

# Supporting Information for

## Two-Phase Flow Oxidation of Valeraldehyde with O<sub>2</sub> in a Microstructured Reactor

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### S1 Assumption of the flow behavior of the two-phase flow oxidation

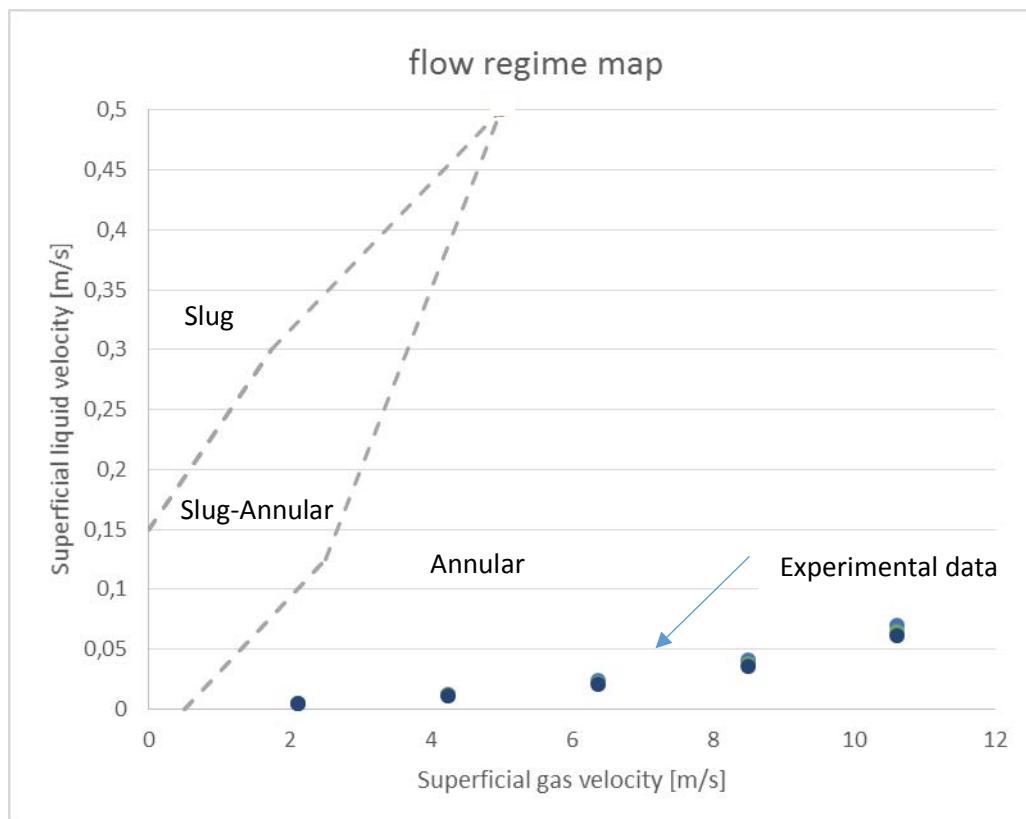
To make an assumption of the flow behavior inside the microreactor the superficial liquid velocity and the superficial gas velocity were calculated and analyzed in a flow regime map of a model system of Isopropanol and Nitrogen.<sup>1</sup>

Liquid phase:

flow rate [mL/Min]	density [g/cm <sup>3</sup> ]	mass flow rate [g/Min]	flow rate [m <sup>3</sup> /s]	cross-sectional area [m <sup>2</sup> ]	ID: 1 mm	Superficial liquid velocity [m/s]
0,24	0,81	0,19	4,00E-09	7,85E-07	5,09E-03	
0,6	0,81	0,49	1,00E-08	7,85E-07	1,27E-02	
1,13	0,81	0,92	1,88E-08	7,85E-07	2,40E-02	
1,94	0,81	1,57	3,23E-08	7,85E-07	4,12E-02	
3,29	0,81	2,66	5,48E-08	7,85E-07	6,98E-02	
0,22	0,81	0,18	3,67E-09	7,85E-07	4,67E-03	
0,56	0,81	0,45	9,33E-09	7,85E-07	1,19E-02	
1,05	0,81	0,85	1,75E-08	7,85E-07	2,23E-02	
1,81	0,81	1,47	3,02E-08	7,85E-07	3,84E-02	
3,06	0,81	2,48	5,10E-08	7,85E-07	6,49E-02	
0,21	0,81	0,17	3,50E-09	7,85E-07	4,46E-03	
0,52	0,81	0,42	8,67E-09	7,85E-07	1,10E-02	
0,99	0,81	0,80	1,65E-08	7,85E-07	2,10E-02	
1,7	0,81	1,38	2,83E-08	7,85E-07	3,61E-02	
2,87	0,81	2,32	4,78E-08	7,85E-07	6,09E-02	

