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Optimal Design of a Multifunctional Reactor for Catalytic Oxidation of Glucose with Fast Catalyst Deactivation

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1. Introduction

Oxidations of organic compounds in liquid phase by oxygen have been applied for years in many important industrial and waste water treatment processes. There are several variants of technical design of these processes – ranging from homogeneous through heterogeneous to biotechnological routes. As an example, the process of gluconic acid production by glucose oxidation can be arranged in all of these variants.

Bioprocesses are usually carried out in aqueous media at ambient temperature and atmospheric pressure in the presence of living microorganisms and their enzymatic apparatus (e.g. *Aspergillus niger*), or by using pure enzymes (glucose oxidase and catalase), (Sikula, et al. (2006), (2007)). In the former case, the biomass represents a solid phase in the reaction system, whereas in the latter case, the reaction system is homogeneous – liquid. Some drawbacks are also inherent with the bioprocesses – e.g. strong sensitivity of microorganisms to impurities present in the reaction system, losses of the substrate transformed to carbon dioxide or utilized for the microorganisms growth, low solubility of oxygen in the reaction system owing to the presence of ionic salts and nutrients (e.g. glucose) with a high rate of oxygen consumption by the microorganisms on the other hand, frequent occurrence of non-newtonian hydrodynamic properties of biomass suspension, foam formation, etc. For such bioprocesses, gas-lift reactors (known as air-lift reactors) (GLRs) are often used for their capability of delivering oxygen to the growing culture at a sufficient rate, while maintaining low shear stress.

Heterogeneous catalyst application to the oxidation process is advantageous compared to homogeneous catalytic systems with respect to simpler separation of a catalyst from the reaction mixture by filtration. At the heterogeneous variant however, a catalyst selection and its optimization is one of the crucial points to be considered. Another one is the reactor type selection and its design (estimation of the geometry and the size of the reactor selected). Neither the authors' experience, nor literature search provide many generalizations on selection of a reactor type for which a counter-example could not be thought up. An open

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mind and good ideas are probably more important here than any generalization. Furthermore, because of complexity in scale dependency of various reactor selection criteria, the authors incline to agree with the statement of Bisio & Kabel (1985) : „*You cannot design a reactor until you have selected its type, and you cannot know if your type selection was wise until you have designed it*”. Thus, the selection – design optimization is an iterative procedure, the “building blocks” of which may use dynamic models to various extents.

Heterogeneously catalyzed wet air oxidation of glucose (Glc) to gluconic acid (Glcac) in aqueous alkaline solution serves as a model reaction. Palladium on activated carbon commercial catalyst enables to run the reaction selectively at ambient conditions. On an industrial scale, biotechnological routes of Glcac production currently prevail over the catalytic one. This is mainly because of the Glcac broad utilization in the food industry. The other reason is a problem with activity of the catalysts used. Pt-group catalysts suffer from gradual reversible deactivation due to an action of oxygen during the reaction course.

One way to overcome the problem leads through the catalyst optimization. Recently, good activity, selectivity and long-term stability were reported for supported gold catalysts (Biella, et al. (2002), Comotti, et al. (2006), Thielecke, et al. (2007)).

Another approach to solve the problems with the catalyst activity deals with the process and/or reactor optimization. It is based on correct choice of a reactor type for a chemical process, the reactor well-suited design and on setting an appropriate mode of the reactor operation. These are the crucial aspects for maximizing the technological output.

The text is focused on solving the problem with the catalyst unstable activity through the reactor / reaction step optimization. Optimization of continuous stirred tank reactor (CSTR) and gas-lift reactor (GLR) productivity through the gas feed modulation is attempted. For any input operational conditions the task is to find conditions of the highest possible productivity of the reactors, i.e. to find conditions where the reaction and reactivation times are shared optimally, so that neither any time is wasted in prolonged activation process, nor is an insufficient activation time provided.

Beneficial effect of composition modulation on a CSTR performance is demonstrated. The catalyst activity can be maintained long-term steady by periodically alternating the gas feed composition. In the case of CSTR, period length and the period split represent independent variables. They both can be varied independently within one CSTR unit of a given construction. It is demonstrated here that for any period length always a split value exists, where the maximum reactor productivity is achieved. By connecting the points of optimal split for every period length, trajectory of the maximal CSTR productivity is obtained.

GLR was selected as the reactor type suitable to carry out the model reaction in. A GLR natural operation enables the catalyst to be periodically exposed to reaction and activation conditions, in the riser and downcomer sections of the GLR, respectively. Such reactors are in their nature multifunctional. In a GLR both, the period length and the split value are bound with geometry of the GLR given. Therefore only one geometrical optimum exists for given set of input operational conditions. The maximal GLR productivity is guaranteed only in this geometrical optimum, because the residence time in riser (reaction time) and the residence time in downcomer (activation time) are only here shared optimally.

1.1 The model reaction kinetics

Glucose (Glc) wet air oxidation over palladium on activated carbon catalyst is used as the model reaction. It takes place in three-phase medium. Advantage of the catalyst is its ability to catalyze the reaction selectively towards gluconic acid (Glcac) at mild conditions. Its

drawback is fast deactivation during the oxidation reaction, when oxygen forms surface oxides or penetrates from the topmost Pd layer to subsurface layer forming subsurface oxide (Simmons, et al. (1991), Lundgren, et al. (2002), Ketteler, et al. (2005)). These Pd-O phases are less active compared to chemisorbed oxygen (oxygen adsorbed above the first metallic layer), and will be referred to as those responsible for change in the catalyst activity. This deactivation was proved reversible (Vleeming, et al. (1997)).

Activation and reactivation of the catalyst is based on reduction of the catalyst active sites. Glucose is good reduction agent to pre-reduce the catalyst. Existence of optimal activation times depending on the reaction mixture composition was observed (see Gogová & Hanika (2009,a) for details).

