Chemical Engineering Journal 160 (2010) 827–833

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Capillary type thermal mass flow sensors for monitoring esterification reactions in residence time micro-reactors

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ARTICLE INFO

Article history:
Received 27 July 2009
Received in revised form
19 November 2009
Accepted 6 January 2010

Keywords:
Inline process analysis
Thermal mass flow sensor
Microstructured reactor
Esterification
Homogeneous catalysis

ABSTRACT

In this contribution capillary type thermal mass flow sensors based on the thermo-transfer principle were applied for monitoring esterification reactions in residence time micro-reactors. A novel micro-reactor with an integrated sensor network was developed that enables the inline analysis of six stages of chemical conversion in parallel. The device was optimized for residence times in the range of several tens of minutes. Conversion can be monitored by means of changes in the isobaric heat capacity. Methods for the compensation of offsets and flow pulsation in the linear operation range of the sensor were developed. The novel micro-reactor was used for studies on the homogeneously catalyzed synthesis of butyl acetate. The phase separation at a certain residence time could be successfully detected. The formation of aggregates/plugs with different phases led to oscillations in the measurement signal. Insofar, robust sensors emerge as low cost tool for the inline analysis and control of esterification reactions.

1. Introduction

Micro-process engineering or micro-reaction technology in chemical, biochemical and pharmaceutical industry became a growing field, e.g. for the intensification and development of novel chemical processes. Several devices for unit operations like mixing, reaction and heat exchange were reported and are commercially available [1–4]. The high surface to volume ratio in micro-fluidic channels involves high mass and heat transfer coefficients. Thus, compared to conventional batch reactors, micro-reactors enable fast mixing under isothermal conditions and a well-defined interface to a solid or liquid catalyst in a continuous process. Among other types the residence time micro-reactor is one of the most important reactors. Devices were extensively used e.g. for the processing of single or multiple stage liquid phase reactions in organic synthesis. The hydraulic diameter, typically $\sim$1 mm and less, is mainly governed by the required residence time, through-put, maximum pressure drop and the risk of plugging. After mixing of the educts in a micro-mixer the reactive system enters the micro-reaction channel and remains e.g. until chemical equilibrium state is present. Ideally, the equilibrium state is located nearby the outlet of the micro-reactor, i.e. the residence time is matched to the kinetics of the reaction. Recently, the analysis of esterification reactions in micro-reactors became of interest. A carboxylic acid and an alcohol are converted to the corresponding carboxylate ester in the presence of a strong acidic catalyst. For the homogeneously catalyzed esterification reaction strong mineral or organic acids are used. While for the heterogeneously catalyzed synthesis ion exchange resins are employed. Carboxylate esters are used as high quality organic solvents with significant industrial relevance, e.g. used for lacquer production. Butyl acetate is of special relevance for several industrial applications, thus a large data set of reaction kinetics based conventional batch processing is available. Further details can be found in [5–12]. In a previous work the homogeneously [13] and the heterogeneously [14] catalyzed synthesis of butyl acetate in a custom made residence time micro-reactor were studied. Focus was e.g. on the kinetics of the equilibrium limited chemical reaction dependent on the flow regime, process temperature and the catalyst concentration. Experimental results were based on conventional off-line analytics, e.g. gas chromatography. Understanding of the static and dynamic behavior of the micro-reactor, respectively micro-plant is fundamental for the development, optimization and control of novel integrated chemical processes. Hence, for the analysis and optimization of esterification reactions in residence time micro-reactors an integrated inline analytics is required. Relevant process parameters are e.g. conversion rate, reaction kinetics, phase changes, residence time distribution and dispersion effects. Up to now, there is a lack in sensitive, robust and low priced sensors for inline chemical process monitoring. Quite expensive spectro-

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doi:10.1016/j.cej.2010.01.006

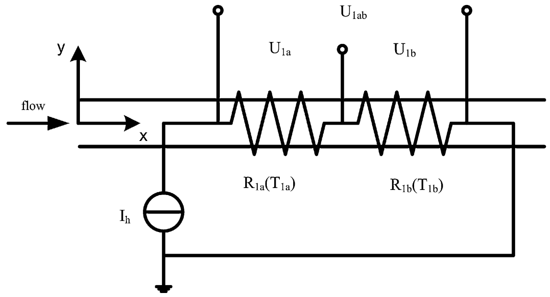

Fig. 1. Schematic of the capillary type thermal mass flow sensor optimized for mass flow rates in the range of ~g/h.

scopic techniques are state of the art for the inline/on-line chemical process analysis by means of absorption/transmission measurement in the UV/VIS/NIR range [15,16]. The scaling up for multiple measurement positions inside the reactor, respectively several micro-reactors/micro-reaction channels in parallel is a problem.

