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Tubular reactor for liquid reactions with gas release

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Abstract

A design procedure for tubular reactors is developed for liquid-phase reactions with gas release in horizontal tubes of small diameters. It is based on a one-dimensional calculation approach, which assumes a stationary turbulent flow. For each stream-wise position on the tube axis, the model delivers the actual temperature, void fraction, chemical composition and slip of the mixture. The possible retardation of the gas release from the liquid proves to be a decisive factor. Approaches to handle this phenomenon are described. The calculation of the tubular flow reactive system requires the knowledge of the reaction macro kinetics. It can be determined separately in suitable small scale batch experiments as shown. Experiments with a homogeneous model reaction in a tubular pilot plant validate the theoretical method.

Keywords: Tubular reactor; Retardation; Reaction; Multiphase flow

1. Introduction

Profitable chemical reactions often require critical reaction conditions. In case of fast exothermic or endothermic reactions, large reaction volumes lead to difficulties in controlling the process variables pressure and temperature. Conducting the reaction in small volumes enables not only a proper control, but prevents also severe damages in case of inhomogeneities or instabilities. Thus, it is often advisable to prefer continuous processing to batch processing [1,2]. The two basic continuous reactor types are the continuous stirred-tank reactor and the tubular plug-flow reactor.

Tubular reactors are simple and easy to construct. Furthermore, a narrow residence time distribution can be achieved by turbulent flow conditions. In case of small tube diameters, the geometry allows operation at high pressures. The favorable ratio of surface to volume enhances heat transfer and thus simplifies the adjustment of a desired axial temperature profile. These advantages make the turbulently operated tubular reactor with small diameter the most recommendable continuous reactor type for critical reaction processes.

Tubular reactors are however disadvantageous for slow reactions, which require long reactor tubes, that cause high pressure drops. The same is true for highly viscous liquids. In this case uneconomic high pumping power can only be avoided, if solely the most critical phase of the reaction is conducted in the tubular reactor.

The design and calculation of tubular reactors can cause problems, because fluid mechanics, reaction kinetics and thermodynamics are coupled and difficult to describe mathematically especially in case of reactions with phase transitions. In practical use this means that a special reactor design is required for each application in order to achieve an optimal process [2–4].

The aim of this work is to develop a design method for homogeneous liquid-phase reactions with gas release in horizontal tubes with small diameters. This includes a one-dimensional calculation approach,

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which—assuming a stationary turbulent plug-flow—takes into account both the fluid dynamics and the reaction process. For each stream-wise position on the tube axis, the model delivers the actual temperature, void fraction, chemical composition and slip of the mixture. It is compared to experiments, carried out in a pilot facility, that allowed measurements also within the reaction zone.

2. Reactor dimensions

In order to be able to assume a turbulent plug-flow, it is necessary to dimension the reactor in a way that the axial dispersion of the reacting phase—here the liquid phase—can be neglected. For superficial liquid Reynolds numbers of $Re_L > 10{,}000$ Lali et al. [5] find independently of the flow pattern a constant axial dispersion, which is not higher than that of liquid single-phase flow at same Reynolds numbers.

For smaller Reynolds numbers $Re_L < 10{,}000$ the axial dispersion of two-phase flow can be significantly higher than the dispersion of single-phase flow.

The internal diameter d of the reactor tube has to be chosen small enough to remove almost instantaneously the heat released by an exothermic reaction, respectively, to supply the necessary heat for an endothermic reaction. This means that thermal stability must be guaranteed along the tube axis. Fluidmechanic design fundamentals, i.e. pressure drop calculation, critical flow, hold up, are summarized by Stahl [6].

3. Model reaction

The autocatalytic oxygen releasing reaction of potassium permanganate with hydrogen peroxide under acid conditions is chosen as model reaction:

$$5H_2O_2 + 2MnO_4^- + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

H_2SO_4 is used as acid. The reaction is homogeneous, all reactants are in aqueous solutions. It features a color change, as the degradation of the permanganate ions leads to a decolorization of the initially violet solution.

The knowledge of density ρ, viscosity η, specific heat capacity c_p and thermal conductivity λ and solubilities as a function of temperature and pressure of all reactants and products and their aqueous solutions is needed to describe the continuous reaction process thoroughly and predict the behavior within the tubular reactor.