Equations (1) and (2) form the kinetic model of the model reaction (Gogová & Hanika (2009,b)). They describe mathematically processes of the main surface reaction, the catalyst deactivation and the catalyst reactivation. Change in the catalyst activity is described through a change in fractional coverage by inactive oxygen species, θ_{so} .

$$\dot{\xi}_w = \frac{k_w c_{Glc} \sqrt{c_O} (1 - \theta_{so})^2}{(1 + K_{Glc} c_{Glc} + K_{Glac} c_{Glac})(1 + K_O \sqrt{c_O})^2}$$

(1)

$$\frac{d\theta_{so}}{dt} = \rho_c W^L (\dot{\xi}_D - \dot{\xi}_A) = \rho_c W^L \left(\frac{k_D \sqrt{c_O} (1 - \theta_{so})^2}{(1 + K_O \sqrt{c_O})} - \frac{k_A \theta_{so} (1 - \theta_{so})}{(1 + K_O \sqrt{c_O})} \right)$$

(2)

This kinetic model applies all the time except when oxygen concentration in the liquid phase approaches zero. Then the reaction and reactivation mechanism changes: inactive oxygen species (responsible for the catalyst deactivation) take over the function of the chemisorbed oxygen in the main surface reaction. When the mechanism changes, its mathematical description also changes, and equations (3) and (4) apply as the kinetics model instead of equations (1) and (2).

$$\dot{\xi}_w = k_w^+ c_{Glc} \theta_{so} (1 - \theta_{so})$$

(3)

$$\frac{d\theta_{so}}{dt} = \rho_c W^L (\dot{\xi}_D - \dot{\xi}_A) = \rho_c W^L k_A \theta_{so} (1 - \theta_{so})$$

(4)

Expressions of the lumped rate and adsorption constants of equations (1) - (4) are listed in Table 1.

Rate and adsorption constant	Dimension	Value
k_w	$[m^{4.5}kg^{-1}mol^{-0.5}s^{-1}]$	0.00313
K_{Glc}	$[m^3mol^{-1}]$	0.0169
K_O	$[m^{1.5}mol^{-0.5}]$	4.50
K_{Glac}	$[m^3mol^{-1}]$	0.384
k_D	$[m^{1.5}mol^{-0.5}kg^{-1}s^{-1}]$	0.00612
k_A	$[kg^{-1}s^{-1}]$	0.00518
k_w^+	$[m^3kg^{-1}s^{-1}]$	$5.47 \cdot 10^{-5}$

Table 1. Parameters of equations (1) - (4), (Gogová & Hanika (2009,b)).

In the kinetic model (equations (1) and (2) or alternatively (3) and (4)), the change in the catalyst activity is expressed through the change in the fractional coverage by inactive oxygen species, θ_{so} . Relation between θ_{so} and the activity is explained below.

Relative activity of the catalyst at time t is defined as the ratio of the reaction rate at time t and reaction rate on a fresh catalyst at the same concentrations and temperature:

$$a(t) = \frac{\dot{\xi}_w(t)}{\dot{\xi}_w^0} \quad [T, \bar{c}] = \text{const.} \quad (5)$$

Thus the relative activity is useful parameter that characterizes changes in the reaction rate as the catalyst deactivates, and it is obtained conveniently from the experimental results. The equation (5) applies to all deactivation processes, no matter if the rate equation is separable or not according to the concept of separability (Szépe & Levenspiel (1970), Butt & Petersen (1988)).

A rate equation is separable if it can be expressed as a product of two terms – the reaction rate on the fresh catalyst and the catalyst activity in the following form:

$$\dot{\xi}_w = \dot{\xi}_w^0(\bar{c})a(\alpha) \quad [T] = \text{const.} \quad (6)$$

Active fraction α is defined as the ratio of the number of active sites per unit mass of the catalyst and the number of all sites, i.e. it gives for this case the following:

$$\alpha = (1 - \theta_{so}) \quad (7)$$

The rate equation (1) is separable. Combination of the equations (1), (6) and (7) gives the following relation between the catalyst activity and the active fraction:

$$a = (1 - \theta_{so})^2 = \alpha^2 \quad (8)$$

Thus the activity depends only on the amount of inactive oxygen species.

1.2 Reversible deactivation of the Pd/C catalyst

Figure 1 provides an insight into the findings made during the model reaction kinetics study. Several regions can be recognized there. Before each experiment in semi-continuous stirred tank reactor (SSTR), the catalyst was activated in the reactor by its reduction with Glc as a component of the reaction mixture in inert atmosphere. The reaction was started up replacing nitrogen flow by flow of nitrogen/oxygen mixture with the desired partial pressure of oxygen. Each experiment consisted of one or more consecutive oxidation runs. Between these oxidation runs the catalyst was reactivated in inert atmosphere with Glc.

The reaction rate at the beginning of the second reaction cycle in SSTR (full circles in Figure 1) is lower because of change in the reaction mixture composition during the first reaction cycle in the batch system (SSTR). To prove full reversibility of the Pd/C catalyst deactivation, the primary experimental data in Figure 1 were corrected for the reaction mixture composition change (empty circles in Figure 1). To serve this purpose, the Glc and Glc_{ac} concentrations at the reaction start-up were applied in the kinetic model (equations (1) and (2) with parameters of Table 1).

Figure 1 indicates possibility of improving the reactor performance by periodically exchanging the reaction and reactivation cycles. In the text below, this approach is analyzed

in process of selection and optimization of a target reactor suitable to carry out the model reaction in.

Fig. 1. Transient reaction rate and extent of the catalyst deactivation (represented by θ_{so}) during Glc oxidation in SSTR (reprinted from Gogová & Hanika (2009,b)). Primary experimental data (●); data recalculated for concentrations at the reaction start-up (○); lines – the SSTR experimental data predicted by the kinetics model. Conditions: SSTR; $c_{0,Glc} = 100.6 \text{ mol/m}^3$; $c_{0,Glcac} = 0 \text{ mol/m}^3$; $\rho_c = 1 \text{ kg/m}^3$; $D_p = 45 \text{ }\mu\text{m}$; $p_{O_2} = 0.1 \text{ MPa}$; $\omega = 600 \text{ min}^{-1}$; $T = 303 \text{ K}$; $pH = 8.1$; kinetic regime (i.e. negligible effect of internal and external diffusion).

1.3 Strategy for elimination of the catalyst deactivation

The advantage of the Pd/C catalyst is its ability to catalyze the model reaction efficiently at mild conditions maintaining high selectivity towards Glcac. Its drawback is fast deactivation during the oxidation reaction. In one hour the catalyst activity can drop to less than 40% of its original value depending on the reaction conditions. Although reversible, the deactivation rate presents a crucial problem for industrial implementation of the process.

This text is devoted to one of many strategies aimed to eliminate the problems with unstable activity of the catalyst. It leads through the process and/or reactor optimization. This approach deals with correct choice of a reactor type for a chemical process, the reactor well-suited design and with setting an appropriate mode of its operation. These are the crucial aspects for maximizing the technological output.

For process similar to the model one, Markusse, et al. (2001) found that the catalyst activity can be maintained steady by periodically switching between oxygen and nitrogen flow to a CSTR. In general, the term “periodic operation” refers to operation regimes in which one or more reactor parameters vary in time. Modulation of mostly composition and/or feed flow rate was researched by e.g.: Boelhouwer, et al. (2002), Silveston & Hanika (2002), Tukač, et al. (2003), Silveston & Hanika (2004), Liu, et al. (2008) etc., with the aim to improve chemical reactors performance through forcing the reactor to operate under transient rather than steady-state conditions. Silveston (1998) in his monograph pays attention to several catalytic processes operated in this way.