In this context low cost capillary type thermal mass flow sensors based on the thermo-transfer (calorimeter) principle [17–19] are focused for the inline monitoring of esterification reactions. Devices are state of the art for the control of mass flow rates in micro-fluidic systems. It is known, that the sensor signal is sensitive to changes in the isobaric heat capacity of the liquid. In a previous work [20] two commercially available mass flow meters [19] connected in series were used for monitoring relative changes in the isobaric heat capacity of liquids. It was shown that for a homogeneous liquid phase the evaluation of the differential sensor signal leads to a sufficient elimination of flow pulsation. In this contribution a novel residence time micro-reactor containing six capillary type thermal mass flow sensors for the inline monitoring of esterification reactions is presented. The device was applied for studies on the homogeneously catalyzed synthesis of butyl acetate with sulfuric acid as catalyst. The measurement sensitivity, impact of flow pulsation, offsets and dispersion effects as well as electrical noise on the sensor signal were of special interest.

2. Measurement principle and sensor design

Capillary type thermal mass flow sensors based on the thermo-transfer (calorimeter) principle mainly consist of two ohmic resistor coils around the outer surface of a cylindrical capillary embedded in an epoxy matrix. Hence, the sensing elements are not in direct contact with the reactive mixture. Insofar, sensors are of low complexity, respectively low costs and involve a high chemical, temperature as well as pressure stability up to 100 bar. A schematic of the sensor is shown in Fig. 1 that was optimized for low mass flow rates the range of ~g/h. With this approach quite long residence times can be achieved for processing chemical reactions with comparable slow reaction kinetics in the range of several tens of minutes. Both resistors act simultaneously as heater and temperature sensor. At flow rates $\gg 0$ g/h heat is mainly convectively transferred to the fluid and conductively along the capillary wall and the surrounding polymer. Hence, the measurement sensitivity and the response time of the sensor are mainly influenced by the thermal coupling between the coil and wall.

The fluid is heated up with an almost linear increase in the temperature along the wall and in the middle of the capillary [20]. Local temperature maxima exist at the wall nearby the end of each heating coil, while the temperature gradient increases with rising heating power. A change in the isobaric heat capacity leads to a change in temperature of the capillary wall, respectively the ohmic resistance of each coil. The relationship between the temperature T_i of a single resistor coil and the dissipated electrical power P_{eli}, respectively heat Q_{thi} can be expressed with Eq. (1). While α_{th} is the temperature coefficient of the resistor, I_h is the heater current and U_i the voltage drop, T_{ref} and R_{ref} are the corresponding reference temperature and resistance.

$$P_{eli} = Q_{thi} = U_i \cdot I_h = I_h^2 \cdot R_{ref}(1 + \alpha_{th}(T_i - T_{ref})) \tag{1}$$

When using sensors in a micro-residence time reactor, the liquid is immediately cooled down to the process temperature after passing the sensor. In commercially available mass flow meters both resistor coils are integrated in a Wheatstone bridge [19]. The circuit is operated in constant power mode, while the bridge voltage U_b is a meter for the mass flow rate. In general, the relationship between isobaric heat capacity c_p, mass flow rate m' and U_b is non-linear. It is determined during calibration procedure with a predefined reference liquid. After linearization and calibration Eq. (2) can be used as a simple approximation for the relationship between U_b, m' and c_p in the operation range of the sensor. The conversion factor K_s is dependent on the physical properties of the sensor, e.g. heating power, geometry and housing materials.

$$U_b = K_s \cdot c_p \cdot m' \tag{2}$$

Further details about the working principle and the performance of devices can be found in [19]. Thus, in single phase regime at least two sensors are required to distinguish in between sensor signal changes due to chemical conversion and flow pulsation. Even when using high quality pumps in the micro-plant, the impact of flow pulsation must be taken into account for the sensor signal analysis [20]. In general, the measurement sensitivity increases almost linear with the amount of dissipated heat, hence a higher overtemperature of the resistor coil. This approach enables the operation of the sensor at higher mass flow rates, while keeping the overtemperature constant. A compromise between the required sensitivity and the tolerable heat has to be found.

