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Structured packed bubble column reactor for continuous production of vanillin from Kraft lignin oxidation

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ABSTRACT

In this work we have studied the lignin oxidation with oxygen to produce vanillin in a continuous gas–liquid co-current bubble column reactor. Using Mellapak structured packings within the reactor, it was possible to increase in 35% the oxygen transfer to liquid phase. A simulation study was performed to gather the effect of different operating conditions (gas and liquid flow rates, temperature, pressure and oxygen mass transfer rate) to achieve improved operating conditions to increase reactor performance. This study allowed us to propose a set of operating conditions that can approach the maximum vanillin conversion obtained in a batch reactor. It was verified that the oxygen mass transfer constant should be significantly increased. This can represent an opportunity to develop new tailored internals for this application.

1. Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is an aromatic compound with a wide spectrum of applications divided in three main branches: flavouring agent in the food industry, perfumery and pharmaceutical intermediate [1,2]. Nowadays, the supply of natural vanilla is not fulfilling market requirements and chemical routes are employed for its production. Vanillin production from biomass will have a smaller environmental footprint and also comply long-term sustainability. One alternative production route is the oxidation of lignin coming from Kraft pulping process. The oxidation of lignin with oxygen has already been studied [3–8].

In this work, a mathematical model was developed for an upward co-current gas–liquid flow reactor and employed to describe experimental lignin oxidation data with and without the internals and used to determine the effect of the main operating conditions to enhance the reactor performance. A bubble column reactor was chosen due to three main reasons: no shaft sealing is required, enabling the operation of aggressive media at high temperatures and pressures; reasonable price and can be easily adapted and resized; and can provide uniform temperature throughout even with strong exothermic reactions [9]. In order to improve the overall mass transfer performance of the system, the main body of the reactor was filled with Mellapak 750Y structured packing from Sulzer Chemtech (Switzerland). Structured packings are found in several gas–liquid applications as internals in reactive distillation or absorption columns operating in counter-current flow [10–17]. However, there is almost no research focused in the application of these packings in reactors with an upward co-current flow configuration. The objective of this work is to report suitable operating conditions to produce vanillin from a biomass-based process in a continuous bubble column reactor using structured packings to enhance mass transfer of the oxidant to the liquid phase.

2. Materials and methods

2.1. Experimental setup

For each experiment 40 l of an aqueous solution with 60 g/l of lignin and 80 g/l of sodium hydroxide were prepared (inlet pH 14). A flow rate of 3.5×10^{-2} l/min of liquid (lignin source) is inserted into the reactor by a piston pump (Dosapro Milton Roy, Milroyal, USA) at ambient temperature. Before entering the main reactor, there is a pre-conditioning chamber of 0.1 m for pre-heating. Then the gas entering the system is mixed with the pre-heated liquid. The gas flow rate employed was 2 l/min (50% of oxygen and 50% of nitrogen) controlled by two mass flow controllers (Bronkhorst, Netherlands). A gas distributor with 19 holes of 1 mm was employed to widespread the gas over the cross-sectional area of the reactor. The gases are mixed in the main reactor body (height of 0.70 m and a diameter of 0.10 m) where three modules of Mellapak

