Simulation investigation of oxydehydrogenation of ethane in an industrial-scale turbulent fluidized bed over MoVTeNbO catalyst

Estudio por simulación de la oxideshidrogenación de etano sobre un catalizador a base de MoVTeNbO en un reactor de lecho fluidizado turbulento a escala industrial

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Abstract

In this study, simulation of an industrial-scale turbulent fluidized bed reactor for the oxidative dehydrogenation of ethane over a MoVTeNbO catalyst is presented. The reactor model was based on a mechanistic model which assumes that tube internals present in industrial units minimize gas back-mixing, and that as a characteristic of fluidized turbulent regime, vigorous catalyst particles mixing occur. Therefore, it is assumed that gas plug-flow in the dense bed and perfectly mixed particulate phase in the dense bed, while in the freeboard plug flow of both gas and solids was assumed. Reaction kinetics was described by a previously reported model. Analysis of operating conditions on reactor performance in terms of ethane conversion and ethylene yield and selectivity. Reactor bed temperature was studied in the 400-480ºC and ethane feed concentration in the range 1-40%. The effect of fluidization velocity was also considered. Reaction temperature was the variable with most effect on ethane conversion and product yield. Ethylene selectivity above 90% was obtained at reactor temperatures 440ºC, however, higher temperatures worked in favor of oxidation reactions. Finally, present simulations of an industrial-scale turbulent fluidized bed were compared with the simulations for an industrial multitube fixed bed reactor reported in the literature.

Keywords: oxydehydrogenation; fluidization; turbulent regime; ethane; industrial scale.

Resumen

Se simula la deshidrogenación oxidativa de etano en un reactor industrial de lecho fluidizado turbulento con MoVTeNbO como catalizador. El modelo empleado es mecanístico y considera que los tubos inmersos en lechos industriales reducen el retromezclado de gas y que en un lecho fluidizado turbulento existe un mezclado intenso del catalizador. Se supone que en la zona de lecho denso el gas fluye en flujo pistón y el catalizador en mezcla perfecta; en la zona diluida ("freeboard") ambos gas y sólidos fluyen en flujo pistón. El modelo cinético empleado ha sido reportado previamente. Los resultados se analisan en términos de la conversión de etano y el rendimiento y selectividad del etileno. La temperatura de reacción se varió en el intervalo 400-480ºC y el porcentaje de etano en la alimentación entre 1 y 40%. También se evaluó el efecto de la velocidad de fluidización. La temperatura fue la variable con mayor efecto sobre la conversión y rendimiento. A 440ºC las selectividad de etileno superó el 90%, pero a temperaturas mayores se favorecieron reacciones de oxidación. Finalmente, los resultados de las simulaciones se compararon con las correspondientes para un reactor industrial multitubo de lecho flijo reportado en la literatura.

Palabras clave: oxideshidrogenación; fluidización; régimen turbulento; etano; escala industrial.

1 Introduction

Light olefins, as ethylene, propylene, and butylenes are essential commodity chemicals employed to produce intermediate chemicals of high importance, solvents, polymers, and many other products. Among petrochemical commodities, ethylene is the largest one produced worldwide, mainly by naphtha steam cracking (Torres Galvis and de Jong, 2013). The oil steam cracking process, however, has several disadvantages, such as being highly energy-intensive, requires relatively high temperatures and suffers from uncontrollable side reactions (Fairuzov *et al.*, 2021). Ethylene market has been growing but also environmental and economic issues associated with current production processes. The selective oxidative dehydrogenation of ethane (ODHE) in the presence of a suitable catalyst has been reported as a promising route to ethylene compared with current processes, as it has the advantages of low energy consumption, high selectivity to ethylene, less by-products and lower carbon footprint (Cavani and Trifirò,1995; Maffia *et al.*, 2016; Najari *et al.*, 2021). Despite intense research activity has been devoted to study ODHE, integration of both an efficient catalyst material selective to ethylene and a proper reaction process, is still a challenge to be solved for ODH to be commercially viable (Luongo *et al.*, 2022). Several catalytic materials have been studied in search of one with adequate properties that would work at lower temperatures, and capable of transforming ethane into ethylene while minimizing oxidation products. It has been suggested that commercial production ethylene via ethane ODH process should be able to convert ethane to ethylene at low temperatures and to significantly reduce the formation of carbon oxides (Bhasin, 2003), e.g. an ethane conversion and ethylene selectivity larger than 60% and 90%, respectively, at operating temperatures below 500ºC. In this regard, several research groups have studied a multimetallic mixed oxide that represents one of the most efficient catalysts for the ODHE, based on MoTeVNb materials (Chen *et al.*, 2023). Valente *et al.* (2014) studied a MoVTeNb multimetallic mixed oxide catalyst and report the simultaneous effect of temperature and space-time that allowed ethane conversions and ethylene selectivity that met the aforementioned criteria for possible commercial interest. The operating temperature was varied from 400 to 480ºC in their work as it allowed an ample range of ethane conversions and ethylene selectivities.

