

Preliminary Model of a Packed Bed Oxidation Reactor



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Introduction

This study was carried out at EuroResinas – Indústrias Químicas, S.A., of group Sonae Indústria, at Sines Portugal. The company trades formaldehyde-based resins, where the formaldehyde is also produced at the industrial unit by partial oxidation of methanol in a packed bed multitubular reactor using an iron-molybdenum oxide catalyst. As it is typical in very exothermic reactions, to avoid hot-spots the catalyst is mixed with inert, followed by pure catalyst layers at the end to improve conversions (Figure 1.). The top and the bottom layers are filled with inert rings to improve the heat transfer between the boiling heat transfer fluid (HTF) and the incoming reaction mixture, as well as between the HTF and the exit gas.

In this study a one-dimensional pseudo-homogeneous model was developed in *gPROMS® Model Builder* and the simulation temperature profiles compared with data from the industrial reactor.

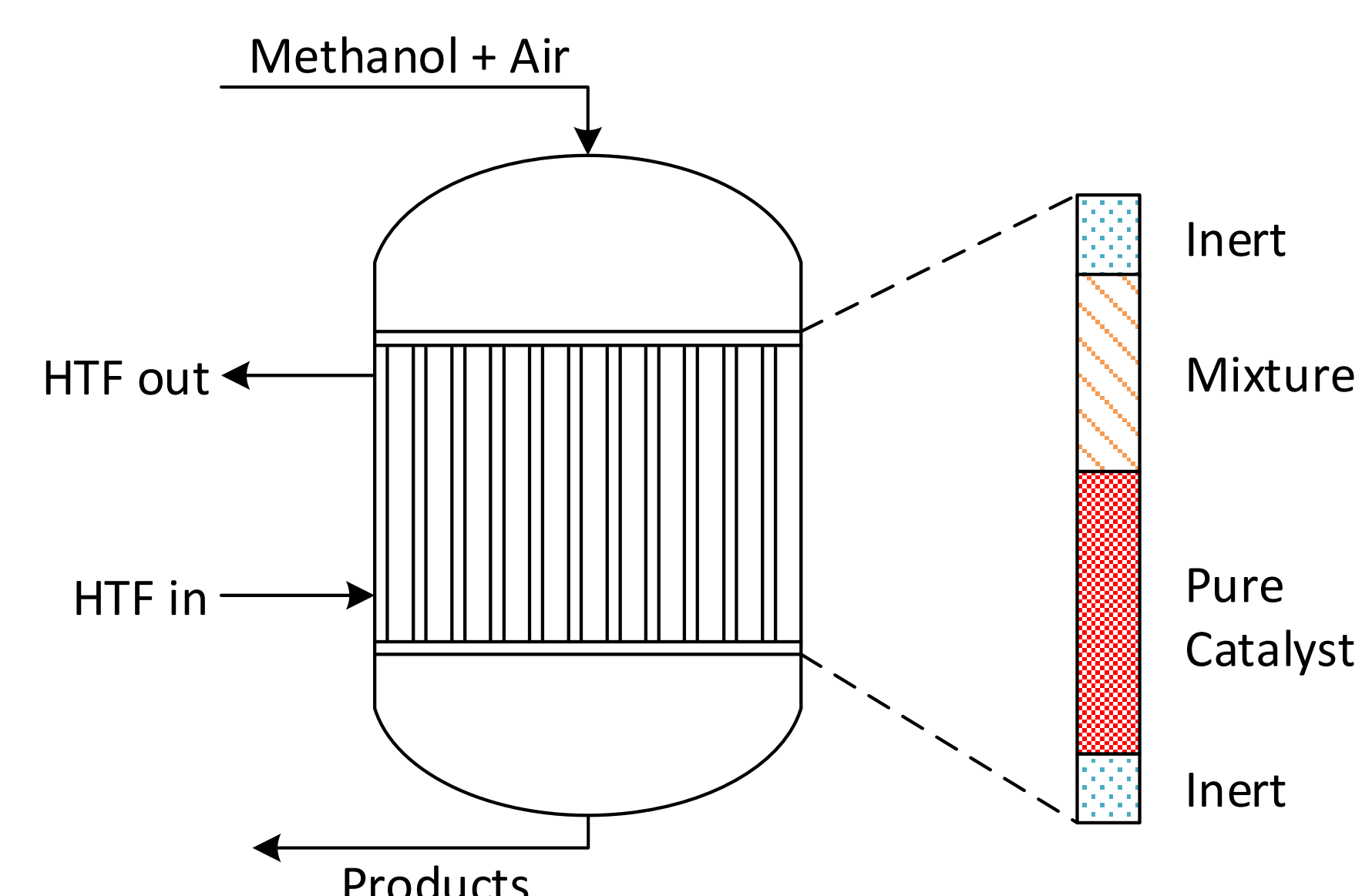
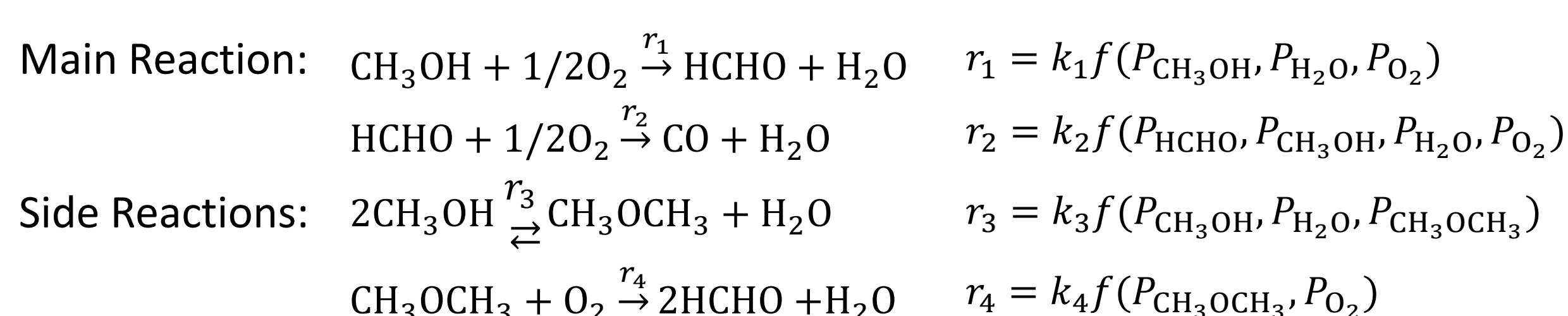


