Intensification of the Capillary-Based Kolbe–Schmitt Synthesis from Resorcinol by Reactive Ionic Liquids, Microwave Heating, or a Combination Thereof

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Abstract:

The continuous Kolbe–Schmitt synthesis of 2,4-dihydroxybenzoic acid from resorcinol was carried out using a setup with a capillary reactor of mm-internals and a micro heat exchanger. The process intensification potential of microwave irradiation for heating up the reactant solution and/or of using ionic liquids as carbonating reactants was evaluated. For the Microwave assisted Aqueous Kolbe–Schmitt synthesis (MAKS), power-to-temperature graphs were calibrated with water and real-case (ion-containing) solutions, revealing several features relevant for process control. Due to higher mean reaction temperatures inside the reactor thanks to faster heating, the yields of all MAKS experiments were higher as compared to the Conventionally Heated (oil bath) aqueous Kolbe–Schmitt synthesis (CHKS) without use of microwave irradiation. The highest yield (before isolation and purification) obtained by MAKS was 52% (at 160 °C, 8 bar, 1 L/h, 90 s), exceeding the yield of CHKS by 5% (at 140 °C, 40 bar, 84 mL/h, 390 s) at a concurrent reduction of reaction time. The MAKS productivity, although lower than possible due to setup limitations (large internal volumes), was up to 67 g/h being in the same range as the CHKS productivity from 25 g/h (39%, 43 s) to 86 g/h (34%, 11 s). Two solutions of ionic liquids were used as CO_2 donating agents, a diluted (1.57 mol/L) and concentrated one (3.2 mol/L) with ethyl based methyl imidizoalium hydrogen carbonate (EMIMHC) and a concentrated one (2.7 mol/L) with butyl based methyl imidizoalium hydrogen carbonate (BMIMHC). The yield obtained for the ethyl based ionic liquid (e-CHILKS) operation was 44% (at 180 °C, 35 bar, 0.17 L/h, 130 s) at a productivity of 5.9 g/h. The yield of b-CHILKS was 59% under the same conditions, yet with a higher productivity of 14.2 g/h. For the Microwave assisted butyl Ionic Liquid Kolbe–Schmitt synthesis (e-MILKS) a yield of 58% at a productivity of 25.3 g/h was derived.

1. Introduction

1.1. Manufacture of Carboxylated Phenols and Kolbe–Schmitt Synthesis. The production of carboxylated phenols is of great importance for the manufacturing of different kinds of pharmaceutical chemicals and other fine organic chemicals. The introduction of the carboxylic acid moiety into mono- or

Scheme 1[a]
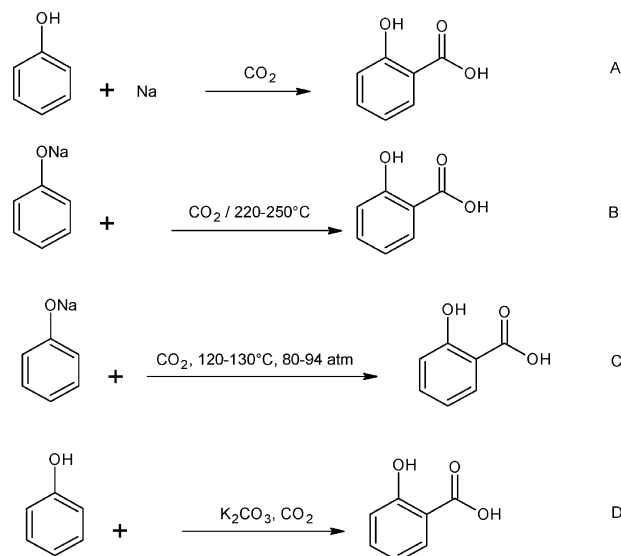
[a] (A) Original Kolbe synthesis. (B) Kolbe reaction starting from sodium phenoxide. (C) Batchwise Kolbe–Schmitt reaction presently used in industry under harsh conditions. (D) Marasse synthesis with even simpler procedure but more expensive reactants.

polyhydroxybenzenes is usually done starting from carbon dioxide (possibly with HCO_3^- precursors added) and the alkaline salt of the phenol (phenoxide; possibly formed by reaction from phenol and the alkali metal, typically sodium). The process variations of this joint route are known as the Kolbe,[1] Kolbe–Schmitt,[2] and the Marasse[3] reactions, which are exemplified at the synthesis of 2-hydroxybenzoic acid (see Scheme 1).

Common to all these routes are harsh reaction conditions, e.g., for the Kolbe–Schmitt reaction the use of the strong base phenoxide and CO_2 under pressures up to 100 bar at temperatures of ~125 °C. Thereby, a 100% product yield is achieved.[2] Reactive phenols, i.e., with two or more electron-donating OH groups, can be processed by much more convenient conditions in a solution-wise manner at atmospheric pressure, different from the powder-based autoclave reactions discussed above.[4,5] This solution-based process is amenable for transfer into a

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Scheme 2. Reaction scheme of the KS reaction carried during this reaction

$$M^+ HCO_3^- / \text{3-40 bar} / \text{100-180°C}$$
$$M = K \text{ or imidazolium derivation}$$
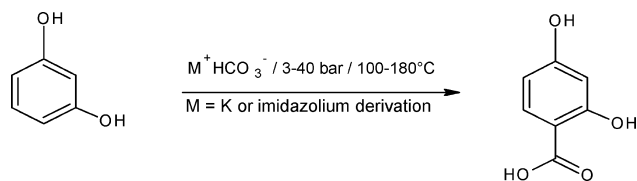
continuous process, and the process intensification by use of a capillary reactor with a millimeter-sized diameter operated in a novel process window,[6] termed high-p,T conditions, was demonstrated.[7,8]

1.2. Process Intensification by Novel Process Windows in Milli- Or Microreactors. Milli and micro process engineering[9–15] facilitates operation at high pressures and temperatures due to the small internal volumes.[7,8,16,17] This allows safe operation in regimes that are otherwise dangerous or difficult to reach, unless a high degree of technical expenditure is accepted. This can, e.g., be used to massively expand the upper operational limit for solvents, which for conventional processing practically is often determined by the solvent boiling point (reflux condition).[7,8,16] A moderate increase in pressure can shift the latter substantially and thus extend the temperature window. Boiling points are for water 100 and 250 °C at 1 and 40 bar, respectively.

Following this motivation, the solution-based Kolbe−Schmitt reaction with resorcinol and $KHCO_3$ giving 2,4-dihydroxybenzoic acid has been successfully processed in a continuous way by making use of capillary reactors (milli process technology)[7] (see Scheme 2).

Yields up to 47% were reached, which almost equals the performance of the Kolbe−Schmitt synthesis by an aqueous batch procedure. By virtue of the much higher temperatures applied (up to 120 °C more), reaction times were up to 1000 times lower, i.e., coming down from hours to tens of seconds.

It was expected and proven by experiment that yields for continuous and batch processes are roughly the same under the same pressure and temperature, since no pronounced heat and mass transfer effects are known for the Kolbe−Schmitt synthesis. However, it has to be considered that the actual temperatures (including the temperature average) in the continuous processes may differ from that of the batch, even when the set temperature (of the oil bath or from the microwave calibration) is the same as the oil bath temperature of the batch process. This is due to axial temperature gradients from processing with an incoming cold solution being gradually heated up. The motivation to use microprocess technology in the context of this paper thus is to explore the impact of novel process windows,[6] e.g., by applying high temperatures and pressures to considerably shorten reaction times and increase space-time yields.

1.3. Microwave as Alternative Energy Source for Reactor Heating. Microwaves are electromagnetic waves which upon irradiation of a solvent can induce (pseudo) separated charges in a molecule, which cause increasing heat. Microwaves have been used for more than two decades for organic synthesis, mainly in batch mode, as demonstrated by a large number of successfully carried out organic reactions.[18–21] Recently, researchers started to investigate continuous microwave processing in capillaries, and more rarely also with microdevices.[22–26] The potential of microwaves for solvent and support-free organic synthesis has been outlined.[27] Microwave equipment manufacturers meanwhile offer special tools for continuous processing, and reports were made about microwave scale-up and mini-plant application.[28,29] It was demonstrated that the combination of microwave heating and micro/milli process technology has advantages over the single approaches and conventional technology.

