Supporting Information

OpenFOAM computational fluid dynamic simulations of two-phase flow and mass transfer in an Advanced-Flow Reactor

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Formulation of mass transfer of species in the OpenFOAM framework

The formulation of the Haroun[1,2] equations within the interFoam framework is included in Table SI - **1** together with the Marschall [3]et al. formulation for comparison.

Table SI - 1: Species conservation equation (CEqn.H) included in OpenFOAM formulation to solve for mass transfer including approaches of Haroun and Marschall.

Haroun et al	Marschall et al
surfaceScalarField phiCi= ((fvc::interpolate(DT)*(1- He)/(fvc::interpolate(alpha1)+(1- fvc::interpolate(alpha1))*He))*fvc::snGrad(alpha1))*mesh.magSf(); solve (fvm::ddt(T) + fvm::div(phi,T) - fvm::laplacian(fvc::interpolate(DT),T) + fvm::div(phiCi,T), mesh.solver("T"));	surfaceScalarField phiCi= ((DT1-DT2/He)/(fvc::interpolate(alpha1)+(1- fvc::interpolate(alpha1))/He)*fvc::snGrad(alpha1))*mesh.magSf(); surfaceScalarField phiD= (fvc::snGrad(DT))*mesh.magSf(); solve (fvm::ddt(T) + fvm::div(phi,T) - fvm::laplacian(fvc::interpolate(DT),T) - fvm::div(phiD,T) + fvm::div(phiCi,T), mesh.solver("T"));
T is the species concentration *DT1, DT2* are the diffusion coefficients of component T in Phase 1 and Phase 2 *He* is the Henry constant defined as the equilibrium ratio concentration of component in Phase 2 with respect to its concentration in Phase 1 *DT* is calculated in createFields.H as a weighted average of *DT1* and *DT2* or using the harmonic approach	

In most chemical engineering applications, reactions also occur. It is thus essential to modify the above solvers incorporating into the species conservation equations the reaction term. An irreversible reaction is first considered, where A is consumed and B is formed (A → B). The piece of code incorporated into the CEqn.H in the solvers is given in Table SI - 2. The kinetic constant in phase 1 is k_1 and in phase 2 is k_2. Normally, reactant A will react only in one phase, but this formulation considers the more general possibility of A reacting in phase 1 and phase 2. In order to convert the two-phase formulation into a single

equation for the entire domain as the VOF formulation, the kinetic constant is calculated as the weight-average. Component B species conservation equation is analog to component A's equation but the sign of the kinetic constant is positive, since B is formed.

Table SI - 2: Modified species conservation equation (CEqn.H) in HarounMassTransfer solver for irreversible reaction A→B

Component A
solve (fvm::ddt(A) + fvm::div(phi,A) - fvm::laplacian(fvc::interpolate(DA),A) + fvm::div(phiCi,A) == fvm::Sp(k12,A))
Component B
solve (fvm::ddt(B) + fvm::div(phi,B) - fvm::laplacian(fvc::interpolate(DB),B) + fvm::div(phiCi,B) == - k_{12}*A)

For an equilibrium reaction A ↔ B the species conservation equation the reversible reaction needs to be considered. The kinetic constant k_{rev12} is the weight-average of k_{rev1} (kinetic constant of the reverse reaction B → A in phase 1) and k_{rev2} (kinetic constant of the reverse reaction B → A in phase 2). The modified equation is shown in Table SI - 3. The kinetic constants need to be defined according to the reaction in the 'transportProperties'. For instance, in this particular example k_{12} is negative for component A and k_{rev12} is positive.

Table SI - 3: Modified species conservation equation in CEqn.H in HarounMassTransfer solver for reversible reaction A ↔ B

Component A
solve (fvm::ddt(A) + fvm::div(phi,A) - fvm::laplacian(fvc::interpolate(DA),A) + fvm::div(phiCi,A) == fvm::Sp(k12,A) + krev12*B)
Component B
solve (fvm::ddt(B) + fvm::div(phi,B) - fvm::laplacian(fvc::interpolate(DB),B) + fvm::div(phiCi,B) == -k12*A - fvm::Sp(krev12,B))

Mass transfer solver validation using OpenFOAM

The first simple validation case is the transport of species across a planar interface between two immiscible fluids. The schematic of the system of study is presented in Figure SI - 1. The boundary and initial conditions for this 1D problem are given in Table SI - 4. Simulation results for different values of diffusion coefficients and Henry constants were performed using the HarounScalarTransportFoam and MarschallScalarTransportFoam solvers. In general, we found no difference in the performance of these two solvers. Results were compared with the ones obtained using Matlab by solving the species conservation equation in one dimension (z coordinate) for each phase (Eq 1), considering the boundary conditions of equal concentration fluxes and jump in concentrations at the interface. When the mesh is fine, the Matlab result can be considered as a close enough representation of the analytic solution.

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i \qquad (1)$$

Table SI - 4: Boundary and initial conditions for 1D validation case.

Time (s)	Position (m)	Condition	Value
0	z	Fixed value	0
t	0	Fixed value	1
t	0.1	Zero gradient	0

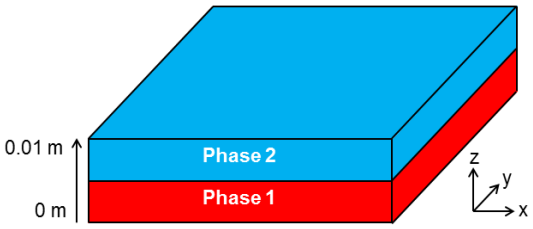


Figure SI - 1: Schematic of the system for validation of mass transfer of species under static conditions and constant volume fraction field.

