

Two-Phase Flow Oxidation of Valeraldehyde with O₂ in a Microstructured Reactor

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Supporting Information

ABSTRACT: Microstructured reactors are the ideal device for highly exothermic reactions. In this work, the highly exothermic two-phase reaction of valeraldehyde with oxygen to valeric acid was carried out in a microreactor. The used device from one-A Engineering Austria GmbH is designed for process development and intensification and can be applied in the scale-up process to small-scale commercial production. The atom economic oxidation of valeraldehyde is performed at 0 to 40 °C with a catalytic amount of manganese(II) acetate. A continuous flow oxidation of aldehydes in such reactors can be a safe and beneficial alternative to commercial batch processes.

INTRODUCTION

Aldehydes can be obtained by the economically efficient transition-metal-catalyzed hydroformylation of olefins known as the oxo synthesis.¹ The oxidation of aldehydes with oxygen to the corresponding carboxylic acids has been widely studied in terms of reaction mechanism,^{2,3} kinetics,⁴ and the influence of different catalysts^{5,6} and solvents.⁷ Vanoye et al.⁸ recently reported the oxidation of different aldehydes in a perfluoroalkoxy alkane (PFA) tubing microreactor with promising results. One beneficial reason for the use of microstructured reactors is the improved mass transfer of oxygen. Due to the low solubility of oxygen in aldehydes⁹ and the fast chemical reaction, the progress of reaction in conventional reactors like stirred tank reactors and bubble column reactors are limited by the mass transfer of O₂.

A further benefit of microstructured reactors is the increased process safety, which is achieved by a low hold up of critical material and the fast removal of reaction heat. Due to the efficient heat transfer, a critical hot spot or a thermal runaway is unlikely.¹⁰ This is an important factor, especially for fast and exothermic reactions such as the oxidation of aldehydes with pure oxygen.

In this paper, a general demonstration of the valeraldehyde oxidation with pure oxygen in a microstructured reactor is presented (Scheme 1). The reactor design is based on meander-shaped pipes from a nickel based alloy which are mounted in a metal housing. Due to the capillary design with periodically arranged narrowings, the microreactor is especially suited for multiphase oxidation reactions with oxygen, ozone,

or hydrogen peroxide. By modifying the periodic narrowings along the complete reactor channel, the degree of mixing and the generation of the gas–liquid interface can be seamlessly adjusted to the reaction conditions. Due to the robust metallic design, the microreactor can be used from lab scale to production scale.

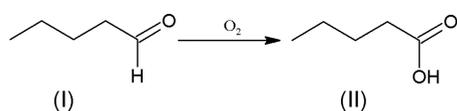
From a green chemistry perspective, oxygen is the ideal oxidizing agent. Furthermore, because of the mild reaction conditions and the high atom efficiency the metal catalyzed oxidation with oxygen has some advantages over other reported aldehyde oxidation methods.¹¹

MATERIALS AND METHODS

The conversion of valeraldehyde to valeric acid with oxygen was carried out in a microstructured reactor from one-A Engineering Austria GmbH (Figure 1a). The reactor was engineered for research and development and can be applied in production processes. Due to the modular design, the reactor can be used in various settings. For the conducted reaction, a setting with 10 microchannels in series (length: 750 mm; internal diameter: 1 mm) and a total volume of 5.82 mL was used. The inserted capillaries were made of Hastelloy with periodical narrowings to increase the mixing performance for an improved mass transfer (Figure 1b).

All substrates were obtained from commercial suppliers and were used without further purification. The homogeneous valeraldehyde solution, containing the manganese(II) catalyst and the octanoic acid, was added continuously into the reactor by a syringe pump (SyrDos 2 with 10 mL syringes, HiTec Zang GmbH, Germany) and preheated in 2 of the 10 available microchannels. The oxygen flow rate (purity: 99.5%, Linde AG, Germany) was measured with a rotameter (Model E: 0.1–0.8 L

Scheme 1. General reaction of valeraldehyde (I) with oxygen to valeric acid (II)