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Nomenclature

A	reaction rate constant for vanillin oxidation, $m^3\ mol^{-1}\ s^{-1}$
A_R	internal cross-section area of the column, m^2
A_W	difference between the external and the internal cross-section area of the column, m^2
B	reaction rate constant for vanillin oxidation, m^3/mol
$C_{i,1}$	concentration of species i in the stirred tank 1, mol/m^3
$C_{i,2}$	concentration of species i in the stirred tank 2, mol/m^3
C_i	concentration of species i in the liquid phase of the column, mol/m^3
C_i^*	concentration of species i in the liquid in the gas–liquid interface, mol/m^3
$C_{P,i}$	heat capacity of substance i, $J\ kg^{-1}\ K^{-1}$
D	vanillin oxidation products
D_{ax}	axial dispersion coefficient, m^2/s
I	ionic strength of the liquid medium, mol/l
k_La	liquid side mass transfer coefficient, s^{-1}
k_1	kinetic constant for vanillin formation, $(m^3/mol)^{1.75}\ s^{-1}$
k_2	kinetic constant for vanillin oxidation, $m^3\ mol^{-1}\ s^{-1}$
K_a	acid dissociation product of the acid species formed during lignin oxidation
L	lignin
M_n	lignin mean molecular weight, g/mol
P_{O_2}	oxygen partial pressure, bar
Q_G	gas flow rate, SLPM
Q_L	liquid flow rate, l/min
r_1	rate of formation of vanillin, $mol\ m^{-3}\ s^{-1}$
r_2	rate of oxidation of vanillin, $mol\ m^{-3}\ s^{-1}$
R_1	radius of the internal wall of the reactor column, m
R_2	radius of the external wall of the reactor column, m
R_3	radius of the internal wall of the outer jacket tube, m
T	reactor temperature, K
T_F	thermo fluid temperature inside the jacket, K
u_{GS}	superficial gas velocity, m/s
u_{LS}	superficial liquid velocity, m/s
U	overall heat transfer coefficient from the thermo fluid in the jacket to the liquid inside the reactor, $W\ m^{-2}\ K^{-1}$
V	vanillin
V_{ST}	volume of each stirred tank, m^3
X	acid products formed in the lignin oxidation

Greek letters

α	lignin stoichiometric coefficient on the lignin oxidation reaction
$\Delta H_{R,1}$	heat of reaction of lignin oxidation, J/mol
$\Delta H_{R,2}$	heat of reaction of vanillin oxidation, J/mol
ε_G	gas hold-up
ε_L	liquid hold-up
ε_S	volume fraction of the structured packing
λ_{ef}	effective thermal dispersion coefficient, $W\ m^{-1}\ K^{-1}$
υ_1	oxygen stoichiometric coefficient on the lignin oxidation reaction
υ_2	acid products stoichiometric coefficient on the lignin oxidation reaction
$\nu_{i,k}$	stoichiometric coefficient of compound i in the reaction k
ρ_i	density of substance i, kg/m^3

Subscripts

F	thermo fluid
G	gas phase
L	lignin or liquid phase
O_2	oxygen
S	structured packing
V	vanillin
W	wall
X	acid products formed in the lignin oxidation

750Y from Sulzer Chemtech (Switzerland) can be placed. Finally, gas and liquid are separated in a widened separation head (height of 0.12 m and diameter of 0.23 m). The liquid stabilization chamber and the main body are fully jacketed. The pressure in the reactor was 10 bar read by a pressure transducer (Lucas Schaevitz, UK) placed at the top of the separation head. Temperature inside the reactor was monitored in three different locations: 0.25, 0.40 and 0.80 m from the liquid feed. Samples were collected from the liquid stream exiting the separation head during 8–9 h. Details about each of these steps, and on the analytical procedure to quantify vanillin in the collected samples are presented elsewhere [18].

3. Modeling and simulations

We have employed a detailed mathematical model to describe the lignin oxidation in a bubble column reactor (BCR) and in a structured packed bubble column (SPBCR). The mathematical model takes into account the liquid pre-heating section and the main body of the bubble column reactor. For both packed and simple bubble columns, the axial dispersion model is the most widely used model to characterize the flowing of liquid phase [19–22]. The one-dimensional version of this flow model was assumed to represent the liquid hydrodynamics in the column section. The assumptions of the mathematical model are the following:

- Constant gas composition with the axial position and time.
- Isobaric reactor.
- The oxygen gas–liquid mass transfer is dominated by the resistance in the liquid film: the resistance in the gas film was neglected and we have considered that the dissolved oxygen is in equilibrium with the gas at the interface.
- Ideal behaviour of the gas phase.
- For the same axial position, the temperatures of the packing, gas and liquid phases are equal (pseudo-homogeneous model for the energy balance).
- The external tube of the reactor jacket is thermally insulated from the surroundings, and the temperature of the outer tube of the column is equal to the temperature of the thermo fluid flowing inside the jacket.
- No heat losses in the thermo fluid between the exit of the bath and the entrance of the reactor jacket.