Che-Galicia *et al.* (2014, 2015) reported a kinetic study and claimed that Langmuir-Hinshelwood-Hougen-Watson kinetic formalism was the most suitable for describing the oxidative dehydrogenation of ethane over MoVTeNbO catalyst. It was also concluded that for this catalyst the 400 to 480ºC temperature range was essential for achieving high selectivities to ethylene, which does not represent only an important economic feature, but also a critical one from the operation control perspective, as reduction of combustion reactions is an important issue regarding reactor temperature control. As it is evident, due to the high exothermicity of the reactions, besides of finding an efficient catalyst for ODHE, it is also necessary to evaluate different reactor configurations for the process. Different reactor configurations are discussed in the literature for ODHE, among which fixed and fluidized bed reactors are the main two types (Ullah *et al.*, 2022). One of the most traditional configuration used in petrochemical industry for partial oxidation reactions is that of multi-tubular fixed bed reactors, where a high number of tubes offers high heat transfer area between the tubes and cooling agent, which although is helpful in removing heat generated, tube radial temperature gradients under extreme conditions can cause heat points that can represent a security issue (Che-Galicia *et al.*, 2015; Chen *et al.*, 2023). Membrane reactors is another reactor configuration that has been suggested to reduce oxygen concentration along a tubular reactor. In a conventional tubular fixed bed reactor oxygen is fed at the reactor entrance and consumed along the reactor, which allows high oxygen concentrations at the reactor entrance that results in undesirable reactions to CO_x products. A membrane reactor has the ability to feed and distribute oxygen in a controlled manner along the reactor wall which can work in favor of ethylene selectivity and detrimental to oxidation reactions. The disadvantage of this configuration, however, appears to be the high cost of this reactors that has limit their application commercially (Asadi-Saghandi and Karimi-Sabet, 2017). Another reactor configuration that has received a recent push in design is the chemical looping oxidative dehydrogenation. In this technology instead of co-feeding ethane and O_2, the oxidizing agent in this process is the lattice oxygen contained in a red-ox catalyst (oxygen carrier), which reacts with ethane. The catalyst oxygen es afterwards reoxidized in a regenerator and then transported back to the reactor, in a cyclic operation (Li *et al.*, 2020; Zhu *et al*, 2020; Cai *et al.*, 2023). Although great efforts have been made in the development of oxygen carriers to optimize the ODH processes and chemical looping process in particularly, the reported materials are still not satisfied in the economic aspects (Fairuzov, 2021). Fluidized bed reactors is another suggestion suitable for temperature control. A number of commercial gas-solid fluidized-bed reactors aimed at different processes, particularly where highly exothermic or endothermic reactions are involved, take advantage of the uniform temperature field that characterizes these systems (Lintz and Retzmann, 2007; Ahumada *et al.*, 2022). Many industrial fluidized bed reactors are routinely operated in the turbulent fluidization regime (Du *et al.* 2002), which is a flow regime that commonly takes place between bubbling and fast fluidization regimes (Bi *et al.*, 2000). This flow regime is characterized by vigorous solids mixing and by suppressed bubble formation (Lee and Kim, 1990), both of which results in an isothermal bed and in excellent contact between gas and solid phases, that makes of this flow regime ideal to enhance reactor performance (Boonprasop *et al.*, 2019). There are, however, some problems that can limit applicating fluidization technology. In contrast to much simpler mechanical properties of fixed bed catalysts, fluidized bed catalysts have to be designed to resist attrition due to prevailing severe fluidization conditions. Furthermore, catalyst fluidity parameters and gas flow patterns have to be considered which makes process design a difficult task (Lintz and Reitzmann, 2007; Ullah, *et al*, 2022).

Although over the years of research some attempts may have been devoted to the industrial development of ODHE to ethylene, no commercial unit appears to be implemented

Table 1 Mechanistic Kinetic model of ODHE over MoVTeNbO catalyst.

	Reaction	Rate equation	
1	$C_2H_6 + 0.5O_2 \rightarrow C_2H_4 + H_2O$	$r_1 = k_1 p_{C_2H_6} \theta_O$	(1)
2	$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$	$r_2 = k_2 p_{C_2H_6} \theta_O^{m_2}$	(2)
3	$C_2H_6 + 2.5O_2 \rightarrow 2CO + 3H_2O$	$r_3 = k_3 p_{C_2H_6} \theta_O^{m_3}$	(3)
4	$C_2H_4 + 3O_2 \rightarrow CO_2 + 2H_2O$	$r_4 = k_4 p_{C_2H_4} \theta_O^{m_4}$	(4)
5	$C_2H_4 + 2O_2 \rightarrow CO + 2H_2O$	$r_5 = k_5 p_{C_2H_4} \theta_O^{m_5}$	(5)

up to date (Chen *et al.*, 2023). In this line of process development, information on the performance of reactor options at industrial-scale is of paramount importance. Therefore, in the present contribution the performance of the ODH reactor is compared between two reactor configurations well stablished in petrochemical industry for highly exothermic reactions, both operating with the same catalyst material. First, simulation is reported of ODHE to ethylene over MoVTeNbO catalyst in a fluidized bed reactor at industrial scale under turbulent regime, and reactor performance has been evaluated by parametric analysis . The model used adopts a two-regions approach (Romano *et al.*, 2016) which has been previously employed in the parametric sensitivity analysis of an industrial unit for the partial oxidation of n-butane to maleic anhydride with satisfactory results. Then, in order to contrast potential operating conditions of both reactor configurations for the ODH of ethane, the simulation results obtained for the fluidized bed are subsequently compared with simulations reported in the literature for ODHE in an industrial-scale multi-tubular fixed bed over the same MoVTeNbO catalyst, with both reactor systems operated under similar temperature and ethane feed concentration conditions.

2 Methodology

2.1 Catalyst kinetic model

A mechanistic kinetic model reported by Che-Galicia *et al.* (2015) based on the Langmuir-Hinshelwood-Hougen-Watson mechanism was developed for ODHE over MoVTeNbO catalyst was used. The kinetic model considers both parallel and consecutive reactions which are summarized in Table 1. In this reaction scheme ethylene is produced by ethane dehydrogenation (r1), while CO and CO_2 are produced by both ethane and ethylene oxidation (r2-r5). The kinetic rate equations are written as a function of the partial pressures of gas phase reactants and consider the effect of adsorbed oxygen and water on reaction rates. In these equations ki denotes rate constant, K_n an adsorption equilibrium coefficient for the n-th component, θ_o oxygen fraction coverage of active sites and p_j partial pressure of reactants. Active sites fraction coverage by oxygen and water are related by a global balance of fraction sites by Eq. (6):

$$\theta_{H_2O} + \theta_O + \theta_* = 1, \qquad (1)$$

where θ_{H_2O} and θ_* correspond respectively to the fraction coverage of water and of active sites, and according to Che-

Galicia *et al.* (2015) are calculated as follows:

$$\theta_O = (p_{O_2} K_{O_2})^{0.5} \theta_* \qquad (2)$$

$$\theta_{H_2O} = p_{H_2O} K_{H_2O} \theta_* \qquad (3)$$

$$\theta_* = \frac{1}{1 + (p_{O_2} K_{O_2})^{0.5} + p_{H_2O} K_{H_2O}} \qquad (4)$$

The kinetic rate constants and adsorption equilibrium coefficients are expressed in terms of Arrhenius and Van´t Hoff equations.

$$k_i = \exp\left[A_i' - \frac{E_{A,i}}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \qquad (5)$$

$$K_n = \exp\left[\frac{\Delta S_n^o}{R} - \frac{\Delta H_n^o}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)\right] \qquad (6)$$

For the *i*-th reaction, A_i' corresponds to the natural logarithm of the pre-exponential factor, $E_{A,i}$ the activation energy factor, T the reaction temperature, T^* the averaged reaction temperature, ΔS_n^o the standard adsorption entropy of each component, ΔH_n^o the standard adsorption enthalpy of each component, and R the universal gas constant.

The kinetic and thermodynamic constants required for Eqs. (1)-(11) were determined by Che-Galicia *et al.* (2015) and are presented in Table 2.

Table 2. Kinetic parameter values of ODHE over MoVTeNbO catalyst.

