A Study on the effects of thermodynamic non-ideality and mass transfer on multi-phase hydrodynamics using CFD methods

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Abstract—Considering non-ideal behavior of fluids and its effects on hydrodynamic and mass transfer in multiphase flow is very essential. Simulations were performed that takes into account the effects of mass transfer and mixture non-ideality on hydrodynamics reported by Irani et al. In this paper, by assuming the density of phases to be constant and Raullt's law instead of using EOS and fugacity coefficient definition, respectively for both the liquid and gas phases, the importance of non-ideality effects on mass transfer and hydrodynamic behavior was studied. The results for a system of octane/propane (T=323 K, P =445 kpa) also indicated that the assumption of constant density in simulation had major role to diverse from experimental data. Furthermore, comparison between obtained results and the previous report indicated significant differences between experimental data and simulation results with more ideal assumptions.

Keywords—multiphase flow, VOF, mass Transfer, Raoult's law, non-ideal thermodynamic, CFD

I. INTRODUCTION

MANY processes in chemical and petrochemical industries involve gas–liquid mass transfer with accompanying reactions between components in the gas or the liquid phase. Despite this fact and substantial research efforts devoted to understand detailed knowledge on the fluid flow ,mass transfer and chemical reactions, thermodynamic behavior as well as their interactions are still lacking. In the past decade, the reaction engineering community has been active in exploring the possibilities to utilize computational fluid dynamics (CFD) in the modeling of multiphase flow phenomena.

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However, in most of the studies, mixture non-ideality and mass transfer are not considered simultaneously.

The direct application of CFD to chemical processes faces several problems; however, even in single phase flow, flow and mass transfer are described by highly non-linear terms that often cause numerical instabilities. More complex phenomena, such as multiphase flow and interfacial mass transfer with rigorous non-ideal behavior, are encountered in multiphase flow in chemical processes [1].

Recently, "hybrid" approaches have emerged as an alternative. In those, CFD is employed only for hydrodynamic simulation, while the chemical phenomena are resolved in a custom-built compartmental model [2]. Although this decoupling cannot be applied to cases where the coupling between hydrodynamics and chemistry is very strong, such as in combustion, many chemical reactors such as slurry reactors. Bauer and Eigenberger [3, 4] used a "zone model" to study a bubble column reactor; Bezzo, Macchietto and Pantelides developed an interface of communication between the gPROMS modeling software and a commercial CFD code; [5]. Zauer and Jones [6] used a segregated feed model in conjunction with CFD to study precipitation in a stirred tank. However, a fundamental weakness of all multizonal models is the difficulty of characterizing the mass and energy fluxes between adjacent zones. However, this fails to take into account the fact that the fluid properties are functions of system conditions (e.g. composition, temperature and pressure) which are themselves unknown. This framework is applicable to systems the physical properties of which are relatively weak functions of intensive properties [6].

Krishna and van Baten, has studied the interphase mass transfer and reaction (first order reaction rate) for one species without considering mixture non-idealities .In their study, densities were constant and they had estimated equilibrium constants with Henry's coefficients. They had also neglected the effect of mass transfer on hydrodynamics behavior of the system [7].

Later Breach has modeled non-ideal vapor–liquid phase equilibrium, mass and energy transfer in a binary system (H2O, H2O2). Because of operating conditions in his work, (P =100 kpa, T=433 K) he has neglected non-idealities in calculations of liquid density and gas phase equilibrium calculations. He has also ignored the effect of non-idealities on the calculation of gas and liquid phase internal energies [8].

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Also Banerjee has modeled evaporation of a binary mixture of ethanol and iso-octane into air flowing in an inclined 2D channel. Simulation has been carried out at atmospheric pressure and temperature ranging from 300 to 340 K. The liquid phase density was calculated based on the averaged mass fraction of individual components and the gas phase has considered as ideal gas. He has considered two-phase cells as interface in which the gas and the liquid are in equilibrium. Therefore the size of meshes should have been very fine around of interface. [9].

