

Demonstration of NIR inline monitoring for hops extraction and micronization of benzoic acid in supercritical CO₂

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ABSTRACT

The use of supercritical CO₂ as solvent for separation processes and chemical reactions is widespread. Many industrial extraction processes using CO₂ consume a huge amount of energy and hence are very cost-intensive. In the past, the duration of extraction was often longer than required for an optimum result. Therefore, an inline monitoring device for terminating CO₂ extraction processes at the right time has been desirable. In collaboration between KIT and SITEC-Sieber Engineering, Switzerland, a mobile near infrared (NIR) inline monitoring device has been developed to close this gap and to offer an opportunity to implement it into industrial extractions processes using CO₂ and to use the data for process optimization. NIR spectroscopy with fiber optics adaption has been proven to be a very good choice, because the CO₂ bands are well separated from all other bands of interest caused by the extracts (organics and water). The NIR inline monitoring device can easily be implemented into industrial plants to visualize the extraction progress and to terminate the process at the right time in order to save energy and money. Measurements on customer's demand are available for extraction and reaction processes in supercritical CO₂.

This paper will actually focus on two applications. Firstly, in collaboration with NATECO₂, Germany, the NIR inline monitoring device has been implemented into a plant for hops extraction with supercritical CO₂. Extractions have been performed and successfully monitored for the varieties Hallertauer Magnum, Hallertauer Herkules, and French Strisselspalter at 60 °C and 25 MPa, 28 MPa, and 50 MPa, respectively. The detectability was 0.1 wt% of hops in CO₂.

Secondly, the applicability of this NIR inline monitoring method on processes for the production of submicron particles in supercritical CO₂ has been demonstrated in a feasibility study. For this purpose, a RESS (Rapid Expansion of Supercritical Solution) high pressure plant (160 ml, max. 35 MPa, max. 120 °C) was built and the NIR inline monitoring device integrated. Two syringe pumps were coupled for an almost pulsation-free-feeding. Benzoic acid was used as a reference solid. In this feasibility study, the focus has not been to perform an optimized RESS process, but rather to monitor the loading of the CO₂ phase with benzoic acid continuously, as this information is crucial for the optimization of a RESS process and has not been available up to the present. The experiments have been carried out at 55 °C and 25 MPa as reference conditions. The performed calibration resulted in a detection limit of 0.1 mg benzoic acid per g CO₂. The loading of the CO₂ phase has been successfully and continuously monitored and can now be applied for other systems.

A side effect of these investigations has been the finding that this NIR inline monitoring device can also be used for very precise solubility measurements and to visualize the establishment of thermodynamic phase equilibrium as a function of time, especially in cases of low solubility of a substance in CO₂. The NIR inline monitoring device can also be used for the inline monitoring of reactions producing data for kinetic modeling and process optimization.

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1. Introduction

Supercritical CO₂ is widely used as a solvent for separation processes and also in some cases for chemical reactions in order to

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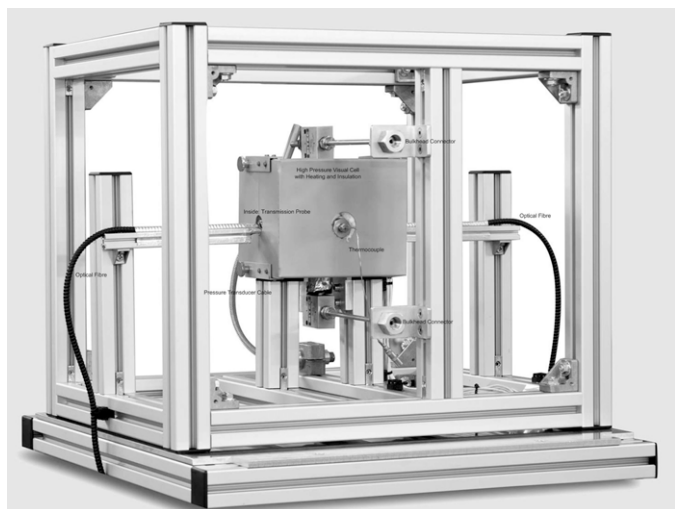


Fig. 1. NIR inline monitoring device SINASCO.

obtain kinetic data for process optimization [1,2]. Industrial extraction processes using supercritical CO₂ are state-of-the-art: several thousand tons of hops, coffee, tea, cocoa and seeds are refined annually and worldwide applying this technology. However, in the operating procedures applied today, valuable processing time often gets lost by the lack of direct measurements inside the high pressure system in order to terminate the process at the right point. Consequently, the Karlsruhe Institute of Technology (KIT) and the company SITEC-Sieber Engineering AG, Switzerland, have developed a mobile system, SINASCO¹ (Fig. 1), which enables near infrared (NIR) inline monitoring for extraction pressures up to 100 MPa [3–6]. Previously, according to the state-of-the-art, only high pressure visual cells have been available for either high temperatures at low pressures (300 °C and 2.5 MPa) or for high pressures at relatively low temperatures (50 °C and 30 MPa). The need for applications in extraction with supercritical CO₂, however, was seen in the range of 40–80 °C up to 75 MPa (or higher), and for reactions up to 200 °C and 35 MPa (or higher). Since 2009, this market gap is closed. The details concerning the construction and set-up of the NIR inline monitoring system SINASCO have been published previously [7,8]. Fig. 1 shows the high pressure visual cell with heating and insulation, the fiber optic adaptation with transmission probes outside the sapphire windows, thermocouple and pressure transducer (which are in contact with the fluid), and the bulkhead connectors.