For the reaction of Glc oxidation by air over reversibly deactivating Pd catalyst, it was indicated in Figure 1 that CSTR productivity can be enhanced by the gas feed flow modulation. Beneficial effects of composition modulation on a CSTR performance were studied in Gogová & Hanika (2009,b) with the model reaction. The task was to share optimally the reaction and reactivation times within given period length, so that neither any time is wasted in prolonged activation process, nor an insufficient activation time is provided.

2. Dynamic operation of CSTR with feed periodic modulation

Possibility of improving the reactor performance by exchanging the reaction and reactivation cycles is indicated in Figure 1. For deeper insight into the model system behaviour under periodic mode of operation, the kinetic model (equations (1) and (2); or (3) and (4)) was implemented in mathematical model of a CSTR (equations 9-12) operating at constant Glc and Glcac concentrations in time and with varying volumetric flow rate of the liquid feed stream according to the value of immediate reaction rate, $\dot{\xi}_w$.

$$\dot{V}_f^L = \frac{W^L \rho_c \nu_{Glc} \dot{\xi}_w}{c_{Glc,f} X_{Glc}} \quad (9)$$

$$\frac{dc_O}{dt} = \frac{\dot{V}_f^L (c_{O,f}^L - c_O^L)}{W^L} + k_L a (c_O^* - c_O^L) + \nu_O \rho_c \dot{\xi}_w \quad (10)$$

$$\frac{d\theta_{so}}{dt} = \rho_c W^L (\dot{\xi}_D - \dot{\xi}_A) \quad (11)$$

with initial conditions:

$$t = 0: \quad c_O^L = c_{O,0}^L \quad \theta_{so} = \theta_{so,0} \quad \dot{V}_f^L = \dot{V}_f^{L,0} \quad (12)$$

where c_{Glc} and c_{Glcac} are constant, and the expressions for $\dot{\xi}_w$, $\dot{\xi}_D$ and $\dot{\xi}_A$ are defined in equations (1) or (3) and (2) or (4), respectively. Inlet and outlet liquid volumetric flow rates are assumed to be equal, i.e. the liquid density is independent on the conversion degree. Inlet and outlet concentrations of oxygen in the CSTR gas streams are assumed identical. Therefore the above CSTR mathematical model consists of liquid phase material balances only.

The value of $k_L a$ was set constant and far enough from a region where G-L external diffusion affects the overall reaction rate (see Gogová & Hanika (2009,a) for details).

Oxygen saturation concentration in the liquid phase, c_O^* , was calculated according to data of Eya, et al. (1994) on oxygen solubility in Glc aqueous solutions, by using the following regression equation:

$$c_O^* = p_{O_2} (1.162 \cdot 10^{-5} - 2.380 \cdot 10^{-8} (c_{Glc} + c_{Glcac})^{0.69}) \quad (13)$$

The kinetics model (equations (1) and (2) or alternatively (3) and (4)) embedded in model of CSTR enables to separate the effect of the reagents concentrations from the effect of the

change in the catalyst activity itself on deviation of the reaction rate in time. The CSTR model makes it possible to express the catalyst activity directly through the ratio of the immediate to the initial reaction rate (i.e. by using equation (5)), and reveals directly the progress in the extent of the catalyst deactivation, see Figure 3. Figure 2 illustrates the effect of varying oxygen partial pressure in the gas feed stream on performance of the CSTR operated under O₂/N₂ periodic mode.

Fig. 2. Simulations of four reaction / reactivation cycles in CSTR operating in periodic O₂/N₂ mode for various oxygen molar fractions in the gas feed stream. Time course of a) immediate rate of Glcac formation, b) the catalyst fractional coverage by inactive oxygen species (reprinted from Gogová & Hanika (2009,b)). Conditions: $t_R = 3600\text{s}$; $t_A = 1800\text{s}$; $\rho_c = 1\text{kg/m}^3$; $W_R = 860\text{ cm}^3$; $c_{Glc} = \text{const.}$; $X_{Glc} = 2\%$; $c_{Glc,f} = 100\text{ mol/m}^3$; $c_{Glcac,f} = 0$.

Fig. 3. Time course of the catalyst activity, expressed through ratio of the immediate to the initial rate of Glcac formation in CSTR as a function of a) oxygen molar fraction in the gas feed stream, b) Glc concentration in the reaction mixture (reprinted from Gogová & Hanika (2009,b)). The case „a)” corresponds to the conditions of the second reaction cycle of Fig. 2. Figure 2a shows the rate of Glcac formation in time and Figure 2b reveals the progress in the catalyst fractional coverage by the inactive oxygen species, which stand behind the catalyst

deactivation. It can be seen that in addition to the observed inhibition effect of oxygen on the Glc oxidation rate (Vleeming, et al. (1997), Gogová & Hanika (2009,a), (2009,b)), also the rate and the extent of the catalyst deactivation are influenced by oxygen concentration in the liquid phase. With its raise, both the θ_{so} steady-state value as well as the transient one increase (Figure 2b), and the catalyst's transient and steady-state activity decreases (Figure 3). Less important is the effect of Glc concentration in the reaction mixture on the catalyst deactivation extent (Gogová & Hanika (2009,b)).

2.1 Optimization of the CSTR under forced periodic operation

The CSTR operation was optimized in the conditions outlined above with equations (9) – (12), i.e. at constant Glc and Glcac concentrations in time and varying volumetric flow rate of the liquid feed stream according to the immediate reaction rate. The reactor is now operated under on-off periodic mode, i.e. with alternating cycles of switching on and off air feed stream. The catalyst reactivation in this case takes over in the oxygen-free intervals.

The period length is defined as a sum of reaction and reactivation times:

$$P = t_R + t_A \quad (14)$$

The split of period is the time the reaction takes in relation to the entire period length:

$$S = t_R / (t_R + t_A) \quad (15)$$

The reactor productivity is represented by cycle-time-averaged reaction rate, $\bar{\xi}_w$, which is a reaction rate averaged over the entire period length:

$$\bar{\xi}_w = \frac{1}{P} \int_{t_0}^{t_0+P} \dot{\xi}_w(t) dt \quad (16)$$

In case of CSTR, period length and the period split value represent independent variables. They both can be varied independently within one CSTR unit of a given (and constant) construction. Beneficial effect of the gas feed modulation on the CSTR performance is showed in Figure 4.