1.4. Solventless Processing and Ionic Liquids. Solvents help to bring reactants together in one phase, which otherwise would stay separate and would not or only slowly react. Solvents may also dilute a hazardous mixture to a concentration level which can be handled. However, solvents increase the reaction volume and thus increase the size and cost of equipment, may be flammable, may be poisonous, require purification (stripping, distillation) and respective equipment, and produce additional waste. By diluting the reactants, the presence of solvents lowers the productivity of reactors.

For all these reasons, there is a trend in modern chemical processing towards solvent-free processing to help keep the

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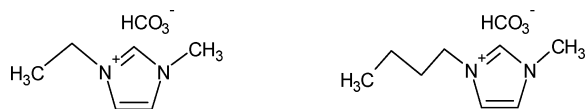(29) Bierbaum, R.; Nüchter, M.; Ondruschka, B. *Chem. Eng. Technol.* **2005**, *28*, 427.

Figure 1. Ionic liquids for the continuous capillary-based Kolbe−Schmitt synthesis: 1-ethyl-3-methylimidazolium hydrogen carbonate, EMIMHC (left), and 1-butyl-3-methylimidazolium hydrogen carbonate, BMIMHC (right).

environment clean, improve operational safety, and offer cost advantages for the converter. In addition, there is the potential to overcome common limits for achieving high space-time yields and thus high process intensification in organic synthesis due to the solubility of the reactants. The typical range of reactant concentrations used for laboratory organic synthesis is from 0.1 to ∼2.0 mol/L, in rarer cases from 2.0 to ∼5.0 mol/L.[30] Industrial processing typically utilizes concentrations at the upper end of that range. In some cases, such high concentrations can be processed in microreactors,[10] since they may involve solids (suspensions) or lead to precipitation during processing. For the industrially piloted phenyl boronic acid synthesis, the concentration of the Grignard reactant had to be decreased from 2.0 to 0.5 mol/L to solve clogging problems, when changing from batch to continuous-flow processing.[31]

Actually for the study under investigation, the solubility of the reactants and the molar concentrations are already quite high according to the above given classification, being in the molar range for resorcinol (0.83 mol/L) and $KHCO_3$ (2.5 mol/L). In addition, water as solvent does not have most of the drawbacks given above, since it is harmless and not flammable (but still may require some purification and cause waste). Nonetheless, in a generic way the reaction in this paper serves also to show how solvent-free processing can be realised, as this model-type processing can be transferred to other and more appropriate examples of use.

The innovation is to use ionic liquids[32−36] which can be tailored to facilitate dissolution and which bear one of the reactant moieties on their own, i.e., acting as reactive solvent without any additional dilution, thereby eliminating the need for $KHCO_3$. Hydrogen carbonate containing ionic liquids were identified as such candidates for reactive solvents in the Kolbe−Schmitt synthesis. In this study, 1,3-dimethylimidazolium hydrogen carbonate derivatives were used, which exchange upon reaction of their hydrogen carbonate anion by $OH^{[37]}$ (see Figure 1). This new class of materials has since recently become available from the Sigma-Aldrich Company.

A drawback of the current innovation is that these ionic liquids are not stable as pure substances. Thus, the addition of a water/methanol mixture is necessary; i.e., a solvent-free operation was not possible, but (at best) only an operation with

a lesser amount of solvent (solvent-less operation). The concentrations for the EMIMHC and BMIMHC mixtures as received were 23.24 and 2.72 mol/L, respectively. Assuming that the pure ionic liquids could have been used, concentrations of 7.2 and 6.9 mol/L for EMIMHC and BMIMHC, respectively, would have set the upper limit for the process intensification, which is at the upper end of laboratory and industrially used concentrations as given above. There is hardly more room for concentration increase by use of new ionic liquids, since the molecular weight of EMIMHC is already quite low so that the above given concentrations approximately set the upper limit in concentration when using reactive ionic liquids. The only remaining option then is to use the ionic liquids simultaneously as reactants and solvents (for $KHCO_3$ or another carbonating species). This approach has not been explored in the present study.

Reuse of these ionic liquids after reaction could principally be achieved by ion exchange[38] or even by addition of pressurized CO_2 in a moderately acidic environment,[39] recovering the original hydrocarbonate containing reactant. Some articles even reported the synthesis of ionic liquids by making use of microwaves; actually this still has been done only for the alkylation reaction of imidazole components.[35]

Ionic liquids have the additional advantage of being strong microwave absorbers.

2. Experimental Section

2.1. Conventionally Heated Kolbe−Schmitt Synthesis. The Kolbe−Schmitt reaction was conventionally carried out as it had been done before, relying on a tube reactor heated by an oil bath.[7] The same chemical protocol has been used, including keeping the concentrations fixed at 2.52 mol/L $KHCO_3$ and 0.83 mol/L resorcinol dissolved in water. No premixing was used, thereby avoiding the need for mixing in the flow sheet, since reaction at room temperature is negligible.

2.1.1. Capillary Reactor Rig. The reaction setup consisted of a syringe pump (1000D; Teledyne ISCO Inc., Lincoln, NE/USA) which could be operated at pressures from 1 to 40 bar. The heating has been done by an oil bath (HUBER compatible control CC505) with a half-synthetic oil medium (see Figure 2).

The reaction unit was made from a commercial bent-steel tube. Some specifications are given in Table 1. The aim of the reported investigations was to achieve preliminary results in a short time to explore the potential of the different intensification approaches and their combinations. Comparability was aspired to for important parameters such as residence time but could not be fully matched, e.g., for inner volume, due to restrictions of short-term availability or manifacturability.

After reaction, the product mixture was cooled down by a cross-flow microstructured heat exchanger (CRMH) of IMM with the following specifications (see Table 2).

In situ temperature measurements were done after the cooling procedure. The temperature chiller (HUBER Unichiller UC015-

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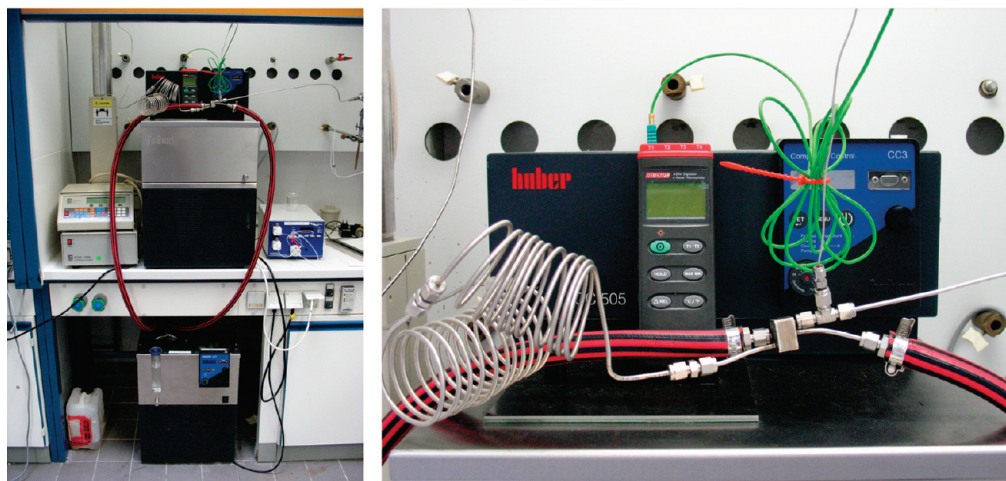(39) Bridges, N. J.; Hines, C. C.; Smiglak, M.; Rogers, R. D. *Chem.—Eur. J.* **2007**, *13*, 5207.
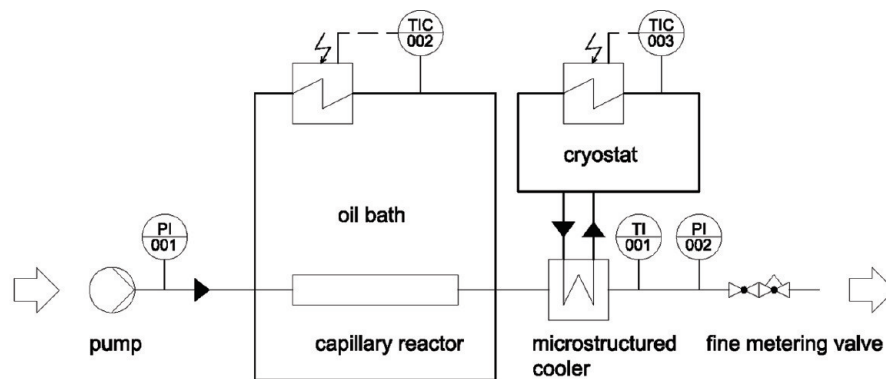
Figure 2. Process flow sheet for conventional heated aqueous Kolbe−Schmitt synthesis using premixed reactants (top). Whole rig and detail of the capillary reactor followed by the micro heat exchanger (bottom).

