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Catalysis Today 105 (2005) 574–581

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Modeling of vanillin production in a structured bubble column reactor

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Abstract

Vanillin is an important flavour. Semi-synthetic vanillin can be produced by the oxidation of lignin. Experimental studies leading to vanillin production in a batch reactor and a structured bubble column reactor (SBCR) lead us to the conclusion that the SBCR could have non-idealities such as dispersion. The radial and axial liquid-phase dispersion within the packed criss-crossing sandwich structures of Mellapak-750Y had been studied. A 2D model accounting for axial and radial velocities and dispersion was formulated and solved. The model predictions were compared with that of an experimental residence time distribution curve. The axial dispersion coefficient of the liquid phase is of the same order of magnitude as the radial dispersion coefficient. The reaction kinetics available in literature is adopted for the present study. Model for the SBCR was formulated and simulated using commercial modeling software. Simulation experiments were conducted in a SBCR. The effect of the following parameters on the yield of vanillin is studied: lignin concentration, lignin molecular weight, oxygen partial pressure and reaction temperature. It can be said that lignin molecular weight is a crucial parameter in vanillin production.

Keywords: Modeling; Vanillin production; Structured bubble column reactor

1. Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is an important flavour in the food industry. It can be extracted from crushed vanilla pods, however this is very expensive compared with other synthetic processes. Popular among these are: oxidation of coniferin by CrO_3, acidification, extraction and oxidation of eugenol or transformation of guaiacol by modified Riedel process. Lignin oxidation route for vanillin production had been practised since the sixties [1,2]. Pulp industry is the most important source of quasi-pure lignin, though it's quality depends on the type of plant or wood. Lignin from gymnosperms is the most appropriate raw material for the production of vanillin since it consists of guaicyl-propane units, which are the precursors for vanillin yield. The Kraft pulping process accounts for two-thirds of the lignin production.

Lignin as a raw material for the production of chemicals has been extensively studied. The breakage of this biopolymer through hydrolysis, pyrolysis, and oxidation leads to phenolic compounds of low molecular weight of great interest. These are produced in low yields. However, higher yields of vanillin and syringaldehyde can be produced by the mild oxidation of lignin in an alkaline medium [3].

Most of the studies of vanillin production were carried out with lignin from waste sulfite liquors. It has been well known since 1920s that lignin heated under reflux conditions for long times in the presence of active alkali produces a maximum yield of vanillin [2]. Pressure, temperature, and reaction time influence the yield and nature of phenolic compounds obtained. However, chemical hydrolysis is not enough to obtain good production yields, though oxidation is needed.

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doi:10.1016/j.cattod.2005.06.044

Nomenclature

C	concentration (mol/l)
C_{in}	feed concentration (mol/l)
D_z	axial dispersion coefficient (cm^2/s)
D_{r}	radial dispersion coefficient (cm^2/s)
k_{Cl}	kinetic rate constant (l/mol/min)
k_{NC}	kinetic rate constant (l/mol$^{1.75}$/min)
L	length of SBCR (cm)
MW	molecular weight (g/mol)
P	Pressure (atm)
r	radial coordinate (cm)
r_1	rate of lignin oxidation (mol/l/min)
r_2	rate of vanillin oxidation (mol/l/min)
r_3	rate of overall vanillin yield (mol/l/min)
t	time (s)
t_{imp}	impulse duration (s)
T	temperature (K)
u	liquid phase interstitial velocity (cm/s)
u_z	axial liquid phase interstitial velocity (cm/s)
u_{r}	radial liquid phase interstitial velocity (cm/s)
z	axial coordinate (cm)
ε	holdup

Subscripts

G	gas
Li	lignin
O_2	oxygen
Va	vanillin

Tarabanko et al. [4] studied the kinetics and selectivity of the retroaldol reaction of vanillideneacetone in the alkaline media. The reaction is of first order with respect to substrate and alkali concentration. The pH dependencies of the rates of vanillin formation in the processes of lignosulfonates and vanillideneacetone oxidation agree almost quantitatively. This indicates that the retroaldol reaction plays an important role in the alkaline oxidative destruction of lignins.

Borregaard is one of the world's largest producers of vanillin, offering vanillin from two different processes, based either on guaiacol or lignosulfonates (sulfite-spent liquor from cellulose production) as raw materials [5,6]. The first part of the work carried out in our laboratory dealt with process optimization for the production of vanillin from lignin of *Pinus* spp. (a gymnosperm). The best results were obtained by oxidation of lignin with a concentration of 60 g/l, a temperature of 120 °C, in alkaline medium containing NaOH at 80 g/l (2 N) under oxygen partial pressure of 4 atm [7].

