

Continuous Synthesis of a High Energetic Substance Using Small Scale Reactors

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For the industrial production of chemicals a safe process design is required to avoid harm to people and environment. It becomes tremendous important if one or more of the following points are characteristic for the synthesis: high heat release, explosive atmosphere, presence of toxic and/or of thermal unstable substances. One substance group, known for being unstable, is the group of organic peroxides. They are potential high energetic substances. Many syntheses of organic peroxides are carried out in semi-batch mode to control the heat release in a good manner. With the aim to increase process control, the advantages of continuous reaction mode, combined with micro reaction technology, are used for the synthesis of one specific organic peroxide in this work.

This approach is not only characterised by shorter residence time, good heat transfer, but also by smaller quantities of managed chemicals, and, therefore, by a lower hazard potential. Often yield and selectivity can be improved additionally.

For the study a peroxyester, namely tert-Butyl peroxy-2-ethylhexanoate (TBPEH), with known thermal hazard potential was chosen. The two phase liquid/liquid reaction was carried out in three types of reactors. A small scale tubular reactor, stressed by ultrasound, and two different micro structured reactors were used. One of them had a meandering and the other a split-and-recombine channel structure. Synthesis temperature was also varied.

From preliminary studies it was known that the side reaction of the involved carboxylic acid chloride to the corresponding acid can become more important in continuous mode compared to semi-batch mode. The effect of reactor type and temperature on selectivity and therefore yield of TBPEH was analysed and compared.

In result the reaction could be carried out in a safe manner. The high heat-exchanging efficiency of the used reactors and the short residence time allowed synthesis temperature near the onset temperature of decomposition of TBPEH. In relation to the results of the capillary tube and of the reactor with meandering channel structure (MR), the results for the split-and-recombine reactor (SAR) showed the best trend line. Further studies have to underline the result. Compared to the traditional reaction path (the semi-batch mode), a higher space time yield could be achieved. This promising information is accompanied by the fact of low reaction volumes. In consequence the productivity is low without a numbering up of reaction channels or a scaling up of it. The nowadays existing philosophy of producing a specific quantity of product by a company, followed by the transport to the customer may change. Just organic peroxides, used in small quantities, e.g. as initiators for polymerisation processes or as resin hardeners, provide the opportunity for an on-demand-production.

1. Introduction

The interesting substance group, organic peroxides, is characterised by its O-O-bound. Peroxides are known for their potential instability, due to heat, impact, UV-light and/or other types of energy input or due to impurities. The resulting decomposition is mostly connected with high energy release and gas production. Therefore, the hazard potential during synthesis of this substance group is not only affected by the thermal potential of the reaction itself, but also by the possibility of decomposition. Preferred reaction modes for a good temperature control during synthesis are commonly semi-batch or continuous mode.

The chosen example TBPEH belongs to the group of peroxyesters of monocarboxylic acids. It is used as polymerisation initiator e.g. for ethylene, styrene, acrylonitrile and acrylates. The traditional synthesis is a two-step-reaction (Milas and Surgenor, 1946; DP, 1972) in semi-batch mode according Figure 1. The final reaction mixture of the second step consists of an aqueous phase with the dissolved KCl and an organic phase, which consists mainly of TBPEH. The mass ratio is approximately 65 % aqueous phase to 35 % organic phase. Beside the product TBPEH, also the reactant tert-Butyl hydroperoxide (TBHP) and the intermediate tert-Butyl potassium peroxide (TBKP) belong to the substance group of organic peroxides.

