Multiphysics Simulation of a Packed Bed Reactor

Alfredo E Varela* and Juan C García
University of Carabobo, Valencia, Venezuela 2001
*Email: avarela@uc.edu.ve

Abstract: Most reactor designs are based on pseudo homogeneous models. This paper studies the COMSOL simulation of a packed bed reactor using a 2-D heterogeneous model. The inter-pellet regions have been approximated with uniform gaps representing uniform void fraction, in consideration of the problems on mesh quality and limitations in memory capacity for a high number of degree of freedom. The case considered was a packed reactor with spherical catalyst for oxidation of o-xylene in air to phthalic anhydride. Large differences in intra-pellet temperature were found in comparison with the average temperatures resulting from simulations reported in the literature using a pseudo homogeneous model.

Keywords: Packed-bed reactor, COMSOL, 2-D model.

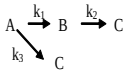
1. Introduction

Packed-bed reactors are employed in the petrochemical and oil refinery industries for a large variety of catalytic processes, ranging from cracking, hydrogenation, dehydrogenation, polymerization to oxidative synthesis. The reactor and catalyst dimensions are selected for the desired heat transfer performance in order to avoid possible undesired reactions, high pressure drops and local overheating.
Pseudo-homogeneous models are most commonly employed for design of packed bed reactors [1, 2]. Due to the simplifying assumptions such as uniform catalyst pellet surroundings, the effects of catalyst pellet design changes in the near-wall environment or around hot spots might be lost. Simulations with heterogeneous models would allow localization hot spots for exothermic reactions and heat effects near wall catalysts for strongly endothermic reactions such as steam reforming [3]. Additionally, they are useful for to improve understanding the effects of changes in operational conditions on fluid flow, temperatures, catalyst activity and product selectivity.

The main characteristic of a fixed-bed reactor design for strongly endothermic or exothermic reactions is the height to diameter scale and the tube to particle diameter ratio. Since it is necessary to have high mesh resolution around the catalyst particle, thus the number of the degree of freedom could be too high for a practical solution along whole reactor.
Several authors suggest that void fraction distribution may change in the direction perpendicular to the flow (References 4 - 7). This variable is associated to packed elements shape and size. Temperature and heat flux values are also associated to this geometrical distribution.

2. 2-D Reactor Model

The example provided by COMSOL [8] from the work developed by Lerou and Froment [9] using the 2D pseudo-homogeneous model is implemented in this study. This is the partial oxidation of o-xylene (A) in air to phthalic anhydride (B) given as



where C denotes carbon monoxide and carbon dioxide, k_i, i=1, 2, 3, are the rate constants. These reactions are highly exothermic, thus the reactor is cooled to avoid overheating.
Figure 1 shows a schematic illustration of a packed-bed reactor. To a first approximation to a model of this complexity, we initially studied the packed bed reactor using a 2-D geometry divided into equally spaced segments as shown in Figure 2.

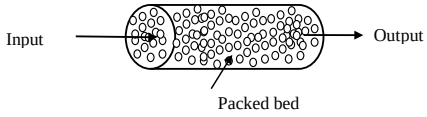


Figure 1. Schematic of a tubular packed-bed reactor.

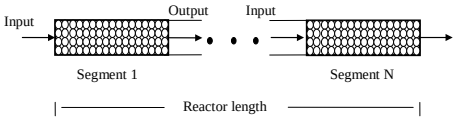


Figure 2. Segmented reactor geometry.

2.1 Reaction Kinetics

All of the rate equations are considered to be pseudo-first-order because of the large excess of oxygen at the reactor input, thus

$$\boldsymbol{r_1 = k_1' p_A,\ \ r_2 = k_2' p_B,\ \ r_3 = k_3' p_A,} \qquad (1)$$

