

OPTICAL DIAGNOSTICS TO STUDY SUPERCRITICAL CO₂ PROCESSES

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Supercritical (sc) carbon dioxide (CO₂) process technologies are inherently interlinked with high pressure. Hence optical access to directly measure in situ the desired quantities is usually restricted. But high pressure at moderate temperatures also results in high molecular number densities (number of molecules per volume). Especially this fact makes high pressure technology a promising field for optical in situ diagnostics. The low scattering cross section (interaction probability between light and matter) of the Raman process is compensated by the many molecules, from which the light can be potentially scattered according to the Raman process. Raman spectroscopy is a powerful optical measurement technique, which provides quantitative information about the number density of particular species, the mixture composition or the mixture temperature.

Other optical measurement techniques, e.g. Shadowgraphy, Interferometry and Foerster Resonant Energy Transfer, are also useful measurement tools for in situ analysis of the supercritical process technology.

The presentation reports several applications of optical measurement techniques to the supercritical process technology and aims to present the potential of such techniques for in situ process studies. The measurement techniques were applied to the supercritical antisolvent precipitation (SAS), the supercritical extraction from emulsions, high pressure phase equilibria and supercritical fluids in micro channels.

INTRODUCTION

Quantitative in situ optical measurement techniques are receiving increasing popularity in the field of supercritical fluid process technology. The increasing demand in these measurement techniques is justified in the motivation of researchers and chemical and biological engineers to understand the mechanisms taking place inside the high pressure equipment, which most probably does not provide optical access to the process interior. Without the possibility to in situ monitor the process taking place inside the apparatuses the development of a comprehensive understanding of the functioning chain of the respective process will be hindered and most probably remain unknown. As only based on a profound knowledge of the process a targeted process optimization may be successful, high pressure apparatuses can be equipped with optical accesses and optical in situ measurement techniques can be adopted. The application of optical in situ measurement techniques until now has contributed significantly to a deeper understanding of the respective processes [1-13].

Regarding the application of optical measurement techniques some considerations have to be made. Once the parameter, which is to be investigated is identified, the therefore most

qualifying optical measurement technique has to be identified from a large pool of available measurement techniques. Different measurement techniques –of course- qualify for the investigation of different parameters. Some measurement techniques, such as shadowgraphy techniques [1-14], qualify to observe phenomenological mechanisms, which do not request for a further investigation, while other more comprehensive measurement technologies can provide exact information about the state variables such as pressure, temperature, density and composition. Some measurement techniques, such as absorption techniques, can provide the desired information line in sight only, which might be sufficient in a homogeneous system, which might be considered a continuously stirred tank reactor. Sometimes, when the composition inside the apparatus might not be considered homogeneous, such as in spray processes, line in sight measurement provide averaged information which has nothing to do with the actual distribution of the desired quantity in the process. Therefore, spatially resolving measurement techniques exist as point wise (0-d), line wise (1-d) [3] or imaging (2-d) strategies [2]. In process with turbulence or temporal fluctuations it might be requested to resolve the fluctuations temporally. Hence measurement techniques down to a temporal resolution of few tens of femtoseconds (10^{-13}) exist. Sometimes transient mechanisms have to be resolved to follow the consequences of an initial event in the subsequent functioning chain. Then measurement techniques with high repetition rates are requested [15].

For the investigation of mixing phenomena Raman scattering is one of the most powerful measurement techniques in high pressure processes. Raman scattering is also frequently applied in ambient pressure processes. Nevertheless the high pressure environment offers the optimum environment to fully exploit the potential of Raman scattering. The two most important advantages of Raman scattering in comparison to other measurement techniques is that

- Raman scattering is species specific and that
- Raman scattering is quantitative.

The most prominent disadvantage of Raman scattering is its small Raman scattering cross section, which is quantifying the probability of the occurrence of a Raman scattered photon, once a molecule interacts with an initial photon. As in high pressure systems the number of molecules (potential Raman scatterers) is more than one order of magnitude higher than compared to ambient pressure processes, the small Raman scattering cross sections are compensated by the high molecular densities of Raman scatterers. Therefore Raman signals of rather high intensity can be detected with relatively simple optical setups. Therefore the two above mentioned advantages of Raman scattering can fully be exploited in high pressure processes.

Raman scattering is species specific

The energy of Raman scattered photons is shifted from the energy of the incident non scattered photons by the energy of the intra molecular transition taking place during the scattering process. In other words, the scattering molecule occupies two different energy levels before and after the scattering process. The energy difference between these two occupied energy levels is transferred onto the photon. As the energy difference between two energy levels is species specific (the energy difference for two different species is never identical, even for isotopes it is different), the energy difference between the scattered and the incident photons carries the information which kind of a molecule has been involved in the scattering process. The energy difference between the incident and the scattered photon can be computed from the wavelength shift of the scattered in comparison to the incident photon.

In mixtures composed of versatile substances, the components can be qualitatively detected. According to the second advantage of Raman scattering, the mixture composition can be quantified, too.

Raman scattering is quantitative

The intensity of the Raman scattering process is directly proportional to the number density of scatterers in the probe volume. In other words, if the amount of scatterers is doubled, the amount of Raman scattered photons is doubled accordingly. Thus, once the Raman setup is calibrated, changed in the mixture under investigation can be followed by monitoring the intensity of a species specific Raman signal. If a whole spectrum, which carries the information of all species present in the mixture under investigation is analyzed simultaneously, the mixture composition can be quantified straight forward.

Based on these advantages partial densities of single species, mixture compositions, supersaturations and the location of first particle precipitation could be quantified, respectively analyzed. A comprehensive overview is given elsewhere [7].