Figure 1. Scheme of the catalyst layers distribution inside the industrial reactor tubes.

Model Description

The gas-phase partial oxidation reaction of methanol is defined by the following reactions



$$k_j = k_{0,j} \exp\left(-\frac{E_{a,j}}{RT}\right), \text{ for } j = 1, \dots, 4$$

The reaction rate equations used in this work are reported in Deshmukh et al.^[1].

Conservation equations for mass and energy are defined as:

Mass Balance: $\frac{dF_i}{dz} = A_s \rho_{bed} \sum_{j=1}^4 v_{i,j} r_j$

Energy Balance: $\sum_{i=1}^6 F_i C_{p,i} \frac{dT}{dz} = \pi d_t U (T_c - T) - A_s \rho_{bed} \sum_{j=1}^4 \Delta H_{r,j} r_j$

The pressure drop along the reactor is neglected and the partial pressures P_i of the components are calculated assuming the ideal gas behavior. The specific heat capacities $C_{p,i}$ were calculated using the Shomate equation and the cooling HTF's temperature T_c is constant. U describes the overall heat transfer coefficient that was considered to be constant. Using the kinetic information reported by Deshmukh et al.^[1] the first simulation results shown in Figure 2.

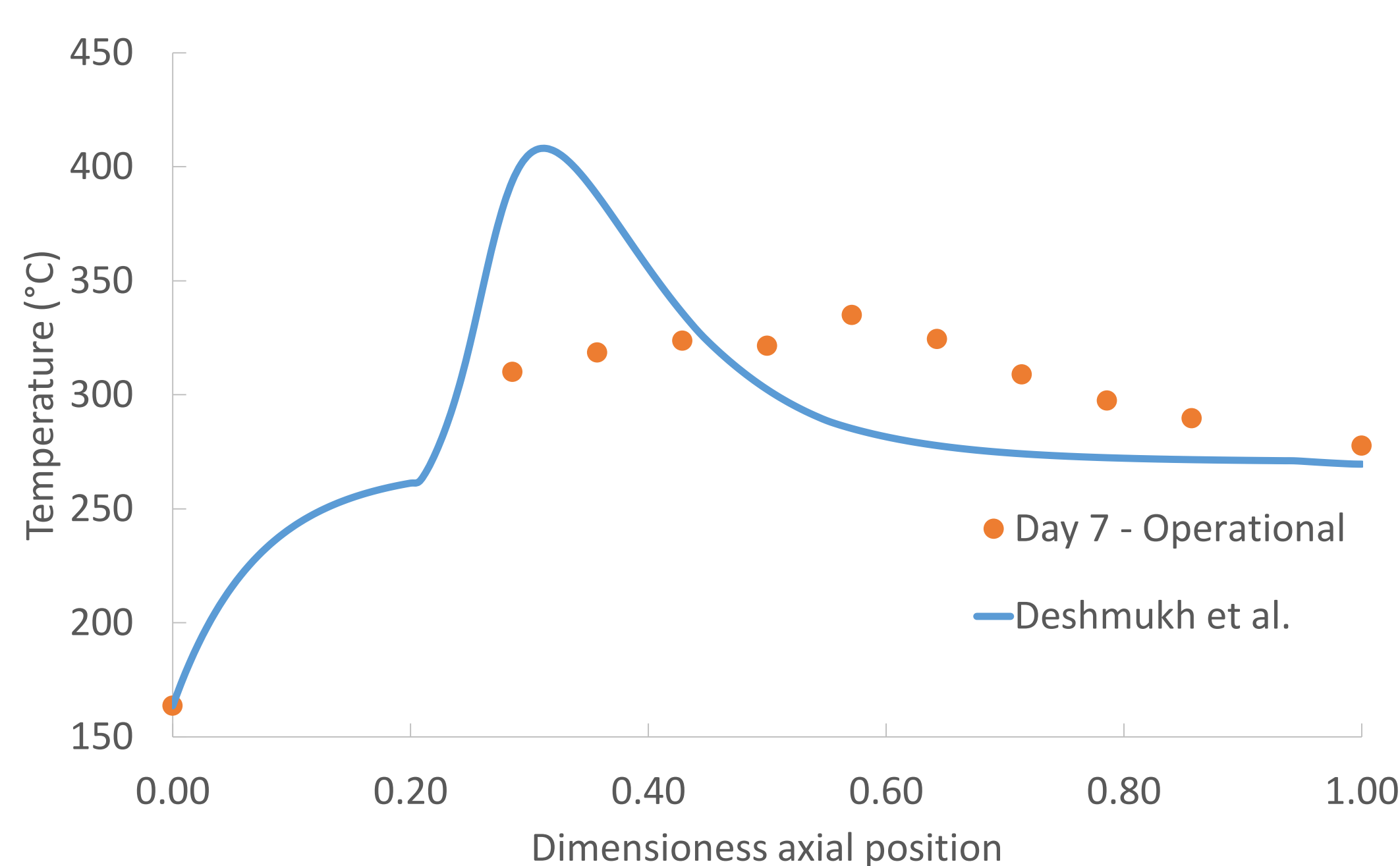


Figure 2. First reactor simulation using the kinetic constants from [1].

The model predictions present a significant deviation from the operational data of the industrial reactor, therefore new kinetic constants ($k_{0,j}$; $E_{a,j}$), as well as a new U , were estimated using *gPROMS®* Parameter Estimation tool.

Parameter Estimation

The parameters were adjusted to four sets of temperatures inside the reactor, corresponding to four operating days, after the fresh catalyst start-up. It was assumed that during this time there was no catalyst deactivation. The results are presented in Table 2 and Figure 3.

Table 1. Operational days used in the estimation of the model parameters.

Operating Day	Methanol Flow F1>F2	Inputs
7	F1	F_i (mol/s)
13		T_{in} (K)
21	F2	T_c (K)
29		$T(z)$ (K)

Table 2. Estimated Values.