Table 1
Mathematical model for the lignin oxidation in the SPBCR and BCR.

Column section (liquid stabilization chamber + main body)	
Mass balance equation	$\varepsilon_L D_{ax}\frac{\partial^2 C_i}{\partial z^2} = u_{LS}\frac{\partial C_i}{\partial z} - \varepsilon_L \sum_k \nu_{i,k} r_k + \varepsilon_L \frac{\partial C_i}{\partial t} - k_L a(C_i^* - C_i)$
Dissolved oxygen in the interface	$C^*_{O_2} = \left(3.559 - 6.659\times10^{-3}T - 5.606P_{O_2} + 1.594\times10^{-5}P_{O_2}T^2 + 1.498\times10^3\frac{P_{O_2}}{T}\right)\times10^{-0.144I}$
Energy balance to the reaction media	$\lambda_{ef}\frac{\partial^2 T}{\partial z^2} = (u_{LS}\rho_L C_{P,L} + u_{GS}\rho_G C_{P,G})\frac{\partial T}{\partial z} - \varepsilon_L\left[(-\Delta H_{R,1})r_1 + (-\Delta H_{R,2})r_2\right] - \frac{2\pi R_2}{A_R}U(T_F - T) + \left(\varepsilon_L\rho_L C_{P,L} + \varepsilon_G\rho_G C_{P,G} + \varepsilon_S\rho_S C_{P,S} + \rho_W\frac{A_W}{A_R}C_{P,W}\right)\frac{\partial T}{\partial t}$
Energy balance to the fluid in the jacket	$\rho_F u_F C_{P,F}\frac{\partial T_F}{\partial z} + \frac{2R_1}{R_3^2 - R_2^2}U(T_F - T) + \rho_F C_{P,F}\frac{\partial T_F}{\partial t} = 0$
Separation head	
Stirred tank 1	$Q_L C_i\vert_{z=0.8\,\mathrm{m}} = Q_L C_{i,1} - V_{ST}\sum_k \nu_{i,k} r_k + V_{ST}\frac{dC_{i,1}}{dt}$
Stirred tank 2	$Q_L C_{i,1} = Q_L C_{i,2} - V_{ST}\sum_k \nu_{i,k} r_k + V_{ST}\frac{dC_{i,2}}{dt}$

After the reactor, there is a gas–liquid separation head that is described by two equal stirred tanks with a dead volume. A detailed description of the mathematical model is given elsewhere [18].

The complete set of equations defining the dynamic non-isothermal model for lignin oxidation in the SPBCR and BCR is detailed in Table 1. Danckwerts boundary conditions for a closed–closed vessel were used [21,22]. The kinetic laws and equations to predict the pH evolution were already reported [3,5] and are compiled in Table 2. The model was solved using gPROMS (PSA Enterprise, UK).

4. Results and discussion

One of the limitations of vanillin production is the oxygen transfer to the liquid phase. One possibility to enhance the oxygen mass transfer rate to the liquid phase is to use a structured packing that will increase the gas–liquid contact area. We have experimentally evaluated the performance of Mellapak 750Y structured packing in a bubble column reactor comparing the performance of the reactor with and without the internals. Furthermore, we have performed a simulation study of the structured packings bubble column reactor (SPBCR) to evaluate the effect of the main operating conditions: liquid and gas feed flow rate (Q_L, Q_G), temperature (T_F^{set}), oxygen partial pressure (P_{O_2}) and the volumetric mass transfer coefficient (k_La).

4.1. Bubble column versus structured packed column

A comparison of the effect of the Mellapak 750Y internals in the vanillin production rate is shown in Fig. 1. The vanillin concentration achieves steady state operation only after 6 h of operation. In steady state, the vanillin concentration results from the trade-off between its conversion from lignin and its oxidation to smaller compounds, according to the reaction scheme shown in Table 1. The temperature increase within the reactor is also shown in Fig. 1. The initial temperature increase is more pronounced for the SPBCR case, which is a result of larger amounts of lignin degradation and consequent higher degrees of vanillin formation. A large thermal dispersion also characterizes both reactor configurations, since a great proximity between the temperature profiles collected at different column heights during the experiments was observed, which is a decisive factor for controlling process units with this kind of exothermic reactions.

