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Review

Chemicals and value added compounds from biomass using sub- and supercritical water

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ABSTRACT

Review summarizes the research on the biomass conversion for production of chemicals and an overview on recent activities of our research group on isolation of substances from biomass using sub- and supercritical water. Herein, hydrothermal processing of biomass waste represents an alternative approach to upswing the productivity chemicals, basic chemicals for synthesis and plant-based pharmaceutical compounds. The processing concepts to obtain products and product classes based on biological raw materials in gaseous, liquid, or solid state are presented. Subcritical water is discussed as a highly reactive media to enhance extraction affinity of value added compounds, such as proteins and amino acids, essential oils, oils and fatty acids, carbohydrates and phenolic compounds from natural sources.

1. Introduction

Development and implementation of sustainable processing concepts promotes reuse of residues of biomass according to a basic concept of biorefineries. This concept comprises extraction of source material and further conversion of residues to a wide range of useful products such as second generation biofuels, base chemicals, biospecial chemicals and bioefficient materials. Partially, the main impetus for this conversion, beside nuclear energy technologies which are also viewed by many researchers and politicians as long term solutions, is driven by a concern to the environment to reduce consumption of conventional solvents and energy. Only renewable biomass has the ability to directly generate hydrocarbon-based liquid fuels that could approach carbon neutrality. Across the full life cycle of these biofuels the net energy balance and environmental impact are changing depending on many factors, but are marginally favorable at best [1]. Their composition varies depending on the type of biomass feedstock, research is focused towards utilization of residues consisting of lignocellulose or fatty acids or oils; and conditions of the process. In advance, high pressure is a tool to design and produce products with completely new specifications by applying available and affordable compounds, such as CO_2, water, ethane, propane and others, as solvents in their sub or supercritical state. Water is known as the cheapest solvent that changes its physicochemical properties dramatically from a solvent for ionic species to a solvent for non-ionic species. Electrochemical properties, e.g. dipole moment decreases from the high value at ambient conditions, but water in the critical region is still as polar as acetone. Reactivity of water increases in the neighborhood of the critical point without as well as with a catalyst [2]. Water has been purposed for treatment of residues, derived from several industrial plants, agriculture and municipal wastes. Hydrothermal conversion of biomass has attracted considerable attention. The increasing global demand for biomass of medicinal plant resources reflects the issues and crisis created by diminishing renewable resources and increasing consumer populations. Extensive research on the hydrothermal conversion of organic waste and low-value organic materials into fuels and chemicals has demonstrated that hydrothermal reactions can convert various natural organic materials directly and efficiently into useful chemicals [3], synthetic organic materials like plastics into oil and ultra-heavy crude oil like bitumen into light oil.

At modest temperatures, ionic and polar species will be extracted. Nonpolar compounds can be dissolved and extracted at higher temperatures and pressures, in the proximity of critical point [4].

Due to the high reactivity, hot pressurized water is frequently used as reaction medium, which is above all, totally environmentally benign. The reactions taking place are commonly summarized as “hydrolysis reactions”. The conversion of glycosylated phenolic compounds (antioxidants) into their respective aglycones after the extraction process represents a side process that allows numerous advantages, especially in later stages of the separation process [5,6].

Whilst supercritical water is currently mostly used for decomposing of harmful substances like polychlorinated biphenyls and sodium sulfate and for treatment of municipal organic waste, on the other hand, subcritical water is employed for milder hydrolysis reactions. In its

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subcritical state, water has been demonstrated to effectively convert cellulosic and proteinaceous biomass such as meat, silk fibroin powder and baker's yeast into useful products [7]. For total extraction of the proteins, near critical and supercritical water has been examined to potentially hydrolyze deoiled byproducts of ceral milling and bran oil industries, into more valuable proteins and amino acids. Protein and amino acids production is strongly influenced by temperature. For protein it increases with an increase in temperature, while that of amino acids decreases with increasing temperature [8].

Water's dielectric constant as a measure of its polarity drops considerably with increasing temperature and pressure; from value 80 at ambient temperature and pressure to value 5 at critical point. At high pressures water becomes a suitable solvent for simple organic compounds. Solvation properties are tuned also by temperature. Gases like nitrogen, air and oxygen, carbon dioxide, hydrogen and methane are completely miscible with supercritical water [1]. Hydrothermal processing of biomass waste represents an alternative approach to upswing the productivity of plant-based pharmaceutical compounds. In the frame of our recent research, water in its subcritical state has been investigated as a green and environmentally friendly extraction medium for the isolation of phenolic compounds from different types of plant materials [9–11].

Using hot pressurized water, lipids and proteins could be extracted. Subcritical water extraction is an alternative and greener processing method for removal of oil from oilseeds.