However, there is considerable interest in the hydrodynamics of bubble column reactors [8]. This interest stems from applications in emerging technologies for conversion of natural gas to liquid fuels [9]. Because of their efficient liquid mixing, bubble columns are suitable reactors for carrying out highly exothermic reactions using vertical cooling tubes. Corrugated packing of the regular type, also called structured packing, have received the greatest attention owing to their favorable performance [10,11].

Iliuta et al. [12] developed a two-zone two-fluid one-dimensional model for the prediction of the irrigated two-phase pressure drop and the total liquid hold-up in gas–liquid counter-current columns containing structured packing and operated in the pre-loading zone. Brunazzi et al. [13] used Mellapak structured packing for the absorption of 1,1,1-trichloroethane by genosorb and determined the interfacial area. Urseanu et al. [14] reports the results of a comprehensive experimental study of the hydrodynamics and mixing in two bubble column reactors of 0.1 and 0.24 m in diameter with KATAPAK-S® as packing material.

An alternative to the conventional slurry reactor is the structured bubble column reactor (SBCR). Structured catalytic bubble columns are new, promising types of multiphase reactors. Their configuration lies basically between slurry reactors and trickle bed reactors. The reactor is made up of several structured sections. Each section consists of Mellapak-750Y elements, supplied by Sulzer Chemtech. The structure consists of two pieces of rectangular corrugated metal sheets aligned in a criss-cross fashion. The inclination of the corrugated sheets is $\alpha = 45^\circ$.

The presence of internals significantly affects both large-scale recirculation and local dispersion. The most common approach to model liquid mixing is the one-dimensional axial dispersion model (ADM). This has been validated innumerable times in small bubble columns without internals. There is no information available in literature regarding the lignin oxidation reaction either in a bubble column or in a SBCR.

The objectives of the present study are as follows:

- To model the vanillin production in the following reactors: batch reactor and structured bubble column reactors.
- To evaluate the non-ideality of a medium-sized structured bubble column reactor.
- To evaluate the feasibility of vanillin production in a continuous flow reactor by studying the batch reactor performance and extending its knowledge to the SBCR.

2. Experimental

2.1. Batch reactor

Vanillin production experiments were carried out in a laboratory autoclave reactor (Buchi, Switzerland). It is fully jacketed to maintain constant temperature. The range of temperature of this study is from ambient temperature to

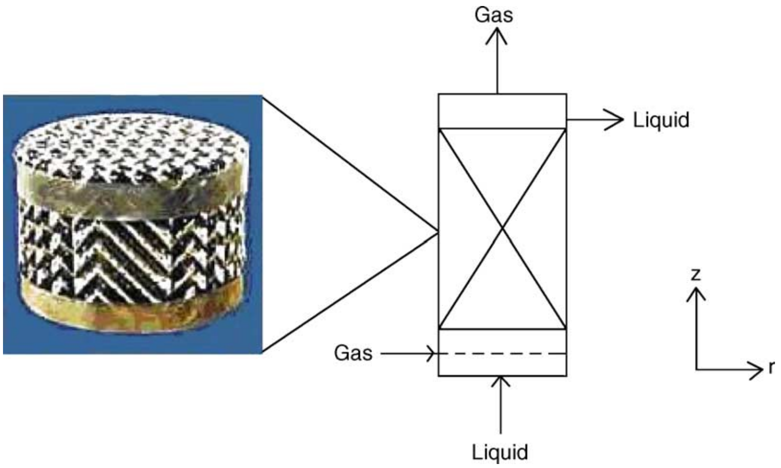

Fig. 1. Schematic of the structured bubble column reactor (SBCR).

170 °C. The heating fluid used for this purpose was a high temperature stable silicone oil (Silicex 322, Spain), circulated by a thermostatic bath (Haake, Germany). Initially the cold lignin solution is fed to the reactor. Mixing of the reactor contents is achieved by a Planetroll motor stirring at 1100 rpm. The temperature inside the reactor is measured by a thermocouple type K. Total pressure is measured with the help of a pressure transducer (Kulite, USA). The reactor is heated under nitrogen pressure up to the desired temperature. Nitrogen is added to the reactor till the pressure is 4–5 bar. Then oxygen is continuously introduced to maintain its desired partial pressure in the reaction system. The samples are collected at regular time intervals and vanillin concentration is measured by gas chromatography, as described by Hartley [15].