One criterion for comparison between solvers is to compare the computed jump in concentration with the theoretical value that should be obtained depending on the Henry constant given as input to the simulation. A comparison between solvers for different diffusion coefficients and Henry constants is

included in Table SI - 5. For cases 1-7 where the diffusion coefficients are equal in both phases to 10^{-5} m^2/s, there is no difference in performance between the two different solvers. The jump in concentration at the interface is well captured by both solvers, with errors below 0.5% for Henry constants between 0.01 and 10, and below 5% for Henry constants up to 100. For longer times, even for Henry constant values of 100, the jump in concentration also achieves the correct value. A second set of simulations were performed for different diffusion coefficients, being DT1 = 10^{-5} m^2/s and DT2 = 10^{-7} m^2/s and different Henry constant values (Table SI - 6). It is observed that longer times are needed in order to achieve the correct concentration jump especially for large Henry constants. However, when comparing the concentration profiles along the entire domain, both solvers provide a good response compared to the value obtained with Matlab (Figure SI - 2 and Figure SI - 3).

Table SI - 5: Jump concentration at interface at 5 s from CFD results as function of Henry constant

Case	DT1 (m^2/s)	DT2 (m^2/s)	He	Jump concentration at interface	Error in jump concentration (%)
1	10^{-5}	10^{-5}	1	0.99945	-0.06
2	10^{-5}	10^{-5}	5	4.98815	-0.24
3	10^{-5}	10^{-5}	10	9.953796	-0.46
4	10^{-5}	10^{-5}	100	95.64985	-4.35
5	10^{-5}	10^{-5}	0.2	0.199963	-0.02
6	10^{-5}	10^{-5}	0.1	0.099986	-0.01
7	10^{-5}	10^{-5}	0.01	0.009999	-0.01

*Same values observed for MarschallScalarTransportFoam and HarounScalarTransportFoam

Table SI - 6**:** Jump concentration at interface from CFD results for different diffusion coefficients as function of Henry constant

Case	He	1 s	5 s	10 s	20 s	50 s	100 s	Error at 1 s (%)	Error at 100 s (%)
8	5	4.761	4.876	4.934	4.973	4.993	4.998	-4.78	-0.04
9	100	52.45	70.10	81.73	91.71	97.80	99.21	-47.55	-0.79

*Same values observed for MarschallScalarTransportFoam and HarounScalarTransportFoam

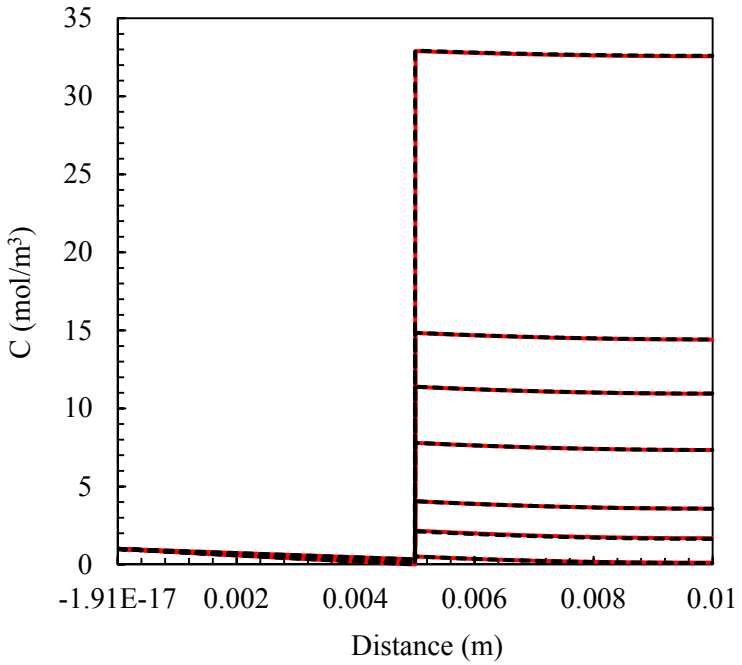


Figure SI - 2: Comparison of concentration profiles using Matlab and OpenFOAM for DT1 = DT2 = 10^{-5} m^2/s, He = 100 for different times = 1 s, 5 s, 10 s, 20 s, 30 s, 40 s, 100 s. Legend: —, OpenFOAM; ----, Matlab

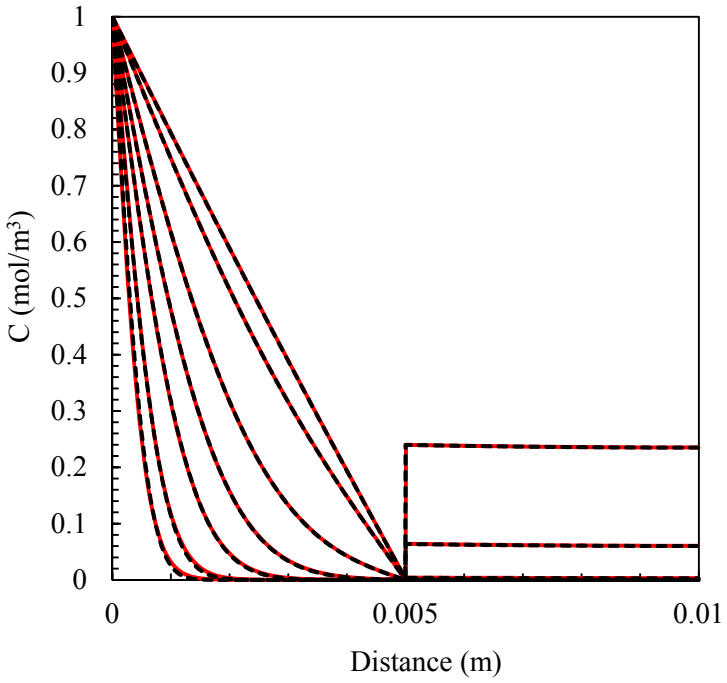


Figure SI - 3: Comparison of concentration profiles using Matlab and OpenFOAM for DT1 = 10^{-5} m^2/s, DT2 = 10^{-7} m^2/s, He = 100 for different times = 1 s, 2 s, 5 s, 10 s, 20 s, 50 s, 100 s. Legend: — , OpenFOAM; ----, Matlab

