Rate Based Modeling of a Sulfite Reduction Bioreactor

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DOI 10.1002/aic.10398
Published online March 23, 2005 in Wiley InterScience (www.interscience.wiley.com).

A novel biological sulfite/sulfate reduction process has been evaluated using a rate-based mathematical model. The principle of this process is that sulfate reducing bacteria reduce sulfate or sulfite to sulfide using H_2 and CO_2 as energy and carbon source under anaerobic conditions. The H_2S gas resulting from the biological sulfate reduction is simultaneously stripped off and, in a separate stage, absorbed and oxidized to elemental sulfur. In this novel process, the biological sulfate/sulfite reduction reaction is accompanied by absorption of H_2 and CO_2, chemical reactions in the liquid phase and the subsequent desorption of the volatile reaction product, H_2S. As a result of the complicated nature of this process, accurate simulation of the system is essential for the precise design, parameter estimation and control of the process. The proposed model adopts the film theory and includes both instantaneous equilibrium reactions and reactions with finite rates. Mass transfer resistance in the gas phase is also taken into account. The rate based process model was implemented in a packed-bed bioreactor model to obtain reactor dimensions as a function of operational variables. A sensitivity analysis was conducted on the mathematical model to define the key parameters of the process design and performance, and to establish the optimal reactor operational conditions. *AIChE J,* 51: 1429–1439, 2005
Keywords: sulfite reducing bacteria, sulfur dioxid, flue gas, multiphase reactions, mathematical modeling

Introduction

Combustion of fossil fuel results in the generation of flue gas containing SO_2 which is a major air pollutant causing several serious environmental pollution problems, such as photochemical smog and acid rain. Flue gas desulfurization (FGD) is effective to prevent SO_2 emission. The most commercially important flue gas desulfurization technology at present is the use of solid, throwaway adsorbents, such as limestone and dolomite. This type of process results in the production of large amounts of gypsum, that is, calcium sulfate, which imposes a significant disposal problem, since only part of the produced gypsum can be used as construction material [1].

As an alternative to the conventional FGD process, a new regenerable biotechnological process for flue gas desulfurization has been developed by Paques Bio systems B.V. and Hoogovens Technical Services [2]. This Bio-FGD process combines a conventional caustic scrubber for the removal of SO_2 from the flue gas and two bioreactors for processing the liquid from the scrubber. In the scrubber, SO_2 is absorbed by a water phase buffered by carbonate. The bisulfite/sulfate is then transferred to the anaerobic bioreactor, where the sulfite and sulfate

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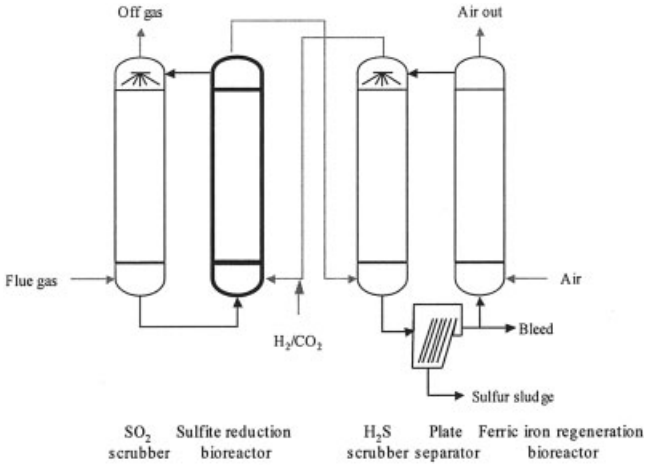

Figure 1. Combined chemical/biological process for conversion of SO_2 to H_2S.

The thick line denotes the sulfite reduction bioreactor modeled in this study.

from the absorber liquid are reduced to sulfide through sulfate-reducing bacteria. Finally, the sulfide containing liquid is fed to an aerobic bioreactor where sulfide is converted to elemental sulfur. Elemental sulfur is removed from the solution by a separator, and the regenerated bicarbonate solution is recirculated to the absorber.

BIO-FGD offers many advantages compared with conventional FGD processes. It results in considerably reduced costs for waste gas desulfurization, high SO_2 removal efficiency and low reagent consumption. Moreover, the mass of the end product is reduced by more than 80% and the end product is reusable (valuable) elemental sulfur. The main disadvantage of the Bio-FGD process is coupling of the reactors by one large liquid cycle. Due to hydrogen sulfide inhibition in the anaerobic reactor, a large cyclic water flow is needed to keep a low hydrogen sulfide concentration. Since all of the reactors are connected by this liquid cycle, a large liquid flow has to be circulated, and most reactors are hydraulically limited. Consequently the reactors become wider due to the limited superficial liquid velocities in combination with the large cycle flow.

To overcome the limit in the Bio-FGD process, we have developed an alternative biotechnological process for flue gas desulfurization [3]. In this process, the sulfide produced in the sulfite reducing bioreactor is stripped off to the gas phase and, hence, no need for the recirculation of a large liquid flow. In this way, instead of one large liquid cycle two small liquid cycles and one gas cycle are applied which makes the process more flexible. In the mean time, two liquid loops are working in a bioscrubber concept and there is no need to separate the biomass from the liquid phase. Also, a suspended growth bioreactor can be used and the liquid containing suspended cells circulating between absorbers and bioreactors.

The first liquid loop contains a sulfur dioxide absorber, which converts SO_2 into HSO_3^-, and a sulfite reduction bioreactor where HSO_3^- is converted by microorganisms into H_2S under anaerobic condition, using H_2 and CO_2 as energy and carbon source, respectively (Figure 1). The H_2S gas resulting from the sulfite/sulfate reduction is simultaneously stripped off and transferred into a gas phase, which carries H_2S to a second loop where H_2S is absorbed and oxidized to elemental sulfur.

Two options are proposed for the second loop: (1) using alkalophilic bacteria, in this case H_2S gas is absorbed into an alkaline solution and subsequently biologically oxidized to elemental sulfur, which is separated from the water phase, [4] and (2) using acidophilic bacteria, in this case an aqueous $Fe_2(SO_4)_3$ solution is used as H_2S absorbent. H_2S is absorbed and chemically oxidized to elemental sulfur, while Fe^{3+} is reduced to Fe^{2+} [5]. Elemental sulfur is removed from the solution by a separator, and the reactant Fe^{3+} is regenerated from Fe^{2+} by biological oxidation in an aerated bioreactor, which is connected to the chemical H_2S oxidizer with a liquid cycle.

