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Microwave-assisted synthesis of ethyl hexanoate following a Ping-Pong Bi-Bi kinetics with inhibition by both substrates

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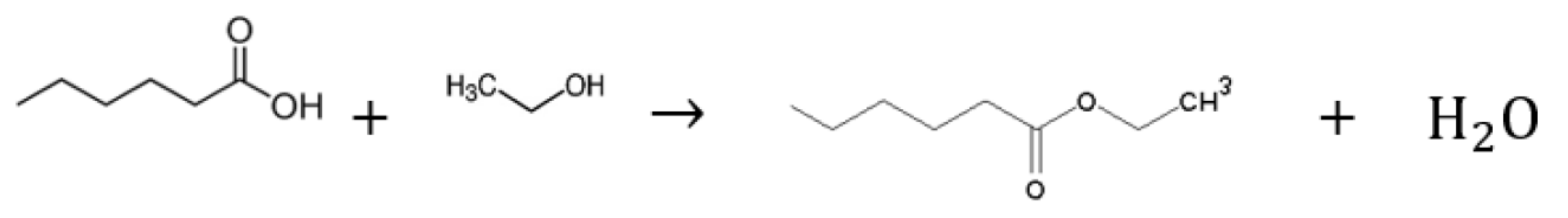
The reaction



$$C_6H_{12}O_2 \;+\; C_2H_6O \xrightarrow{enzyme} C_8H_{16}O_2 \;+\; H_2O$$

$$A \;+\; B \xrightarrow{enzyme} P \;+\; W$$

- Optimum conditions to carry out this reaction, whose rate equation can be described by the Ping Pong Bi Bi mechanism, are reached when temperature is around 50 °C, enzyme dose is about the 2% w/w and molar ratio acid to alcohol is 1:3

- Since the reaction is endothermic (ΔHr = 23000 J/mol), a microwave heating is provided to prevent its shutdown. Microwaves allow to maintain the temperature in an optimal range for enzymes and they can be successfully used in organic synthesis to reach high conversions

Modeling and Simulation

$$-2v_z\frac{\partial C_A}{\partial z}+\mathfrak{D}\frac{\partial^2 C_A}{\partial z^2}+\mathfrak{D}\left(\frac{1}{r}\frac{\partial C_A}{\partial r}+\frac{\partial^2 C_A}{\partial r^2}\right)-(-r_A)=\frac{\partial C_A}{\partial t}$$

$$-2\rho c_p v_z\frac{\partial T}{\partial z}+k\frac{\partial^2 T}{\partial z^2}+k\left(\frac{1}{r}\frac{\partial T}{\partial r}+\frac{\partial^2 T}{\partial r^2}\right)-(-r_A)(-\Delta H_r)+\pi f\varepsilon_0\varepsilon''|E_z|^2=\rho c_p\frac{\partial T}{\partial t}$$

$$(-r_A)=\frac{(-r_A)_{max}C_AC_B}{C_AC_B+k_BC_A\left(1+\frac{C_A}{k_{iA}}\right)+k_AC_B\left(1+\frac{C_B}{k_{iB}}\right)}$$