The validation above considered a sharp interface. In reality, the volume fraction field as calculated by interFoam almost always presents a diffuse interface, where the phase volume fraction gradually transitions from 0 to 1 across several grid cells. Therefore, we have constructed another test case where the phase interface is not a sharp step function, but varies smoothly from one phase to another over 5 cells. It can be seen from Figure SI - 4 that there is still a very good agreement between the Matlab solution and the OpenFOAM solution even with a diffuse interface, indicating the robustness of the new solver when coupled with the interFoam solver and applied to real problems.

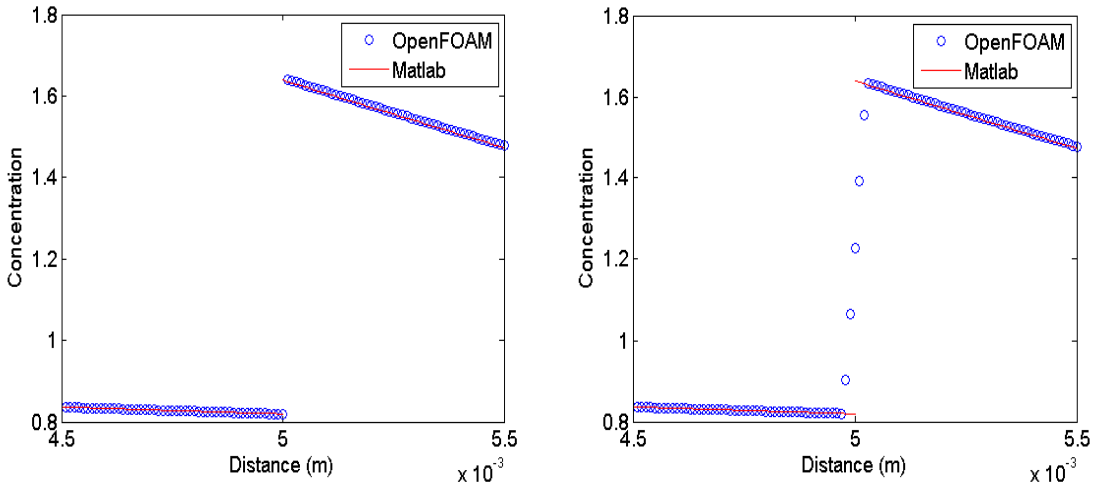


Figure SI - 4: Comparison of concentration profiles using Matlab and OpenFOAM for a sharp interface (left) and a diffuse interface (right). In both cases, there is a good agreement between the Matlab and OpenFOAM solutions.

The validation performed above corresponds to static conditions, for zero velocity and a fixed volume fraction field. The next step is to validate the solvers for cases of fixed volume fraction field and constant velocity profiles. One example for this validation is the parallel flow of two immiscible phases between two planar surfaces, as shown in Figure SI - 5.

Figure SI - 5: Schematic of the system for validation of mass transfer of species under dynamic conditions and constant volume fraction field.

The velocity field is first calculated analytically for 1D dimension and used as an input for the velocity field in the OpenFOAM solvers. Assumptions of steady-state, unidirectional flow (x-component), fully developed flow (x-component of the velocity does not depend on x), no slip at the walls, and no effect of gravity forces:

$$0 = -\frac{\partial P}{\partial x} + \mu\left(\frac{\partial^2 v_x}{\partial z^2}\right) \qquad (2)$$

With no-slip boundary condition at the walls, and for a fixed pressure drop, the velocity field $v_x(z)$ is given by eq 3:

$$v_x(z) = \frac{1}{2\mu_1}\frac{\partial P}{\partial x}z^2 + \alpha_1 z + \beta_1 \qquad 0\text{ m} < z < 0.005\text{ m} \qquad (3)$$

$$v_x(z) = \frac{1}{2\mu_2}\frac{\partial P}{\partial x}z^2 + \alpha_2 z + \beta_2 \qquad 0.005\text{ m} < z < 0.01\text{ m}$$

where $\alpha_1 = \frac{\left(\frac{\partial P}{\partial x}\right)\frac{\mu_2 H}{\mu_1}\left(\frac{3}{\mu_2}+\frac{1}{\mu_1}\right)}{\frac{\mu_2}{\mu_1}+1}$, $\alpha_2 = \alpha_1\frac{\mu_1}{\mu_2}$, $\beta_1 = 0$ and $\beta_2 = -H\alpha_2 - \frac{H^2}{2\mu_2}\left(\frac{\partial P}{\partial x}\right)$

Validation of HarounScalarTransportFoam and MarschallScalarTransportFoam solvers was performed for the same two fluid system with the above velocity field and a very low diffusivity (DT1 = DT2 = 10^{-9} m^2/s), such that convection dominates over diffusion. The CFD results were compared with results obtained with Matlab for a simplified problem, described by eq 4 and boundary conditions in Table SI - 7. The comparison of concentration profiles evolution with time obtained using