Estimated Parameter	Value	Estimated Parameter	Value
$k_{0,1}$	$6.5 \times 10^5 \text{ mol kg}^{-1} \text{ s}^{-1}$	$E_{a,1}$	64.8 kJ mol^{-1}
$k_{0,2}$	$5.0 \times 10^3 \text{ mol kg}^{-1} \text{ atm}^{-1} \text{ s}^{-1}$	$E_{a,2}$	51.6 kJ mol^{-1}
$k_{0,3}$	$4.2 \times 10^6 \text{ mol kg}^{-1} \text{ atm}^{-1} \text{ s}^{-1}$	$E_{a,3}$	$240.6 \text{ kJ mol}^{-1}$
$k_{0,4}$	$3.8 \times 10^7 \text{ mol kg}^{-1} \text{ s}^{-1}$	$E_{a,4}$	$166.7 \text{ kJ mol}^{-1}$
U	$112.8 \text{ W m}^{-2} \text{ K}^{-1}$		

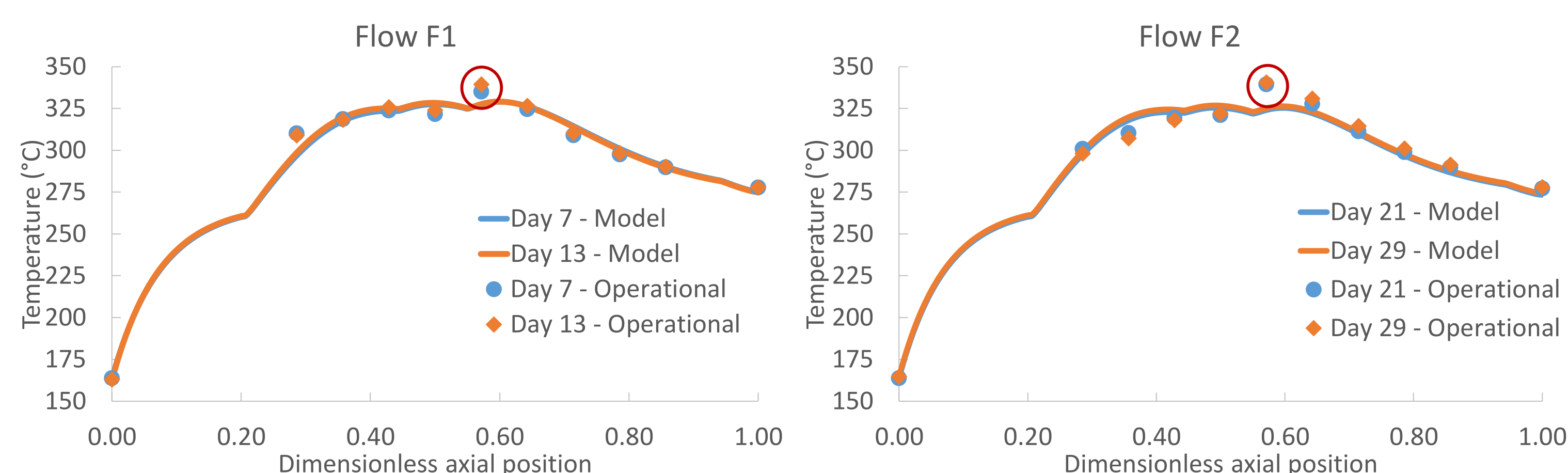


Figure 3. Temperature profiles obtained with the estimated parameters.

The simulation results showed a relative average deviation for the four days below 2 % from the operational data. Moreover, the model was able to reproduce the influence of the different catalyst layers in the reactor temperature profile, but presented a slight difference between the experimental and model temperatures at the hot-spot position.

Axial overall heat transfer coefficient $U(z)$

The next attempt to improve the reactor model was to calculate an overall heat transfer coefficient as a function of the axial position of the reactor. Dixon et al.^{[2][3]} proposed the following equation to calculate U as a function of the wall heat transfer coefficient, h_w , the effective radial thermal conductivity of the catalyst bed, k_r , and the reactor diameter, d_t .

$$\frac{1}{U} = \frac{1}{h_w} + \frac{d_t}{6k_r} \frac{\text{Bi} + 3}{\text{Bi} + 4}$$

New kinetic parameters were estimated (PE 2) and the resulting temperature profile is presented in Figure 4. Table 3 shows the results summary for the simulation of operational day 7. The inclusion of an axial U reduces the average deviations, but with a great decrease in the reaction yield.

