Sensors and Actuators A 162 (2010) 215–219

Contents lists available at ScienceDirect

Sensors and Actuators A: Physical

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

Real-time monitoring of a high pressure reactor using a gas density sensor

Johannes K. Sell [a,*], Alexander O. Niedermayer [a], Sebastian Babik [b], Bernhard Jakoby [a]

[a] Institute for Microelectronics and Microsensors, Johannes Kepler University Linz, Altenbergerstr. 69, 4040 Linz, Austria
[b] PO Polymer Design, Borealis Polyolefine GmbH, Linz, Austria

ARTICLE INFO

Article history:
Received 30 September 2009
Received in revised form 7 December 2009
Accepted 4 January 2010
Available online 15 January 2010

Keywords:
Gas density sensor
Quartz crystal resonator
Pressure dependence

ABSTRACT

We investigate a gas density sensor based on quartz crystal resonators for high pressure (2.5×10^6 Pa) and high temperature (340 K) application. The suitability of tuning fork resonators for density measurement in pure gases has been demonstrated. Furthermore, thickness shear-mode resonators are commonly used for viscosity and density measurement in liquids. In our contribution, these devices are compared with respect to their sensitivity to gas density for the target application in a polymerization reactor, involving high ambient pressures. It was confirmed, that tuning fork resonators are mainly sensitive to density, whereas shear-mode resonators are more suitable for viscosity measurement. Moreover, a density sensor for density measurements in unknown gases and gas mixtures, based on two tuning forks, is presented. At high pressures, an additional pressure-dependent frequency shift has to be considered.

1. Introduction

Maintaining constant gas composition in a gas polymerization process is crucial to obtain a uniform polymerization and the development of new polymers. Due to the typical polymerization conditions in a polymerization reactor ($T \approx 340$ K, $p \approx 2.5 \times 10^6$ Pa), standard procedures such as mass spectroscopy or gas chromatography cannot be applied to directly monitor the gas composition inside the reactor in real-time.

We are currently working on a density sensor, which will be part of a prototype sensor system for monitoring the gas composition in a pressure vessel during the polymerization process. The density sensor is based on a quartz crystal resonator in contact with the gases. It was shown, that thickness shear-mode resonators can be used for density and viscosity measurements in liquids [1]. Moreover, tuning fork resonators have successfully been applied for density measurement in SF_6[2]. Tuning fork and thickness shear-mode devices provide fast response times and are therefore suitable for real-time monitoring of physical properties of fluids. In our contribution, these devices are investigated with respect to their suitability for density and viscosity measurement in gases and gas mixtures.

2. Frequency shift of resonators in contact with fluids

In general, the resonance frequency of a resonator in contact with a surrounding media is shifted. The magnitude of the shift depends on the properties of the surrounding media, the geometry of the resonator, and its vibration mode.

2.1. Tuning fork resonator

A tuning fork resonator can mathematically be described as a cantilever, vibrating in flexural mode. The resonance frequency of the resonator in contact with a fluid (liquid or gas) is shifted; the relative change is given by [2]:

$$\frac{\Delta f}{f_0} = \frac{-t}{2\rho_q w}\left(\frac{c_2}{\sqrt{\pi f_0}}\sqrt{\eta\rho_g} + c_1\rho_g\right) \quad (1)$$

where f_0 is the resonance frequency in vacuum, ρ_g is the density of the surrounding gas, ρ_q is the quartz density, t is the thickness of the tuning fork, w its width, η is the viscosity of the surrounding gas and c_1 and c_2 are geometry dependent constants. A more detailed derivation can, e.g., be found in [3].

2.2. Thickness shear-mode resonator

When a thickness shear-mode resonator is brought in contact with a fluid, a strongly attenuated shear wave is excited in the fluid. This effect is based on an entrainment of the fluid with the vibrating sensor surface, which leads to a damping of the resonator (due to viscous losses) and to a frequency shift (due to the entrained mass). The latter is given by [4]:

$$\frac{\Delta f}{f_0} = -\frac{f_0^{1/2}}{\sqrt{\pi\rho_q\mu_q}}\sqrt{\eta\rho_g} \quad (2)$$

* Corresponding author. Tel.: +43 732 2468 6250; fax: +43 732 2468 6252.
E-mail address: johannes.sell@jku.at (J.K. Sell).

0924-4247/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.sna.2010.01.013

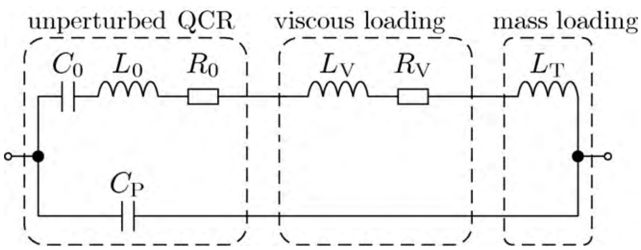

Fig. 1. Butterworth–van Dyke model of a quartz crystal resonator. The elements of the unperturbed QCR are extended with L_L and R_L for viscous loading and with L_T for mass loading.

where μ_q is the elastic shear modulus of the quartz resonator. An additional frequency shift has to be considered, if the surface roughness of the resonator is in the order of the decay length $\delta = (2\eta/(\omega\rho_g))^{1/2}$ of the shear wave. In this case, fluid is trapped which behaves much like an ideal mass layer; the relative frequency shift then can be calculated by [1]:

$$\frac{\Delta f}{f_0} = -\frac{f_0^{1/2}}{\sqrt{\pi\rho_q\mu_q}}\left(\sqrt{\eta\rho_g} + (4\pi f_0)^{1/2}\rho_g h\right) \qquad (3)$$

with h being the effective thickness of the trapped layer.

