Synthesis of pigments in a three-stage microreactor pilot plant—an experimental technical report ☆

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Abstract

This serialized paper, going on from an IMRET 6 paper [1], describes from a technical point of view further application progress of microreaction technology (MRT) in the field of azo-chemistry at Clariant. Reproducibility of MRT-lab data in the MRT-pilot plant, which includes a numbering-up concept, was confirmed for a second MRT-pigment. Screening tests of commercially available microdevices disclose a need of further improvement of them. Additionally, first experimental data of an on-line process-control prove that a so-called multi-scale approach [2], which means integration of microdevices in conventional equipment, is a promising and successful way for a broader application of MRT in industrial applications.
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1. Introduction

Recently, Clariant has reported a successful start of a three-stage continuous microreaction technology (MRT)-pilot plant, which was used, first, for synthesis of a yellow azo-pigment with improved coloristic properties [1]. To prove principal feasibility and suitability of the numbering-up concept of the transfer from lab to pilot plant scale [3,4], further work was done.

For former investigations as well as experiments described in this study, two model azo-pigments were chosen, of which one is yellow colored and the other one red colored, respectively. Thus, they are called yellow and red model pigment in the following. From time to time, both model pigments were used for comparison of scaling-up versus numbering-up, for evaluation of reproducibility of results and process stability in microdevices and, finally, for testing an experimental set-up with respect to the so-called multi-scale approach.

In general, azo-pigments are synthesized by two main reaction steps, namely diazotation and coupling. (Some azo-pigments need an additional laking-step, which is not discussed here.) In Fig. 1 reaction schemes are shown for diazotation and coupling, respectively.

Diazotation is a reaction of a primary aromatic amine (Ar-NH$_2$) with a nitrosating agent such as sodium nitrite (NaNO$_2$) [5]. This reaction requires an excess of acid (HY) [5]. The resulting diazonium ion (ArN$^+$≡NY$^-$), which can exist in suspended or dissolved form, is then consumed in the following coupling reaction. The coupling reaction itself is an exothermic electrophilic substitution of the diazonium compound with a nucleophilic partner (coupling component (RH)). Besides formed pigment (Ar-N=N-R) in this reaction free acid (HY) is produced.

2. Experimental procedure

To investigate continuous coupling of the yellow and red model pigment, respectively, in several microdevices under various aspects (see Sections 3.1 and 3.2), both diazonium components and coupling components were prepared in a batch-wise manner.

For both model pigments starting materials are a primary aromatic amine (Ar-NH$_2$) and a coupling component (RH). Each primary aromatic amine is suspended in water and 2 eq. of acid (HY) are added. Then this suspension is cooled down to 5 °C and kept at this temperature. Afterwards, sodium nitrite solution is added continuously within

$$Ar-NH_2 + NaNO_2 + 2\,HY \xrightarrow{\text{Diazotation}} Ar-N\overset{+}{\equiv}N\,Y^- + NaY + 2\,H_2O$$

$$Ar-N\overset{+}{\equiv}N\,Y^- + RH \xrightarrow{\text{Coupling}} \underset{R}{\overset{Ar}{N=N}} + HY$$

Ar: (hetero-) aromatic group
R: couling component residue
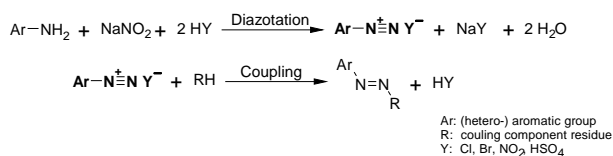Y: Cl, Br, NO$_2$ HSO$_4$

Fig. 1. Reaction schemes of diazotation and coupling reaction, respectively.

some minutes. This reaction mixture is stirred with a slight excess of nitrite. In case of the yellow model pigment the formed diazonium salt remains suspended. In contrast to this, the diazonium salt of the red model pigment is dissolved. In each case, final concentration of diazo component is adjusted so that it can be handled in microdevices without any problems.

In parallel, the coupling component is prepared by dissolving in an alkaline solution. After preparation of coupling and diazo component in a batch-wise manner, they are continuously fed into the microdevices using multiple piston pumps. Coupling of the yellow model pigment is performed at room temperature and a set-value of pH = 6.3. Set-value of coupling temperature of the red model pigment is the same, but coupling pH value is 5.0. pH-values are adjusted by use of an additional pump for dosing of an alkaline solution as buffer. Result of the coupling reaction is a suspension with a pigment concentration of below 5%.