Recently the effects of the non-ideal behavior of phases on their hydrodynamic behaviors studied based on a CFD framework in which the properties of each phase are rigorously modeled as a function of temperature, pressure and concentration of phase constituting components using equation of state [11]. Mass transfer during condensation and vaporization was modeled by chemical potential at the liquid–vapor interface. Mass transfer resulting from the chemical potential field is determined by T-P flash calculation at the liquid-vapor interface. The equilibrium calculations were performed using the fugacity coefficient definition for both the liquid and gas phases The CFD framework developed based on Eulerian – Eulerian model. A finite volume scheme was used to solve the equations of motion.

In this paper, two cases were considered. The obtained results of these cases were compared with the case (case 0) in Irani's study[11]. In the first case (case 1) density of phases were assumed to be constant, and in the second case (case 2) they were calculated by equation of state (Peng-Robinson). In both cases Rault's law was used instead of fugacity coefficient definition for both the liquid and gas phases in order to study affection intensity of non-ideality on hydrodynamic behavior. The mathematical model of the system is described in section 2, and the bench mark used in this study is explained in section 3. Section 4 goes through the comparison between simulations and experimental results.

II. Mathematical Model

Continuity Equation for the Liquid and Gas phases

The variation of liquid holdup with time and position is obtained by solving the continuity equations for the liquid and gas phases. The continuity equation for the flowing liquid and gas is written in terms of the accumulation and convection terms balanced by the total mass transferred to and from the other phases (written in terms of interphase fluxes for gas-liquid equations, discussed in the next section).

Since gas and liquid phases do not interpenetrate into each other in the reactor, the VOF approach is used. In this approach, the motion of all phases is modeled by formulating local, instantaneous conservation equations for mass and momentum [10].

The Continuity equation for a phase, 'q', in a multiphase flow problem is as follows:

$$\frac{\partial}{\partial t}(\alpha_q \rho_q) + \nabla \cdot (\alpha_q \vec{v} \rho_q) = S_{pq} \tag{1}$$

$$S_{qp} = -S_{pq}$$

The velocity vector $\vec{v}$ comes from solving the Navier-Stokes Equations (NSE).

The right-hand (S_{pq}) side describes mass transfer from phase p to q. Where α_q is the volume fraction of phase q, which needs to satisfy the relation (2).

$$\sum_{q=1}^{N} \alpha_q = 1 \tag{2}$$

One of the most important characteristics of a multi-phase system is fractions of various phases. Thus, it is necessary to know the volume fraction, α_q of each phase, q, in the entire computational domain.

Momentum transfer equations

The variation of velocity with time and position is calculated by solving the momentum balance equation. The properties appearing in the transport equations are determined by their averaging based on phase volume-fraction.

$$\frac{\partial}{\partial t}(\rho \vec{v}) + \frac{\partial}{\partial x_j}(\rho \vec{v} \vec{v}) = \tag{3}$$

$$-\frac{\partial p}{\partial x_i} + \frac{\partial}{\partial x_j}\mu\left(\frac{\partial \vec{v}}{\partial x_j} + \frac{\partial \vec{v}}{\partial x_j}\right) + \rho g_i$$

$$\rho = \sum_{i=0}^{n} \rho_q \alpha_q \qquad \mu = \sum_{i=0}^{n} \mu_q \alpha_q$$

$$\frac{\partial}{\partial t}\alpha_g C_{ig} + \nabla \cdot (\alpha_g \vec{v} C_{gi} - D_{ig}\alpha_g \nabla C_{ig}) = \alpha_g N_i^{gl} \tag{4}$$

$$\frac{\partial}{\partial t}\alpha_l C_{il} + \nabla \cdot (\alpha_l \vec{v} C_{il} - D_{il}\alpha_l \nabla C_{il}) = -\alpha_l N_i^{gl} \tag{5}$$