Table 1. Specification of the capillary reactor

reactor type	bend capillary
mixer material	stainless steel SS 316Ti
tube inner diameter	1.39 mm
tube outer diameter	3.14 mm
total length[a]	4.0 m
total tube volume	6.07 mL
total reaction volume[a]	6.11 mL

[a] Including connector.

Table 2. Specification of the cross-flow microstructured heat exchanger (CRMH)

micro heat exchanger	CRMH
material	stainless steel SS 304
number of microchannels per plate	9
number of microstructured plate	52
channel width	0.7 mm
channel depth	0.2 mm
channel total length	12.0 mm
sealing	diffusion bonding
dimensions of outer device	22 mm × 22 mm × 14 mm
total volume flow	Up to 130 L/h
operational temperature	Up to 300 °C
system pressure	Up to 50 bar
heat transfer coefficient	4000 W/(m^{2}K) for water at 30 L/h
specific heat transfer area	12 800 m^2/m^3
active inner volume	15 mm^3
pressure drop	1 bar at 72 L/h watery fluid

3) operating with water was controlled based on this measurement by manual modifications to ensure a sufficient quenching capacity of the product fluid to give a desired final temperature of 35 °C. A buildup of high pressures in the tube was realized by a Swagelok valve, which was adjusted manually.

2.1.2. Chemicals. 2,4-Dihydroxybenzoic acid ($C_7H_6O_4$, 154.12 g/mol, Fluka, >98%), resorcinol ($C_6H_6O_2$, 110.11 g/mol, Aldrich, 99%), and potassium hydrogen carbonate ($KHCO_3$, 100.12 g/mol, Fluka, >98%) were used. The water was deionised by a membrane deionizer. The aqueous solutions were degassed by exposure to ultrasound and subsequently bubbled with nitrogen to remove the oxygen contents before use, because dissolved oxygen could lead to undesired oxidation reactions at the high temperatures envisaged.

2.1.3. Chemical Protocol. The reactants used were both separately solved in water, which was especially for $KHCO_3$ a difficult and time-consuming task, as the solubility limit was approached (limit 333 g/L; actual value 253 g/L; for compari-

son: limit for resorcinol 1254 g/L; actual value 92 g/L). The dissolving process of $KHCO_3$ should be done by adding the water in a stepwise manner. Heating does not lead to pronounced solubility improvements but rather could initiate the reaction already above 70 °C.

After dissolving the two components separately in water, both solutions were added in an 800 mL bottle which was kept at room temperature, to prevent any chemical reactions.

The composition of the solution and the respective concentrations of the reactants were as follows:

Table 3. Variation in flow rates at 180 °C and 40 bar

temp (°C)	pressure (bar)	flow rate (mL/h)	reactor volume (mL)	reaction time (s)
180	40	500	6.11	43
180	40	1000	6.11	22
180	40	2000	6.11	11

- 202.0 g (2.02 mol) of $KHCO_3$ (final concentration in reaction mixture of 2.5 mol/L)
- 73.5 g (0.67 mol) of resorcinol (final concentration of 0.83 mol/L)
- 669.0 g of water totally

For carrying out the chemical reaction in a continuous mode, pressure and temperature were set to be constant but the flow rates were varied (see Table 3).

2.1.4. HPLC Product Analysis. HPLC (Shimadzu VP series with UV−vis detector) was used to qualify and quantify the species in the reaction mixture. An acidic eluent was selected to ensure that the acidic sites on the molecules will not be deprotonated. For this purpose a solution of 0.5 mol/L KH_2PO_4 was prepared and mixed with a solution (50:50 vol%) of water/acetonitrile with 1 vol% of H_3PO_4. This resulted in a mixture consisting of a ratio of the acidic solution/acetonitrile/water of 2:1:1 vol%, respectively, at a pH of 2.5−3.5. The eluent was conditioned at an isocratic flow of 0.6 mL/h in a 250 mm × 4.0 mm Nuceosil 120 C18, 5 μm column (Macherey Nagel, Düren/Germany purchased via MZ-Analysentechnik, Mainz/Germany). The reaction components were detected by UV detection at 220 and 260 nm.

Samples were taken from solutions having passed the exit valve. To calculate product concentrations, both the reactants and products were calibrated by HPLC with stock solutions of known concentrations (1, 1.5, and 2 mmol/L). In this way, a calibration curve was obtained, being applied for all samples under the only approximately valid assumption that no side products were formed (selectivity ≈ 100%). The calibration line has been checked for linearity with the university statistics software package STATGRAPHICS, by checking different test parameters for linearity. This was checked for each batch of samples by analyzing a mixture of known molarities of reactant and product.

2.1.5. Isolation and Purification. In the case of the aqueous Kolbe−Schmitt synthesis, the product could be isolated and purified as follows: At the reactor outlet, the reaction mixture is introduced into a solution of 40 mL of deionised water and 15 mL of hydrochloric acid of at least 32% puriss. p.a. (pH: 1.0). The precipitated product is then filtered out (pore size <5 μm), washed with ice-cold water, and dried. The filter residue is then again dissolved in water, recrystallised, and filtered. In this way, the product 2,4-dihydroxybenzoic acid can be separated from the educts and the byproduct 2,6-dihydroxybenzoic acid. The loss of product due to isolation and purification is in the range of 15% of the originally synthesized amount. In the frame of this explorative study, in the case of the Kolbe−Schmitt synthesis with ionic liquids an isolation method had not been developed yet.

2.2. Microwave Heated Kolbe−Schmitt Synthesis.
2.2.1. Capillary Reactor Rig. The capillary reactor rig had to be adjusted for microwave operation. Glass and PTFE capillary reactors were used. The differences in reactor volume were compensated by varying the volume flows so that a comparable residence time as that for the conventional steel capillary resulted (see Figure 3).

The PTFE capillary had exactly the same dimensions as those of the original steel capillary,[7] whereas the available glass capillary was different with an inner diameter of 3 mm, different from the original steel capillary, and a total volume of 24 mL. This capillary was inside the microwave oven joint to the inlet and outlet tubes (PTFE) using PTFE tube connectors. A special manufactured glass capillary reactor with the same inner volume as that of the original steel capillary[7] was ordered, but was not delivered within the period of investigation.

2.2.2. Microwave Oven and Insertion of Capillary Reactor Rig. A microwave oven (Anton Paar Multiwave 3000) was used with the glass capillary (see Figure 3) mounted on a holder. This construction should guarantee safety and a good volumetric flow control. The other operational items (pumping, cooling, pressure built-up by valve) were the same as those for the conventional heating.[7]

2.2.3. Temperature Programming and Measurement. Power-to-temperature graphs served to show the feasibility of safe high-temperature operation and provide basic settings of the micro-wave equipment ("calibration"); see the more detailed discussion under 3.1. Experiments were done in a process window which is comparable with previous experiments done with conventional heating methods.[7] The reactions were carried out in two sequences, with the first part at low power input and the second one at high power input. When using ionic liquids, the first part is a safe way to compare the behaviour of the dissolved reactant salts with the power temperature calibration curves of water at the same power input.

The duration of irradiation was varied from 4 to 8 min. As a response to microwave irradiation, first a fast temperature increase was observed followed up by a gradual decrease of the temperature derivative, and at long enough irradiation times hardly any change from the maximum reachable temperature was visible anymore. At high power, the set temperature is reached in less than 4 min, while temperature equilibration takes more than 8 min at low power. This is also a function of the flow rate.

