Chemical Engineering Journal 223 (2013) 129–134

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

In situ measurement of the temperature of water in microchannels using laser Raman spectroscopy

A. Ewinger, G. Rinke *, A. Urban, S. Kerschbaum

Karlsruhe Institute of Technology (KIT), Institute for Micro Process Engineering, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

HIGHLIGHTS

- ▶ In situ measurement of water temperature between 30 °C and 58 °C within a microchannel.
- ▶ Linear dependence between peak intensities and temperatures.
- ▶ Temperature determination achieved an accuracy of ±1.2 °C.
- ▶ Application of laser Raman spectroscopy with a spatial resolution of 15 μm in width and 25 μm in depth.

ARTICLE INFO

Article history:
Received 9 October 2012
Received in revised form 16 January 2013
Accepted 23 January 2013
Available online 9 February 2013

Keywords:
Raman spectroscopy
Microchannel
Temperature measurement
Spatial resolution

ABSTRACT

For an improved understanding of physical and chemical processes in microreactors and their optimization, it is important to know the temperature distribution within microchannels. For this purpose, laser Raman spectroscopy can be applied. In this work, a 32 mm long microchannel with 0.4 mm width and 0.2 mm depth was used. Its temperature was controlled between 30 °C and 58 °C. The beam of a continuous argon ion laser was coupled into the tube of a microscope and focused through a quartz plate into the microchannel. The scattered Raman light of the molecules was measured with a spectrometer and a CCD camera. For first investigations, pure water was used. The broad vibrational Raman band of the OH stretch is bimodal with peaks at about 3250 cm^{-1} and 3450 cm^{-1} and leads to different shapes, which are dependent on temperature. The dependence of the peak intensities on temperature shows a linear course, and the temperature can be determined with an accuracy of ±1.2 °C. Further own investigations with the same Raman system show that the measuring procedure used here has a lateral local resolution of approximately 15 μm and a depth resolution of 25 μm. Therefore, the temperature profile inside microchannels can be determined with this spatial resolution.

1. Introduction

1.1. Micro-chemical engineering

The use of micro-structured components for process engineering has gained increasing importance in chemical, pharmaceutical and life sciences applications during the last years. Reactors, heat exchangers, static mixers and other process components can be fabricated in configurations scaled in millimeters with embedded micrometer-sized channels [1–8]. Due to large specific wall surface area, devices with such small channel dimensions provide more efficient mass and heat transfer. This can result in greater selectivity and higher yield for chemical reactions [3,5].

At the Karlsruhe Institute of Technology (KIT) micro-structured devices can be manufactured with widths and depths of microchannels down to 0.1 mm. Examples are cross or counter flow micro-heat exchangers, electrically powered micro-heat exchangers, micromixers as well as micro-structured reactors for chemical reactions with liquid or gaseous media [9]. These components are pressure resistant up to several hundred bars and have high heat transfer coefficients. For example cross flow micro-heat exchangers with an outer volume of 1×10^{-6} m^3 can have a heat transfer coefficient of up to 30 kW m^{-2} K^{-1}, when run with water in both passages. With cold water inlet temperature of 8 °C in one passage, warm water inlet temperature of 95 °C and a mass flux in both passages of 2000 kg m^{-2} s^{-1}, a thermal power of 20 kW can be transferred. With this operating conditions, the pressure drop in both passages is about 5 bar [9].

The production of these micro-structured devices is based on mechanical micro-machining of metal foils. Micromechanical processes are for instance precision turning and precision milling. The following materials can be used: stainless steel as standard, hastelloy, aluminum alloys and different metals like silver, palladium,

* Corresponding author. Tel.: +49 721 608 23556; fax: +49 721 608 23186.
E-mail address: Guenter.Rinke@kit.edu (G. Rinke).

1385-8947/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2013.01.076

rhodium and copper. The foils are joined by thermal diffusion bonding at high temperatures and the diffusion-bonded body is then welded in a standardized housing. These micro-heat exchangers and microreactors have already found industrial applications. Areas of applications are for example chemical production [9–13] and biodiesel production [14].

1.2. In situ temperature measurements

Common methods which are a state of the art for in situ temperature measurements in microchannels are IR thermometry [15–17] or thermocouples and thin-film resistance temperature detectors [15], which can be used to determine local temperatures of the channel wall or near this wall, but do not achieve a spatial resolution within the liquid volume. Other methods as laser-induced fluorescence thermometry [18–20] and Liquid Crystal Thermography [20] require temperature sensitive fluorescence dyes and Liquid Crystals and they are comprehensive in equipment and analysis. Furthermore, their fluorescence properties may change with time. Kim et al. [21] used micro-Raman spectroscopy for steady state measuring of temperatures in microchannels, but without specifying spatial resolution within the volume of a microchannel, probably integrated over the height of the microchannel.

1.3. Laser spectroscopy for concentration measurements

In order to obtain a better understanding of the physical and chemical processes within such components and to optimize these devices it is desirable to measure concentration profiles and temperature profiles within microchannels. For this purpose, laser Raman spectroscopy can be used. This method is very selective for individual chemical compounds, allows a good spatial resolution and gives a quantitative analysis. Raman spectroscopy can be combined with a microscope and confocal apertures to measure small volumes.