Gas phase:

ID: 1 mm				
flow rate [mL/Min]	flow rate [L/Min]	flow rate [ $m^3/s$ ]	cross-sectional area [ $m^2$ ]	Superficial gas velocity [m/s]
100	0,1	1,67E-06	7,85E-07	2,12
200	0,2	3,33E-06	7,85E-07	4,24
300	0,3	5,00E-06	7,85E-07	6,37
400	0,4	6,67E-06	7,85E-07	8,49
500	0,5	8,33E-06	7,85E-07	10,61
100	0,1	1,67E-06	7,85E-07	2,12
200	0,2	3,33E-06	7,85E-07	4,24
300	0,3	5,00E-06	7,85E-07	6,37
400	0,4	6,67E-06	7,85E-07	8,49
500	0,5	8,33E-06	7,85E-07	10,61
100	0,1	1,67E-06	7,85E-07	2,12
200	0,2	3,33E-06	7,85E-07	4,24
300	0,3	5,00E-06	7,85E-07	6,37
400	0,4	6,67E-06	7,85E-07	8,49
500	0,5	8,33E-06	7,85E-07	10,61



Due to the results we assumed annular flow inside the microreactor channels. The calculation shows that the flow regime is far away from slug-flow.

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(1) Wälchli, S.; Two-Phase Flow Characteristics in Gas-Liquid Microreactors, Swiss Federal Institute of Technology, Zürich (2005)

## S2 Calculation of the liquid hold-up (Lockhart-Martinelli)

The liquid and the gas hold-up are approached by Lockhart-Martinelli.<sup>1</sup> The correlation between the Lockhart-Martinelli parameter and the liquid hold-up is according to the calculations of Abduul-Majeed.<sup>2</sup>

The calculation were carried out for the lowest and the highest mass flow rate for the liquid solution.

Gas:		
flow rate [mL/Min]	density [g/cm^3]	mass flow rate [g/Min]
100	0,00143	0,14
500	0,00143	0,71
Liquid:		
flow rate [mL/Min]	density [g/cm^3]	mass flow rate [g/Min]
0,21	0,81	0,17
3,29	0,81	2,66

$$\chi = m_l / m_g * \sqrt{(\rho_g / \rho_l)}$$

where:

$\chi$ : Lockhart-Martinelli parameter

$m_l$ : liquid phase mass flow rate

$m_g$ : gas phase mass flow rate

$\rho_g$ : gas density

$\rho_l$ : liquid density

Lockhart-Martinelli parameter <sup>1</sup>	Liquid-Holdup [-] <sup>2</sup>	Liquid-Volume [mL]	Liquid-Volume [%]	Gas-Holdup [-]	Gas-Volume [mL]	Gas-Volume [%]
0,050	0,023	0,11	2,3	0,98	4,56	97,7
0,157	0,05	0,23	5,0	0,95	4,44	95,0

Calculation of the film thickness by assuming a cylinder geometry:

$$V = \pi * r^2 * h$$

$$0.23 \text{ mL} = \pi * r^2 * (8 * 750 \text{ mm}) \quad // \text{capillary length: } (8 * 750 \text{ mm})$$

$$230 \text{ mm}^3 = \pi * r^2 * (6000 \text{ mm})$$

$$0,0122 \text{ mm}^2 = r^2$$

$$r = 0,11 \text{ mm} \triangleq 110 \mu\text{m}$$

Calculation of the specific interface:

$$S_V = (\pi * 2 * (r - \text{film thickness})) / \pi * r^2$$

$$S_V = (2 * (0.5 - 0.11)) / 0.5^2$$

$$S_V = 0.78 / 0.25$$

$$S_V = 3.12 \text{ mm}^2 / \text{mm}^3 \triangleq 3120 \text{ m}^2 / \text{m}^3$$

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## S3 Calculation of the heat transfer time

The heat transfer time is calculated for two different scenarios.