IR and NIR spectroscopy for the quantitative analysis of fluids at high pressures and temperatures has been a well-known method for many years, e.g. by Buback et al. for basic structural investigations of high pressure systems and kinetic studies of polymerizations as well [9,10]. A survey of all relevant activities and on the instrumentation alternatives can be found elsewhere [7].

In the present case, the task has been to select the best method for the monitoring of (industrial) extraction processes and reactions in supercritical CO₂. When extracting natural substances for the food, cosmetics, and pharmaceutical industries as well as for cleaning processes with CO₂, it has been impossible so far to directly observe these energy-intensive processes. Hence, the duration of extraction in the past was often longer than required for an optimum result. Here, inline tools for monitoring concentrations of chemical compounds indicating the progress of e.g. an extraction process, a chemical reaction, or for control of constant

concentrations of substances prior to supercritical particle formation processes are often desired, but have not yet been readily available. Fiber optics adapted NIR spectroscopy has proven to be the best method for inline monitoring in processes using supercritical and also liquid CO₂, because the bands of CO₂ and all other substances relevant for this process (organics and H₂O) are well separated and can easily be quantified. Using the mobile NIR device SINASCO, such processes can now be visually monitored inline continuously during the whole run, therefore enabling termination of the run at the right point in time. The available NIR inline monitoring device has several advantages: compact, mobile, flexible, and easily and quickly integrated into industrial extraction plants. Due to the reduced operation time for the individual processes, it is possible to run more extractions per day than before and to increase production capacity. Finally, a considerable amount of money and energy are also saved.

This NIR inline monitoring module SINASCO has already been used for several applications. In this paper, two different examples are addressed:

- (i) a SINASCO module was installed in one of NATECO₂'s extraction plants and tested in real terms for hops extraction;
- (ii) in a feasibility study, the applicability of this NIR inline monitoring method on processes for the production of submicron particles in supercritical CO₂ was investigated.

A “side effect” of these investigations has been the finding that this NIR inline monitoring device can also be used for very precise solubility measurements and to visualize the establishment of thermodynamic phase equilibria as a function of time.

2. Application of NIR monitoring for hops extraction

2.1. Materials and methods

For the NIR inline monitoring experiments for hops extraction, one of NATECO₂'s lab scale plants designed for a maximum of 80 °C and 100 MPa has been used (Fig. 2). It consists of a 3 L extraction vessel and 2 separators. The optical cell for the NIR inline monitoring has been installed between the extractor and the separation vessel of the extraction plant, as shown in Fig. 2. The mobile NIR inline monitoring device has been calibrated for hops and water in the solubility region from zero up to 7.5 wt% of hops (which is generally taken as the solubility limit for the non-volatile components of the hops extract) and up to the solubility limit of about 1×10^{-5} g water/gram CO₂ at 60 °C and 25 MPa. The OPUS QUANT integral method provided by the Bruker spectrometer software is used with a detection limit of 0.1 wt% for hops. For every calibration point, 10 spectra have been averaged. In general, the characteristic spectra of hops extract are mainly caused by the bitter compounds called “alpha-acids” and “beta-acids”, which have varying concentrations in different types of hops. Therefore, the first calibration has been carried out with the hops variety French Strisselspalter and has been supplemented by calibration data from the hops varieties Hallertauer Magnum and Hallertauer Herkules. The calibration for the NIR inline monitoring of hops extraction has been performed at 60 °C and 25 MPa using hops extracts, which contain the usual amount of water. Therefore, the calibration data have to be corrected for the individual water content, which is also measured within the same run spectroscopically and then subtracted. No pure substances have been used for the hops calibration.

The present NIR method can track the hops and the water content of the extraction fluid continuously. The water content is very important for the quality of many extracts of natural substances. Other own investigations, which have not yet been published, have

¹ Set-up for inline NIR spectroscopic analysis in supercritical carbon dioxide.