In Fig. 1, two experiments with similar operating conditions are shown with (BCR configuration) and without using the packing modules (SPBCR configuration). The steady state vanillin concentrations obtained were around 0.73 and 0.56 g/l, for the SPBCR and the BCR experiments, respectively. There is a clear improvement of the vanillin conversion using the SPBCR. However, the vanillin concentration is still far from the maximum of 2.0 g/l obtained for the oxidation of the same Kraft lignin in a batch reactor [18].

In Fig. 1, the solid lines correspond to the mathematical model shown in Table 1 using k_La as a fitting value. The parameters employed for the simulations are listed in Table 3. The values of k_La are $8.05\times10^{-4}\,s^{-1}$ using structured packing against $5.98\times10^{-4}\,s^{-1}$ without packing. Thus, it is demonstrated that the mass transfer coefficient increases 35% using packed internals. Calculated values of mass transfer coefficient k_La with different correlations available in literature [17] are within the same order of magnitude. However, the application of existing correlations is doubtful since these equations were developed for co-current downflow or counter-current systems.

The lignin oxidation is still limited by the poor mass transfer of oxygen from gas phase to the liquid phase. In order to overcome

Table 2
Kinetic laws for the reaction media of lignin oxidation with oxygen, and set of equations to estimate the pH evolution.

Kinetic laws	
Reaction rate	*Lignin oxidation*: $\alpha\mathrm{L} + \upsilon_1\mathrm{O_2}\xrightarrow{r_1}\mathrm{V} + \upsilon_2 X$ *Vanillin oxidation*: $\mathrm{V} + \mathrm{O_2}\xrightarrow{r_2}\mathrm{D}$
Rate of lignin oxidation	$r_1 = k_1 {C_{O_2}}^{1.75} C_L;\quad k_1 = 1.289\,exp\left(-\frac{4000}{T}\right)$
Rate of vanillin oxidation	$\mathrm{pH}\geq 11.5,\ r_2 = k_2 C_{O_2} C_V;\quad k_2 = 72.6\exp\left(-\frac{5530}{T}\right)$
	$\mathrm{pH} < 11.5,\ r_2 = A f(\mathrm{pH}) C_V^2;\quad f(\mathrm{pH}) = \left(\frac{B\times10^{(3-\mathrm{pH})}}{1+B\times10^{(3-\mathrm{pH})}}\right)^2,\qquad A = 0.0679\exp\left(-\frac{3103.7}{T}\right);\quad B = 8.88\times10^9\exp\left(-\frac{1936.6}{T}\right)$
Equations for pH prediction	
$C_X < 1\mathrm{N}$	$\mathrm{pH} = 14$
$1\mathrm{N} < C_X < 1.9955\mathrm{N}$	$\mathrm{pH} = 14 + \log_{10}(2 - C_X)$
$1.9955\mathrm{N} < C_X < 2\mathrm{N}$	$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\left[\frac{C_X - (K_W C_X/K_a)^{1/2}}{(K_W C_X/K_a)^{1/2}}\right];\quad K_a = 10^{-\mathrm{p}K_a}$
$C_X < 2\mathrm{N}$	$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\left(\frac{2}{C_X - 2}\right)$