Simultaneous extraction of oil- and water-soluble phase from sunflower seeds with subcritical water has been carried out by Ravber and co-workers [12,13]. Antioxidant activity of the obtained extracts has increased considerably compared to the one of extracts, obtained by conventional extraction procedures. The most probable explanation is that hydrolysis of ester and glycoside bonded antioxidants occurred, which produced oils with high antioxidant capacities [12].

Advantages of processing at hydrothermal conditions instead of using conventional hydrolysis media are numerous. Yields of the desired product, higher than 90% could be obtained at relatively mild hydrothermal conditions, temperatures lower than 200 °C and pressures about 200 bar. Compared to the conventional extraction processing, short reaction times are required [13–15].

In supercritical state, water offers excellent transport properties due to its high diffusion ability and low viscosity, a control mechanism depending on solubility and new reaction possibilities for hydrolysis and oxidation [16]. The process of destructive oxidation of organic waste is commonly termed as Supercritical water oxidation (SCWO). In the presence of oxygen, organic waste, which is highly miscible with water at these conditions, reacts to carbon dioxide, water, and some other small molecules. Partial oxidation of organic molecules, for example of methane to methanol, can be achieved by a proper selection of operating conditions (temperature and pressure) as well [17].

Supercritical water oxidation is an environmentally acceptable technology which produces a disposable clean liquid (pure water), clean solid (metal oxides, salts), and clean gas (CO_2, N_2) [18]. Therefore, the technology can be classified as green chemistry according to the sustainable development. At high temperature in a dense, single phase environment, oxidation reactions are rapid and complete in supercritical water [19].

Operating at high pressures may result in processes that require much lower amounts of energy and maybe also in new processes which are capable of performing new types of reactions that produce completely new bio-based products. The production of value-added products from waste biomass, such as waste from agriculture, food or forestry industry is a topic of the intense research which tends to reduce the operating temperature and energy requirements by processing biomass with water at much higher pressures or adding supercritical CO_2 to the reaction mixture.

Another possibility is lowering the energy barrier by the addition of catalysts. Such treatment of biomass would be a completely new process. However, the data on the mechanisms and kinetics of reactions are scarce. Additionally, the total yields of the final products are practically unknown for these unconventionally high-pressures and temperatures for the multi-component systems.

Considering the above mentioned facts, it is highly important to investigate how water and CO_2 in such a system would affect the biomass conversion reactions and what products would form, how different ratios and conditions affect the conversion and if it is possible to perform the reactions that normally occur above critical point at milder conditions. This knowledge will open completely new possibilities in biomass conversion, which could also lead to new types of reactions and products [6,20].

Limitations of processes operating at the mentioned high temperatures and unconventionally high pressures are their investment costs that are significantly higher compared to ambient pressure technologies. Nevertheless, many recent studies have suggested that classical large-scale reactors needed for biomass conversion are maybe not necessary for processes involving supercritical water as reaction medium. It has been proven, that reaction kinetics of near-critical water and supercritical water with organic compounds are extremely fast and that long contact times should therefore be avoided.

This contribution is a review on the waste biomass conversion for production of chemicals and an overview on recent activities of our research group on isolation of substances from biomass using sub- and supercritical water at pressures up to 1000 bar.

2. Chemicals from biomass

Even if the switch from crude oil to biomass is not as simple as it first appears, significant developments have been achieved in the field of biomass-derived chemicals and materials over the last two decades. The driving force for the research was enhanced by the idea of using sustainable non-depleting resources and the application of more environmentally benign synthetic methods. Chemicals produced from biomass contain greater functionality than those derived from the fossil fuels. That could be explained from the fact that biomass is a complex feedstock for production of fine chemicals due to its chemical composition that varies by species, season and location and also contains substantial number of heteroatoms.

Development of new technologies for hydrolysis of lignocellulosic feedstocks and fermentation of the resulting sugars to a variety of chemicals is based on intense research carried out in the past decades. Investigations are yielding advances in protein engineering, synthetic biology and metabolic pathway engineering [21]

An overview on the use of different types of biorenewable resources in the 21st century for production of chemical products, materials and energy has been published by Clark and Deswarte in 2015 [22]. Particularly lignocellulosic, organic waste and algae dominate as feedstock [23].

Water in proximity of its critical point recently received considerable attention especially as a reaction medium for reforming wastes and by-products, being attractive from an environmental point of view. The method is sustainable and is able to convert very wet biomass (up to 90% water content) and liquid streams to gases or other bio-based chemicals. By applying this method residues from different industries can be further used to obtain value added products. Problems related to waste disposal after domestic and industrial wastewater treatment, wastes from oil and biodiesel industry and wastes from food, biomass processing and chemical industry can be minimized or even avoided. Sub- and supercritical fluid reforming is based on the capacity of this media to hydrothermally degrade organic compounds via different reactions (hydrolysis, dehydration, carboxylation, aromatization etc.), leading to the formation of bio-oils, liquid compounds and gases. Obtained products can be further used as raw materials in chemical reactions or as energy carriers, thus improving the overall economic efficiency of the industrial process [3].