Monitoring of Gas Mixtures by Means of a Flexible IR-Sensor System Utilizing Tunable Filters

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Abstract

We present the implementation of a cost-effective infrared sensor solution, dedicated for real-time measurement of the overhead gas composition in bench scale polymerization reactors. The system is based on a tunable IR-filter. It is integrated into a sampling pipe and operated at ambient pressure. First test measurements of the system with binary mixtures and their evaluation with modern algorithms are presented. Furthermore, as an outlook, the potential of the developed calibration for application in ternary gas mixtures is discussed.

Keywords: IR, infrared absorption, ambient pressure, ternary gas analysis, bench scale polymerization

1. Introduction

The work was stimulated by the original task of measuring the overhead gas composition in experimental bench scale polymerization reactors. Infrared (IR) absorption measurement has been identified as a suitable method for real-time monitoring of the ongoing process. However, the usage of FTIR systems, suitable for this task, often is not attractive for companies, due to the high investment costs. In this contribution we give insight on the implementation of our IR system, dedicated for measurement in a gas stream at ambient pressure, and discuss challenges for the evaluation of IR transmission measurements when measuring at ambient pressure. Furthermore, measurements in binary gas mixtures are presented and the development of calibration models, suitable for the evaluation of these (and potentially also ternary) mixtures, is discussed.

2. Infrared absorption

In a single component gas, the transmittance of a monochromatic light source is given by the Beer-Lambert-Law [1]:

\[ T(\nu) = \frac{I(\nu)}{I_0(\nu)} = e^{-\alpha(\nu)b} \] (1)
where $\alpha(\tilde{\nu})$ is the linear absorption coefficient at the wavenumber $\tilde{\nu}$ and $b$ is the length of the transmission path through the sample.

Often, the law is also given in terms of molar concentration $c$ and molar absorptivity $\varepsilon(\tilde{\nu})$. In our evaluation we use the mass concentration $c' = c/M$ and the mass attenuation coefficient $\varepsilon'(\tilde{\nu}) = \varepsilon(\tilde{\nu})M$, where $M$ is the molar mass of the gas.

The absorbance of a gas sample can then be defined by

$$A(\tilde{\nu}) = \log \left( \frac{I(\nu)}{I_0(\tilde{\nu})} \right) = \varepsilon(\tilde{\nu})' c' b$$ (2)

In an $N$-component mixture, all constituents contribute to the absorbance, which then is given by:

$$A(\tilde{\nu}) = \sum_{i=1}^{N} \varepsilon_i'(\tilde{\nu}) c_i' b$$ (3)

Beer’s law and its extension to mixtures is valid only if the following assumptions, also made in the derivation of the theory, are met [1]: monochromatic radiation, independent absorbers, collimated radiation, homogeneous sample without scattering, no saturation of absorptions and linearity of the detectors. Most of these criteria are easily met nowadays, but the first two may pose some challenges, which will be briefly discussed in the following section.

Normally, broadband light sources are used for IR transmittance measurements. The transmittance at a specific wavenumber is determined with a narrow-band filter or by application of FTIR spectroscopy. In both cases, the bandwidth $bw$ around the observed wavenumber $\nu_0$ is finite, resulting in an effective measured transmittance of:

$$T_{eff}(\tilde{\nu}) = \frac{\int_{\nu_0 - bw/2}^{\nu_0 + bw/2} I_0(\tilde{\nu}) e^{A(\tilde{\nu})} d\tilde{\nu}}{\int_{\nu_0 - bw/2}^{\nu_0 + bw/2} I_0(\tilde{\nu}) d\tilde{\nu}}$$ (4)

In mixtures, $A(\tilde{\nu})$ in general is a nonlinear function of the mixture composition$^1$ due to collision broadening [2]. Furthermore, $A(\tilde{\nu})$ varies over the filter bandwidth. Despite these effects, which rule out the usability of eq. (3), evaluation of the composition of a mixture can be achieved by application of modern evaluation algorithms (like, e.g., partial least squares regression (PLS), neural nets, stepwise regression, ...). A good overview of these algorithms can be found in [3].