For the discrimination between chemical conversion, respectively changes in the isobaric heat capacity and flow pulsation in the two phase regime more than two measurement positions are required. Two or more liquid phases with different average isobaric heat capacities may cause an alteration in the signal similar to the impact of flow pulsation, when passing the sensor. With regard to Eq. (2) the impact of flow pulsation on the signal can be compensated with at least a pair of sensors in contact with a homogeneous liquid phase.

3. Residence time micro-reactor

Fig. 2 shows the novel residence time micro-reactor made of stainless steel containing a network of thermal mass flow sensors. The network consists of six sensors as illustrated in Fig. 1 (μ-Flow series from Bronkhorst High-Tech, The Netherlands) with an inner diameter of 1 mm. Hence, it enables the inline analysis of six stages of chemical conversion in parallel. Each sensor hangs in an isolated cavity to ensure a precise temperature control and stability, while minimizing parasitic heat conduction path. As shown in Fig. 2 sensors are interconnected in series by conventional 1/16″ capillaries made of PTFE. This approach allows an easy and flexible adjustment of the residence time in between two consecutive sensors by means of the capillary volume. Therefore, the position of each sensor in the micro-reactor can be adapted to the kinetics of the reaction. For processing the synthesis of butyl acetate, capillaries with an inner diameter of 1 mm matched to the sensor capillary and segments with 40, 80, 160, 320 and 640 cm corresponding to internal volumes of 314, 628, 1257, 2513 and 5027 μL are employed. Due to the short capillary length ~4 cm residence time in each sensor compared to the polymer capillaries in between can be neglected. The total internal volume of the residence time micro-reactor is ~10 mL, including

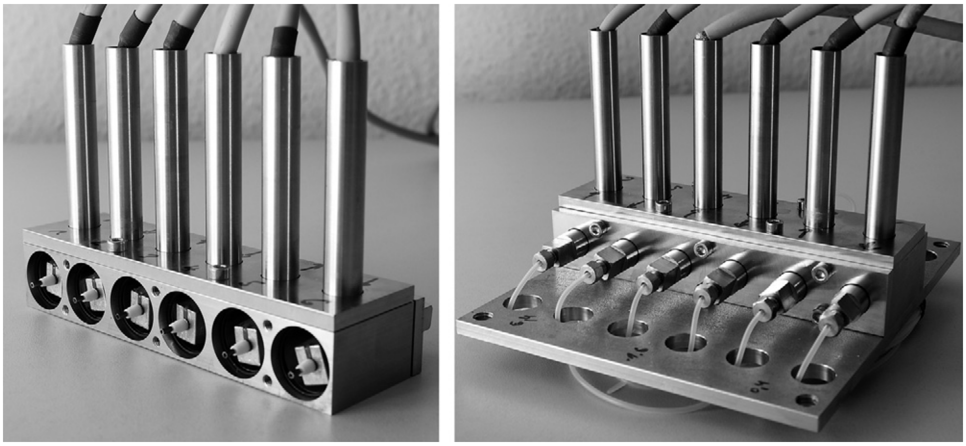

Fig. 2. Residence time micro-reactor made of stainless steel containing six capillary type thermal mass flow sensors for the inline analysis of homogeneously catalyzed esterification reactions by means of relative changes in the isobaric heat capacity.

6 sensor capillaries, each ~33 μL, and 5 PTFE capillaries as mentioned above. For precise temperature control the device is fully immersed in a thermostat bath. Water flow around the capillaries ensures that the reactive mixture is cooled down to the process temperature after passing the sensor. After mixing of the educts the reactive mixture enters the micro-reactor and passes all six sensors Si starting from S1 to S6. Insofar, the position of each sensor in the micro-reaction channel corresponds to a certain residence time. Fig. 3 illustrates the structure of the micro-reactor. It is apparent that from theory all sensors are affected simultaneously by changes in the mass flow rate. While differences in between offset compensated sensor signals can be attributed to chemical conversion. The absolute mass flow rate entering the micro-reactor is known due to mass flow meters at each inlet of the micro-plant. The four-wire technique is used for current feed and voltage measurement.

Alternatively a single resistor coil or both coils of each sensor can be connected to a programmable current source. A constant current in the range of 10–40 mA dependent on the overall flow rate is applied for heat generation. Chemical conversion, respectively changes in the isobaric heat capacity can be monitored by alterations of the voltage at each resistor coil.