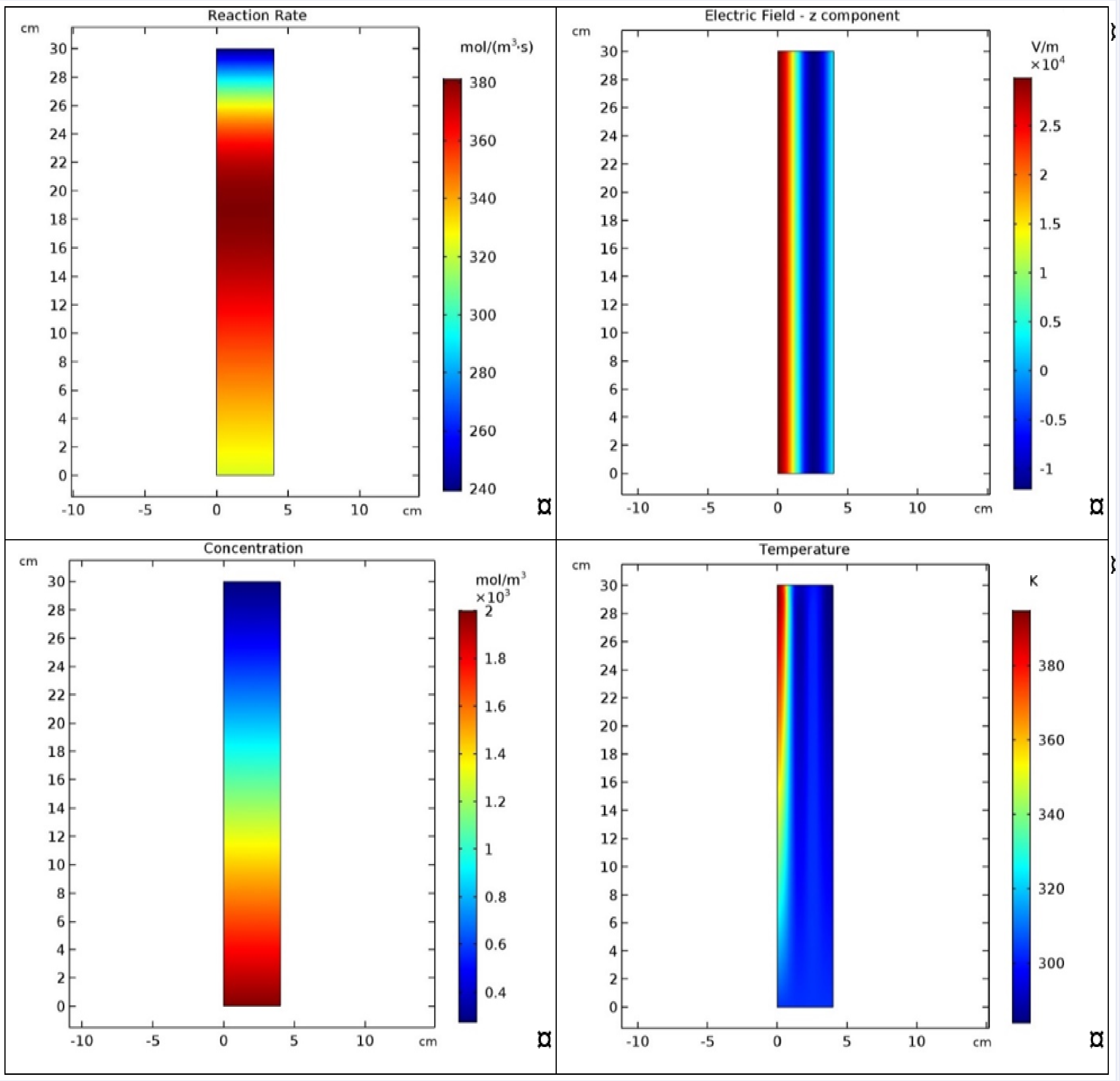
$$\frac{1}{r}\frac{\partial E_z}{\partial r}+\frac{\partial^2 E_z}{\partial r^2}+k^2E_z=0$$

$t=0$	$C_A=0$	$T=T_0$		$\forall r,\forall z$
$r=0$	$\frac{\partial C_A}{\partial r}=0$	$\frac{\partial T}{\partial r}=0$	$\frac{\partial E_z}{\partial r}=0$	$\forall z,\forall t>0$
$r=R$	$\frac{\partial C_A}{\partial r}=0$	$\frac{\partial T}{\partial r}=0$	$E_z=E_{z0}$	$\forall z,\forall t>0$
$z=0$	$C_A=C_{A0}$	$T=T_0$	$E_z=0$	$\forall r,\forall t>0$
$z=L$	$\frac{\partial C_A}{\partial z}=0$	$\frac{\partial T}{\partial z}=0$	$E_z=0$	$\forall r,\forall t>0$

Solved with the
Finite Element Methods

COMSOL MULTIPHYSICS®

Results



Conclusion

The concentration follows the decay typically observed in a PFR reactor; the reaction rate increases from the inlet until a maximum (due to the substrate inhibition at high concentration) and then it decreases until the outlet section. Both the endothermicity of the reaction and the microwave heating, that play in an opposite way, affect the temperature, keeping it in an acceptable range to let the enzyme work. However, temperature profile is strongly uneven, mainly due to the electric field distribution.

Bibliography (References)

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