The rate equations are written consequently [8, 9]

$$\begin{aligned} \boldsymbol{r_1} &= \boldsymbol{\rho_b y_o y_{Ao} k_1 (1 - x_A)} \\ \boldsymbol{r_2} &= \boldsymbol{\rho_b y_o y_{Ao} k_2 x_B} \\ \boldsymbol{r_3} &= \boldsymbol{\rho_b y_o y_{Ao} k_3 (1 - x_A)} \end{aligned} \qquad (2)$$

where x_A is the total conversion of o-xylene, and x_B is the conversion of o-xylene into phthalic anhydride. If x_C is the conversion into carbon monoxide and carbon dioxide, then the total conversion of A is $x_A = x_B + x_C$. Consequently, the reaction kinetics are represented by

$$\begin{aligned} \boldsymbol{r_B} &= \boldsymbol{y_{Ao} y_o c_{tot} [k_1 (1 - x_B - x_C) - k_2 x_B]} \\ \boldsymbol{r_C} &= \boldsymbol{y_{Ao} y_o c_{tot} [k_2 x_B + k_3 (1 - x_B - x_C)]} \end{aligned} \qquad (3)$$

Rate constants are defined by the Arrhenius equations

$$\boldsymbol{k_i = A_i \exp\left(-\frac{B_i}{T}\right),\ \ (i = 1, 2, 3)} \qquad (4)$$

where T is the temperature in kelvins, and A_i and B_i are characteristic parameters for each reaction. These parameters are given [9] as: A_1 = exp(19.837), A_2 = exp(20.86), A_3 = exp(18.97), all in kmol/kg h, and B_1 = 13588 K, B_2 = 15803 K, and B_3 = 14394 K.

The model used for this system ([8, 9]) consist on a mass balance and an energy balance:

$$\begin{aligned} \boldsymbol{\nabla \cdot (-D_{eff} \nabla x_i + u_s x_i)} &= \boldsymbol{\frac{1}{c_{tot} y_{Ao}}} \\ \boldsymbol{u_s \rho_g C_p \nabla \cdot T - \nabla \cdot (-k_{eff} \nabla T)} &= \boldsymbol{\sum_{i=1}^{3} (-\Delta H_i) r_i} \end{aligned} \qquad (5)$$

where the heats of reaction (ΔH_i) are given by [9]: ΔH_1 = -1.285x10^6 J/mol, ΔH_2 = -3.276 x10^6 J/mol, and $\Delta H_3 = \Delta H_1 + \Delta H_2$.

The boundary conditions are insulation for the mass transfer equations at the axis symmetry, or reactor centerline (0,z) and heat flux for the heat balance equation at the reactor wall (R,z), as seen in Figure 3, which are resented by

$$\boldsymbol{\frac{\partial x_B}{\partial r}(0, z) = \frac{\partial x_C}{\partial r}(0, z) = 0, \frac{\partial T}{\partial r}(0, z) = 0} \qquad (6)$$

$$\boldsymbol{\frac{\partial x_B}{\partial r}(R, z) = \frac{\partial x_C}{\partial r}(R, z) = 0, k_{eff} \frac{\partial T}{\partial r}(R, z) = -\alpha (T - T_o).} \qquad (7)$$

the mass transport and the heat transport dominate At the reactor inlet, the concentrations are zero and the temperature equals T_0. At the outlet, assume that the convective parts of.

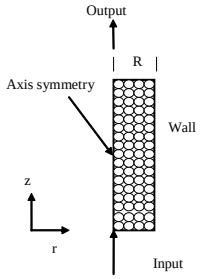


Figure 3. Schematic 2-D representation of the reactor.

3.Model Implementation Using COMSOL Multiphysics

In order to simplify the geometry of packed bed reactor to a 2D geometry, we need to select a uniform void fraction. This is determined as

$$\boldsymbol{\varepsilon = (LA - W_{cat} \rho_s / LA_c)} \qquad (8)$$

where L and A_c are the tube length and cross sectional area, W_{cat} and ρ_s the catalyst weight and density, respectively. Then each segment inlet is defined by

$$\boldsymbol{L = j\, L_s,\ j = 0, \ldots, N_s,} \qquad (9)$$

here L_s = 0.00873 m, is the chosen segment length, and N_s is the maximum number of elements.

The reactor segment is described by 2D axis symmetry geometry as shown in Figure 4 using reactor centerline as the z axis and radius as the r axis. We choose a segment length of 0.00873 m and a radius of 0.0127 m. This model is an arrangement of six circles of 0.00159 m radius, describing six catalyst spherical pellets with 0.00079 m of separation, which represents a packed bed with uniform void fraction.