Interphase Mass Transfer

The interphase mass transfer is related to the diffusion at the interface that is related to the concentration gradients at the interface, too [12]. Concentration gradient of species in each phase was approximated using Finite Difference approach. In fact mass transfer coefficient based on Film theory is originally obtained through this approach. According to this approach various elements of concentration gradients of phase 'q' can be obtained as follows:

$$\frac{\partial C_{iq}}{\partial x_j} \approx \frac{C_{iq} - C_{iq}^*}{\Delta x_j}$$

Where C_{iq} is the concentration of i-th component in phase q right at the interface and C_{iq}^* is the concentration of this component when phase q is at equilibrium with the other phase in the mixture (Fig 1). This is based on the fact that in a multiphase system, they are assumed to be at equilibrium right at their interface.

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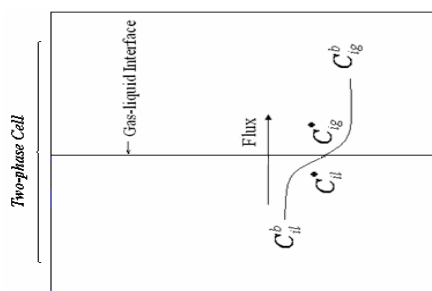Vol:3, No:10, 2009

Fig. 1 Schematic of two-phase cell and equilibrium at the interface

For a mixture containing vapor and liquid the equilibrium concentration of various components can be obtained through isothermal flash calculations which are presented at all chemical engineering thermodynamic text books [13, 14]. Details of flash calculation algorithm and equations were given in appendix.

The concentration of various species in vapor and liquid phases are obtained based on equations 4 and 5, respectively. Having obtained equilibrium concentrations, one can obtain the flux of species transfer (N_i^q) and the rate of inter-phase mass transfer (S_{pq}, which is source of Equation 1.) through equations 6 and 7 respectively, in which Mi is molecular weight for i-th species. Calculated flux for component 'i' (N_i^q) in one phase is a source or sink for the same component in the other phase because there is no accumulation at the interface.

$$N_i^q = D_{im} \frac{C_{iq} - C_{iq}*}{\Delta z_j} \qquad (6)$$

$$N_i^p = -N_i^q$$

$$S_{pq} = \sum_{i=0}^{n} N_i^q M_i \qquad (7)$$

Simulation procedure

The transport equations (Eq.'s 1, 3, 4, and 5) were discretized by control volume formulation [15]. UPWIND method was used for discretization. A segregated implicit solver method with implicit linearization was used to solve discretized momentum equations. These equations have been obtained through the application of the first-order upwind method on Eq.3, and for the pressure velocity coupling, the SIMPLE method has been used [15]. For the pressure equation, the pressure staggering option (PRESTO) method was used [15].

The structure of the program code is explained below. The program first reads the structured data from pre-processing section (in which the mesh representing the equipment has been built), before it goes into two nested iteration loops. Inner loop iterations are performed within each time step using the equations corresponding to the discretized version of the proposed model, while the outer loop goes through simulation times until it gets to the final time or steady state whichever happens sooner. At each time step, before going into the inner loop the fluid properties in each cell are calculated.

In the inner loop, all the discretized equations are solved in three steps. In the first step the physical properties such as density is updated based on the current solution. If the calculation has just begun, the fluid properties will be updated based on the initialized solution. In the second step the flash calculation is performed in order to obtain the equilibrium concentrations based on which the source terms of the species concentrations and continuity equations are obtained. In the third step, equations of continuity, momentum are solved and after obtaining the velocity and pressure fields, equations corresponding to species concentration are solved in order to obtain the profiles of the concentration of various species. In this step with the help of Eulerian-Eulerian approach (VOF approach), the trajectory of interface between two phases (liquid and gas) is determined. At the end of this step, convergence checking based on the norm of errors is done [14].