2.2. Residence time distribution (RTD) experiments

The bubble column used in the present study has a cylindrical jacketed main body with a diameter of 10 cm and a height of 66 cm, filled with three modules of a Sulzer Chemtech structured packing (Mellapak-750Y) to enhance mass transfer. This packing has been used by industry for over 20 years and has proved itself in performance. Fig. 1 depicts Mellapak-750Y structured packing. The upper part is kept empty, as in an ordinary bubble column. The column is also equipped with a perforated plate gas distributor that has seventeen holes of 0.5 mm diameter. The gas can be fed to the reactor as a mixture of N_2 and O_2, or pure streams. Flows are controlled by two mass flow controllers (Bronkhorst, Netherlands): 0–1 SLPM and 0–2 SLPM for O_2 and N_2, respectively. The gas inlet was divided into four equally distinct streams made of 1/8 in. tubes to provide a more homogeneous bubble distribution. The liquid was fed through a piston pump (Dosapro Milton Roy, USA) in the range of 1.3–13 l/h.

As it is a medium sized bubble column, the pulse duration was longer so that the tracer could be easily detected at the outlet. The column was filled with water at a given flow rate which resulted in a liquid phase velocity of 0.0228 cm/s. Nitrogen was bubbled through the reactor. Vanillin was used as a tracer with a pulse concentration of 42.653 mg/l and a duration of 246 s. Samples were collected at regular intervals at the column outlet, after the tracer had been injected. The purpose of this experiment is to understand the non-ideality of the bubble column. Vanillin concentration in the collected samples was measured spectrophotometrically at 348 nm.

3. Modeling

3.1. Batch reactor modeling

The following assumptions are made:

- The dissolved oxygen concentration in the solution was calculated from a semi-empirical correlation.
- The reactor is perfectly mixed.
- There is no mass transfer limitation from the gas to liquid phase.

3.1.1. Reaction kinetics

Reaction kinetics as developed by Mathias [16] is adopted for the present study. The following assumptions are made:

- The experimental kinetic study was based on the concentration of vanillin as a function of time, as it was neither possible to measure the concentration of lignin nor by-products of the oxidation.
- The dissolved oxygen concentration in the solution was calculated from a semi-empirical correlation.
- The lignin is composed of precursors (or nuclei N) that will create only vanillin.

- The lignin oxidation reaction into vanillin is irreversible.
- The production rate of vanillin is the same for all the fragments of lignin.
- The reactor is perfectly mixed.
- There is no mass transfer limitation from the gas to liquid phase.
- Isothermal operation.

3.1.2. Oxidation of lignin

Lignin + oxygen → vanillin

The reaction is carried out at high pH (pH >12) in 2 N NaOH solution.

The rate equation for vanillin production [17] can be written as:

$$r_1 = k_{\mathrm{NC}}[C_{\mathrm{O_2}}]^{1.75}[C_{\mathrm{Li}}] \tag{1}$$

$$k_{\mathrm{NC}} = 1.376 \times 10^7 \exp\left(-\frac{3502}{T}\right) \tag{2}$$

3.1.3. Oxidation of vanillin

Vanillin + oxygen → products

The rate equation for vanillin oxidation [18] can be written as:

$$r_2 = -k_{\mathrm{Cl}}[C_{\mathrm{O_2}}][C_{\mathrm{Va}}] \tag{3}$$

$$k_{\mathrm{Cl}} = 4.356 \times 10^6 \exp\left(-\frac{5530}{T}\right) \tag{4}$$

The overall rate of vanillin production can be written as:

$$r_3 = k_{\mathrm{NC}}[C_{\mathrm{O_2}}]^{1.75}[C_{\mathrm{Li}}] - k_{\mathrm{Cl}}[C_{\mathrm{O_2}}][C_{\mathrm{Va}}] \tag{5}$$

3.1.4. Dissolved oxygen concentration correlation

Mathias [16] proposed the following correlation:

$$C_{\mathrm{O_2}} = \Big(3.559 - 6.659 \times 10^{-3}T - 5.606P_{\mathrm{O_2}} + 1.594 \times 10^{-5}P_{\mathrm{O_2}}T^2 + 1.498 \times 10^3\frac{P_{\mathrm{O_2}}}{T})(10^{-0.144I})(10^{-3}) \tag{6}$$

3.1.5. Lignin mass balance

$$\frac{\mathrm{d}C_{\mathrm{Li}}}{\mathrm{d}t} = -k_{\mathrm{NC}}[C_{\mathrm{O_2}}]^{1.75}[C_{\mathrm{Li}}] \tag{7}$$

3.1.6. Vanillin mass balance

$$\frac{\mathrm{d}C_{\mathrm{Va}}}{\mathrm{d}t} = k_{\mathrm{NC}}[C_{\mathrm{O_2}}]^{1.75}[C_{\mathrm{Li}}] - k_{\mathrm{Cl}}[C_{\mathrm{O_2}}][C_{\mathrm{Va}}] \tag{8}$$

Initial conditions:

$$C_{\mathrm{Li}} = 0.0526\,\mathrm{mol/l}, \qquad C_{\mathrm{Va}} = 0\,\mathrm{mol/l} \tag{9}$$