The catalyst activity can be maintained long-term steady by periodically alternating the reaction and activation periods of the catalyst operation. As can be seen in Figure 4, for any period length always a split value exists, where the maximal reaction rate is achieved. The CSTR optimization task was to find conditions that guarantee the highest reactor productivity at any period given. In other words, the optimal reaction-reativation time-share had to be found within any given period length. The maximal CSTR productivity is only guaranteed in the split optimum, where no time is wasted in prolonged activation process, neither an insufficient activation time is provided. Figure 4 maps the CSTR performance for selected input conditions. By connecting the points of optimal split for every period length, trajectory of the maximal CSTR productivity is obtained. For illustration, the trajectory is highlighted in Figure 4.

In the direction of decreasing the values of P and S in Figure 4, the system approaches operation of such a hypothetical CSTR that runs without the periodic on-off mode, but with lower content of oxygen in gas feed stream (compared to oxygen content in the on-mode of the original system). In the opposite direction the system approaches operation of such CSTR that runs without reactivation of the catalyst and the cycle-time-averaged reaction rate

Fig. 4. Simulation of the model reaction run in CSTR operated under on-off periodic mode; cycle-time-averaged reaction rate as a function of period length and split value with trajectory of the CSTR maximal productivity (dots). (The model solution is only approximate in $P \rightarrow 0$, see the text below). (reprinted from Gogová & Hanika (2009,b)).

Conditions: $\rho_c = 1 \text{ kg/m}^3$; $W_R = 860 \text{ cm}^3$; $Y_{O,f} = 0.21$; $c_{Glcac,f} = 0$; $X_{Glc} = 2\%$; $c_{Glc,f} = 100 \text{ mol/m}^3$.

approaches value of steady-state reaction rate of such system. It should be noted that the model solution in Figure 4 ought to be taken as an approximation in the region near $P=0$. A relation between the gas flow rate to the reactor and the gas holdup in it becomes important in this region. The model doesn't take it into account (see the model assumptions at the beginning of Section 2).

3. Multifunctional gas-lift reactor (GLR) employment

3.1 Characteristics of gas-lift reactors

What makes gas-lift reactors attractive for chemical and biotechnological applications is their relatively simple construction with possible segregation into various reaction zones, low and homogeneously distributed shear forces, good (and cheap) mixing with elimination of backmixing, and whole lots of possible design modifications.

Gas-lift reactor (GLR) consists of four main sections (see Figure 5): riser, gas-liquid separator, downcomer and bottom of the reactor. Operation of the GLR is relatively simple. It is based on spontaneous circulation of the reaction mixture along these four sections of the reactor as a result of difference in apparent density of the media present in riser and downcomer of the GLR. Successful application of these reactors to a specific (bio)chemical process is closely related with proper design of the reactor and on optimization of the mode of its operation.

However, in a GLR of a given construction (geometry), superficial gas velocity is the only independent variable that affects the entire hydrodynamics within the reactor - see the scheme in Figure 5, which documents the complexity of phenomena that occur in a GLR. Understanding of such hydrodynamic phenomena as gas hold-up, flow regimes or circulation velocity leads to more insight into the resulting mixing, heat and mass transfer.

Gas hold-up is the volumetric fraction of gas in the gas-liquid (G-L) or the gas-liquid-solid (G-L-S) dispersion. This phenomenon indicates a potential for mass transfer (higher gas hold-up = larger interfacial area) and the difference in gas hold-up between the riser and the downcomer is the driving force for liquid circulation. The **liquid velocity**, in turn, determines the residence times of the liquid in various zones of the reactor and controls important reactor parameters such as gas-liquid mass transfer, heat transfer, mixing and turbulence. For biochemical applications, oxygen mass transfer is one of the most important design parameters. Any shortage of oxygen significantly affects the process performance. Ideally, a reactor should have a maximum transfer rate, with efficient mixing, at minimum energy input.

When a GLR is employed for Glc production with living cultures, then quite contrary to the catalytic route, oxygen has to be present in riser, as well as in downcomer, to ensure living conditions all over the GLR circulation loop. But since the difference in the gas hold-up in riser and that in downcomer ($\varepsilon_{GR} - \varepsilon_{GD}$) represents the liquid circulation driving force, this requirement is only satisfied at the expense of decreased circulation velocity. Thus, an optimal ε_{GD} should be assured in the bioprocess by correctly designed separator of the reactor (Blažej, et al. (2004)).

The geometric design of GLR (scale of reactor, separator design, slighness of the reactor, ratio of cross-sectional areas of the downcomer and the riser etc.), the superficial gas velocity, pressure drop (friction) along the flow path and physical properties of the liquid phase have a strong influence on both the gas hold-up and the liquid velocity.

Fig. 5. Interrelated processes in a GLR (adopted from Blažej (2004)).

In a gas-lift (air-lift) reactor the hydrodynamics, transport and mixing properties, gas hold-up, interfacial areas and interphase mass transfer coefficients depend strongly on the prevailing flow regime. Following regimes occur in direction of increasing flow rate and can be deduced from both visual observation and gas hold-up:

Bubble flow (homogeneous flow regime): Small, spherical and equally sized gas bubbles that are distributed more or less uniformly over the column's cross section characterize this flow regime.

Churn turbulent (heterogeneous flow regime): Bubbles of widely varying size and shape can be observed as well as bubble coalescence and break-up.

Slug flow regime: With Newtonian media, this regime can be observed only at high superficial gas velocities and in airlift reactors with small riser diameter. Practical importance of slug regime is low. But if the liquid phase changes its physico-chemical properties during the process in such a way that the initially Newtonian behaviour changes into non-Newtonian (as a result of the biomass growth), then churn flow may transform into slug flow (see Godó, et al. (1999)).

3.2 Natural periodic operation of GLR

Gas-lift reactor (GLR) was selected as the reactor type suitable to carry out the model reaction in. GLR natural operation resembles the above mentioned forced periodic operation of the CSTR as follows: In GLR, the model reaction, as well as the catalyst reactivation proceeds within one multifunctional reactor unit. In principle, GLR operation is based on spontaneous circulation of the catalyst dispersion in liquid, which results from difference in apparent density of the reaction mixture present in riser and downcomer sections of the reactor. Therefore, if complete separation of the gas phase is ensured after the reaction media passes the riser where the main reaction (and the catalyst deactivation) takes part, the downcomer serves as reactivation zone of the reactor.

Fig. 6. Sketch of tanks-in-series model (right) linking hydrodynamics with kinetics that occur in the individual sections of continuously operating three-phase gas-lift reactor (left).