Special Issue: Oxidation and Oxidative Reactions

Received: June 1, 2015

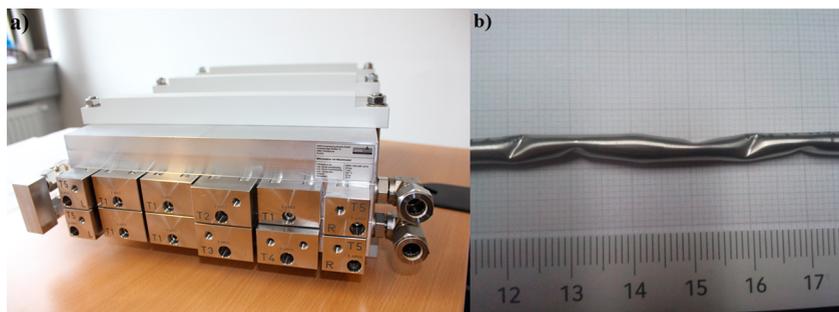


Figure 1. Microreactor MRM 1026-0261-2014 from one-A Engineering Austria GmbH (a), employing microchannels with periodical narrowings (length: 750 mm; internal diameter: 1 mm) (b).

min^{-1} , VAF Fluid-Technik GmbH, Germany). The gas and the liquid stream are contacted inside the reactor in a T-Mixing chamber. The conversion was carried out in the 8 remaining capillaries, with a total volume of 4.76 mL. Figure 2 shows the experimental setup.

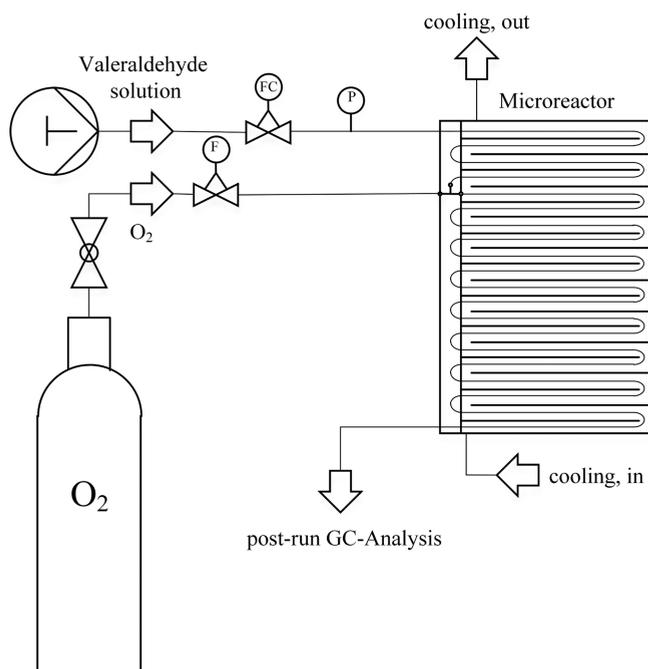


Figure 2. Microreactor setup for the two-phase flow oxidation of valeraldehyde with O_2 .

The used operating parameters are displayed in Table 1. Samples to analyze the reaction progress were diluted with methanol in a ratio of 10/1 (v/v). Quantitative analyses of the oxidation reaction for the determination of the valeraldehyde conversion were carried out by GC (7820A with flame ionization detector (FID), Agilent Technologies Inc., United States of America) equipped with an HP5 column (length: 30 m; diameter: 0.320 mm; film thickness: 0.25 μm), injection volume 0.5 μL . The GC spectra were measured with an initial column temperature of 60 $^\circ\text{C}$ and two temperature ramps (first: 10 $^\circ\text{C min}^{-1}$ to 150 $^\circ\text{C}$, second: 30 $^\circ\text{C min}^{-1}$ to 250 $^\circ\text{C}$). A constant flow rate of 1.5 mL min^{-1} (split flow: 150 mL min^{-1}) of N_2 carrier gas was used. The method was calibrated for valeraldehyde and valeric acid.