Parameter	Value
A_1', mmol $(g_{cat}\ h)^{-1}$	5.50
A_2', mmol $(g_{cat}\ h)^{-1}$	0.686
A_3', mmol $(g_{cat}\ h)^{-1}$	1.58
A_4', mmol $(g_{cat}\ h)^{-1}$	2.60
A_5', mmol $(g_{cat}\ h)^{-1}$	0.787
$E_{A,1}$, kJ mol^{-1}	90.5
$E_{A,2}$, kJ mol^{-1}	165
$E_{A,3}$, kJmol^{-1}	150
$E_{A,4}$, kJ mol^{-1}	139
$E_{A,5}$, kJ mol^{-1}	132
$-\Delta S_{O_2}^o$, J mol^{-1}	215
$-\Delta S_{H_2O}^o$, J mol^{-1}	42
$-\Delta H_{O_2}^o$, J mol^{-1}	45.6
$-\Delta H_{H_2O}^o$, J mol^{-1}	128
m_2	0.922
m_3	0.906
m_4	1.23
m_5	0.905

2.2 Reactor simulation

The model used herein for simulating the fluidized bed reactor adopts a two-regions approach similar to those reported by Abba *et al.* (2003) and Romano *et al.* (2016). As mentioned earlier, no industrial facility appears to exist as yet for the ODHE, therefore, for the purpose of the present work, the industrial turbulent fluidized-bed reactor configuration simulated corresponds to that of an actual commercial-scale n-butane partial oxidation reactor (Romano *et al.*, 2016). In the model, the main features of the industrial reactor can be schematized as in Fig.1. Two distinct regions can be observed, a dense bed at the lower end of the reactor, containing most of the catalyst inventory, followed by the freeboard, containing entrained catalyst particles that are recirculated tot the bottom of the reactor after separation by cyclones. Reactions can occur in both regions and the heat of reactions is transferred to immersed heat-exchanger tube bundles.

Turbulent fluidization regime offers distinct operational features that have been determined experimentally either at laboratory or industrial-scale units. In terms of temperature, it is characterized by intense solids back-mixing that allows a uniform bed temperature field (Du *et al.*, 2002; Kobayahi *et al.*, 2010; Romano *et al.*, 2016; Jia *et al.*, 2017). Regarding fluid-dynamics features, good gas-solid contact prevails, and hence mass and energy transfer is favored in this regime as compared with bubbling fluidized regime; furthermore, it has also been reported that gas back-mixing is restrained due to the presence of internals in the reactor, such as heat transfer tubes used for temperature control (Kunii and Levenspiel, 1991; Zhang *et al.*, 2008).

The above characteristics of this fluidization regime, among some others, have been the base to the main assumptions of the model which are as follows:

- Steady state operation;

- The reactor operates under turbulent fluidization regime;

- the presence of tube internals and baffles in the dense bed minimizes gas back-mixing and hence plug-flow behavior is assumed for the gas phase;

- particulate phase in the dense bed are perfectly mixed;

- uniform and constant bed temperature as a result of good solids mixing and efficient heat removal;

- negligible temperature difference between gas and solid phases;

- negligible effect of pressure drop due to bed weight;

- both entrained solids and gas in plug flow in the freeboard;

- complete separation of catalyst particles in the cyclone.

Considering the above assumptions, the reactor mass balance equations are given as follows:

$$\frac{dF_j}{dZ} = A_R \rho_B \sum_{i=1}^{5} v_{ij} r_i, \quad j = 1,\ldots,6 \quad (7)$$
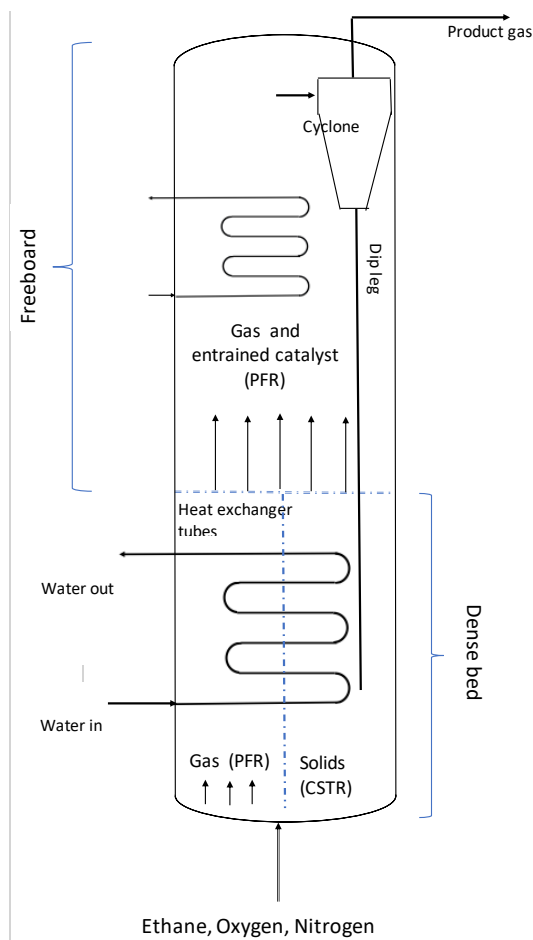

Fig. 1. Model representation of the industrial fluidized bed reactor.

where the index j denotes a reactant or product.

$$\int_0^{L_{db}} \rho_{cat}(1-\varepsilon) \cdot A_R dZ + \int_{L_{db}}^{L_{fb}} \rho_b(Z) \cdot A_R dZ = M_{cat} \quad (8)$$

The first term on the left-hand side of Eq. (13) corresponds to the catalyst mass in the dense region and in which the catalyst density per unit bed volume can be estimated from the dense bed height. La latter was estimated by a modified Richardson-Zaki equation, which relates the average bed porosity with superficial gas velocity and particle cluster terminal velocity (Avidan and Yeruslami, 1982; Lee and Kim, 1990; Bi *et al.*, 2002):

$$\frac{U}{U_{ct}} = \varepsilon^n \quad (9)$$

where U_{tc} and n for turbulent fluidization were estimated from expressions provided by Venderbosch (1998).

The second integral corresponds to the catalyst mass in the freeboard volume and in this reactor region ρ_b is a function of height (Z). The catalyst volume fraction can be assumed to decrease exponentially with bed height, from the value at the top surface of the dense bed (i.e., ϕ_{fb} ($Z = L_{db}$) = $1 - \varepsilon_{db}$ ($Z = L_{db}$) (Kunii and Levenspiel, 1991):

$$\phi = \phi^* + (\phi_{db} - \phi^*)\exp(-aZ_{fb}) \quad (10)$$

where *a* is an empirical constant given by Abba *et al.* (2003) and,

$$\phi^* = \frac{G_E}{U - U_T} \tag{11}$$

In Eq. (16) U_t is the particle terminal velocity and $G_E = F_E A_R$ is the elutriation catalyst flux at the top of the reactor, which can be assumed constant above the Total Disengagement Height (TDH).

