Modeling of Partial Oxidation in Gas–Solids Downer Reactors

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Selective partial oxidations represent an important class of reactions in the process industry. Of particular interest is the partial oxidation of n-butane to maleic anhydride (MAN), which is arguably the largest commercialized alkane partial oxidation process. Partial oxidation of n-butane, which uses vanadium phosphorous oxide (VPO) as a heterogeneous catalyst, is believed to operate through a unique mechanism in which lattice oxygen oxidizes n-butane selectively to MAN. Past work has shown that performing partial oxidation reactions in gas–solids riser configuration is realizable and commercially viable, which has lead to commercialization of this technology in the last decade. Though the riser configuration allows optimal and independent control of the oxidation and reduction steps, the riser unit suffers from solid backmixing at walls, which in turn result into lower conversion, nonoptimal selectivity and diminished overall yield of desired product. In recent years, there has been growing interest in downers involving cocurrent downflow of both solids and gas phases, hence offering relatively uniform flow characteristics. In this contribution, we explore through modeling the implications of effecting partial oxidation reactions in a downer (gas–solids cocurrent downflow) compared to that in a conventional riser reactor (gas–solids cocurrent up flow) operated under equivalent *operating conditions. Further, we explore the operational space of downers for these reactions, suggesting ways for improving the productivity of downer for partial oxidation applications.* © 2009 American Institute of Chemical Engineers *AIChE J,* 56: 2150–2162, 2010

Keywords: CFB downer, CFD, hydrodynamics, lattice oxygen, riser, selective oxidation

Introduction

Maleic anhydride (MAN) is one of the most industrially important multifunctional chemical intermediates used mainly in the manufacture of unsaturated polyester resins (50% of total MAN production[1]), and well as in other chemical industries such as lubricating oil additives agricultural chemicals, textile chemicals, paper reinforcement additives, food additives and pharmaceuticals.[2] In the late 1990s, DuPont announced the commissioning of a plant for manufacturing Tetrahydrofuran (THF), in which a transport bed reactor (riser) for partial oxidation of n- butane to MAN is a key component of the overall process.[3] This marked a major development in the commercial manufacturing of MAN, and partial oxidation process in general.

Historically, maleic anhydride was first produced commercially by National Aniline and Chemical Company in 1933 by oxidation of benzene in packed bed reactor using

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vanadium oxide catalyst. This process was highly atom inefficient[4] (atom economy of 44%), because benzene with six carbon atoms is used to produce a C4 compound, wasting two carbon atoms per molecule of reactant used. In 1966,[5] a new process for the manufacture of maleic anhydride directly from n-butane (C4 compound) feedstock was proposed. As compared to benzene oxidation process which offered atom economy[4] of 44%, butane oxidation process offered an atom economy of about 65%, thus making it ‘‘greener’’ process. In the present day context of global warming issues, the latter route is definitely preferred as the earlier process released two molecules of CO_2 per molecule of reactant (benzene) used. Rapid increase in the price of benzene and strict pollution control norms in the next few decades necessitated commercialization of n-butane process and the first commercial plant was commissioned operational in 1974 by Monsanto. In subsequent decades, a variety of reactors such as multitubular fixed bed reactor,[6,7] fluidized bed reactor[8] and circulating fluidized bed reactor[8,9] have been used for n-butane oxidation process. Multitubular fixed bed reactors suffered from hot spot formation owing to the highly exothermic nature of this reaction. Fluidized bed reactors[8] allowed fine catalyst particles to be used, thus reducing temperature and concentration gradients with efficient use of the particle surface, and were thus the next logical choice. Rapid movement of catalyst particles prevented formation of a flame front and hence the reactor could be operated with higher butane concentration.

In 1996, DuPont commercialized the n-butane oxidation process based on circulating fluidized bed (CFB) technology,[3] in which oxidation and reduction processes were carried out in separate vessels. Independent optimization of oxidation and reduction allowed significant increase in the selectivity of maleic anhydride. For instance, at 50% conversion at 360^0C the riser showed a selectivity of 70%, as against 50% selectivity demonstrated in the fluidized bed reactor.[3] Though the riser offers better gas solids contacting as compared to that of fluidized bed reactor, it is well documented that it suffers from solids backmixing at walls under high flux operation conditions.[10,11] Also, counter-gravity flow sets up instabilities resulting in locally high slip velocities which leads to the nonuniform distribution of the catalyst particles, and in turn the desired products. Roy et al.[12] proposed a phenomenological model for the partial oxidation of n-butane in a gas–solids riser reactor using steady state kinetics,[13] as well as unsteady state kinetics.[14] Roy et al.[12] studied the effect of catalyst deactivation, n-butane feed concentration and solids backmixing, and in summary concluded that the highly backmixed solids phase and corresponding exposure to longer residence times for a fraction of the catalyst inventory results in reduced selectivity of the process to the desired product (MAN).

In last two decades, a new ‘‘quick’’ reactor concept, the so called ‘‘downer’’ reactor[15,16] has been proposed to overcome the limitations of riser reactor. Downer is a counterpart of riser in which both gas and solids phase are moving cocurrently downwards at high velocities (in the range of 3–15 m/s). As compared to riser operating at same operating conditions, a downer is claimed to offer more uniform and dilute flow with a shorter average contact time. Emig et al.[17] have studied partial oxidation reaction in downer reactor with a fluidized bed regenerator. These authors proposed a reactor for downer reactor as well as fluidized bed regenerator and it was found that lattice oxygen distribution in the oxidized catalyst modeled via ‘‘oxygen loading distribution’’ is one of the most important factors influencing the performance of the reactor. It was found that to achieve higher selectivity, the catalyst should be uniformly loaded with sufficient amount of oxygen. The issues related to ‘‘lattice oxygen distribution chemistry’’ are further discussed below.

Aside from the work of Emig et al.,[17] no other contribution has been reported in the open literature discussing the potential of downers for synthesis reactions. In particular, literature is scant in benchmarking the potential of downers vis-à-vis risers for a chosen application. In this work, an attempt is made to seek to highlight these issues through the coupling of CFD simulations of gas solids flow in rises and downers and their reactor modeling for partial oxidation reaction.

Kinetics of n-Butane Oxidation

n-Butane oxidation is highly exothermic in nature and the main products are carbon monoxide, carbon dioxide and water, in addition to the desired product, maleic anhydride. Stoichiometry of the three principal reactions involved are as follows:

$$\text{n-}C_4H_{10} + 3.5\ O_2 \rightarrow C_4H_2O_3 + 4H_2O$$
$$\Delta H_{R-298K} = -1261\ \text{kJ/mol},\quad \Delta G_{298K} = -1248\ \text{kJ/mol} \quad (1)$$

$$\text{n-}C_4H_{10} + 4.5\ O_2 \rightarrow 4CO + 5H_2O$$
$$\Delta H_{R-298K} = -1526\ \text{kJ/mol},\quad \Delta G_{298K} = -1684\ \text{kJ/mol} \quad (2)$$

$$\text{n-}C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$$
$$\Delta H_{R-298K} = -2659\ \text{kJ/mol},\quad \Delta G_{298K} = -2701\ \text{kJ/mol} \quad (3)$$

As butane behaves as a weak base towards metal oxides, vanadium phosphorous oxide (VPO) having acidic properties and several oxidation states of Vanadium is used as the catalyst[13,18] for this process. After the first breakthrough,[19] a significant number of studies have been carried out focusing on various aspects of n-butane oxidation by VPO catalyst. The participation of lattice oxygen and capability of VPO catalyst to store lattice oxygen are now well established facts in VPO oxidation literature.[20] However, there is ambiguity about the exact role played by lattice oxygen and what role butane plays in the reaction mechanism. Buchanan and Sundaresan[21] as well as later researchers like Huang et al.,[22] assumed that lattice oxygen from the catalyst reacts with the adsorbed butane, whereas Schneider et al.[23] assumed that lattice oxygen reacts with gas phase oxygen. Huang et al.[22] further postulated that lattice oxygen is responsible only for the formation of MAN whereas butane oxidizes to CO_x via participation of adsorbed oxygen. In contrast, Mills et al.[14] and Lorences et al.[24] proposed a mechanism in which only ‘‘lattice oxygen’’ is responsible for MAN formation as well as CO_x formation.