For a first evaluation of an on-line process control concept (see Section 3.3) continuous diazotation of the primary aromatic amine (Ar-NH$_2$) for production of the red model pigment was investigated. To realize this, the aromatic amine was suspended and stirred in acid (HY), cooled down to 10 °C and kept at this temperature in a batch vessel. For continuous diazotation in a microdevice, this hydrochloride suspension as well as sodium nitrite solution (NaNO$_2$) were fed separately into the microdevice. There, after mixing of species continuous diazotation takes place under isothermal conditions (15 °C).

After working-up of the pigment, which includes its separation from the pigment suspension, drying and milling, both model pigments were tested with respect to coloristic properties for the respective application field (yellow model pigment: plastic application; red model pigment: printing application).

For specification as well as comparison of pigments color impression with a standard, measurement systems are used, e.g. the so-called CIELAB system [6]. For this, coloristic properties like color shade, strength or lightness are measured, e.g. by visual evaluation. Color (C) itself describes whether the pigment is yellow or red and color shade (H) describes nuances of a deviation from this color, say, yellow with a slight green nuance; color strength, which tells, how strongly it is colored given in percent. Color lightness (L) of a pigment is given by the gray equivalent [5].
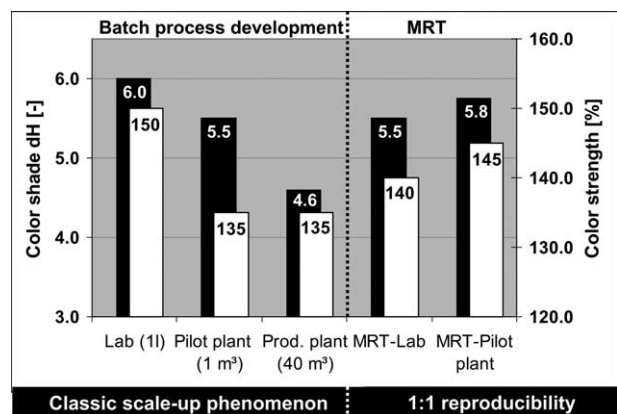

Fig. 2. Pigment quality: scaling-up (batch-synthesis) vs. numbering-up of CPC-microreactors for small-scale production of a yellow model pigment.

3. Results and discussion

3.1. Scaling-up versus numbering-up, reproducibility of pigment quality formed in microdevices

Investigations of the yellow model pigment using the advantages of microreaction technology (MRT) discloses potential to reduce costs through faster process and product development. Fig. 2 shows reproducibility of coloristic properties (color shade and color strength) of the yellow model pigment formed by a classic batch process development and in CPC[1]-microreactors, respectively. (Output of one pilot plant batch operation is about 80 kg per batch operation and hour, that one of the MRT-pilot plant is about 1 kg/h. Internal reproducibility of each scale is about ±3%, which is true for batch as well as MRT-synthesis.)

Although the yellow model pigment produced in the batch lab slightly exceeds the quality of the MRT-lab pigment, this quality level cannot be formed in batch production scale (left half in Fig. 2). This is primarily due to increased reaction volume by a factor of 40,000 and, thus, due to the loss of mixing quality when transferring the batch process from lab scale to pilot scale and ultimately full production scale.

In contrast to this, reaction and mixing volumes do not change from MRT-lab to pilot plant scale and, therefore, pigment quality of MRT-lab is reproducible in the MRT-pilot plant. Indeed, pigment produced in the MRT-pilot plant is slightly superior to that out of the MRT-lab. The reason is, that with standard dosing equipment the accuracy of exact stoichiometric dosing of reactants at strong flow rates (output of MRT-pilot plant is about 30 l/h) is higher, than when working in the lab range of several 10 ml/min.

Using CPC-microreactors, the reproducibility of MRT-lab pigment quality in the MRT-pilot plant as well as accelerated process and product development time could be underlined for a further MRT-pigment. A detailed MRT-lab study regarding the red model pigment met the requirements for

Table 1
Reproducibility of coloristic quality data of a red model pigment formed in MRT-lab and pilot plant, respectively, using CPC-microreactors

Coloristic property	MRT-lab pigment	MRT-pilot plant pigment
Color dC	1.58	1.52
Color strength (%)	111	118
Color shade dH	0.40	0.38
Color lightness dL	0.42	0.4

In each case compared to an internal pigment standard.

a fast process transfer from the lab to the pilot plant, which took less than 1 week. In contrast to this, for this special pigment transfer of the batch-process from lab to pilot plant scale took 2–3 weeks. This can be explained by the need of re-adjustment of process parameters due to scaling-up effects. The reproducibility of MRT-pigment properties is shown in Table 1.