HarounScalarTransportFoam and Matlab is shown in Figure SI - 6**:** Concentration profiles obtained using (left) OpenFOAM; (right) Matlab, formulation with boundary conditions at interface. Concentration is treated as a passive scalar for fixed velocity profiles.. The CFD simulations were seen to yield the same concentration profiles at different times as the Matlab solution.

$$\frac{\partial C}{\partial t} + v_x(z)\frac{\partial C}{\partial x} = 0 \qquad (4)$$

Table SI - 7**:** Boundary conditions for validation of mass transfer solvers

Time (s)	Position (m)	Boundary condition	Value	Units
t	x = 0	Fixed value	1	mol/m^3
t	x > 0	Fixed value	0	mol/m^3

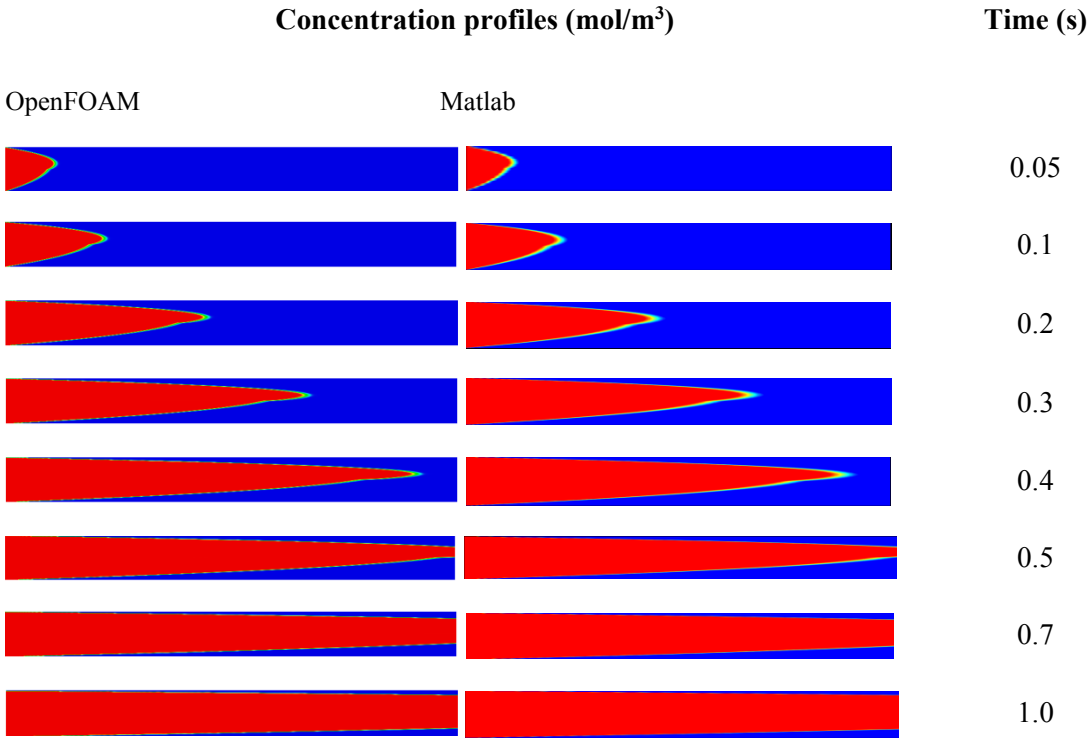
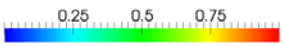


Figure SI - 6: Concentration profiles obtained using (left) OpenFOAM; (right) Matlab, formulation with boundary conditions at interface. Concentration is treated as a passive scalar for fixed velocity profiles. Legend: 

Dynamic simulations of mass transfer using OpenFOAM

Transient simulations have been performed using the modified solvers to account for mass transfer using OpenFOAM. The species of interest (acetone) is transferred from water (continuous phase) to hexane (dispersed phase) over time. Several variables are monitored over time, since the droplets start to be formed at the inlet of the reactor when the two phases start contact: a) concentration of species in the hexane phase; b) droplet diameter; c) specific interfacial area; d) hexane holdup; e) individual mass transfer coefficient; f) overall mass transfer coefficient.

The effect of the total flow rate in the mass transfer process is shown in Figure SI-7. Larger overall mass transfer coefficients are achieved at the largest flow rates thanks to the enhanced individual mass transfer coefficients that are obtained operating at larger Reynolds numbers. One limitation to these results is the numerical coalescence of droplets observed at the largest flow rates, which yields largest droplets than what would be expected experimentally. The values for the overall mass transfer coefficients are therefore underpredicted.

The effect of viscosity of the continuous phase is shown in Figure SI-8. As it is shown here, the overall effect of viscosity on the overall mass transfer coefficient is not significant. However, the effect of surface tension is stronger as shown in Figure SI-9. Lower surface tension decreases the mass transfer efficiency. First, the bulk concentration of acetone in hexane is lower and the maximum concentration possible is higher, therefore, decreasing the efficiency from 83 % to 60 %. In addition, the specific interfacial area is smaller, and, although the individual mass transfer coefficient is slightly larger for the lower surface tension, the overall effect is to decrease the overall mass transfer coefficient. Therefore, although having lower surface tension is advantageous to achieve smaller droplets sizes (more breakup), in order to have a better performance, it would be necessary to increase the hexane flow rate so that the hexane holdup increases and the total interfacial area also increases (a), contributing to an overall larger mass transfer rate.