3.2. Residence time distribution modeling

Fig. 1 is a schematic of the structured bubble column reactor (SBCR). The following two-dimensional convective diffusion equation is used to simulate the experimental RTD curve obtained from the structured bubble column. The mass balance equation is characterized by both axial and radial convective and dispersive terms.

$$\frac{\partial C}{\partial t} = D_z\frac{\partial^2 C}{\partial z^2} + D_{\mathrm{r}}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C}{\partial r}\right)\right] - u_z\frac{\partial C}{\partial z} - u_{\mathrm{r}}\frac{\partial C}{\partial r} \tag{10}$$

Initial conditions:

$$C = 0$$
$$C_{\mathrm{in}} = \begin{cases} 42.653\,\mathrm{mg/l}, & \text{for } 0 < t < t_{\mathrm{imp}} \\ 0, & \text{for } t > t_{\mathrm{imp}} \end{cases} \tag{11}$$

Boundary conditions:

$$uC_{\mathrm{in}} = uC - D_{\mathrm{ax}}\frac{\partial C}{\partial z} \quad \text{at } z = 0 \tag{12}$$

$$\frac{\partial C}{\partial z} = 0 \quad \text{at } z = L$$

$$\frac{\partial C}{\partial r} = 0 \quad \text{at } r = 0$$

$$\frac{\partial C}{\partial r} = 0 \quad \text{at } r = R$$

The radial and axial velocity components are calculated as follows:

$$u_z = u\sin(45^\circ) \tag{13}$$

$$u_r = u\cos(45^\circ) \tag{14}$$

3.3. Structured bubble column reactor modeling

3.3.1. Mass balance

A mass balance for lignin and vanillin in the reactor yields the following continuity equations. Both axial and radial convective and dispersive terms are taken into consideration. Cylindrical coordinates are used.

Lignin:

$$\frac{\partial C_{\mathrm{Li}}}{\partial t} + u_z\frac{\partial C_{\mathrm{Li}}}{\partial z} + u_{\mathrm{r}}\frac{\partial C_{\mathrm{Li}}}{\partial r} = D_z\frac{\partial^2 C_{\mathrm{Li}}}{\partial Z^2} + D_{\mathrm{r}}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{\mathrm{Li}}}{\partial r}\right)\right] - r_1 \tag{15}$$

where r_1 is the rate of disappearance of lignin.

Vanillin:

$$\frac{\partial C_{\mathrm{Va}}}{\partial t} + u_z\frac{\partial C_{\mathrm{Va}}}{\partial z} + u_{\mathrm{r}}\frac{\partial C_{\mathrm{Va}}}{\partial r} = D_z\frac{\partial^2 C_{\mathrm{Va}}}{\partial Z^2} + D_{\mathrm{r}}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial C_{\mathrm{Va}}}{\partial r}\right)\right] + r_3 \tag{16}$$

where r_3 is the effective rate of vanillin production.

Initial conditions:

$$C_{\mathrm{Li}} = 0.0526\,\mathrm{mol/l}, \qquad C_{\mathrm{Va}} = 0 \tag{17}$$

Boundary conditions are the same as those presented in Eq. (12).

The high heat capacity of the liquid phase and its favorable heat transfer properties ensure temperature equilibrium within the reactor. Hence, isothermal operation is assumed.

3.3.2. Gas phase

Dissolved oxygen concentration in the reactor is assumed to be uniform throughout the column and is given by the following correlation, i.e. Eq. (6). Dissolved oxygen is responsible for the lignin oxidation.

3.4. Numerical solution

All the model equations with relevant initial and boundary conditions were solved using gPROMS software package [19]. It is used for modelling and simulation of processes with both discrete and continuous as well as with lumped and distributed characteristics. A third order orthogonal collocation on finite elements method (OCFEM) was used for this purpose. Backward finite difference method (BFDM) is used for the axial domain. Two elements were used in the axial domain with 10 collocation points. Three finite elements were used in the radial domain with five collocation points. All simulations were performed on a Pentium IV processor with 512 MB RAM. Simulation parameters for batch reactor are shown in Table 1. Table 2 gives simulation parameters for SBCR model.

4. Results and discussion

4.1. Batch reactor

Optimisation exercise was carried out with the following parameters as variables: lignin concentration, lignin molecular weight, partial pressure of oxygen, reaction temperature. Fig. 2 shows the curve fit obtained for the vanillin yield curve. The following experimental conditions were maintained: $C_{\mathrm{Li}} = 0.0526$ mol/l (60 g/l, MW = 1141), $T = 393$ K (120 °C), $P_{\mathrm{O_2}} = 3.6$ atm. Lignin was dissolved in 4 N NaOH. Vanillin concentration is reasonably predicted qualitatively.