### 1. Calculation for homogenous filled capillary with valeraldehyde

Calculation of Heat transfer time $\tau$	
$\tau = L^2 / (\alpha * Nu)$	Roberge, D. M.; Kockmann, N.; Scale-up concept for modular microstructured reactors based on mixing, heat transfer, and reactor safety, Chemical Engineering and Processing, Vol. 50 (2011), 1017-1026
$L =$	0,1 cm // capillary diameter
$Nu =$	3,66 - // laminar flow through capillary (assumption)
with	
$\alpha = k / (\rho * c_p)$	// thermal diffusivity
$k =$	134 W/(m * K) // thermal conductivity Natan, B.; Vargaftik, Lev. P.; Handbook of Thermal Conductivity of Liquids and Gases, CRC Press, Inc (1994), p. 172
$\rho =$	810 kg / m^3 // density Material Safety Data Sheet, Sigma Aldrich (12.03.2015)
$c_p =$	2020 J / (kg * K) // heat capacity Korkhov, A.D.; Dyakova, G.N.; Vasilev, I.A., Heat capacity of pivalaldehyde and valeraldehyde, (1983)
$\alpha =$	0,82 cm^2 / s
$\tau =$	<u>0,003332</u> s

### 2. Calculation for a film thickness of 0,11 mm (calculated from the liquid hold up (S2))

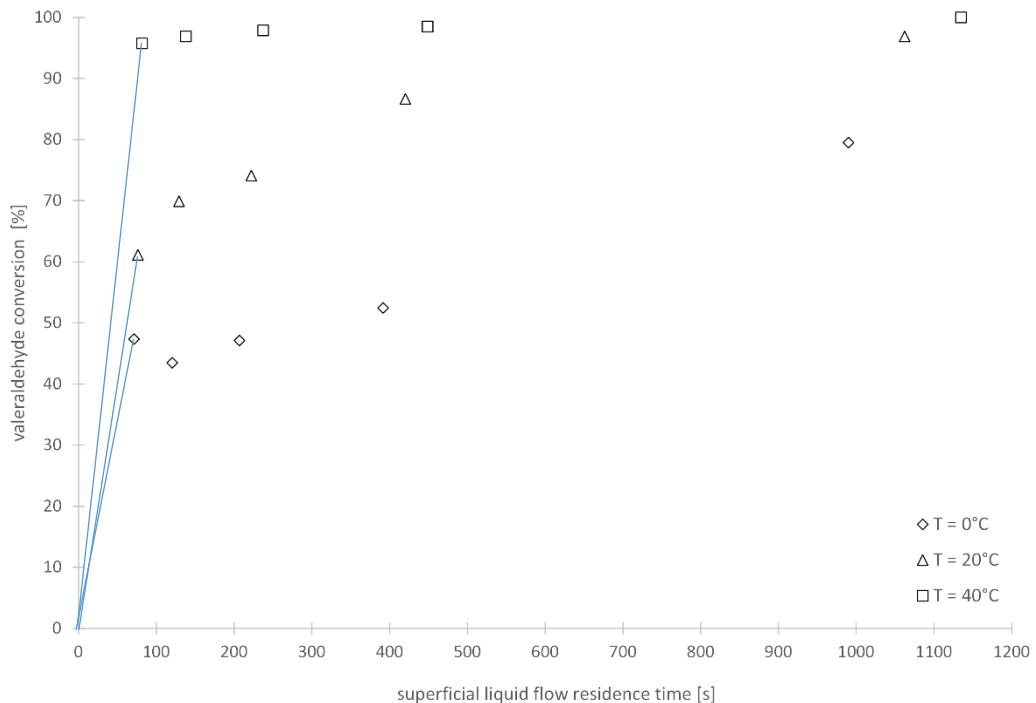
Calculation of Heat transfer time $\tau$	
$\tau = L^2 / (\alpha * Nu)$	Roberge, D. M.; Kockmann, N.; Scale-up concept for modular microstructured reactors based on mixing, heat transfer, and reactor safety, Chemical Engineering and Processing, Vol. 50 (2011), 1017-1026
$L =$	0,011 cm // capillary diameter
$Nu =$	3,66 - // laminar flow through capillary (assumption)
with	
$\alpha = k / (\rho * c_p)$	// thermal diffusivity
$k =$	134 W/(m * K) // thermal conductivity Natan, B.; Vargaftik, Lev. P.; Handbook of Thermal Conductivity of Liquids and Gases, CRC Press, Inc (1994), p. 172
$\rho =$	810 kg / m^3 // density Material Safety Data Sheet, Sigma Aldrich (12.03.2015)
$c_p =$	2020 J / (kg * K) // heat capacity Korkhov, A.D.; Dyakova, G.N.; Vasilev, I.A., Heat capacity of pivalaldehyde and valeraldehyde, (1983)
$\alpha =$	0,82 cm^2 / s
$\tau =$	<u>4,0317E-05</u> s