4. Micro-plant and experimental procedure

Fig. 4 illustrates the structure of the custom made micro-plant as used for the homogeneously catalyzed synthesis of butyl acetate. The setup mainly consists of two mass flow meters (mini CORI-FLOW from Bronkhorst, The Netherlands) combined with two micro-annular gear pumps (mzr-4605 from HNP, Germany) for educt feed, two pressure sensors and a pressure regulator (EL-Press series from Bronkhorst) as well as a T-type micro-mixer. Valves at the inlets V-S_{Ei} are used for the selection of educts, respectively solvents for calibration, offset compensation and flushing. Additional valves V-L_{Ei} in between micro-reactor and pressure sensors enable the easy change in between different liquids, hence flushing the inlet independently of the micro-reactor. All micro-fluidic devices are interconnected by conventional PTFE capillaries. The residence time micro-reactor with micro-mixer directly attached to the inlet is placed in a thermostat (RE307 from Lauda, Germany). An analog PC plug-in card with 16 programmable current sources (NI-4704 from National Instruments, USA) is used for heat generation. Resistor voltages are measured at a sample rate of 20 Hz with a PC plug-in card with >16 analog inputs (NI-6259 from National Instruments, USA). For noise reduction sensor signals are filtered by a moving average, window size 10. A custom made LabView based software running on a standard PC is used for process control and sensor signal acquisition. All measurements were done at 80 °C and an overpressure of 4 bar defined at the pressure controller. All chemicals were of analysis grade. An equimolar feed of 1-butanol and acetic acid premixed with sulfuric acid was used for the synthesis of butyl acetate. The mole fraction x of the catalyst was in the range of 0.001 and 0.01. First, the micro-reactor was flushed several times with 1-butanol to ensure well-defined start conditions. Second, inlet E1 was flushed till V-L_{E1} with acetic acid/sulfuric acid. Third, the equimolar feed of both educts was started, after stable mass flow rates were present, the overpressure regime was applied. Hence, when starting the esterification reaction, the reactive mixture was to displace pure 1-butanol starting from V-L_{E1}. Samples were collected at the end of the capillary to visually verify, whether one liquid phase or two separated liquid phases were present.

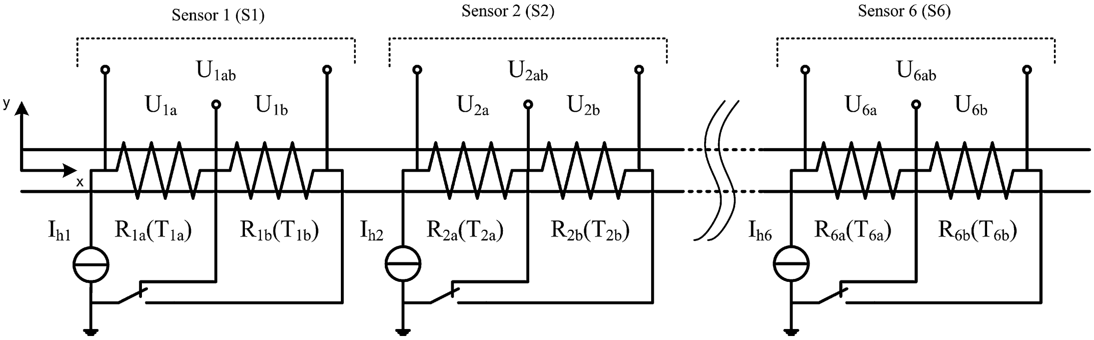

Fig. 3. Structure of the micro-residence time reactor containing a network of six capillary type thermal mass flow sensors connected in series, each with two resistor coils, while alternatively a single or both coils can be connected to a programmable current source.