Another important issue which requires further attention is the mechanism of diffusion of sub-surface oxygen. Most of the studies agree that subsurface oxygen is several monolayers thick[14,21,22]; however, the mechanism of sub-surface diffusion is not clear. Wang and Barteau[25] argued that this process is fast enough as compared to the butane oxidation step, whereas other studies[14,22] have reported that subsurface oxygen diffusion is relatively slow. The role of ‘‘subsurface oxygen diffusion’’ becomes crucial especially if the reactor is a short contact time reactor (such as some elements of a circulating fluidized bed loop), as butane oxidation could become limited by the extent of regeneration of the catalyst and the ability (or lack thereof) of the subsurface oxygen to contact the gas–phase oxygen at the catalyst surface.[26] Additionally, if the solids flow in the reactor is nonuniform then partially reduced catalyst may get permanently deactivated finally resulting into lower MAN yields after some passes following system startup.[27] In summary, if reactors such as risers, fluidized beds or downers are to be investigated for VPO oxidation then there is need of more kinetic investigation which will unveil the role of butane, adsorbed oxygen and comparative rates of lattice oxygen diffusion.

In the current work, unsteady state kinetics from Mills et al.[14] has been used to evaluate the performance of the downer reactor on a comparative basis with an equivalent riser reactor. As compared to other researchers, including relatively recent publications,[22,28] Mills et al.[14] advocate the role of subsurface oxygen diffusion explicitly in their kinetic mechanism. Further, they show clear evidence of this mechanism through their kinetics work using a TAP (‘‘Temporal Analysis of Products’’) reactor, a millisecond microreactor setup wherein it is possible to temporally segregate oxygen-rich and oxygen-lean environments. One notes that it is precisely the periodicity that a typical VPO catalyst particle ‘‘sees’’ in its sojourn through the partial oxidation reactor and regenerator in a circulating fluidized bed loop. Hence we find it prudent to adopt the kinetic scheme proposed by Mills et al.,[14] owing to its generality and attempt to explicitly account for the lattice oxygen diffusion step.

Mills et al.[14] proposed that the VPO catalyst contains a thin layer of vacant sites in which atmospheric oxygen can diffuse in and penetrate into the lattice. This is referred to as ‘‘subsurface oxygen.’’ During the reoxidation of the catalyst (in the regeneration of the vessel), filling of gas phase dioxygen (O_2) continues until the subsurface oxygen vacancies approach saturation. Subsequently, the VPO catalyst is subjected to the oxygen lean environment (such as in the vessel where the partial oxidation of n-Butane occurs) this subsurface oxygen act as a reservoir for the supply for oxidation (both partial and complete) and surface lattice sites vacated due to the chemical reaction gets replenished by this diffusing subsurface oxygen. Thus, the depletion of lattice oxygen at the surface (reacting with gas phase n-butane) creates a concentration gradient between surface and core of a catalyst particle, which drives further diffusion from the core to the surface. This concept is depicted in Figure 1. Clearly, a key for this mechanism to work smoothly is to have sufficient replenishment of surface lattice oxygen at an adequate rate.

Our goal in this contribution is not to criticize the various reported mechanisms, which is a distinct challenge for chemists as of today. We will focus in this paper on the possibilities of efficient gas–solids contacting with partial oxidation chemistry, in which the lattice oxygen diffusion has a distinct role. As argued above, the kinetics reported by Mills et al.[14] offers the possibility for exploring this objective with a CFD and reactor modeling framework.

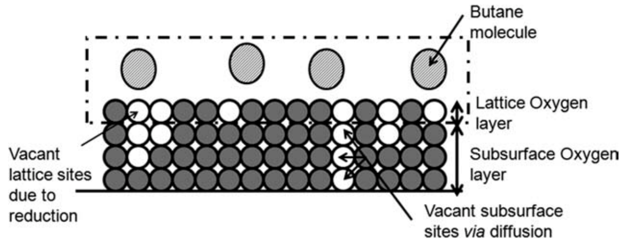


Figure 1. Conceptual diagram showing the role of subsurface oxygen diffusion in selective oxidation of butane (Only reactant species are shown).

The kinetic model can be described as (Mills et al.[14]):

$$\text{n-}C_4H_{10} + 7(O)_{\text{lattice}} \rightarrow C_4H_2O_3 + 4H_2O + 7(.)_{\text{lattice}} \quad \text{(r1)}$$

$$\text{n-}C_4H_{10} + 9(O)_{\text{lattice}} \rightarrow 4CO + 5H_2O + 9(.)_{\text{lattice}} \quad \text{(r2)}$$

$$\text{n-}C_4H_{10} + 13(O)_{\text{lattice}} \rightarrow 4CO_2 + 5H_2O + 13(.)_{\text{lattice}} \quad \text{(r3)}$$

$$r_i = k_i[C_4H_{10}]\theta_i^{a_i} \quad i = 1, 2, 3$$
$$a_1 = 0.412;\ a_2 = 1;\ a_3 = 0.865 \text{ at } T = 653K$$

In the above, (.) represents a vacant lattice oxygen site. The net rate of butane disappearance and of product formation can be obtained as the linear combination of the reaction rates r_1, r_2 and r_3.

Modeling: CFD and Reactor Model

The model developed in the current work follows the earlier approach of Roy et al.[12] First, an Euler–Euler CFD simulation of vessel of interest (downer) is performed and the flow parameters such as mean velocity, mean phase fraction and dispersion numbers are extracted from this CFD simulation. Next, a scalar transport simulation is performed using CFD imposed on the fully developed flow field simulated by the hydrodynamic model. Using the residence time distribution (RTD) curves thus generated, dispersion coefficient for each phase is extracted by matching the moments of the simulated RTD and that from the axial dispersion model with closed-closed boundary conditions. Using this hydrodynamic picture, a reactor model is developed incorporating the key elements of the full CFD simulation and the reaction kinetics. Note that a more ‘‘exact’’ alternative to this approach would have been to have an Euler–Lagrange model of the hydrodynamics and track the fate of each catalyst particle in its sojourn through the vessel of interest. Such a computation would be prohibitively expensive from a computational viewpoint. The approach that has been used, however, is almost equally predictive because essentially it classifies the solids catalyst phase into ‘‘bins’’ or ‘‘packets’’ of residence times, and tracks the fate of each ‘‘packet’’ through the reactor of interest. In essence, our approach is similar to assuming ‘‘segregated flow’’ of the various packets within the field that has been computed *a priori* by CFD.

CFD modeling of downer reactor

As discussed in the above section, an Euler–Euler CFD model is formulated for the downer flow. The ensemble

Table 1. List of the Important Parameters used in the CFD Simulation of Downer

Downer Specification (Zhang et al. 1999, 2000)	$L \times D$	9.1 m × 0.1 m
Solid Properties	Apparent particle density	1500 kg/m^3
	Sauter mean diameter	67 microns
Model	Solver	2D, axi-symmetric,
	Multiphase	Eulerian- Eulerian
	Turbulence	Standard K-ε Model
Grid	Radial × Axial (uniform)	15 × 1860
KTGF Parameters	Granular temperature	1e-5 m^2/s^2
	e_p, e_w	0.95,0.90
	Specularity coefficient	0.5
Wall Boundary Condition	Gas Phase	No-Slip condition
	Solid Phase	Johnson Jackson

averaged "two fluid" conservation equations[29] that are solved for the phases are as follows (assuming no mass exchange between phases)

Continuity (fluid phase):

$$\frac{\partial}{\partial t}\left(\varepsilon_f \rho_f\right) + \nabla \cdot \left(\varepsilon_f \rho_f \vec{u}_f\right) = 0 \tag{4a}$$

Continuity (solids phase):

$$\frac{\partial}{\partial t}(\varepsilon_s \rho_s) + \nabla \cdot (\varepsilon_s \rho_s \vec{u}_s) = 0 \tag{4b}$$

Momentum (fluid phase):

$$\frac{\partial}{\partial t}(\varepsilon_{\mathrm{f}} \rho_{\mathrm{f}} \vec{u}_{\mathrm{f}}) + \nabla \cdot (\varepsilon_{\mathrm{f}} \rho_{\mathrm{f}} \vec{u}_{\mathrm{f}} \otimes \vec{u}_{\mathrm{f}}) = -\varepsilon_{\mathrm{f}} \nabla p + \nabla \cdot \bar{\bar{\tau}}_{\mathrm{f}} + \varepsilon_{\mathrm{f}} \rho_{\mathrm{f}} \vec{g} + \beta_{\mathrm{sf}}(\vec{u}_{\mathrm{s}} - \vec{u}_{\mathrm{f}}) + \vec{F}_{\mathrm{f}} \tag{5a}$$