It was noted that the Teflon parts were the most sensitive part of the setup with regard to high temperature and pressure operation. Especially for operation at temperatures close to boiling points, bubble formation was observed in the capillary which result in a breakdown of the Teflon connectors.

The temperature was measured on the surface of the capillary via a fibre optical temperature sensor. This method has a lot of inaccuracies but was the only possibility for obtaining information about the axial temperature profile. Thus, averaged values were taken, and a benchmark temperature measurement was added to prove consistency. For the latter reason thermocouples were connected just after the exit point of the capillary and were connected to software. This way, a very accurate temperature profile over time was measured. For all reactive experiments,
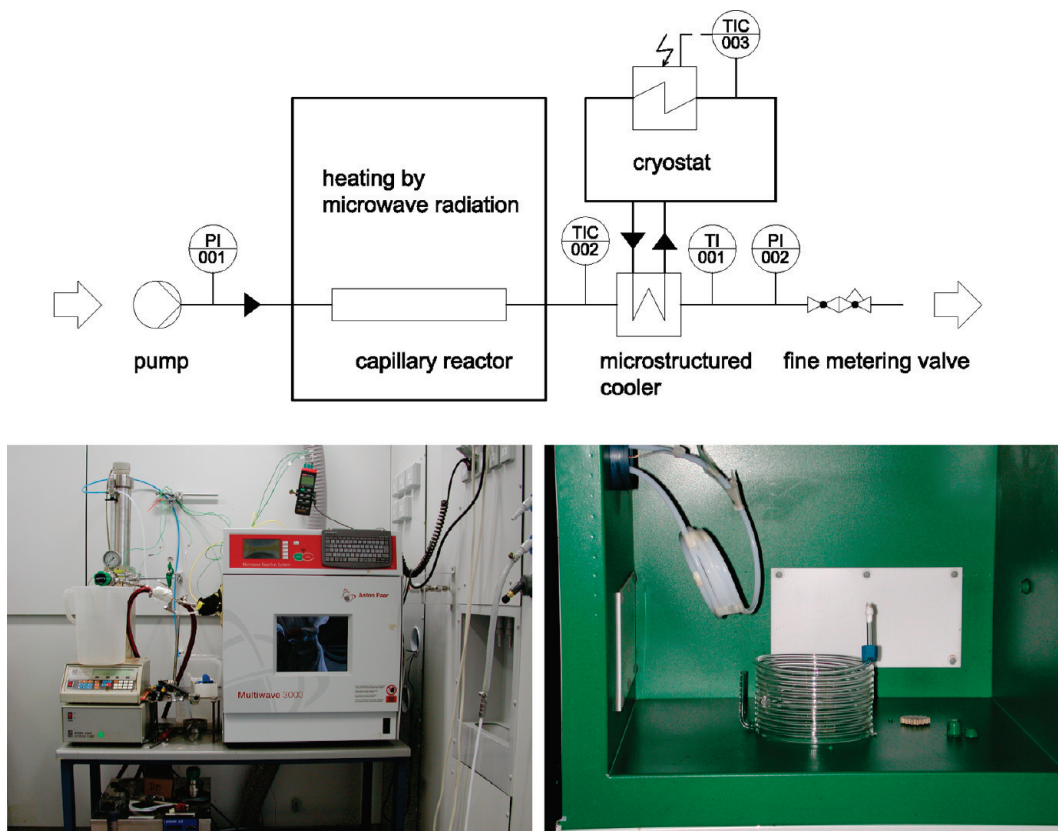
Figure 3. Process flow sheet for microwave assisted aqueous Kolbe−Schmitt synthesis using premixed reactants (top). Whole rig and detail of the capillary reactor (bottom).

the reaction temperature was measured directly after leaving the microwave oven by a dipped thermocouple.

2.3. Oil Bath and Microwave Heated Kolbe−Schmitt Synthesis Using Ionic Liquids. *2.3.1. Ionic Liquid Stock and Reaction Solutions.* The ionic liquids used (1-ethyl/1-butyl-3-methylimidazolium hydrogen carbonate, EMIMHC, and BMIM-HC, respectively) were newly launched products of SIGMA-Aldrich and as expensive chemicals were available only in small quantities.[37] The ionic liquids are not deliverable as pure chemicals (due to instability), but are dissolved in solvents. The ethyl-based ionic liquid solvent was given as a 50% mixture with MEOH/H_2O 2:3, which amounts to a HCO_3^- concentration of 3.2 mol/L. The butyl based ionic liquid solvent was supplied as a 50% mixture in water, which amounts to a HCO_3^- concentration of 2.7 mol/L. In a first run, a similar concentration of the ionic liquids was prepared from these stock solutions as has been used for the conventional Kolbe−Schmitt reaction with $KHCO_3$, but this resulted in a reduction of the total volume which limited the number of potential experiments.

EMIMHC was used for both the oil bath heated and microwave heated Kolbe−Schmitt reaction. For the oil bath application, EMIMHC was diluted with water to a concentration of 1.57 mol/L, while, for the microwave oven application, the concentration was kept at 3.2 mol/L. Also BMIMHC was used for both the oil bath and the microwave oven processing at a concentration of 2.7 mol/L. The reaction capillary (PTFE) used in the microwave oven had an ID of 3 mm and a total inner volume of 9.23 mL.

3. Results and Discussion

3.1. Temperature Mapping and Feasibility of Safe High-Temperature Operation. Temperatures are measured as a function of power and the flow rate for pure water flows followed then by the real-case solution used for the Kolbe−Schmitt reaction (see 3.4), containing a high concentration of ionic species, $KHCO_3$, with a high absorption of microwaves.

In this way, some insight should be obtained about start-up, heating rate, temperature distribution, limits, safety, and dynamics of the microwave heating, and in particular on

- if there are *start-up effects* such as thermal equilibration (radial profile by heat conduction via capillary wall to air) and how long it takes for stable operation
- if a true *high temperature operation* ("Novel Process Windows") can be reached, i.e., temperatures much above 100 °C and ideally close to 200 °C for the case investigated, at stable operation (pressure fluctuation, e.g., by bubbles)
- *temperature mapping* by providing correlations from power setting to measured temperature ("calibration")
- temperature development in the capillary (*axial profile*)
- if and how the *presence of ionic species contributes to faster heating*
- if a *multilevel power setting* can aid safe operation (no thermal overshooting)

3.1.1. Start-up Effects, Temperature Mapping, and Maximum Temperature for Water Flow. Start-up was done with a lower power of 75 W which was gradually increased to higher
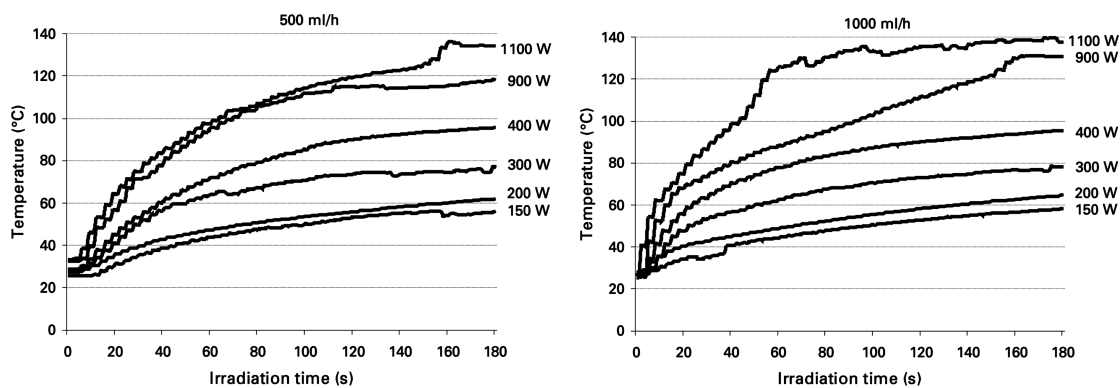
Figure 4. Temperature response of a water flow upon microwave irradiation at various power inputs for flow rates of 500 and 1000 mL/h.
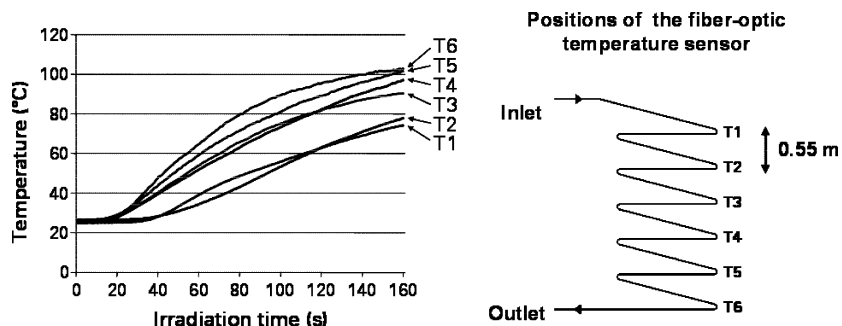

Figure 5. Temperature profile determined at various equally spaced locations along the capillary upon microwave irradiation, with T1 being at the entrance and T6 at the exit (1000 mL/h; 800 W).

values of power around 1100 W which corresponds to the upper limit (1400 W) of the microwave equipment used.