In order to get stable and meaningful results the time step must be very small (in the order of 10^{-4} s). In general, the time-stepping strategy depends on the number of iterations by time step needed to ensure very low residuals values (less than 10^{-7} for concentration and 10^{-6} for momentum and continuity). Computational time is within 3–4 weeks for the two dimensional simulations. Calculations have been carried out on a 4GB RAM, 3.2 GB CPU computer.

III. BENCHMARK FOR VALIDATION OF SIMULATION

We used experimental results, which were taken for validation of simulation [8]. A cylindrical vessel (Fig 2) filled with vapor and liquid hydrocarbons were selected as the benchmark. The liquid hydrocarbon was chosen to be pure Octane and the hydrocarbon in the gas phase was assumed to be Propane. Because of isothermal assumption in our simulation a circulator was used to fix system temperature at favorite value.
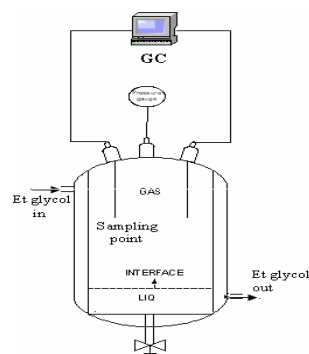

Fig.2 Schematic of Experimental set up

IV. RESULT AND DISCUSSION

Fig. 3 shows initial condition of the simulations for case 1 and 2 at which the concentration of octane in gas phase and propane in liquid phase set to zero. It was also assumed that there is no movement in the system and hence the velocity

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was set to zero for the whole domain. As time goes on, species are transferred between phases. This leads to a time varying concentration profiles in both phases and a general velocity field for the whole fluid that both of them originated from interphase mass transfer. The simulation results for concentration profiles and velocity field at certain time, for both cases are shown in Figs 4 to 9. As Figs 5 and 8 shows, octane was transferred from liquid phase to gas phase and concentration of octane in liquid was decreased whereas concentration of octane in gas was increased.
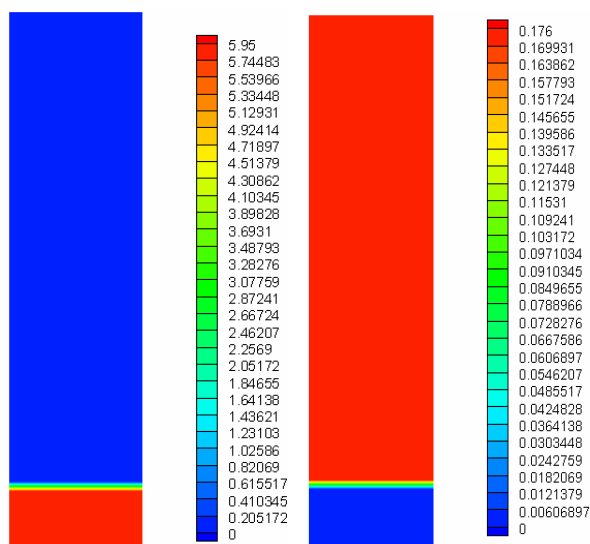
Fig. 3. Contour of octane concentration (left) and propane concentration (right) [mol /liter] and at t=0.0 second (case 1, 2)
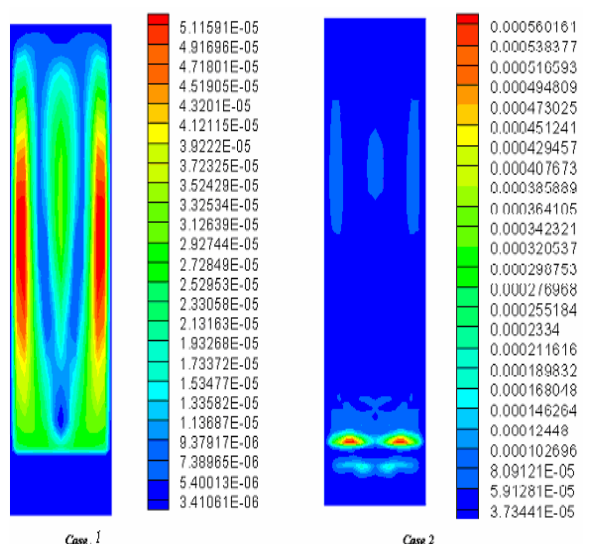