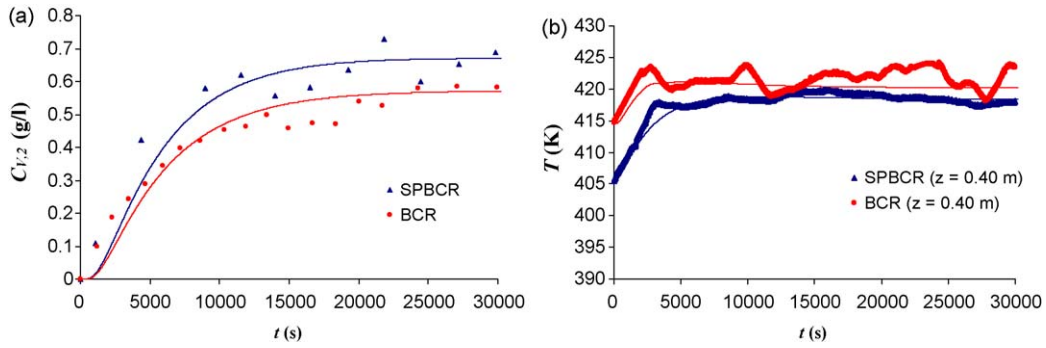

Fig. 1. Vanillin concentration at the exit stream of the reactor (a) and temperature history (b) at a column height of 0.4 m for experiments without internals (BCR) and using three Mellapak 750Y structured packing modules (SPBCR). Operating conditions are: liquid flow rate = 3.5×10^{-2} l/min, 1 SLPM of O_2, 1 SLPM of N_2, pressure = 10 bar, Feed pH 14, Feed lignin concentration = 60 g/l.

Table 3
Model parameters used in the simulation of the lignin oxidation experiments using the SPBCR and BCR configuration.

	SPBCR	BCR		SPBCR	BCR
Flow model parameters					
ε_L ($z \geq 0.1$ m)	0.880	0.969	ε_L ($z < 0.1$ m)	1	1
ε_G ($z \geq 0.1$ m)	0.078	0.031	ε_G ($z < 0.1$ m)	0	0
ε_S ($z \geq 0.1$ m)	0.042	0	V_{ST} (m^3)	0.45×10^{-3}	0.45×10^{-3}
D_{ax} (m^2/s)	2.2×10^{-4}	9.6×10^{-4}			
Heat transfer parameters					
U (W/m^2 K)	36.8	60.0	λ_{ef} (W/m K)	1531	4110
Properties of the reaction system					
α	0.5		M_n (g/mol)		2325
υ_1	1.56		$\Delta H_{R,1}$ (J/mol)		-29.7×10^6
υ_2	114		$\Delta H_{R,2}$ (J/mol)		-0.267×10^3

the kinetic limitations of the reactor, we have made a simulation study to explore which operating conditions should be changed to improve the reactor performance.

4.2. Study for improvement of the reactor performance

Our simulation study covers operating variables like liquid feed flow rate (Q_L), gas feed flow rate (Q_G), set point of the thermostatic bath (T_F^{set}), and the oxygen partial pressure (P_{O_2}). The effect of the mass transfer parameter, k_La, was also added to represent the possibility of changing the internals of the reactor.

Operating conditions and mass transfer coefficient values should satisfy a trade-off situation between high lignin conversion with small (or none) oxidation of vanillin. The simulation results of the steady state vanillin concentration in the SPBCR reactor for the operating conditions covered in this study are detailed in Fig. 2.

It can be observed from Fig. 2(a) that for the higher liquid flow rates (0.083 and 0.167 l/min), increasing the reactor temperature leads to an increase in the vanillin amounts obtained in the exit stream. This behaviour is opposed to the one predicted for the lower liquid flow rate (0.033 l/min) in the same set point range. When the liquid residence time is increased, the lignin degrades more extensively and the pH starts to decrease promoting vanillin degradation and thus reducing its overall concentration at the end of the reactor.

An increase in the gas flow rate Q_G results in a higher gas superficial velocity; in the experimental range of Q_G studied, the k_La increased almost linearly with the gas superficial velocity. A linear dependency between the k_La and the gas superficial velocity was extrapolated in the range of gas flow rates (up to 10 SLPM) used in Fig. 2(b). Higher steady state vanillin concentrations in the exit stream were obtained for higher gas flow rates, due to the increase in k_La. The degree of vanillin formation is smaller for higher liquid flow rates, since there is less available oxygen per mass of lignin.

