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Phase Transfer Catalyzed Reaction in Micro Flow Chemistry

The cost attractive alternative

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Summary

This application Note describes the benefits of micro flow chemistry for biphasic liquid-liquid reactions with a Phase Transfer Catalyzed (PTC) type of reaction. For a model reaction Flowid realized a 3 times higher production rate per day with a higher selectivity (99%) as compared to batch reactions. Due to the continuous nature of the process and the micro dimensions of the reactor internals, hardly any operational costs are required while reaction parameters are precisely controlled and product consistency is improved.
Scale up to industrial production capacities is relatively straight-forward.

This makes flow chemistry an attractive alternative for PTC reactions.
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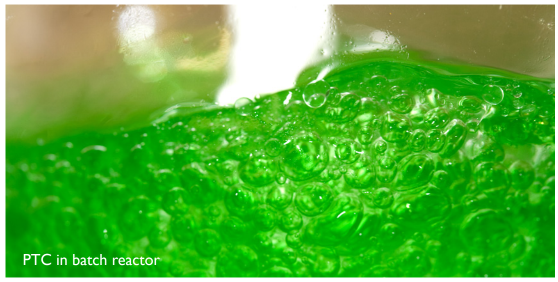
Reactor	Conversion	Selectivity	Reaction time
Micro structured reactor	99%	98,7%	10 sec.
Batch reactor	46%	86%	30 min.


PTC in batch reactor

Phase Transfer Catalyzed Reactions

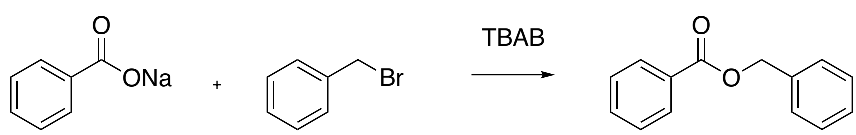
PTC reactions represent a class of green reactions that circumvent the use of aggressive reactants and expensive solvents. By utilizing a phase transfer catalyst it is possible to induce reactivity between an anionic compound dissolved in water and a reactant dissolved in the organic phase. The phase transfer catalyst acts as a carrier of the reactants between the phases. PTC reactions are environmentally friendly and can result in higher yields while using less expensive chemicals, thus making them an attractive and widely used reaction method in laboratory and production environments.

The conventional batch methods for PTC reactions most often suffer from heat and mass transfer limitations, hot spot formation and broad droplet size distribution throughout the reactor. These drawbacks are amplified even more when the process is scaled up, resulting in a decrease in performance and a deteriorated product consistency.

These drawbacks can be eliminated by performing PTC reactions in micro structured reactors under continuous flow conditions. Due to the small internal dimensions of these reactors, mass transfer rates are high and heat transfer limitations are avoided, ensuring a consistent temperature gradient throughout the whole reactor. Additionally, micro structured reactors are ideal for the formation of liquid-liquid dispersions with a controllable and narrow droplet size distribution, resulting in a high and consistent product quality.

Model reaction

As a model PTC reaction, the reaction of sodium benzoate with benzyl bromide to benzyl benzoate was used in this study. Herein, benzyl bromide is a hazardous reactant with strongly lachrymator (tear gas) properties. Therefore, it is clear that the operational safety in the production is essential. The product is commonly used as an insecticide or artificial additive in the food and flavor industry. The cheap and soapy-like tetra butyl ammonium bromide (TBAB) is used as phase transfer catalyst.



