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Sonochemical synthesis of peracetic acid in a continuous flow micro-structured reactor

P.D. Jolhe [a], B.A. Bhanvase [b], V.S. Patil [a], S.H. Sonawane [c,*]

[a] University Institute of Chemical Technology, North Maharashtra University, Jalgaon 425001, India
[b] Department of Chemical Engineering, Laxminarayan Institute of Technology, Rashtrasant Tukadoji Maharaj Nagpur University, Nagpur 440033, India
[c] Department of Chemical Engineering, National Institute of Technology, Warangal 506004, India

HIGHLIGHTS

- Continuous microstructured reactor for the preparation of PAA in the presence of ultrasound.
- The effect of different parameters was studied on the formation of PAA.
- Reaction rate increases due to the formation of H_2O_2 because of cavitational events.
- Reaction time was less than 10 min compared to that of conventional batch reactors.

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ABSTRACT

In the present work, a continuous flow micro-structured reactor was used for the preparation of peracetic acid (PAA) in the presence of ultrasonic irradiations. The effect of several parameters such as acetic acid: hydrogen peroxide molar ratio (1:0.45–1:2.5), flow rate (20–40 mL/h), temperature (20–60 °C) and catalyst loading (340–707 mg/cm^3) were investigated in the presence of ultrasound during the preparation of peracetic acid. The deactivation of the Amberlite IR-120H catalyst was studied in micro-structured reactor. The optimum values of the molar ratio of acetic acid:hydrogen peroxide, flow rate, temperature and catalyst loading were found to be 1:1, 30 mL/h, 40 °C and 471 mg/cm^3, respectively. In the present study, the reaction time observed was less than 10 min compared to that of conventional batch reactors. This drastic decrease in the reaction time was attributed to the use of micro-structured reactor in which heat and mass rates are significantly higher compared to conventional reactors. Also, use of ultrasound drastically enhances the reaction rate due to the formation of H_2O_2 from the chemical effects of ultrasound.

1. Introduction

Peracetic acid is powerful, environmentally friendly and a very cheap oxidizing agent that has great commercial potential in many industries. It can be used as a bleaching agent and to prevent biofilm formation in paper and pulp industries, as a disinfectant in water treatment, for epoxidation of olefins and so on [1–5]. It is also an exceptional active reagent for epoxidation of unsaturated triglycerides for obtaining low cost plasticizers with good performance from natural and renewable sources [5]. Also, PAA pre-treatment has been proved to improve enzymatic digestibility of sugarcane bagasse without the need of high temperature [6,7]. Regardless of these applications of the peracetic acid, limited literature is available on the preparation of PAA. The kinetics of the formation of PAA has been studied by very few researchers, especially in conventional batch reactors. Zhao et al. [8] have studied and developed a homogeneous kinetic model for the preparation of PAA from acetic acid and hydrogen peroxide using Sulfuric acid as a catalyst in the liquid phase. It has been reported that the synthesis of PAA was first-order reactions with respect to reactant concentrations and H^+ concentration. It has been further reported that the rate-determining step in the synthesis of PAA is the reaction between H_2O_2 with active carbonyl intermediary. Further the kinetics of the formation of PAA in a batch process has been investigated by many researchers [9,10]. Peracetic acid is an unstable substance due to its fast thermal decomposition, and therefore, safety aspects in the production of PAA need to be considered. Due to this reason, studying the reactions on small scale is evident. Microreactor safety is based on a small reaction volume, which also

* Corresponding author. Tel.: +91 870 2462626.
E-mail address: shirishsonawane@rediffmail.com (S.H. Sonawane).

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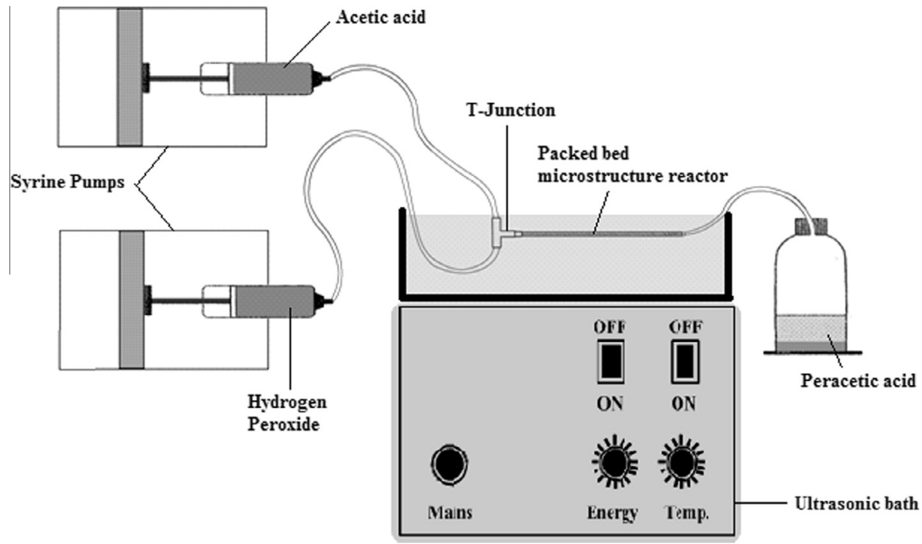

