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Steady-State Simulation of a Fixed-Bed Reactor for the Total Oxidation of Volatile Organic Components: Application of the Barkelew Criterion

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Abstract: A steady-state tubular reactor for total oxidation reaction under typical industrial conditions in the removal of volatile organic components (VOC) is described using a one-dimensional heterogeneous reactor model with intraparticle diffusion, using a fully developed Langmuir–Hinshelwood reaction rate expression. The effectiveness factor, accounting for these intraparticle diffusion limitations, is calculated with a generalized Thiele modulus. The actual inclusion of this factor shows that higher operational reactor temperatures can be possible, since this diffusion limitation restricts the heat production inside the catalyst particle. Special attention is given to the outlet concentration of propane, taken as the model VOC, and runaway criteria, reported in the literature, are evaluated. Furthermore, the well-known Barkelew criterion (to evaluate runaway for exothermic reactions) is implemented for practical and safe reactor design. This work identifies that the critical couples populating the Barkelew diagram are positioned lower (up to a 50% difference, compared to Barkelew’s original report), so that operation of the reactor under higher hydrocarbon molar inlet fractions is possible while maintaining safe performance.



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1. Introduction

According to Theloke and Friedrich [1], four main sources of volatile organic components (VOC) can be distinguished, namely transport (37%), solvent use (55%), production and storage processes (4%), and combustion processes (4%). One third of all emitted gases are alkanes. The emissions coming from mobile sources, most of them automotive, can be eliminated by the use of monolith reactors [2]. The stationary emissions can be destructured using the same reactor type, but the use of tubular reactors is preferred, since industrial effluents have a higher flow rate than car exhaust gases. Furthermore, for highly exothermic reactions, as is the case for total oxidation reactions, this type of reactor, embedded in molten salt, is definitely preferred for its heat transfer [3]. In this type of reaction, exothermicity cannot be neglected; therefore, hotspots and runaway are the origins of a poor oxidation reactor operation. Literature overviews of these phenomena are given by Baptista et al. [4], Velo et al. [5], and Quina et al. [6]. Excessive temperatures during runaway may lead to serious damage to the reactor, catalyst sintering and deactivation, and, last but not least, hazardous situations for the operators. It is clear that these phenomena should be

avoided at all times. A recent report deals with thermal runaway for wall-cooled multi-tubular fixed-bed catalytic reactors (MTR), using an n th order reaction in multiple stacked reactor configuration [7]. Regarding safe reactor operation, Calverley et al. suggest the loading mixtures of active and inert catalyst pills into multi-tubular reactors. This process produces natural variations in catalyst activity [8]. Nevertheless, their commercial-scale reactor simulations for the partial oxidation of *o*-xylene to phthalic anhydride suggest that this variation can still cause a significant fraction of the reactor tubes to run away, even though the reactor is operating well within its stable range when a perfect activity profile is assumed. A very comprehensive overview in terms of runaway prevention is given by Kummer and Varga [9]. They consider the appropriate design of the reactor, the operation strategy, and an early warning detection system. Reactor runaway criteria can indicate thermal runaway early, which can be addressed via three criteria classes (based on geometry, sensitivity, and stability). Furthermore, the works of Westerterp and Molga [10] and Yang et al. [11] on criteria for runaway phenomena are recommended.

In this work, a steady-state non-isothermal plug flow reactor is simulated for the total oxidation of volatile organic components (VOC), for which propane is taken as a model molecule, using a fully developed Langmuir–Hinshelwood reaction rate expression. Intraparticle gradients are accounted for by means of an effectiveness factor, calculated with a generalized Thiele modulus [3]. After the discussion of a base case, several variations in inlet and reactor conditions are presented. Special attention is paid to the runaway phenomenon in terms of the well-known Barkelew graph [3,12,13], which can occur when the reaction is exothermic and the generation rate of heat exceeds the rate of its removal. The simulation results using a fully developed kinetic model including intraparticle diffusion limits will be compared to the results of Barkelew in terms of reactor operation (temperature, inlet hydrocarbon molar fraction).