Biological sulfite reduction is an important subprocess in this new integrated chemical-biological process for SO_2 removal, which is the focus of this study. For this purpose, the use of autotrophic sulfate reducing bacteria in a suspended growth type bioreactor is proposed in which, hydrogen gas is used as an electron donor. The use of suspended biomass is advantageous compared to the use of biofilm because diffusion limitation is absent. By using a closed liquid loop a suspended biomass culture can be recirculated between the two reactors as long as the HRT in the SO_2 scrubber can be neglected, which is normally the case. An aqueous $NaHCO_3$ solution is used for SO_2 absorption, and subsequently bicarbonate is regenerated via biological reduction of sulfite in the bioreactor.

The overall sulfite conversion rate in H_2 utilizing bioreactors is often determined by the mass transfer capacity for H_2 [6]. The application of suspended growth type bioreactors for this purpose offers several advantages over biofilm bioreactors. In the suspended growth bioreactors there is no need for space and expensive carrier material. The only mass transfer barrier is transfering compounds from the gas phase to the liquid phase due to the absence of the mass transfer resistances as a result of the compounds transport to the biofilm and diffusional resistance within the biofilm.

In the suspended growth bioreactor, the SRT can be easily selected by the amount of bleed. In the sulfite reduction bioreactor using hydrogen as the electron donor, a strong competition exists for hydrogen between hydrogenotrophic sulfite reducer and hydrogenotrophic methanogens (converting H_2 to undesired CH_4) occurs [6]. The bleed can be set in such a way to select a residence time short enough to prevent growth of competing hydrogenotrophic methanogenic bacteria in the system.

Sulfate reducing bacteria (SRB) are obligate anaerobes, which convert sulfate or sulfite as electron acceptor to sulfide as end product. They are known to grow both heterotrophically using small organic molecules, and autotrophically using H_2 as the electron donor and CO_2 as the carbon source [7]. Synthesis gas is considered to be highly attractive for the sulfate removal process for the following reasons [8]:

- Low biomass yield is achieved using autotrophic sulfate reducing bacteria.
- Synthesis gas is easily produced on site from gasification of the coal.
- Low-grade coal, containing sulfur deposits can safely be used for synthesis gas production, as sulfur compounds would be treated by the system.

In this study the feasibility and engineering aspect of the sulfite reduction bioreactor were investigated. In this bioreactor

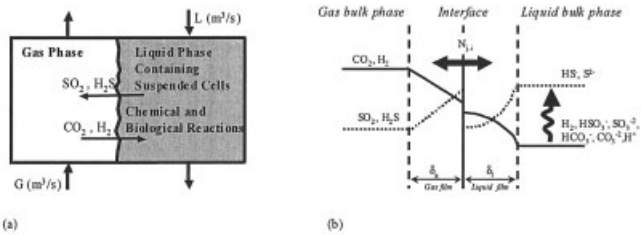

Figure 2. Complex reaction system.

(a) Overall mass transfer frame in the countercurrent flow contactor; and (b) concentration profiles in the two film model for a cross section of the column.

biological reaction is accompanied with several chemical reactions in liquid phase, transport of H_2 and CO_2 from gas phase, and the subsequent desorption of a volatile reaction product, H_2S. Due to the complicated nature of this process, an accurate simulation of the process is essential for the precise design. In this regard, a rate based model has already been developed in the previous research [3] and modified to apply for the design and simulation of the sulfite reduction bioreactor.

Mathematical Model Development

Process description

The sulfite reduction process is considered as a system where a sulfite containing liquid is contacted with a gas flow containing H_2 as energy source and CO_2 as carbon source. The liquid is fed at the top of the bioreactor at a flow rate L, and it comes in countercurrent contact with a gas flow at volumetric rate G. H_2 and CO_2 from the gas phase must be transferred to the liquid phase, where the biological reaction occurs and sulfite is converted to sulfide. The produced sulfide is transferred to the gas phase as H_2S. In the liquid phase, in addition to the biological reaction a series of chemical reactions occur. The chemical reactions must be taken into account in the model since they are relevant to transport and reaction rates calculation as well as the pH. A representation of the system is depicted in Figure 2. In the proposed model, the following assumptions have been made to simplify the analysis of the bioreactor:

- Steady-state condition
- Mass transfer between the gas and liquid phase is described based on the two film theory.
- No reaction takes place in the gas phase.
- The contactor used is packed bed and the gas and liquid are in plug flow.
- The temperature differences can be neglected.

Model Reactions

Autotrophic sulfate reducing bacteria use carbon dioxide as their sole carbon source to produce organic matter. A stoichiometric equation for bacterial growth on hydrogen can be derived from the biomass yield on H_2 ($1/Y_{sx}^{\max}$ is the moles of H_2 consumed per C-mol biomass produced), the elemental balances on, C, H, O, N and the charge balance and by assuming that the biomass composition is represented by $CH_{1.8}O_{0.5}N_{0.2}$ [9]

$$CO_2 + 0.2NH_4^+ + \frac{1}{3}\left(\frac{1}{Y_{sx}^{\max}} - 2.1\right)HSO_3^- + \frac{1}{Y_{sx}^{\max}}H_2 \rightarrow CH_{1.8}O_{0.5}N_{0.2} + \frac{1}{3}\left(\frac{1}{Y_{sx}^{\max}} - 2.1\right)HS^- + \left(\frac{1}{Y_{sx}^{\max}} - 0.6\right)H_2O + 0.2H^+ \quad (1)$$

Besides growth, bacteria also use the energy created from H_2 and sulfites for maintenance necessities. The simplified catabolic stoichiometric equation that applies to the bacterial maintenance reaction can be written as

$$H_2 + \frac{1}{3}HSO_3^- \rightarrow \frac{1}{3}HS^- + H_2O \quad (2)$$

The rate equation for the specific rate of hydrogen utilization with simultaneous inhibition by the product H_2S can be described by the following equation[6]

$$q_{H_2} = q_{H_2}^{\max} \cdot \frac{C_{HSO_3^-}}{K_{HSO_3^-} + C_{HSO_3^-}} \cdot \frac{C_{H_2}}{K_{H_2} + C_{H_2}} \cdot \left(1 - \frac{C_{H_2S}}{C_{H_2S,\max}}\right) \quad (3)$$

Accordingly, the conversion rate of H_2 based on the reactor liquid volume r_{H_2} (in mol of $H_2/m^3.h$) is

$$r_{H_2} = -q_{H_2} \cdot C_x \quad (4)$$

By considering the biomass specific substrate consumption rate (q_{H_2}) and maintenance (m_s) as independent rates and using the Pirt equation [10], the following relation for specific growth rate can be obtained

$$r_x = \mu C_x = Y_{sx}^{\max}(q_{H_2} - m_{H2})C_x \quad (5)$$

Consequently, the relations between other conversion rates and r_x can be obtained by the stoichiometric coupling of the above growth and maintenance reactions (Eqs. 1 and 2)

$$-r_C = r_x \quad (6)$$

$$-r_{NH_3} = 0.2r_x \quad (7)$$

$$-r_{SIV} = r_{SII} = \frac{1}{3}\left(\frac{1}{Y_{sx}^{\max}} - 2.1\right)r_x + \frac{1}{3}m_sC_x \quad (8)$$

The values of the kinetic parameters and maintenance coefficient are estimated using correlations proposed by Heijnen et al.[9] and reported literature data as shown in Table 1.