Kluytmans, et al. (2003) proposed application of GLR for reaction similar to the model one. To design the target three-phase GLR that would suit the reaction of Glc oxidation over the Pd/C catalyst, we constructed GLR mathematical model (see Gogová & Hanika (2009,c))

that is presented and applied in the following text. For any input operational conditions maximal productivity of the reactor is only guaranteed in the point of the target GLR optimal geometry. The GLR model proposed employs tanks-in-series mixing model sketched in Figure 6 to combine hydrodynamics of a real GLR (Bello, et al. (1984), Blažej, et al. (2004), Blažej, et al. (2004), Juraščík, et al. (2006), Sikula, et al. (2007), Sikula (2008), Sikula & Markoš (2008)) and the kinetics of the model reaction from Section 1.1. This GLR model is much simpler and a bit more realistic than that of Kluytmans, et al. (2003) who employed axial dispersion mixing model with hydrodynamics measured in small-scale 2D bubble-column reactor and considered intra-particle diffusion.

3.3 Modelling and optimization of the GLR productivity

Optimization of GLR productivity is attempted in the following couple of sections. In the case of GLR it is impossible to move along a trajectory of maximal productivity as was the case with the CSTR of Section 2.1, without reconstruction of the GLR itself, as both, the period length and the split value, are bound with geometry of the GLR given. Since both, the reaction and the reactivation times in GLR are set by the reaction mixture residence times in riser and downcomer of the GLR, respectively, only one geometrical optimum exists for given set of input conditions. The maximal GLR productivity is guaranteed only in this geometrical optimum. The optimization task in this case therefore is to find these geometrical optima for any set of input conditions.

GLR mathematical model was derived and applied to aid the target reactor design. The GLR model consists of two main parts (Figure 7). In the first one (hydrodynamics cycle), hydrodynamics and optimal geometry of the reactor is iteratively calculated. The second part (reactor performance cycle) uses the results of the first part, links them up with the model reaction kinetics and iteratively calculates the actual GLR steady-state performance.

Tanks-in-series model (as sketched in Figure 6) is employed in the second part of the GLR mathematical model to grasp the way of mixing in real GLR. Every tank of the tanks-in-series model is described by a set of nonlinear algebraic equations (NAE) linking hydrodynamics and kinetics that apply in the given section of GLR. Tanks-in-series and axial dispersion models are the most frequently used mixing models for GLRs. Both were applied recently for simulation of the biotechnological equivalent of the model reaction run in GLR (Znad, et al. (2004), Sikula, et al. (2006), (2007), Sikula & Markoš (2008)).

The following set of assumptions applies with the derived GLR mathematical model:

1. The GLR operates in steady state in the region of homogeneous bubbly flow.
2. The downcomer gas hold-up is zero; this is achievable by correct design of separator (Gogová, et al. (2002)).
3. The number of tanks that form riser and downcomer corresponds to the extent of axial dispersion in these sections. Plus, there are two tanks for each – the bottom and the separator. In the latter two tandems, the sizes of the individual twin tanks vary depending on the respective volumes taken up by either liquid (then they become a functional part of downcomer) or G-L dispersion (and then act as a part of riser).
4. Each of the tanks in series operates isothermally and is perfectly mixed.
5. The mathematical model combines description of the GLR hydrodynamics with the kinetics of the glucose oxidation reaction and the catalyst deactivation and reactivation.
6. The reactor operates at low Glc conversion, up to 10%. Then, according to Kunz & Recker (1995) assumption of 100% selectivity towards Glcac can be taken.

7. The Pd/C catalyst particles (45 μm) are assumed to be homogeneously dispersed in liquid phase. Then it is justifiable, for the mathematical description purpose, to accept a concept of pseudo-homogeneous reaction phase. However, apart from the liquid phase, the catalyst does not leave the reactor.
8. Constant liquid volumetric flow rate within the reactor sections is assumed, i.e. the liquid density is constant – independent on the conversion degree.

3.3.1 Algorithm for the GLR mathematical model solution

The GLR model is used to firstly aid the target GLR design for any given input conditions, and secondly, to predict steady state characteristics of the target reactor. The simulations presented were run by using commercial software Matlab.

Algorithm of the GLR mathematical model is sketched in Figure 7. The GLR model input adjustable parameters are: degree of Glc conversion, all the feed (and start-up) concentrations, the catalyst concentration, kinetics parameters, temperature (fixed, 30°C), atmospheric pressure (fixed), superficial gas velocity, number of tanks and basic geometrical parameters. The basic geometrical parameters (the reactor type – internal-loop gas-lift reactor (ILGLR), the GLR volume, its separator volume, its bottom height, the liquid height, the outer column diameter and the riser wall thickness) were adopted from experimental GLR, volume 40L (see Blažej, et al. (2004), Blažej, et al. (2004), Juraščík, et al. (2006), Sikula, et al. (2007), Sikula (2008), Sikula & Markoš (2008)). This particular reactor has been a source of many hydrodynamic correlations employed in the GLR model. Non-adjustable parameters have complex dependencies on the input adjustable ones. The procedure pictured in Figure 7 is applied to calculate them. See Gogová & Hanika (2009,c) for more details on the GLR mathematical model.

The one-tank model is an integral part of the GLR mathematical model (see Figure 7). It uses concept of one CSTR, which for the period of t_R operates as reactor (and the gas phase is being introduced to it) and for duration of t_A works as activator (with no gas introduced). In both of these cases, the liquid phase is being continuously introduced and discharged at a constant, cycle-time-averaged volumetric flow rate. (In this parameter the CSTR of the one-tank model differs from the CSTR optimized in Section 2).

The one-tank model serves to estimate a first approximation of the optimal split value (defined in Eq.(15)) for the target gas-lift reactor. At the optimal split, the target GLR productivity reaches its maximum (given by the cycle-time-averaged reaction rate). The S_{opt} value found by the one-tank model is only optimal for CSTR of the one-tank model (i.e. for conditions of ideal mixing), and therefore it is necessary to correct it for conditions given by hydrodynamics of the target reactor. The split correction takes the following aspects into account. In the GLR model, mixing in the target GLR was described by dividing riser into 7 + 2 tanks (one tank of bottom(R) and one tank of separator(R)) and downcomer into at least 7 + 2 tanks (one tank of bottom(D) and one tank of separator(D)). These values are based on experimentally determined local and overall Peclet numbers (Sikula (2008), Sikula & Markoš (2008)). Depending on the actual GLR geometry and hydrodynamics, the portion separator contributes to either riser or downcomer varies. One-tank model doesn't count with this variation, which therefore has to be included in the split correction, too. Different mixing in CSTR and GLR is closely related with different distribution of the reaction mixture components between reactor and activator modes of the one-tank model and that of tanks-in-series model. The split value is therefore corrected for formation of concentration profiles along the GLR, as well.