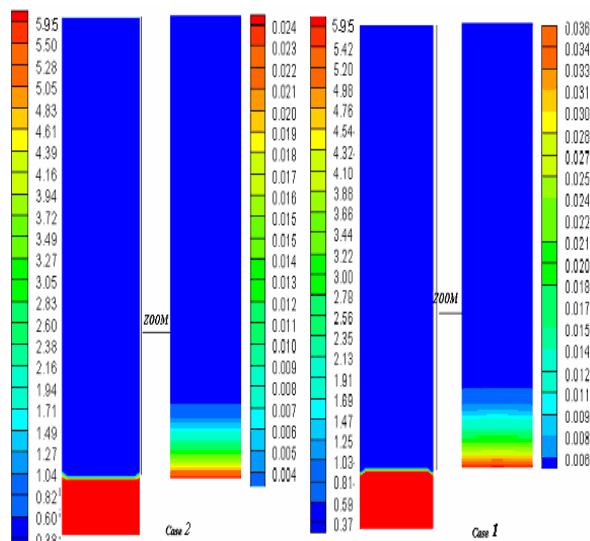Fig. 4. Contour of velocity (m/sec) at t=185 seconds (case 1, 2)

Fig.5. Octane concentration (mol /liter) at t=185 s (cases 1, 2)

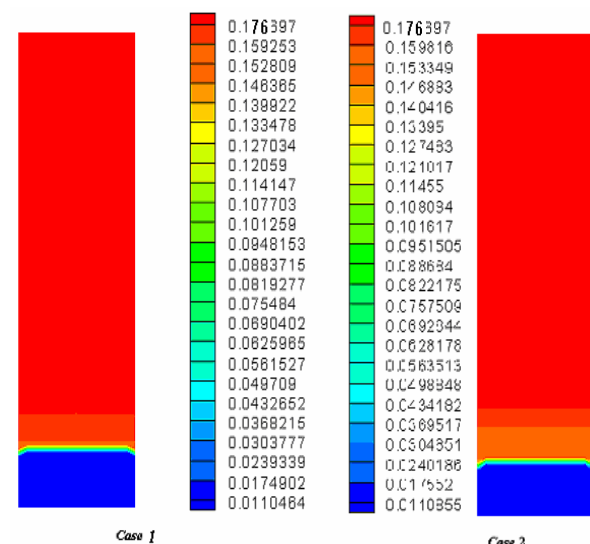
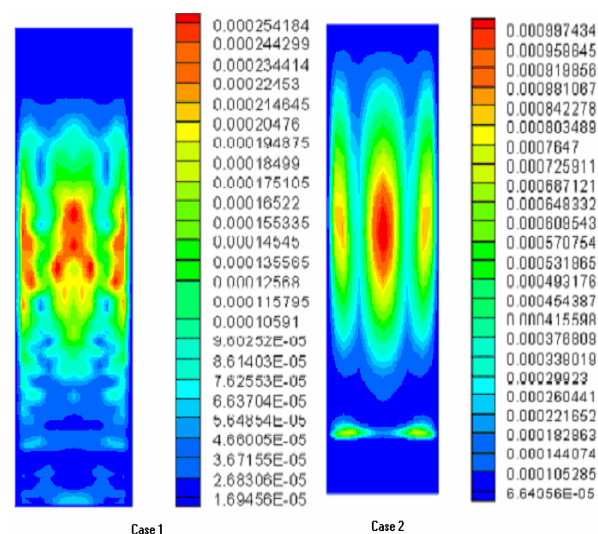Fig. 6. Propane concentration (mol /liter) at t=185 s (case 1 and 2)