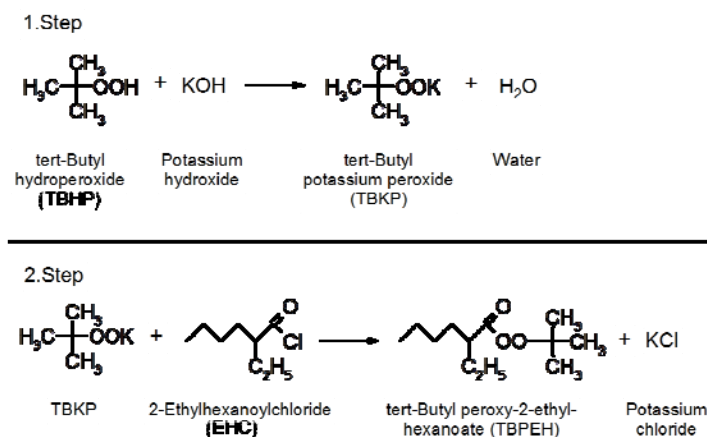


Figure 1: Reaction scheme of TBPEH synthesis

Already in the 1970s a continuous route was described to produce peroxyesters in an industrial plant (Kohn, 1978). Some continuous routes are described in patents (DD, 1977; DE, 1996). Nevertheless is the handling with high amounts of organic peroxides attended with a high hazard potential. With the introduction of micro structured reactors several workers used the advantage of this technology for the production of organic peroxides, e.g. Ebrahimi et al. (2011) for the production of performic acid and Zhang et al. for the production of methyl ethyl ketone peroxide. A patent was applied for the synthesis of several organic peroxide classes (EP 2006).

The main safety characteristics of the TBPEH synthesis and the decomposition behaviour of the involved peroxides were determined earlier (Fritzsche and Knorr, 2009) and are presented in Table 1. The adiabatic temperature rise is a term to assess and to compare the thermal potential of exothermic reactions in a first approach. It reflects worst case conditions: a batch mode is supposed, where the total reaction heat is accumulated in the reaction mixture due to adiabatic conditions. Adiabatic temperature rise higher than 50 K implies a medium or even high severity of reaction and requires specific regard (Stoessel, 2008).

Table 1: Safety characteristics of the two-step synthesis of TBPEH

	Total reaction heat kJ/mol	Adiabatic temperature rise K	Onset temperature of decomposition °C	Decomposition energy kJ/kg
1 st step: Formation of (TBKP) _{aq}	-23	25	(TBHP) _{aq} : 100 (TBKP) _{aq} : no onset found	-1320 -
2 nd step: Formation of TBPEH	-128	76	organic phase, containing TBPEH 93 % by weight: 67	-1120

Looking at the decomposition behaviour of the involved peroxides, no decomposition of the aqueous solution of TBKP could be recorded. Although the aqueous TBHP solution is characterised by a notable decomposition energy, it is not the most critical part. It is added controlled in the first step and converted without accumulation. TBPEH is produced in the second step and enriched in the organic phase. Comparing both, the thermal potential of the reaction steps and the decomposition characteristics of substances or mixtures, the second reaction step is the one with the higher hazard potential. Therefore only this step was realised in continuous mode.

In the 2nd reaction step a good mixing is necessary, because the reactants are non dissoluble in each other. Reaction takes place at the phase boundary. The reaction rate will be controlled by mass transfer without a good mixture.

In the past several microstructured reactors with different mixing strategies were developed for such liquid/liquid reactions. Known are passive mixers, which are working without external disturbance effects, and active mixers, which apply some kind of physical effect like pressure or electrohydrodynamics (Ngyuen and Wu, 2005). To the group of passive mixers, where the channel structure provokes mixing of the reactants, belong e.g. interdigital and microjet mixers. Bošković et al. (2011) characterised e.g. a split-and-recombine reactor, a serpentine channel based reactor and one with a herringbone structure. Illg et al. used a caterpillar micro-mixer (2011) and an orifice microreactor (2012) to synthesize a similar peroxyester, namely tert-Butyl peroxyvalate (TBPP). For an active mixing e.g. the use of ultrasound was reported (Hübner et al., 2012). Own measurements in a capillary tube without and with ultrasound showed the advantages of the active mixing device (Fritzsche and Knorr, 2013).

