

Captions to Figures

Scheme 1: Scheme of the reactor solid/gas. The enzyme in the solid state is packed between two glass wool layers in a glass tube and constitutes a fixed bed, in the second thermostated oven. This bed is percolated by gaseous nitrogen, which simultaneously carries gaseous substrates and removes reaction products. The gaseous stream is formed in the first oven, that includes four lines of nitrogen regulated by flowmeters; three of them are used for the saturation of flasks containing substrates and possibly an additional non-reactant component. It is assumed that in each line, the carrier gas after bubbling in a flask, is in equilibrium with the liquid and that the partial pressure of the substrate in the gas leaving the flask is equal to the bubble point pressure above the pure compound. The three lines are then mixed together with the fourth one which is used for the adjustment of the total molar flow and of the partial pressure of the different component in the final gas. After mixing of all lines the thermodynamic activity of each compound in the microenvironment of the enzyme can be calculated.

The gas leaving the reactor is injected in a gas chromatograph and all parameters are monitored on-line by a computer.

Figure 1: The kinetic resolution of racemic pentan-2-ol through acylation using methyl propanoate, methyl butanoate, methyl hexanoate, methyl isobutanoate and methyl decanoate ($n=1,2,3,4,5$) as acylating agent and *Candida antarctica* lipase B (CaLB) catalyst.

Figure 2:

(A)-Effect of acyl donor and temperature on enantioselectivity of immobilized CaLB (Novozym 435[®]) in kinetic resolution of pentan-2-ol through acylation reaction in continuous

solid/gas reactor, with different methyl esters. (*R*)-enantiomer is the preferred one except with methyl isobutanoate as acyl donor at 100°C. Standard deviations were calculated using three values of enantiomeric ratio (*E*). (B) Effect of acyl donor and temperature on enantioselectivity of free CaLB (Lipozyme[®]) in kinetic resolution of pentan-2-ol through acylation reaction in a continuous solid/gas reactor, with different methyl esters. (*R*) is the preferred enantiomer. Standard deviations were calculated using three values of activity and of enantiomeric ratio (*E*).

Figure 3:

(A) Effect of imprinting on enzyme enantioselectivity in the kinetic resolution of pentan-2-ol in continuous solid/gas reactor. Immobilized CaLB (Novozym 435[®]) was co-dried with (*R*)-2-aminohexane, (*S*)-2-aminohexane or 1-aminohexane, using methyl propanoate as acyl donor and at 70°C. Standard deviations were calculated using three values of enantiomeric ratio (*E*). (B) Effect of imprinting on enzyme activity in the kinetic resolution of pentan-2-ol in continuous solid/gas reactor. Immobilized CaLB (Novozym 435[®]) was co-dried with (*R*)-2-aminohexane, (*S*)-2-aminohexane or 1-aminohexane, using methyl propanoate as acyl donor and at 70°C. Standard deviations were calculated using three values of activity.

Figure 4:

Effect of sol-gel immobilization of free CaLB on enzyme enantioselectivity in the kinetic resolution of pentan-2-ol in continuous solid/gas reactor and of the addition of (*R*)-2-aminohexane, (*S*)-2-aminohexane or 1-aminohexane, with methyl propanoate as acyl donor and at 70°C. Standard deviations were calculated with three values of activity and of enantiomeric ratio (*E*).

Figure 5: Synthesis pathway of the *meso*-symmetric diol (7) from the commercial cycloocta-1,2-diene in two steps : epoxidation followed by ring opening in acidic conditions

Figure 6: Enantioselective acylation of *meso*-symmetric diol (7) using vinyl ethanoate, vinyl propanoate and vinyl butanoate as the acylating agents ($n=0,1,2$) and (A) free or immobilized CaLB (Novozym 435[®]) catalyst and (B) free or immobilized BC Lipase catalyst.