In both scenarios the heat transfer time is much faster than the reaction time. Therefore we can assume isothermal conditions.

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## S4 Calculation of the activation energy Ea.

The activation energy Ea is roughly calculated by using the initial reaction rate (primary slope in Figure 3). A zero order reaction rate was assumed.

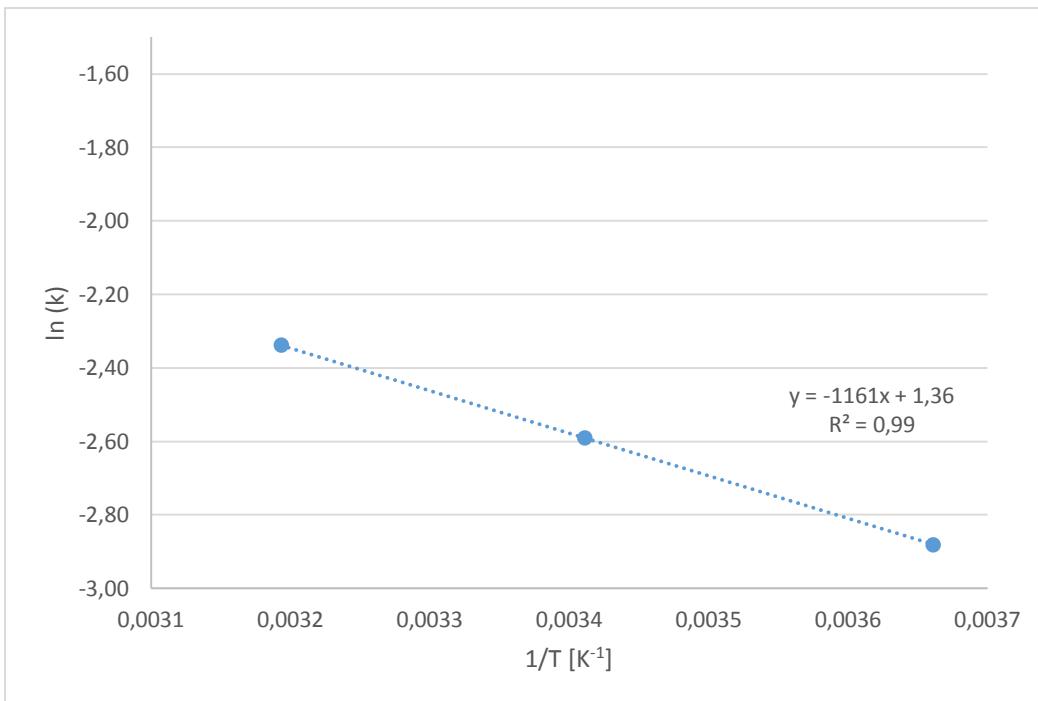


**Figure 3.** Valeraldehyde conversion for the catalyzed oxidation reaction with manganese(II) acetate and octanoic acid in a microreactor (one-A Engineering, Austria) at different reaction temperatures (0 °C, 20 °C, and 40 °C).