An expression for the reaction macro kinetics is necessary in order to calculate tubular reactors. Simoyi et al. [7] found the reaction between the permanganate ions and hydrogen peroxide under acid conditions to occur in three stages: a fast initial, an induction period and a main autocatalytic step. While the first two steps take a few milliseconds, the main step can last several seconds.

In the literature, no complete reaction kinetics is given for all three steps. For the essential autocatalytic main step, the following rate law may be applied [8]:

$$\frac{dc_{MnO_4^-}}{dt} = kc^{a}_{MnO_4^-}(c_{MnO_4^-,0}+c_{Mn^{2+},0} - c_{MnO_4^-})^{r} \tag{1}$$

According to the measurements of Simoyi et al. the exponents can be approximated with $a = 1$ and $r = 1.5$.

In order to determine the dependency of k, measurements of the reaction time are conducted in a batch facility. The reaction times were measured optically by evaluation of videorecordings (50 pictures per second).

The trend of the obtained data corresponds to literature data at lower absolute concentrations [9]. The reaction time is found in the range between 0.8 and 10 s. An increase of temperature and initial surplus of sulfuric acid leads to higher reaction rates, while a higher surplus of hydrogen peroxide inhibits the autocatalytic reaction. Thus, varying the initial hydrogen peroxide concentration is an elegant means to adjust the reaction time to a desired value.

Eq. (2) directly gives the following relation between k and the reaction time t_R:

$$t_R = \frac{C}{k^{1.5}_{MnO_4^-}} \tag{2}$$

For a 99% degradation of the permanganate ions, the constant is $C \sim 12$. Thus, a correlation for the reaction kinetics is resulting with the measured reaction times t_R. It has to be kept in mind that this macro kinetics does not give any information about the reaction mechanism.

To transfer the obtained macro kinetics to the tubular reactor, it is necessary that both reactors have similar mixing times. The mixing time of the tubular reactor used is given in Section 4. The comparability of heat transfer in both reactors is ensured by the analogy of geometry, wall material (glass) and wall thickness, as well as the choice of the same heat carrier (water). A sufficiently high heat transfer within the heat carrier is assumed.

4. Experimental

A tubular reactor pilot plant was designed to conduct the experimental work. Its reactor tube has a length of 5 m (five modular elements, each 1 m long) and an internal diameter of 7 mm. Fig. 1 shows the experimental set-up schematically.

The maximum total volume flow is 12 l/min, what leads to a maximum entrance Reynolds number of $Re_{\mathrm{in}} = 30{,}000$ at ambient temperature. At mixture temperature of $T = 50\,^{\circ}\mathrm{C}$ this value increases to $Re_{\mathrm{in}} = 60{,}000$, due to the lower viscosity. Before entering the reactor, the three solutions pass a heat exchanger, which allows a stationary tempering at temperatures between $T = 15$ and $50\,^{\circ}\mathrm{C}$.

While the $KMnO_4$- and the H_2SO_4-solution, which do not react with each other, are premixed before the inlet, the H_2O_2-solution is added in a coaxial mixing nozzle at the reactor entrance. The tube jacket enables temperature control by heat exchange. The modular design offers the possibility to provide measuring points for temperature, pressure and void fraction in the couplings between the modules. Furthermore, elements as orifice plates can be inserted here, in order to disturb and homogenize the flow.

Experiments were conducted in a temperature range between $T = 15$ and $50\,^{\circ}\mathrm{C}$ and in a mass flow range between $M^*_{\mathrm{tot}} = 0.028$ and 0.112 kg/s. At ambient temperature these mass flows correspond to entrance Reynolds numbers of $5000 \le Re_{\mathrm{in}} \le 20{,}000$. The $KMnO_4$-massflow fraction $x^*_{\mathrm{KMnO_4}} = M^*_{\mathrm{KMnO_4}}/M^*_{\mathrm{tot}}$ was varied between $x^*_{\mathrm{KMnO_4}} = 0.39 \times 10^{-3}$ and 5.8×10^{-3}, that leads to volume flow fractions of the released oxygen at the reactor outlet (ambient pressure) of $0.1 \le \varepsilon^*_{\mathrm{G}} \le 0.7$. The volume flow fraction is defined as $\varepsilon^*_{\mathrm{G}} = V^*_{\mathrm{G}}/V^*_{\mathrm{tot}}$.