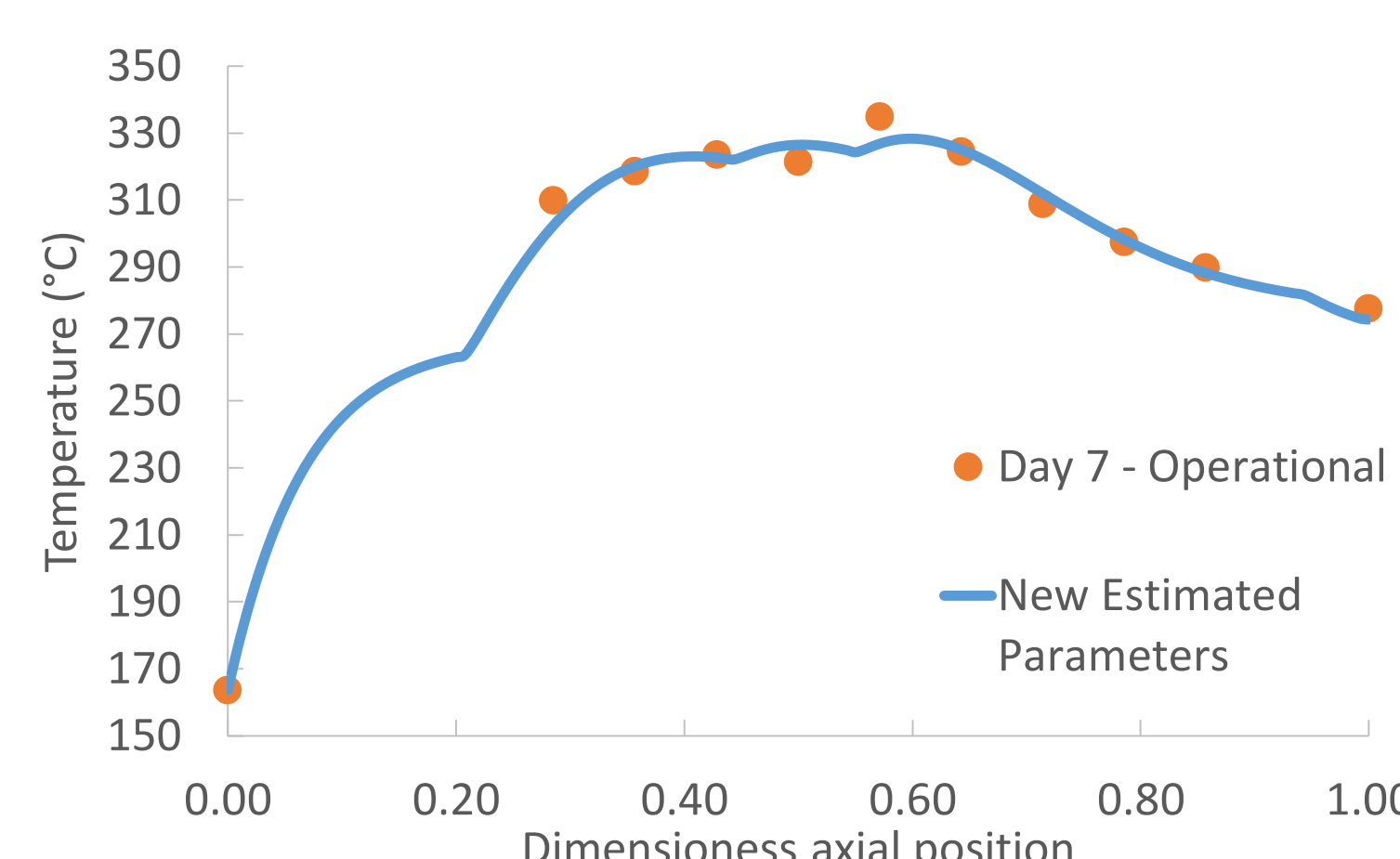


Figure 4. Temperature profiles obtained with new estimated parameters.

Table 3. Day 7 results summary

	Deshmukh	PE 1	PE 2
Av. Dev. (%)	11.6	1.3	1.0
Conv. (%)	98.7	92.8	93.2
Yield (%)	96.2	93.0	65.0

Conclusions and Future Work

- A one-dimensional model for the partial oxidation reaction of methanol was developed and a good correlations with the industrial reactor temperature profile was achieved based on parameter estimations.
- The lack of information relatively to the composition of the outlet stream of the reactor adds great difficulty in the development of a more reliable model of the process.
- The next step will include the catalyst deactivation in the reactor model. This effect will be described by a factor that depends on the different bed properties and temperatures along the reactor length

References

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