Momentum (solids phase):

$$\frac{\partial}{\partial t}(\varepsilon_{\mathrm{s}} \rho_{\mathrm{s}} \vec{u}_{\mathrm{s}}) + \nabla \cdot (\varepsilon_{\mathrm{s}} \rho_{\mathrm{s}} \vec{u}_{\mathrm{s}} \otimes \vec{u}_{\mathrm{s}}) = -\varepsilon_{\mathrm{s}} \nabla p - \nabla p_{\mathrm{s}} + \nabla \cdot \bar{\bar{\tau}}_{\mathrm{s}} + \varepsilon_{\mathrm{s}} \rho_{\mathrm{s}} \vec{g} + \beta_{\mathrm{sf}}(\vec{u}_{\mathrm{f}} - \vec{u}_{\mathrm{s}}) + \vec{F}_{\mathrm{s}} \tag{5b}$$

Total volume conservation:

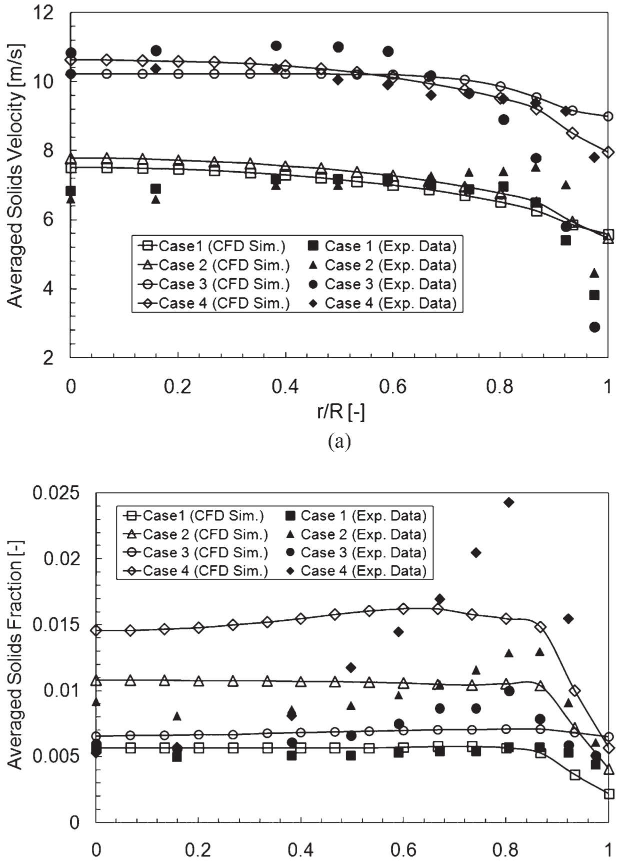
$$\varepsilon_{\mathrm{s}} + \varepsilon_{\mathrm{f}} = 1 \tag{6}$$

Details of the CFD simulation and parameters have been reported in an earlier work.[30] In case of high velocity gas–solids dispersed flow such as in a downer, the gas–solids drag is found to be the dominating interaction. The authors have reported earlier[30] that the formalism due to Matsen[31] for drag was the most suitable closure for predicting the high slip velocities of dilute gas–solids downer flows. This finding was in contrast to popularly used closures such as that due to Wen and Yu.[32]

The open literature is scarce in experimental data on hydrodynamics in downers. To validate the CFD model, data published by Zhang et al.[33,34] was used as a reference. The downer dimensions and other geometrical and process parameters were chosen as per that publication. Four operating conditions were chosen for the current study, namely:

- Case 1: Low superficial gas velocity and low solids circulation flux ($U_{\mathrm{g}} = 3.7$ m/s, $G_{\mathrm{s}} = 49$ kg/m^{2}s)
- Case 2: Low superficial gas velocity and higher solids circulation flux ($U_{\mathrm{g}} = 3.7$m/s, $G_{\mathrm{s}} = 101$ kg/m^{2}s)
- Case 3: Higher superficial gas velocity and lower solids circulation flux ($U_{\mathrm{g}} = 7.2$ m/s, $G_{\mathrm{s}} = 101$ kg/m^{2}s)
- Case 4: Higher superficial gas velocity and higher solids circulation flux ($U_{\mathrm{g}} = 7.2$ m/s, $G_{\mathrm{s}} = 208$ kg/m^{2}s)

Two-dimensional, unsteady state, axisymmetric simulations were carried out using commercial software package FLUENT 6.2.16. Table 1 lists the important parameters used in the CFD simulation. Kinetic theory of granular flow (KTGF) was used to model solids phase interactions. These CFD simulations were checked for the sensitivity to the numerical parameters such as grid independence and time step and model parameters such as parameters for turbulence model and KTGF model parameters. As the flow in downers is dilute, CFD simulations were not found to be sensitive to the KTGF parameters (such as specularity coefficient and granular temperature). Figure 2a and 2b show the results of the CFD simulations using Matsen's[31] closure for drag, and



(a)

(b)

Figure 2. Comparison of time-averaged hydrodynamics profiles predicted by CFD model with that of experimental data (Zhang et al.[33,34]) in fully developed region of downer (a) mean solids velocity (b) mean solids fraction.

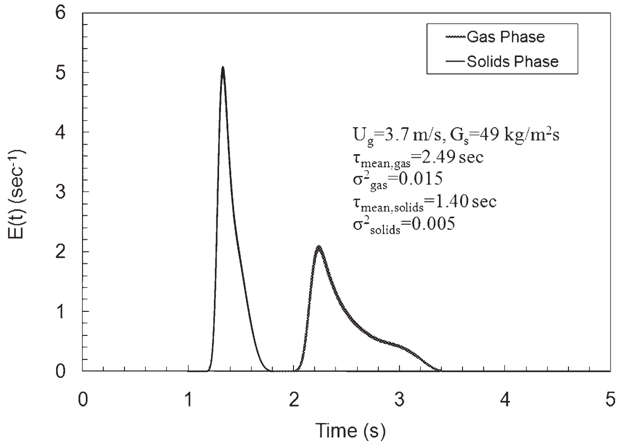


Figure 3. RTD curve for gas and solid phase in downer from scalar transport simulation for U_g = 3.7 m/s and G_s = 49 kg/m^{2}s.

its comparison with experimental data.[33,34] The simulations were able to predict the experimentally observed velocity profiles to acceptable accuracy.[30]

Scalar transport simulation

The underlying philosophy of the scalar transport equation is to tag each phase with an inert tracer, and simulate its distribution over time and space, and in particular at the exit of the vessel of interest (downer). One notes that the global dispersion (about the mean velocity profile) in any convection dominated system is driven primarily by multiscale convective transport (through eddy dispersion or deviation from the mean velocity profile). This is in analogy to the convective contribution to the axial dispersion coefficient in Taylor–Aris dispersion,[35,36] which originates in the parabolic profile of laminar flow in a tube. As there is no mass exchange between phases, in the present case one may tag each phase independently. With that understanding, the scalar transport equation in the kth phase is given by:

$$\frac{\partial}{\partial t}\left(\varepsilon_k\rho_k\phi_k^n\right)+\nabla.\left(\varepsilon_k\rho_k\overrightarrow{u_k}\phi_k^n-\varepsilon_k\Gamma_k^n\nabla\phi_k^n\right)=0 \qquad (7)$$

In Eq. 7, ϕ_k^n is the nth scalar in the kth phase. The simulation is implemented as follows. First, the fully developed velocity and phase fraction profiles simulated via CFD using Eqs. 4–6 are solved. Under the reasonable assumption that the hydrodynamic profiles are not altered by the scalar transport, the scalar injection is simulated by setting the scalar concentration at the inlet (0^-) to a fixed value, such as unity. The transient simulation for ϕ_k^n is executed (with precalculated profiles of ε_k and $\overrightarrow{u}_k$ in Eq. 7), and the flow averaged (‘‘mixing-cup’’) concentration at the exit plane is evaluated as a function of real time. The flow-averaged concentration or ‘‘mixing cup concentration"[37] is defined as:

$$\left\langle\phi_k^n(t)\right\rangle=\frac{\int_A c\,\overrightarrow{u}\cdot\overrightarrow{n}\,dA}{\int_A \overrightarrow{u}\cdot\overrightarrow{n}\,dA} \qquad (8)$$

Table 2. List of the Important Parameters Extracted from RTD Tracer Simulation of Downer

Case No.	U_g (m/s)	G_s (kg/m^{2}s)	Gas Phase τ_g (s)	Gas Phase σ^2_g (-)	Solid Phase τ_s (s)	Solid Phase σ^2_s (-)
1	3.7	49	2.49	0.015	1.40	0.005
2	3.7	101	2.49	0.011	1.35	0.005
3	7.2	101	1.30	0.006	0.97	0.003
4	7.2	208	1.28	0.005	0.95	0.004