Pressure and temperature are measured at the reactor in- and outlet as well as within the reactor between the modules. The temperature is detected by NiCr–Ni-thermocouples, the pressure is transduced by ceramics diaphragm sensors (Type Endress + Hauser Cerabar). The void fraction is measured at the couplings, too. The chosen method is gamma-densitometry with an Iodine-125 gamma-source.

5. Calculation method

The basic requirements of a calculation method for tubular reactors are summarized in Section 1. In Fig. 2, a schematic flowsheet of the calculation procedure is shown. The one-dimensional calculations are carried out iteratively, basing on the method of finite differences. The following input data is needed: the

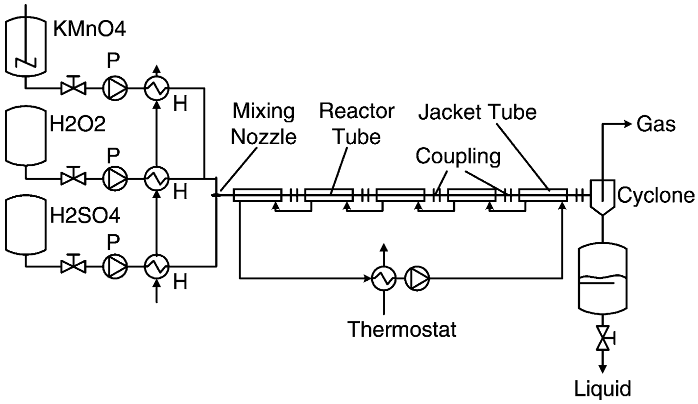

Fig. 1. Schematic representation of the test set-up. P: membrane pumps, H: heat exchanger.

