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Research Note

In Situ Attenuated Total Reflection Infrared Spectroscopic Monitoring of Supercritical CO_2 Extraction for Green Process Applications

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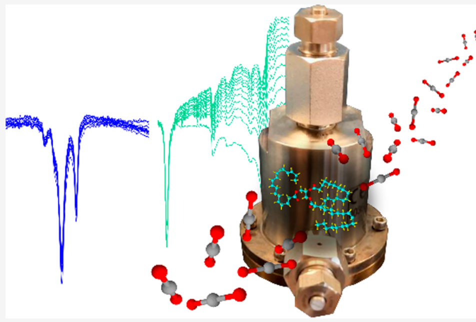
ABSTRACT: Supercritical CO_2 ($scCO_2$) extraction of valuable chemicals from food, biomass, and residues thereof has recently been recognized as a sustainable process. In this study, we present a new design of an attenuated total reflection infrared (ATR-IR) spectroscopic cell for monitoring the extraction of fatty acid from almonds under $scCO_2$ conditions. The newly designed ATR-IR cell allows in situ monitoring of changes of the composition of the almonds during the $scCO_2$ extraction process at a pressure of up to 450 bar. Extracted components can be spectroscopically followed at a time resolution of 30 s. This allows fast and facile optimization of $scCO_2$ conditions such as temperature, pressure, and extraction time.



Supercritical CO_2 extraction ($scCO_2$) has had a great deal of interest and attention for the extraction of chemical compounds from natural products.[1−4] CO_2 behaves as a supercritical fluid under relatively mild conditions (above 31.0 °C and 73.8 bar). This supercritical condition enables efficient, organic solvent-free extractions without any considerable degradation or oxidation of target compounds. There are several successful applications with $scCO_2$ extraction such as patchouli essential oil for cosmetics,[1] lipids/fatty acids extraction,[2,4] and antioxidants extraction.[3] Especially, the $scCO_2$ extraction of fatty acids from plants and food is a rapidly growing market.[5−13] A major component of the fatty acids, i.e., triglyceride, is generally obtained by a conventional multistep method including vacuum distillation, crystallization using urea, and extraction by hexane.[14] Hence, $scCO_2$ extraction simplifies the whole extraction process considerably. Besides, $scCO_2$ extraction contributes to the utilization of CO_2 and recycling of natural resources, which are the scopes of sustainable development goals (SDGs). The extraction efficiency strongly depends on the conditions. For example, the oil yield from tiger nuts increases with the extraction time and pressure.[8] An optimal extraction temperature is ca. 60 °C, above which the yield decreases. However, the viscosity increased with the extraction temperature together with fatty acid constituents. A similar trend was observed for the fatty acid extraction from sesame seeds[9] and sapucaya nuts.[10] The flow rate of $scCO_2$ through the extraction vessel is also a key factor to enhance the process efficiency. A higher flow rate contributes to better yield for the extraction from betel nuts.[11,15] The extraction condition is optimized to suit industrial applications of the extracted compounds. Generally, the process optimization requires a number of time-consuming experiments using analytical tools such as gas or liquid chromatography. After each experiment, cleaning and reloading of the extraction reactor are also required. Therefore, real-time analysis of the extraction is desired. Due to the required high pressure (up to ca. 450 bar) for some cases, the development of an in situ analytical tool has been challenging. There have been only a few online spectroscopic applications reported to date.[16,17] In situ Raman spectroscopy was successfully applied for monitoring the $scCO_2$ extraction of hops.[16] A Raman sensor was located between the extraction chamber and separator, whose configuration allows in situ monitoring of the $scCO_2$ phase under extreme conditions (up to 95 °C and 1000 bar). In situ near-infrared (NIR) spectroscopy was also applied in a similar way. The NIR sensor installed between the extraction vessel and separator allows real-time monitoring of the benzoic extraction from hops.[17] However, NIR shows broad IR bands and has difficulties in simultaneous monitoring of several components without extensive calibrations. To our knowledge, there has been no report on real-time direct monitoring of materials themselves using Fourier transform mid-infrared (FT-IR) spectroscopy in such a high-pressure range. There have been some reports by Kazarian et al.[18−25] and Baiker et al.[26−33] with

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mid-infrared spectroscopic analyses under $scCO_2$ conditions, which were applied for a variety of chemical phenomena. However, their cell design is limited with maximum pressure and cannot withstand 450 bar to monitor the solid phase.