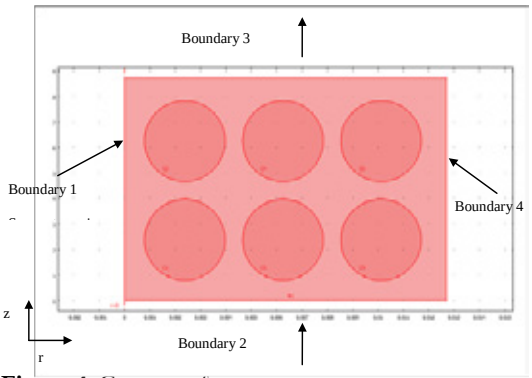


Figure 4. Geometry for a reactor segment.

The application modes used, for a steady state analysis, were selected from the Chemical Engineering Module as: Momentum Balance (Incompressible Navier-Stokes) for subdomain 1 (rectangle R1 in Figure4), and Mass Balance (Convection and Diffusion) and Energy Balance (Convection and Conduction) for subdomains 2-6 (circles C1-C6). Models equations and their respective boundary and initial conditions for these application modes are given in Tables 1 to 3.

Table 1: Navier-Stokes equations (Subdomain 1)

$$\boldsymbol{\rho_g u \cdot \nabla u = \nabla \cdot [-pI + \mu(\nabla u + (\nabla u)^T)]}$$
$$\boldsymbol{\nabla \cdot u = 0}$$

Initial conditions $\begin{cases} \boldsymbol{u_{to} = 0} \\ \boldsymbol{v_{to} = 0} \\ \boldsymbol{p_{to} = p_o} \end{cases}$
Boundary 1: Symmetry $\boldsymbol{n \cdot u = 0}$, $\boldsymbol{t \cdot [-pI + \mu(\nabla u + (\nabla u)^T)]n = 0}$
Boundary 2: Inlet
Segment 1 $\begin{cases} \boldsymbol{u_o = 0} \\ \boldsymbol{v_o = u_s} \end{cases}$;
Other segments $\begin{cases} \boldsymbol{u_o = u_{prev}} \\ \boldsymbol{v_o = v_{prev}} \end{cases}$
Boundary 3: Outlet $\boldsymbol{p_{to} = p_o}$, $\boldsymbol{\mu(\nabla u + (\nabla u)^T)n = 0}$
Boundary 4 and 5-28 (circle segments): No slip, $\boldsymbol{u = 0}$

Table 2: Convection and diffusion equations

Subdomain 1

$$\boldsymbol{\nabla \cdot (-D \nabla c_B) = -u \cdot \nabla c_B, u = [u\ v]^T}$$
$$\boldsymbol{\nabla \cdot (-D \nabla c_C) = -u \cdot \nabla c_C, u = [u\ v]^T}$$

Subdomains 2, .., 7 (circles)

$$\boldsymbol{\nabla \cdot (-D_{eff} \nabla c_B) = r_B / y_{Ao}},$$
$$\boldsymbol{\nabla \cdot (-D_{eff} \nabla c_C) = r_C / y_{Ao}}$$

Initial conditions $\boldsymbol{c_{Bto} = 0, c_{Cto} = 0}$
Boundary 1: Axial symmetry $\boldsymbol{r = 0}$
Boundary 2: Concentration
Segment 1, $\boldsymbol{c_{Bo} = 0, c_{Co} = 0}$,
Other segments, $\boldsymbol{c_{Bo} = c_{B,prev}, c_{Co} = c_{C,prev}}$
Boundary 3: Convective flux $\boldsymbol{n \cdot (-D \nabla c_B) = 0}$, $\boldsymbol{n \cdot (-D \nabla c_C) = 0}$
Boundary 4: Insulation $\boldsymbol{n \cdot N = 0, N = -D_{eff} \nabla c_B + c_B u}$, $\boldsymbol{n \cdot N = 0, N = -D_{eff} \nabla c_B + c_B u}$

The inlet conditions (boundary 2), $z = 0$, are uniform concentrations, uniform temperature, and uniform velocities. Thus, for j=1, u = 0, v = v_s, $c_B = c_C = 0$ and $T = T_o$, and for j>1, $c_B = c_{B,prev}$, $c_C = c_{C,prev}$, $T = T_{prev}$, $u = u_{prev}$, $v = v_{prev}$. Here the sub index *prev* denotes variables determined at the segment output of the previous segment. The inlet, at boundary condition, $z = 0$, for each segment are considered to be the outlet average property values of previous segment at $z = L_s$. From output data, the average values at boundary 3 (output) over a circular cross section of the reactor segment of area $A = \pi R^2$ of are evaluated as

$$\tilde{\varphi}_i = \frac{2}{R^2} \int_0^R \varphi_i(r) r\, dr \qquad (9)$$

where φ_i denotes velocity components (u, v), conversions (x_A, x_B, x_C) or temperature (T).