The frequency shift of a tuning fork vibrating in flexural mode and of a thickness shear-mode resonator hence are both depending on viscosity and density. The relative frequency change for both can be generally described by

$$\Delta f = A\sqrt{\eta\rho_g} + B\rho_g \qquad (4)$$

where A and B are resonator dependent constants. Tuning fork resonators and thickness shear-mode resonators both can be used for density and viscosity measurement in fluids, e.g. gases. Their suitability for a particular application is determined by the coefficients A and B.

3. Equivalent circuit model for quartz crystal resonators

Mechanical quartz crystal resonators can be described by electrical equivalent circuit models, the most commonly being the Butterworth–van Dyke model [5]. It consists of a motional branch with a capacitance in parallel (see Fig. 1). The motional branch is a resonant circuit, formed by a series connection of resistor, capacitor and inductance, which corresponds to the mechanical resonance behavior of the quartz. The parallel capacitance comprises the static capacitance of the resonator and parasitic capacitances, e.g. stray or cable capacitances.

The interaction of the resonator with a surrounding fluid can be modeled by adding lumped elements to the motional branch. Viscous entrainment of fluid can be described by a series combination of an inductor and a resistor, mass loading with fluid by another inductance [1].

The admittance of the motional branch is given by

$$Y_m = \left(R_0 + R_V + i\left(\omega(L_0 + L_V + L_T) - \frac{1}{\omega C_0}\right)\right)^{-1} \qquad (5)$$

The admittance of the a quartz crystal resonator in contact with a liquid then is given by

$$Y = i\omega C_p + Y_m \qquad (6)$$

At series resonance, the inductance and the capacitance of the motional branch cancel, the admittance of the motional branch is maximum and real.

In the admittance locus plot (see Fig. 2), which is the representation of the admittance in the complex plane, the admittance of the motional branch is given by a circle with its center on the x-axis. For high Q resonators, most of the circle's circumference corresponds to frequencies close to the series resonance frequency ω_0. Due to the parallel capacitance of the resonator, the circle is approximately shifted by $i\omega_0 C_p$ parallel to the y-axis. The admittance corresponding to the series resonance frequency ω_0 of the motional branch thus has an additional imaginary part. ω_0 therefore be monitored, by tracking the frequency, at which the real part of the admittance is maximal. This can, e.g. be achieved by measuring the complex impedance of the resonator with an impedance analyzer (see, e.g., [6]). Alternatively, phase-lock-loop techniques (see, e.g., [7]) or oscillators circuits (see, e.g., [8]) can be used, if the parallel capacitance is compensated.

4. Experimental setup

The experiments where conducted in a pressure vessel, which is equipped with a pressure sensor, a temperature sensor and a heating sleeve. The pressure sensor has a range of 2.5 MPa with an accuracy of ±0.5 %, temperature can be measured with an accuracy of ±0.1 K. The vessel is connected to ethene (C_2H_4), propene (C_3H_6) and tetrafluoromethane (CF_4) gas cylinders. It can be filled with pressures up to 2.5 MPa with C_2H_4 and CF_4; C_3H_6 can only be filled up to its critical vapor pressure of 1.0 MPa at room temperature.

The frequency-dependent impedance of the resonators (details are provided below) was measured with an impedance analyzer. From the impedance characteristics, the series resonance frequency was extracted as described in Section (3).

5. Results

The shift of the series resonance frequency of various quartz crystal resonators in contact with surrounding gases was measured in dependence on the gas pressure. The gases used have been C_2H_4, C_3H_6 and CF_4; the measurements have been conducted at room temperature. In detail, the performance of standard 32.768 kHz tuning fork resonators and a 5 MHz thickness shear-mode resonators is presented.

The density–frequency shift relation was obtained by measuring the series resonance frequency vs. the pressure and calculating the density of the gases at the prevailing pressure and temperature. The density can be computed by a series expansion of the virial equation:

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots \text{higher orders} \qquad (7)$$

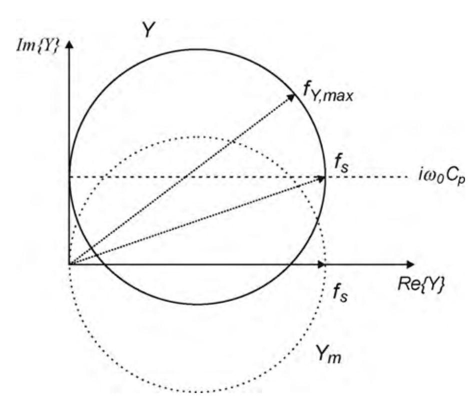

Fig. 2. Admittance locus plot of a quartz crystal resonator. The dashed circle is the admittance of the motional branch, the solid circle is the admittance of the resonator with parallel capacitance. It is approximately shifted by $i\omega_0 C_p$, compared to the admittance of the motional branch.