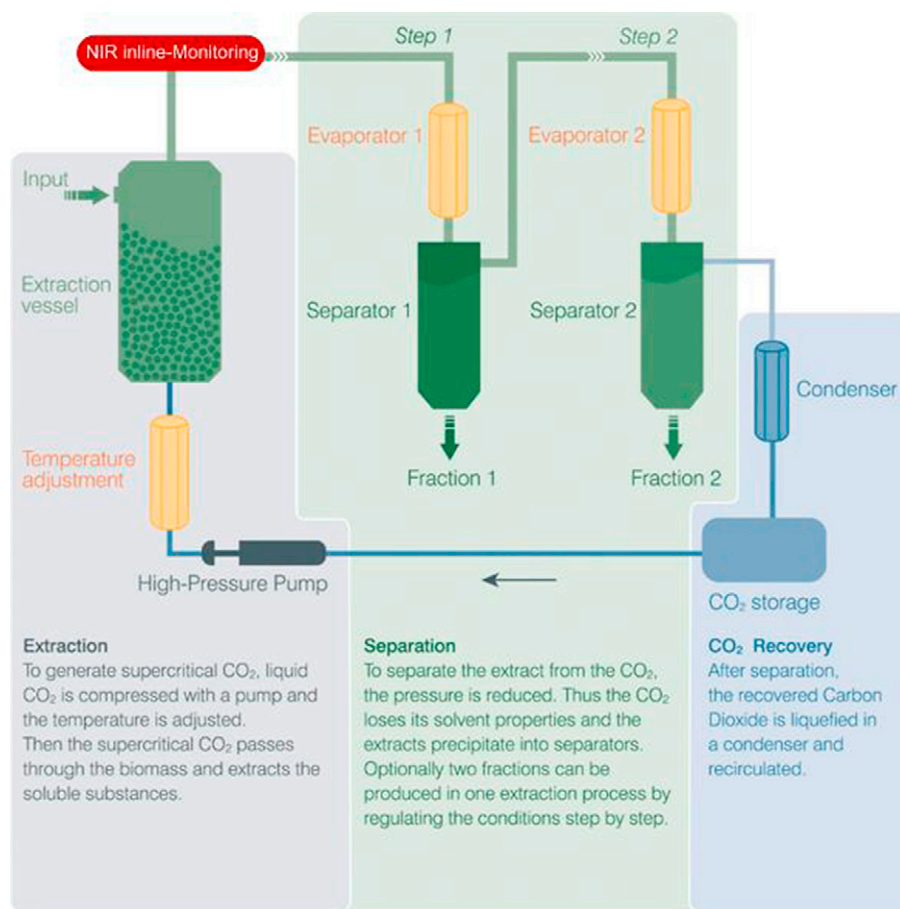


Fig. 2. Scheme of a CO₂ extraction plant with integrated NIR inline monitoring device.

also shown that the use of a co-extract (like isopropanol) does not negatively affect the quantitative data obtained.

For the hops extraction process, the extractor was filled with common hop pellets and the extraction parameters were adjusted to the conditions of 60 °C and 25 MPa, 28 MPa, and 50 MPa, respectively. CO₂ was recycled emission-free, starting with liquid CO₂ out of the storage tank, which was then compressed and heated to supercritical conditions. The CO₂ flows through the extractor and dissolves the extract, which is separated by decompression of the CO₂. The CO₂ is condensed again and re-circulated. The extract yield is determined by weight. These data are correlated with the data from the NIR inline monitoring in order to evaluate the quality of the measurements.

2.2. Results and discussion

The results for three representative experiments at 60 °C and 25 MPa, 28 MPa, and 50 MPa, respectively, are shown in Figs. 3–5. Every run has been carried out only once, because the extraction curve as a function of time appeared as expected, and hence the results have been satisfactory. For the visualization of the extract concentration as a function of time, a method is implemented using software called “Opus Process” (delivered by Bruker together with the NIR spectrometer).

Fig. 3 shows the concentration of hops extract in the CO₂ as a function of time for the extraction at 60 °C and 25 MPa on the left side. On the right side are the corresponding spectra for the whole run.

Figs. 4 and 5 show the concentration of hops as a function of time at 60 °C, 28 MPa and 50 MPa, respectively. In these figures, also the

water content is shown (which is the lower curve in the left figure). On the right side are the spectra at the corresponding conditions.

All extraction runs show the typical behavior with a fast increase and a slow exponential decrease in concentration, as expected. The maximum concentration of hops extract is about 12.2 wt% at 25 MPa, and about 18.4 wt% at 28 MPa, respectively, which corresponds to the experiences from previous experiments. But at 50 MPa, the hops concentration is about 38.1 wt%, which is much too high according to previous extraction experiences. Here, the data show two initial peaks, which result from pressure inconsistencies during startup of the extraction. They cause density fluctuations with changes in the solubility and can occur during pressurizing the extraction plant. The graph shows that the NIR inline monitoring is a very sensitive method.

These results show, that the present calibration can be extrapolated from 25 MPa to 28 MPa at the same temperature, as the density difference is comparably low (0.0274 g/cm³). Between 25 MPa and 50 MPa, however, the density difference is 0.12674 g/cm³. Here a separate calibration has to be performed extending the pressure range up to 50 MPa in order to get quantitative data.

The solubility power of CO₂ depends strongly on the density. At higher densities, other components can be dissolved out of the extraction matrix than at lower densities. A change in density due to extraction of (several) components from a matrix can affect the results, e.g. in order to produce hops extract for beer brewing, the pressure is usually 25–30 MPa. At higher pressures up to 100 MPa some polyphenols can be extracted, which are not soluble at the lower pressures.

