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Pressurized fluid systems: Phytochemical production from biomass

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ABSTRACT

Pressurized fluids, such as subcritical water, pressurized aqueous ethanol and pressurized aqueous ionic liquids, are considered as environment-friendly solvents that can be used for the production of phytochemicals from a variety of biomasses. Phytochemicals, such as phenolic acids and carbohydrates, have innumerous applications in the food, pharmaceutical and other industries. In this study, the current status of pressurized fluids and production of phytochemicals are presented. Research in our laboratory has focused on the use of pressurized fluids to obtain phytochemicals from potato peel, lentil husk, barley hull, lupin hull, among others to later be used in some applications. Experiments with pressurized fluids were performed using a dynamic flow high-pressure system at different temperatures, pressures, time, static holding time and pH. Results indicated that the total phenolic and carbohydrate contents and antioxidant activity of these biomass systems increased with temperature. The optimum phytochemical production and total antioxidant activity of each biomass were obtained using specific pressurized fluids. For example, the highest carbohydrate extraction from barley hull was obtained using pressurized aqueous ethanol, but this pressurized fluid was not the best for phenolics removal. Then, pure phenolics were used in two applications: enzymatic synthesis of ferulic acid in flaxseed oil in SC-CO_2 media and added to milk to retain valuable components using high pressure processing assisted by temperature. Important reaction pathways for specific systems were also discussed. Phytochemical production from selected biomasses using pressurized fluids and its uses in reactive system applications were demonstrated.

1. Introduction

Phytochemicals are produced by plants and comprise a number of compounds, such as phenolics (flavonols, anthocyanins, catechins), polysaccharides (sugars, starch, hemicellulose, cellulose) and others (alkaloids, essential oils, *etc.*). Phytochemicals, such as phenolic acids, have antioxidant and antimicrobial activities and their consumption have been correlated with a lower incidence of cancer, heart disease, and diabetes. Polysaccharides are also considered important phytochemicals that can be used in a number of food, pharmaceutical and fuel applications like bioethanol. These phytochemicals are found in fruits (grapes, mango, pomegranate, citrus fruits), vegetables (cabbage, potato, onion, peppers), cereals (barley, rice, flax) and herbs (green tea, rosemary, oregano, ginseng).

Phytochemicals have been commonly obtained using conventional extraction methods with petrochemical solvents, such as methanol, ethyl acetate, chloroform and others, which require their complete removal by a subsequent evaporation process before being used as nutraceuticals or ingredients for the food, cosmetic and pharmaceutical industries. Government regulations on the use of organic solvents are getting stricter and the safety of these residual solvents in the final products is being questioned. Emerging pressurized fluid technologies use green and environmentally friendly solvents, such as subcritical water (sCW), pressurized aqueous ethanol (PAE) and supercritical CO_2 (SC-CO_2) that can be utilized for production of phytochemicals from a variety of biomasses. The use of SC-CO_2 has been extensively reviewed and discussed [1]. But, there is limited information on the use of subcritical water technology and other pressurized fluids. Brunner [2] has well discussed and reviewed principles and phase behavior of subcritical fluids as well as its potential for hydrolysis. Studies that used subcritical water technology include extraction of bioactives, such as damnacanthal from roots of *Morinda citrifolia*, shikimic acid from *Illicium verum* [3,4], and flavor compounds from *Rosmarinus officinalis* [5]. Even though the use of pressurized fluids like water had an advantage of short extraction time, the formation of aldehydes and browning compounds in some extracts cannot be avoided. For example, Qui and Xiuyang [6] reported that batch pressurized water reaction at 10 MPa, 180 °C and 30 min converted ~10% of glucose to 5-hydroxymethylfurfural. The amounts of aldehydes and browning compounds in the extracts have also been

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Nomenclature

Abbreviations

BHT	butylated hydroxytoluene
GAE	gallic acid equivalent
GRAS	generally recognized as safe solvent
HD	hydrodistillation
IL	ionic liquid
sCW	subcritical water
HMF	hydroxymethyl furfural
PAE	pressurized aqueous ethanol
PAIL	pressurized aqueous ionic liquid
PLA	polylactic acid
SC-CO_2	supercritical CO_2
P	pressure (MPa)
R	ratio
T	temperature (°C)

Symbols

ε	permittivity
pKw	ionic strength

measured at absorbance values of 294 and 420 nm, respectively [7]. In addition, to increase the extraction of phenolics, and minimize oxidation compared to aqueous ethanol solutions, the mixture ethanol + water + CO_2 has been reported [8]. Recently, pressurized aqueous solvents like neoteric ionic liquids (ILs) with low melting point, high thermal stability and negligible vapor pressure have been used [9].