This clearly demonstrates that there is no loss of pigment quality, when successfully applying the concept of numbering-up from lab to pilot scale. Furthermore, a continuous process based on microreactors can form pigment with a constant level of high quality.

Fig. 3 shows color strength of the yellow model pigment versus operating time. It is illustrated that due to a continuous process, which is the basis of MRT, constant product quality is intrinsic with a continuous process. Provided measures are taken with respect to on-line process control (e.g. see Section 3.3). Thus, considering high-quality MRT-pigments with a potential market volume up to 100 t per annum, it is expected to reduce costs for achieving final product standardization.

Regarding these promising aspects of MRT in industrial chemical research and development, microreactors are considered as additional standard tools for process/product development and optimization in several departments and divisions at Clariant. For this reason, Clariant, as a potential manufacturer of MRT-specialities, needs to be awarded of the latest state of microdevices for process intensification. Thus, thinking of a potential production plant based on microreactors requires the evaluation of selected commercially

available microdevices. These devices should be designed and evaluated to fulfill maximum heat transfer and optimum mixing properties, in general. Therefore, a screening of microdevices for application in the field of azo-chemistry was done.

3.2. Screening of several commercial microdevices

At Clariant in a first approach, two microdevices (CPC-microreactors and IMM[2]-caterpillar mixer) were used for analyzing scaling-up phenomenons of classic process development in the field of azo-coupling. Data not shown here, demonstrate that under continuous process conditions the mixing stage of the reactants has a far greater influence on final coloristic properties of a pigment than a temperature increase due to release of reaction enthalpy under adiabatic conditions.

For example performing azo-coupling under adiabatic conditions at room temperature in IMMs caterpillar mixer revealed just a slight increase of temperature in a range between 3 and 7 °C, which was measured at the outlet of the microdevice. This temperature increase is caused by buffering of free acid, formed during reaction, to keep pH value constant.

Comparing now coloristic properties of MRT-pigment, formed under adiabatic conditions, with pigments, that were synthesized under isothermal conditions in CPC-microreactors, showed no significant effect of temperature on coloristics within this temperature range.

Therefore, it can be concluded that – regarding azo-coupling reactions at room temperature – the focus of process optimization has to be concentrated on mixing. For this reason, at the beginning of reactor screening selected commercial microdevices were characterized with respect to mixing using the well-known Villermaux-reaction [7], which was already used for such concerns in the past [8]. Nevertheless, next to a conventional 0.5 in. helical static mixer,[3] a standard caterpillar mixer of IMM and a Micro-Jet reactor[4] – the latter equipped with two coaxial nozzles ($\varnothing = 400 \mu m$) – a PCR-microreactor[5] with an integrated heat exchanger, similar to formerly used CPC-microreactors, were investigated. Fig. 4 shows these microdevices, Table 2 gives a rough review of some specifications.

Taking the positive effect of volume rate and, thus, turbulence on mixing into account, microdevices were characterized with only one single total flow rate of 60 kg/h, which is representative for MRT-pilot plant scale. Following the preparation of NaAc–KI–KIO$_3$- and HCl-solution for a flow rate ratio of 1:1 described in [8], solutions were fed into the microdevices by piston membrane pumps. In each case mass rate was 30 kg/h. Analysis was done off-line using an
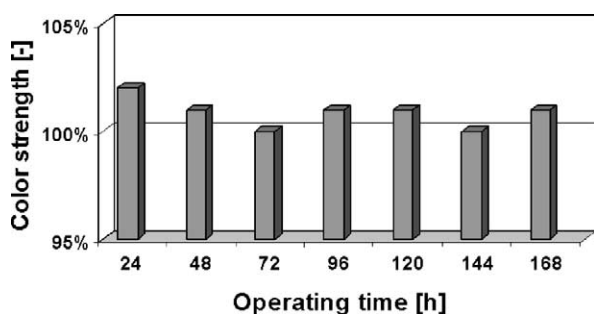

Fig. 3. Coloristic strength of a yellow model pigment, produced in a MRT-pilot plant, as a function of operating time. Data are compared to an internal MRT-pigment standard.