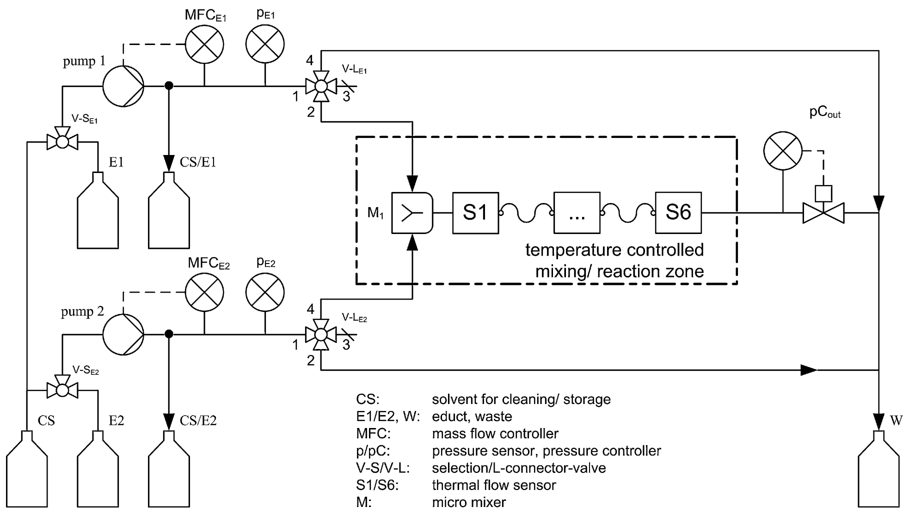

Fig. 4. Structure of the micro-plant with integrated micro-residence time reactor/thermal flow sensor network for the processing and inline analysis of homogeneously catalyzed esterification reactions at low mass flow rates in the range of ~g/h.

5. Experimental results

5.1. Offset compensation

In general due to fabrication tolerances sensors exhibit slightly different electrical and thermal properties. Fig. 5 shows the response of the sensor network for 1-butanol after switching on the current sources. Fig. 6 shows the corresponding curves with offset compensation referred to S1.

Even when the micro-reactor was flushed with a non-reactive liquid, sensor signals differed within the measurement accuracy. Thus, before processing esterification reactions offsets, mainly due to a different ohmic resistance of each coil, had to be compensated. After compensation all sensors exhibited the same signal within the measurement accuracy, when non-reactive liquids were dispensed into the micro-reactor. Experimental results showed that those offsets can be modeled as a constant factor. For the compensation one sensor was taken as reference, here S1, and deviations of all other sensors were referred to this sensor. Initially, the reactor was flushed with 1-butanol and after thermal equilibration, voltages of all sensors were sampled at least for 10 min and the average voltages U_{mSi} were calculated. According to Eq. (3) a correction factor C_{Si} for each sensor was determined, while U_{mSref} is the average voltage of the reference resistor. Then, the offset compensated signals U_{cSi} of all sensors were calculated according to Eq. (4). Maximum accuracy of the compensation could be achieved, when the correction factors were determined at the same flow rate ratio as used for the esterification reaction.

$$C_{Si} = U_{mSi} \cdot U_{mSref}^{-1} \tag{3}$$

$$U_{cSi}(t) = U_{Si}(t) \cdot C_{Si}^{-1} \tag{4}$$

5.2. Pulsation compensation

Even though the sensor network was used for monitoring changes in the isobaric heat capacity, it was also sensitive to changes in the mass flow rate. Hence, for the monitoring of esterification reactions the impact and compensation of flow pulsation induced sensor signal changes was an important factor. Fig. 7 shows the response of the network due to the propagation of pulsation, an offset of 10 mV was added to S2–6 for better illustration. Alterations in the signals were mainly due to the control loop of the pumps and electrical noise.

As shown in Fig. 7 the influence of flow pulsation was correlated in between sensors, while the influence of electrical noise not.

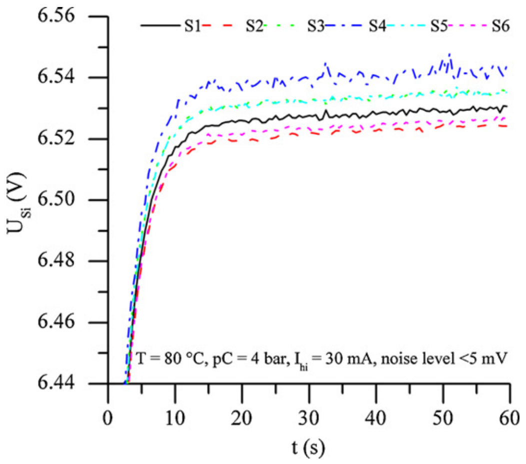

Fig. 5. Response of the thermal flow sensor network without offset correction after switching on the current sources, when 1-butanol was dispensed at a constant rate of 41.2 g/h into the residence time micro-reactor.