The biological sulfite reduction process using H_2 and CO_2 as respiration energy and carbon source also involves the exchange of SO_2, CO_2, H_2 and H_2S between the liquid and gas phases. In addition a complex system of parallel and consecutive ionic dissociation/association reactions in the liquid phase takes place. The basic reactions considered are

Table 1. Kinetic Parameters for Sulfite Reducing Bacteria, with H_2 and CO_2 as Energy and Carbon Source at 55°C[9,12,13]

Kinetic Parameter	Value	Units
$q_{H_2}^{max}$	19.1	$molH_2/C\text{-}mol \cdot h$
K_{H_2}	2.2×10^{-4}	$kmol/m^3$
$K_{HSO_3^-}$	3.1×10^{-4}	$kmol/m^3$
$Y_{H_2}^{max}x$	0.06	$C\text{-}mol/molH_2$
m_{H_2}	1.0	$molH_2/C\text{-}mol \cdot h$
$C_{H_2S}^{max}$	0.016	$kmol/m^3$

$$SO_2 + H_2O \rightleftarrows H^+ + HSO_3^- \quad (9)$$

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-} \quad (10)$$

$$CO_2 + H_2O \rightleftarrows H^+ + HCO_3^- \quad (11)$$

$$CO_2 + OH^- \rightleftarrows HCO_3^- \quad (12)$$

$$HCO_3^- \rightleftarrows H^+ + CO_3^{2-} \quad (13)$$

$$H_2O \rightleftarrows H^+ + OH^- \quad (14)$$

$$H_2S \rightleftarrows HS^- + H^+ \quad (15)$$

$$HS^- \rightleftarrows S^{2-} + H^+ \quad (16)$$

Reactor model

The steady state mass balances for SO_2, CO_2, H_2 and H_2S in the gas phase assumed in plug flow through the reactor can be written as

$$\frac{1}{RTS} \cdot \frac{dGp_{j,b}}{dz} = -N_{j,i}^g a \quad (17)$$

where j represents the above gaseous species.

The steady state mass balance for each species j in the bulk liquid phase, also assumed in plug flow, is

$$\frac{L}{S}\frac{dC_{j,b}}{dz} = -N_{j,b}^l a - r_{j,b}^l \varepsilon_l \quad (18)$$

where fluxes into or from bulk liquid are

$$N_{j,b}^l = -D_j \left.\frac{dC_j}{dx}\right|_{x=\delta_l} \quad (19)$$

Mass balances for individual chemical species can be combined to balances for total sulfite(SIV), total carbonate (C), total sulfide (SII) and hydrogen as follows

$$\frac{L}{S}\frac{dC_{SIV,b}}{dz} = \left(D_{SO_2} \left.\frac{dC_{SO_2}}{dx}\right|_{x=\delta_l} + D_{HSO_3^-} \left.\frac{dC_{HSO_3^-}}{dx}\right|_{x=\delta_l} + D_{SO_3^{2-}} \left.\frac{dC_{SO_3^{2-}}}{dx}\right|_{x=\delta_l} \right) a - r_{SIV,b}^l \varepsilon_l \quad (20)$$

$$\frac{L}{S}\frac{dC_{C,b}}{dz} = \left(D_{CO_2} \left.\frac{dC_{CO_2}}{dx}\right|_{x=\delta_l} + D_{HCO_3^-} \left.\frac{dC_{HCO_3^-}}{dx}\right|_{x=\delta_l} + D_{CO_3^{2-}} \left.\frac{dC_{CO_3^{2-}}}{dx}\right|_{x=\delta_l} \right) a - r_{C,b}^l \varepsilon_l \quad (21)$$

$$\frac{L}{S}\frac{dC_{SII,b}}{dz} = \left(D_{H_2S} \left.\frac{dC_{H_2S}}{dx}\right|_{x=\delta_l} + D_{HS^-} \left.\frac{dC_{HS^-}}{dx}\right|_{x=\delta_l} + D_{S^{2-}} \left.\frac{dC_{S^{-2}}}{dx}\right|_{x=\delta_l} \right) a - r_{SII,b}^l \varepsilon_l \quad (22)$$

$$\frac{L}{S}\frac{dC_{H_2,b}}{dz} = D_{H_2} \left.\frac{dC_{H_2}}{dx}\right|_{x=\delta_l} a - r_{H_2,b}^l \varepsilon_l \quad (23)$$

Equations 17 and 20 to 23 contain the fluxes at the gas/liquid interface and from liquid film/liquid bulk. These fluxes are related to the concentration gradients of the different components at the gas/liquid interface and bulk liquid (see also Eqs. 34 to 38). Therefore, the concentration profiles of different components in the liquid film are required. For this purpose, the mass balance equations in liquid film for different species have to be integrated into the mass balances for the axial direction of the reactor. Note that, because of CO_2 hydrolysis reaction in the liquid film and changes in pH, concentrations of individual species change in the film. However, because it is assumed that no biological reaction takes place in the film, the total fluxes of SII, SIV and C are not affected. Consequently, Eqs. 20 to 23 could also be formulated, based on the fluxes of H_2S, SO_2, CO_2 and H_2 at the gas/liquid interface.

Film region

The differential equations describing the diffusion of each component j into or from the gas phase without reaction are

$$\frac{dN_j^g}{dx} = 0 \quad (24)$$

where j is for SO_2, CO_2, H_2S and H_2.