Table 1
Simulation parameters for batch reactor

S.no.	Parameter (units)	Value
1	Partial pressure of oxygen (atm)	4
2	Temperature (K)	393
3	Ionic strength (I) (N)	2
4	MW of lignin (g/mol)	1141
5	Volume (l)	0.5

Table 2
Simulation parameters for SBCR model

S.no.	Parameter (units)	Value
1	L (cm)	66
2	C_{Li} (mol/l)	0.0526
3	ε_{L}	0.863
4	ε_{G}	0.1
5	ε_{S}	0.037
6	u (cm/s)	0.00232
7	u_z (cm/s)	0.00164
8	u_{r} (cm/s)	0.00164
9	D_{r} (cm^2/s)	0.1
10	D_z (cm^2/s)	0.2
12	$P_{\mathrm{O_2}}$ (atm)	4
13	T (K)	393

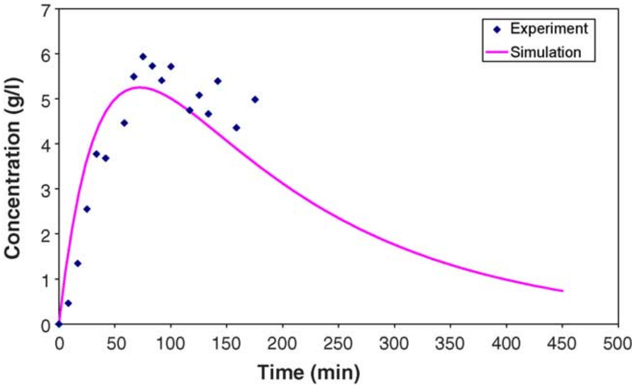

Fig. 2. Base case vanillin yield curve ($C_{\mathrm{Li}} = 0.05256$ mol/l (60 g/l, MW = 1141), $T = 393$ K (120 °C), $P_{\mathrm{O_2}} = 3.6$ atm). Experimental data by Mathias [16].

The effect of initial lignin concentration on vanillin yield is displayed in Fig. 3. Experimental conditions are: $C_{\mathrm{Li}} = 0.0263$ mol/l, $P_{\mathrm{O_2}} = 3.8$ atm. Lignin concentration is 30 g/l (MW = 1141), $T = 393$ K. As the initial lignin concentration is reduced, there is less vanillin yield. It is to be noted that though the simulation results show that higher initial concentrations of lignin yield higher vanillin yields, it

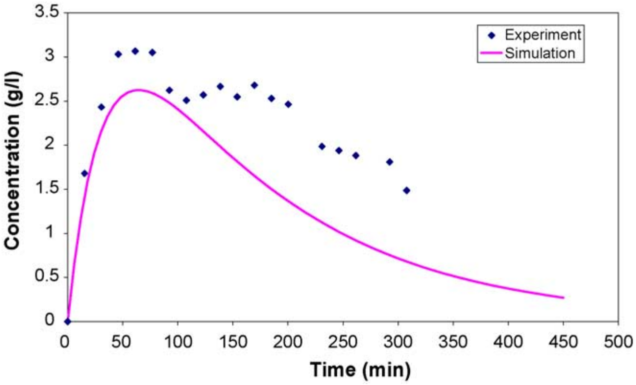

Fig. 3. Vanillin yield curve for an initial lignin concentration of 30 g/l ($C_{\mathrm{Li}} = 0.0263$ mol/l (30 g/l, MW = 1141), $T = 393$ K (120 °C), $P_{\mathrm{O_2}} =$ 3.6 atm). Experimental data by Mathias [16].

has been found to be untrue. Sixty grams per liter of initial lignin concentration gave an optimum vanillin yield.

The properties of the macromolecules made soluble reflect the properties of the network from which they are derived. Lignin in the true middle lamella of wood is a random three-dimensional network polymer comprised of phenyl–propane monomers linked together in different ways. Lignin in the secondary wall is a non-random two-dimensional network polymer. The chemical structure of the monomers and linkages, which constitute these networks differ in different morphological regions (middle lamella versus secondary wall), different types of cell (vessels versus fibers), and different types of wood (soft woods versus hard woods) [20]. The lignin is composed of precursors (or nuclei N) that will create only vanillin. NMR of the lignin samples could be done to determine the quantity of these precursors. It could be imagined that the amount of precursors and the amount of lignin may have a linear proportion. Instead of basing the kinetics on moles of lignin basis, it is interesting to base the calculations on precursor moles.