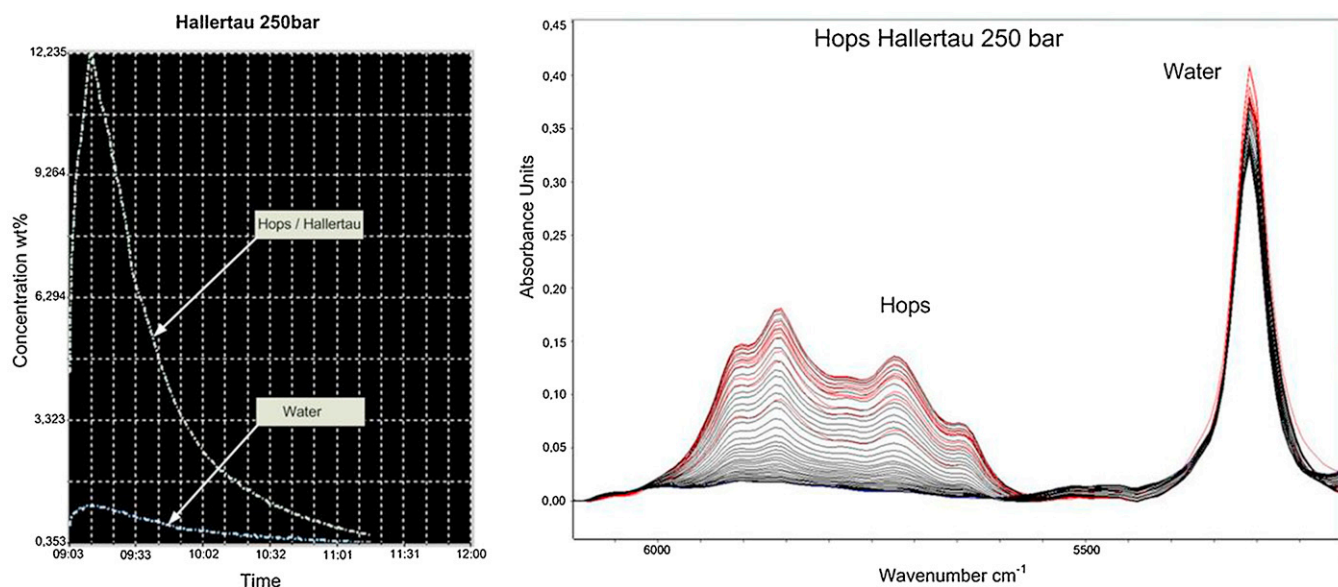


Fig. 3. Result of inline monitoring for hops extraction at 60 °C und 25 MPa.

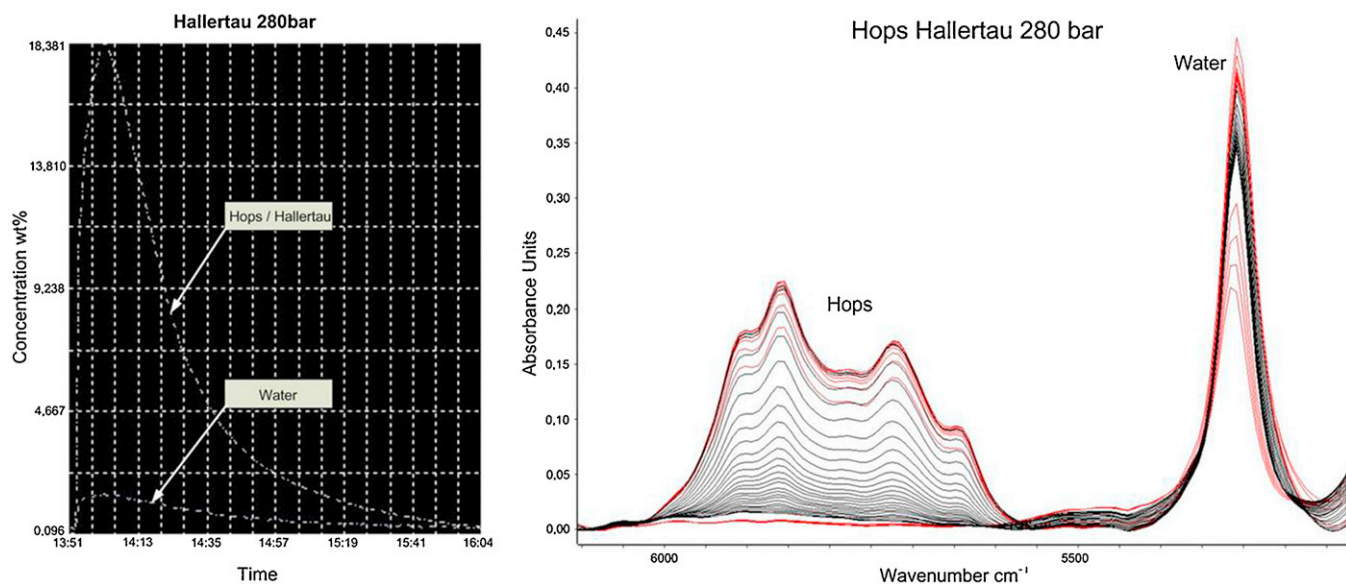


Fig. 4. Result of inline monitoring for hops extraction at 60 °C und 28 MPa.