In Eq 8, ‘‘A’’ is the area of the exit plane and $\vec{n}$ is the unit outward normal to the plane. Subsequently the flow of these scalars is evaluated as a function of time and the flow weighted concentration of injected scalar in the specified phase at the exit of the downer is monitored. By normalizing these concentrations, the residence time distribution for each phase in downer is obtained for all the four cases. First moment of the curve (mean residence time) and second central moment normalized by square of the first moment is reported for each phase in all the four simulation cases. Figure 3 shows the RTD curve for one of the cases, namely, Case 1: U_g = 3.7 m/s; G_s = 49 kg/m^{2}s. RTD curves show that for all of the cases, both phases in downer show plug flow like behavior which is always claimed as one of the distinct advantages of downer configuration in literature. Table 2 lists the mean residence times and dispersion coefficient for each phase for all the four cases extracted from scalar transport simulations. If one assumes ‘‘axial dispersion

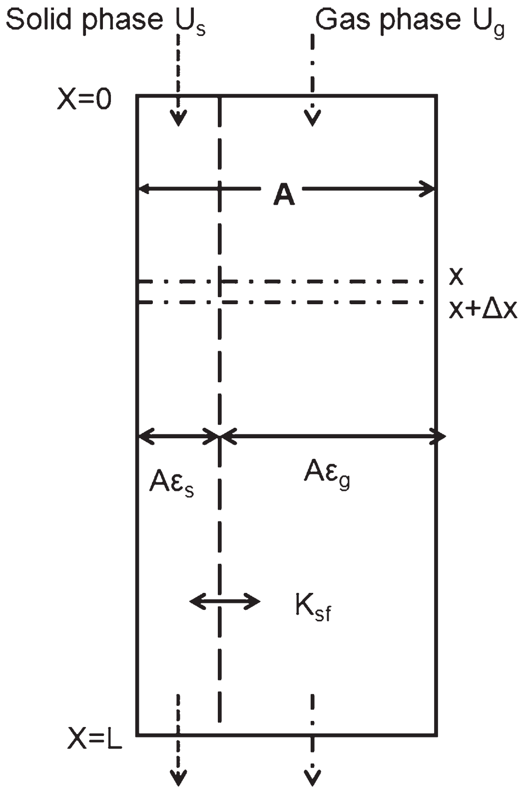


Figure 4. Development of reactor model for partial oxidation of n-butane in downer: Schematic of approach followed.

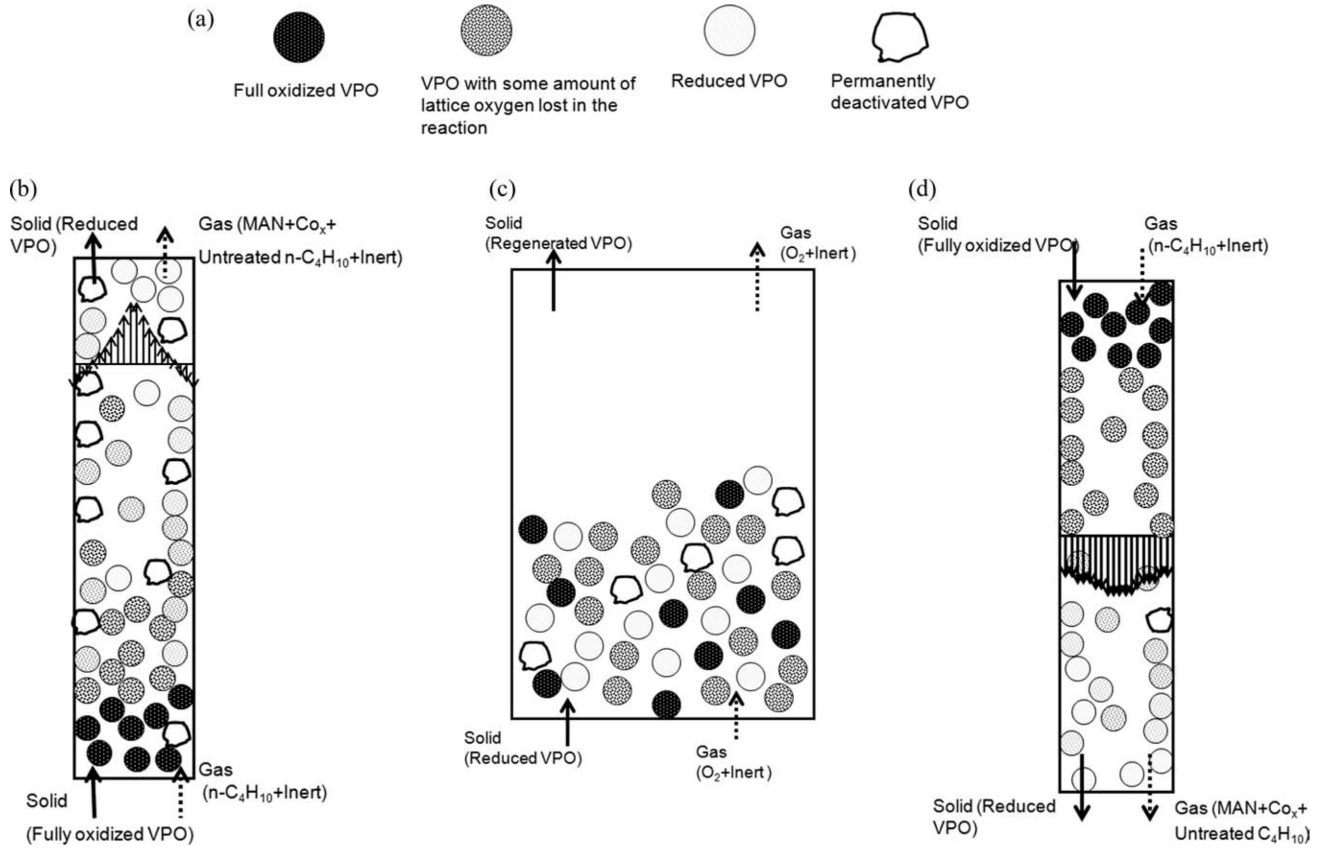


Figure 5. Conceptual diagram showing fate of VPO catalyst in various configurations (a) various stages of oxidation of the VPO catalyst (b) Riser reactor (c) Fluidized bed Regenerator (d) Downer reactor.

model'' for each phase then by matching the variance of the RTD curve of given phase with the dispersion number, one can determine the effective ''dispersion coefficient'' of that phase.

Though the CFD simulation is done for 9.3 m downer column (same as that of experimental setup[33,34]), for the reactor model simulation, a downer of length 22 m is chosen as base case and the flow parameters are subsequently scaled up for this column. This scaling was essential to allow sufficient residence time for solids phase in the reactor. This ensured adequate mean residence time to the catalyst, which was not a consideration in the purely hydrodynamic cold-flow experimental study.[33,34]

Reactor model for downer

The reactor model for the downer is developed by coupling the axial dispersion model[36] with the hydrodynamic parameters extracted from CFD simulations and scalar transport simulations. Figure 4 shows a schematic diagram for the reactor model development. Note that it is assumed that the gas is sufficiently dilute in reactants so that U_g does not change along the length of the reactor.

Mass balance for *ith* species in the solid phase:

$$\varepsilon_s \frac{\partial C_{s_i}}{\partial t} = -u_s \varepsilon_s \frac{\partial C_{s_i}}{\partial x} + \varepsilon_s D_{ax} \frac{\partial^2 C_{s_i}}{\partial x^2} - K_{sf}\left[C_{si} - C_{fi}\right] + R_{si} \quad (9)$$

Danckwerts' boundary condition at the inlet:

$$u_s C_{si}^{-} = u C_{si}^{+} - D_{ax} \frac{\partial C_{si}}{\partial x} \quad (10)$$

Boundary condition at exit:

$$\frac{\partial C_{si}}{\partial x} = 0 \quad (11)$$

Initial condition:

$$At\ t = 0 \quad C_{si} = C_{fi} \quad (12)$$

Similar balance is written for species in gas phase. Following Mills et al.,[14] the transient diffusion of lattice oxygen on each catalyst particle is modeled *via* one-dimensional transient diffusion model. The governing equation for this description is:

$$\frac{\partial \theta_0}{\partial t} = \frac{1}{\tau_d} \frac{\partial^2 \theta_0}{\partial \xi^2} \quad (13)$$

At the surface of the catalyst:

$$\xi = 1: \quad \frac{\partial \theta_{0,s}}{\partial t} = -\frac{1}{\tau_d} \frac{\partial \theta_0}{\partial \xi} + \frac{R_{(0)}}{C_{tot}} \quad (14a)$$

