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2- and 3-Stage temperature ramping for the direct synthesis of adipic acid in micro-flow packed-bed reactors

Minjing Shang [a], Timothy Noël [a], Qi Wang [a], Yuanhai Su [a], Keisuke Miyabayashi [b], Volker Hessel [a,*], Shinji Hasebe [b]

[a] Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven 5600 MB, The Netherlands
[b] Department of Chemical Engineering, Kyoto University, Kyoto 615-8510, Japan

HIGHLIGHTS

- Application of micro-flow packed-bed reactors for hazardous multiphase reaction.
- In-line temperature monitoring enables tight process control (e.g. of hot spots).
- Temperature ramping improved the yield effectively to 66%.
- The space–time yield is much higher than those obtained in batch reactors.

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ABSTRACT

The synthesis of adipic acid from cyclohexene and hydrogen peroxide was investigated in micro-flow packed-bed reactors. The isolated yield of adipic acid increases with increasing residence time in micro-flow packed-bed reactors. The addition of phosphoric acid cannot effectively improve the isolated yield of adipic acid though it is generally known to reduce the decomposition of H_2O_2. Then, different temperatures were tested along the reactor length, since the adipic acid synthesis is known to consist of 6 elementary reactions with different temperature needs. For experiments with 2-stage temperature ramping, 70 °C and 100 °C, respectively, are the optimal temperatures for the first stage and second stage reactor, which lead to 63% isolated yield of adipic acid. Furthermore, 3-stage temperature ramping improves the yield of adipic acid to 66%. Multi-injection of hydrogen peroxide at different stages does not lead to a further increase in adipic acid yield. Although high temperatures are used in this transformation, the in-line recording of temperature profiles along the flow axis shows that safe operation for this exothermic reaction can be realized in the micro-flow packed-bed reactors. Notably, the space–time yields in micro-flow packed-bed reactors are more than one order of magnitude higher than those obtained in batch reactors.

1. Introduction

Adipic acid is one of the most widely used dicarboxylic acids in the chemical industry, and can be used for the manufacture of nylon 6,6 polyamide, polyurethanes, plasticizers as well as other pharmaceutical chemicals [1]. Nylon 6,6 polyamide is one of the most common building blocks of textile and plastics. In 2010, the global adipic acid capacity was about 2.6 million tons per year, and will reach 3.3 million tons per year in 2016 [2]. Currently, most adipic acid is produced industrially in two steps. The first step is the aerobic oxidation of cyclohexane to obtain cyclohexanone and cyclohexanol, which employs cobalt salts as catalysts. In the second step, the cyclohexanone and the cyclohexanol are oxidized by nitric acid to obtain adipic acid. However, in order to maintain high selectivity of cyclohexanone and cyclohexanol in the first step, it is necessary to keep the conversion of cyclohexane low (e.g. 3–8 mol%) [3]. Furthermore, this traditional process releases a great amount of nitrous oxide due to the utilization of nitric acid, which represents 5–8% of the worldwide anthropogenic N_2O emission. Nitrous oxide causes serious environmental problems, such as air pollution, greenhouse effect, and ozone depletion. Driven by environmental restrictions and large cost of dealing with nitrous oxide, research has been inspired to explore a more environmentally friendly strategy for adipic acid synthesis.

* Corresponding author. Tel.: +31 40 2472973.
E-mail address: V.Hessel@tue.nl (V. Hessel).

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One alternative is the oxidation of cyclohexene with H_2O_2 to produce adipic acid. Although the current commercial process for producing hydrogen peroxide is an energy and pollution intensive process [4], H_2O_2 itself is considered as an eco-friendly chemical since its sole degradation product is water [5]. The first process employing hydrogen peroxide for producing adipic acid was reported by Sato et al. [6]. This process employed cyclohexene as the starting material and allowed to obtain 90% yield of adipic acid at 90 °C after 8 h. This landmark paper has inspired several other research groups to develop new strategies to achieve a more efficient adipic acid synthesis starting from cyclohexene and H_2O_2 [7]. These reports have been mainly focused on the development of novel catalysts and the optimization of new reaction processes. Cheng et al. [8] modified an SBA-15 mesoporous catalyst with tungsten oxide and then used it to catalyze the cyclohexene oxidation to produce adipic acid. In this process, the yield of adipic acid reached 30% after 13 h at 85 °C. Furthermore, aiming to improve the mixing efficiency between H_2O_2 (aqueous phase) and cyclohexene (organic phase), mesoporous oxides with built-in active tungsten oxide were applied to produce adipic acid, inside which the immiscible two phases contacted with each other and reacted under the effect of immobilized catalyst. In this operational mode, the yield of adipic acid could reach 95% at 80 °C after 24 h, but the reusability of catalyst still needed to be improved [9]. Vafaeezadeh et al. [10] developed silica-supported ionic liquid catalysts to create an amphiphilic reaction environment for the oxidation of cyclohexene, and obtained 87% yield of adipic acid within 18 h at 75 °C. For most processes utilizing a heterogeneous catalyst [8–11], extremely long reaction times were needed and thus rather low space–time yields of adipic acid were achieved. Homogeneous catalysts can also be used and can reduce the reaction time significantly. Jin et al. [12] have used peroxy tungstate as catalyst and studied the influence of reaction conditions on the adipic acid production. They obtained 95% yield of adipic acid at 80–95 °C after 9 h reaction time. Wen et al. [13] prepared a homogeneous catalyst complex that included H_2WO_4, H_3PO_4 and H_2SO_4, and applied it to produce adipic acid in a series of continuous stirred-tank reactors (CSTRs). The highest yield for adipic acid that could be reached was 93% at 73–90 °C with 8 h reaction time. However, the space–time yield for homogeneous catalysis with conventional reactors was still low.