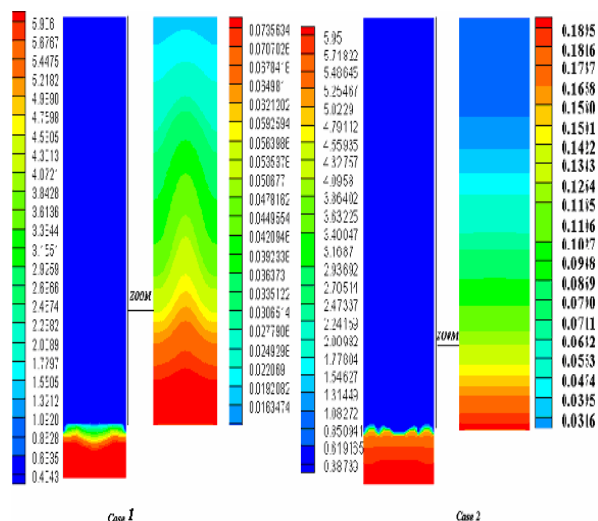Fig. 7. Contour of velocity (m/sec) at t=3500 s (case 1 and 2)

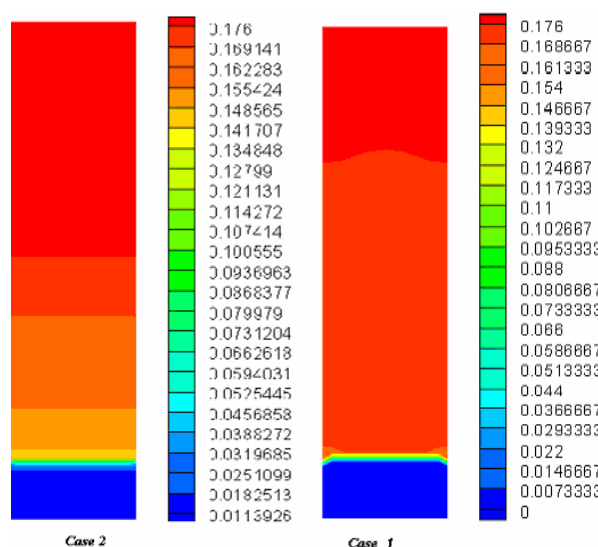Fig. 8. Octane concentration (mol /liter) at t=3500 s (case 1 and 2)

Fig. 9. Propane concentration (mol /liter) at t=3500 s (case 1 , 2)

As a result of mass transfer in the interface, velocity in this region is higher than others (Figs 4 and 7).

As seen in Figs 4 and 7 since the dissolution of octane in gas has not considered in calculation of gas phase density (case 1), velocity fields were different for cases 1 and 2. Thus bulk species concentrations in gas and consequently gradients in gas-liquid interface were solved differently. Therefore mass fluxes of species were different too. Due to difference in bulk species profile, the flux of species was also different (inter-phase mass transfer for cases 1 and 2 were .025 and .05 kg/ (m^3.s) respectively).

On the other hand Propane dissolved in liquid phase which leads to its concentration decrease in gas phase, it can be seen right at the interface the Propane concentration has its least value for gas phase and the largest value for the liquid phase (Figs 6, 9).

In order to see deviation of mentioned cases from experimental data quantitative comparisons were done between data obtained for Octane concentration in gas phase