It can be observed in Fig. 2(c) that an increase in the partial pressure of oxygen results in an increase in vanillin yield. The explanation is again related to the oxygen transfer rate to the liquid. The oxygen mass transfer rate depends not only on the k_La but also on the concentration driving force between the gas–liquid interface and the liquid bulk. The oxygen partial pressure has a major influence in the oxygen solubility in the liquid and thus in the mass transfer driving force. When the P_{O_2} is increased, the oxygen solubility is higher promoting a media with a higher oxidative capacity.

Other situation tested was keeping all operating conditions constant and change the values of the volumetric mass transfer coefficient (k_La). This study has the objective of determining the effect of mass transfer constant in the overall performance of the reactor. In a real reactor, improvements in the mass transfer conditions can be achieved by using much higher gas flow rates. The results are presented in Fig. 2(d) and reveal an increase in the vanillin production with higher k_La values, with the exception of the results for Q_L of 0.033 l/min. In this case, there is a maximum level of vanillin formation with k_La, and then the productivity starts to decrease by undesired vanillin oxidation. This suggests that for a given amount of liquid fed to the reactor, there is an oxidative capacity of the media that should lead to a maximum vanillin yield.

Based on the information gathered above, it is possible to define a new set of conditions that could improve the vanillin yield. To increase the productivity of the system, a larger oxidative capacity of the media should be provided and the liquid residence time should be adjusted to avoid excessive vanillin oxidation. The oxidative capacity could be achieved by increasing the gas flow rate (Q_G) to improve the mass transfer coefficient, and also using pure oxygen