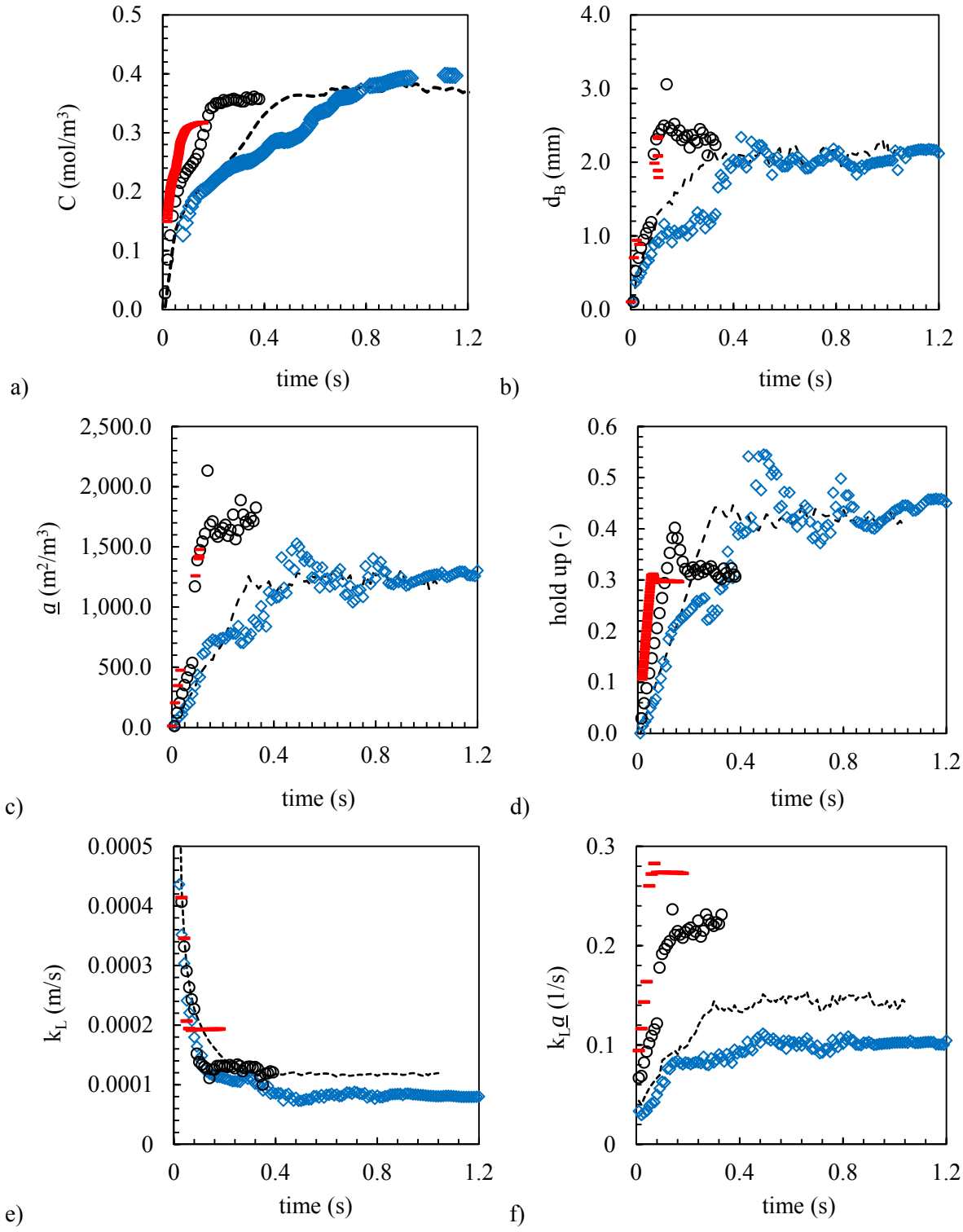


Figure SI-7: Effect of total flow rate at hexane to water flow rate ratio = 1 on a) concentration in hexane; b) average drop size; c) specific interfacial area; d) hexane hold-up; e) individual mass transfer coefficient; f) overall mass transfer coefficient. Total flow rate (mL/min): ◇, 20; - - -, 40; ○, 80; –, 160