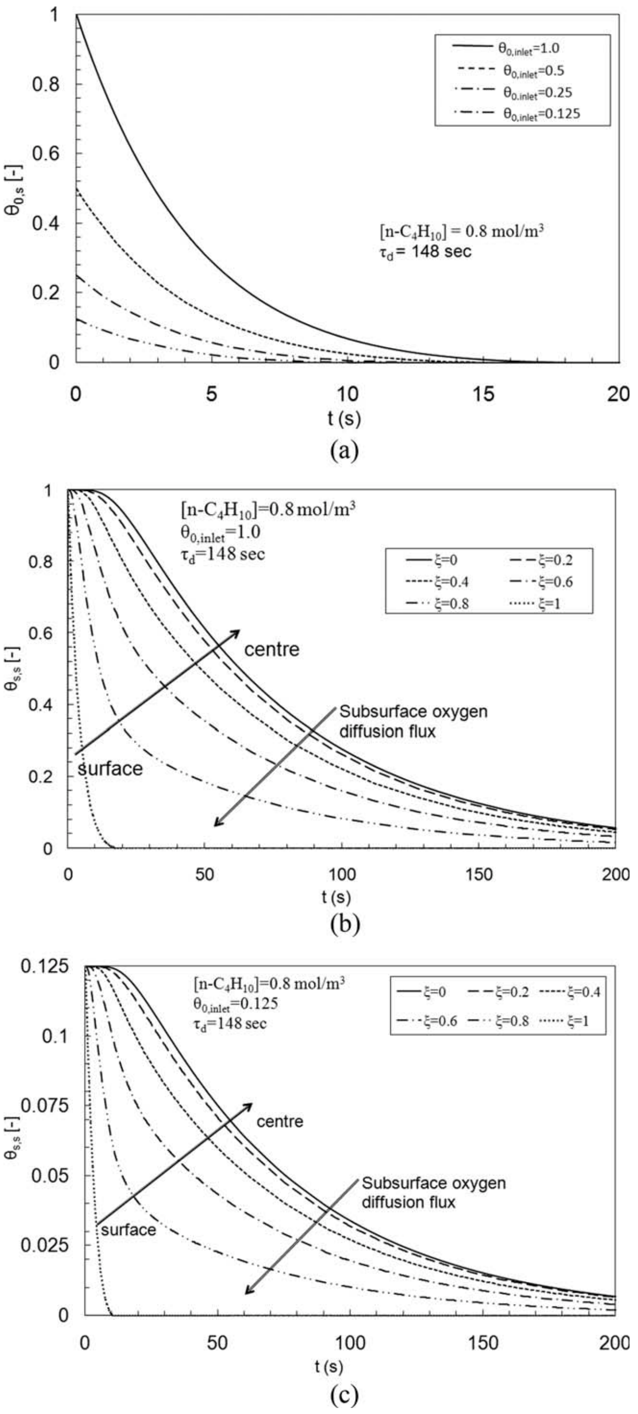


Figure 6. Lattice oxygen profiles without reactor transport (a) Lattice oxygen concentration at the surface of catalyst depending on the initial oxidation degree of the catalyst (under catalyst reduction condition) (b) Lattice oxygen concentration through the subsurface for $\theta_{0,\mathrm{inlet}}$ = 1.0 (under catalyst reduction condition) (c) Lattice oxygen concentration through subsurface for $\theta_{0,\mathrm{inlet}}$ = 0.125 (under catalyst reduction condition).

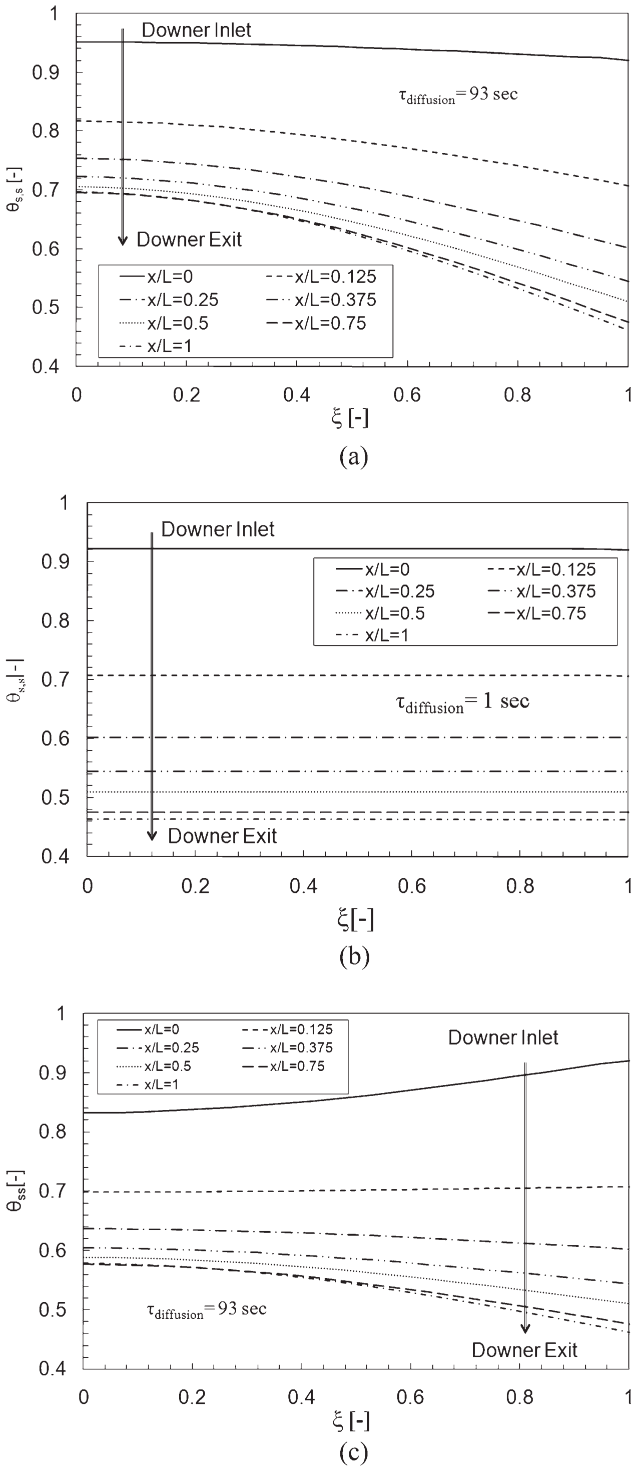


Figure 7. Lattice oxygen profile at the end of reaction for U_g = 3.7 m/s and G_s = 49 kg/m^{2}s at various axial position in the downer, with (a) uniformly and fully oxidized catalyst at the inlet and $\tau_{\mathrm{diffusion}}$ = 93 sec (b) uniformly and fully oxidized catalyst at the inlet and $\tau_{\mathrm{diffusion}}$ = 1.0 sec(c) linearly oxidized catalyst (at ξ = 0, θ_0,s = 0.1 and at ξ = 1.0, θ_0,s = 1.0) at the inlet and τ_{difusion} = 93 s.

Table 3. The Contact Times for Each Phase in Riser and Downer for the Four Operating Conditions (a) at Same Gas Phase Residence Time (b) at Same Solid Phase Residence Time

		Downer		Riser	
Case No.	Operating Conditions	τ_g (s)	τ_s (s)	τ_g (s)	τ_s (s)
(a) Same Gas Phase Residence Time					
1	$U_g = 3.7$ m/s, $G_s = 49$ kg/m^{2}s	5.9	3.4	5.9	10.0
2	$U_g = 3.7$ m/s, $G_s = 101$ kg/m^{2}s	5.9	3.2	5.9	9.9
3	$U_g = 7.2$ m/s, $G_s = 101$ kg/m^{2}s	3.1	2.2	3.1	4.8
4	$U_g = 7.2$ m/s, $G_s = 208$ kg/m^{2}s	3.1	2.2	3.1	4.2
(b) Same Solid Phase Residence Time					
1	$U_g = 3.7$ m/s, $G_s = 49$ kg/m^{2}s	17.8	10.0	5.9	10.0
2	$U_g = 3.7$ m/s, $G_s = 101$ kg/m^{2}s	18.9	9.9	5.9	9.9
3	$U_g = 7.2$ m/s, $G_s = 101$ kg/m^{2}s	5.8	4.8	3.1	4.8
4	$U_g = 7.2$ m/s, $G_s = 208$ kg/m^{2}s	5.8	4.2	3.1	4.2

At the center of the catalyst:

$$\xi = 0: \quad \frac{\partial \theta_O}{\partial \xi} = 0 \tag{14b}$$

where $R_{(O)}$ is a linear combination of the reaction rates r_1, r_2, and r_3 and ξ is nondimensional radial coordinate. Note that the boundary condition is a function of time. Figure 5 shows "conceptual diagram" depicting the fate of VPO catalyst in the various parts of riser reactor, downer reactor as well as fluidized bed regenerator.