Fig. 4 is a fit obtained for a lignin whose molecular weight is 3050. Initial conditions: $C_{\mathrm{Li}} = 0.02$ mol/l, T = 393 K (120 °C), $P_{\mathrm{O}_2} = 6.5$ atm. The vanillin concentration peaked quickly. Higher partial pressures of oxygen leads to more dissolved oxygen concentration, which in turn leads to better vanillin production. But the dissolved oxygen in turn oxidizes vanillin to further products. The overall yield of vanillin decreases. It is recommended to go in for lower operating pressures. The simulation results are shown in the form of smooth lines. The one, which gave a good fit was simulated using a lignin concentration of 0.02 mol/l, other conditions remaining the same.

As the molecular weight of lignin is more, the lesser the vanillin yield. It is essential that lower molecular weight lignin is used for the oxidation reaction. Lower molecular weight lignins could contain more amounts of precursors which are responsible for vanillin yield. The lignins used in the experimental studies are from different lots, though from the same supplier, i.e. MeadWestvaco, North Charleston, South Carolina, USA. The molecular weights of lignin are: 1141 and 3050. These molecular weights were measured by high-performance liquid chromatography (HPLC). After acidification and extraction with THF, 20 μl of sample solution was injected into the chromatograph using Shodex AC802/S (8 mm × 250 mm) column. The column was then eluted with THF flow-rate of 1 ml/min The molecular weights were determined relative to toluene and polystyrene that were used as standards.

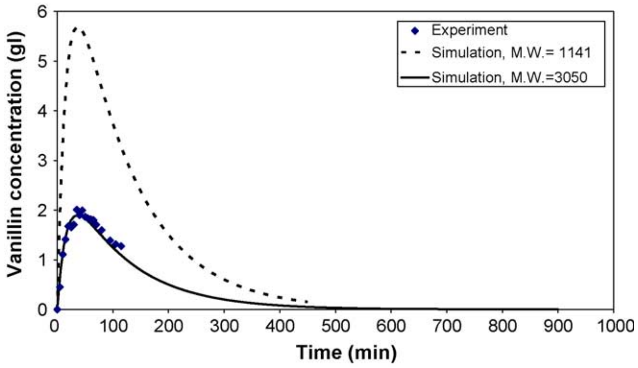

Fig. 4. Effect of lignin molecular weight on the yield of vanillin ($C_{\mathrm{Li}} = 0.02$ mol/l (60 g/l, MW = 3050), T = 393 K (120 °C), $P_{\mathrm{O}_2} = 6.5$ atm). Experimental data by Araujo [21].

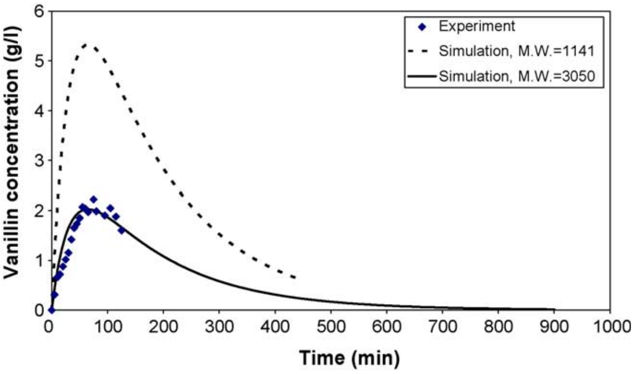

Fig. 5. Effect of oxygen partial pressure on vanillin yield (Li = 0.02 mol/l, T = 393 K (120 °C), $P_{\mathrm{O}_2} = 4$ atm). Experimental data by Araujo [21].

Fig. 5 shows the effect of partial pressure on the yield of vanillin for a lignin with a MW of 3050. Initial conditions: $C_{\mathrm{Li}} = 0.02$ mol/l, T = 393 K (120 °C), $P_{\mathrm{O}_2} = 4$ atm. The vanillin concentration reached it's peak somewhat slowly compared to that of the previous curve. At lower pressures, the degradation of vanillin into by-products is less compared to that at higher pressures. The simulation results are shown in the form of smooth lines. The one, which gave a good fit was simulated using a lignin concentration of 0.02 mol/l, other conditions remaining the same.

With this information in hand, it is desired to see what happens when the lignin oxidation is carried out in a continuous reactor such as a structured bubble column reactor. In this direction, RTD experiments were carried out to see if any non-idealities exist in the SBCR. In the next section, the modelling of RTD in a SBCR is presented.

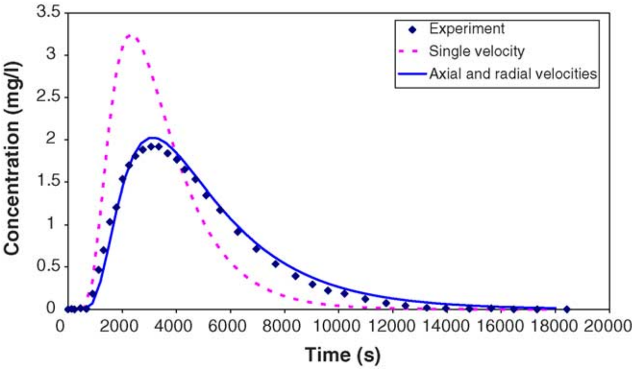

Fig. 6. Comparison of RTD data for tracer experiment. Experimental data by Araujo [21].