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[2] Institut für Mikrotechnik Mainz GmbH (IMM), D-55129 Mainz.
[3] Statiflow, D-51643 Gummersbach.
[4] Synthesechemie GmbH, D-66822 Lebach.
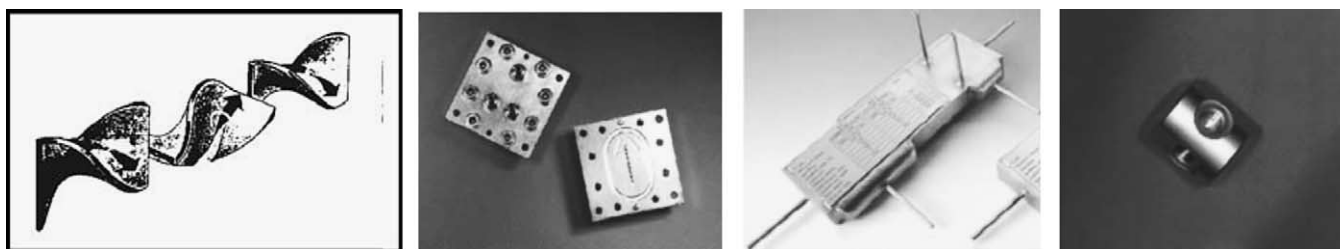[5] Heatric, Poole, Dorset BH16 6LT, UK.

Fig. 4. From left to right: sketch of a helical static mixer, caterpillar mixer, PCR-microreactor (source: Heatric), Micro-Jet.

Table 2
Specifications of microdevices investigated in this study and shown in Fig. 4

	Material	Hold-up (ml)	Mixing is due to	Other specifications
Static mixer	Steel 1.4571	16	Diffusion/turbulence	12 Removable helical mixing elements
Caterpillar mixer	Titanium	1.5	Diffusion/turbulence	Two-plate design, two inlets, up to 5 MPa
PCR-reactor	Duplex-steel	18	Diffusion	Diffusion bonded, three inlets, integrated heat exchanger, up to 10 MPa/100 °C
Micro-Jet	Steel 1.4571	1	Impinging jet	Welded nozzles, two inlets, up to 10 MPa

UV-Vis spectrometer, in which a sample was analyzed 1 min after generation with respect to absorption of formed iodine at $\lambda = 352$ nm. The higher the detected iodine concentration, the less effective is the mixing. Fig. 5 shows the results.

Macro-mixing in multi-laminating microdevices is more effective and superior over macro-mixing in a conventional static mixer [9]. Therefore, as expected, absorption of iodine in microdevices is at least one order of magnitude lower than in a conventional mixing device. This corresponds to a better mixing.

Regarding IMMs standard caterpillar mixer and PCR-microreactor excellent mixing results can be explained by immediate micro-mixing after contacting and relates to molecular diffusion of species between lamellas in flat channels. In each case maximum channel height amounts to 1 mm compared to a diameter of 0.5 in. of the static mixer.

The experiment reveals best mixing properties of the Micro-Jet reactor. This is not surprising, because here two mass transfer accelerating effects coincide: first, mixing in small volumes as mentioned above for caterpillar mixer and PCR-microreactor. Secondly, mixing in the Micro-Jet profits by maximum transformation of kinetic energy of two fluid beams into mixing energy, which meet each other in a collision point in the center of a mixing zone.