Here a Raman based measurement technique is proposed, which provides quantitative information about mixture compositions from mixtures inside a capillary. Similar strategies have been proposed by others for the quantification of heating values of fuel gases before combustion in turbines [16].

METHODS

A capillary of internal diameter of 1 mm, which is coated highly reflective for the visible light is considered as a high pressure phase equilibrium cell. The Raman excitation laser is focused through the capillary windows into the capillary, where the excitation laser light travels along the capillary. Hence along the capillary the incident excitation photons pass many potential scatterers. The Raman scattered photons, which originally are scattered into all directions, can exit the capillary, which is coated highly reflective for the visible spectrum, only through the front and the back windows. Hence 50 % of “all” the Raman scattered photons, which have been generated along the capillary can be detected through the front or the back window. This increases the intensity of the Raman signals dramatically

RESULTS

By using a capillary, which is internally coated highly reflective for the visible spectrum, Raman measurements for the analysis of phase equilibria can be carried out with low power excitation lasers. With increasing length of the capillary, the detectable Raman scattering signals can be increased up to 15 times. For capillary length longer than 40 cm a stagnation of the Raman signal intensity increase is observed. Consequently species, which are present in a mixture in minor species concentrations might be detectable with a setup like this. The capillary allows for cheap construction of high pressure view cells. The test studies are still in progress. More comprehensive results will be presented at the “The Hague” meeting.

CONCLUSION

Capillaries have the potential to become a serious substitute for high pressure view cells, as they can be produced cost effective and allow direct optical access. Due to their elongated

design they promote Raman scattering applications, which are first choice for phase equilibria studies without the need for taking samples.

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REFERENCES:

- [1] A. Braeuer, R. Adami, S. Dowy, M. Rossmann, A. Leipertz, Observation of liquid solution volume expansion during particle precipitation in the supercritical CO₂ antisolvent process, *The Journal of Supercritical Fluids* 56 (2011) 121-124.
- [2] A. Braeuer, S. Dowy, A. Leipertz, Simultaneous Raman and elastic light scattering imaging for particle formation investigation, *Optics Letters* 35 (2010) 2553-2555.
- [3] A. Braeuer, S. Dowy, A. Leipertz, R. Schatz, E. Schluecker, Injection of ethanol into supercritical CO₂: Determination of mole fraction and phase state using linear Raman scattering, *Optics Express* 15 (2007) 8377-8382.
- [4] A. Braeuer, S. Dowy, R. Schatz, M. Rossmann, E. Schluecker, A. Leipertz, Supercritical Antisolvent Particle Precipitation: In Situ Optical Investigations, *Chemical Engineering & Technology* 33 (2010) 35-38.
- [5] A. Braeuer, S. Dowy, R. Schatz, E. Schluecker, A. Leipertz. Antisolvent Precipitation: Interaction of Mixing, Phase behaviour and Particle formation. in 9th international Symposium on Supercritical Fluids. 2009. Arachon: ISASF.
- [6] A. Braeuer, R. Schatz, E. Schluecker, A. Leipertz. Characterization of the spray dynamics in a pulsed antisolvent Spray Precipitator. in ICLASS. 2006. Koyoto, Japan.
- [7] A. Braeuer, E. Torino, S. Dowy, S. Luther, E. Schluecker, A. Leipertz, E. Reverchon, Analysis of the supercritical antisolvent mechanisms governing particles precipitation and morphology by in situ laser scattering techniques, *Chemical Engineering Journal* accepted for publication (2011).
- [8] S. Dowy, A. Braeuer, A. Leipertz. CO₂ partial density distribution under dynamic mixture generation conditions in the supercritical antisolvent process. in 11th European Meeting on Supercritical Fluids. 2008. Barcelona: ISASF.
- [9] S. Dowy, A. Braeuer, K. Reinhold-Lopez, A. Leipertz, Laser analyses of mixture formation and the influence of solute on particle precipitation in the SAS process, *The Journal of Supercritical Fluids* 50 (2009) 265-275.
- [10] S. Dowy, A. Braeuer, K. Reinhold-López, A. Leipertz, In situ optical monitoring of the solution concentration influence on supercritical particle precipitation, *The Journal of Supercritical Fluids* 55 (2010) 282-291.
- [11] S. Dowy, A. Braeuer, R. Schatz, E. Schluecker, A. Leipertz, CO₂ partial density distribution during high-pressure mixing with ethanol in the supercritical antisolvent process, *The Journal of Supercritical Fluids* 48 (2009) 195-202.
- [12] S. Dowy, A. Braeuer, R. Schatz, E. Schluecker, A. Leipertz. Particle Nucleation and Mixture Formation Characterized by a combination of Raman and Mie Scattering. in 9th international Symposium on Supercritical Fluids. 2009. Arachon: ISASF.
- [13] S. Dowy, E. Torino, S.K. Luther, M. Rossmann, A. Braeuer, Imaging the supersaturation in high-pressure systems for particle generation, *Chemical Engineering Journal* 168 (2011) 896-902.
- [14] E. Reverchon, E. Torino, S. Dowy, A. Braeuer, A. Leipertz, Interactions of phase equilibria, jet fluid dynamics and mass transfer during supercritical antisolvent micronization, *Chemical Engineering Journal* 156 (2010) 446-458.

- [15] A. Braeuer, S.R. Engel, S. Dowy, S. Luther, J. Goldlücke, A. Leipertz, Raman mixture composition and flow velocity imaging with high repetition rates, *Opt. Express* 18 (2010) 24579-24587.
- [16] M.P. Buric, K. Chen, J. Falk, R. Velez, W. S.: *Raman sensing of fuel gases using a reflective coating capillary optical fiber*, in *Proceedings of the Spie* U. Eric, D. H., and A. Wang, Editors. 2009. p. 731608.