The differential equations describing the process of diffusion with simultaneous reaction of each species j in the liquid phase are

$$\frac{dN_j^l}{dx} = r_j \quad (25)$$

Where Fick's law is used to express the diffusive flux of each species:

$$N_j = -D_j \frac{dC_j}{dx} \tag{26}$$

After replacing the fluxes Eq. 26 in Eq.25, the mass balances for individual species can be combined to obtain the following balances for total sulfite, total sulfide, total carbonate and total sodium

$$D_{SO_2} \frac{d^2C_{SO_2}}{dx^2} + D_{HSO_3^-} \frac{d^2C_{HSO_3^-}}{dx^2} + D_{SO_3^{2-}} \frac{d^2C_{SO_3^{2-}}}{dx^2} = 0 \tag{27}$$

$$D_{CO_2} \frac{d^2C_{CO_2}}{dx^2} + D_{HCO_3^-} \frac{d^2C_{HCO_3^-}}{dx^2} + D_{CO_3^{2-}} \frac{d^2C_{CO_3^{2-}}}{dx^2} = 0 \tag{28}$$

$$D_{H_2S} \frac{d^2C_{H_2S}}{dx^2} + D_{HS^-} \frac{d^2C_{HS^-}}{dx^2} + D_{S^{2-}} \frac{d^2C_{S^{2-}}}{dx^2} = 0 \tag{29}$$

$$D_{H_2} \frac{d^2C_{H_2}}{dx^2} = 0 \tag{30}$$

$$D_{Na^+} \frac{d^2C_{Na^+}}{dx^2} = 0 \tag{31}$$

By using Eq. 27 to 31, the biological reaction in the liquid film is neglected as can be justified by the small volume of the liquid film compared to the overall liquid volume.

Because the reactions 9, 10 and 13 to 16 includes proton transfers, instantaneous equilibrium is assumed for these reaction throughout the liquid film; therefore, the chemical equilibrium relations of these reactions also apply at all points in liquid phase.

The hydrolysis reaction of CO_2 is slow, therefore, instead of a chemical equilibrium equation a separate material balance for CO_2 has to be included

$$D_{CO_2} \frac{d^2C_{CO_2}}{dx^2} = r_{CO_2} \tag{32}$$

r_{CO_2} represents the CO_2 hydrolysis reaction rate and is a function of the reactive species involved, and the reaction may proceed according to Eq. 11 or 12 depending on the pH [3].

It has been shown that the impact of any electric potential gradient on the flux of ions may be disregarded under low solute concentration conditions as long as the mass flux equations are combined with a flux charge equation [11]. Therefore, the last equation needed to close the system of balance equations in the liquid film is the flux of charge

$$\sum z_j \cdot D_j \cdot \frac{dC_j}{dx} = 0 \tag{33}$$

Boundary conditions

The model system consisting of mass and charge balances Eqs 27 to 33 and six chemical equilibrium relations for the reactions 9, 10 and 13 to 16 must be completed by the boundary conditions relevant to the film model at the gas liquid interface ($x = 0$) and boundary conditions in bulk liquid ($x = \delta_l$) δ_l is the thickness of mass transfer boundary layer in the liquid phase which can be estimated using the mass-transfer coefficient k_l and the diffusivity for H_2S as reference $\delta_l = D_{H_2S}/kl_{H_2S}$.

Boundary conditions at the gas liquid interface($x = 0$)

The transfer rate of SO_2 is equal to the sum of the fluxes of the sulfite species at the gas-liquid interface, which also must be equal to the flux of SO_2 in the gas film

$$N^g_{SO_2,j} = \frac{k_{g,SO_2}}{RT}(p_{SO_2,b} - p_{SO_2,j}) = -\left(D_{SO_2}\left.\frac{dC_{SO_2}}{dx}\right|_{x=0} + D_{HSO_3^-}\left.\frac{dC_{HSO_3^-}}{dx}\right|_{x=0} + D_{SO_3^{2-}}\left.\frac{dC_{SO_3^{2-}}}{dx}\right|_{x=0}\right) \tag{34}$$

where

$$p_{SO_2,j} = H_{SO2}C_{SO2,i} \tag{35}$$

and similarly for H_2S and H_2

$$N^g_{H_2S,i} = \frac{k_{g,H_2S}}{RT}(p_{H_2S,b} - p_{H_2S,i}) = -\left(D_{H_2S}\left.\frac{dC_{H_2S}}{dx}\right|_{x=0} + D_{HS^-}\left.\frac{dC_{HS^-}}{dx}\right|_{x=0} + D_{S^{2-}}\left.\frac{dC_{S^{-2}}}{dx}\right|_{x=0}\right) \tag{36}$$

$$N^g_{H_2,i} = \frac{k_{g,H_2}}{RT}(p_{H_2,b} - p_{H_2,i}) = -D_{H_2}\left.\frac{dC_{H_2}}{dx}\right|_{x=0} \tag{37}$$

Since the rate of the hydrolysis reaction is slow, the flux of CO_2 in the gas film is equal to the flux of dissolved CO_2 at the interface

$$N^g_{CO_2,i} = k_{g,CO_2}/RT(p_{CO_2,b} - p_{CO_2,i}) = -D_{CO_2}\left.\frac{dC_{CO_2}}{dx}\right|_{x=0} \tag{38}$$

The flux of HCO_3^- and CO_3^{2-} at the interface must be zero because the transport of carbon species is represented by CO_2

$$D_{HCO_3^-}\left.\frac{dC_{HCO_3^-}}{dx}\right|_{x=0} + D_{CO_3^{2-}}\left.\frac{dC_{CO_3^{2-}}}{dx}\right|_{x=0} = 0 \tag{39}$$

The flux of Na is zero at the interface

$$D_{Na^+}\left.\frac{dC_{Na^+}}{dx}\right|_{x=0} = 0 \tag{40}$$

and also the net flux of charge must be zero at $x = 0$

$$\sum z_j \cdot D_j \cdot \left.\frac{dC_j}{dx}\right|_{x=0} = 0 \tag{41}$$

Since instantaneous equilibrium is assumed for the reactions 9, 10 and 13 to 16 at the interface, the equilibrium equations for these reactions apply also at $x = 0$.