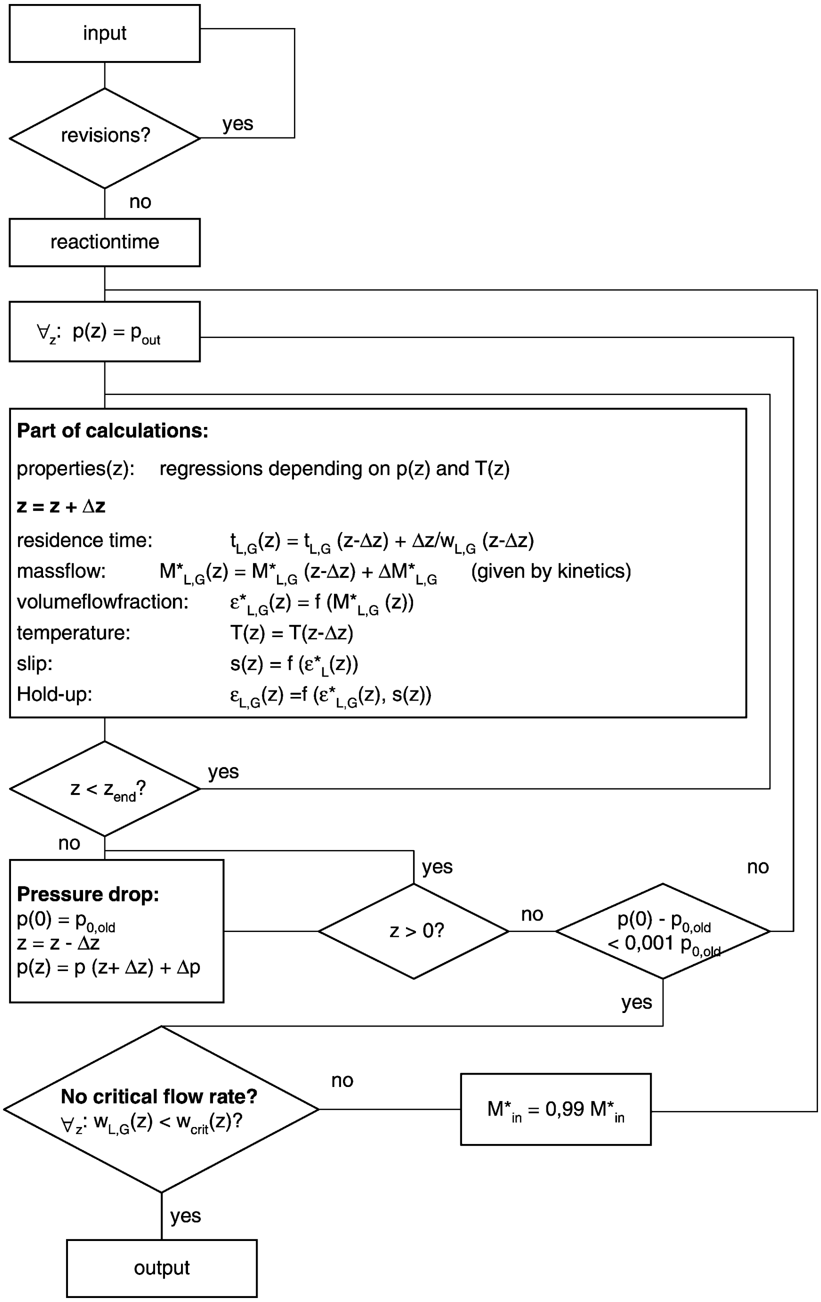

Fig. 2. Schematic flowsheet of the calculation procedure [10].

tube geometry (length, diameter, orifice plates), the entrance conditions (temperature, mass flow, concentrations) and the pressure at the reactor outlet. The program calculates for each stream-wise position the tube axis pressure, temperature, chemical composition, void fraction and the velocities of both phases. All other quantities can be derived from this. For further details see [6].

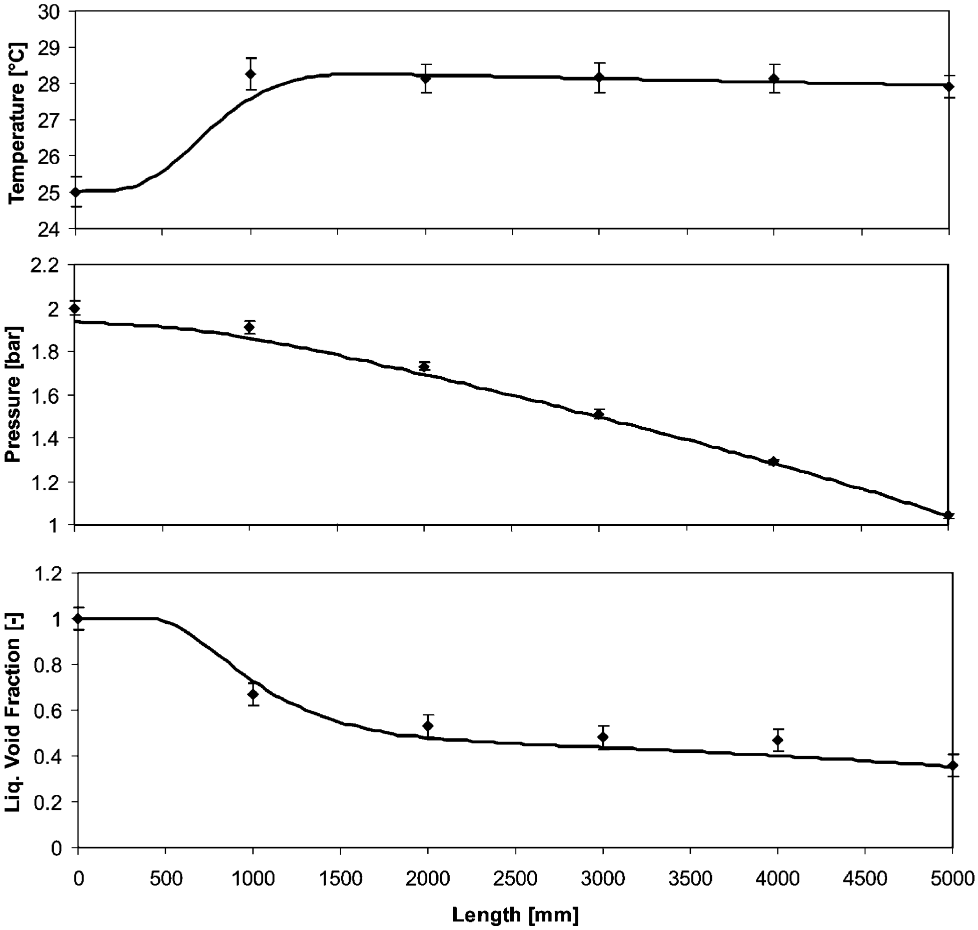

Fig. 3. Undisturbed tubular reactor flow: comparison of calculated and measured temperature, pressure and void fraction development. Mass flow: $M^* = 0.061\,\mathrm{kg/s}$, entrance Reynolds number $Re_{\mathrm{L,in}} = 12{,}400$, initial concentrations: 5.96 g $KMnO_4$/kg solution, 24.25 g H_2O_2/kg solution, 21.06 g H_2SO_4/kg solution, entrance temperature $T_{\mathrm{in}} = 25\,°\mathrm{C}$, jacket temperature $T_{\mathrm{jack}} = 26\,°\mathrm{C}$.