and their corresponding simulated results that is shown in Fig. 10. Since it was not possible to use the GC for dynamic measurement of more than one point, only five experimental data have been obtained and compared against their corresponding points obtained by simulation. Only the gas concentrations can be measured online due to impossibility of measurement liquid phase. As illustrated in Fig. 10, the maximum amount of difference between simulations and experimental data would occur at the start of simulation (t = 0). The mentioned difference was due to the delay in Gas Chromatograph injection during fixing the system pressure. Because of using Rault-law in equilibrium calculation instead of fugacity coefficient definition for the liquid and gas phases in both cases, flux of species are calculated incorrectly. As seen in Fig.13 the difference between simulations in the cases and experimental intensified in comparison with previous study [9]. In case 1, since the densities of phases were assumed constant, the effects of dissolved components on density of phases and buoyancy effect aren't considered; consequently incorrect velocity field and species concentrations in addition of the mass transfer flux are predicted.
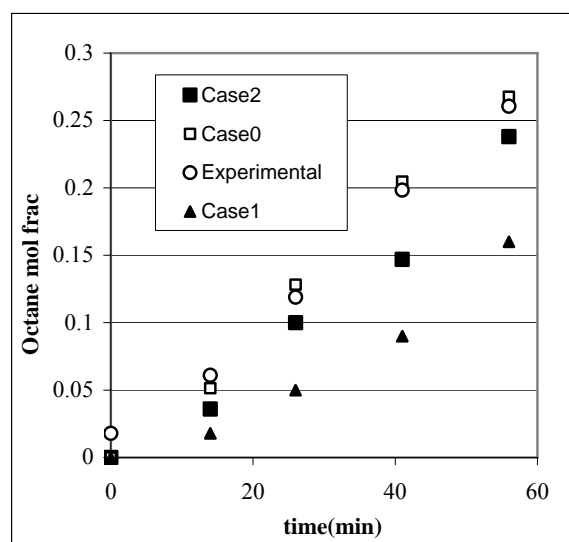

Fig. 10. Comparison of Experimental and simulations

Table 1 shows the simulated and measured concentration of Octane in gas phase along with their relative difference. As this table shows, the errors in Octane mole fraction in gas phase at all times are less than five percent while we considered all of non idealities (case0). Since, the system is not at equilibrium and the mass transfer is simulated based on the CFD approach, and no empirical correlation has been used in the simulation, these small errors can be used as a rational for the accuracy of the simulation results including the velocity and gas phase volume fraction profiles. The errors in case 2 and case 1 were higher (21-31%) and (38-65%) respectively. These errors show that such simplifications in similar modeling cases lead to wrong predictions.

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TABLE I COMPARISON BETWEEN SIMULATION AND EXPERIMENTAL DATA AND RELATIVE ERRORS

time	experimental	Case0	Case2	Case1	Error(case0)	Error(case2)	Error(case1)
0	0.018	0	0	0	100	100	100
14	0.0528	0.0515	0.036	0.018	2.46212121	31.818182	65.909091
26	0.1273	0.128234	0.1	0.05	0.73369992	21.445405	60.722702
41	0.1983	0.2047	0.147	0.09	3.22743318	25.869894	54.614221
56	0.26053	0.2676	0.238	0.16	2.713699	8.6477565	38.586727

V. CONCLUSIONS

The aim of this paper was to study the importance and effects of considering non-ideal thermodynamic in the simulation, which was presented in previous study [11].

For this purpose, the benchmark was simulated by using numerical method based on a macroscopic model and the finite volume method. In this simulation, non-ideality wasn't considered in the cases. Rault-law was used in equilibrium calculation instead of fugacity coefficient definition for the liquid and gas phases in both cases, and in the case 1 density of phases was assumed constant.

Quantitative validation of simulated system with experimental data was based on online analyzing of gas phase flow by Gas Chromatograph. The predictions in both cases were compared with the experimental measurements and the simulation data in our previous work. It was found that the difference between the gas species concentrations in experiment and simulation increased by assumption of more ideality. The results also indicated that the assumption of constant density in simulation had major role to diverse from experimental data. (Fig.10). It is worth to mention here that the closure for the mass transfer is not as mature as the closures used for the hydrodynamics. However, we got confident that if a more accurate closure for the mass transfer with considering non-ideality to be applied; the present model would give a closer comparison with the experimental investigation as has been shown in this study. Our model in our previous work is based on the Eulerian – Eulerian approach and combines hydrodynamics, mass transfer and mixture non-ideality is able to predict behavior of a multiphase reactors. The model and results presented in this work would be useful for extending the application of CFD based models for simulating large multiphase reactors.

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