Table 3: Energy balance equations.

Subdomain 1

$$\nabla \cdot (-k \cdot \nabla T) = -\rho_g C_{pg} u \cdot \nabla T;$$
$$u = [u\ v]$$

Subdomains 2, .., 7 (circles)

$$\nabla \cdot (-k_{eff} \cdot \nabla T) = (-\Delta H_1) r_B + (-\Delta H_2) r_C - \rho_g C_p u \cdot \nabla T$$

Initial condition $T_{to} = T_0$;
Boundary 1: Axial symmetry $r = 0$
Boundary 2: Temperature
Segment 1, $T_{to} = T_0$;
Other segments, $T_{to} = T_{prev}$.
Boundary 3: convective flux $\boldsymbol{n \cdot (-k \cdot \nabla T) = 0}$
Boundary 4: heat flux $\boldsymbol{n \cdot q = -\alpha(T - T_0)}$, $\boldsymbol{q = -k \cdot \nabla T + \rho_g C_{pg} T u}$

The approach using COMSOL GUI and COMSOL Script can be summarized as follows:

a. First set up the 2D-axis-symmtry geometry, as shown in Figure 4, and application modes.

b. Mesh generation by selecting a maximum element size of 1×10^{-4} m for boundaries 1, 2, 3 and 4, and 0.5×10^{-5} for interior circle boundaries.

c. Next set up subdomains 1 and subdomains 2-6 for the different application modes and boundary conditions.

d. Now solve the problem. First choose the Navier-Stokes equations to compute the velocity components (u, v) for subdomain 1. Then save variables and solve energy and mass balance equations.

e. Save the above process as a matlab file and modify it for the successive changes in boundary and input conditions of each reactor segment.

f. Execution of the matlab file and analysis of results under Comsol Script environment.

4. Results and Discussion

Model parameters are given in references [8] and [9]. For a reactor radius of R = 1.27 cm, a superficial velocity v_s = 1.064 m/s, (m/s), inlet temperature T_0 = 627 K, operating pressure $\boldsymbol{p_o = 1.013x10^5}$ **Pa**, inlet total concentration c_{tot} = 44.85 mol/m^3 mol/m, inlet mole fraction of o-xylene y_{Ao} = 0.00924, inlet mole fraction of oxygen y_0 = 0.208, catalyst bulk density ρ_b = 1300 kg/m^3, gas density ρ_g = 1293 kg/m^3, gas heat capacity C_p = 1046 J/(kg K), heat transfer coefficient α = 156 W/(m^2 K).

The effective diffusion constant is D_{eff} = 3.19e-7 m^2/s, the diffusivity of xylene in air is D = 8.074x10^{-5} m^2/s (estimated form reference [10]), effective thermal conductivity k_{eff} = 0.779 W/(m K), and gas thermal conductivity [10] k = 0.0318 W/(m K).

Figure 5 shows preliminary results of temperature for the first (j = 1) and sixteen (j = 16) segments respectively. Fig. 5a suggests that the temperature increase is about 5 K near reactor inlet. However, intra-pellet hot spots are observed at j = 16 and temperatures differences could reach values up to about 200 K. Simulations further than this high temperature levels cause unstable solutions.

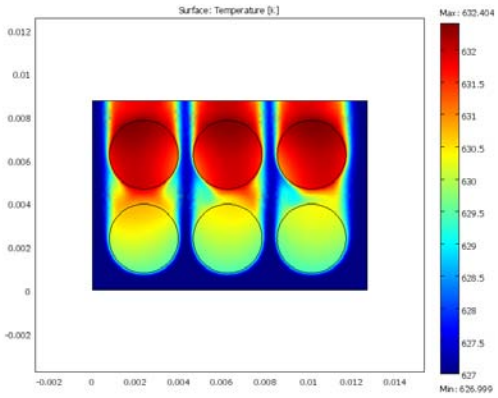


Figure 5a. Temperature distributions for segment 1. (L = 0.00873 m).