Figure 4 shows that start-up takes more than 180 s of irradiation time. The temperature increase becomes smaller but still is not constant. The latter time is longer than the residence time of the flow; i.e., the flow was renewed during that time. Thus, there has to be an additional effect besides the heating time of the cold flow which probably is due to the heating up of the cold capillary wall (not warmed up by microwaves) by heat conduction and to compensate for the heat losses by air. Only after these effects are in equilibrium temperatures within the liquid are constant.

Higher temperatures can be reached by a higher power setting, which is to be expected. The experiments show a large amount of scattering in temperature data. The temperature increase is not as gradual as the corresponding power changes (sometimes the curves are close to overlapping), and there is other scatter (bumps, see 1000 mL/h plot). This may be caused by the intrinsic nonuniform field over the capillary in a multimode instrument which may differ also from experiment to experiment by small dislocations of the capillary on the holder which alters the efficiency of absorption by differing reflections at the capillary surfaces.

The experiments determine as well the maximum temperature reachable, which was close to 140 °C under the given conditions, i.e., for pure water operation with the equipment used. The efficiency of microwave absorption is expected to decline with increasing temperature, a trend which is evident from Figure 4. This relates to the drastic increase of the penetration depth of microwaves and a corresponding increase in the loss factor. The latter is however partly compensated by

using multimode operation and multiple internal reflections in the microwave chamber.

3.1.2. Axial Capillary Temperature Profile for Water Flow. The PTFE tube consisted of six coils each with a measurement point at equal distance so that the same volume is given between two points of measurement. A temperature sensor made of optic glass fibers was used.

A curved increase in temperature is found (see Figure 5). The temperature changes over the whole length of the capillary from ∼75 to 100 °C. Thus, the average temperature is ∼10 °C lower than the set temperature. Such axial gradients are, however, intrinsic to the heating concept under continuous-flow conditions, particularly if no heat exchanger is set upfront.

3.1.3. Increase of Heating Rate by Presence of Ionic Species (Real-Case Solution). The heating rate was determined for pure water and the real-case Kolbe−Schmitt mixture, revealing the effect of stronger absorbing ionic species. Figure 4, top shows that ∼170 s are needed to reach 100 °C for a pure water solution at 500 mL/h and 500 W (by extrapolation between the 400 and 600 W values, which are nearby). The same temperature is achieved within 50 s for the real-case Kolbe−Schmitt mixture; see Figure 6. It is also shown here that by setting the power to 600 W a fast switch to ∼180 °C can be achieved. The operation is less stable as compared to the pure water processing, since the temperature data are more scattered and there is even a loss of operation control indicated by a downwards bump, probably due to sudden bubble release and/or solvent evaporation (by pressure instability) and corresponding cooling effects. Thus, the microwave irradiation was turned off which induces a slow cooling of the liquid mixture.
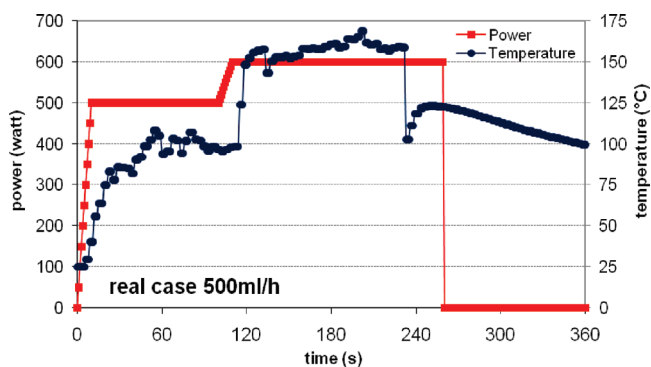
Figure 6. Temperature response (outlet temperature) of a flow of a real-case Kolbe−Schmitt reaction mixture heated in a glass capillary via microwave irradiation with leveled power input at flow rates of 500 mL/h.
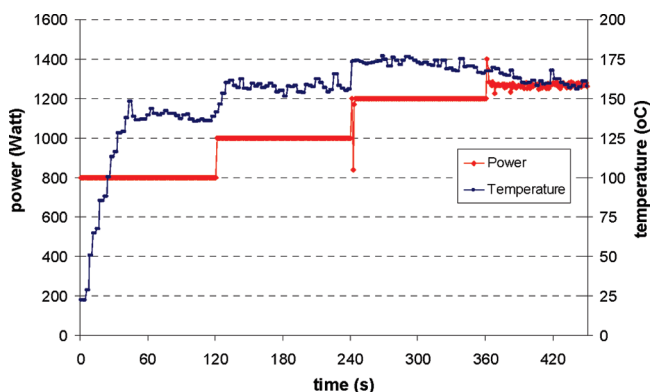

Figure 7. Temperature response (outlet temperature) during heating in a glass capillary for preprogrammed microwave power input for real-case Kolbe−Schmitt reaction mixture at a flow rate of 1400 mL/h.

3.1.4. Multilevel Power Setting for Exploring High-Temperature Operation. In the phase of exploring new power settings and new process conditions (e.g., new solutions) and especially when targeting high temperatures, it is not advised, for reasons of safe operation, to use a single (high) power setting to reach the temperature in one step. Otherwise, thermal overshooting up to the stop of operation of the microwave oven or even destruction of the flow-through components and leakage of solutions may occur. A proper measure is a preprogrammed stepwise increase of the power setting and thus the temperature (see Figure 7).

Multilevel power setting can be done as well in a decline fashion to step to a lower temperature, including complex sequences of declining and rising power (see Figure 8).

3.1.5. Stability of Operation with Real-Case Fluids at High Temperature. The instable operation shown in Figure 6 was caused by the low resistance at high pressures of the glass capillary rig due to the connection points. Therefore, a switch to PTFE as material was necessary, allowing a stable high-pressure operation. The following experiments were conducted with a PTFE tube with dimensions (OD × ID × length: 6 mm × 3 mm × 1.3 m) similar to the glass tube.

Figure 9 shows that using the improved connection a much more stable operation is given for the real-case Kolbe−Schmitt reaction mixture, since the temperature fluctuations reduced a lot.
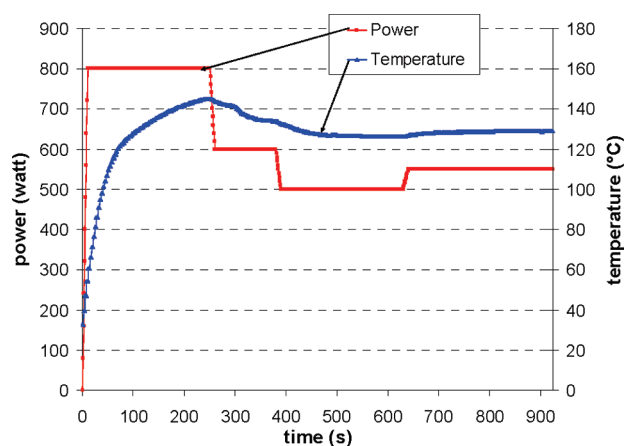

Figure 8. Temperature response (outlet temperature) of a water flow heated in a glass capillary via preprogrammed microwave power input−multilevel power setting.