Boundary conditions in bulk liquid ($x = \delta_l$)

Equilibrium is assumed for all the reactions in the bulk liquid; therefore, besides the equilibrium equations for reactions 9, 10 and 13 to 16, also the equilibrium equation can be written as follows

$$\frac{C_{H^+} \cdot C_{HCO_3^-}}{C_{CO_2}} = K_3 \tag{42}$$

together with other four equations obtained from mass balances for total sulfur species, total carbon species, Na^+,H_2 and a charge balance

$$C_{tot,SIV} = C_{SO_2,b} + C_{HSO_3^-,b} + C_{SO_3^{2-},b} \tag{43}$$

$$C_{tot,SII} = C_{H_2S,b} + C_{HS^-,b} + C_{S^{2-},b} \tag{44}$$

$$C_{tot,C} = C_{CO_2,b} + C_{HCO_3^-,b} + C_{CO_3^{2-},b} \tag{45}$$

$$C_{tot,H_2} = C_{H_2,b} \tag{46}$$

$$C_{tot,Na} = C_{Na^+,b} \tag{47}$$

$$\sum Z_j C_j = 0 \tag{48}$$

The system of seven Eqs 27 to 33 together with the six equilibrium equations for the reactions 9, 10 and 13 to 16 and the described boundary conditions are used to find the concentration profiles of the 13 unknown species (H_2, H_2S, HS^-, S^{2-}, SO_2, HSO_3^-, SO_3^{2-}, CO_2, HCO_3^-, CO_3^{2-}, Na^+, H^+, OH^-) in the liquid film at each z position in the column height. These concentration profiles allow the calculation of the fluxes of SO_2, H_2S, H_2 and CO_2. The fluxes are needed for integration of differential mass balance equations in the bulk gas and liquid along the column in Eqs. 17 and 20 to 23.

The liquid film thickness and reactor height were both discretized in a spatially uniform grid and second-order finite differencing was applied. The resulting system of nonlinear algebraic equations was solved numerically with a traditional Newton-based method.

Results and Discussion

In a previous work we have described the model based design of a scrubber for SO_2 removal from the flue gas in a 600 MW power plant using an aqueous $NaHCO_3$ solution [3]. The flue gas flow rate considered was 2×10^6 Nm^3/h containing 1,000 ppm SO_2, and the partial pressure of CO_2 in the flue gas was 0.14 bars. In this study, the model proposed will be applied for the design of a sulfite reduction bioreactor for the regeneration of the absorbent used in the SO_2 scrubber. The temperature and the total pressure were assumed to be 55°C and 1.1 bar, respectively, equivalent to the conditions in the first column. A packed bed reducing contactor is proposed. The packing material is considered to be 35 mm plastic pal rings. The liquid phase with suspended cells enters the bioreactor at the top and flows countercurrently with the gas phase. The bioreactor diameter is based on the 85% flooding condition. The height of the bioreactor is determined for full conversion ($<$ 99%) of sulfite to sulfide and 99% desorption of sulfide produced to the gas phase. The correlations used for estimation of the physical properties and model mass transfer parameters are the same as described previously [3].

Bioreactor performance

In the integrated process for SO_2 removal described in the introduction, a closed liquid loop between the SO_2 scrubber and sulfite reduction bioreactor is proposed. Hence, the absorbent liquid from the SO_2 scrubber is directly transferred to the bioreactor and the outgoing liquid from the bioreactor is recirculated to the SO_2 scrubber. Biomass is proposed to grow as a suspension in the bioreactor and the cells are transferred with the liquid phase between two reactors without separation stage. Hence, the objectives to be met in the sulfite reduction bioreactor are:

- Transfer of CO_2 and poorly soluble H_2 from the gas phase to the liquid phase
- Biological sulfite reduction.
- Transfer of sulfide as H_2S to the gas phase.

To prevent subsequent desorption of H_2S in the SO_2 scrubber, the outlet liquid from the bioreactor should be free of H_2S. Therefore, H_2S resulting from sulfite reduction should be either stripped off simultaneously in the sulfite reduction bioreactor or removed in a separate stage. Single stage H_2 absorption and desorption of H_2S in the sulfite reduction bioreactor is preferred to keep the configuration of the integrated process for flue gas desulfurization as simple as possible.

Representative input conditions and design parameters and some model results for the sulfite reduction bioreactor are summarized in Table 2. These conditions are considered in the simulations.

Regeneration of bicarbonate solution

Typical results when the bioreactor is designed to regenerate the bicarbonate solution used as SO_2 absorbent are discussed. Composition of the inlet liquid into the SO_2 reduction bioreactor is the same as the outlet liquid from the SO_2 scrubber. Typical interfacial mass-transfer rate profiles of the components along the bioreactor height are shown in Figure 3. Positive and negative values of the component flux correspond to absorption and desorption, respectively.

The initial concentration of CO_2 in the gas phase, the concentration of the carbonate species in the liquid phase and the consumption rate of CO_2 determine the direction of the CO2 flux at the gas/liquid interface. In this case in the major part of the bioreactor the partial pressure of CO_2 in the gas phase, is higher than the partial pressure of CO_2 in the liquid phase and, hence, absorption of CO_2 occurs. And only at the top of the bioreactor desorption of CO_2 occurs, some degree.

Table 2. Typical Design Parameters for Sulfite Reduction Bioreactor

Bioreactor temperature, $T(K)$	328
Bioreactor pressure, $P(bar)$	1.1
Flow rates	
Inlet liquid flow rate, $L(m^3/s)$	1.11
Inlet gas flow rate, $G(m^3/s)$	11.1
Inlet liquid composition	
C_{Na} $(kmol/m^3)$	0.036, 0.114*
C_{SV} $(kmol/m^3)$	0.022
C_{CIV} $(kmol/m^3)$	0.0138, 0.0125*
C_P $(kmol/m^3)$	0.0, 0.072*
C_X (kg/m^3)	10
Inlet gas phase composition	
H_2 (%)	70
CO_2 (%)	30
Maximum sulfite conversion	>99%
Maximum sulfide desorption	>99%
Interfacial area, a (m^2/m^3)	125
% Flooding	85
Liquid hold up	10%
Mass transfer coefficients	
k_{g,H_2S} (m/s)	0.032
k_{g,CO_2} (m/s)	0.071
k_{g,H_2} (m/s)	0.071
k_{g,SO_2} (m/s)	0.024
k_{l,H_2S} (m/s)	0.0009
k_{l,CO_2} (m/s)	0.0010
k_{l,H_2} (m/s)	0.0016
k_{l,SO_2} (m/s)	0.0010
liquid film thickness, δ_l (mm)	0.0035
Calculated column height (m)	30.4, 21.8*
Calculated column diameter (m)	6.13

In case of phosphate buffer.

H_2S is produced in the liquid phase and subsequently desorbed to the gas phase. At the top of the bioreactor the partial pressure of H_2S is higher than the partial pressure of the H_2S in the fresh solution; therefore, H_2S absorption occurs. However, overall H_2S is transferred to the gas phase in the bioreactor.