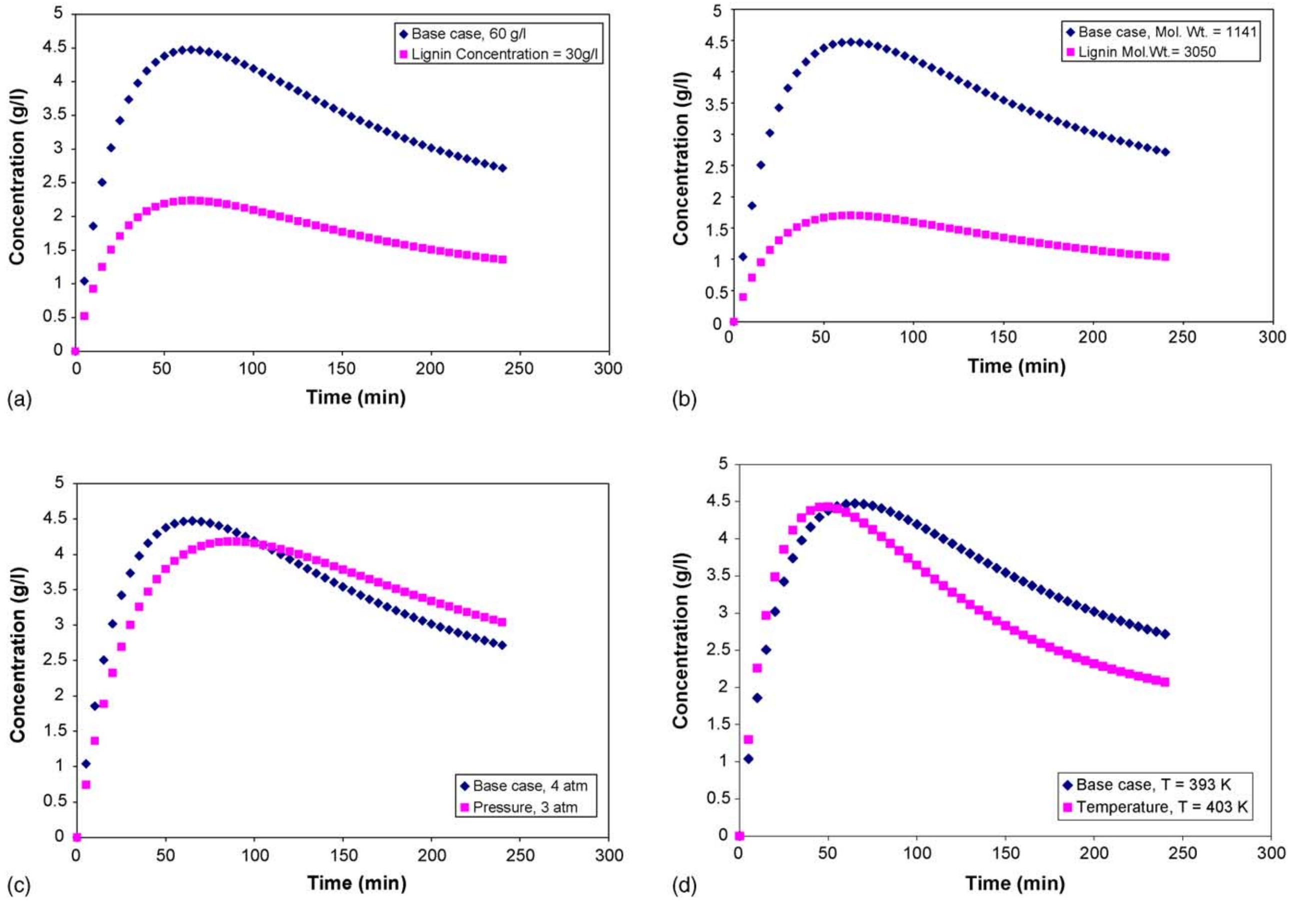

Fig. 7. (a) Effect of lignin concentration and (b) effect of lignin molecular weight on the yield of vanillin in a SBCR. (c) Effect of oxygen partial pressure on the production of vanillin in a SBCR. (d) Effect of reaction temperature on the yield of vanillin in a SBCR.

4.2. RTD studies

Fig. 6 shows the curve fit obtained by simulating the tracer experiment: liquid phase velocity is 0.0228 cm/s, pulse concentration is 42.653 mg/l, with a duration of 246 s. Gas phase flow rate is 0.25 l/min. Tracer experimental data are simulated with $u_z = u_r = 0.0161$ cm/s, $D_z = 0.2$ cm^2/s and $D_r = 0.1$ cm^2/s.