Fig. 7. Algorithm of GLR model for calculation of design and performance of the target GLR suited for the model reaction accompanied with the catalyst reversible deactivation. (reprinted from Gogová & Hanika (2009,c))

3.4 Optimal design of the target GLR

To optimize GLR productivity, optimal residence times in the riser and downcomer sections have to be found. Optimal value of split, S_{opt} , guarantees the GLR maximal productivity (represented by cycle-time-averaged reaction rate). By shifting the split value, the reaction-reactivation time-share changes, and so does the geometry parameter (downcomer-to-riser cross sectional area ratio, A_D/A_R) of the target GLR. This dependency is demonstrated in Table 3. The GLR productivity reaches maximum in conditions of its optimal geometry. It is the case "b" in Tab. 3 with the optimal split value. Increase in the S_{opt} of 20% triggers shift of A_D/A_R in such a way, that the reaction gets favoured at the expense of the catalyst activation. The cycle-time-averaged catalyst fractional coverage by inactive oxygen, $\bar{\theta}_{so}$, then settles on higher values (see Tab. 3, case c). Change in $\bar{\theta}_{so}$ indicates change in the catalyst activity. The higher the $\bar{\theta}_{so}$ is, the more the catalyst's activity drops (see Section 1.1). If the opposite trend is attempted, i.e. if the optimal split is 20% reduced, the activation gets favoured. But even though the catalyst is more active for the reaction (see the lower value of the cycle-time-averaged catalyst fractional coverage by inactive oxygen in Tab. 3, case a), the reaction time portion is not long enough to cover the overall time loss spent by the catalyst activation and the reactor productivity drops down again.

Case	$\bar{\xi}_w$ [mol/kg/s]	$\bar{\theta}_{so}$ [-]	A_D/A_R [-]	D_R [m]	$D_{D,Eqv.}$ [m]
a) $0.8 \times S_{opt}$	0.00286	0.0658	1.6989	0.0909	0.1184
b) S_{opt}	0.00349	0.1332	0.8588	0.1084	0.1005
c) $1.2 \times S_{opt}$	0.00287	0.2380	0.4065	0.1236	0.0788

Table 3. Effect of deflection from the optimal split value. (reprinted from Gogová & Hanika (2009,c)). Simulation conditions: ILGLR; $N_R=N_D=7$; $N_{Sep}=N_B=2$; $U_{GR}=0.04$ m/s; $P_W=80\%$; $c_{f,Glc}=100$ mol/m³; $c_{f,Glcac}=0$ mol/m³; $Y_{f,O}=0.21$; $X_{Glc}=0.02$

Figure 8 shows effect of superficial gas velocity U_{GR} and molar fraction of oxygen in the gas feed stream $Y_{O,f}$ on the location of the GLR optimal geometry (plot a), which is where the maximum reactor productivity is achieved (plot b). Similar effect is showed in Figure 9 for various Glc liquid feed stream concentrations.

It can be seen in Fig. 8, that a change in $Y_{O,f}$ is compensated to large extent by change in A_D/A_R and the reaction rate responds only slightly to it. In the case of increasing Glc concentration (Fig. 9), the GLR productivity increases significantly (in the point of the GLR optimal geometry). As the Glc concentration rises up, the rate of the catalyst reactivation increases as a result of quicker consumption of oxygen. As a consequence, the downcomer zone of GLR, required for the catalyst reactivation, shrinks, too.

Fig. 8. Influence of oxygen concentration in the gas feed ($Y_{OG-feed}$) stream at various U_{GR} levels on a) location of the target GLR optimum geometry; b) cycle-time-averaged reaction rate in the point of optimal geometry. (reprinted from Gogová & Hanika (2009,c)). Conditions: $c_{Glc,f}=100$ mol/m³; $c_{Glcac,f}=0$; $X_{Glc}=2\%$; $N_R=N_D=7$; $N_{Sep}=N_B=2$; $P_W=80\%$.

It was found during the model reaction kinetics study that the reaction rate is inhibited by oxygen. Moreover, oxygen affects the extent of the catalyst deactivation. The variation range of oxygen content in gas feed stream is therefore limited. Figure 8 covers major part of the target GLR operational window in terms of U_{GR} and $Y_{O,f}$. In the region of low $Y_{O,f}$ and U_{GR} (Figure 8) or high $c_{Glc,f}$ and low U_{GR} (Figure 9) the catalyst reactivation is sufficient enough and the downcomer reaches only a couple of cm in diameter there. It gives raise the impression that even bubble column reactors (BC) can be used to carry out the reaction under these conditions. The impact of backmixing (characteristic for BCs) on the catalyst behaviour may, however, be detrimental. Another limitation in terms of the GLR operational window arises at high U_{GR} , where the riser diameter may become critically

small. Here, the flow regime is more likely to change from homogeneous bubbly flow to slug flow (see a flow map in e.g. Shah, et al. (1982)).

Fig. 9. Effect of glucose concentration in the liquid feed stream at various U_{GR} levels on a) location of the target GLR optimum geometry; b) cycle-time-averaged reaction rate in the point of optimal geometry. (reprinted from Gogová & Hanika (2009,c)). Conditions: $Y_{O,f} = 0.21$; $c_{Glcac,f} = 0$; $X_{Glc} = 2\%$; $N_R = N_D = 7$; $N_{Sep} = N_B = 2$; $P_W = 80\%$.

For the input operational parameters given by the points on the $U_{GR} - c_{i,f}$ and $U_{GR} - Y_{O,f}$ coordinates in Figures 8a and 9a, respectively, the 3D-plane of solutions represents the optimum geometry with the only possible reaction-reactivation time-share to achieve the highest possible cycle-time-averaged reaction rate in the target GLR. Every geometrical solution either above or below the optimum plane would lead to either too long or too short reactivation time, respectively. Any of these two deviations results in depression in cycle-time-averaged reaction rate compared to that achieved in GLR of optimal geometry.

As proved above, depending on the input conditions the optimum reaction-reactivation time-share varies and so does the optimum in the target GLR geometry, which is also reflected in the profiles of the reaction rate and the concentrations along the GLR. In Figure 10, calculated profiles of the actual concentrations and reaction rates along the circulation loop are presented for selected set of input parameters. Each symbol in Figure 10 represents one tank of the tanks-in-series within the loop (their abbreviations are for illustration marked at the top of the Figures 10a, b). The space time in Figure 10 is defined as follows:

$$\tau_{\Sigma k} = \frac{\sum_{j=1}^k W_j^L}{\dot{V}^L}; \quad k = 1, 2, \dots, N_{tot} \quad (10)$$

The target GLR operates continuously. In the profiles, inlet and outlet points in the reactor are visible (compare with Figure 6). For the input conditions listed with Figure 10, the calculated reactor productivity (cycle-time-averaged reaction rate) is 3.49 mmol Glcac per 1 kg of the catalyst per second.