In the dense bed temperature is controlled by immersed cooling surfaces. The characteristics and operating conditions of an industrial tube bank heat exchanger described by Kobayashi *et al.* (2010) were here considered. The energy balance for the pressurized cooling water can be expressed as:

$$\int_0^{L_{db}} hAS(T_W - T_{db})dx = F_W C_{p,W}(T_{W,in} - T_{W,out})$$
$$+ fF_W \Delta H_V \tag{12}$$

In the case of partial water vaporization *f* corresponds to the fraction of cooling water vaporized (Kobayashi *et al.*, 2010). Heat transfer coefficients are reported for this particular system by Kobayashi or they can be estimated as suggested by Vreedenberg (1958).

3   Results

In order to characterize the performance of a turbulent fluidized bed (TFB) reactor for the ODH reaction, temperature, space-time, and inlet gas composition are the key operating variables considered in the present study, and the corresponding responses expressed in terms of reactant conversion, product yield, and selectivity.

3.1   *Bed voidage along the bed height and its effect on conversion*

In this section, simulation results of the TFB reactor voidage and its effect on ethane conversion are presented in Fig. 2, and where $Y(z)$ corresponds to ethane conversion at reactor height z and $Y(L)$ to that at reactor exit. As it is shown, a sharp increase in bed voidage occurs in the freeboard region as compared to the dense bed value. As a consequence of the relatively low catalyst concentration in the freeboard, the increase of ethane conversion in this section was found to be relatively negligible. The above results are in accordance with experimental industrial findings reported by Romano *et al.* (2016), in terms of pressure drop in an industrial reactor operated under turbulent regime, where pressure drop in the freeboard appears to be, in average, no more than 5 percent of the total reactor pressure drop. By assuming pressure gradients are entirely due to the weight of the catalyst holdup per unit reactor height and negligible inertial and wall effects, we estimated the corresponding freeboard voidage fraction in the industrial reactor to be close to *ca.* 0.98, which is very similar to 0.96 voidage fraction value in our reactor. Furthermore, the above work report that reaction rate in the reactor freeboard is quite small and that temperature is maintained essentially constant by heat exchanger tubes.
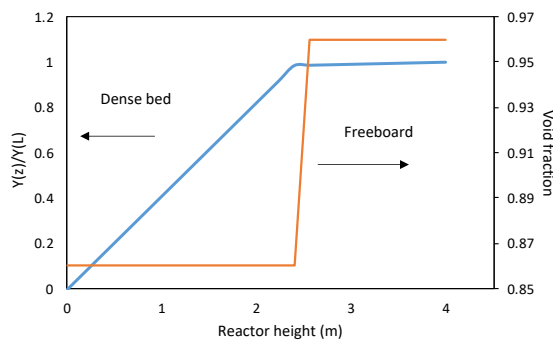

Fig. 2. Bed voidage along reactor height.

3.2   *Comparison with experimental grain catalyst data*

These part of the work deals with a comparison between turbulent fluidized bed predictions and some of the experimental data reported by Che-Galicia *et al.* (2014), on which the kinetic model used is based. Figure 3a shows the effect of temperature on the conversion of ethane and oxygen for a feed mixture containing ethane, oxygen, and nitrogen, with a molar ratio $C_2H_6/O_2/N_2 = 9/7/84$, and 0.28 g_{cat} h mol^{-1}_{ethane} space-time. It is evident that ethane conversion increases with reaction severity as a result of temperature increase. Oxygen consumption follows closely that of ethane at lower temperatures, reaction conditions where ethylene product predominates, however, at higher temperatures (e.g. 480ºC) a relatively larger O_2 conversion rate appears associated to reactions towards CO_x products. For the sake of comparison, the experimental ethane conversion obtained from a fixed bed at laboratory scale, where transport limitations for the main reaction was assessed (Che-Galicia *et al.*, 2014). It is clear that the experimental ethane conversion was always higher than the corresponding one for the TFB (e.g. at 440ºC, experimental ethane conversion was 30 % higher than in TFB), and as temperature and molar feed composition was the same for both systems, the significantly larger space-time of the experimental system (23 g_{cat} h mol^{-1}_{ethane}) appears attributable to such difference. In this regard, it is worth mentioning that the space-time for the TFB was limited by the hydrodynamic gas flow rate boundaries as dictated by the fluidized bubbling and fast fluidization regimes (Lee and Kim, 1990).

Figure 3b depicts yield of ethylene and total carbon oxides (CO_x) predicted for the TFB as a function of reaction temperature, within the region 400-480ºC and 0.28 g_{cat} h mol^{-1}_{ethane}, and a mixture feed containing ethane, oxygen and nitrogen with a molar ratio ethane to oxygen of 1.3. Furthermore, experimental ethylene yield (Che-Galicia *et al.*, 2014) are also presented for the purpose of comparison. From this side, it is evident that for the TFB reactor ethylene production increases with reaction temperature at a larger rate than CO_x products, in such a way, that at the highest temperature considered (480ºC) ethylene yield reaches 44% and CO_x 11%. Moreover, the experimental ethylene yields presented in this figure are higher than those predicted for the TFB reactor for the temperature range, which can be considered a consequence of the corresponding larger conversions of the experimental data compared with TFB (see Figure 3a).
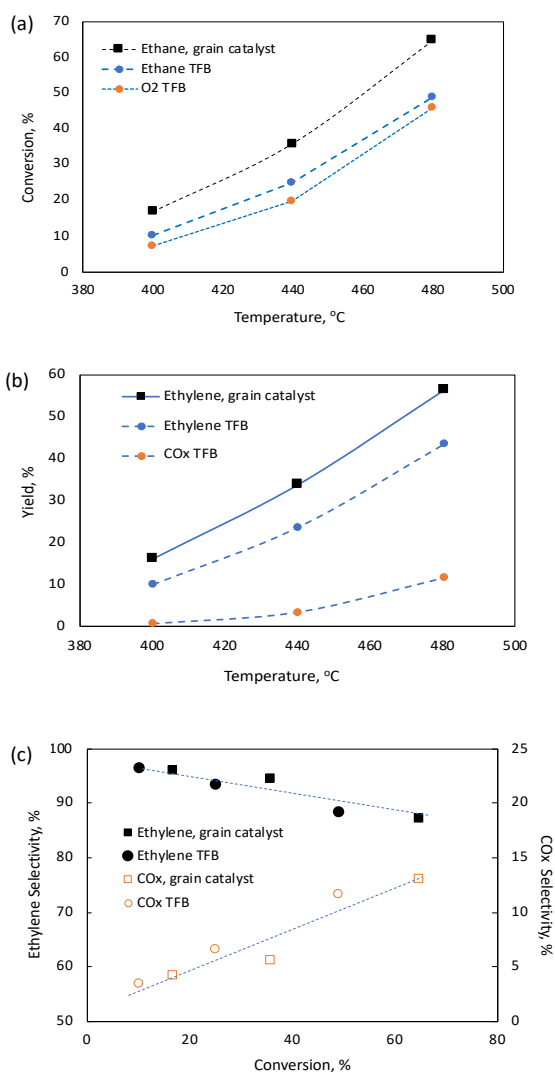
(a)