For a very large power input of 1200 W and a very high temperature around 190 °C, stable operation over a time of ∼120 s was achieved. An attempt to ramp to an even higher temperature by increasing the power to 1400 W was not successful and showed the limits of the microwave rig. The system automatically shut down and came back to stable operation by lowering the power input to 1250 W, albeit the power fluctuations were larger from there on. This did not largely affect the temperature response; only the fluctuations became somewhat larger with average deviations of ∼5−10 K. Still in view of achieving such high temperatures, as hardly reported before for continuous microwave operation, the temperature setting was regarded to be acceptable, as this quality of operation could be held for time of a few minutes at least which is enough to perform reaction experiments.

3.2. Reaction Experiments. For the aqueous Kolbe−Schmitt reaction, for both conventional and microwave heating, the product 2,4-dihydroxybenzoic acid was formed from resorcinol and potassium bicarbonate in an aqueous solution. In the case of the Kolbe−Schmitt synthesis using reactive ionic liquids instead of the aqueous potassium bicarbonate solution, resorcinol was directly solved in the 50 or 25 weight percent ionic liquid solution.

3.2.1. Results of the Conventionally Heated Kolbe−Schmitt Reaction (CHKS). To check for comparison with the previous work[6] one selected experiment at 180 °C and 500 mL/h is repeated in this paper for the conventionally heated Kolbe−Schmitt reaction (see Table 4). To broaden the database, two quick variations in flow rate/reaction time were added, changes which can be quickly done, once oil bath temperature is in equilibrium.

For operation at 180 °C and 500 mL/h, a 39% yield was found in the present work and 43% in the previous work. The difference can be due to a certain change in dimensions in the capillary from the previous to the present work and thus to a corresponding change in residence time. Both yields are comparable to a batch run undertaken in the previous work, showing a 40% yield in 2 h of operation.
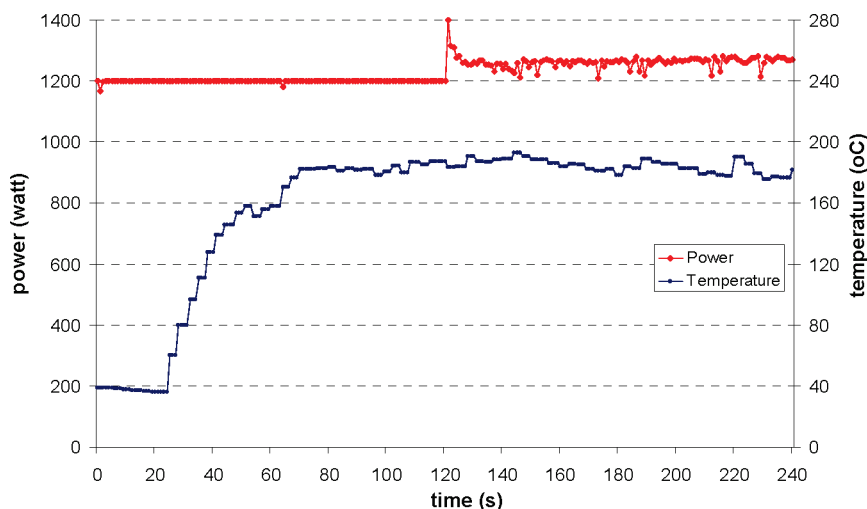
Figure 9. Temperature response (outlet temperature) during heating in a PTFE capillary via preprogrammed microwave power input for real-case Kolbe−Schmitt reaction mixture at a flow rate of 3000 mL/h.

Table 4. Yield for the conventionally heated Kolbe−Schmitt reaction (CHKS)[a]

source	temp (°C)	pressure (bar)	flow rate (mL/h)	reactor volume (mL)	reaction time (s)	yield (%)
previous work[6]	180	40	500	9.03	65	43
redone work here	180	40	500	6.11	43	39
redone work here	180	40	1000	6.11	22	35
redone work here	180	40	2000	6.11	11	34

[a] Results from previous work and redone in this paper to confirm functionality of the new setup.
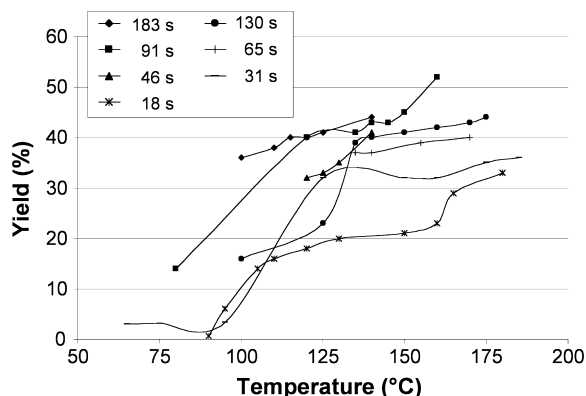

Figure 10. Yield performance of the microwave heated Kolbe−Schmitt reaction (MAKS).

3.2.2. Results of the Microwave Heated Kolbe−Schmitt Reaction (MAKS). The yields obtained by the microwave heated Kolbe−Schmitt reaction (MAKS) were determined as a function of reaction time and temperature (see Figure 10).

A trend of increased yields at longer residence times and higher temperature is visible, as to be expected. Concerning the latter, a plateau is reached beyond a certain temperature threshold. The temperatures for a given yield are lower as compared to the CHKSS, indicating that the actual temperatures are higher in the case of MAKS. Also, the data scatter, e.g., the curves, intersect (without a meaningful explanation for that)

which indicates that the operation is not fully stable, e.g., that temperature fluctuations are present. The highest yield obtained by MAKS was 52% (at 160 °C, 8 bar, 1 L/h, 90 s), exceeding the yield of CHKS by 5% (at 140 °C, 40 bar, 84 mL/h, 390 s) at a concurrent reduction of reaction time (see Figure 10).

The results for reaction times of 18, 31, and 65 s were selected for comparison against respective results obtained by the conventionally heated Kolbe−Schmitt synthesis (see Figure 11).

For all residence times the microwave heating resulted in higher yields than those given for conventional heating at a comparable set temperature. This is related to the higher actual temperatures inside the capillary due to faster heating by the strong absorption of the microwaves as a consequence of the salty nature of the reactants. In both cases, the inlet temperature of the reactants was room temperature, and an axial temperature profile up to the measured outlet temperature is formed. The slope of the profile is, in the case of oil bath heating, dependent on the (constant) surface of the capillary and the mean temperature difference, whereas, in the case of microwave heating, the profile depends on the intensity of irradiation, the microwave absorption properties of the reaction mixture, and the reactor shape. In the former case, the deviation of the mean reaction temperature from the set temperature and the measured outlet temperature decreases with the rise in set temperature; in the latter case, it can be assumed that the slope of the temperature profile is almost independent from the reaction temperature measured at the outlet, aside from heat losses to ambient air. In summary, the faster heating under microwave irradiation leads to higher conversions for the same residence times due to the higher mean temperature inside the capillary reactor.