T [K]	c <sub>V<sub>A</sub></sub> t = 0 [mol/L]	c <sub>V<sub>A</sub></sub> t = 1 [mol/L]	Δ c	t <sub>1</sub> [s]	k [mol/ L *s]	LN (k)	1/T [K <sup>-1</sup> ]
273,15	4,7	0,7	4,0	71	0,06	-2,88	0,0037
293,15	6,8	1,1	5,7	76	0,08	-2,59	0,0034
313,15	8,0	0,2	7,8	81	0,10	-2,34	0,0032

c<sub>V<sub>A</sub></sub> t = 0 initial concentration of valeraldehyde

c<sub>V<sub>A</sub></sub> t = 1 valeraldehyde concentration at t<sub>1</sub>



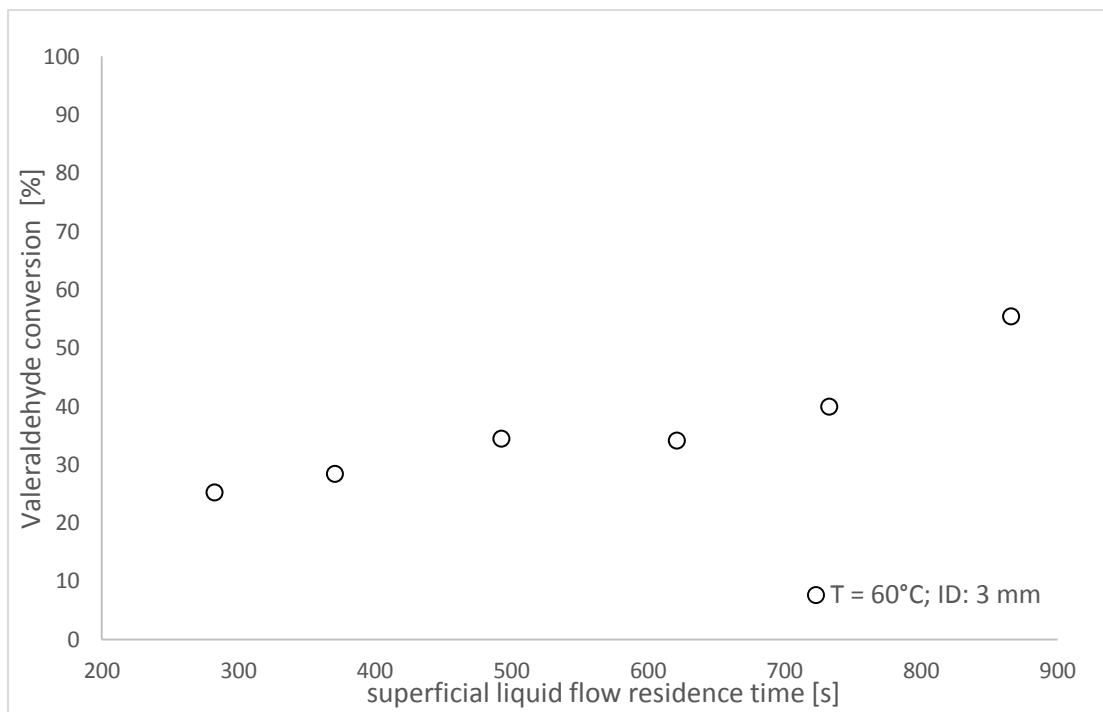
$$E_A = m * (-R)$$

$$E_A = -1161 \text{ K} * (-8,314 \text{ J / mol K})$$

$$E_A = 9652 \text{ J / mol} \approx \underline{9,5 \text{ kJ / mol}}$$

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## S5 Results of the scale-up experiment to 3 mm internal diameter capillary



