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Prospects: Facing current challenges in high pressure high temperature process engineering with *in situ* Raman measurements

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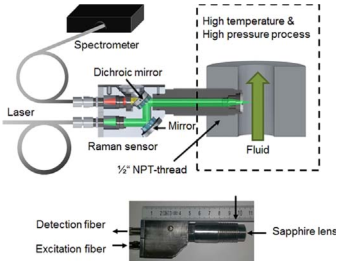
GRAPHICAL ABSTRACT



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ABSTRACT

Prospects are given how Raman spectroscopy can provide valuable insights into the understanding of processes that are operated at high pressures and high temperature. At high pressures and high temperatures Raman spectroscopy has been an efficient tool for the *in situ* analysis of mechanisms such as heat transfer, mass transfer, reaction, crystallization, decomposition, condensation, hydrolysis and others. Its future potential is discussed treating three specific example processes; (i) the extraction of valuable compounds from biomass, (ii) the conversion of biomass to platform chemicals and fuels and (iii) the decontamination of wastewaters containing organics. What is discussed for these three example processes can be transferred to other processes that do not have to take place at high temperature and high pressure. A brief introduction into applied Raman spectroscopy is provided in the context of these processes. Then it is described where in these processes the application of Raman spectroscopy can make substantial contributions to the understanding of the processes. Finally, some strategies are mentioned how Raman spectroscopy can be applied to high pressure and high temperature processes.

1. Introduction

Today, humanity is confronted with a lot of serious challenges, such as pollution, climate change, energy supply, nutrition of a growing world population, urbanization, waste management and many more. High temperature and high pressure (HTP) process engineering has encountered these challenges and may possibly contribute to overcome them in the future. Examples are the substitution of harmful solvents with benign green solvents such as compressed carbon dioxide (CO_2) [1] or hydrothermal water [2] in a variety of processes, carbon capture

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and sequestration [3], high pressure treatment for food pasteurization [4], hydrothermal conversion of biomass and waste to biofuels or platform chemicals [5,6], HTP carbonization of sewage sludge [7], supercritical water oxidation (SCWO) for the decontamination of wastewaters from organic loads and others [8].

Unfortunately, HTP processes, simply because of high pressure and high temperature, represent delicate scenarios for the adoption and application of *in situ* measurement techniques. Thus, knowledge about the mechanisms (heat transfer, mass transfer, reaction, crystallization, decomposition, condensation, hydrolysis…) and their kinetics taking place inside these HTP processes is not as comprehensive as it is for processes that take place at ambient pressure and temperature. Thermodynamic data, such as solubility, vapor liquid equilibria, specific volume and others are not comprehensively available at HTP conditions, too. *In situ* measurement techniques can help develop a comprehensive understanding of HTP processes, which is the basis of the successful but also efficient operation of HTP processes. Therefore *in situ* measurement techniques will not only help to face current challenges in HTP process engineering, but can potentially contribute to overcome some of humanity's serious challenges. The technological challenge is the adoption of the *in situ* and non-invasive optical measurement techniques to the HTP processes that are operated at conditions rather harsh for the successful application of optical diagnostics.

The applications of Raman measurement techniques, not all of them applied *in situ*, have provided valuable insights into a variety of fields that are related to supercritical fluid science and technology and to high temperature and/or high pressure processes in general. These fields, among many more, cover thermodynamics [9–11], physical chemistry [12–16], reactions [17–23], thermal process engineering [24–29], heat and mass transfer [30–42] and material sciences, geology, as well as mineralogy [12,43,44]. The majority of *in situ* Raman applications at HTP conditions have been carried out in idealized colorless systems, from which interference-free Raman spectra were recorded and from which the desired information could be extracted in a straight forward manner. But to better understand the mechanisms in real processes, Raman spectroscopy has to be applicable to non-idealized, chromatic (not colorless), close-to-reality or even real processes. HTP application fields for which I see that Raman spectroscopy can make substantial contributions are the exploitation of biomass (1) and the decontamination of wastewaters from organics (2). The exploitation of biomass covers the extraction of valuable compounds from biomass (1a) and the conversion of biomass to platform chemicals and fuels (1b). Of course there are other seminal fields of application, but because of their great relevance with respect to current humanity's challenges (sustainable supply of resources and energy and waste deposition of mega cities) I decided to pick those two. It should be underlined that there already have been *in situ* Raman studies with respect to the decontamination of wastewater under idealized conditions [18,21,45], but, to the knowledge of the author, not under close-to-reality-conditions and not with respect to the exploitation and the conversion of biomass.