3.2.3. Results of Oil Bath Heated Ionic Liquid Kolbe− Schmitt Reaction. It is obvious that, for potential industrial applications, currently expensive reactive ionic liquids should not be consumed but have to be recycled to a great extent. The development of such a recycling method was not a subject of the reported investigations. Potential approaches could based, for example, on ion exchange methods. In some cases, nonreactive and cheaper ionic liquids may have advantages as
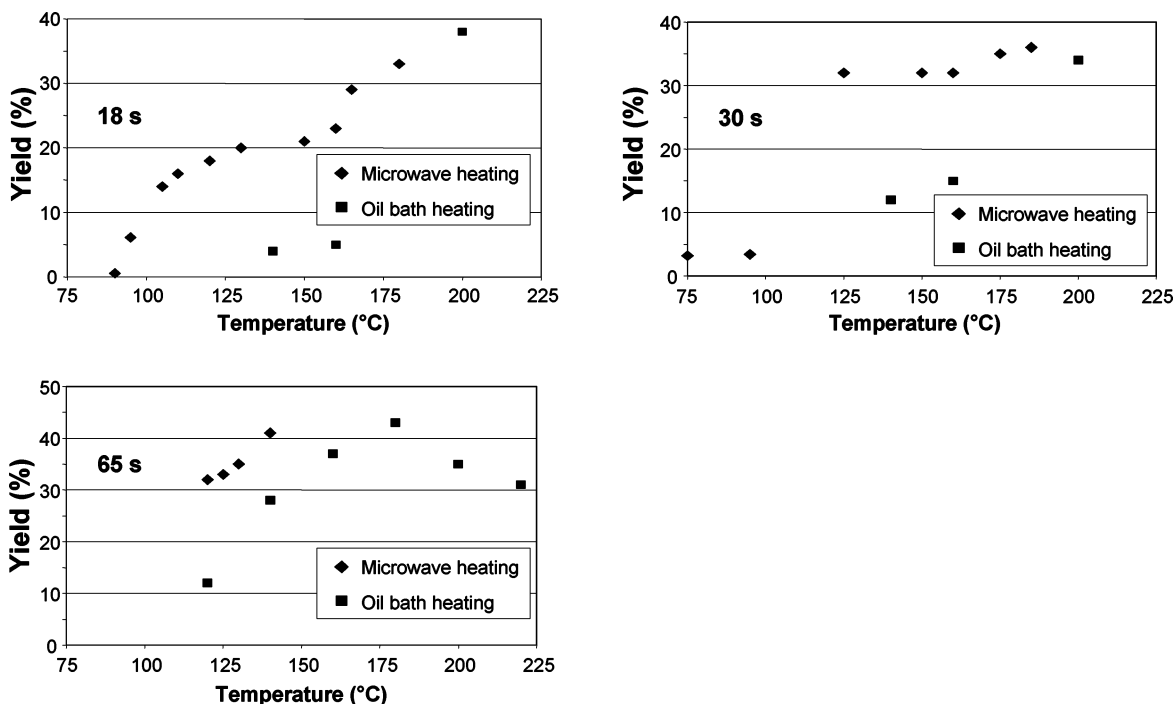
Figure 11. Comparison of the yield performances for the conventionally and of the microwave heated Kolbe–Schmitt reaction at a reaction time of 18, 31, and 65 s (from left up to right up to left down).

Table 5. Process parameters and yield performance for the e-CHILKS process with diluted EMIMHC

flow rate (mL/h)	pressure (bar)	temp (°C)	residence time (s)	yield (%)
170	35	180	130	44

solvents and as highly effective microwave absorbers. Furthermore, this model reaction was only chosen to explore the capability of new process regimes and open the door for real applications, e.g., in fine or specialty chemistry, facilitating the synthesis of higher valuable products.

3.2.3.1. Oil Bath Heated Kolbe–Schmitt Reaction with the Diluted Ethyl Based Ionic Liquid (e-CHILKS). The first reaction done with the ethyl based ionic liquid has been used as a trial, to test for the feasibility of the ionic liquids to act as carboxy donating species. 20 g of EMIMHC mixture (50% in MEOH/H_2O = 2:3; 10 g of ionic liquid), 2.47 g of resorcinol, and 19.2 g of water were used for the feed solution. The capillary volume was 6.11 mL.

The dilution of the EMIMHC mixture with water resulted in a concentration of 1.57 mol/L, while the HCO_3^- concentration was 1.3 mol/L. The reaction parameters and the yield of this reaction are given in Table 5.

The feasibility of using HCO_3^- carrying ionic liquids as carboxylating agents for the Kolbe–Schmitt synthesis was thus demonstrated for the first time. Although the HCO_3^- concentration was significant lower, the yields of the ionic liquid Kolbe–Schmitt reaction are comparable to the conventional aqueous synthesis.

3.2.3.2. Oil Bath Heated Kolbe–Schmitt Reaction with Concentrated Butyl Based IL (b-CHILKS). The second reaction was similar to the one above but used the butyl based ionic liquid (BMIMHC). No additional water was needed as added solvent for resorcinol, but rather resorcinol was directly dis-

Table 6. Process parameters and yield performance for the b-CHILKS process with concentrated BMIMHC

flow rate (mL/h)	pressure (bar)	temp (°C)	residence time (s)	yield (%)
170	35	150	130	40
170	35	160	130	51
170	35	170	130	54
170	35	175	130	57
170	35	180	130	59

solved in the ionic liquid solution. 40 g of BMIMHC mixture (50% in mixture of H_2O; 20 g of ionic liquid, 2.7 mol/L) and 4.26 g of resorcinol were mixed, resulting in concentrations of 0.9 mol/L for resorcinol and 2.4 mol/L for BMIMHC. The capillary volume was 6.11 mL. The parameters and yield of this reaction are given in Table 6.

Yields that were increased in the CHILKS process are generally superior to those of CHKS and reach up to 59%, thus being 11% higher than that for the conventional oil bath heated process and 8% higher than that of the best literature operation by a laboratory batch process[30] (see Figure 12). The yields also exceed the performance of the low concentration run (e-CHILKS).

3.2.4. Microwave Heated Kolbe–Schmitt Reaction with Concentrated Ionic Liquids. 3.2.4.1. Microwave Heated Kolbe–Schmitt Reaction with Concentrated BMIMHC (b-MILKS). This reaction has been done with BMIMHC by microwave heating. A PTFE tube with an inner diameter of 3 mm and outer diameter of 6 mm was used, having a total inner volume of 9.23 mL and a reactor length of 1.31 m. The reactor was 6-fold coiled and was stable at that temperature and pressure. The reaction conditions were exactly the same as those for the oil bath heated BMIMHC reaction, but using a different capillary, thus done with different flow rate. 40 g of BMIMHC
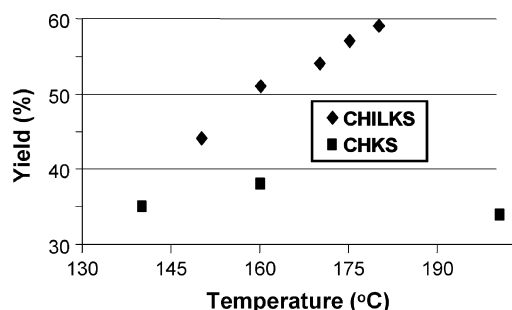
Figure 12. Comparison of the yield performances for the conventionally heated Kolbe−Schmitt reaction using an aqueous KHCO₃ solution or reactive ionic liquids (concentrated BMIM-HC).

Table 7. Process parameters and yield performance for the b-MILKS process with concentrated BMIMHC

flow rate (mL/h)	pressure (bar)	temp (°C)	residence time (s)	yield (%)
320	10	100	104	38
320	10	110	104	42
320	10	120	104	49
320	10	130	104	56
320	10	140	104	57

Table 8. Process parameters and yield performance for the e-MILKS process with concentrated EMIMHC

flow rate (mL/h)	pressure (bar)	temp (°C)	residence time (s)	yield (%)
320	14	80	104	33
320	14	90	104	35
320	14	110	104	46
320	14	115	104	47
320	14	118	104	49
320	14	127	104	56
320	14	135	104	58
320	14	140	104	58

mixture (50% in mixture of H_2O; 20 g of ionic liquid, 2.7 mol/L) and 4.26 g of resorcinol were mixed, resulting in 2.4 mol/L of BMIMHC in the reaction mixture. The parameters and yield of this reaction are given in Table 7.

Thus, the ionic liquid based Kolbe−Schmitt reaction could also successfully combine with microwave operation with high product yields. The maximal yield of 57% is 10% higher than that for the conventional oil bath heated process and 7% higher than that of the best literature operation by a laboratory batch process.[30] It was, however, unexpectedly not possible to reach high temperatures, even though high power input from the microwave could be used.

3.2.4.2. Microwave Heated Kolbe−Schmitt Reaction with Concentrated EMIMHC (e-MILKS). For the reaction of the ethyl based ionic liquid, 40 g of EMIMHC mixture (50% in MEOH/H_2O = 2:3; 20 g of ionic liquid, 3.2 mol/L) and 4.52 g of resorcinol were mixed. The concentration of EMIMHC in the reaction mixture was 2.6 mol/L. The capillary volume was 9.23 mL. The parameters and yield of this reaction are given in Table 8.