For this study TBPEH synthesis was carried out at varying process temperature with two passive mixer types, a reactor with a meandering channel structure (MR) and a split-and-recombine reactor (SAR). Additionally a capillary tube, stressed by ultrasound was applied. They will be described in the following.

2. Reactors and test assembly

Capillary tube: Two commonly available sizes, 1/16 inch and 1/8 inch, were applied. The tubes, made of PFA, had a length of 1 m and an inner diameter of 1 mm (1/16" tube) and 1.65 mm (1/8" tube), respectively. For the tests with ultrasound the corresponding tube was inserted in an ultrasonic bath (Bandelin electronic, RK 156 BH, 35 Hz) over a length of 0.45 m.

Micro structured reactor with meandering channel (MR): Two reactors of this type, different in channel dimension, were used in the tests. The glassy reactor is characterised by a meandering channel (Figure 2). The reactor named as MR1 had a channel diameter of 500 µm and a length of approximately of 1.5 m, whereas the reactor named as MR2 had a channel diameter of 300 µm and a length of approximately 3.0 m. The repeating switch of the reaction mixture along the channel provokes a disorganization and reorientation of the two liquid phases. Both reactors provide the opportunity to work with three reactants. For the synthesis of TBPEH two inlets were used and the third was blocked.

Split-and-recombine reactor (SAR): The specific attribute of this glassy reactor is the structure of the channel, which is split and recombined repetitively over the whole length. Due to the repeating splitting of the channel, the reactant stream is separated, twisted and united again, a multilamination occurs. As result the contact surface of the liquid/liquid phases is enlarged. Figure 3 shows the reactor schematically and a detail of the channel structure (detail given by Bošković et al., 2011). Channel dimensions are 600 µm in width, 300 µm in height and 1.64 m in length.

All micro structured reactors (MR and SAR) and the drawings, except detail in Figure 3, were supplied by the company mikrogas chemtech GmbH (Mainz, Germany).

For the specific test run the reactors were embedded in a bench scale unit, which consisted for all runs of the same components. In case of the capillary tubes, the reactant streams were first mixed in a y-shaped mixer. The other reactors were supplied directly with the reactants via the pumps because the mixing feature is already part of the reactor structure. The intermediate was supplied with a HPLC pump (Sykam S1221) and the acid chloride with a syringe pump (Postnova PN1610D). The reactants were supplied at room temperature. Individual flow rates of TBKP and EHC were adjusted in a molar ratio of 1:1. The total flow rate was adjusted to 0.3 ml/min. For the variation of the process temperature, the reactors were inserted in a bath, regulated by a thermostat. Temperature varied for the capillary tubes between 10 °C and 40 °C, for MR1 and MR2 between 20 °C and 40 °C and for the SAR between 20 °C and 50 °C in 10-K steps.

The produced reaction mixture was continuously transferred to a separation funnel, already filled with approximately 100 ml deionised water to quench the reaction.

The separated organic phase was analyzed offline with HPLC. Samples were diluted with a mixture of methanol and ethanol (4:1 V/V). As eluent a mixture of water and acetonitrile (4:6 V/V) was used. The HPLC parameters are: sample loop 10 ml, flow rate 1 ml/min, reversed phase column Sunfire C18 (186002559, length 150 mm, inner diameter 4.6 mm, particle size 3.5 µm). Detection was made with a refractive index detector by Waters (Model 2414). Retention times of the substances are as following TBKP 2.63 min, 2-Ethylhexanoic acid 4.62 min, 2 Ethylhexanoyl chloride 12.92 min, TBPEH 23.16 min.