The first NIR inline monitoring measurements for hops extraction showed a discrepancy between the detected hops extract concentration and the quantity of extract in the separator. One reason was the fact, that the calibration was performed with the total extract, which is a mixture of water and hops components. Subsequently the water content was analyzed, a calibration with water was carried out, and the hops extract calibration was corrected. Another influencing factor was identified as the high amount of volatile hops oil components which are present in the CO₂, especially at the beginning of the extraction process. The oil component peaks overlap with the other hops extract peaks in the spectra. During the run, depletion is observed due to deposition of the volatile components in the extract. Hence, the final yield of extract correlated with the quantity indicated by the inline concentration measurement sufficiently. It was verified, that inline measurements of extract concentration have been performed successfully with a detection limit of 0.001 g/hops/g CO₂ (or 0.1 wt% hops in CO₂). The whole extraction runs have been

visualized quantitatively and are normally terminated far away from the detection limit at around 1–2 wt%. Therefore, the NIR inline monitoring is a useful tool for the right termination and process optimization of hops extraction processes with CO₂. Further measurements should increase the know-how about application and performance of the optical cell by extracting complex matrices.

3. Application of NIR inline monitoring for micronization processes

3.1. Materials and methods

In a feasibility study, the applicability of NIR inline monitoring for measuring the loading of CO₂ by benzoic acid for the production of submicron particles has been investigated. Benzoic acid² has

² Benzoic acid EMSURE® Reag.Ph.Eur. p.A. by Merck.

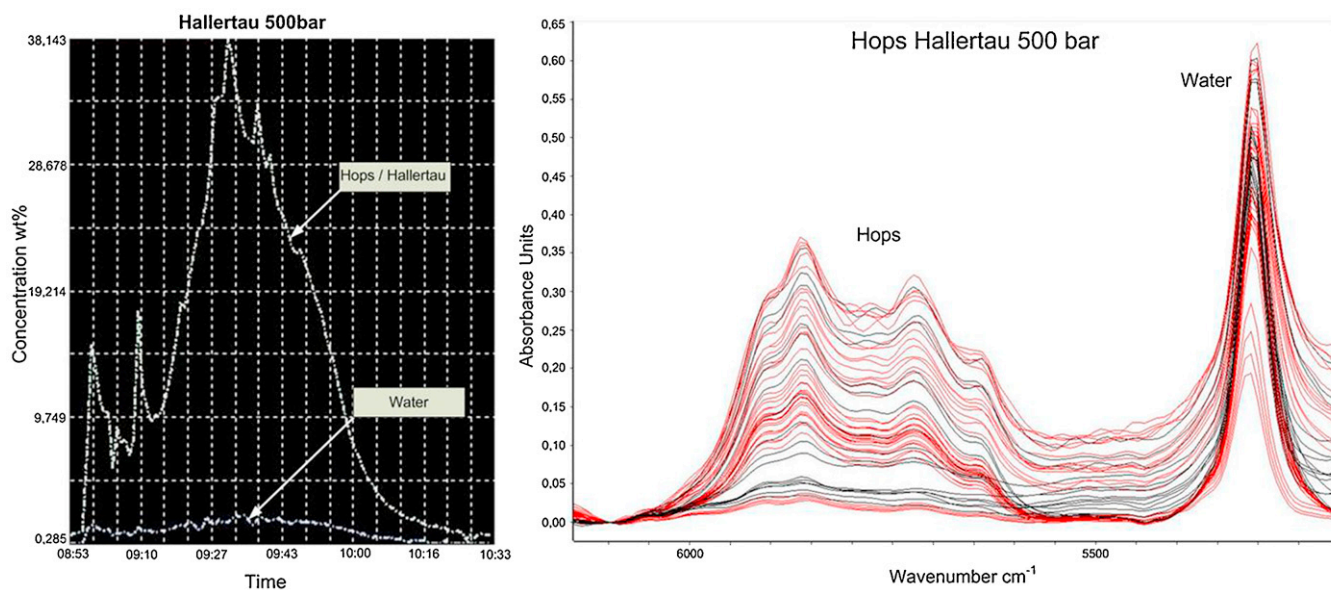


Fig. 5. Result of inline monitoring for hops extraction at 60 °C und 50 MPa.

been used as reference material to measure the loading of the CO₂ phase by NIR inline monitoring prior to a micronization process, since the solubility in CO₂ in the relevant pressure and temperature ranges is reported in the literature [11,12].