The maximal yield of 58% compares to the best CHILKS performance and is 11% higher than that for the conventional
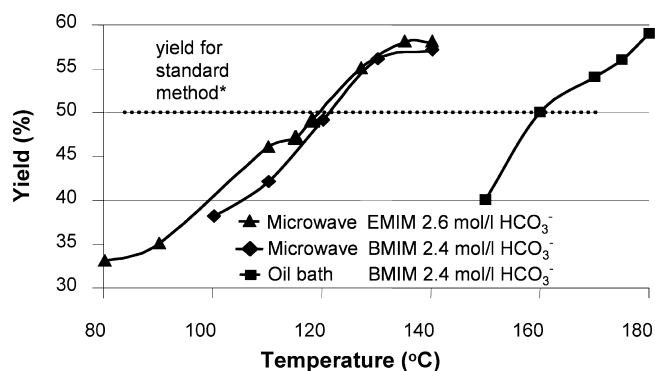
Figure 13. Oil bath and microwave heated Kolbe−Schmitt reaction with different ionic liquids: comparison of CHILKS and MILKS performances. The given concentrations refer to the reaction mixture.

oil bath heated process and 8% higher than that of the best literature operation by a laboratory batch process.[30]

3.2.5. Comparison of All Capillary Reactor Processes Conducted (CHKS, MAKS, CHILKS, and MILKS). In Figure 13, a comparison of all ionic liquid based reactions is given.

The slopes of the yield−temperature plots are similar and so are the maximal yields. However, both MILKS plots reach the maximal yield at a much lower (set) temperature (see Figure 13). This is another indication that the actual temperature in the MILKS process is (on average) closer to the set value than that for the CHILKS process. From Figure 14 it is also evident that the microwave assisted process MAKS (without use of ionic liquids; with KHCO₃) has superior performance compared to the conventionally heated CHKS process.

3.2.6. Space-Time Yield As Measure for Process Intensification. In Table 9, the mass flows achieved and the space-time yields are given as a measure for process intensification. This is complemented by process parameter data and yields.

The new microwave and ionic liquid based processes do not reach the high space-time yields reported for CHKS in ref 6. This is mainly due to limitations in the precious ionic liquid materials and choice of capillaries suited for microwave operation. The first reason limits the maximal flow, and the second has led to an increase in capillary diameter (for the glass and PTFE capillaries) which lowers the reaction time for a given flow rate. Thus, it can be said that for the new processes reasonable space-time yields were reached which, however, allow for greater intensification by the measures mentioned. To corroborate this, two outlooks were made for the MILKS process. The first assumes a much larger flow rate of 2000 mL/h and a reduced reaction time of 1 min. The second additionally takes into account a doubling of the resorcinol concentration and a reduction of the excess of KHCO₃. The projected increase in space-time yield reaches a value approximately half or equal to the benchmark of the CHKS process, respectively, and will be subject of future investigations.

4. Conclusions and Outlook

To establish microwave heating for the Kolbe−Schmitt synthesis, calibration curves were monitored, yielding the temperature response on power input. As to be expected, the heating of water depends on the wattage input, and the heating
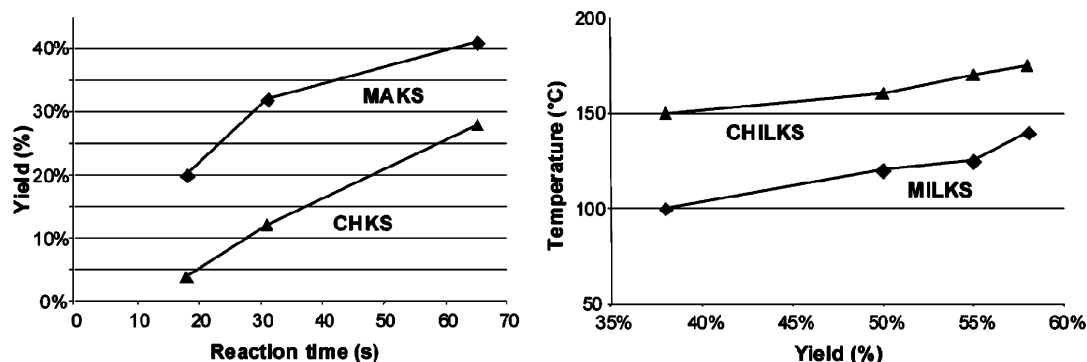
Figure 14. Comparison of the best results for all methods. Left: Oil bath and microwave heated aqueous Kolbe−Schmitt reaction. Right: Oil bath and microwave heated Kolbe−Schmitt reaction using different ionic liquids.

Table 9. Process intensification of the current microwave and ionic liquid based processes as compared to a batch process and future projection

Process	Way of heating	CO_2-donating agent	Yield (%)	T (°C)	P (bar)	Volume flow (mL/h)	Concentration resorcinol (g/L)	Concentration M^+ HCO_3^- (g/L)
Batch (2 h, 1 L)	oil bath	$KHCO_3$	40%	100	0	500	92	253
CHKS	oil bath	$KHCO_3$	47%	140	40	84	92	253
CHKS	oil bath	$KHCO_3$	38%	200	40	2000	92	253
MAKS	microwave	$KHCO_3$	52%	160	8	1000	92	253
e-CHILKS	oil bath	IL dilut.	44%	180	35	170	56	227
b-CHILKS	oil bath	IL conc.	59%	180	35	170	101	476
e-MILKS	microwave	IL conc.	58%	135	10	320	97	457
b-MILKS-Outlook 1	microwave	IL conc.	58%	135	10	2000	101	476
b-MILKS-Outlook 2	microwave	IL conc.	58%	135	10	2000	211	422

Process	Way of heating	Molar ratio $M^+HCO_3^-$/resorcinol	Reaction time (s)	Reactor volume (mL)	Mass flow product (g/h)	Space Time Yield (kg/(h m³))
Batch (2 h, 1 L)	oil bath	3.02	7200	1000	20.6	21
CHKS	oil bath	3.02	390	9	5.1	564
CHKS	oil bath	3.02	16	9	97.7	10859
MAKS	microwave	3.02	92	24	66.9	2786
e-CHILKS	oil bath	2.59	130	6	5.9	962
b-CHILKS	oil bath	2.58	130	6	14.2	2329
e-MILKS	microwave	2.58	104	9	25.3	2740
b-MILKS-Outlook 1	microwave	2.58	60	33	164.6	4943
b-MILKS-Outlook 2	microwave	1.10	60	33	342.2	10276

rate is higher for higher wattages. Thus, less time is needed to reach equilibrium temperature with higher vs lower wattages. Due to the heating, an axial profile of temperature results in the capillary, with end temperatures being higher up to 30 °C compared to entrance temperatures. The actual temperatures under process conditions with a high concentration of microwave absorbing reactant salts were still not exactly at set temperature but rather fluctuated. Although this does not stop lab-scale feasibility studies, this is a major technical hurdle to be solved for a continuous pilot-scale process which has to have constant temperature for, e.g., 10 h.

The microwave heated Kolbe−Schmitt synthesis (MAKS) was carried out with yields up to 52% with lower reaction times and temperatures measured at the outlet as compared to the conventionally heated process (CHKS). This can be explained with faster reaction rates due to a higher mean reaction temperature inside the capillary reactor thanks to faster heating in the case of microwave irradiation. In this manner, an easy upgradeable microwave-oven rig with a maximal mass flow of 67 g/h and a space-time yield of 2800 kg/(m³ h) (CHKS: 98 g/h and 10860 kg/(m³ h)) is achieved.

Ionic liquids were used as HCO_3^- donating agents for the Kolbe−Schmitt reaction, which eliminate the need for solvents with all the advantages discussed and principally make it possible to reach high reactant concentrations (which could not fully been exploited for the reasons given). The conventionally heated ionic liquid Kolbe−Schmitt synthesis resulted into product yields up to 59% with approximately similar productivity as that of the CHKS process.

A future goal is to reach much higher pressures by improving the capillary material and the pressure resistance of the PTFE capillary. The current work was done close to critical physical

parameters of endurance and limit of conceptual feasibility (if multiphases occur, i.e., at the onset to bubble formation) which cannot be tolerated for operation in an industrial setting. Another goal is the future provision of higher concentrated ionic liquids as used in this study to reduce the amount of solvent and to increase the space-time yield. In the same manner, the dissolution of $KHCO_3$ in ionic liquids can be used to increase also the space-time yield, in this case, then using the ionic liquids (non-hydrogen carbonate based) only as solvent and using $KHCO_3$ separately as a carboxylating agent. Further, gaseous CO_2 may be directly added as a reactant, also in combination with ionic liquids.