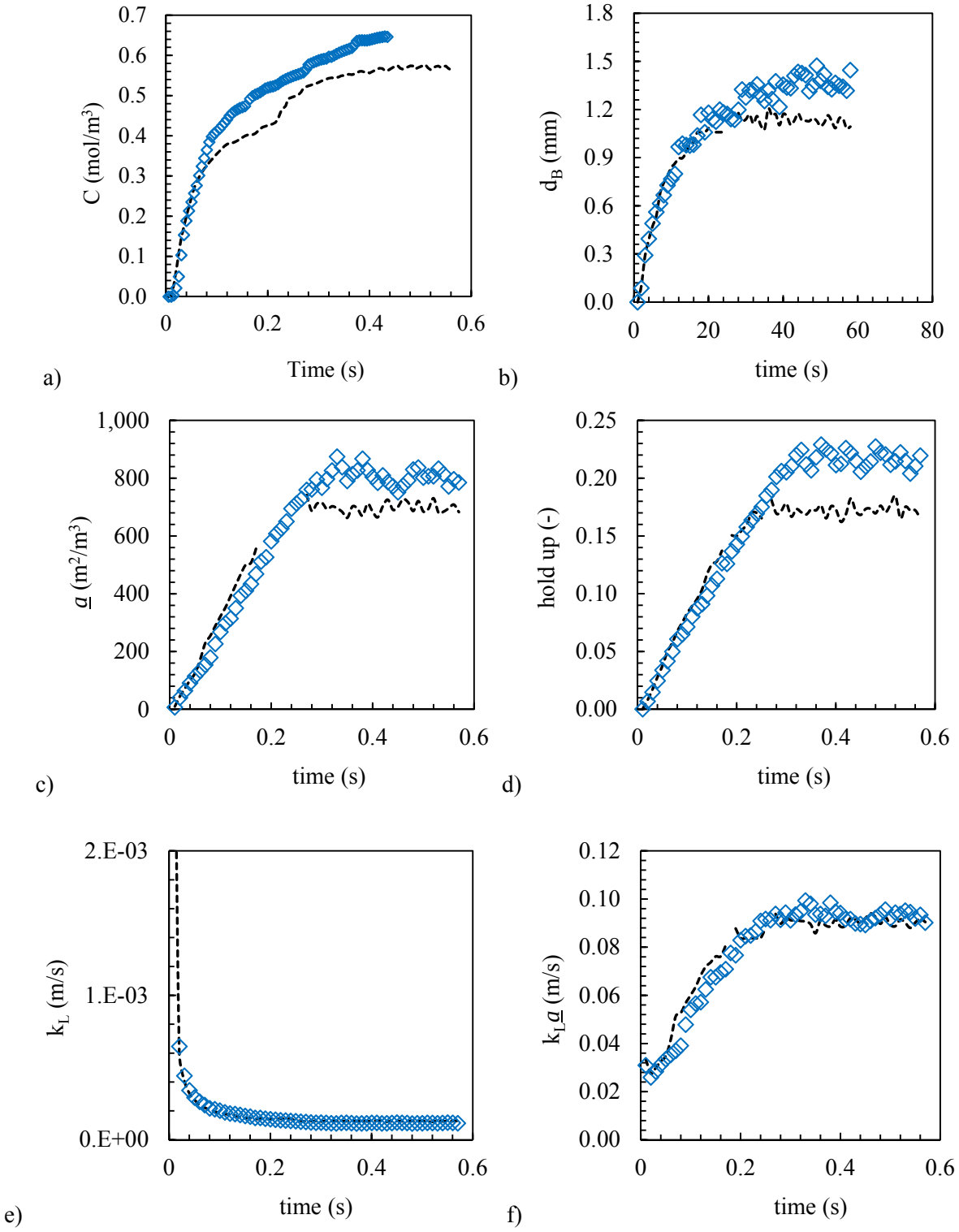


Figure SI-8: Effect of viscosity on a) concentration in hexane phase; b) droplet size; c) specific interfacial area; d) hold-up; e) individual mass transfer coefficient; f) overall mass transfer coefficient. Legend: ◇, 0.001 Pa s; ----, 0.01 Pa s

