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Online monitoring of the supercritical CO_2 extraction of hop

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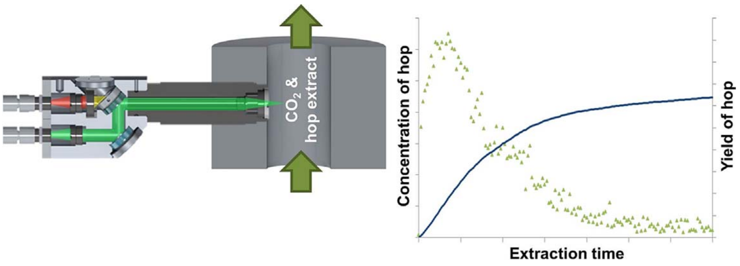
GRAPHICAL ABSTRACT



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ABSTRACT

An *in situ* Raman measurement system is introduced, which allows the real-time monitoring of the supercritical CO_2 extraction of hop. During the extractions, which were performed in a lab-scale extraction plant at NATECO$_2$, the hop extract concentration in CO_2 and also the amount of α-lupulic acids in the extract were measured. For the required optical access, a high pressure Raman sensor was designed and constructed, which could be easily installed inline between extractor and separator. The applicability of the presented measurement system is shown by monitoring the scCO$_2$ extractions of two different hop varieties under relevant extraction conditions of 333 K and 20 MPa, 24 MPa and 28 MPa, respectively.

1. Introduction

For more than three decades, industrial supercritical fluid extraction (SFE) processes have been used in the food and nutrition industry, e.g. for the decaffeination of coffee beans and tea leaves or for the extraction of oils or resins from natural products such as hops, sesame, algae and many more [1–3]. Especially for oxidation sensitive, thermolabile, high value or minor components, supercritical carbon dioxide (scCO$_2$) is often the favored extraction solvent, as it combines gentle critical conditions regarding temperature (304.13 K) and pressure (7.38 MPa) with its non-toxicity, high availability, non-corrosiveness and non-flammability [1,3]. In general, the use of a compressible gas like CO_2 as extraction agent offers the advantage of receiving highly selective extracts by varying pressure and temperature [4]. Furthermore, its usage allows an easy and residue-free solvent removal, qualifying it in particular for food and nutrition applications [1,3].

Most of the scCO$_2$ extraction plants are operated in a similar way: firstly, supercritical CO_2 is generated by pressurizing liquid CO_2 with a pump and heating it up in a heat exchanger. Then, the supercritical solvent flows through the extractor, which is charged with biomass.

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After the extraction the homogenous CO_2/extract mixture is separated through pressure reduction into a gaseous CO_2 and an extract phase. The extract can be removed from the process while the gaseous CO_2 is recycled again. If required, fractionation of the extract can be realized by reducing the pressure step-by-step.

Besides the characteristics of the raw material like moisture content or particle size, the applied process parameters, such as temperature, pressure, CO_2-flow rate and extraction time have a major influence on the product quality and the manufacturing costs [5]. Operating the process under non-optimal extraction parameters engenders high costs and can lead to undesired products. Furthermore, changes of the ingredients in the natural raw materials, caused by cultivation conditions like crop area or crop year [6], can require adjustments of the process parameters to ensure a consistent product quality. For economical and ecological reasons, especially the determination of the optimal extraction time is of great importance. At too short extraction times, too much of the valuable and desired ingredients remain in the raw material, while at too long extraction times the additional energy costs of the processes exceed the revenues of additional extract amounts.

To determine the optimal process parameters conventionally, extract and raffinate are offline analyzed after the termination of the extraction process and yield as well as selectivity are quantified. Then, an iterative procedure follows, in which the process parameters are adjusted and the extraction process is repeated until the desired product properties are reached. Depending on the consistence of the extract, also a sampling out of the separator during the extraction and a subsequent offline analysis could be possible. For the offline analysis, gas chromatography (GC), high performance liquid chromatography (HPLC) or absorption spectroscopy (AS) are used [7]. As these methods show a non-neglectable time delay between sampling and effective knowledge of the extract composition, often the extraction parameters can be optimized not for the current extraction but only for the following one. Furthermore, the physical sampling under high pressure conditions during the extraction may be incorrect, due to demixing or adherences in the separator [8,9].