Table 1. Set-up parameters for the two-phase flow oxidation of valeraldehyde

parameter	range
reactor volume	5.82 mL (total volume); 4.76 mL (reaction volume)
microchannels	2 tubes for preheating; 8 tubes for reaction
internal diameter of the microchannels	1 mm
oxygen flow rate	100–500 mL min^{-1}
valeraldehyde flow rate	0.21–3.29 mL min^{-1}
octanoic acid flow rate	0.046–0.732 mL min^{-1}
molar ratio of valeraldehyde to octanoic acid	1:0.15
molar valeraldehyde feed rate	0.0019–0.0309 mol min^{-1}
molar oxygen feed rate	0.0058–0.0928 mol min^{-1}
molar oxygen excess	2 equiv (relative to valeraldehyde)
manganese(II) acetate catalyst	1000 ppm (mol/mol relative to valeraldehyde)
temperature	0–40 $^\circ\text{C}$
pressure	0.5–3.2 bar (reactor inlet)

RESULTS

At the beginning of the study, the reaction conditions have been optimized in batch experiments. The results of the batch experiments from Lehtinen et al.⁴ could be confirmed for the oxidation of valeraldehyde. They found a fast and selective air oxidation of 2-ethylhexanal with manganese(II) acetate and the addition of octanoic acid. The reaction has an autocatalytic potential. The final product valeric acid catalyzes the reaction. Any carbon acid shows this behavior; octanoic acid (high boiling point, low-priced) was used for practical reasons.

The experiments were carried out with a large molar excess of oxygen (2 equiv). Because of this excess and the low density of oxygen, compared to the liquid, the dominant phase in the capillary is the gas phase. Therefore, an annular flow pattern can be assumed (see Supporting Information). Due to the large excess of oxygen, the phase ratio is nearly constant over the entire reaction process. These process parameters were selected to achieve a high mass transfer rate, since the oxidation process is described with a mass transfer limitation.⁸

Furthermore, a safe oxidation process with oxygen has been developed. A dilution of valeraldehyde for safety reasons is not necessary. The calculation of the heat transfer time is included in the Supporting Information. However, to achieve a fast conversion of the aldehyde, the addition of octanoic acid is important. An increase of the reaction rate of about 2.1 times was observed. The conversion of valeraldehyde at 0, 20, and 40 $^\circ\text{C}$ with addition of octanoic acid and manganese(II) acetate

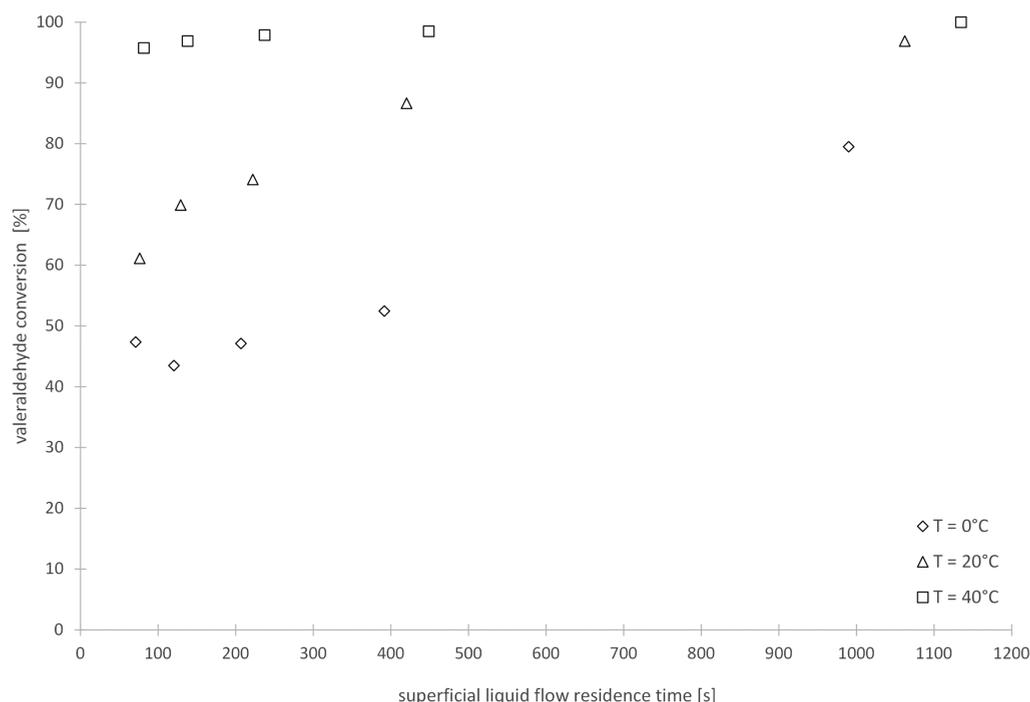


Figure 3. Valeraldehyde conversion for the catalyzed oxidation reaction with manganese(II) acetate and octanoic acid in a microreactor (one-A Engineering, Austria) at different reaction temperatures (0, 20, and 40 °C).