6. Comparison with experimental results

Fig. 3 shows in detail the comparison of the calculation with the experimental results for one example. The flow is not disturbed, that means no orifice plates are inserted into the reactor. The experiment is conducted at ambient temperature with an entrance Reynolds number of $Re_{\mathrm{L}} = 10{,}000$ ($M^*_{\mathrm{L,in}} = 0.062\,\mathrm{kg/s}$). The initial concentrations are listed in Fig. 3.

The essential quantities to compare are reaction time, temperature and pressure development, void fraction development and the mass flow of released oxygen. The following table shows the comparison. Since the gas mass flow is only measured at the reactor outlet, it is not included in Fig. 3.

	$\varepsilon_{\mathrm{L,out}}$	$M^*_{\mathrm{G,out}}$ (g/s)	p_{in} (bar)	T_{out} (°C)	t_{R} (s)
Theory	0.352	0.181	1.96	27.95	0.79 ± 0.05
Experiment	0.36 ± 0.04	0.17 ± 0.01	1.99 ± 0.03	27.91 ± 0.32	0.72 ± 0.04

Experiment and measurement show a good agreement, that is within the measurement accuracy.

All experiments with undisturbed flow agree well with the calculations for reaction time and temperature development. However, the void fraction development often displays a deviation between the measured and predicted values, that cannot be explained with the uncertainties in measurement. These deviations result from an erroneous estimation of the retardation of gas release. The equilibrium assumption, that all gas passes directly into the gaseous state when the liquid is saturated with solved gas, is not justified in most cases. Usually the system is in non-equilibrium after reaction, i.e. the mass of gas solved in the liquid exceeds the equilibrium solubility. The liquid is super-saturated and the release of the gas phase is retarded.

Deviations in the prediction of the void fraction always cause errors in the prediction of pressure drop, too.

The experiments concerning disturbed flow were carried out using an orifice plate in order to disturb the reacting flow. It is inserted in 2 m distance from the reactor inlet what is according to the reaction zone length, adjusted by the reaction time.

The flow disturbance proves to reduce the retardation of gas release. The experiments do not indicate that the orifice diameter necessary for an instantaneous gas release depends on the Reynolds number, whereas this diameter obviously depends on the amount of produced oxygen, as shown in the following table.

$KMnO_4$-concentration (g/kg solution)	0.39	1.20	2.65	5.8
$\varepsilon^*_{G,out}$	0.1	0.3	0.5	0.7
Orifice-ϕ (mm)	2	2	3	4

7. Conclusion and outlook

The design of gas–liquid tubular reactors requires significantly more effort than in the single-phase case. In this work tubular reactors for homogeneous liquid reactions with gas release were examined. A design procedure for turbulent flow conditions was elaborated and experimentally verified on the basis of a model reaction. This method includes criteria to determine the reactor dimensions, the measurement of a reaction macro kinetics and a program for reactor calculation. This program is based on experimentally verified suitable correlations to calculate the pressure drop, the slip, the temperature development and the critical flow phenomenon for small tube diameters. It does not need any adjustable parameters. Besides the reaction kinetics and the pressure drop correlations, the gas release proves to be an important parameter to describe the process. It does not depend on the reaction kinetics alone, as the gas can be released retarded from super-saturated reaction mixture. The retardation time can be influenced by flow perturbation.

Future work will focus on the formulation of a more basic and universal correlation in order to predict this retardation as a function of physical properties, flow conditions and perturbation. The examination of heterogeneous liquid–liquid reactions will be a further task, as this reaction type is industrially relevant. The oxidation of 2-octanol with nitric acid is an example for such a heterogeneous reaction with an undesired side reaction, since NO_x-gases are formed [10]. The prediction and measurement of the specific phase interface between the liquid phases will have high significance, because it governs the mass transfer and thus influences the reaction macro kinetics.

Acknowledgements

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