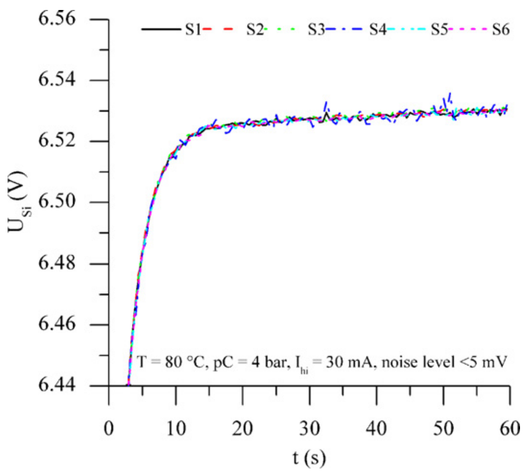

Fig. 6. Response of the thermal flow sensor network with offset correction after switching on the current sources, when 1-butanol was dispensed at a constant rate of 41.2 g/h into the residence time micro-reactor.

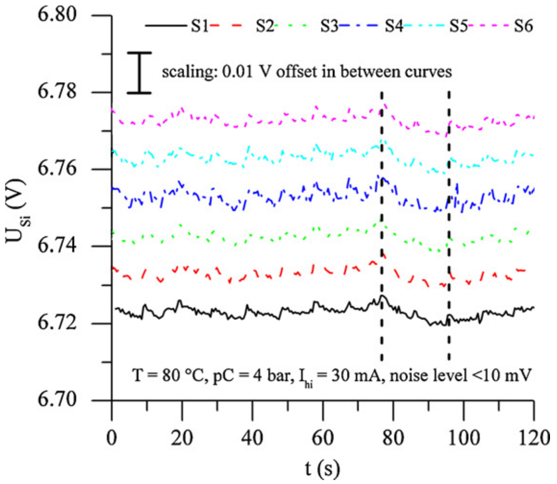

Fig. 7. Response of the thermal flow sensor network due to the propagation of flow pulsation, when 1-butanol was dispensed at a constant rate of 20.4 g/h into the residence time micro-reactor.

Although capillaries with a length up to several meters were placed in between sensors, flow pulsation affected all sensors almost instantaneously. No phase shifts or significant damping of the peaks referred to the base line could be observed during propagation through the micro-reactor. For the compensation of flow alterations differential sensor signals were evaluated. One sensor was taken as reference, where single phase regime could be premised, usually S1. After offset compensation the differential signals of S2–6 in reference to S1 were calculated. Fig. 8 shows the differences in the sensor signals of S2–6 in reference to S1, when 1-butanol was dispensed into the micro-reactor. As long as a non-reactive liquid flows through the micro-reaction channel differential signals must be zero. When comparing Fig. 7 and Fig. 8 it is apparent that the evaluation of differential sensor signals significantly lowered the impact of flow pulsation.

The noise level could be reduced from ∼10 to ∼2 mV, while the remaining fluctuations were mainly due to electrical noise induced by the limited stability of the current sources. When the signal changes due to pulsation were small in reference to the average mass flow rate, the sensor network response could be regarded as linear. Thus, it could be treated as an offset added to sensor signal shifts due to chemical conversion. When the amplitude of flow pulsation was too high, the sensor response showed non-linear behavior. In that case the differential signal significantly differed from zero, which is apparent in Fig. 9 directly after applying overpressure.

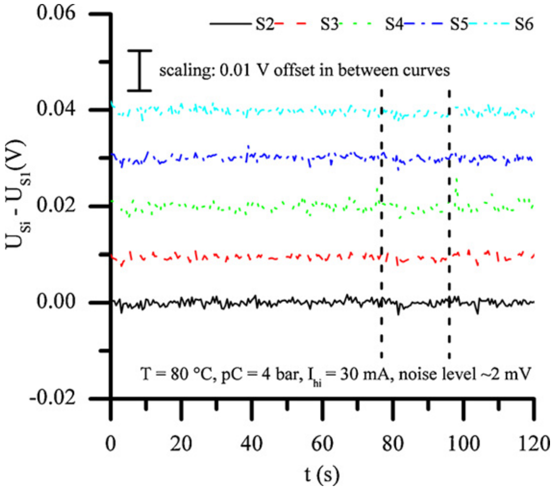

Fig. 8. Differences in the sensor signals S2–6 referred to S1 in the presence of flow pulsation, when 1-butanol was dispensed at a constant rate of 20.4 g/h into the residence time micro-reactor.