H_2 is transferred from the gas phase to the liquid phase where it is consumed by sulfate reducing bacteria. In the lower part of the bioreactor, no substantial transfer of H_2 is observed, whereas H_2S desorption occurs. Therefore, it can be concluded that in this region there is no biological sulfite reduction reaction to consume H_2. In Figure 4, the reaction rate profiles along the bioreactor are shown, which clearly indicate that sulfite conversion is accomplished in the uppermost of the bioreactor. Therefore, it can be concluded when a bicarbonate buffer solution is used in the SO_2 scrubber, the bioreactor height becomes considerably higher due to the need for H_2S desorption. The function of the bottom part of the bioreactor is only desorption of the remaining H_2S in the liquid phase. The bioreactor height based on sulfite conversion would be about 60% of the total bioreactor height needed for the H_2S stripping.

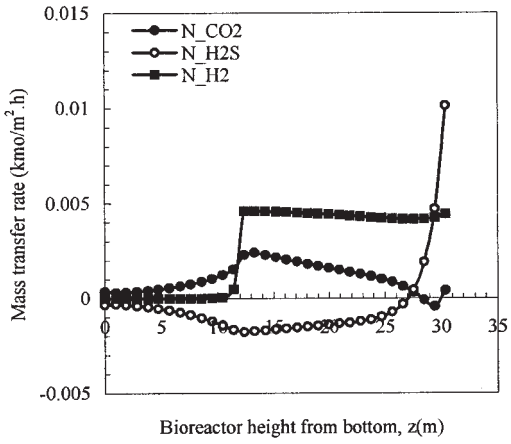

Figure 3. Interface mass-transfer rate profile of various gases along the bioreactor in case of bicarbonate buffer.

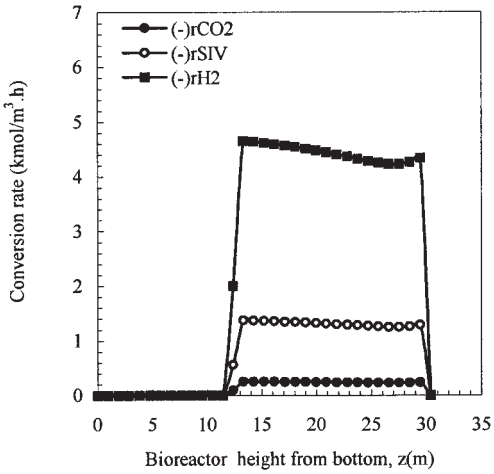

Figure 4. Conversion rate profile of various components along the bioreactor, in case of bicarbonate buffer.

The desorption of sulfite species, as SO_2 to the gas phase is negligible, less than 0.004% of total the sulfite species in the liquid phase transfers to the gas phase as SO_2 (simulation not shown).

Stimulation of H_2S desorption using phosphate buffer

Simulation results show that H_2S desorption is a physical mass transfer process without significant chemical enhancement. However, appropriate pH adjustment helps H_2S desorption. The adjustment of pH impacts the H_2S desorption by altering the relative amount of H_2S, HS^- and S^{2-} species. A decrease in the pH permits an increase in the relative ratio of H_2S to the total sulfide concentration. The fraction of H_2S concentration to the total sulfide concentration in the bulk liquid using the equilibrium relations is given by

$$C_{H_2S}/C_{tot,SII} = 1(1 + K_1/10^{-pH} + K_1K_2/10^{-2pH}) \qquad (49)$$

where K_1 and K_2 are the first and second dissociation constants of H_2S, respectively. This equation indicates that the percentage of the H_2S is 4.5%, 32 and 82% when the pH is adjusted at 8, 7 and 6, respectively. Therefore, the H_2S desorption can be stimulated utilizing an acidic buffer, but inhibition of the bioreaction limits the allowed pH. Buffer capacity, on the other hand, can be increased to reduce pH change of the solution along the bioreactor. In the case of bicarbonate buffer, increasing bicarbonate concentration to achieve a better buffering is actually unfavorable to the process because it causes an increase in pH as well.

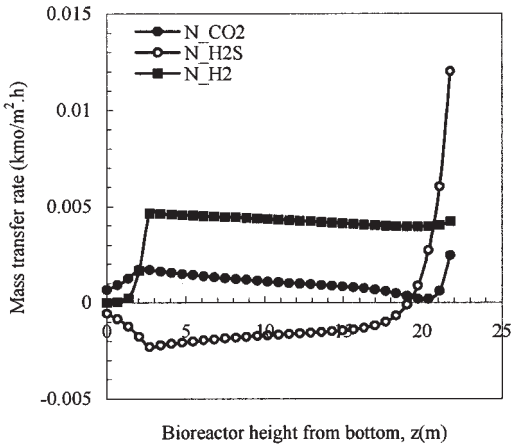

Figure 5. Interface mass-transfer rate profile of various gases along the bioreactor, in case of phosphate buffer.

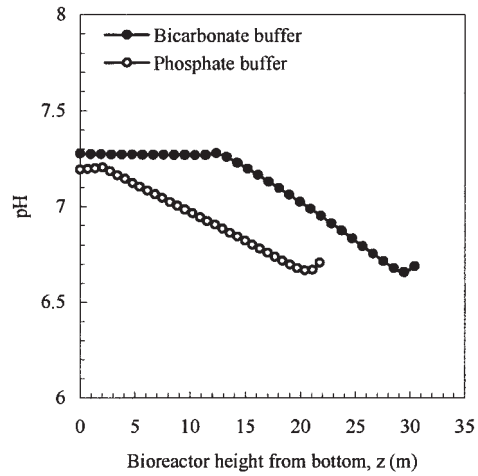

Figure 7. pH profile in the liquid bulk along the bioreactor.

A combined bicarbonate-phosphate buffer solution was tested as an alternative for the pure bicarbonate buffer described previously. The simulation results obtained when a phosphate buffer is used at the same inlet liquid pH of the bicarbonate buffer (pH = 6.7) are shown in Figure 5. The results indicate that by using a phosphate buffer nearly simultaneous desorption of H_2S in the reaction zone along the bioreactor can be achieved. The bioreactor height substantially decreases, about 30%, resulting in a more economical process. A similar behavior is presented by reaction rate profiles along the bioreactor in Figure 6.

