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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.