Figure 5a depicts the various stages of oxidation of the VPO catalyst. In a riser (Figure 5b), while one expects the VPO to be progressively reduced as one goes up in the vessel, because of solids backmixing there is a significant fraction of VPO particles that are almost completely reduced but are backmixed to upstream locations in the reactor. Such particles may eventually get completely deactivated due to over reduction and hence constitute dead weight in the catalyst inventory. In Figure 5c, a similar and arguably worse situation is shown in which the solids are more or less completely backmixed. In Figure 5d, in a downer one expects a better situation because fresh butane contacts freshly reactivated catalyst which progressively reduces down the reactor as the butane is also depleted. One expects minimal permanent deactivation in this case. Thus the "trick" would be to watch the catalyst residence times, solids loading and characteristic times of lattice oxygen diffusion steps and kinetic steps, to obtain optimal selectivity and yield.

In Eq. 9, the reaction rate term (R_{si}) for each species is evaluated from Mills' kinetics.[14] At every time step, lattice oxygen concentration is obtained by employing the "subsurface oxygen diffusion" model. Subsequently, this oxygen concentration is used as an input in the next time step. As explained in the reaction kinetics section, VPO actually acts as an "oxygen carrier" in which subsurface oxygen diffusion plays vital role. Therefore in addition to the reactor scale equations, at every time step, lattice oxygen at the surface of the catalyst is obtained by the balance of reduction of catalyst and replenishment of oxygen via diffusion from subsurface of the catalyst (as conceptually depicted in Figure 1).

A single mass exchange coefficient, K_{sf} is employed to take into account the interphase mass transfer for given species. This parameter takes into account physical mass transfer due to gas–phase film diffusion (not to be confused with "subsurface oxygen diffusion") and convection at the surface of the catalyst particle as well as adsorption and surface transport of gas phase species on the surface of catalyst particle. At present sufficient quantitative information is not available for the mass transfer in downer, hence in this work K_{sf} is chosen such that mass transfer from solids to gas phase is not limiting under any conditions.

As in the literature[16,38] as well as in the present work, the downer is proposed as an alternative to gas–solids contacting in risers, it is prudent to investigate its "comparative" potential. Most works reported in the literature on downer hydrodynamics relate to fluid catalytic cracking application[38,39]; the present contribution is arguably one of the first considerations of a synthesis reaction for making a chemical intermediate in a downer. The comparison of downer and riser as a potential contactor for partial oxidation is based on the two criteria:

- Same gas phase residence time
- Same solids phase residence time

At selected operating conditions, solids velocity and solids fraction for riser reactor is evaluated from the correlations proposed by Patience et al.[40]

Reactor Simulation

Lattice oxygen diffusion

Lattice Oxygen Diffusion Without Reactor Transport. The equations were discretized using the Crank Nicholson algorithm[41] and implemented on MATLAB 7.0. At each time step in the main reactor code, the lattice oxygen diffusion model is solved in a coupled fashion.

To understand the role of "lattice oxygen diffusion" in deciding the reactor performance, some simulations were done without the reactor transport effect. Both butane oxidation and catalyst reoxidation cases were considered. For catalyst reduction case, four situations with different *initial* lattice oxygen concentration were considered such as: case (*L*1) $\theta_{0,\text{inlet}} = 0.125$; case (*L*2) $\theta_{0,\text{inlet}} = 0.25$; case (*L*3) $\theta_{0,\text{inlet}} = 0.5$; case (*L*4) $\theta_{0,\text{inlet}} = 1.0$. Constant butane concentration of 0.8 mol/m^3 in the bulk was assumed and characteristic diffusion time of 148 s[14] was taken. Figure 6a shows variation of concentration of lattice oxygen at the surface of the catalyst with time. As expected, if the initial catalyst reoxidation degree is lesser, catalyst will get "dried up (depleted

Table 4. Time Scales Involved in the Various Transport Processes

Process	Time Scale (typical)		Factors on Which it Depends
Reaction kinetics	Reaction step	τ_{rxn}	Catalyst characteristics, operating temperature
	$nC_4H_{10} \rightarrow$ MAN	8	
	$nC_4H_{10} \rightarrow CO$	9.5	
	$nC_4H_{10} \rightarrow CO_2$	1.6	
Lattice oxygen Diffusion	∼100 s		Catalyst characteristics, operating temperature
Mean Flow	3–10 s		Hydrodynamics of reactor (superficial gas velocity and solids mass flux)
Dispersion	∼100–1000 s (solids phase) ∼1000 s (gas phase)		Hydrodynamics of reactor

of lattice oxygen)'' quickly. Figure 6b shows variation of subsurface oxygen concentration when $\theta_{0,\text{inlet}} = 1.0$, initially and Figure 6c shows similar case $\theta_{0,\text{inlet}} = 0.125$. Though the trends of the profiles are qualitatively similar in both the cases, for lesser degree of initial lattice oxygen concentration, higher subsurface oxygen concentration gradient is observed. This can be a very crucial factor in the catalyst reoxidation. Moreover, one observes that the lattice oxygen at the outer surface of the catalyst depletes very quickly (owing to the presence of n-butane in the bulk), in about 10 s or so, while diffusion from the core takes about 148s.[14] As a result, even if the catalyst is sufficiently reoxidized, it may not help the reaction simply because the surface is ''starved'' of the lattice oxygen. If such a catalyst particle is backmixed, indeed some of the lattice oxygen locked-in the core of the particle would be released eventually but that may not contact fresh butane. Hence, overall productivity will suffer. In a downer configuration, this is however less of a problem because as the surface gets depleted of lattice oxygen, the bulk butane partial pressure also falls (downstream in the reactor), and this may contribute to enhanced productivity.

Lattice Oxygen Diffusion in Downer Reactor. A base case simulation was done with downer of length 50 m and operating conditions, $U_g = 3.7$ m/s and $G_s = 49$ kg/m^{2}s with uniform and fully oxidized catalyst and butane concentration 1.865 mol/m^3 at the inlet of the downer. Gas phase mean residence time for this case is 13.5 s and solid phase mean residence time is 7.8 s. Figure 7a shows lattice oxygen profile through subsurface layer of the catalyst at the various axial positions of downer ($x/L = 0$ corresponds to the entrance of the downer) at the end of the reaction with $\tau_d = 93$ s, i.e., around two orders of magnitude higher than characteristic time of solids phase. Figure 7b shows a simulation was done with $\tau_d = 1.0$ sec and keeping all other parameters same. Figure 7b indicates that for lower value of τ_d (i.e., the solid state lattice oxygen diffusion time), of the same order as that of reactor scale solids phase characteristic time, lattice oxygen profiles are relatively more uniform (i.e., uniform depletion of oxygen occurs). If the lattice oxygen profile at the inlet of the downer is nonuniform, with higher degree of reoxidation near surface than core as the oxygen must penetrate inside during the reoxidation phase then for τ_d (=93 sec) $\gg \tau_{\text{solids,mean,}}$ lattice oxygen profile becomes more and more nonuniform after the reduction of the catalyst, as shown in Figure 7c. This lattice oxygen profile is very important from the point of view of the regeneration/reoxidation of the catalyst. If the VPO catalyst used in the process has higher diffusion time than solids mean residence time, and the reoxidation process is inefficient (i.e., catalyst is not reoxidized fully and uniformly), then a time can come when the VPO catalyst gets dried completely and becomes inactive resulting into the selectivity losses.

Even though Figure 6 and 7 shows simulations done with a constant bulk butane partial pressure, the ''story'' almost completely emerges from these calculations. Essentially, the interplay between lattice oxygen diffusion times and flow characteristic times determine how the gas solids contactor will perform. The gradient in species concentration in the

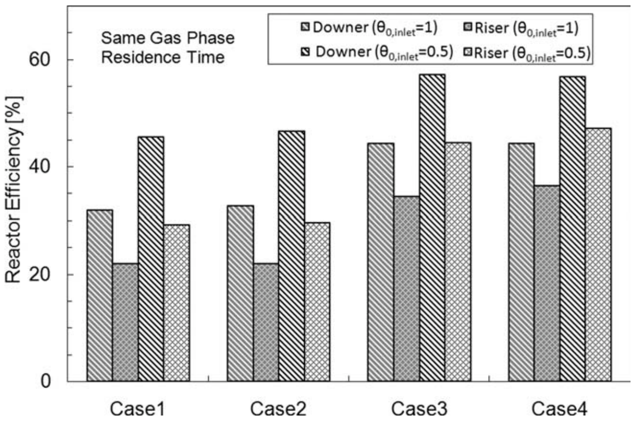


Figure 8. Reactor efficiency for downer and riser at same gas phase residence time with fully oxidized catalyst at the inlet and partially oxidized catalyst at the inlet.