Microreactor technology provides a powerful approach for process intensification, and shows its importance for chemical industry and continuous-flow chemistry [14–18]. Extremely large surface-to-volume ratios of microreactors lead to fast heat transfer and mass transfer rates, which are beneficial for strong exothermic reactions or mass transfer controlled reactions, respectively. Furthermore, it is easy to apply harsh reaction conditions (e.g. high temperature, high pressure and high reactant concentration) in microreactors. The reduction of mass transfer limitation and the potential to employ harsh process conditions can effectively reduce reaction time and finally improve space–time yield. Such conditions refer to the Novel Process Windows (NPW) concept [19–21]. For the oxidation of cyclohexene with H_2O_2, NPW intend to involve the use of high temperature and high concentration of H_2O_2 which can speed up the intrinsic kinetics of different reaction steps, and thus facilitate the overall reaction process (chemical intensification field). However, it is challenging to realize such chemical intensification in batch reactors, due to an insufficient mass and heat transfer rate and easy decomposition of H_2O_2 at high temperature and high concentration. In contrast, the high heat and mass transfer rates in microreactors can accommodate such harsh reaction conditions and offers a safe and reliable process [22,23].

Recently, we demonstrated that we could obtain 50% isolated yield of adipic acid by using 50 wt% H_2O_2 in a single micro-flow packed-bed reactor at atmospheric pressure and 100 °C with 20 min residence time [22]. However, we observed that in this process a large amount of H_2O_2 decomposed and the efficiency of H_2O_2 was just about 45%. Thus, it is of great importance to reduce the decomposition of H_2O_2 [24] in order to further increase the yield of adipic acid and avoid the potential explosion hazards. In addition and as illustrated in Fig. 1, there are six consecutive elementary reactions included in the direct synthesis of adipic acid from cyclohexene and H_2O_2, which have all distinct reaction rates [6]. For the sake of reducing the H_2O_2 decomposition and improving heat control inside the reactors, two engineering solutions can be envisioned, namely multi-temperature ramping and multi-injection [25–27]. Multi-temperature ramping refers to the application of different reaction temperatures in different sections of the reactor. For an ionic liquid synthesis as an example for an ultra-fast highly exothermic reaction, it was demonstrated that multi-temperature ramping can avoid thermal runaway and reduce useless consumption of reactants and products, finally leading to a significant increase in space–time yield [24]. Another possible solution is the multi-injection, which refers to distributing reactants along the reactor length by using different inlets. This is in a way a speed-up flow counterpart of the drop-by-drop addition of reactants in batch synthesis. This solution proved also to be beneficial to keep the heat management under control in the whole reaction system, leading to an enhanced product yield [28,29].

In this work, the effects of operational parameters on the yield of adipic acid synthesis starting from cyclohexene and H_2O_2, such as residence time and the addition of phosphoric acid, have been investigated in micro-flow packed-bed reactors. In order to further improve the adipic acid synthesis, we applied a multi-temperature ramping strategy for micro-flow packed-bed reactors. Moreover and as a means of comparison to the latter, the performances of single-injection and multi-injection were compared. The concepts of Novel Process Windows were clearly embodied in this work.

It has to be pointed out that the intention of this paper is not to perform kinetic or analytical experiments, but rather to make process chemistry research under 'realistic', production-near conditions. We follow approaches using packed-bed micro-flow reactors, as developed by Santacesaria et al. in the EU Large-Scale project COPIRIDE heading for new modular production concepts [30–32]. Under such harsh conditions (high concentration and high temperature) and given the intrinsic fastness and exothermicity of

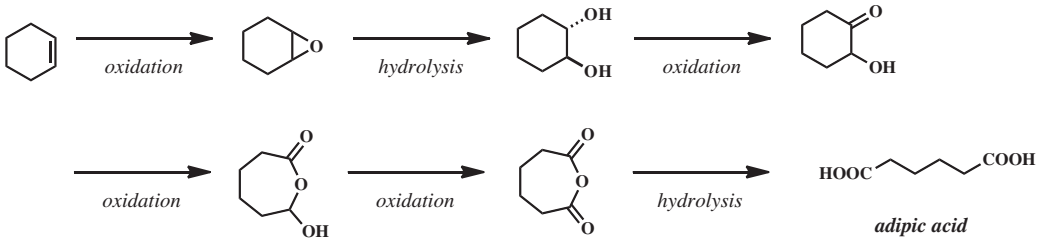

Fig. 1. Proposed reaction pathway for the synthesis of adipic acid [5].