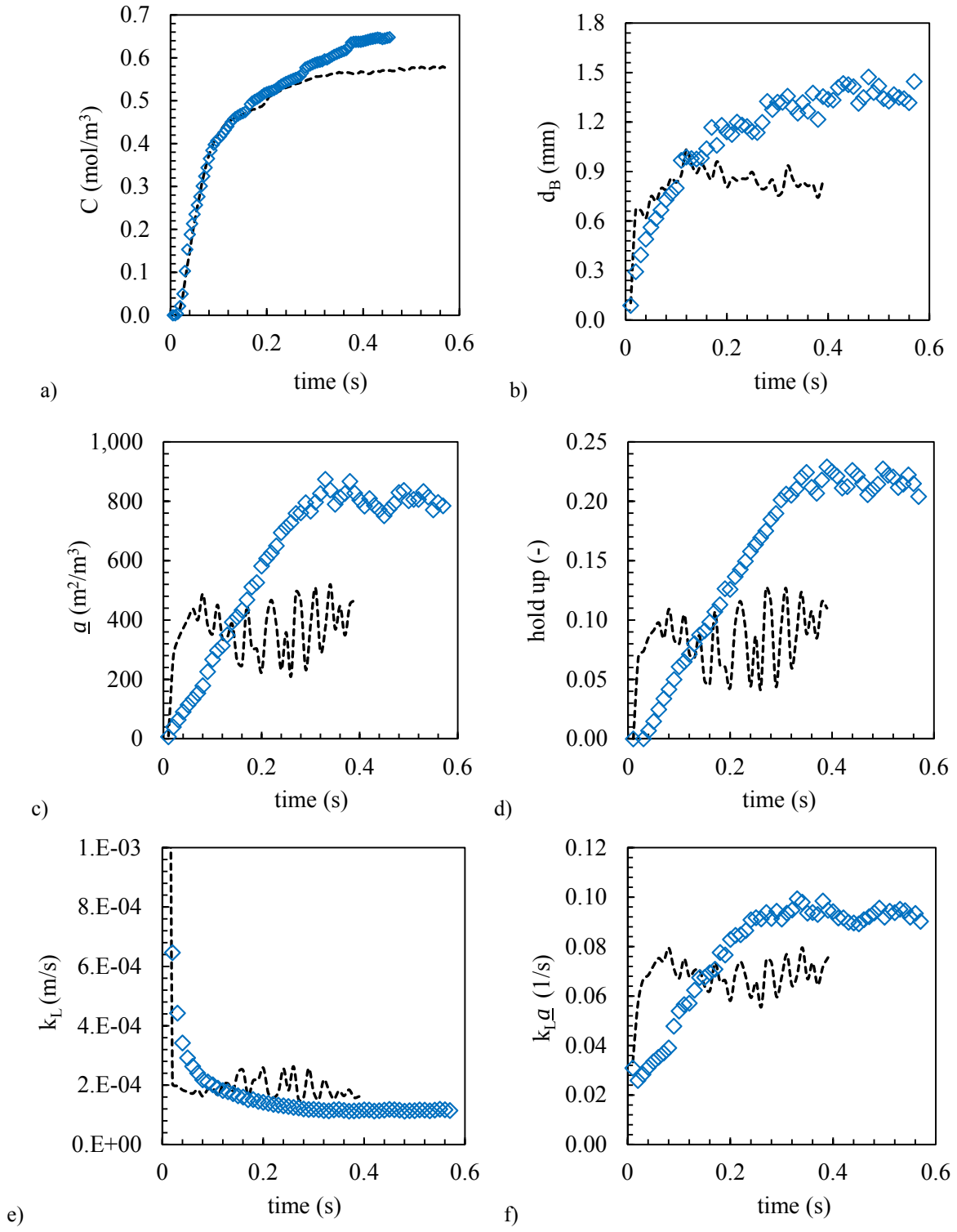


Figure SI-9: Effect of surface tension at 40 mL/min water and 10 mL/min hexane on a) concentration in hexane phase; b) average drop size; c) specific interfacial area; d) hexane holdup; e) individual mass transfer coefficient; f) overall mass transfer coefficient. Legend, σ (N/m): ◇, 0.052; ----, 0.0068

The effect of contact angle for fixed flow rates of water (40 mL/min) and hexane (10 mL/min) is shown in Figure SI-10. It is observed that, as a consequence of the different flow patterns formed at different contact angles, the droplet size, holdup and specific interfacial areas are greatly affected. However, the individual mass transfer coefficient remains almost unchanged. For hexane wetting the walls partially (for a contact angle of water of 0 °, water wets completely the walls; for increasing contact angles, hexane wets partially the walls), the interfacial area available for mass transfer gets reduced and the overall mass transfer coefficient decreases.

The effect of reactor design is presented in Figure SI-11. It was observed that the main flow patterns do not change significantly among the three different reactor designs. Only the droplet size and holdup change, affecting the interfacial area. The overall mass transfer coefficients are on the order of 0.1 s^{-1} for all the three designs, with slightly larger values for the design with dot.

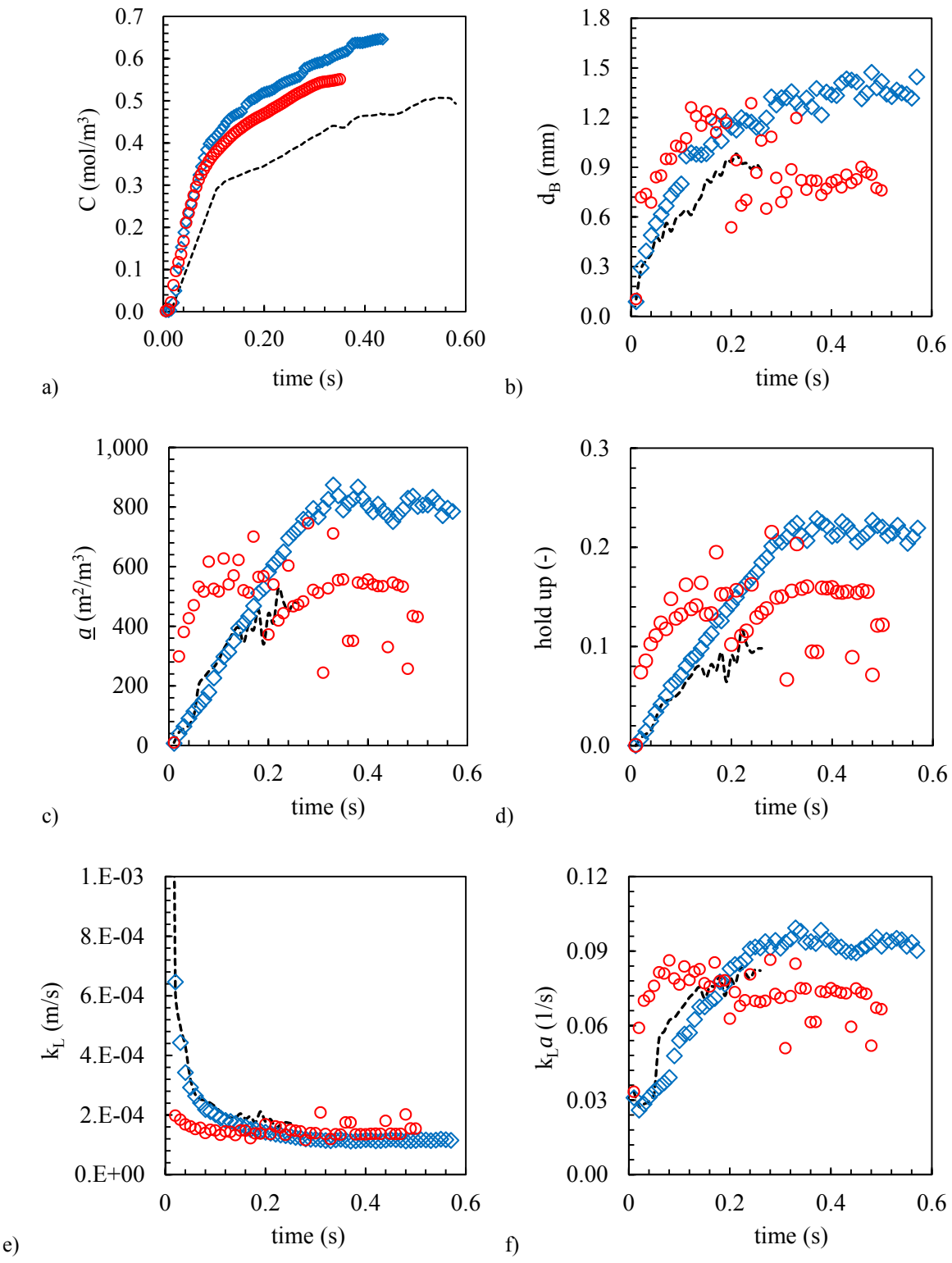


Figure SI-10: Effect of contact angle at 40 mL/min water and 10 mL/min hexane on a) bulk concentration in hexane; b) average drop size; c) specific interfacial area; d) hexane holdup; e) individual mass transfer coefficient; f) overall mass transfer coefficient Legend: ◇, 0º; ----, 75º; ○, 150º