2. Model Description

This section contains an explanation of the reactor model that was used for the simulations (Section 2.1). In Section 2.2, it is proven that a pseudo-homogeneous is sufficient for the current simulations. Section 2.3 describes the details of the total oxidation kinetic model that was used. Details of the solution procedure are summarized in Section 2.4. This section ends with a reflection on the typical reactor duty for total oxidation reactions (Section 2.5).

2.1. Reactor Model

For the simulation of the total oxidation of propane, a one-dimensional reactor model is used, in which it is assumed that concentration and temperature gradients only occur in the axial direction. The continuity equation for propane is given by Equation (1), in which $F_{C_3H_8}$, ρ_b , Ω , and R_{w,C_3H_8} represent the molar flow rate of propane through the reactor, the bed density, the cross section of the reactor, and the specific production rate of propane. The energy equation is given by Equation (2), in which u_s , ρ_f , T , $c_{p,f}$, $(-\Delta_r H)$, U , d_t , and T_r are the superficial velocity, gas density, bulk fluid temperature, the specific heat of the gas mixture, reaction enthalpy, overall heat transfer coefficient, reactor tube diameter, and reactor temperature, respectively. Equation (3) is the momentum equation, in which p_t , f , and d_p are the total pressure along the axis of the reactor, the friction factor, and the equivalent particle diameter, respectively.

$$\frac{dF_{C_3H_8}}{dz} = \rho_b \Omega R_{w,C_3H_8} \quad (1)$$

$$u_s \rho_f c_{p,f} \frac{dT}{dz} = (-\Delta_r H) \rho_b (-R_{w,C_3H_8}) - \frac{4U}{d_t} (T - T_r) \quad (2)$$

$$-\frac{dp_t}{dz} = f \frac{\rho_f u_s^2}{d_p} \quad (3)$$

The conditions at the inlet of the reactor are $F_{C_3H_8} = F_{C_3H_8,0}$, $T = T_0$, and $p_t = p_{t,0}$. In the above continuity Equations (1) and (2), the only mechanism of transport is plug flow. In all the performed simulations, the Péclet numbers for mass and heat transfer Pe'_{ma} and Pe'_{ha} , as a measure of the deviation from the plug flow regime, are calculated at the reactor inlet. When the rate monotonically decreases in the reactor bed, Young and Finlayson [14] point out that the critical position where the importance of axial mixing has to be assessed is the bed inlet.

$$\frac{R_{w,C_3H_8,0} \rho_p d_p}{u_s C_{C_3H_8,0}} \ll Pe'_{ma} \quad (4)$$

$$\frac{\rho_p (-\Delta_r H) d_p}{u_s \rho_f c_{p,f} (T - T_r)} \ll Pe'_{ha} \quad (5)$$

The Péclet numbers for axial mass transfer, Pe'_{ma} , and axial heat transfer, Pe'_{ha} , are obtained from Equations (6) and (7), where Sc and Pr are the dimensionless Prandtl and Schmidt number. The static contribution for axial heat transfer, $\lambda_{e,a,b}$, and typical values for constant C are given by Kulkarni and Doraiswamy [15].

$$\frac{1}{Pe'_{ma}} = \frac{0.5}{1 + \frac{3.8}{Sc Re_p}} + \frac{0.3}{Sc Re_p} \quad (6)$$

$$\frac{1}{Pe'_{ha}} = \frac{\lambda_{e,a,b}}{\lambda_f} \frac{1}{Pr Re_p} + \frac{14.5}{d_p \left(1 + \frac{C}{Pr Re_p}\right)} \quad (7)$$

Corresponding to base case conditions (see Table 1), it was concluded from the obtained values in Equations (6) and (7) (see Table 2) that axial mixing is not significantly present, and hence no additional second-order terms, accounting for axial diffusion, were to be added to Equations (1) and (2).