In this context, an online and real-time monitoring of the progress during the $scCO_2$ extraction would drastically enhance and accelerate the optimization of the process parameters. In general, optical metrology provides a variety of techniques, which are potentially applicable for remote and *in situ* measurements in high pressure processes, such as absorption spectroscopy, laser induced fluorescence or Raman spectroscopy [10]. However, not all of these mentioned techniques are perfectly suitable to monitor the extraction of natural materials. Natural material usually contains water, which is also extracted in small amounts from the CO_2 out of the raw material. Due to the very strong absorption cross section of water in the mid-infrared and far-infrared spectral regions, already small amounts of water extinguish the incident light and thus make mid- and far-infrared absorption measurements without previous sample-preparation-steps impossible. Therefore, absorption measurements can only be carried out in the near-infrared region, as it was demonstrated for the extraction of hop by Böhm et al. [5]. However, due to the characteristics of the near-infrared absorption spectrum, the quantification of the absorption spectra in terms of concentrations or compositions was complex, as calibration measurements had to be made for each individual operational condition (pressure and temperature) [5].

Fluorescence based techniques suffer from the fact that the fluorescence emissions depend on the operational conditions and are heavily influenced by intermolecular interactions. Thus, as the composition of natural raw materials varies, a quantification of the fluorescence signals in terms of concentrations or compositions is challenging and time consuming.

Raman spectroscopy is based on an inelastic scattering mechanism between the incident laser light and the investigated substance. The energy difference between the incident and the scattered photons, which is called Raman shift, is species specific. Thus, the Raman spectrum contains information about the species contained in the investigated substance. Additionally, Raman spectroscopy is known to be a quantitative measurement technique with respect to the mixture composition [11]. Especially at high pressures, the low Raman scattering cross sections are compensated by the high densities of the fluids resulting in high Raman signal levels [12]. However, natural materials contain usually pigments and can be excited by the Raman excitation laser to fluoresce. Then, the desired Raman signals are superimposed by fluorescence interferences, which are orders of magnitude more intense. It is known that the Raman signal intensity increases with decreasing excitation wavelengths, but also the fluorescence probability of the system increases.

If the Raman process is excited in the near-infrared spectral region, the fluorescence interferences could be minimized, but also the Raman signal level is low. Additionally, − with respect to the excitation wavelength − red-shifted Raman signals can be absorbed by the water or by molecules with hydroxyl groups dissolved in the extraction solvent. A Raman excitation wavelength in the ultraviolet spectral region is also applicable, but, as already mentioned, at lower wavelengths the undesired fluorescence interference is enhanced. Consequently, Raman excitation wavelengths in the visible spectral range are a compromise of quantifiable Raman signal levels on the one hand and still sufficiently low undesired fluorescence interferences on the other hand. Therefore, the experiments were carried out with an excitation wavelength of 532 nm.

For the elimination of remaining fluorescence interferences from the Raman spectra, various methods are discussed in literature [13–16]. In this study the implementation of the so called shifted excitation Raman differential spectroscopy (SERDS) measurement technique [17–19] allowed to suppress the disturbing fluorescence interference and online monitor the supercritical CO_2 extraction of hop in a lab-scale extraction plant of the collaboration partner $NATECO_2$ (Germany; www.nateco2.de).

In the sections that follow, first the extraction plant and the Raman measurement device are described, then the methodology of eliminating the interfering fluorescence emissions from the obtained spectra and the spectra evaluation are depicted. Finally, the obtained results are shown.

2. Materials and methods

2.1. Experimental setup

All experiments were performed in a lab-scale extraction plant of $NATECO_2$, which can withstand pressures up to 100 MPa and temperatures up to 368.15 K and which is shown in a simplified flowchart in Fig. 1. The main components of the plant are the extractor with an internal volume of 3 L and the separation unit. In cases, where additional fractioning is needed a second separation unit can be integrated after the first one. For the Raman measurements a short stainless steel pipe including a self-developed Raman sensor (see photo insert in Fig. 2) was installed inline between extractor and separator. The entire optical system is robust and reliable even under the harsh measurement conditions in an industrial extraction hall (high humidity, high temperature, vibrations etc.). In order to avoid the precipitation of hop extract during the experiment inside the pipe, the pipe was kept on extraction temperature using an electrical cartridge heating.

The Raman measurement system, illustrated in Fig. 2, works on the principle of the shifted excitation Raman differential spectroscopy (SERDS), which will be described in detail below. It includes two continuous wave frequency doubled Nd:YAG lasers (Samba, Cobolt AB, Solna, Sweden) with a maximum output power of 1000 mW each, and emission wavelengths of 531.93 nm and 532.20 nm, respectively, resulting in an excitation energy difference of 9.5 cm^{-1} (1/531.93 nm - 1/532.20 nm). The two lasers emit linear polarized light. In order to couple the two lasers efficiently into the glass fiber that is connected