(b)

(c)

Fig. 3. Comparison of turbulent fluidized bed reactor simulation with grain catalyst experimental data (molar percent feed $C_2H_6/O_2/N_2 = 9/7/84$).

Figure 3c displays the evolution of selectivity to ethylene and CO_x as a function of ethane conversion. It is observed that, as the reaction conditions increase in severity, in terms of temperature and space-time, ethane conversion and CO_x selectivity grow, in detriment of ethylene selectivity. For instance, for the experimental system, although an ethane conversion increment from 16 to 65% was observed by a 400 to 480°C temperature increase, it also resulted in an ethylene selectivity reduction from 96 to 87%. Similarly, TFB simulation for the same temperature increase produced an ethane conversion increment from 10 to 47% but also a selectivity reduction from 97 to 88%.

It is evident that ethylene selectivity for the TFB appears to follow closely the evolution of the experimental data, which reflects the relatively good gas-solid contact that prevails in a turbulent fluidized bed reactor (Lee and Kim, 1990; Boonprasop *et al.*, 2019).

3.3 Effect of temperature and feed composition

In order to explore the optimum range of operating conditions for ethane ODH in a TFB reactor at industrial scale, the effect of feed composition and reactor temperature on reactant conversion and ethylene yield have been investigated. The feed composition comprises ethane, oxygen and nitrogen, the latter, an inert gas added for temperature control due to high exothermicity of reactions. Figure 4 presents the effect of ethane percent in feed (1-40%) at three operating temperatures (400, 440, and 480°C), and where oxygen composition (at 7 percent), pressure, and flowrate were maintained constant. For 1% ethane in feed and 480°C temperature, ethane conversion was found to reach nearly 100 percent, but showed a significant decrease at lower temperatures (Fig. 4a). It is evident from this results that for a given operating temperature, an increase in ethane concentration (higher C_2H_6/O_2 ratio) leads to lower ethane conversions, the effect being more obvious for 1:7 and 9:7 ethane-to-oxygen ratios where ethane is the limiting reagent, than for 18/7 and 40/7 ratios, where ethane is the excess reagent. This result is in accordance of previous results (Che-Galicia *et al.*, 2014) that report that reaction rates over the MoVTeNbO catalyst are less sensitive to changes in the partial pressure of oxygen than it is to corresponding changes of the hydrocarbon. From the above results, it is apparent that operating at relatively high ethane to oxygen molar ratios would result in a large amount of ethane unconverted the would need, afterwards, separation and recycle to the reactor inlet.

Also shown in Fig. 4a is the proportion of O_2-to-C_2H_6 consumed, from which it is clear that the oxygen consumed is directly proportional to the amount of ethane converted, and that the proportionality constant increases with reaction temperature; this is attributable to side reactions that are favored at high temperatures, and are relatively more O_2 consuming.

Ethylene yield is presented in Fig. 4b, and results appear very similar to those found for ethane conversion (vide Fig. 4a). It increases with temperature, for instance, at 1% ethane in feed, ethylene yield increased from 17 to 87% respectively for a temperature increase of 400 to 480°C; however, for a given temperature it decreases with ethane percentage. At a fixed temperature, however, for lower C_2H_6/O_2 ratios (1:7 to 9:7) ethylene yield decreased sharply, but at higher ethane percentages in feed (18:7 to 40:7 C_2H_6/O_2 ratios), where oxygen is the limiting reactant, it reduces comparatively at a lower rate and a stabilizing trend was observed. Also presented in Fig. 4b is the CO_x yield, which was affected by temperature and ethane composition similarly to that observed for ethylene yield, that is to say, fairly affected by temperature and ethane feed composition, mainly, where C_6H_6/O_2 molar ratio < 14:7; for higher C_6H_6/O_2 ratios than this the effect of ethane composition becomes comparatively less important compared with temperature.

In terms of ethylene selectivity, it was found that values above 90% were obtained for temperatures not exceeding 440°C. The highest selectivity obtained for the present conditions was 96%, however, the corresponding ethane conversions were always below 30% (vide Fig. 4c).
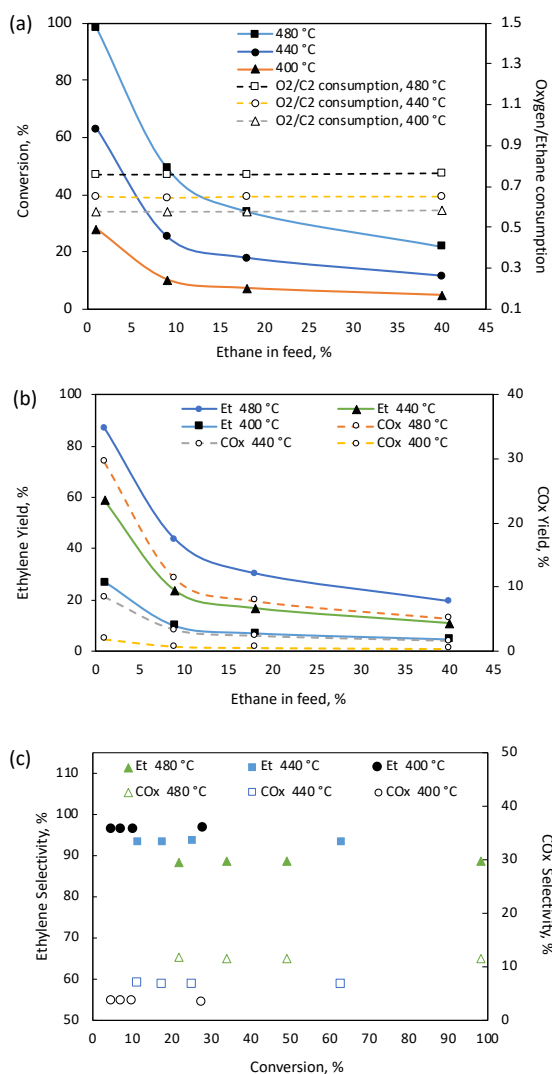
Fig. 4. Effect of temperature and feed composition: a) Ethane conversion; b) Ethylene yield; and c) Selectivity.