The impact of phosphate buffer on pH of the liquid bulk along the bioreactor as compared to the bicarbonate solution is presented in Figure 7. Because the sulfite species are converted to the sulfide species and subsequently are transferred to the gas phase as H_2S, increase in pH of the liquid phase from the top to the bottom of the bioreactor is expected. However, the resulting changes in pH in the case of phosphate buffer due to higher buffer capacity are smaller than those occurring for the bicarbonate buffer. The low pH of the liquid bulk in the case of the phosphate buffer results increase of the relative ratio of H_2S to the total sulfide concentration and, hence, the enhancement of H_2S desorption.

The partial pressure profiles of H_2, CO_2 and H_2S in the gas bulk along the bioreactor are shown in Figure 8. Changes in the partial pressures are the results of the gas/liquid interfacial mass transfer and change in the gas flow rate. As the gas phase moves up, H_2 and CO_2 are transferred to the liquid phase and consumed by sulfate reducing bacteria. H_2S produced desorbs to the gas phase, but based on the stoichiometry of the biological sulfite reduction reaction H_2S production is about one third of the H_2 consumed; therefore, the gas flow rate decreases along the bioreactor height.

The concentration profiles of the total sulfite and total sulfide and H_2S in the liquid bulk along the bioreactor are depicted in Figure 9. The concentration of the sulfite species decreases from the top to the bottom of the bioreactor, due to the biological conversion to sulfide. The concentration profile of the total sulfide species in the liquid bulk is the result of

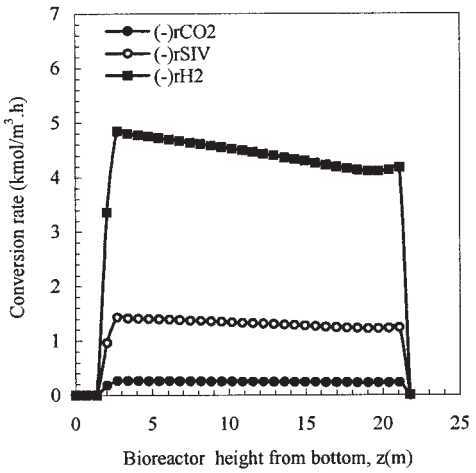

Figure 6. Conversion rate profile of various component along the bioreactor, in case of phosphate buffer.

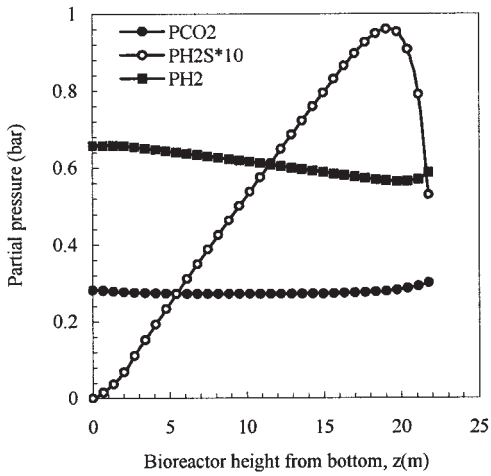

Figure 8. Partial pressure profile of various gases along the bioreactor, in case of phosphate buffer.

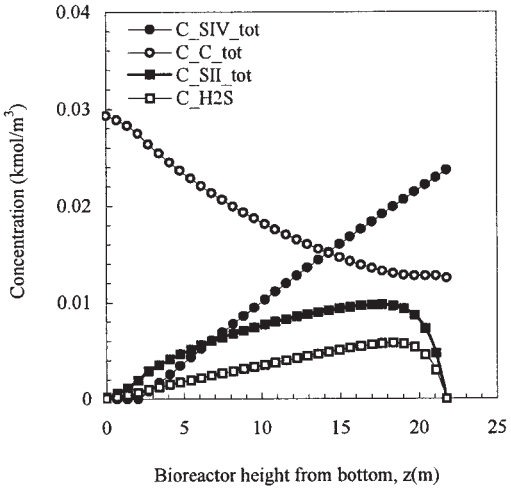

Figure 9. Concentration profile of total sulfite, carbonate, sulfide and hydrogen sulfide along the bioreactor, in case of phosphate buffer.

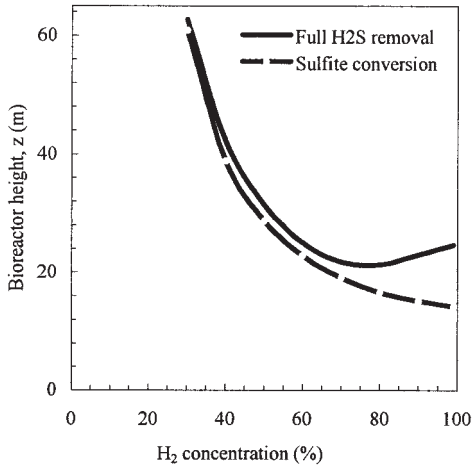

Figure 10. Effect of inlet gas H_2 concentration on the bioreactor height at constant total gas pressure; the height required for H_2S stripping equals the height for full H_2S removal minus the height required for sulfite conversion.

absorption/desorption and production. The sulfide species is produced and eventually stripped off to the gas as H_2S. It is clear that the H_2S concentration in the liquid bulk along the bioreactor is far from the toxicity level, 1.6×10^{-2} kmol/m^3 [12].

Sensitivity analysis

A sensitivity analysis is performed to quantify the effect of some of the model input parameters on the process performance and to establish the optimal operating conditions. Below the dependence of the reactor height on three independent variables, the partial pressure of H_2, the suspended cells concentrations and the total pressure are described.

Effect of H_2 partial pressure on the bioreactor height

The required bioreactor height to obtain full conversion of sulfite without considering 99% desorption of H_2S, is shown in Figure 10. The bioreactor height decreases significantly by increasing the partial pressure of H_2 due to increase in the H_2 gas/liquid interfacial flux. By further increasing of H_2 partial pressure the sulfite reduction process switches from mass transfer limited to kinetic limited regime, therefore, decrease in the bioreactor height for sulfite conversion slows down.

Figure 10 shows also how increasing H_2 concentration in the inlet gas to the bioreactor alters bioreactor height required for full H_2S desorption. The bioreactor height decreases by increasing H_2 partial pressure in the inlet gas. However, further increase of H_2 partial pressure results in an increase of the bioreactor height. Since the inlet gas flow and pressure are assumed to be constant high H_2 partial pressure is corresponded to the low CO_2 partial pressure. And at the low inlet CO_2 partial pressure the pH at the bottom of the bioreactor increases resulting in poor H_2S desorption and, therefore, the higher bioreactor height.