A RESS process (Rapid Expansion of Supercritical Solution) is a fast depressurizing of a fluid, which contains a dissolved solid substance, through a nozzle in order to produce micro size particles. In this case study, a RESS process serves as background to monitor the loading of the fluid phase with a solid. In the present case, carbon dioxide is used as fluid and benzoic acid as reference solid. They form a so-called asymmetric mixture, which is explained elsewhere in more detail [8]. Fig. 6 shows a combination of the generalized phase situation for the possible operation conditions and the schematic sequence of the RESS process [13,14]. The lower boiling substance is CO₂ (index "1"). The process must be operated above the critical point of CO₂ (CP1). The substance to be micronized, in this case benzoic acid (index "2"), is dissolved in supercritical CO₂ and then rapidly expanded through a very narrow nozzle of a 50 μm diameter. In order to avoid a melting of the solid and consequently a plugging of the nozzle, the applicable operation area is bounded by the S₂LG line of the benzoic acid in order to achieve the desired micron particles. Practically, the RESS process in this system has to be performed at elevated temperatures between

75 °C and 145 °C and pressures between 20 MPa and 30 MPa at the nozzle.

For performing a RESS process run, liquid CO₂ is pressurized, heated, loaded with the substance to be micronized, in this case benzoic acid, and then sprayed through a heated 50 μm nozzle to produce submicron particles. In contrast to the extraction processes, here no recirculation of the CO₂ is normally provided. A lab-scale apparatus for operation up to 120 °C and 30 MPa has been developed, designed, built, and put into operation. The loading experiments have been performed at 55 °C and 25 MPa, as reference conditions in this case study. The nozzle had been heated up to 75 °C in order to avoid an early precipitation or plugging.

At these conditions, the calibration of the NIR inline monitoring system for the mixture consisting of (benzoic acid + CO₂) has been performed in a different recirculation apparatus [7,8] in order to assure full solubility, as shown in Fig. 7 [15].

For every calibration point (more than 50 in total), a corresponding amount of benzoic acid has been weighed into the high pressure system and dissolved in CO₂, up to the solubility limit, which is detected automatically by this procedure. Here, complete solubilization has been achieved, when the spectra reach their maximum. The spectra have been measured in absorbance units (AU).

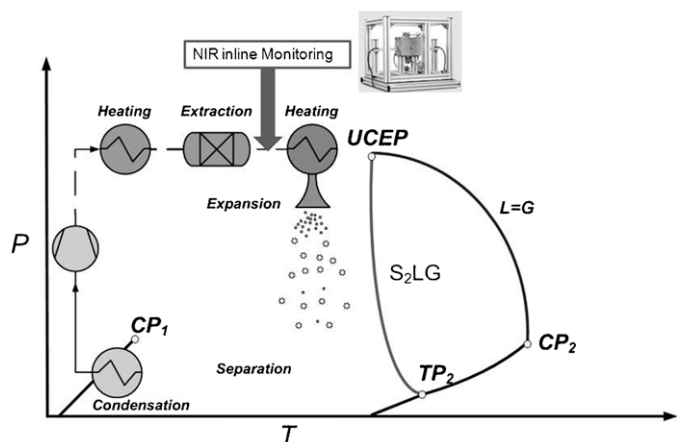


Fig. 6. Scheme of RESS process with integrated NIR inline monitoring.

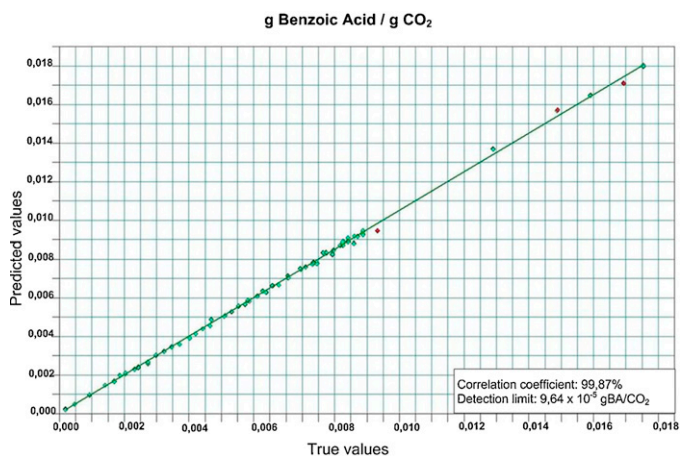


Fig. 7. PLS calibration for the system (benzoic acid + CO₂), predicted versus true values.

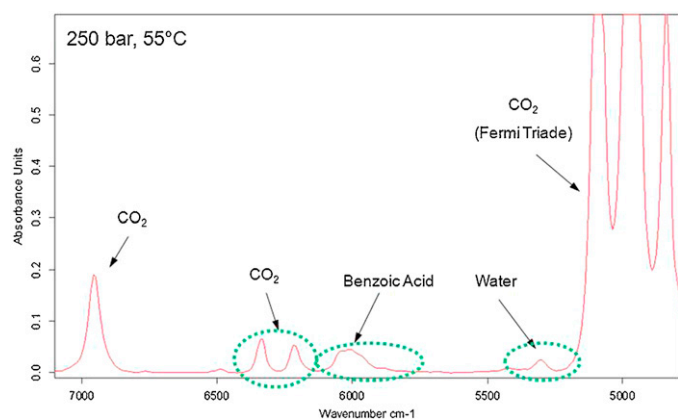


Fig. 8. Sample spectrum for the system (benzoic acid + CO₂), 55 °C, 25 MPa, 0.009 mg benzoic acid/g CO₂.