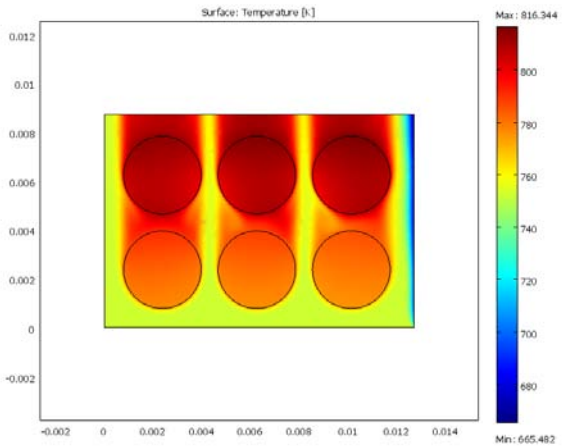


Figure 5b. Temperature distributions for segment 16. (L = 0.13968).

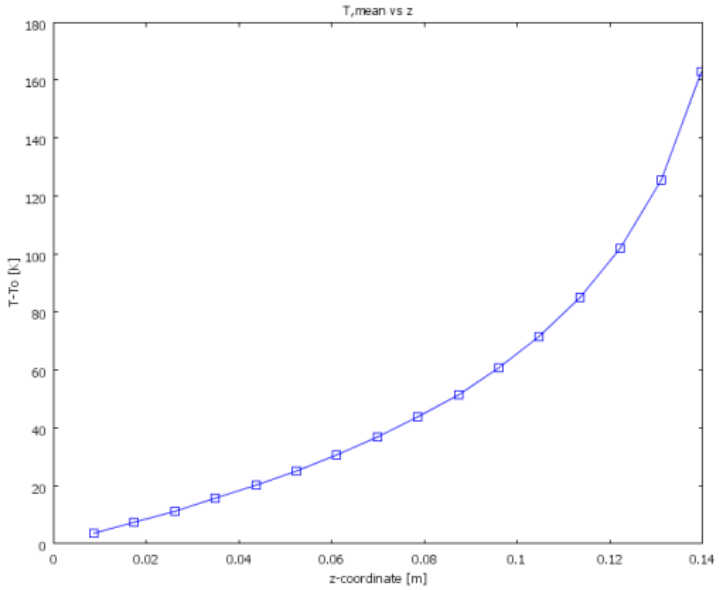


Figure 6. Average temperature profile, L = 0.13968 m.

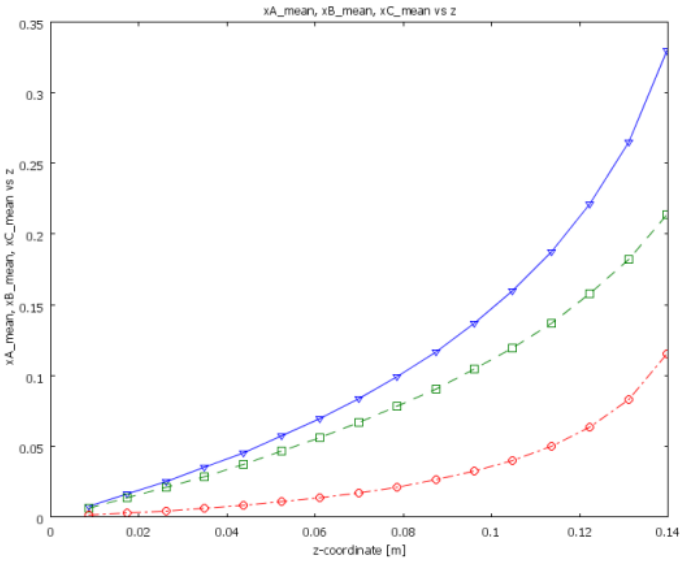


Figure 7. Average conversions, L = 0.13968 m.

The average temperature difference, $T - T_o$, and average conversions (x_A, x_B, x_C) along the axial direction, for a reactor length of L = 0.13968 m, are given in Figures 7 and 8, respectively. Although, this location is close the reactor inlet, for a typical 3m reactor length, these variables increase exponentially indicating the reactions are very rapid and the heat transfer through the wall might not be enough to maintain the temperature close to the inlet temperature T_o. Too high temperatures, the so called hot-spots, as indicated in Fig. 5b could affect catalyst activity. Figure 7 presents the distribution of conversion x_A for segments 1 and 16, respectively. The maximum stream conversion is about 35%, while the maximum intra pellet conversion is 100%.