These simulations are carried out by considering the radial and axial velocity components of the fluid. The bubble velocity seems to affect the RTD curves. The geometry of the packing suggests that there are radial and axial velocity components. As a starting point, it is assumed that both axial and radial velocities are equal. The experimental data are in terms of symbols. The simulated data are represented by smooth curves. The dashed line curve with a higher peak height is the simulation result considering only axial velocity, which is equal to the liquid phase velocity. Mellapak-750Y has a void fraction of 0.963.

4.3. Structured bubble column reactor

The effect of the following parameters on the yield of vanillin had been studied: lignin concentration, lignin molecular weight, oxygen partial pressure and reaction temperature.

Fig. 7(a) shows the effect of lignin concentration on the yield of vanillin. The base case curve is simulated using $C_{\mathrm{Li}} = 0.0526$ mol/l (60 g/l, MW = 1141), $T = 393$ K (120 °C), $P_{\mathrm{O_2}} = 4$ atm, $u = 0.00232$ cm/s. The vanillin concentration is plotted on the ordinate in terms of g/l (MW of vanillin = 152.15). The above parameters were arrived at through simulation. The vanillin yield is comparable to that of the batch reactor. The vanillin yield in the SBCR can match that of batch reactor in cases of longer residence times. A compromise should be arrived at in which case the residence time is not very long. This time was found to be around 8 h. It is to be noted that though the simulation results show that higher initial concentrations of lignin yield higher vanillin yields, it has been found to be untrue in the case of batch reactors. Sixty grams per liter of initial lignin concentration gave an optimum vanillin yield.

The effect of lignin molecular weight on the yield of vanillin is shown in Fig. 7(b). The base case curve is simulated using $C_{\mathrm{Li}} = 0.0526$ mol/l (60 g/l, MW = 1141), $T = 393$ K (120 °C), $P_{\mathrm{O_2}} = 4$ atm, $u = 0.00232$ cm/s. Lower molecular weight lignin seems to contain more amounts of precursors which are responsible for the vanillin yield.

The effect of oxygen partial pressure on the production of vanillin is shown in Fig. 7(c). The base case curve is generated using the following conditions: $C_{\mathrm{Li}} = 0.05256$ mol/l, $T = 393$ K (120 °C), $P_{\mathrm{O}_2} = 4$ atm, $u = 0.00232$ cm/s. At lower pressures, the oxygen solubility is less compared to that at higher pressures. Hence, the vanillin yield is lower. But the higher the oxygen solubility due to higher pressure, vanillin oxidation results in reduced vanillin yield.

Fig. 7(d) shows the effect of temperature on the yield of vanillin. $C_{\mathrm{Li}} = 0.0526$ mol/l, $T = 403$ K (130 °C), $P_{\mathrm{O}_2} = 4$ atm, $u = 0.00232$ cm/s. As the temperature is raised, the rate of reaction increases. Also, the dissolved oxygen concentration is reduced, which will lessen the vanillin oxidation to by-products. This is the situation in the initial stages. As the reaction progresses, the vanillin oxidation results in less vanillin yield in the case of higher temperature.

5. Conclusions

Vanillin production in a batch reactor has been successfully modeled. The effect of the following parameters on the yield of vanillin had been studied: lignin concentration, lignin molecular weight, and oxygen partial pressure. Armed with this information, the modeling of RTD and vanillin yield in a SBCR are carried out.

Compared with a bubble column reactor, we may conclude that operation of a structured bubble column reactor has the advantage of a reduced back-mixing of the liquid phase. Moreover, in contrast to a bubble column, the superficial velocity in a SBCR, can be varied in a broad range, without significant change in the axial dispersion.

Though one-dimensional axial dispersion model (ADM) was sufficient to model dispersion in small bubble columns without internals, it cannot predict the dispersion in columns with internals. A two-dimensional model, taking into account a radially dependent axial velocity profile, and both axial and radial dispersion, is required to account for the internals on liquid mixing.

The model simulations show that the effective velocity concept is very important in dealing with structured bubble column reactor models. These effective velocities could be used in predicting the vanillin yield also. Gas phase velocity seems to affect the shape of the RTD curves, i.e. dispersion. The curve fitted with a single effective velocity could not give better result. This is an indication that both axial and radial velocities exist in equal magnitude in Mellapak-750Y packing.

Finally, simulation is an essential part of effective experimentation. In this direction, the simulations presented in this manuscript could lead to an optimal selection of the operating parameters for SBCRs.

Acknowledgement

P. Sridhar gratefully acknowledges financial support from FCT (SFRH/BPD/14996/2004).

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