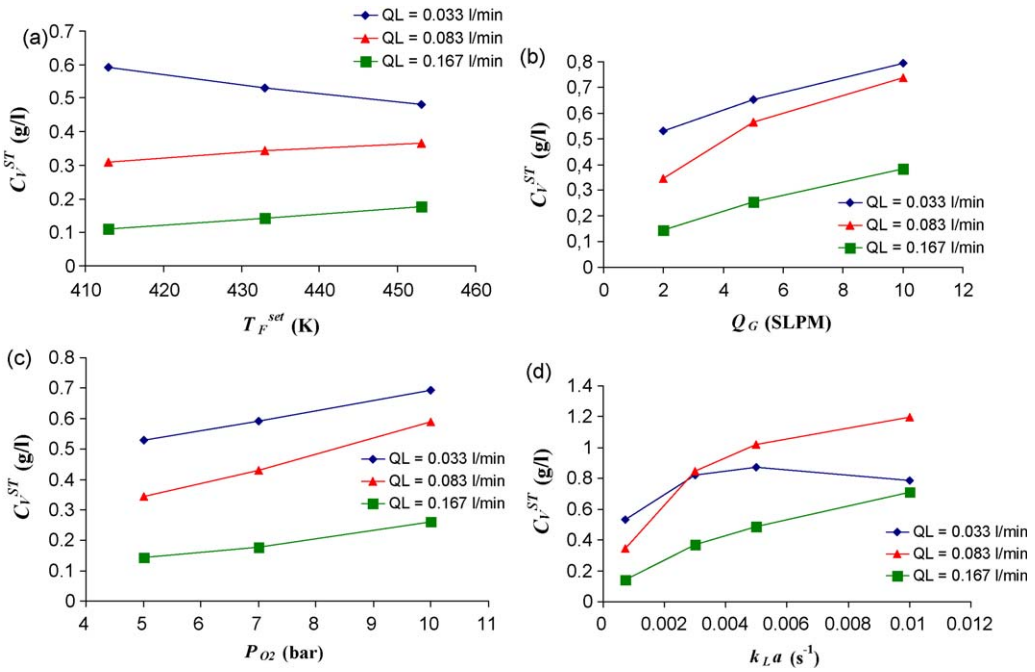

Fig. 2. Predicted values of the steady state vanillin concentration in the exit stream (C_V^{ST}) for different T_F^{set} (a), Q_G (b), P_{O_2} (c) and k_La (d). The fixed values for each case where: (a) Q_G of 2 SLPM, P_{O_2} of 5 bar and k_La of 7.06×10^{-4} s^{-1}; (b) T_F^{set} of 433 K, P_{O_2} of 5 bar and k_La of 7.06×10^{-4} s^{-1} (Q_G of 2 SLPM), 1.36×10^{-3} s^{-1} (Q_G of 5 SLPM) and 2.42×10^{-3} s^{-1} (Q_G of 10 SLPM); (c) T_F^{set} of 433 K, Q_G of 2 SLPM and k_La of 7.06×10^{-4} s^{-1}; (d) T_F^{set} of 433 K; Q_G of 2 SLPM and P_{O_2} of 5 bar. The total pressure was 10 bar for all simulations.

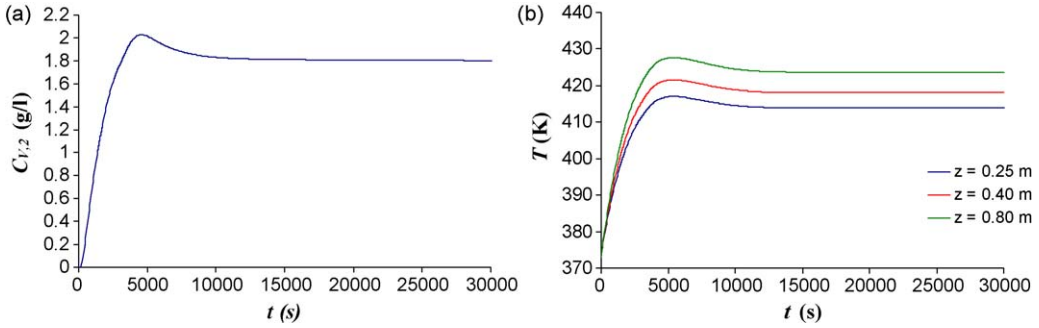

Fig. 3. Simulation results for the vanillin concentration at the exit stream of the reactor (a) and temperature history at three different column heights (b) using improved operating conditions.

increasing its solubility in the liquid phase. With those considerations, a new set of operating conditions is proposed: liquid flow rate (Q_L) of 0.167 l/min; T_F^{set} of 433 K; P_{O_2} of 10 bar with pure oxygen; gas flow rate (Q_G) of 40 SLPM; and k_La of 1.5×10^{-2} s^{-1}. With these proposed operating conditions, the simulation results of the vanillin concentration at the exit of the separation head and different temperature profiles within the reactor are shown in Fig. 3. Other possibility to improve the performance of the reactor is to modify the internals to operate in slug flow regime where values of k_La of the order of 0.4–1 s^{-1} can be achieved [17].

In the Fig. 3(a), the vanillin concentration shows a maximum before achieving its steady state value, that results from the change in the reaction rate equation for vanillin oxidation occurring when the pH gets lower than 11.5. The steady state value of the $C_{V,2}$ is around 1.8 g/l, which is approximately 85% of the maximum levels of vanillin concentration obtained in the batch reactor.

5. Conclusions

In this work we have evaluated the use of structured packings in a co-current bubble column reactor to enhance the vanillin production from lignin oxidation. It was observed that oxygen mass transfer from gas to liquid phase limits the extent of vanillin production. It was experimentally verified that the use of Mellapak 750Y modules have increased in 35% the mass transfer coefficient compared to a reactor without the internals. However, the overall amount of oxygen transferred to the liquid phase was still small and a study of the effect of operating variables was performed: liquid and gas feed flow rates, O_2 pressure, temperature and oxygen mass transfer constant. It was observed that the liquid and gas flow rates should be adjusted to prevent excessive oxidative capacity of the media avoiding excessive vanillin oxidation. It was also observed that oxygen pressure should be increased and eventually using pure oxygen should be considered. A set of operating conditions was proposed enabling us to obtain a vanillin concentration of 1.8 g/l, close to 2.0 g/l that was the maximum concentration of vanillin obtained in batch experiments using this lignin source. It was verified that the oxygen mass transfer constant should be significantly increase. This can represent an opportunity to develop new tailored internals for this application.

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