Fig. 5. Effect of superficial gas velocity: a) Ethane conversion; b) Ethylene yield; and c) Ethylene selectivity.

At 440ºC a 93% ethylene selectivity was found for up to 63% ethane conversion. For 480ºC, ethane conversions above 90% and ethylene selectivity of about 88% were obtained.

3.4 Effect of superficial gas velocity on reactor performance

The effect of superficial gas velocity on reactor performance is presented in Fig. 5 for two temperatures and feed ratio 9/7/84 ($C_2/O_2/N_2$). It is evident from Fig. 5a that for 480ºC, *c.a.* 44% gas velocity increase conversion decreases *c.a.* ten percent points while at 440ºC decreases c.a. seven percent points. This can be attributable to a reduction in catalyst concentration by an increase in particle entrainment and also by a reduction of gas residence time in the dense bed. Similar findings are shown in Fig. 5b for ethylene and CO_x yields, where it is evident the fair effect of temperature as compared with the effect of superficial gas velocity. Furthermore, for the present operating conditions, and from data in Figs. 5a and 5b, ethylene selectivity appears to decrease with an increase of ethane conversion (Fig. 5c).
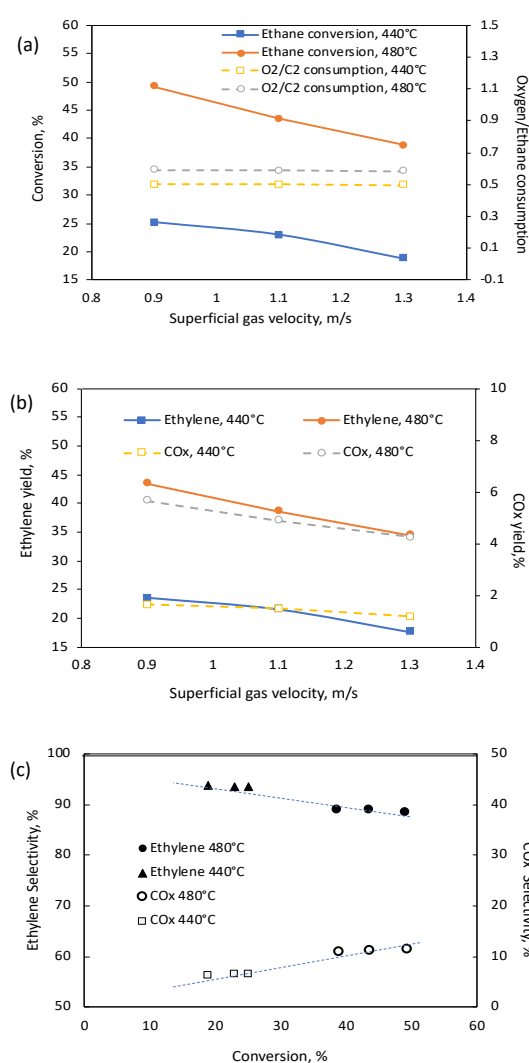
3.5 Reaction heat removal

It is common practice in many fluidized beds where exothermic reactions take place that immersed cooling tubes are immersed in the bed to maintain desired temperatures (Kunii and Levenspiel, 1991). In the present work, the characteristics of bank of cooling tubes employed in an industrial exothermic reactor, reported by Kobayashi and co-workers (2010), was considered in the model. Briefly, the industrial reactor contains 150 m of hairpin cooling tubes (152 tubes, i.d. 78.1 mm) distributed in 12 blocks, fed with pressurized water as the cooling fluid, and saturated or superheated steam at the exit, depending on the heating block. Kobayashi reports heat transfer coefficients for the cooling system and also confirm the nearly isothermal operation within the industrial fluidized bed (temperature gradient of about 3ºC). Based on this heat transfer configuration, in Figure 6 we have compared the amount of heat generated at different operating conditions with the corresponding cooling capacity of the system (Q/Q_{HT}) of the reactor operated at 480ºC (although not presented, similar results were obtained for the bed operated at 440ºC).
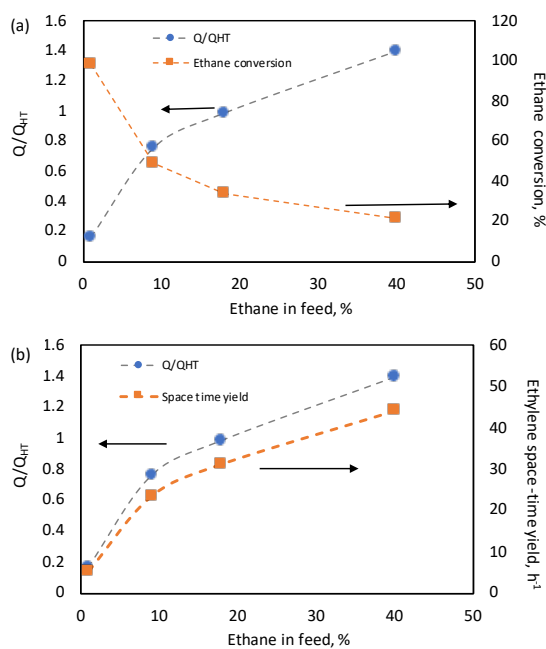
Fig. 6. Effect of ethane percentage in feed on heat generated at 480ºC. a) Cooling capacity of the reactor and ethane conversion; b) Cooling capacity and ethylene space-time yield (kg ethylene/ h·kg$_{cat}$).

Fig. 6a shows that as the percent of ethane in feed increases the reaction heat generated also increases. Although ethane conversion decreases, its combination with the larger amount of ethane fed results in a net increase in ethane consumed and hence of Q, the heat released by reactions. In this regard, Fig.6b depicts a nearly proportional increase of reaction heat and ethylene space yield. For the operating conditions considered, it is also evident that the cooling tube bundle was only able to cope with the heat generated for an ethane feed under 20%, for which the reaction heat generated, Q, is lower than the capacity of heat removal, Q_{HT}. The heat generated from operating at higher ethane percent than this would require a redesign of the heat transfer system considered, so as to augment its cooling capacity.