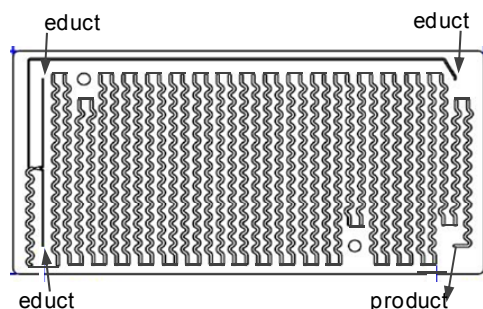


Figure 2: Meandering channel structure of reactor MR1 and MR2

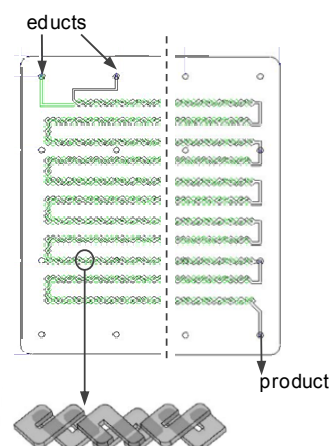


Figure 3: Split-and-recombine reactor (SAR)

3. Results and Discussion

As above mentioned, the organic phase of each reaction mixture was analysed and the conversion of EHC, the yield of TBPEH and the selectivity of TBPEH production calculated. In the following the results are compared regarding the reactor type, the influence of the dimension of the same reactor type and the synthesis temperature.

The synthesis temperature, given in the Figures 4, 5 and 6, reflects primarily the bath temperature. It is assumed that the reactors of MR- and SAR-type are at the same temperature after an equilibration time of a few minutes. Capillary tubes were stressed in the bath by ultrasound, which caused an additional warming. Comparative runs with water, instead of the reaction mixture in the tubes, showed a temperature difference to the adjusted bath temperature between 4 K and 6 K for the 1/16" tube and between 3 K and 4 K for the 1/8" tube, respectively. The measured offset was taken into account for the synthesis temperature for the capillary tubes. The total flow rate was 0.3 mL/min for all runs. The single points in the following figures are the measured values, whereas the lines should show a trend for the specific reactor dependent on the temperature.

Figure 4 shows the conversion of the reactant EHC. Comparing the reactors, the highest conversion of EHC was detected in the SAR. With ongoing temperature the conversion rises clearly and reaches at 50 °C nearly 100 %. High EHC conversion takes place also in the capillary tubes. The conversion in the 1/8" tube seems to be at lower temperature better than in the smaller tube. This difference is neutralised with higher temperature. But for both capillary tube reactors is the temperature influence rather small. The reactors MR1 and MR2 show in contrast to the others a strong temperature dependency. At higher temperatures (40 °C) values between 90 % and 100 % are attained.

A total conversion of EHC does not promise necessarily a good yield of the target product TBPEH. Side reactions, e.g. the formation of the corresponding acid, can occur. This fact illustrates Figure 5. Although the EHC conversion in the SAR is high, the yield of TBPEH at lower temperatures is small. The SAR results show a strong dependence on temperature. MR1 and MR2 show the trend of a higher yield of TBPEH with increasing temperature as well. The yield in the capillary tubes is almost independent of the temperature. The effect of ultrasound seems to be more important than the temperature variation for this specific test arrangement.

Values for the selectivity of TBPEH are seen in Figure 6. Tendencies for the specific reactors change in different manner with increasing temperature. With higher temperature the selectivity becomes for all reactors smaller, except for the SAR. For this reactor type selectivity rises clearly. The HPLC analytics confirmed a decreasing acid content in the samples of SAR with increasing synthesis temperature.

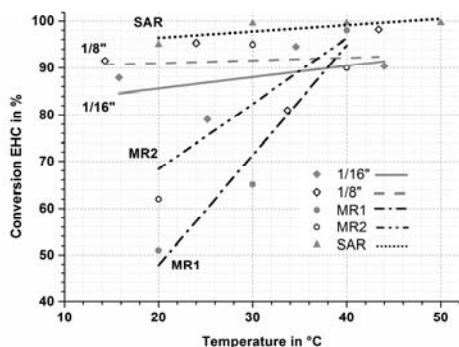


Figure 4: Conversion of EHC in dependency from reactor type and synthesis temperature