In this research note, we report a new design of an attenuated total reflection IR (ATR-IR) spectroscopic cell for monitoring $scCO_2$ extractions. As a model process, the extraction of fatty acids from almonds was selected. Figure 1a and b shows the newly designed IR cell. Samples can be

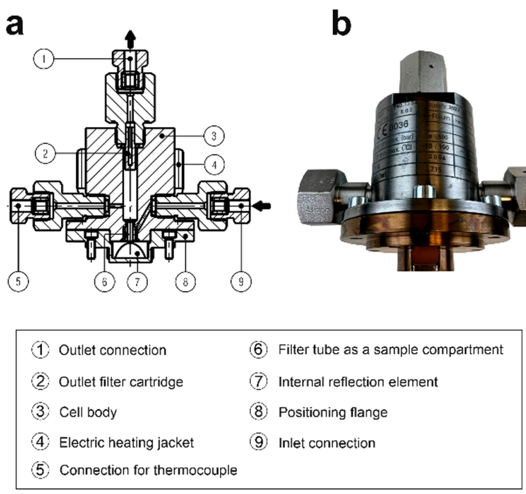

Figure 1. (a) Design of the newly developed in situ ATR-IR cell. (b) Photo of the home-built ATR-IR cell.

placed into a tubular extractor (inner diameter of 3 mm) over an internal reflection element (IRE). The IRE materials can be flexibly selected from ZnSe, Si, and Ge, depending on the extraction conditions. The Ge IRE is suitable for most of the extraction cases because of its tolerance against chemicals and the wide spectral range of 675−5500 cm^{-1}. The herein presented design allows the direct contact of materials and IRE crystal, such that the evanescent wave partially penetrates the materials (almonds in this study). The cell withstands a pressure as high as 1000 bar (Figure S6 in the Supporting Information). Previously reported cell designs did not allow such a high pressure because the area of IRE crystals on which the pressure is applied was large.[19−21,23] In our new design, the inner diameter was only 3 mm, on which the pressure is directly applied. This small area enabled a tolerance against 1000 bar. The $scCO_2$ flows vertically from the bottom to the top of the cell. The temperature is adjusted in the range of 25−80 °C by an electric heating jacket. A thermocouple is inserted into the extraction vessel and ensures the temperature control inside the extraction unit. The $scCO_2$ fluid is introduced from the bottom through a metallic mesh filter and then passes through the sample bed in a plug-flow manner. The IR cell can be placed onto a commercially available optical compartment (VeeMAX III, PIKE Technologies), which is installed on a FT-IR spectrometer (INVENIO R, Bruker) equipped with a mercury−cadmium−telluride (MCT) detector.

Figure 2a shows the typical molecular structure of one of the triglycerides, which are the main components extracted from almonds by $scCO_2$.[34] Three different fatty acid constituents are composed of either saturated or unsaturated fatty acid. The molecular structure is quite simple containing only hydrogen, carbon, and oxygen atoms for alkyl chains and ester group. Therefore, its extraction is ideal to be monitored by the new IR cell as a model extraction. Figure 2b displays the IR spectrum of pure almonds before $scCO_2$ extraction. The asymmetric and symmetric stretching vibrations of the CH_3 group are assigned at 3008 and 2856 cm^{-1}.[35] The IR bands of CH_2 moieties are assignable at 2924 and 2856 cm^{-1}. The ester keto group is assignable at 1746 cm^{-1}. The stretching vibration of the C═C bond of unsaturated fatty acids overlaps with the bending vibration of H_2O. The deformation modes of CH_3 and CH_2 overlap with the stretching vibration of C−C bond. Therefore, ν(C−H), ν(C═O), and ν(C−O), indicated by the yellow, green, and red colors in Figure 2b, were tracked by in situ ATR-IR spectroscopic measurements. Figure 2c shows in situ ATR-IR spectra of the almonds (150 mg) during $scCO_2$ extraction (200 bar, 9.4 kg/h $scCO_2$ flow rate, 46.2 °C) recorded at an interval of 30 s. The spectra were taken at the spectral resolution of 4 cm^{-1}, 64 scans per spectrum, and scanning velocity of 60 kHz with an aperture size of 2.5 mm. Since the background spectrum was taken in the presence of the almonds and $scCO_2$ at the beginning, IR bands of the extracted compounds emerge as negative bands. The extraction of the triglyceride was successfully observed with a high signal-to-noise (S/N) ratio and time resolution. Note that there was no water extracted as evident from the flat band region of 3100−3600 cm^{-1}. This indicates that water stayed in the solid phase of the almonds and that only fatty acids were selectively extracted. A very weak IR band at 1654 cm^{-1} assignable to ν(C═C) of the unsaturated fatty acids was also detected (see the enlarged spectra in Figure S7 in the Supporting

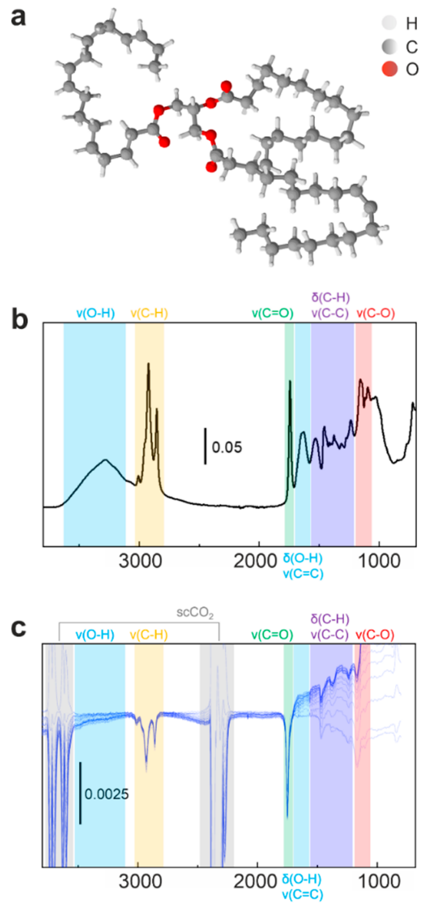

Figure 2. (a) Molecular structure of triglyceride. (b) ATR-IR spectrum of almonds before $scCO_2$ extraction. (c) Time-resolved ATR-IR spectra of almonds during $scCO_2$ extraction.