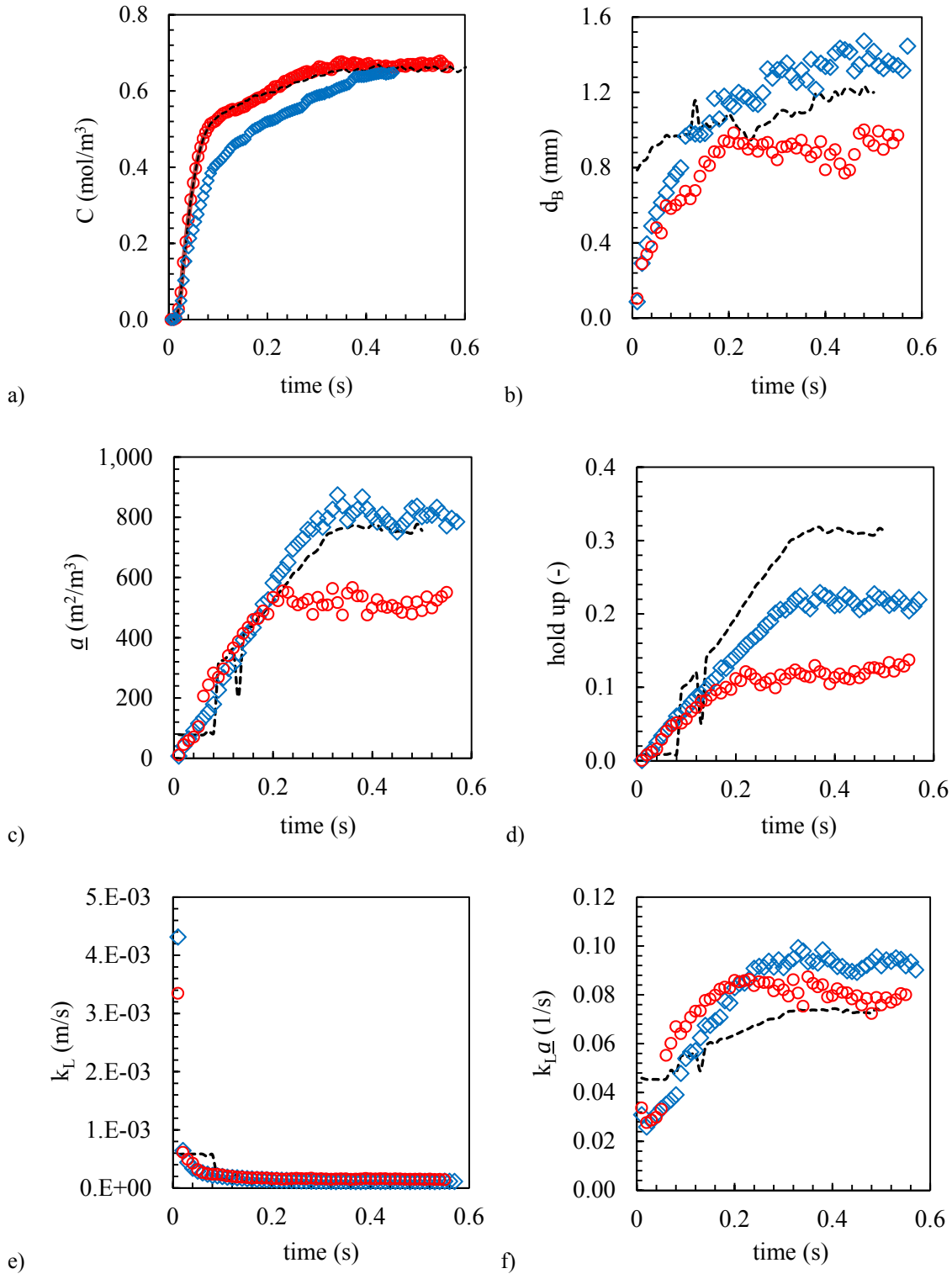


Figure SI-11: Effect of reactor design at 40 mL/min water and 10 mL/min hexane on a) bulk concentration in hexane; b) average drop size; c) specific interfacial area; d) hexane holdup; e) individual mass transfer coefficient; f) overall mass transfer coefficient Legend: ◇, AFR; ----, No Dot; ○, LFR

REFERENCES

[1] Haroun, Y.; Legendre, D.; Raynal, L. Volume of fluid method for interfacial reactive mass transfer: Application to stable liquid film. *Chem. Eng. Sci.,***2010**, *65*, 2896–2909

[2] Haroun, Y.; Raynal, L.; Legendre, D. Mass transfer and liquid hold-up determination in structured packing by CFD. *Chem. Eng. Sci.,* **2012**, *75*, 342–348

[3] Marschall, H.; Hinterberger, K.; Schüler, C.; Habla, F. Hinrichsen, O. Numerical simulation of species transfer across fluid interfaces in free-surface flows using OpenFOAM. *Chem. Eng. Sci.,* **2012**, *78*, 111–127