4 Comparison of turbulent fluidized bed and fixed bed reactors simulations of ethane ODH

In the catalytic oxidative dehydrogenation process, ethylene yield is limited by the reactions that form carbon oxides (CO$_x$), namely, ethane and ethylene combustion reactions. As total oxidation reactions generate, a large amount of heat and reach high temperatures in the reactor that can severely damage the catalyst and even cause reactor runaway (Rodriguez *et al*, 2011). The choice of the reactor configuration and design becomes then a key factor in terms of heat removal and temperature control. A common industrial option to conduct these exothermic processes are

multitube catalytic reactors, containing thousands of tubes of small diameter that facilitate heat removal and minimize radial temperature gradients. Heat removed is transferred to a cooling fluid that flows over the tube bundle. Che-Galicia *et al*. (2015) reported simulation studies for a the production of ethylene out of ethane ODH in a packed bed catalytic industrial reactor, immersed in a cooling fluid, and where MoVTeNbO catalyst particles dt/dp equal to 3.12 were employed. They based their predictions by modeling a single tube assuming that all the tubes in the bundle behave similarly, and for which they used a two-dimensional pseudo-heterogeneous model coupled with the same kinetic model employed in the present work. In order to elucidate the potential operating conditions of both reactor configurations for the ODH of ethane, fluidized and fixed bed, in the present section the simulations reported by Che-Galicia for a fixed bed reactor and co-workers are compared with those for an industrial turbulent fluidized bed.

4.1 Operating temperature

The effect of feed temperature on reactor performance for both, fixed bed (FB) and turbulent fluidized bed (TFB), is presented in Fig. 7 for C$_2$H$_6$/O$_2$/N$_2$ = 9/7/84 feed molar ratio. As it shown in Figure 7a, for both reactor configurations a similar increase of ethane conversion was observed with temperature, which can be interpreted as both reactor configurations being operated under kinetic control. It is also evident from this figure that comparatively more oxygen appears to be consumed for the FB configuration. Such difference in oxygen consumption is mainly detected at the higher temperature considered (480ºC) and can be attributed to reactions towards CO$_x$ products (Fig 7b). According to Che-Galicia *et al*. (2015), this is attributed to heat removal limitations in the FB reactor simulated, mainly at high temperatures (480ºC), for which a pronounced hot spot was predicted with a temperature rise of ca. 56ºC, and hence reactor operation under such severe conditions should be avoided. On the other hand, for the TFR operated at the same conditions heat removal was ca. 75% of the cooling capacity of system, which in principle should allow the removal of the heat generated. Figures 7b and 7c show predicted ethylene yield and selectivity, which were found quite similar for both reactor configurations. It has been reported that high selectivity to ethylene, larger than 90%, is one of the most important desired features for ethane ODH (Valente *et al*., 2014; Asadi-Saghandhi and Karimi-Sabet, 2017), however, for both reactor configurations this was only possible at lower temperatures (Fig. 7c).

4.2 Ethane percentage in feed

The effect of ethane concentration in feed on reactor performance for both, fixed bed (FB) and turbulent fluidized bed (TFB), is presented in Fig. 8 for T=440ºC and as a function of ethane feed molar ratios (expressed as C$_2$H$_6$/O$_2$/N$_2$ = X/7/(93-X)). Figure 8a and 8b show similar ethane conversions and ethylene yields for both reactor configurations, but for the lowest ethane concentration in feed (C$_2$H$_6$/O$_2$/N$_2$ = 1/7/92), where the TFB conversion is ca. 18% larger than the one reported for the FB, and ca. 16% larger for ethylene yield.
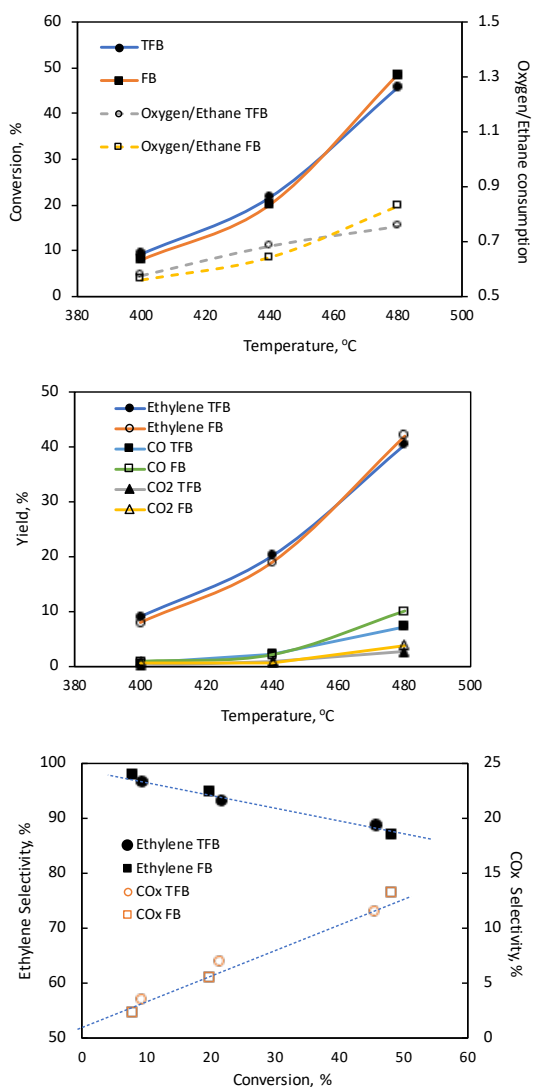
Fig. 7. Turbulent fluidized bed and fixed bed reactors simulations of ethane ODH ($C_2/O_2/N_2$ = 9/7/84). Temperature effect on a) Ethane conversion; b) Ethylene yield; and c) Ethylene selectivity.
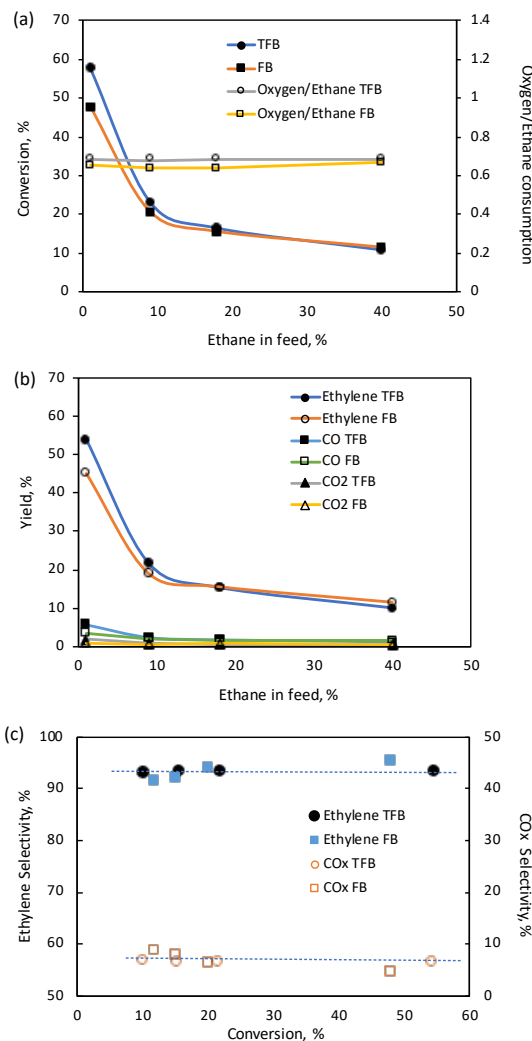

Fig. 8. Effect of feed composition on fixed bed and turbulent fluidized bed reactor configuration: a) Ethane conversion; b) Ethylene yield; and c) Selectivity.