3. Measurement System

The devised IR sensor system consists of an infrared source, a detector, a commercially available tunable filter$^2$ and a gas cell with CaF$_2$ windows (see Fig. 1). The filter is electrically tunable in the range between 3.0 to 4.1 μm with a half-width of 80 nm. The IR source is driven with a square wave with a frequency of 10 Hz; a PbS photoresistor is used as detector. The resistance of the detector is modulated by the radiation of the IR source, the modulation is proportional to the intensity of the incident light. Excitation of the IR source and readout of the detector signal is carried out with a data acquisition (DAQ) module. To measure the shift of the resistance, a constant voltage is applied to the resistor and the current through the resistor is amplified with a current-to-voltage converter (Fig. 2). As the shift of the resistance is small (less than 3 % of the nominal value), the signal has a large offset. This offset is removed by subtraction of an appropriate signal, supplied by the DAQ, using a differential amplifier. The signal of the differential amplifier is read out with the DAQ module, the signal amplitude is obtained by discrete Fourier transformation. By application of the differential amplifier, the modulated output signal covers the whole input range of the ADC (if the amplification is chosen appropriately), instead of only 3 % which would be used otherwise.

$^1$Responsible is the dependence of the full width at half maximum of spectral lines on the composition [2]

$^2$TFP-3041L by InfraTec
4. Measurements & Results

To evaluate the approach, IR absorption measurements were performed in mixtures of propene with N₂, methane with N₂, and propene with methane at ambient pressure and room temperature. For each mixture, IR spectra were measured with 56 points between 2900 nm and 3550 nm; additional points were recorded between 4150 nm and 3800 nm as reference. The concentration of each mixture was determined by measurement of the gas density and application of the van-der-Waals mixing rule with the Peng-Robinson equation of state [4].

As examples, the measured absorbance spectra of propene-N₂ mixtures with different mole fractions of propene are shown in Fig. 3, the dependence of the absorbance on the mole fraction for selected wavelengths is depicted in Fig 4. Here, the nonlinearity of the mass attenuation coefficient, discussed above, can be seen.

Using PLS regression, a model to estimate the propene mole fraction was developed. The spectral data from measurements in propene-methane and propene-N₂ mixtures were included in the calibration to obtain a robust estimation, i.e., that the estimation of the propene content must not be influenced by methane or N₂ content. In Fig. 5, the residuals of the developed model are shown which confirm the suitability of the chosen model. Cross-validation predicts a root-mean-squared error less than 1 % for future measurements.

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The specialized software "DataLab" (http:\\www.lohninger.com\datalab\) was used for the evaluation.
This accuracy can be achieved by measurement at only 7 wavelengths (6 spectral points, 1 reference point), reducing the measurement time, (which is limited by the settling time of the filter) from 75s to about 10s.  
As the estimation of the propene content is not influenced by the other constituents, the calibration model has the potential to also be suitable for ternary propene-methene-N\textsubscript{2} mixtures.

5. Conclusions and Outlook

We have presented an IR system, dedicated for the composition measurement of the gas phase of bench scale polymerization reactors. Due to the flexibility of the system by virtue to the tunable filter, the system can be easily adapted to different gas mixtures. Test measurements in binary gas mixtures containing propene, methene and N\textsubscript{2} were carried out. A calibration model, that predicts the mole fraction of propene without getting influenced by the N\textsubscript{2} or methane ratios was developed. It can be concluded that this calibration has the potential to accurately estimate the propene mole fraction also in ternary propene-methene-N\textsubscript{2} mixtures. We are currently working on an automation of the measurement system in order to process a large number of ternary gas mixtures to be able to confirm the calibration or to adapt if necessary.

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References