In Figures 11 and 12 calculated profiles of reaction rates and molar fraction of oxygen in the gas phase are shown along the GLR circulation loop. The arrows indicate the trends as the $Y_{O,f}$ (Figure 11) and $c_{Glc,f}$ (Figure 12) rise. Optimal geometry of the target reactor varies for varying input conditions (as shown in Figures 8 and 9), and thus the hydrodynamics and the residence times vary, too. Therefore, comparison of the profiles calculated for various input conditions is facilitated through normalized space times along the circulation loop.

Fig. 10. Profiles of a) the actual reaction rates (circles) and the catalyst fractional coverage by inactive oxygen (squares); b) Glc (circles) and dissolved oxygen concentrations (squares) and molar fraction of oxygen in the gas phase (triangles); along the GLR circulation loop (reprinted from Gogová & Hanika (2009,c)). Conditions: $c_{Glcac,f} = 0$; $c_{Glc,f} = 100 \text{ mol/m}^3$; $Y_{O,f} = 0.21$; $X_{Glc} = 2\%$; $U_{GR} = 0.04 \text{ m/s}$; $N_R = N_D = 7$; $N_{Sep} = N_B = 2$; $P_W = 80\%$.

Fig. 11. Profiles of a) the immediate reaction rates, and b) oxygen molar fraction in the gas phase along the GLR circulation loop for various $Y_{O,f}$ (reprinted from Gogová & Hanika (2009,c)). Simulation conditions: $c_{Glcac,f} = 0$; $c_{Glc,f} = 100 \text{ mol/m}^3$; $X_{Glc} = 2\%$; $U_{GR} = 0.04 \text{ m/s}$; $N_R = N_D = 7$; $N_{Sep} = N_B = 2$; $P_W = 80\%$.

Similarly to Figure 10, the maximum immediate reaction rate is achieved in separator(D) tank for every $Y_{O,f}$ (Figure 11) or $c_{Glc,f}$ (Figure 12). As the arrow in Figure 11a indicates, this value even increases with increase in $Y_{O,f}$, and shifts towards lower space times. At the same time, as the maximum immediate reaction rate in separator(D) tank rises with $Y_{O,f}$, the minimum reaction rate in the bottom tanks depresses. Therefore, quite contrary to the trend of immediate rate in the separator(D) tank, the cycle-time-averaged reaction rate decreases slightly as demonstrated in Figure 8b. The above mentioned shift towards lower space times on increasing $Y_{O,f}$ is given by shift in the optimal geometry of the target GLR towards higher A_D / A_R values (see Figure 8a and the rationale to it). The trends in Figure 11a are reflected by the profiles in Figure 11b – rising the $Y_{O,f}$ causes more prompt consumption of oxygen in riser (which corresponds with the steep increase in immediate reaction rate profile along riser – Figure 11a), but duration of this period decreases gradually.

Simulation results in Figure 12 show profiles of the immediate reaction rates and molar fraction of oxygen in the gas phase for various $c_{Glc,f}$. As the arrows indicate, increase in $c_{Glc,f}$ shifts the reaction rate towards higher values and at the same time, it shifts the residence times in downcomer tanks towards lower values (Figure 12a). Analogous trend is observable in the Y_O profiles (Figure 12b). This is in agreement with Figure 9 and the rationale given to it in the text above.

Fig. 12. Profiles of a) the immediate reaction rates, and b) oxygen molar fraction in the gas phase along the GLR circulation loop for various $c_{Glc,f}$ (reprinted from Gogová & Hanika (2009,c)). Simulation conditions: $c_{Glcac,f} = 0$; $Y_{O,f} = 0.21$; $X_{Glc} = 2\%$; $U_{GR} = 0.04 \text{ m/s}$; $N_R = N_D = 7$; $N_{Sep} = N_B = 2$; $P_W = 80\%$.

3.5 Practical aspects

The derived GLR mathematical model was used for computer aided design and optimization of a target multifunctional gas-lift reactor with the aim to solve the main problem of the model reaction - the catalyst unstable activity. Examples of such processes are e.g. wet air oxidation of waste waters or syntheses of chemical specialties. Glucose oxidation (in alkaline aqueous solution) with oxygen in the presence of a palladium catalyst was used as the case study. Application of GLR to this reaction system enabled simultaneous reaction in riser and the catalyst reactivation in downcomer section of the reactor.

The GLR model assumptions lean on the kinetics of the reaction and the catalyst deactivation. All the simulations assume homogeneous bubbly flow of the reaction mixture in riser, zero gas hold-up in downcomer and predict the system steady state operation. The isothermal tanks-in-series mixing model describes axial dispersion of the reaction mixture in the oxidation and the catalyst reactivation sections of the reactor. Hydrodynamic parameters of the GLR model were taken from pilot plant data (Blažej, et al. (2004), Blažej, et al. (2004), Juraščík, et al. (2006), Sikula, et al. (2007), Sikula (2008), Sikula & Markoš (2008)).

The GLR mathematical model proposed helps to overcome the problem with the catalyst unstable activity by appropriate calculation of the target GLR geometry for any given input operational conditions. Moreover, the model is capable of predicting optimal geometry of the target GLR, its maximal productivity and other steady state characteristics for reactions similar to the model one, i.e. for G-L-S oxidations with reversible deactivation of a catalyst due to an action of any substance present in the gas phase. The limitations are only given by meeting the ranges of GLR operational window as explained with Figures 8 and 9.

The GLR model derived is not limited to the model reaction only. It can easily be extended for other G-L-S oxidations with reversible deactivation of a catalyst due to an action of a substance present in the gas phase. The limitation here is given by at least partly overlapping the ranges of a GLR applicability (see the reasoning given with Figures 8 and 9 about the ranges of the model reaction operational window) with the new reaction requirements (set by the new reaction kinetics).

The proposed GLR model can also be extended to non-isothermal process conditions. In future, the area of the GLR model employment may be broadened for process scale-up and the reactor safe control. But, the experimental validation of the model solutions remains a challenge for the future research.

For the biotechnological routes of GlcAc production, GLRs are also of interest due to several advantages that they offer over alternative bioreactors. However, a GLR design for the biotechnological applications is based on different policy, compared to the catalytic application. In the catalytic process the condition of zero gas hold-up in downcomer was directive for the reactor design. On the contrary, in the biotechnological application this condition is no longer relevant as the living conditions for the cell cultures involved have to be ensured all over the GLR circulation loop, i.e. oxygen has to be present in downcomer. Therefore, GLR correctly designed for a bioprocess should provide sufficient G-L mass transfer, and it should operate at an optimal gas hold-up in downcomer.