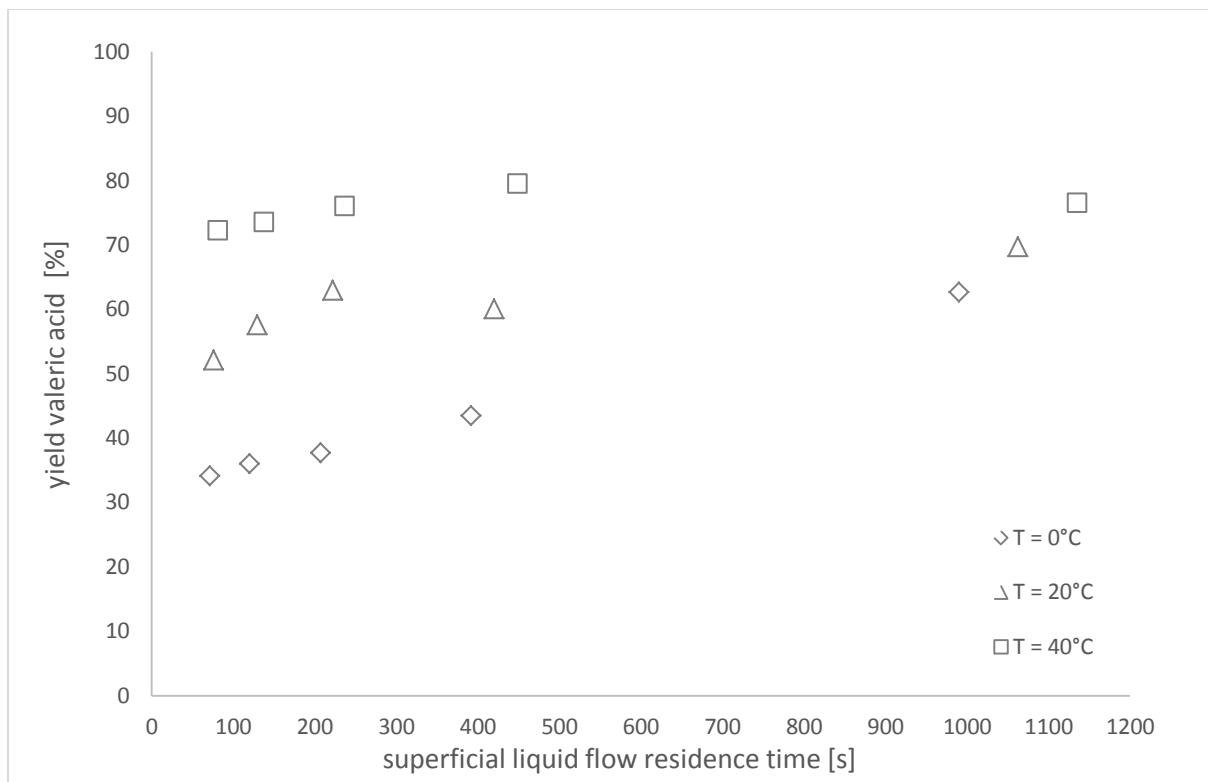
Valeraldehyde conversion for the catalyzed oxidation reaction with manganese(II) acetate in a microreactor (one-A Engineering, Austria) at 60°C.

#### Set-up parameters for the two-phase flow oxidation of valeraldehyde

parameter	range
reactor volume	5.30 mL (reaction volume)
microchannels	2 pre-heating; 1 reaction
internal diameter of the microchannels	3 mm
oxygen flow rate	200 mL min <sup>-1</sup>
valeraldehyde flow rate	0.29 – 1.01 mL min <sup>-1</sup>
molar valeraldehyde feed rate	0.0027– 0.0095 mol min <sup>-1</sup>
molar oxygen feed rate	0.0109 mol min <sup>-1</sup>
molar oxygen excess	3 – 0.15 equivalent (compared to valeraldehyde)
manganese(II) acetate catalyst	100 ppm (mol/mol relative to valeraldehyde)
temperature	60 °C
pressure	0.5 bar (reactor inlet)

The conversion can be accelerated by the addition of octanoic acid.

## S6 Corresponding yields of the experiments from Figure 3



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

The Yield was calculated from the start concentration of the aldehyde and end concentration of the valeric acid. Both concentrations are obtained by the calibrated GC-Method.