Fig. 1. Schematics of the experimental setup for the preparation PAA in micro-structured reactor.

leads to small inventory of dangerous chemicals. Moreover, the efficient heat transfer resulting from the high surface area-to-volume ratio offers efficient temperature control and, therefore, decreases the risk of run-away reactions. So, the present study preparation of PAA was carried in a microreactor. Also acoustic cavitations induced by ultrasound are among the well-explored research topics which represent green chemistry. The purpose of using ultrasound in present study was to check the feasibility of in situ generation and green provision of H_2O_2 during the course of reaction. Ebrahimi et al. [11] have performed continuous synthesis of performic and peracetic acids in a microstructured reactor using corresponding carboxylic acids and hydrogen peroxide in the presence of homogeneous sulfuric acid catalyst. Formation rates of performic and peracetic acids have been studied by Ebrahimi et al. [12] at different temperatures and catalyst concentrations. It has been reported that the reactions are faster than that in conventional reactors. Ebrahimi et al. [12] have also synthesized performic acid in a packed bed microstructured reactor in the presence of a cation exchange resin catalyst at different temperatures, catalyst concentrations, and residence times. It has been reported that with an increase in temperature and catalyst concentration accelerated the performic acid formation rate. Further Kockmann et al. [13] have reported the concept of the scale up of single channel microreactors which can be used to carry out chemical reactions in tiny channels using continuous-flow processes.

In the present work the effect of several parameters such as molar ratio, flow rate, temperature and catalyst loading has been investigated in the micro-structured reactor. The formed PAA is highly unstable and this reaction takes more time (more than 30 h) in batch processes [14]. Due to this higher reaction time, the decomposition of the product can occur. Further, it is very difficult to carry out this type of highly exothermic reaction in batch or continuous stirred tank reactor. Also, if the reaction is fast and strongly exothermic, hot spot and non-uniform temperature distribution might appear in batch or continuous stirred tank reactor. Such problems can be easily eliminated with the use of micro-structured reactor, which operates on a continuous basis [15]. Due to the small dimensions of the micro-structured reactor, the reaction conditions are easier to maintain because of higher heat and mass transfer rates. Further, the use of homogeneous catalysts such as sulfuric acid has a disadvantage like its subsequent separation from product. Therefore, in the present work, a solid Amberlite IR-120H catalyst is preferred.

Also, it has been reported that the use of ultrasound can lead to physical and chemical transformations in the reaction medium [16–22]. When the ultrasonic waves pass through a liquid medium, a large number of micro bubbles are formed which grow and finally collapse (cavitations) in a few microseconds releasing large magnitudes of energy. The adiabatic collapse of cavity results in the generation of very high local temperatures (>10000 K) and pressures (>1000 atm) and results in the formation of radicals ($^{\cdot}OH$ and $^{\cdot}H$), which leads to the formation of H_2O_2. This helps in the enhancement of the PAA formation reaction as formed H_2O_2 can be used in the reaction. Further, the physical effects (i.e. micro-turbulence and shock waves) generated by the ultrasonic irradiations keep the catalyst in suspended condition and decrease the mass transfer resistance that can enhance the PAA formation reaction. Ultrasound can enhance the mass transfer coefficient, specifically in case of liquid–liquid reactions. Small microfluidic devices has issue with micromixing, hence T junction is being used. However, if combination of ultrasound and microreactor is used then both higher micromixing and enhancement in mass transfer is also observed. This work is unique attempt in which two process intensification devices were used to facilitate the highly exothermic reaction. Though it is well known that microreactor and ultrasound independently enhance the selectivity and conversion however there are very few reports in which combination of the two devices studied [23,24].

With these objectives, the preparation of PAA was carried out in a micro-structured reactor in the presence of ultrasound using acetic acid and H_2O_2. The effects of different variables such as molar ratio, flow rate, temperature and catalyst loading have been investigated in micro-structured reactor. Further, the deactivation phenomenon of the used catalysts i.e. Amberlite IR-120H has been studied.

2. Experimental details

2.1. Materials

The chemicals used in the preparation of PAA in the presence of cation exchange resin catalyst were anhydrous acetic acid and hydrogen peroxide (30 wt.%) purchased from S.D. Fine Chem. Cation exchange resin, Amberlite IR-120H, particles (mean diameter = 0.83 mm, density = 1.28 g/cm^3, functional group = sulfonic acid) was purchased from Rohm & Haas. For the analysis of PAA