4. Conclusion

The model reaction chosen appears to be interesting, not only due to its versatility for the industrial applications, but also because it raises many chemico-engineering problems to be solved in unconventional ways. The main problem of the model reaction is fast but fully reversible deactivation of Pd catalyst due to an action of oxygen during the reaction course. Various approaches can be taken to get over the problem. In the work described in this chapter, the problem is tackled through a tailored selection, design and optimization of the catalytic reactor. For reasons explained below, gas-lift reactor (GLR) was selected as the target reactor suitable to carry out the model reaction in. It allows the reaction along with the catalyst reactivation proceed within one reactor unit. Such reactors are in their nature multifunctional.

Deeper insight into the catalyst deactivation is made by analyzing the model reaction behaviour under conditions of a continuous stirred tank reactor (CSTR) operation. Optimization of the CSTR productivity through the gas feed stream composition / flow modulation was attempted. Dynamic mathematical model of CSTR operating under on-off periodic mode was used to aid this task. In the periodic operation, enhancement of the overall reaction rate results from forcing the catalyst to operate under transient conditions. In CSTR, period length, as well as the period split value represent independent variables and can be varied independently within one CSTR unit of a given (and constant) construction. For any period length always a split value exists, where maximum reaction rate is achieved (see Figure 4). The optimization task was to find conditions that guarantee the highest reactor productivity at any period given. In other words, the optimal reaction-reactivation time-share had to be found within a given period length, where the maximum CSTR productivity is guaranteed, because in the period split optimum no time is wasted in prolonged activation process, neither insufficient activation time is provided. Figure 4 maps the CSTR performance for selected input conditions. Benefits of running the model reaction

under conditions of periodic exposure to oxidative and reductive environment were explored and a trajectory of maximal CSTR productivity was defined. A real production plant operational requirements and limitations decide about the position on this trajectory.

GLR (gas-lift reactor) natural operation resembles the above mentioned forced periodic operation of the CSTR as follows: In GLR, the main reaction, as well as the catalyst reactivation proceeds within one multifunctional reactor unit. In principle, GLR operation is based on spontaneous circulation of the catalyst dispersion in liquid, which results from difference in apparent density of the reaction mixture present in riser and downcomer sections of the reactor. Therefore, if complete separation of the gas phase is ensured after the reaction media passes the riser where the main reaction (and the catalyst deactivation) takes part, the downcomer serves as reactivation zone of the reactor. If economic aspects were considered, GLR natural periodic operation would be cheaper than the forced periodic operation of CSTR.

In GLR it is impossible to move along a similar trajectory of the highest reactor productivity (as was the case with CSTR) without reconstruction of the GLR itself. The period value is given by liquid circulation velocity, i.e. the time one circulation loop takes; and the split value is set by the given GLR geometry. Only one geometrical optimum exists for given set of input operational conditions. The maximal GLR productivity is only guaranteed in this geometrical optimum, because the residence time in riser (reaction time) and the residence time in downcomer (activation time) are only here shared optimally. The optimization task for this GLR case was to find the optimal geometry for any set of input conditions. The derived GLR mathematical model was used to aid design of target reactor for reaction of heterogeneously catalyzed glucose oxidation. The model helps to overcome the problem of the catalyst's fast reversible deactivation by appropriate calculation of the target GLR.

In this chapter presented theoretical analysis of the target reactor optimal design procedure also offers several extensions to the future research. It should firstly focus on experimental validation of the presented GLR mathematical model and after that on the model extension for non-isothermal reactions. This would make the GLR model a useful tool for a process scale-up and its safety control.

Another direction of subsequent research efforts might be a critical comparison of chemical and biotechnological oxidation routes for syntheses of chemical specialties. An objective confrontation would be valuable from the viewpoint of technical arrangement of the processes as well as from the viewpoint of the two processes economics.

5. Nomenclature

A	cross-sectional area (m^2)
a	relative activity of the catalyst (-)
c	concentration (mol m^{-3})
D	diameter (m)
D_p	catalyst particle diameter (m)
K	adsorption coefficients (see Table 1 for details and dimensions)
k	rate constants (see Table 1 for details and dimensions)
k_{La}	volumetric mass transfer coefficient (s^{-1})

N	number of tanks (-)
P	period $P=t_R+t_A$ (s)
P_W	portion of separator volume that functionally contributes to riser (%)
p	pressure (Pa)
R_w	specific rate of formation / consumption (mol kg ⁻¹ s ⁻¹)
S	split $S=t_R/(t_R+t_A)$ (-)
T	temperature (K)
t	time (s)
t_C	cycle time (s)
U	superficial velocity (m s ⁻¹)
$\dot{V}$	volumetric flow rate (m ³ s ⁻¹)
W	volume (m ³)
X	conversion (%)
Y	molar fraction (-)

Greek symbols

α	active fraction (-)
ε	gas hold-up (-)
ν	stoichiometric coefficient (-)
θ_{so}	catalyst fractional coverage by inactive oxygen species (-)
ρ_c	catalyst concentration (kg m ³)
τ	space time (s)
$\dot{\xi}_{A(D)}$	specific activation (deactivation) rate (kg ⁻¹ s ⁻¹)
$\dot{\xi}_w$	specific reaction rate (mol kg ⁻¹ s ⁻¹)
ω	stirring frequency (min ⁻¹)

Subscript/superscript

0	initial, at $t=0$ s
-	average; vector (with concentration)
*	saturated
A	activation; activator
B	bottom
D	downcomer; deactivation
Eqv	equivalent (with downcomer diameter)
f	feed
G	gas phase
Glc	glucose
Glcac	gluconic acid

i	i-th species
k	k-th tank
L	liquid phase
O	oxygen
opt	optimal
R	riser; reaction; reactor
Sep	separator
tot	total
w	related to the weight of the catalyst used
Σk	sum from bottom(R) tank to the k-th tank (with space time)

Abbreviations

B	bottom
$CSTR$	continuous stirred tank reactor
D	downcomer
G	gas phase
Glc	glucose
$Glcac$	gluconic acid
GLR	gas-lift reactor
HD	hydrodynamics
$ILGLR$	internal-loop gas-lift reactor
L	liquid phase
R	riser
S	solid phase
Sep	separator
$SSTR$	semi-continuous stirred tant reactor

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When talking about modelling it is natural to talk about simulation. Simulation is the imitation of the operation of a real-world process or systems over time. The objective is to generate a history of the model and the observation of that history helps us understand how the real-world system works, not necessarily involving the real-world into this process. A system (or process) model takes the form of a set of assumptions concerning its operation. In a model mathematical and logical assumptions are considered, and entities and their relationship are delimited. The objective of a model – and its respective simulation – is to answer a vast number of “what-if” questions. Some questions answered in this book are: What if the power distribution system does not work as expected? What if the produced ships were not able to transport all the demanded containers through the Yangtze River in China? And, what if an installed wind farm does not produce the expected amount of energy? Answering these questions without a dynamic simulation model could be extremely expensive or even impossible in some cases and this book aims to present possible solutions to these problems.

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