Effect of biomass concentration on the bioreactor height

In a closed liquid loop bioscrubber concept for gas purification the pollutant gas stream is uncoupled from the absorbent liquid containing biomass. Therefore, there is no need for biomass retention and a bioreactor with suspended biomass can be applied. In a closed loop bioscrubber with in principle infinitely long biomass retention times, much higher biomass concentration can be achieved. The maximum biomass concentration in the bioreactor is achieved when all substrate is used for the growth independent maintenance purposes. However, in practice some bleed is required to a avoid toxicity effect resulting from accumulation of salts and halide ions (that is, F^- and Cl^-). Furthermore, the bleed flow rate can be used to set the cell residence time (SRT) at a desired value to washout undesired slow growing microorganisms. The maximum bleed corresponding to the lower limit of the SRT in the closed loop bioscrubber, which is determined by the washout of the desired, suspended cells.

The maintenance coefficient at 55°C is estimated to be 0.33 molSIV/C-mol.h, using the correlation proposed by Heijnen et al.[9] The total SIV, which should be removed, is about 85 kmol/h. By assuming a 1,000m^3 total operating liquid volume including the scrubber, bioreactor and piping volume, the maximum biomass concentration can be calculated to amount about 60 kg/m^3. A biomass concentration of 2 kg/m^3 corresponds to a SRT of 1.2h.

In Figure 11, the bioreactor height is plotted against the biomass concentration in the inlet liquid.

As biomass concentration in the inlet liquid increases the bioreactor height decreases. However, by further increasing of the biomass concentration the sulfite reduction process switches from the kinetic limited to the mass transfer limited regime, therefore, the calculated bioreactor height remains constant.

Effect of total pressure on the bioreactor height

The bioreactor height is controlled by H_2 absorption rate and H_2S desorption rate. Increasing the total pressure at constant gas flow rate leads to a higher H_2 interfacial mass-transfer rate

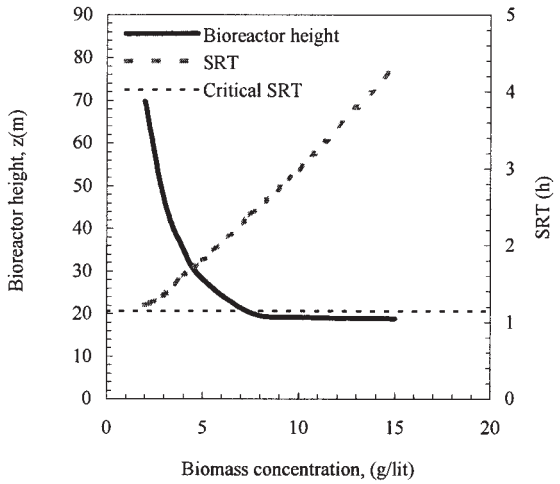

Figure 11. Effect of biomass concentration on the column height, and the SRT required.

and using phosphate buffer allows simultaneous desorption of H_2S. Therefore, the bioreactor height will be decreased.

Conclusions

A novel closed loop bioscrubber concept for flue gas desulfurization was evaluated. This process is based on recycling of the absorbent solution between a scrubber and sulfite reducing bioreactor without separation of the suspended bacterial cells. The main feature of the closed loop bioscrubber concept is that much higher biomass concentration and high mass transfer capacity can be achieved. The integrated biological process seems a very viable option for flue gas desulfurization, and should be further developed for large-scale applications.

Feasibility and engineering aspects of sulfite reduction bioreactor using H_2 and CO_2 as energy and carbon source were studied. In this process the biological reaction is accompanied with several chemical reactions in liquid phase, transport of H_2 and CO_2 from gas phase and the subsequent desorption of volatile reaction product H_2S. To evaluate the process a simple, but realistic mathematical model was developed. The principle of the model is, based on the two film theory which governs the coupling of mass transfer (absorption/desorption of the chemical components), specific features of electrolyte species, biological and chemical reactions. The proposed model comprehensively describes the complicated system of reaction and interface transport. In general the model can be used equally for other reactive separation processes.

The model results show that, simultaneous desorption of H_2S produced during the biological sulfite reduction can best be achieved in the same bioreactor by using phosphate buffer. Therefore, a separate stage for H_2S desorption is not required.

Acknowledgment

The support of this project by STW, the Dutch Technology Foundation, and the support of the first author by Iranian Ministry of science, research and technology are gratefully acknowledged.

Notation

a = specific interfacial area, m^2/m^3
C = molar concentration in the liquid phase, $kmol/m^3$
C_x = biomass concentration, C-$kmol/m^3$
$C^l_{j,b}$ = concentration of the component j in the liquid bulk, $kmol/m^3$
D = diffusion coefficient, m^2/s
G = gas volume flow rate, m^3/s
He = Henry's law coefficient, $atm.m^3/kmol$
k = reaction rate constant
k_g = gas side mass-transfer coefficient, m/s
k_l = liquid side mass-transfer coefficient, m/s
L = liquid volume flow rate, m^3/s
ms = maintenance coefficient of biomass on H_2, mol H_2/C_mol. s
N_j = flux of component j in the liquid film per unit gas/liquid interfacial area, $kmol/m^2$ s
$N^g_{j,i}$ = interfacial flux of component j per unit gas/liquid interfacial area, $kmol/m^2$ s
P = total pressure, atm
p_j = partial pressure of the component j, atm
q_{H_2} = biomass specific H_2 consumption rate, mol H_2/C-mol.s
$q_{H_2,\max}$ = maximum biomass specific H_2 consumption rate, mol H_2/C-mol s
r_{H_2} = H_2 consumption rate, kmol H_2/m^3.s
r_x = bacterial growth rate, C-$kmol/m^3$.s
R = gas constant, m^3.atm/kmol.K
r_j = reaction rate of the component j, $kmol/m^3$.s
S = column cross section, m^2
T = temperature, K
x = spatial coordinate in the liquid film, m
$Y^{\max}_{sx}$ = The maximum yield coefficient of biomass on H_2, C-mol/mol H_2
z = spatial coordinate on the column height, m
z_A = electric charge of species A

Greek letters

δ_g = gas film thickness, m
δ_l = liquid film thickness, m
ε_l = liquid holdup m^3/m^3
μ = specific growth rate, 1/s
μ_{max} = maximum specific growth rate, 1/s

Superscripts

g = in gas phase
l = in liquid phase

Subscripts

b = in the bulk of the gas or liquid phase
i = at gas/liquid interface

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Manuscript received May 28, 2004, and revsion received Aug. 17, 2004.