For verification of these promising mixing results of Villermaux's test reaction, standard caterpillar mixer and Micro-Jet reactor were both used for the synthesis of the yellow model pigment mentioned above. It can be underlined that all of these microdevices are suitable for the synthesis of this yellow model pigment, of which a total amount of 125 kg was produced in a MRT-pilot plant [1]. For example Table 3 shows comparison of coloristic results formed in a CPC-microreactor and IMMs standard caterpillar mixer. Coupling in the CPC-microreactor was operated under isothermal conditions in contrast to adiabatic operation of the standard caterpillar mixer.
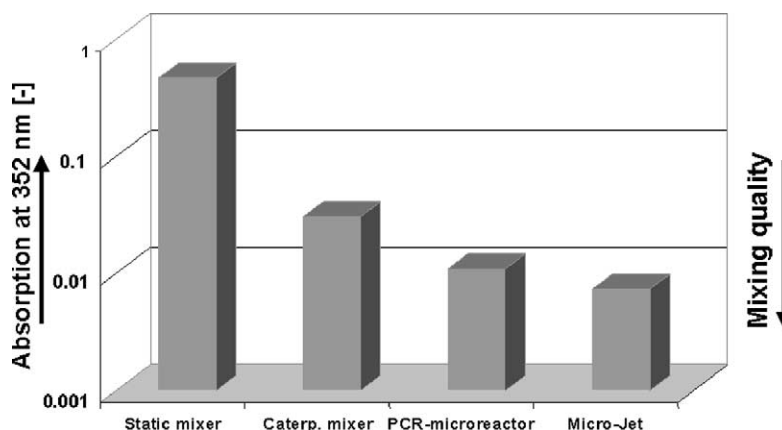

Fig. 5. Absorption of formed iodine at $\lambda = 352$ nm due to continuous mixing of 30 kg/h NaAc–KI–KIO$_3$-solution with 30 kg/h HCl-solution in various devices, residence times are approximately: PCR-microreactor: 1.1 s; helical static mixer: 0.9 s; standard caterpillar mixer: 90 ms; Micro-Jet reactor: 60 ms.

Table 3
Coloristic properties of a yellow model pigment formed under isothermal and adiabatic reaction conditions in a CPC-microreactor and IMMs standard caterpillar mixer, respectively

Coloristic property	CPC-microreactor	IMM caterpillar mixer
Color dC	0.73	0.68
Color strength (%)	143	143
Color shade dH	5.21	5.82
Color lightness dL	1.48	1.64

Data are compared to an internal pigment standard.

Apart from improved color shade (dH), data of IMMs standard caterpillar mixer are in good correlation with data of the CPC-microreactor. These data are a principal proof that continuous mixing in small volumes and – more important – exact dosing of the reactants is the key to MRT-pigments with enhanced properties.

As testing of several commercial microdevices reveals basic suitability for synthesis of MRT-pigments and coloristic results agree, these devices can be evaluated with respect to user handling. In this study, it turned out that none of the commercial microdevices, available at the time of this investigation, meet requirements with respect to application in a pigment production plant. Some aspects are covered in greater detail in the following paragraphs.

After operating up to five various microdevices in the last year, it was clear for applications in azo-chemistry, when at least one suspension has to be handled, that the direction of flow in microdevices has to be set very carefully.

Despite promising coloristics formed in IMMs standard caterpillar mixer, it failed in this study from a technical point of view, when producing the red model pigment. Due to rectangular inlet and outlet geometry at these locations the standard caterpillar mixer tends to total and irreversible blockage. Fig. 6 shows rising formation of coating in the inlet and outlet of the top plate (①, ②), which finally leads to total blockage of the mixing geometry (③) and short circuit flow of reactants (④). However, in the mean time these
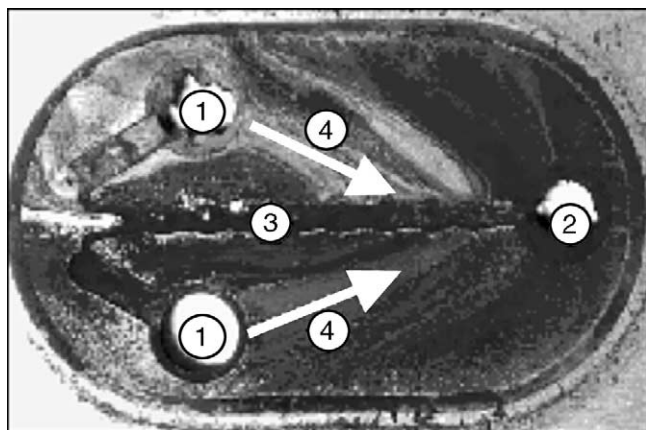

Fig. 6. Mixer geometry in the top plate of IMMs standard caterpillar mixer, which is blocked, when coupling a red model pigment.

Fig. 7. Caterpillar mixer with straight outlet (source: IMM).

problems seem to be solved [10], as there is an improved caterpillar mixer available with straight outlet geometry (see Fig. 7). Alternative anti-fouling concepts for microdevices are discussed in [11,12].