Sodium benzoate Benzyl bromide Benzyl benzoate

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Experimental & Results

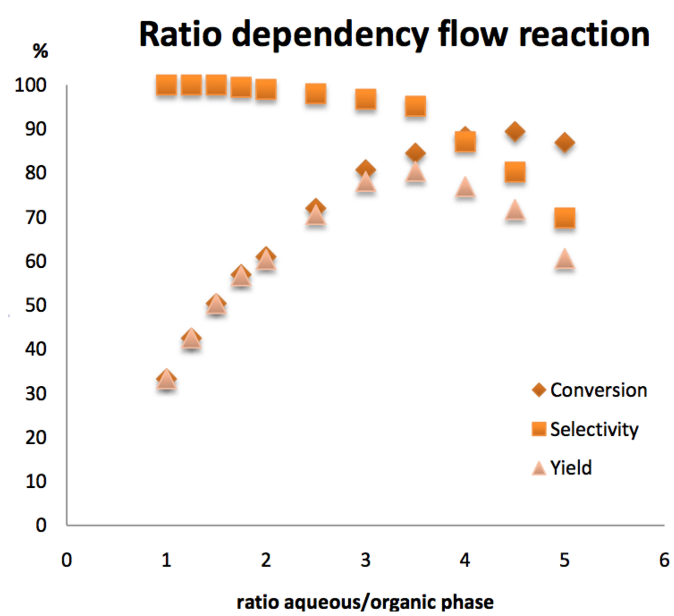
Batch experiments were performed in a 250 ml flask equipped with a turbine stirrer at 105 °C and stirrer speeds of 450 rpm. The flask was loaded with 50 grams organic phase (benzyl bromide) and 50 grams aqueous phase (12 wt% catalyst, 30wt% sodium benzoate). Continuous micro flow experiments were carried out with a stainless steel mixer ideally suited for the generation of emulsions. To facilitate residence time and thus reaction time the mixer was connected to 10 meter of 0.5 mm capillary including measures to circumvent droplet coagulation. The system was heated by an oil bath at a temperature of 105 °C. The aqueous phase contains a similar concentration of catalyst compared to the batch experiments. Sample analyses were performed with a GC. The byproduct, benzyl alcohol, was identified by IR and GC-MS.

The batch experiments showed a maximum conversion of 50% at 30 minutes reaction time, this corresponded to a yield of 35%, due to a decrease in selectivity (70%). Maximum production rates for the batch system were found at a shorter reaction time of 6 minutes, yielding 46% conversion with 80% selectivity. By using a micro structured flow reactor it was possible to operate at much shorter reaction times (10 seconds) compared to batch. Furthermore, higher conversions (99%) and selectivities (98.7%) were attained corresponding to a yield of 98%. Increased interface surface area between the water and organic phase in the micro structured flow reactor is the main cause for the higher yield. The laboratory micro flow set-up used in this study had a product throughput of 79.5 g/hr with plenty of room for scale-up.

Optimization of the process can be achieved by adjusting the ratio between the aqueous and organic phase. This is simply done by tuning the pump speed, instead of performing labor intensive batches for each data point. Increasing the flow ratio leads to an increasing conversion, even up to 99% between flow ratios of 4 to 6, while selectivity stays relatively constant over the complete range of ratios 1 to 4.

Although the product yield increases at high flow ratios, the concentration lowers as well. Therefore, the maximal production rate of benzyl benzoate in mol/s in a micro structured flow reactor was obtained at a ratio of 1. The maximal production rate for the batch reactor was achieved at a reaction time of 6 minutes. Running small batches of 6 minutes is time consuming, has high operational costs, and is subject to operational flaws, safety risks and product inconsistency.

Micro structured flow reactors can be operated continuously for long periods of time. Therefore, the production rate per day is 3.3 times higher compared to batch, based on 4 batches an hour for an 8 hour work day.



Conclusions

In this Note it is demonstrated that benzyl benzoate can be produced with a PTC reaction using a continuously operated micro structured flow reactor with better results compared to conventional batch methods. The selectivity is increased up to 98.7%. The production rate per day is increased with a factor 3, without the need for human intervention, e.g., for cleaning, dosing, or filling the reactor. Operational flaws and safety risks are eliminated while product consistency is improved.

Outlook

For larger scale productions, Flowid can scale up continuous processes based on micro structured reactors, while maintaining process conditions and performance. On the other side, batch reactors will lose efficiency when scaled up due to less effective mixing and to long residence times.