The grams of benzoic acid (BA) loaded into the vessel and also the grams of CO₂ in the vessel and hence also the real concentrations of benzoic acid in CO₂ are known.

For every single point, 10 individual spectra have been taken and averaged. These results have been used to calculate a so-called partial least squares (PLS) calibration. Details on the application of this PLS method for extraction processes with supercritical CO₂ have been published earlier [7,8].

The PLS calibration results are shown in Fig. 7 with the real values versus the predicted values. Therefore, the best result is obtained, when the real value is equal to the predicted value, the diagonal in the graph. The detection limit for this method is 0.1 mg benzoic acid/g CO₂ (corresponding to 0.01 wt%). The error bars are so small that they are within the range of the markers. This proves that the calibration is a very precise method for solubility measurements and NIR inline monitoring of a micronization process as well. Other studies have shown that a deviation from the diagonal may occur at high concentration of dissolved substances in CO₂ [8].

A sample of the spectra used for the calibration is shown in Fig. 8. The peaks caused by CO₂ and benzoic acid are indicated and show that they are well separated. Therefore, the automatic identification and quantification of benzoic acid is working well.

For performing the inline monitoring experiments, the mobile NIR device SINASCO has been implemented easily and rapidly into the RESS lab-scale high pressure apparatus, as shown in Fig. 6. For every run, benzoic acid has been weighed into the “extraction vessel” which is used here as a sample reservoir to perform a micronization process of about 45–60 min of duration. CO₂ is pumped through and loaded with benzoic acid. Two syringe pumps have been coupled to allow a continuous flow-through mode without any pulsation. Finally, the CO₂ phase containing benzoic acid is rapidly expanded through a 50 μm nozzle resulting in micronized benzoic acid without any recirculation, as the NIR inline monitoring of the CO₂ phase loaded with benzoic acid is the matter of interest. Here, it is very important to work within the right temperature regime, as otherwise the nozzle will plug. The process is run until all the benzoic acid has been dissolved and sprayed, which is clearly indicated by zero spectra. Between the extraction vessel and the spray nozzle, the NIR device is implemented and measures inline the concentration of benzoic acid loaded into the CO₂ phase (Fig. 6).

3.2. Results and discussion

The results for the NIR inline monitoring applied for the micronization of benzoic acid out of a supercritical CO₂ phase are shown in Fig. 9. All loading curves of benzoic acid in CO₂ look similar. On the basis of the NIR calibration data (Fig. 7),

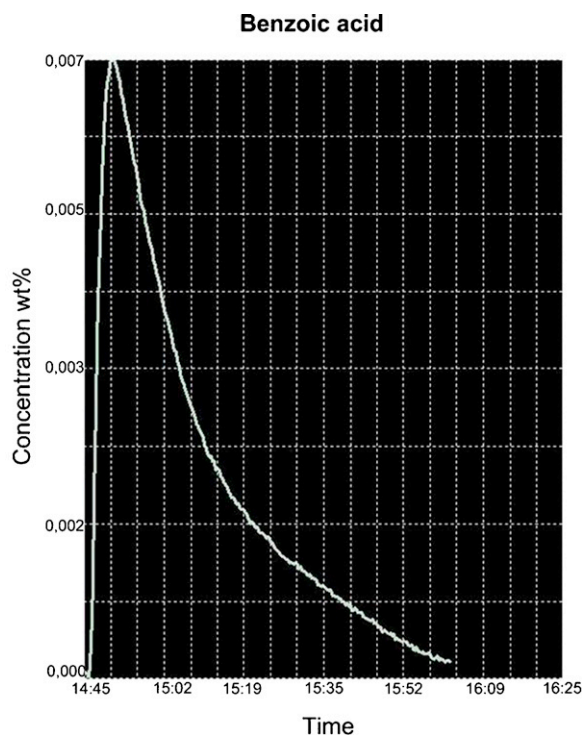


Fig. 9. Example for NIR inline monitoring curve.

all concentrations for the whole micronization run have been monitored quantitatively and visualized continuously. A fast loading in the beginning is followed by a slow decay down to zero. From the NIR calibration data, which have been obtained from the spectral measurements described above, a method with the Bruker Software called “Opus Process” has been implemented. It allows measuring the concentration of benzoic acid in the continuous CO₂ stream quantitatively, as performed within the micronization apparatus used for the experiments. It should be kept in mind, that this lab-scale apparatus has been designed for processing a continuous CO₂ stream loaded with a dissolved solid, which has to be quantified by inline monitoring at every stage of the process. Its task is not to perform an optimized micronization process, just to demonstrate the successful NIR inline monitoring of the CO₂ phase loading for micronization processes.

4. Conclusion

It has been proven that the NIR inline monitoring device SINASCO has been integrated successfully into a hops extraction [16] and a micronization plant [17] as a useful tool to visualize and to optimize the respective process. The spectral measurements can be performed with a detectability of 0.1 wt% hops extract in CO₂, and 0.01 wt% benzoic acid in CO₂, respectively.