Salmon et al. [22] used a Raman microscope to observe the mixing processes of chloroform and methylene chloride within a commercially available micro-device. Park et al. [23] applied both, confocal fluorescence spectroscopy and Raman spectroscopy, to monitor the mixing processes of ethanol and isopropanol in a micromixer. Löbbecke et al. [24] developed a modular microreaction system, which allows to control the reaction with IR and Raman spectroscopy. Fletcher and Haswell [25] used a commercial Raman microscope to monitor the concentration profiles during the synthesis of ethyl acetate within a micromixer, which consists of silicon and Pyrex. Schlüter et al. used laser induced fluorescence to characterize the flow within microchannels [26].

For measurements of concentration profiles within microchannels our working group uses micro-Raman spectroscopy, too [27]. In this work, the same technique was extended to measure temperatures within microchannels.

1.4. Laser Raman spectroscopy for temperature measurements in water

Liquid water shows a strong and broad vibrational Raman band in the region between 2800 cm^{-1} and 3800 cm^{-1} that is due to OH. The Raman spectrum of this OH stretch is bimodal with strong peaks at 3250 cm^{-1} and 3450 cm^{-1} [28]. The shape of the resulting Raman band between 2800 cm^{-1} and 3800 cm^{-1} depends on temperature, which is based on the different behavior of the valence band of different water species [29,30]. There are three-dimensional clusters of hydrogen-bonded (HB) water [21,31,32] or so-called polymer [33] at a wavenumber of 3250 cm^{-1} and non-hydrogen-bonded (NHB) water or monomer at 3450 cm^{-1}. With increasing temperature, the hydrogen bond of clustered water molecules is broken. Due to changes in equilibrium between monomer and clustered water molecules [21,33], the ratio of the Raman intensities at higher wavenumbers to lower wavenumbers becomes larger [32–35]. This means that the monomer concentration systematically increases with rising temperature [36]. Therefore, the temperature of water can be determined from the ratio of the two peak intensities of the bimodal peak at 3250 cm^{-1} and 3450 cm^{-1}.

Paolantoni et al. [37] investigated the relationship from ordered and disordered water molecules at 10–75 °C. Kargovsky [38] differentiated in his model between "heavy" (number of water clusters $n = 4$–6) and "light" water clusters ($n = 1$–3) from −12.5 to 32.5 °C. Starzak et al. [31] introduced a model to determine temperatures between −30 °C and 300 °C for water. They described the predominance of the concentrations of water tetramer and pentamer, while the concentrations of monomer and dimer water are very low at room temperature. Kim et al. [21] gave an example for measuring temperatures (from 53.6 to 54.8 °C) inside a microchannel of a polymerase chain reaction chip using thermochromic liquid crystals and laser Raman spectroscopy. However, no data are presented concerning the lateral and depth resolution. Others dealt with salt influence, not only the effect of temperature [29,35,36]. Burikov et al. [29,30] and Dolenko et al. [36] used the three wavenumber method and an artificial neural network for the determination of temperature and salinity of seawater and water solutions with electrolytes.

This paper deals with first experiments to measure the local temperature of pure water within a microchannel. For this purpose, the temperature dependent spectral shape of the OH-Raman band is used.

2. Experimental setup

2.1. Microchannel device

These experiments were done with a microchannel within a 1 mm thick round metal plate with 50 mm diameter. The microchannel was 32 mm long with 0.4 mm width and 0.2 mm depth. The plate was made of Hastelloy C22. For Raman measurements, a 2 mm thick round quartz plate of 50 mm diameter covered the metal plate containing the microchannel. As gasket an O-ring with 1 mm thickness was fitted into a nut. The microchannel with polished surface, the quartz plate and a thick metal base plate were pressed together with a flange on top and were positioned below the microscope objective (Fig. 1). The base plate contained a heat

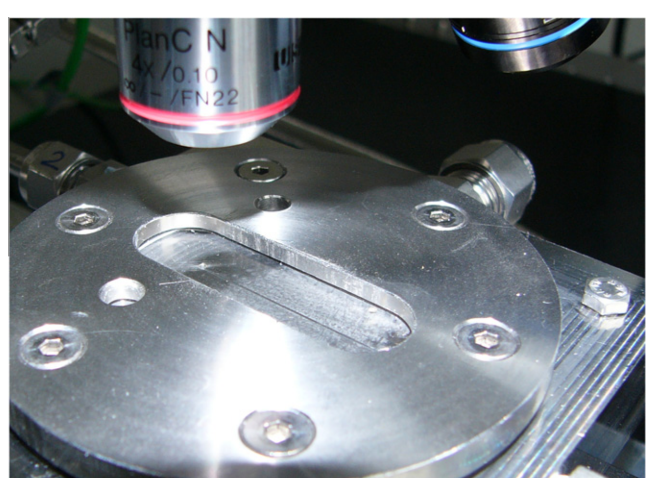

Fig. 1. Photo of the micro-device below the microscope objective.