism or, especially, different types of plants. The molecular level of the organization allows the properties of an individual polymer to be explained, depending on the characteristics of the chemical structure. Consideration of the supramolecular level involves the interaction of the cell wall components. On the one hand, these are the issues of the dynamics of cell-wall synthesis and the self-organization processes that control the formation of chaotic objects of biological origin. On the other hand, the interaction of the plant cell wall components is a question of their thermodynamic compatibility.

Thus, the biochemical processes of synthesis and self-organization of the components of the lignin–carbohydrate matrix lead to the formation of a complex multi-component system considered as a nano-biocomposite, which is a thermodynamically limited ordered system of biopolymers in *quasi*-equilibrium [6].

The proposed concept of the thermodynamic state of the lignin–carbohydrate matrix [7] and the possibility of regulating the areas of thermodynamic compatibility of components due to chemical (selective solvents, catalysts of redox reactions, oxidizing agents, enzymes, etc.) and/or physical (supercritical and subcritical fluid state, steam explosion, ultrasonic and microwave processing, etc.) impact [8] allow us to consider the supercritical fluid technologies (SCFTs) as a tool for directing changes in the biocomposite’s structure and properties at the molecular level and also as a way of creating essentially new technologies for the complex processing of plant raw materials [9].

Analysis of publication activity in scientific journals reveals a constant interest in the use of SCFTs for solving various scientific, technological, and technical problems. There were more than 7600 publications in Chemical Abstracts, 17 840 in Science Direct, and 937 in Web of Science during the period from 2006 to 2013. About a third of the works were devoted to the use of SCFTs for the processing of renewable plant raw materials and the modification of biopolymers to obtain a wide range of target products.

Nowadays, SCFTs are used to produce extracts of lower plants and medicinal, low-tonnage, pharmaceutical, and cosmetic preparations [10, 15] both in Russia and abroad. Another promising object for SCFTs is seaweeds. The high content of biologically active substances in the macrophytes that are effective in the treatment and prevention of a wide range of diseases explains the interest in seaweed. Thus, the supercritical extracts of the lipid-pigment complex of Arctic brown algae contain a significant amount of fatty acids including polyunsaturated omega-3 (eicosapentaenoic and stearidonic) and omega-6 (linoleic and arachidonic) acids and polyphenolic compounds [11].

The use of SCFTs for processing wood and its components should be developed in the following directions: creation of methods for the delignification of plant raw materials; modification of lignin and cellulose and processing them into other products; hydrolysis of plant raw materials and saccharification; production of biofuel and ethanol; extraction of various components from plant raw materials; production of low molecular weight chemicals; and processing of organic waste.

Let us look through the some examples of their implementation.

One of the important aspects of the development of SCFTs for the processing of plant wood raw materials is the possibility of application of supercritical processes for the technologies of deep delignification of wood to obtain the pulp and modify the main components of the wood – lignin and cellulose.

As a prototype of SCFTs in the chemical processing of wood, one can consider the steam explosion (SE) of wood biomass (alternatively called steam cracking or flash-autohydrolysis). Mason (the Masonite process) first performed steam explosion in the 1930s in the US. The essence of the method lies in short-term (from several seconds to several minutes) processing of wood sawdust or wood chips by heated water vapor in the temperature interval of 180–260 °C at corresponding pressures of the saturated steam of 1.2–3.4 MPa followed by a sharp decrease to atmospheric pressure [12]. According to modern concepts, the mechanism of action on the plant matrix during the steam explosion is the reaction of deacetylation of hemicelluloses at increased temperatures with the formation of acetic acid, as well as the generation of formic acid with sugar decomposition. These organic acids act as the catalysts of weak-bond hydrolysis in the lignin–carbohydrate matrix of wood and degradation of hemicelluloses. According to the physico-chemical model of the structure of wood substance [7], the weak-bond hydrolysis leads to a change of the phase state, delamination of the cell wall components, and an increase of the thermodynamic incompatibility of the system because of the destruction of the supernetwork between the lignin and carbohydrates. Besides, the steam explosion affects the diffusion regions in the cellulose microfibrils. As a result, the microfibrils are destroyed; the degree of polymerization decreases, the degree of cellulose crystallinity increases, and the coalescence and partial depolymerization of lignin with the formation of low molecular weight compounds (six to eight phenylpropane units) take place.