Research in our laboratory has focused on solubility determination of selected phenolic acids and sugar compounds in pressurized water [10,11] as well as the use of pressurized fluids to obtain these phenolics and carbohydrates from Canadian biomasses. For solubility of selected phenolic acids and selected sugars in pressurized water, experimental data were obtained at pressures of 1.5–12 MPa and temperatures of 100–180 °C using a dynamic flow high pressure system. Results indicated that solubility of glucose and lactose in pressurized water increase with an increase in temperature but the opposite occurred with the increase of pressure from 1.5 to 12 MPa [10]. Dissolution of selected phenolic acids in pressurized water increased, remained stable (gallic acid) or decreased (3-4-hydroxyphenyl propionic acid and 4-hydroxybenzoic acid) with an increase of temperature [11]. Phenolics and carbohydrates were obtained from potato peel, lentil husk, barley hull, among others through extraction, fractionation, reaction and combination of these unit operations [9,12–14].

The main objective of this review is to provide the current status of subcritical water technology, an overview for the production of phytochemicals from biomass using pressurized fluids and, discuss future trends and perspectives of upcoming potential applications of pressurized fluids as a commercial technology.

2. Current status of pressurized fluids and phytochemical production

Over the past decade, pressurized fluid systems have been used to obtain phytochemicals from different plant matrices without shortcomings associated to conventional techniques, such as large amount of noxious solvents, extended extraction times and further complex separation procedures [15–17]. In general, pressurized fluids at high pressure and temperature have shown to induce higher solubility of chemicals as well as to improve the mass transfer rate, leading to short extraction times and high extraction yields. Hence, due to the particular physicochemical properties of

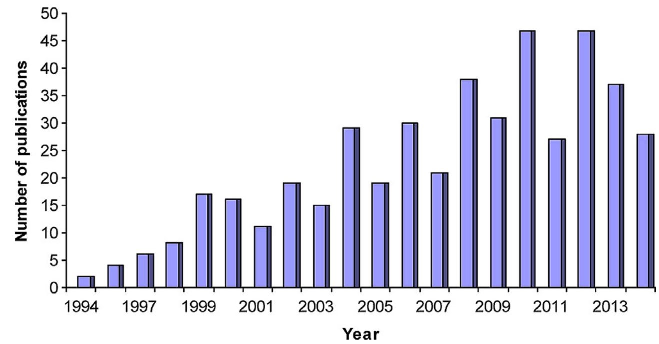

Fig. 1. Number of scientific publications on subcritical water extraction from 1994 to 2013.

pressurized fluids, generally recognize as safe solvents (GRAS) are commonly used for phytochemical production [14,17,18]

The extraction of phytochemicals with pressurized fluids can be approached at either supercritical or subcritical conditions. The use of supercritical fluids as the extraction media of bioactive compounds from a variety of medicinal plants and agricultural co-products has been widely reported. In 2003, more than 70 relevant studies were compiled by the International Society for the Advancement of Supercritical Fluids (I.S.A.S.F) [19]. Moreover, in the past decade, almost 300 new different plants have been studied using supercritical solvents, such as CO_2, ethane and propane [1]. Although supercritical fluids are considered as safe and environmentally friendly solvents, their affinity for non-polar components often requires the addition of a co-solvent like ethanol [1,20]. On the other hand, the use of pressurized fluids at the subcritical state, mainly water and water + ethanol, has shown to be effective when extracting both polar and non-polar chemicals from different matrices [4,9,12,14,21–26].

Subcritical water or pressurized hot water is defined as water in the liquid state under pressure (0.2–21 MPa) and temperatures higher than its boiling point (100 °C) but below its critical temperature (374 °C). At subcritical conditions, the hydrogen-bonded lattice of water is disrupted and its physical and chemical properties are modified [27]. Hence, in this condensed state, the diffusivity, permittivity, viscosity, density and surface tension of water can be tailored to induce solvency of a variety of compounds. For example, when water is heated up to 220 °C, its permittivity (ε) dramatically decreases (Table 1) and leads to a value close to that of organic solvents, favoring the extraction of non-polar components at higher temperatures but polar components at lower temperatures [17,27].

Subcritical water has been used in a wide range of applications since it was first reported in 1994 [28]. The extraction of polycyclic aromatic hydrocarbons, herbicides and pesticides from soil and sediments as well as the extraction of flavors, fragrances and therapeutic compounds from plants and food has been earlier described [15,27,29–31]. According to the Web of Science database, the number of articles and reviews published on subcritical water technology has increased exponentially in the last decade. Figs. 1 and 2 show the number of scientific publications and the growing areas of research on subcritical water extraction from 1994 to 2013, respectively.

According to Fig. 2a, Food Science and Technology is one of the most prominent areas of research on subcritical water utilization after Chemistry and Engineering. The extraction and production of bioactive phytochemicals have shown to be the main driving forces of this particular area. To date, several patents have been filed for potential use on food and pharmaceutical applications. Among them, the isolation of polyphenolic compounds from fruits and vegetables, production of essential oils from plant material and, the extraction of phytochemicals from plant sources have