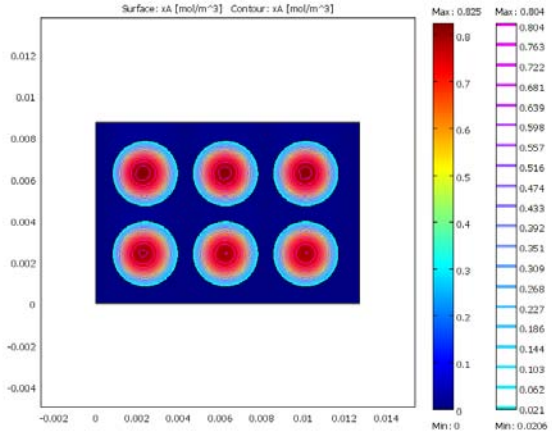


Figure 7a. Conversion of A for segment 1. (L = 0.00873 m).

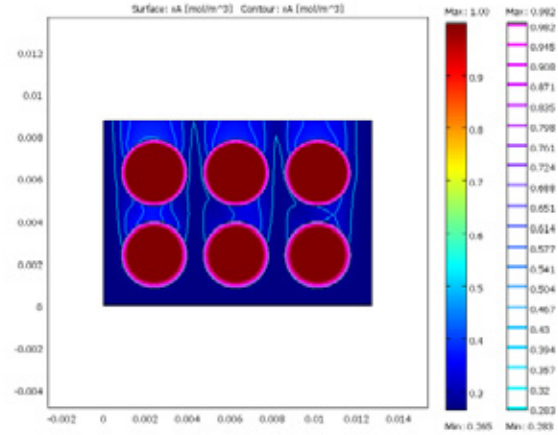


Figure 7b. Conversion of A for segment 16. (L = 0.13968 m).

5. Conclusion

It was concluded for the case examined that high temperatures increases or hot-spots occurred near reactor inlet. In order to study possible undesired conversions and catalyst damage, a more detailed model is desirable. For a future work we suggest consideration of a geometry model with intra pellet gaps and in contact with each other for the packed bed reactor simulation. This study should include sensitivity analysis of inlet temperature and heat transfer through the wall.

6. References

1. J.M. Smith, *Chemical Engineering Kinetics*, 3rd ed., Mc-Graw-Hill, 1981.
2. G.F. Froment and K.B. Bischoff, *Chemical Reactor Analysis and Design*, 2nd ed., John Wiley & Sons, 1990.
3. A. G. Dixon *et. al*, CFD Simulation of Reaction and Heat Transfer Near the Wall of a Fixed Bed, *International Journal of Chemical Reactor Engineering*, Volume 1 2003 Article A22.
4. O. Bey, and G. Eigenberger, Fluid Flow Through Catalyst Filled Tubes. *Chemical Engineering Science*, 52-8, 1365-1376, 1997.
5. M. Giese, K. Rottschäfer and D. Vortmeyer, Measured and Modeled Superficial Flow Profiles in Packed Beds with Liquid Flow. *Aiche Journal*, 44, 484-490, 1998.
6. K. Nandakumar, Yiqiang Shu, and K.T. Chuang, Predicting geometrical properties of random packed beds from computer simulation. *AIChE Journal*, 45, 2286-2297, 1999.
7. G. Muller, Prediction of Radial Porosity Distributions in Randomly Packed Fixed beds of Uniformly Sized Spheres in Cylindrical Containers. *Chemical Engineering Science*, 46, 706-708, 1991.
8. *COMSOL Multiphysics User's Guide*, Version 3.2, COMSOL AB, 2005.
9. J.J. Lerou and G.F. Froment, Velocity, Temperature and Conversion Profiles in Fixed Bed Catalytic Reactors, *Chem. Eng. Science*, vol. 32, pp. 853–861, 1977.
10. W. L. McCabe, J.C. Smith and P. Harriott, *Unit Operations of Chemical Engineering*, 5th Ed., McGraw-Hill, 1993.

7. Acknowledgements

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