According to Villermaux's test reaction results, the Micro-Jet reactor is the best mixer investigated in this study (see Fig. 5). But forming two coaxial fluid beams for a maximum transformation of kinetic energy into mixing has—from our point of view – a crucial disadvantage: results from experiments in the field of azo-pigments revealed, that a maximum flow rate ratio of 1:1.5 should not be exceeded when using, e.g. a nozzle pair (400 μm/400 μm). Otherwise the beam with higher flow rate and, thus, stronger momentum, is too powerful with respect to the weaker fluid beam emerging from the opposite nozzle.

The result in this special case is, that the collision point of both beams moves from the middle of the mixing chamber to its wall in direction of the opposite nozzle. Under extreme conditions, pigment formation and precipitation even may take place in front of the nozzle, which leads to immediate blockage. Obviously the successful use of the Micro-Jet for this special azo-coupling reaction is impracticable and seems not to enable sufficient operation time—especially, as four reactants at highly different flow rates have to be handled. Nevertheless, the Micro-Jet may be a reliable microdevice, if only two reactants with similar flow rates have to be mixed.

Above all, microreactors with integrated heat exchangers like CPC-microreactors are suitable for pigments synthesis in general. But in most cases bonding techniques of microstructured platelets based on solder – more ingenious technology works with diffusion bonding (see Heatric's PCR-microreactor) – are used. This inhibits inspection of the microstructures as well as thorough cleaning for multi-purpose use. Furthermore, no commercial low-cost microdevices are available, which today can be explained by restrained application of them in industry and, consequently, low number of produced pieces.
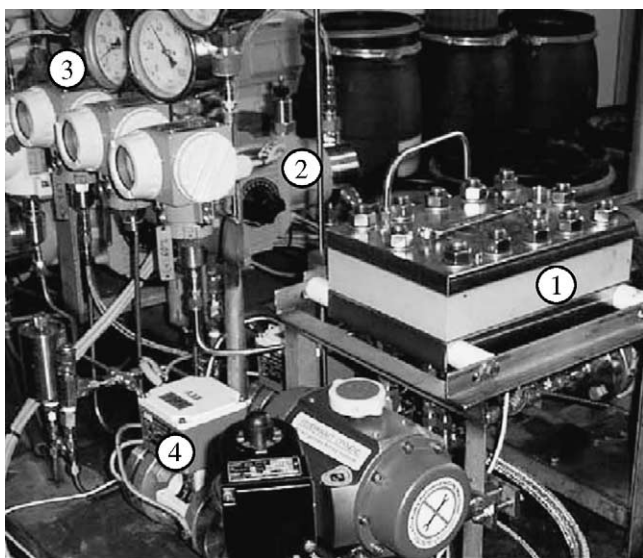
Fig. 8. Example of an experimental set-up according to multi-scale approach.

Fig. 9. Redox-potential plot of a continuous fully automated diazotation in microreactors.

For these reasons, from a technical as well as economic point of view, especially with respect to a production plant based on microreactors, microdevices are needed, which can be disassembled. A first modular design for a high through-put, namely Ehrfeld's[6] micromixer LH 1000, appeared on the market in the last 6 months. This device is also available with an integrated heat exchanger. Another two-plate device is under development. Both designs will be object of future high-priority investigations.

3.3. Multi-scale approach and on-line process control

Today batch-processes dominate in the field of pigments synthesis. For a serious discussion of the application of microdevices for continuous processes at industrial scale, investigations still have to be intensified, even if principal feasibility has already been shown to be successful.

This is especially true with respect to process automation as well as a so-called multi-scale approach, e.g. building-up integrated multi-scale process units with locally micro/mini-structured devices [2] in conjunction with conventional instrumentation equipment like pressure, pH as well as redox-potential sensors and magnetic flowmeters. First promising results were obtained, when establishing a dynamic control of flow rates with redox-potential as steering parameter in the diazotation stage of the MRT-pilot plant.