A “side-effect” of this NIR method is a very precise detection of the solubility of benzoic acid in CO₂, as demonstrated with the calibration measurements. At 25 MPa and 55 °C, a solubility maximum of 9.82 mg benzoic acid/g CO₂ (corresponding to 0.98 wt%) has been found. This is higher than the so far reported maximum solubility of benzoic acid in CO₂ (0.56 wt%) [11,12] and therefore subject to further investigation. The measurements will be extended to different temperatures and pressures. Also further experimental research with natural substances of interest for micronization will be performed.

Furthermore, it has been shown that the NIR device SINASCO is not only valid for the inline monitoring of industrial extraction processes (e.g., hops extract production for brewing beer [16]), but

also for cleaning processes for precision parts or abrasive slurries or reactions in supercritical CO₂ as the solvent (e.g., the oxidation of hexanal to hexanoic acid [1,2]). Also a big application potential is seen for the monitoring of micronization processes in CO₂ phases [17]. The NIR inline monitoring device SINASCO is ready now for tests in industrial processes. The data gained by this method will give a clear insight into the loading of the CO₂ phase. This knowledge would be helpful to optimize micronization processes with respect to the desired narrow size distribution of the produced particles.

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References

- [1] N. Dahmen, A. Kruse, G. Wiegand, E. Dinjus, Synthese von Hexansäure in überkritischem CO₂, *Chemie Ingenieur Technik* 83 (2011) 1399–1404.
- [2] G. Wiegand, H. Ederer, J. Bürck, S. Roth, H. Mathieu, K. Krämer, Inline NIR reaction monitoring and kinetic modelling for the partial oxidation of hexanal to hexanoic acid in supercritical carbon dioxide, in: *Proceedings of the ISSF*, May 1–4 Orlando, FL, 2005 (#217 on CD).
- [3] KIT Press Release 091/2009. Available from: http://www.kit.edu/55_407.php
- [4] G. Wiegand, S. Johnsen, B. Zehnder, Maßgeschneidertes NIR-inline-Monitoring-Modul. Einsparung bei der Naturstoffextraktion und Teilereinigung mit CO₂, *CITplus* 7/8 (2009) 41–43.
- [5] G. Wiegand, S. Johnsen, B. Zehnder, *ACHEMA 29. Internat. Exhibition Congress for Technical Chemistry*, in: *Environmental Protection, and Biotechnology*, Frankfurt, Germany, May 11–15, 2009.
- [6] G. Wiegand, S. Johnsen, B. Zehnder, Mobile NIR-inline monitoring device for processes with CO₂. *Prep. Pap.-American Chemical Society, Division of Fuel Chemistry* 55 (2010) 77–78.
- [7] J. Bürck, G. Wiegand, S. Roth, H. Mathieu, K. Krämer, Quantitative in-line analysis of squalane in supercritical CO₂ using fiber-optic NIR spectroscopy and multivariate calibration, *J. NIR Spectroscopy* 12 (2004) 29–36.
- [8] J. Bürck, G. Wiegand, S. Roth, H. Mathieu, K. Krämer, Monitoring of technical oils in supercritical CO₂ under continuous flow conditions by NIR spectroscopy and multivariate calibration, *Talanta* 68 (2006) 1497–1504.
- [9] M. Buback, Near infrared spectroscopy of fluid phases, *Journal of Molecular Structure* 347 (1995) 113–130.
- [10] M. Buback, Spectroscopy of fluid phases – the study of chemical reactions and equilibria up to high pressures, *Angewandte Chemie International Edition* 30 (1991) 641–653.
- [11] R.T. Kurnik, S.J. Holla, R.C. Reid, Solubility of solids in supercritical carbon dioxide and ethylene, *Journal of Chemical and Engineering Data* 26 (1981) 46–51.
- [12] M. Türk, G. Uppel, P. Hils, Formation of composite drug–polymer particles by co-precipitation during the rapid expansion of supercritical fluids, *Journal of Supercritical Fluids* 39 (2006) 253–263.
- [13] A. Klotz, Diploma Thesis, KIT, Germany, January 2011, p. 86.
- [14] T. Grau, Bachelor Thesis, KIT and Hochschule Offenburg, Germany, July 2011, p. 66.
- [15] E. Kaczowka, Master Thesis, KIT and Hochschule Offenburg, Germany, October 2010, p. 97.
- [16] G. Wiegand, S. Johnsen, N. Igl-Schmid, J. Schulmeyr, A. Wuzik, B. Zehnder, Optimization of CO₂-extraction processes by inline monitoring, in: *Proceedings of the 10th International Symposium on Supercritical Fluids*, San Francisco, P-0303, 2012, p. 2.
- [17] D. Böhm, T. Grau, S. Johnsen, E. Kaczowka, A. Klotz, M. Türk, G. Wiegand, B. Zehnder, NIR-inline-Monitoring for Micronization Processes in Supercritical CO₂, in: *Proceedings of the 10th International Symposium on Supercritical Fluids*, San Francisco L-219, 2012, p. 4.