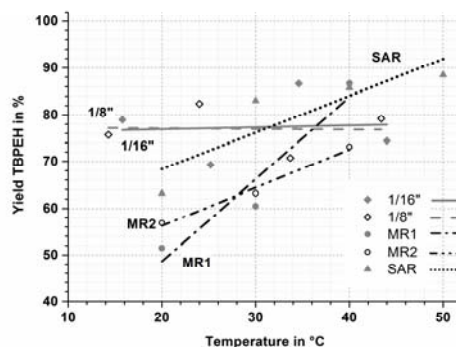


Figure 5: Yield of TBPEH in dependency from reactor type and synthesis temperature

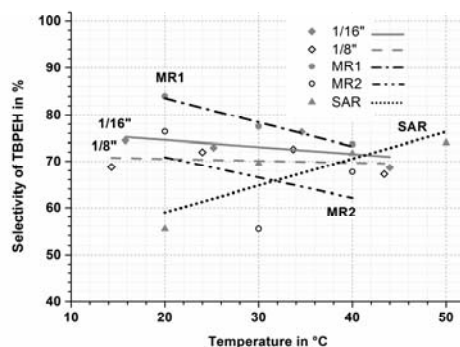


Figure 6: Selectivity of TBPEH in dependence from reactor type and synthesis temperature

The residence time for the specific reactors was assessed from the approximate volume of the reactor and the flow rate. In order of decreasing residence time the sequence is: 1/8" capillary tube (425 s), 1/16" capillary tube (155 s), SAR (145 s), MR1 (60 s) and MR2 (40 s). Not regarded is the influence of the mixing structure on residence time and residence time distribution. In consequence is a detailed comparison of the several reactors at different conditions at the moment difficult. Estimation of residence time and its distribution are going to be an aspect for further studies.

4. Conclusion

All of the three tested reactor types, capillary tube (stressed by ultrasound), MR and SAR, can be used to produce the chosen peroxyester. For two reactor types two different channel sizes were applied. The results showed clearly a differentiation between the reactor types and the channel geometry, respectively. The conversion of EHC, the yield and selectivity of TBPEH were examined for rating.

Best results were achieved with the SAR. The SAR allowed a very good mixing of the two liquid phases and an enlargement of the phase boundary by its channel structure. Due to these facts and a sufficient residence time, the reactor enables a nearly total conversion of EHC. Higher synthesis temperatures seem to favour the formation of TBPEH instead of the side reaction.

The results, obtained with the capillary tubes, showed only small alteration regarding temperature variation and different channel dimension. Obviously the effect of ultrasound plays the major role. In comparison to the passive mixers, the use of ultrasound is another possibility to achieve a good mixing of the reactants. In the specific case of organic peroxide production, the treatment with ultrasound can cause a safety problem. It is known, that bubbles in liquids can be produced by ultrasound. The bubbles can collapse by pressure and cause local heating or a so called hot spot. Rivas et al. (2012) reported about this phenomenon in micro structured reactors. Such a cavitated system facilitates the transition from a thermal decomposition via deflagration into a detonation. Also induced detonations can be propagated better in cavitated sys-

tems (Mader, 1965). Wandrey and Wehrstedt (1997) discussed the influence of cavitation on the decomposition behaviour of liquid organic peroxides. TBPEH, technical pure, does not propagate a detonation (UN, 2009), but is able to do so in the cavitated test version (measurements at BAM following UN (2009), results not published). This test is carried out in tubes with an inner diameter of 50 mm. At the moment it is not known if the effect of cavitation on the decomposition behaviour appears in small dimensioned tubes as well.

The reactors with the meandering structure, MR1 and MR2, seem to perform poorly in contrast to the other reactor types. On the other hand they had the shortest residence times, what could be reason for the results.

The comparison of the reactors is at the moment not finalized. It is necessary to estimate the residence time and residence time distribution for the reactors. Additionally the knowledge about the influence of the reactor structure on the formation of the phase boundary has to be increased. More information about the kinetics and thermodynamics of the main reaction and the side reaction is needed.

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