(1000 ppm, mol/mol relative to valeraldehyde) is displayed in Figure 3. A rapid conversion of valeraldehyde was achieved with the applied reaction conditions (superficial liquid flow residence time: 82 s; conversion: 95%). The corresponding yields of the experiments are shown in Figure 3S in the Supporting Information. The reaction is accelerated by increasing the reaction temperature. A rough calculation of the activation energy E_A (9.5 kJ mol^{-1}) was performed by using the initial reaction rate (see Supporting Information). The activation energy below 20 kJ mol^{-1} indicates a mass transport limited reaction. Due to the fast reaction rate, it is supposed that the reaction took place in the liquid boundary layer.

Typical byproducts in the oxidation process of aldehydes with oxygen are ketones, alcohols, and small chain hydrocarbons. We observed no additional peaks in the GC analytics within the detection range of 0.01 wt % (wt %). By analyzing the mass balance of valeraldehyde and valeric acid, we observed a selectivity of 80% to 85%. This could indicate low boiling hydrocarbons as byproducts. Without the catalyst and the octanoic acid, we observed a lower selectivity of 51% to 55%. The selectivity increase is mainly due to the manganese(II) catalyst and the octanoic acid. According to Lehtinen et al.,⁴ octanoic acid has the ability to reduce the acyl radical formation from the aldehyde, while the manganese(II) catalyst enhances the conversion of the intermediate to the carboxylic acid. The interaction of both factors leads to the increased selectivity.

The experiments were also conducted with a smaller amount of catalyst. With the lowest amount of the manganese(II) catalyst (50 ppm, mol/mol relative to valeraldehyde), the reaction rate was 7.5 times slower compared to the result with 1000 ppm. However, this can be compensated with longer residence times. A scale-up to bigger microchannels (3 mm) was carried out, but it is not straightforward due to the change of hydrodynamic mass transfer. The results of the scale-up experiment are included in the Supporting Information.

In a future production process, the autocatalytic behavior could be leveraged by a recycle stream of the product to the reactor entrance. This way, the octanoic acid can be avoided. Based on these results, a production capacity of 0.049 kg h^{-1} and a high space-time-yield of about $10\,290 \text{ kg h}^{-1} \text{ m}^{-3}$ was calculated. By comparing the space-time-yield with the results from the Patent WO 2010/108586 A1,¹² which describes the noncatalytic oxidation of valeraldehyde with oxygen in a microstructured reactor, nearly the same space-time-yield of about $10\,000 \text{ kg h}^{-1} \text{ m}^{-3}$ could be found. By further optimization, especially of the phase ratio and the reaction temperature, the space-time-yield can be enhanced.

CONCLUSION

The catalytic oxidation of valeraldehyde with dioxygen has been demonstrated using a Hastelloy microreactor. The used microreactor is ideal for scale-up processes to small-scale commercial production. With the benefits of microreaction technology, it is possible to carry out a safe oxidation process without any prior dilution of the aldehyde. A fast conversion of valeraldehyde could be achieved with the addition of manganese(II) acetate (1000 ppm, mol/mol relative to valeraldehyde) and octanoic acid. This oxidation process of valeraldehyde shows high productivity (space-time-yield $10\,290 \text{ kg h}^{-1} \text{ m}^{-3}$) and selectivity (80% to 85%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.oprd.5b00173.

Assumption of the flow behavior of the two-phase flow oxidation (S1); calculation of the liquid hold-up (Lockhart-Martinelli parameter) (S2); calculation of the heat transfer time (S3); calculation of the activation energy E_A (S4); results of the scale-up experiment to 3

mm internal diameter capillary (S5); corresponding yields of the experiments from Figure 3 at 0, 20, and 40 °C (S6) (PDF)

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Notes

The authors declare no competing financial interest.

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