Fig. 8 shows a section of the diazotation stage with microreactors housing (①), double piston membrane pumps for dosing (②), pressure sensors and indicators (③) and finally flow meters (④). As total output of the diazotation stage is about 15 l/h conventional commercially available processing and instrumentation equipment could be used. Suppliers
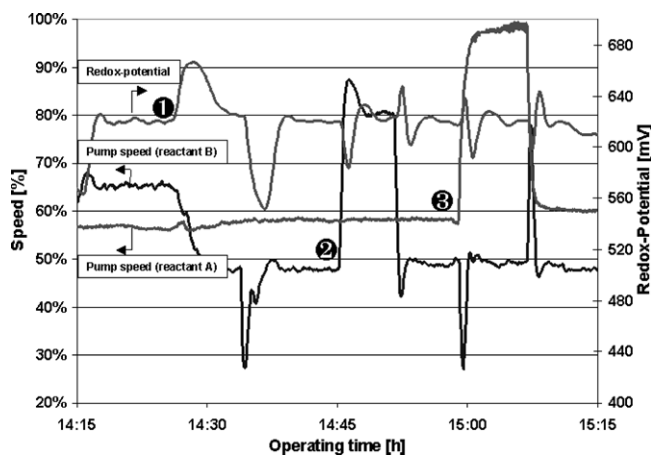
were ABB, Endress ∉ Hauser, Mettler Toledo, Schott and Prominent.

For a better understanding of following results, when investigating the controlled continuous diazotation in microdevices, the correlation between redox-potential and dosage of the nitrosating agent is explained. As underlined in Section 2 a slight excess of nitrosating agent is needed for a complete diazotation. This can be detected in a batch process very easily, as redox-potential is very sensitive to the nitrosating agent. That is, a rising excess of nitrosating agent provokes a significant sharp increase of the redox-potential. This is also true for continuous diazotation in microdevices, but for process control the dosage of nitrosating agent has to be correlated not with the slope of the jump response (like in the batch-process), but with an absolute value of redox-potential under steady-state dosing conditions, see Fig. 9.

In Fig. 9 recorded plots of the redox-potential, measured at the outlet of the microreactor, the speed of two pumps, which dose reactant A (aromatic amine) and reactant B (nitrosating agent), respectively, are shown versus operating time of a fully automated continuous diazotation in a stack of microreactors. According to experimental data, it is known that a redox-potential of 620 mV is an optimum operating point for the red model pigment. This value ensures complete diazotation and an acceptable excess of reactant B.

Dosing pump of reactant A (aromatic amine) acts as the master pump. It determines the speed of dosing reactant B (nitrosating agent) by a master–slave correlation. The control concept of diazotation does not provide a static ratio between flow rates of reactant A and B, but a dynamic one. The speed factor of pump B depends on the redox-potential as follows: if a redox-potential of 620 mV is exceeded, the flow rate of reactant B, thus the ratio of speed pump B to speed pump A, has to be reduced and vice-versa.

By provoking complications in the process, the optimized set of PID-control parameters was tested (see marks ❶ to ❸ in Fig. 9): at mark ❶ reactant A (aromatic amine) was diluted, which leads instantaneously to a sharp increase of

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[6] Ehrfeld Mikrotechnik AG, D-55234 Wendelsheim.

redox-potential, because for a short time too much of reactant B (nitrosating agent) is fed into the reactor. But within some minutes the speed of reactant B is reduced so that the optimum redox-potential value of 620 mV is reached again. The same is true for marks ❷ and ❸ , when each time one pump head of a double piston master/slave pump is deactivated manually. Then, this is compensated by increasing the speed. Again, the plot of redox-potential clearly shows, how fast the applied control concept eliminates deviation from the optimum operating point.

For processes based on microreactors, these data are motivation enough for further improvement of an automated control, while using conventional and commercially available electronic, measurement as well as control equipment. Furthermore, it can be concluded that the multi-scale approach is not of academic nature. But it is a practicable way to promote the challenging industrial application of devices for process intensifications like microreactors/mixers.

4. Conclusion

Applying micromixers/reactors in lab as well as pilot plant scale shows, how efficient microdevices work. This working principle has a positive impact to process optimization, faster process development and potentially new products. Nevertheless, one essential message of this paper should be, that quality as well as availability of microdevices have to be improved. According to the state of art of manufacturing technologies, these devices have to meet requirements for a broader, more convenient use in pilot plants and most importantly in production plants. If this challenge is accepted, everyone should be encouraged to increase the participation in the field of multi-scale concepts. The data discussed in this paper is conclusive proof that multi-scale concepts can be successful. This primarily can be achieved when a combination of conventional instrumentation set-up is used in conjunction with microdevices.

It has to be pointed out that these conclusions, especially the evaluation of microdevice applied in the field of azo-chemistry, are relative in the sense that they are only valid for the two investigated model azo-pigments. Other applications may lead to a different evaluation and ranking of microdevices.

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