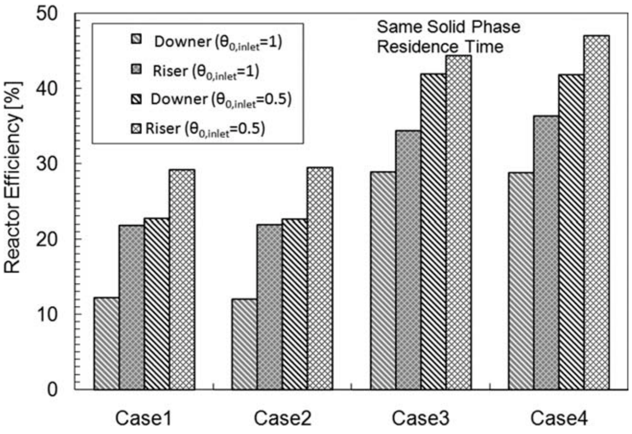


Figure 9. Reactor efficiency for downer and riser at same solid phase residence time with fully oxidized catalyst at the inlet and partially oxidized catalyst at the inlet.

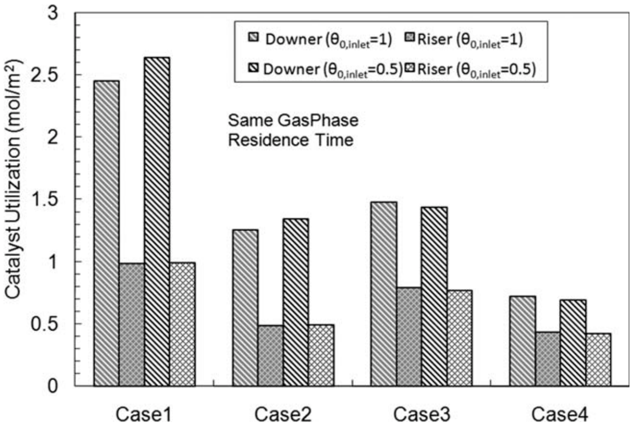


Figure 10. Catalyst utilization for downer and riser at same gas phase residence time with fully oxidized catalyst at the inlet and partially oxidized catalyst at the inlet.

bulk gas would modify this picture somewhat, and this is done in full CFD-coupled reactor simulation that is reported below.

Reactor performance of downer vs. riser

As explained earlier, downers are generally looked forward as the better option as compared to that of risers owing to its advantages such as forward mixing and uniform flow characteristics. In the present case, downer and riser performance for butane oxidation is compared on the basis of same gas phase mean residence time and same solid phase residence time. Four operating conditions for which hydrodynamic performance was evaluated, *viz*. Case 1: $U_g = 3.7$ m/s, $G_s = 49$ kg/m^{2}s, Case 2: $U_g = 3.7$ m/s, $G_s = 101$ kg/m^{2}s, Case 3: $U_g = 7.2$ m/s, $G_s = 101$ kg/m^{2}s and Case 4: $U_g = 7.2$ m/s, $G_s = 208$ kg/m^{2}s, are considered for the comparison. Performance is compared by comparing ‘‘reactor efficiency’’ and ‘‘catalyst utilization.’’ Table 3 summarizes the contact times for each phase in riser and downer for the four operating at same gas phase residence time as well as at same solids phase residence time. In addition, the effect of regeneration of catalyst is also modeled.

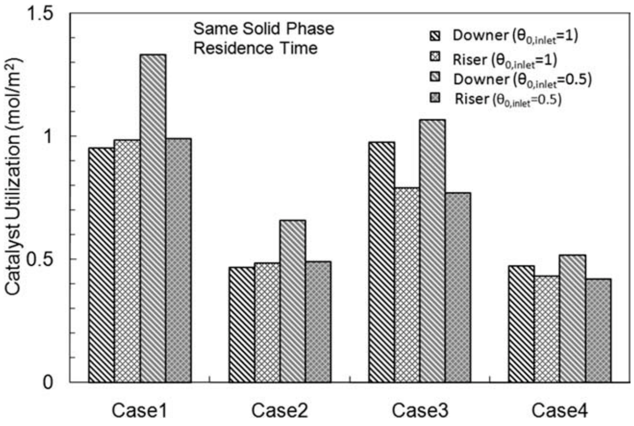


Figure 11. Catalyst utilization for downer and riser at same solid phase residence time with fully oxidized catalyst at the inlet and partially oxidized catalyst at the inlet.

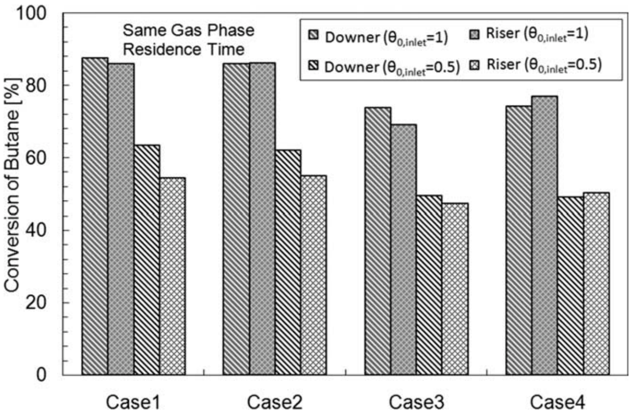


Figure 12. Conversion of butane in riser and downer at same gas phase residence time with fully oxidized catalyst at inlet and partially oxidized catalyst at inlet.

Reactor efficiency

Reactor efficiency[42] is defined as the ratio of total amount of desired product produced (maleic anhydride in this case) to the amount of desired product produced if all the catalyst was exposed to the gas phase reactants at the reactor inlet. Reactor efficiency is one of the measures which reflect the effect of flow pattern of the phases involved on the reaction kinetics. It is essential to use such a metric here rather than the conventionally use LHSV or WHSV based reactor activity. This is in view of the multistep kinetics, the multitude of time scales involved (Table 4) and our desire to make a comparative study of downers and risers.

Figure 8 shows the comparison of reactor efficiency for riser and downer at same gas phase residence time with fully oxidized catalyst at the inlet and half regenerated catalyst at the inlet. Downer shows higher reactor efficiency, the

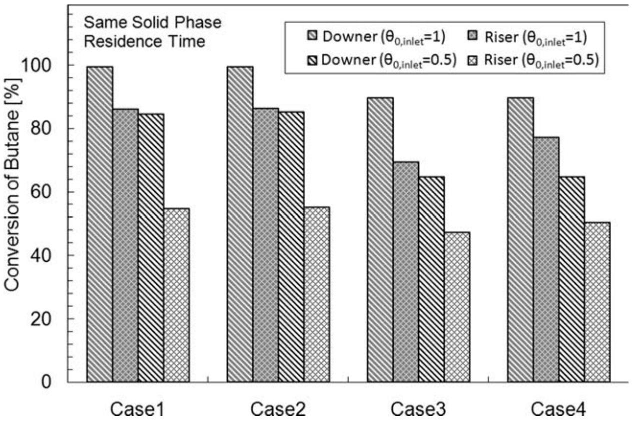


Figure 13. Conversion of butane in riser and downer at same solid phase residence time with fully oxidized catalyst at inlet and partially oxidized catalyst at inlet.

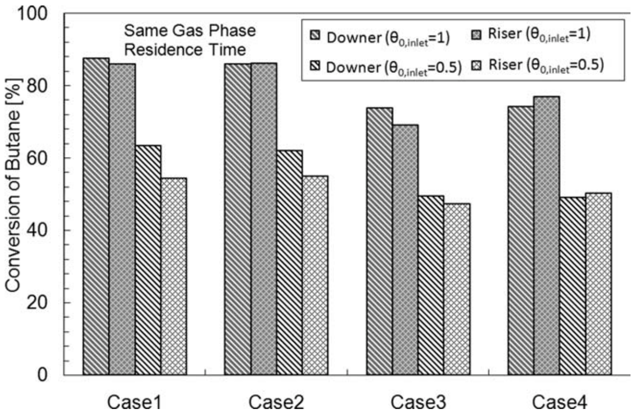


Figure 14. Yield of MAN in riser and downer at same gas phase residence time with fully oxidized catalyst at inlet and partially oxidized catalyst at inlet.