The listed processes, apparently, occur in the processing by supercritical (SC) $CO_2$, in which the main constituents of the actions are also the addition of the solvent and increased temperature and pressure. The absence of delignifying ability of pure SC $CO_2$ necessitates the addition of modifying additives [13]. The mechanism of chemical reactions during SC-processing is determined by the action on weak chemical bonds; it can be considered similar to the mechanism of the processes during SE [14].

The low-temperature oxidative delignification of fir wood (operating temperature: 100 °C) [15], including the thermal treatment of raw material in the presence of SC $CO_2$ and $H_2O_2$ as the oxidizer, makes it possible to obtain an intermediate product having greater whiteness and increased strength properties in comparison to the coniferous kraft pulp. Extraction with the use of SC $CO_2$ can be applied to expand the raw material sources, for example, to non-wood raw materials such as straw and bamboo [16].

Another intensively developed direction of SCFTs is modification of plant biopolymers, based on the principles of thermodynamic *quasi*-equilibrium of phases in solid and solvated in solvent states.

Lignin is the second most abundant natural material on the Earth, accounting for a quarter to a third of the entire plant biomass. Nowadays, economic possibilities have opened up for creating new technologies for lignin applications and the production of valuable products with high yields. The modification of lignin is reduced, as a rule, to action on carbon–carbon bonds with the destruction of the spatial network that leads to oxidative fragmentation of lignin and the formation of valuable low-molecular weight compounds [17, 18].

The works on production and application of cellulose esters can be separated into individual and sufficiently scaled directions of cellulose modification with the use of the SCFTs. Therefore, for example, one of the products of esterification, cellulose carbamate, is an ecologically safe material that represents a good alternative to oil-based polymers due to its renewability, biodegradability, and solubility in simple solvents

[19, 20]. The other very common ether of cellulose is ethyl cellulose, which can be applied, for example, in systems for prolonged drug delivery [21]. Apart from the production of esters, other types of cellulose modification include the production of aerogels, hydrogels, and other products based on cellulose materials [22].

A significant number of works published in the area of supercritical processing of plant raw materials are dedicated to the hydrolysis of cellulose and hemicelluloses and saccharification [23]. In comparison with the conventional techniques of acid hydrolysis and enzymatic saccharification, supercritical hydrolysis technology has advantages such as high efficiency, easy processing, and environmental safety. It is possible to use steam explosion as a pre-treatment before SC-hydrolysis for a wide range of plant materials such as hard and soft wood, wastes from the forestry and wood processing industries, sugar cane, cellulose, artificial fibers based on cellulose, straw, and spruce bark.

In addition to the lignocellulosic raw materials, algae biomass, for example, *Chlorella* sp. [24], preliminarily dried in SC $CO_2$, is a promising source for ethanol production. Green algae are dried for 40–60 min at low temperatures (40 °C). Subsequent fermentation of raw materials is performed in the presence of cellulase, α-amylase, glucoamylase, and the yeast *Saccharomyces cerevisiae*. The advantages of this method are the increased ethanol yield and the reduction of losses of polysaccharides contained in algae.

The production of different fuel types (including biodiesel) is another promising area of plant biomass processing [25]. As such fuels are renewable, sustainable, and environmentally friendly, researchers often suggest them as an alternative to petrol and diesel. SCFTs are promising technologies for future large-scale fuel production, especially from wastes from forestry and agricultural industries. Compared to conventional methods of biofuel production, SCFTs have several advantages such as fast reaction kinetics, high capacity, and lack of a need to use catalysts. The main factors that limit the application of SCFTs in this area are the tough conditions of the process and high requirements for the raw materials.

## Conclusions

The results presented in this report clearly show the prospects for the development of modern methods of complex processing of plant raw materials based on the principles of “green” chemistry and “nature-like” technologies. At the same time, the fundamental factor in the successful solution of technological problems is the application of the laws of the fundamental cycle of “structure – functional nature – properties” for characterization of both individual biopolymers and plants as nanobiocomposites. From this point of view, the most promising route is the supercritical fluid technologies. However, the development of supercritical technologies is still in the process of being established. Therefore, their wide implementation in practice requires both the optimization of the technological solutions and fundamental research into the mechanism and kinetics of ongoing processes.

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