For a larger ethane concentrations in the feed of $C_2H_6/O_2/N_2$ = 9/7/84, where ethane is still the limiting reactant, both conversion and ethylene yield decrease steeply; and afterwards, at larger ethane percentages (where ethane is no longer the limiting reactant), they both decrease slightly in comparative terms. Ethylene selectivity is presented in Fig 8c, which was always above 90% for both FB and TFB, and for ethane conversions of up to ca. 55%. These high ethylene selectivity values result from the catalytic properties of MoVTeNb that at temperatures 440ºC and below is much less active towards formation of CO_x products. Therefore, it appears that operating under such industrial conditions would also allow manageable heat rates generated from the exothermic reactions.

Conclusions

The central point of the present paper was the simulation of an industrial scale turbulent fluidized-bed reactor for the oxidative dehydrogenation of ethane to ethylene, which was limited to the case where ethane and oxygen are co-fed to the reactor. The reactor model used, which consists of mass and energy balance equations and constitutive expressions, was based on one reported elsewhere that successfully described the partial oxidation of n-butane to maleic anhydride in an actual industrial fluidized bed reactor operated in the turbulent regime. The parametric sensitivity analysis was performed considering the effect of reactor bed temperature, ethane feed concentration, and inlet flow rate. Reactor simulations were compared with experimental laboratory data for the grain catalyst, and although expected differences in ethane conversions and ethylene yields due to different space-times between scales, similar trends were observed for ethylene selectivity.

Reactor temperature was found to be the parameter that most affected reactants conversion and products yield, followed by ethane feed concentration and comparatively less by the gas superficial velocity. Ethane conversion is favored by temperature increase but at a temperature of ca. 480ºC chemical reactions towards CO_x products punishes ethylene yield. Ethylene selectivities above 90% were obtained only at lower temperatures such as 440ºC and below. The effect of ethane percent in feed was more evident for compositions where ethane was the limiting reagent while a much smaller effect resulted from ethane being the excess reagent. Ethane conversion and ethylene yield both increased as the ethane feed composition was reduced, but this effect was significant only for ethane under 9% in feed. The fluidized bed simulation results were compared with the corresponding simulations reported in the literature for an industrial scale fixed-bed reactor, having both configurations the same catalyst mass per reactor volume. Similar conversions and yields were observed for both reactor configurations regarding the effect of feed temperature and ethane composition. The main difference, however, resulted from the removal of the heat generated by the chemical reactions under extreme operating conditions (higher conversions at 480ºC), as for which the presence of significant heat-points were reported for the fixed bed reactor, while the fluidized-bed industrial cooling system appeared to be comparatively better suited for dealing with this issue.

On the basis of the results obtained herein it can be concluded that high values of selectivity to ethylene, above 90%, at levels of ethane conversion ca. 60% can be achieved in a TFB reactor, however this was only the case for 1% ethane feed. This appears to be a disadvantage of co-feeding ethane and O_2 to the catalytic reactor, as it then requires an inert atmosphere (diluted with an inert gas as N_2) to keep the reaction mixture from entering the ignition conditions. This sub-optimal composition is a constraint that limits reactor performance but that can be addressed by distributing the O_2 feed along the reactor height so as to avoid the problem of feed flammability. As several design parameters associated on feeding can be considered (e.g., number and location of feeding points and distribution of O_2 flow along reactor height), an optimization study of this type of TFB reactor is needed from the perspective of ethane conversion and ethylene selectivity.

Acknowledgment

Nomenclature

A	Heat-transfer surface area per unit reactor volume [m^{-1}]
A_i	Natural logarithm of pre-exponential factor of reaction rate i [mmol (g$_{cat}$ h)$^{-1}$]
a	Decay constant [m^{-1}]
C_D	Particle drag coefficient based on the superficial gas velocity [dimensionless]
Cp	Heat capacity [kJ mol^{-1}K^{-1}] [kJ kg^{-1}K^{-1}]
D_t	Cooling tube diameter [m]
dp	Particle equivalent diameter [m]
E_{Ai}	Activation energy of reaction i [kJ (mol)$^{-1}$]
Fg	Gas flow rate [mol s^{-1}]
Fw	Water flow rate [kg s^{-1}]
g	Acceleration of gravity [m s^{-2}]
h	Overall bed-to-surface heat-transfer coefficient [kJ s^{-1}m^{-2}K^{-1}]
ki	Reaction rate constant of reaction i [mmol (g$_{cat}$ h)$^{-1}$]
k_w	Water thermal conductivity [kJs^{-1} m^{-1} K^{-1}]
K_n	Adsorption equilibrium constant for component n [(Pa^{-1})]
L	Overall reactor height [m]
L_{db}	Dense bed height [m]
L_{fb}	Freeboard height [m]
Ms	Overall catalyst inventory [kg]
Nu	Nusselt number Nu = h$_{win}$D$_t$/k$_w$ [dimensionless]
P	Reactor pressure [atm]
pi	Partial pressure of component i [Pa]
Pr	Prandtl number Pr = $c_p\mu/k$ [dimensionless]
ri	Specific reaction rate of reaction i [mmol (g$_{cat}$ h)$^{-1}$]
Re	Reynolds number, $Re = \rho DtU/\mu$ [dimensionless]
S	Bed cross-sectional area [m^2]
T	Temperature [K]
U	Superficial velocity [m s^{-1}]
U_t^*	Particle terminal velocity [m s^{-1}]
Z	Axial Coordinate [m]
Greek letters	
ΔH	Heat of reaction [kJmol^{-1}]
ΔH_n^0	Standard enthalpy of adsorption for component n [kJ (mol K)$^{-1}$]
ΔS_n^0	Standard entropy of adsorption for component n [J (mol K)$^{-1}$]
ε	Void fraction [dimensionless]
μ	Viscosity [Pa s]
ρ	Density [kg m^3]

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