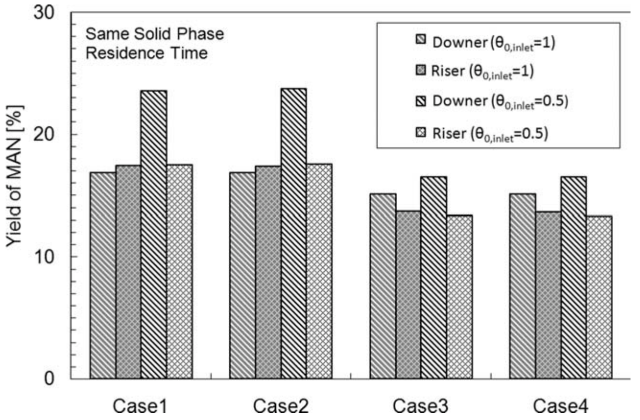


Figure 15. Yield of MAN in riser and downer at same solid phase residence time with fully oxidized catalyst at inlet and partially oxidized catalyst at inlet.

improvement being dramatic at lower superficial gas velocity. Similar trends are observed for the condition when catalyst is half regenerated but the quantitative difference between the reactor efficiency of the two reactors increases. Thus, actually there exists an optimal time of contact for which downer show beneficial behavior as compared to riser. Also, catalyst regeneration seems to be one of the most critical factors affecting the reactor performance. At very low contact times, difference between the riser and downer narrows down. At constant solid phase residence time, for fully oxidized catalyst at the inlet as well as half oxidized catalyst at the inlet (Figure 9); reactor efficiency for the riser is slightly higher as compared to that of downer. Thus, the main advantage of downer as compared to riser comes from the shorter contact time of solid catalyst.

The crucial point to be recognized here is that while it is easy to change parameters of mean residence times of risers and downers at will in a simulation, in reality it is not so. Normally in a circulating fluidized system, one has very little control on the solids inventory in each leg and also the solids circulation rate. Indeed, this has been a topic of dedicated research[40,43] and as often a matter of speculation. Once the gas flows and solids flux is established inside a circulating fluidized bed system, the flows and volume fraction adjust themselves in a manner (accounting for slip between phases) that one has a little control in the final residence times. Thus, results such as shown in Figure 8 and 9 could lead to further nonoptimality in case of the riser in a real setup. It suffices to state that in general, because flows in downers are aided by gravity, the solids mean residence times tend to be shorter compared to that in risers. Thus, for short time scale reaction it turns out to be a better option.

Catalyst utilization

In gas–solids catalyzed reactors, one of the key contributions to the operating cost come from the cost of the catalyst: so it is important to see how efficiently catalyst itself is utilized in the reactor. We have chosen to define, catalyst utilization as:

$$\text{Catalyst Utilization} = \frac{\text{Amount of desired product produced}}{(\text{vol. fraction of solids phase}) \times (\text{length of the column})} \tag{15}$$

Figure 10 compares catalyst utilization by downer and riser at same gas phase residence time with fully oxidized catalyst at the inlet as well as partially oxidized catalyst. Catalyst utilization is much better as compared to that in riser for all four operating conditions for both fully and partially oxidized catalyst. Even when compared at the same solid phase residence time, downer offer slightly better catalyst utilization for both fully regenerated catalyst at the inlet, as well as half regenerated catalyst at the inlet, (Figure 11). This is because, in case of downer, ''forward mixing'' occurs, i.e., solids have higher velocity as compared to gas therefore gas always get contacted with fresher catalyst whereas in case of riser, gas is followed by solid catalyst so gas always ''meets'' older catalyst (or partially depleted). This advantage is offset when solid phase residence time in downer approach that in riser. Similar to reactor efficiency, from the catalyst utilization point of view, downer seems to be better at optimal time of contact, beyond which distinction between riser and downer becomes lesser.

Comparison of Figure 10 and 11 suggests that on a ''per catalyst mass'' (or catalyst volume) basis, the downer mode of contacting is definitively superior to riser for partial oxidation reaction. On a per reactor volume basis, the riser may outperform the downer (Figure 12–15) however, because of lower velocities the riser can support higher solids fraction. Therefore it is possible, depending on how the numbers play out that riser has higher volumetric productivity than the downer even though the downer has better catalyst utilization. Coupled to this is the additional costs related to complete homogeneous combustion of butane which may offset the reactor performance metrics.

Summary and Conclusions

The inspiration for the current work comes from the belief that particularly for reactions involving selective intermediates, such as partial oxidations, the gas–solids downflow contacting mode may be arguably superior to the gas–solids upflow mode (riser). Indeed, some recent reports in the open literature hint towards such a possibility, and it was prudent to explore the potential particularly for partial oxidation reactions, such as that of n-butane to maleic anhydride (MAN).

However, doing so is not a trivial task, as downflow gas–solid reactors (as like any other gas–solid flow systems) is characterized by high velocity and turbulent flow fields which are not easy to characterize experimentally or computationally. Thus, the Euler–Euler CFD model is employed for simulating the flow in downers and risers under comparable conditions. On those CFD simulations, a scalar transport model was overlaid to quantify the backmixing of the phases. This ‘‘effective hydrodynamic model’’ thus extracted from the CFD models was then converted to a reactor model which was used to assess the relative performance of downers and risers for partial oxidation applications.

In summary, therefore, there have been two accomplishments in this work. First, a methodology has been laid out for employing, by ‘‘reduction of order’’, the hydrodynamic fields computed in an Euler–Euler model in an effective reactor model. Second, specific to the application of partial oxidations, the modeling framework has been use to make quantitative comparisons of downers and risers.

The other important piece that has been dealt with in this work, and specifically to the application of partial oxidation, is the lattice oxygen diffusion model that is inherent to the kinetics of partial oxidation of n-butane, as per Mills et al.[14] Arguments have been put forth as to why the kinetics due to Mills et al.[14] is preferred. Subsequently, a particle scale model which mimics the lattice oxygen flux at the particle level due to the gas phase environment around the particle has been simulated and presented. From the numerous simulation results that have been presented, the ‘‘big picture’’ that emerges is that the crux of the partial oxidation process lies in matching the flow time scales and dispersion time scales as the reactor level, and the lattice oxygen diffusion time scales at the catalyst level. Key to optimizing yield of desired product (MAN) is to get optimally reoxidized VPO catalyst into the reactor, transporting it through the reactor over an optimum time scale which allows optimal evolution of lattice oxygen to surface to participate in the partial oxidation reaction, and then to get the catalyst out of the system before it gets over-reduced so that the regeneration becomes prohibitive.

The above concepts were used to interpret the CFD/reactor modeling results. It is clear from the reactor/CFD modeling work that *on a catalyst mass basis*, catalyst in downer is always better utilized than in a riser, in that the yield of the desired intermediate is higher. The overall productivity of the downer reactor is however; marginally lower than that of a riser operating under equivalent conditions, and that is only because riser generally supports a higher solids holdup than a downer. Thus, for the same moles of n-butane in the feed, even though the riser may be a relatively inefficient reactor, more moles of MAN are produced simply because the n-butane conversion is higher (more moles of biproducts are produced as well). In the downer, in contrast, for every mole of MAN produced, fewer moles of biproducts are produced, in general.

Each catalyst particle is however, always much better utilized in a downer. The downer configuration looks even more promising in the event when the catalyst enters the process vessel (either downer or riser) in a partially regenerated state. Usually, this is the case in industrial practice. When catalyst is partially regenerated, the side reactions are preferred in the riser mode as the relatively higher times of residence and higher backmixing (marginal effect) leads to the catalyst getting ‘‘cooked’’ for longer, taking the oxidation to completion. Thus, less moles of MAN are produced in the riser, in general.

In conclusion, it may be said that the principal advantage of downer over riser mainly stems from shorter contact time for solid catalytic phase and forward mixing characteristics. The main story that emerges is that the partial oxidation process lies in matching the flow time scales and dispersion time scales as the reactor level, and the lattice oxygen diffusion time scales at the catalyst level. These objectives are better realized in the downer, hence it should be taken as the preferred mode of gas–solids contacting in the future. This is particularly true for selectively driven reaction processes, such as partial oxidation.

The only aspect that offsets the benefits of the downer are the lower solids holdup. Clearly, there is a need to design units where larger solids holdup can be achieved. Search for ways to have high density downers seem imperative.

Notation

C = concentration of species (mol/m^3)
d = particle diameter (μm)
e = restitution coefficient (-)
G = external circulation rate (kg m^2/s)
K = mass exchange coefficient (1/s)
p = pressure (N/m^2)
r = radial position (m)
R = radius of the column (m)
t = time (s)
u = superficial velocity (m/s)

Greek letters

ρ = density (kg/m^3)
β = interphase momentum exchange factor (kg/m^{3}s)
θ_0 = fraction of surface sites occupied by lattice oxygen (-)
ε = volume fraction (-)
τ = characteristic time (s)
ξ = dimensionless coordinate normal to the surface of the layer (-)
Γ = diffusivity of scalar (kg/m-s)

Subscripts, Superscripts

s,s = subsurface
f = fluid phase
s = solid phase
p = particle

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