In the sections that follow, first an introduction to Raman spectroscopy will be provided. Then I will describe my ideas on how applied Raman spectroscopy can support processes for the exploitation of biomass (provision of fine chemicals, pharmaceuticals, platform chemicals and fuels) and the decontamination of wastewaters resulting especially from sewage sludge HTP carbonization. What I report are my visions and prospects rather than sound standing results.

Besides this prospects article on "Raman spectroscopy", this special issue also contains other articles with a focus on measurement techniques. These are the article of Sergei Kazarian about infrared absorption spectroscopy [46], the article of Eberhard Schlücker about Raman spectroscopy and ultraviolet/visible (UV/VIS) absorption spectroscopy [47] and an article by Monika Johannsen about chromatographic measurement techniques [48].

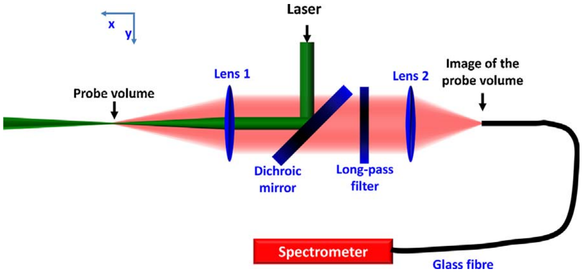

Fig. 1. Sketch of an example experimental Raman setup for signal detection in back scattering configuration (from [50]).

2. Raman spectroscopy

In this section the Raman effect is described in brief, on the basis of a practical experimental setup that is shown in Fig. 1. Textbooks by Long [49] and Braeuer [50] provide comprehensive descriptions of the Raman effect/spectroscopy in general and related to high pressures.

Each Raman spectroscopy setup consists of a laser, a spectrograph, some optical components and a detector. In Fig. 1 the detector is integrated into the spectrometer and thus not labelled separately. The laser radiation is sketched greenish and the detected signals reddish. The dichroic mirror and spherical lens 1 are required to guide and focus the laser radiation into the probe volume. Due to the interaction between light and matter the signals emerge. These signals can be due to elastic light scattering, inelastic light scattering and emissions, three very different interaction mechanisms between light and matter. Lens 1 and lens 2 image the probe volume in backward direction (signal detection under 0°) onto the entrance area of the glass fiber. Then the signals are guided through the glass fiber towards the spectrometer, where the signals are spectrally dispersed and detected as an intensity-over-wavelength spectrum by the detector.

2.1. *Raman spectroscopy, a spatially resolved measurement technique*

As lens 1 and lens 2 image the probe volume on the entrance area of the glass fiber, only the signals that emerge from the probe volume itself are efficiently collected and guided to the spectrometer. Signals emerging from regions before or behind the laser beam focus (laser beam waist) are imaged behind or before the glass fiber entrance area and are thus not efficiently collected. The region around the laser focus from which the signals are efficiently launched into the glass fiber is called depth of field of the Raman sensor and determines the dimension of the probe volume. The exact dimensions of the probe volume depend on the lenses used, the laser beam diameter before it passes lens 1 and on the core diameter of the glass fiber.

2.2. *Raman spectroscopy, a qualitative measurement technique*

If the matter (molecules) in the probe volume cannot absorb the laser photons, the laser photons can only be scattered from the molecules. Similar to the mechanics of colliding spheres, in the case of "photon-molecule-collisions" (or scattering interactions), it is differentiated between elastic and inelastic light scattering. If the laser photon, due to the interaction with the molecule, changes its direction but not its energy, the scattering process is called ELASTIC light scattering or Rayleigh scattering. Then the wavelengths of the scattered radiation and the incident laser radiation are identical. Due to the conservation of energy the scatterer (molecule) does not change its energy. If the laser photon, due to the collision with a molecule, changes its direction and its energy, the scattering process is called INELASTIC light scattering or Raman scattering. Then the wavelengths of the inelastically scattered radiation and the incident laser radiation are different. Due to the conservation of energy, the value of the energy

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