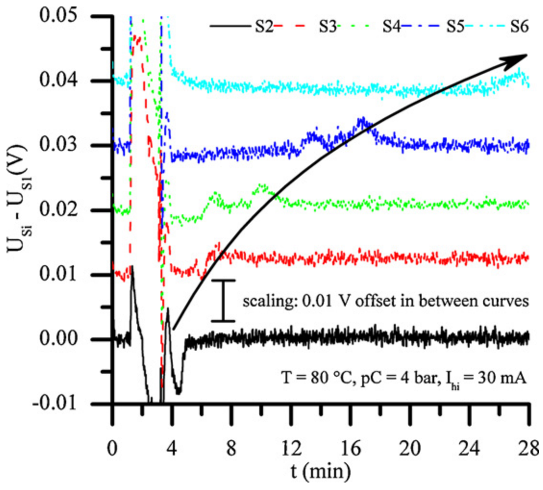

Fig. 9. Synthesis of butyl acetate (acetic acid: 9.3 g/h, 1-butanol: 11.1 g/h, sulfuric acid: $x = 0.01$): transient response of the sensor network by means of changes in the differential signals of S2–6 in reference to S1 after activation of the pressure controller that led to a temporary imbalance of the educt feed.

5.3. *Synthesis of butyl acetate*

After offset compensation procedure as discussed in Section 5.1 the synthesis of butyl acetate was started. Initially, the non-steady state response of the sensor network was of special interest, directly after starting medium feed. The valve V-L_{E1} was switched from 1-butanol to the mixture of acetic acid and sulfuric acid. After stabilization of the mass flow rates an overpressure of pC = 4 bar was set at the pressure controller. Fig. 9 shows the differential sensor signals of S2–6 in reference to S1 after the start of medium feed. The increase in overpressure led to a temporary and non-symmetric decrease in the mass flow rate of each pump. In a time scale of ∼2 min the mass flow rate of acetic acid was more than two times higher than for 1-butanol resulting in a non-equimolar mixing of acetic acid and 1-butanol. Approx. 3 min after applying overpressure regime, mass flow rates of both pumps converged to their steady state value. As shown in Fig. 9, the non-equimolar mixture propagated through the micro-reactor and dispersed as depicted by the arrow in the diagram. Residence times in between sensors corresponded to the internal volume of each capillary segment. Fig. 10 extends Fig. 9 and shows the transient response of the thermal flow sensor network, when the reactive system became biphasic. After ∼33 min the reactive mixture displaced 1-butanol at S6 and the signal started to oscillate, while the signals of all other sensors remained almost constant.

It is known that during the synthesis of butyl acetate at 80 °C a phase transition from one to two liquid phases occurs at a certain mole fraction. As shown in Fig. 10, the system became biphasic in between S5 and S6. The temporary decrease in the signal of S6 referred to the baseline was due to the water-rich phase, when passing the capillary of the sensor. Compared to butyl acetate, acetic acid and 1-butanol, the isobaric heat capacity of water is approx. two times higher. An increase in the isobaric heat capacity led to a decrease in the overtemperature of the resistor coils, thus a decrease in the temperature gradient and in the voltage drop. Fig. 11 shows the steady state response of the thermal flow sensor network within 1 h after the reactive mixture became biphasic. Based on the kinetics of the transient as shown in Fig. 10 it can be

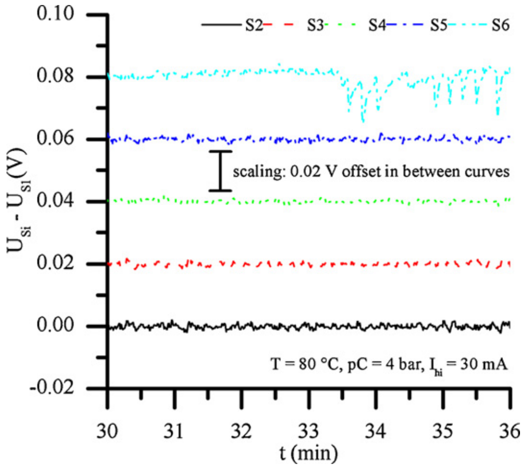

Fig. 10. Synthesis of butyl acetate (acetic acid: 9.3 g/h, 1-butanol: 11.1 g/h, sulfuric acid: $x = 0.01$): transient response of the sensor network by means of changes in the differential signals of S2–6 in reference to S1 30 min after starting the educt feed, when the reactive system became biphasic.