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Information). More than 90% of fatty acids in the almonds are unsaturated. Hence, the reason for the weak intensity of ν(C═C) is that the dipole moment changes of the C═C bond are too low to be detected by mid-IR spectroscopy due to its nearly symmetric configuration. Moreover, intense IR bands of $scCO_2$ overwhelmed all the regions at 2200−2400 and 3550−3750 cm^{-1}. Hence, we expect that nitrile groups (C≡N) cannot be monitored. However, other functional groups containing nitrogen and chlorine atoms can be followed by the newly developed ATR-IR cell. This feature offers an extensive potential for many applications such as pesticide removal and purification of materials by $scCO_2$.

Figure 3 shows the time-resolved evolution of different IR bands. To make it plain and comprehensive, the *y*-axis

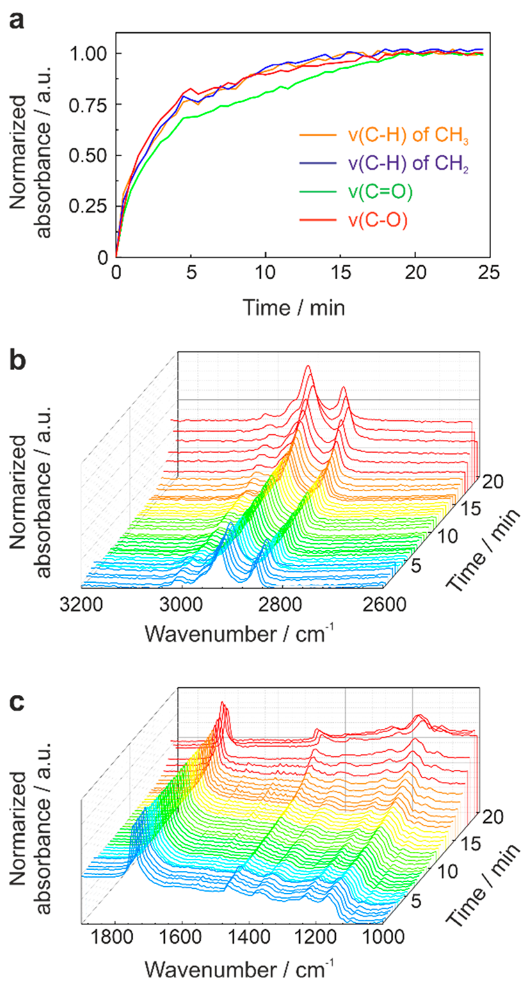

Figure 3. (a) Time courses of different functional groups during $scCO_2$ extraction, and spectral evolution vs extraction time in (b) a high wavenumber region and (c) a high wavenumber region.

(absorbance) was inversed and normalized to be positive values. Figure 3a shows the time course of vibrational modes assigned to the triglyceride obtained from Figure 3b and c. The time evolution of ν(C═O) slightly differed from other vibrational modes such as the stretching vibrations of C−H and C−O. However, all the curves showed almost the same trend. Obviously, the extraction process was not proportional to the extraction period. At the initial 30 s, the extraction occurred rapidly, indicated by the steep slopes of the signals analyzed in Figure 3a, and then gradually slowed down. The complete extraction took ca. 20 min under this condition. A big challenge of in situ IR spectroscopy is the spectra processing. As seen in Figure 3b, the background signal shifted during the course of the experiment, which disturbed obtaining the time evolutions of each moiety. Therefore, particular attention is required to make a plot considering the background shift. This background shift cannot be avoided because upon $scCO_2$ extraction, the density of the solid phase decreases, and thus, the diffraction index for the internal IR reflection changes. As shown in Figure 3c, in the fingerprint region, the baseline shift was observed together with the background shift. Therefore, the data processing at a lower wavenumber region requires both background and baseline corrections.

In summary, we developed a new analytical tool for in situ monitoring of the solid phase during $scCO_2$ extraction. The newly designed ATR-IR cell withstands up to 1000 bar in the temperature range of 25−80 °C. Mid-IR is advantageous because different functional groups can be followed simultaneously on the same time scale. The ATR-IR cell is not limited only to monitor the extraction fatty acids but is applicable for other processes under $scCO_2$ conditions such as purification of raw materials and catalytic reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.2c03558.

Information as mentioned in the text (PDF)

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All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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