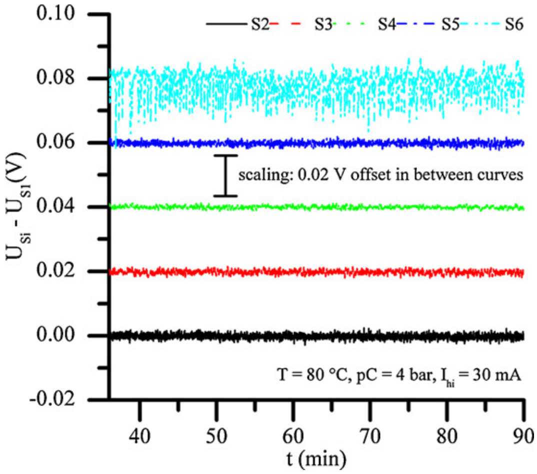

Fig. 11. Synthesis of butyl acetate (acetic acid: 9.3 g/h, 1-butanol: 11.1 g/h, sulfuric acid: $x = 0.01$): steady state response of the sensor network by means of changes in the differential signals of S2–6 in reference to S1 within 1 h after the reactive system became biphasic.

concluded that the phase separation was mediated by the formation of larger aggregates/plugs of at least several tens of μL traveling through the micro-channel.

The sampling accuracy of single aggregates/plugs with alternating liquid phases was limited by the slow response time $t_{98\%} \cong 1$ s of the sensors e.g. compared to [21]. Before the phase separation sensor signal shifts of S2–S5 were comparably small in the range of several mV, when the reactive mixture displaced pure 1-butanol. Hence, it can be concluded that the average isobaric heat of the reactive mixture (1-butanol, acetic acid, butyl acetate, water, sulfuric acid) is close to the value of 1-butanol. Measurement accuracy for a certain mass flow rate can be increased, when the amount of dissipated heat, respectively the overtemperature of the resistor coil is increased. When lowering the mole fraction of sulfuric acid from 0.01 to 0.001, no phase separation could be observed between S5 and S6 at the same overall mass flow rate.

6. Summary and outlook

A novel residence time micro-reactor with integrated capillary type thermal mass flow sensors for monitoring esterification reactions was presented. The device with 6 sensors connected in series was applied for studies on the homogeneously catalyzed synthesis of butyl acetate. Thus, the sensor network enabled the detection of relative changes in the isobaric heat capacity during the esterification reaction at 6 positions in parallel. It was shown that differences in between sensors due to fabrication tolerances can be compensated by a constant correction factor related to a selected reference sensor. After offset compensation the differential sensor signals for a non-reactive liquid were zero within the measurement accuracy. Furthermore, it was shown that all sensors were affected simultaneously by flow pulsation. As long as voltage changes were comparably small referred to the baseline, the impact of flow pulsation could be adequately compensated by evaluating differential sensor signals. This approach enabled the separation of flow and heat capacity induced changes in the sensor signal, even when a biphasic regime was present. When flow alterations were comparable high, the non-linear behavior of the sensor had to be taken into account, i.e. the differential signals differed significantly from zero. In terms of measurement sensitivity, the stability of the current source was the limiting factor. The inline monitoring of the synthesis of butyl acetate revealed that the isobaric heat capacity of the reactive mixture is close to the value of pure 1-butanol. Furthermore, the transition from one to two liquid phases during chemical conversion could be successfully detected by oscillations in the sensor signal. The phase separation mediated by the formation of aggregates/plugs in the capillary is characteristic for a certain mole fraction of the reactive mixture. The propagation of disturbances during the operation of the plant, e.g. a non-uniform mixing due to the switching of valves, oscillation of pumps or changes in overpressure could be detected by the sensor network. In a nutshell, capillary type thermal mass flow sensors can be applied for the inline analysis of esterification reactions in terms of reaction kinetics, phase separation and the formation of plugs. Low complexity and low cost sensors with high pressure, temperature and chemical stability emerge as attractive sensor principle for inline analytics in residence time micro-reactors.

Acknowledgement

We thank Bronkhorst High-Tech B.V. (The Netherlands) for supporting our research activities with thermal flow sensors based on the μ-Flow series.

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