Regarding possible radial variations, earlier work ruled out significant radial influences under the given conditions [16,17]. If higher values for the reactor tube diameter are to be considered, the 1D model probably needs to be replaced by a 2D model using cylindrical coordinates, i.e., including the radial direction [3]. Instructive reports are the works of Donaubauer et al. [18] and Kern and Jess [19].

A heterogeneous reactor model, in which a distinction is made between the conditions in the fluid and the catalyst particle, is advised in the case of rapid reactions or reactions with an important heat effect, e.g., (total) oxidation reactions [3]. Since high flow rates, and hence superficial velocities, are adopted in industrial reactors, the concentration and temperature gradients on the reactor scale are generally smaller than on the catalyst particle scale [3]. External gradients are investigated in more detail in Section 2.2.

Within the catalyst particle, temperature gradients are generally smaller than concentration gradients [3]. In order to account for the concentration gradients inside the catalyst particle, an effectiveness factor η can be calculated. This factor corresponds to the ratio of the rate of reaction with pore diffusion resistance to the reaction rate at surface conditions, i.e., without internal gradients. Hence, the specific production rate in Equations (1) and (2) equals $\eta(-r_{w,C_3H_8})$, with $-r_{w,C_3H_8}$ being the rate of disappearance of propane (see Section 2.3), and it is possible to characterize the situation inside the catalyst particle by means of a single number, η [3]. Nevertheless, it is common to use constant effectiveness factors [20–22], where calculated values for η are updated along the axial position in the reactor. Instructive

examples can be found in Lee et al. [23], investigating the kinetics and effectiveness factor for methanol steam reforming over Cu/ZnO/Al₂O₃ catalyst; Carrasco-Venegas et al. [24], describing the catalytic dehydrogenation of cyclohexanol; Lee et al. [25], reporting on the simulation of a fixed-bed reactor for dimethyl ether synthesis with complex kinetics; and Kim et al. [26], proposing a novel method for an effectiveness factor estimation of two simultaneous reactions in the preferential CO oxidation over CuO/CeO₂.

Table 1. Base case conditions used in the simulations. The oxygen source is air; the total inlet pressure is calculated to have a fixed outlet pressure, p_{atm} .

Parameter	Symbol	Units	Value
reactor configuration			
number of tubes	N_t	-	3000
inner diameter	d_t	m	0.016
wall thickness	d_w	m	0.002
wall heat conductivity	λ_w	$\text{W m}^{-1} \text{K}^{-1}$	$48.9 + 0.0426 T$ [27]
tube length	L_t	m	12.0
bed porosity	ϵ_b	$\text{m}^3 \text{m}^{-3}$	0.49
catalyst			
equivalent particle diameter	d_p	m	2.33×10^{-3}
pore radius	r_p	m	6.34×10^{-9}
particle porosity	ϵ_p	$\text{m}^3 \text{m}^{-3}$	0.62
tortuosity	τ_p	m m^{-1}	2.0 [28]
density	ρ_s	$\text{kg}_{\text{cat}} \text{m}_{\text{cat}}^{-3}$	3254
effective thermal conductivity	λ_e	$\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$	36.0 [27]
operating conditions			
inlet temperature	T_0	K	598
reactor temperature	T_r	K	648
inlet total pressure	$p_{t,0}$	Pa	$2.10 \times 10^{+5}$
inlet total flow rate	$F_{t,0}$	$\text{mol}_{t,0} \text{s}^{-1}$	26.6
inlet mole fractions	$y_{\text{C}_3\text{H}_8,0}$	$\text{mol}_{\text{C}_3\text{H}_8,0} \text{mol}_{t,0}^{-1}$	3.70×10^{-3}
	$y_{\text{H}_2\text{O},0}$	$\text{mol}_{\text{H}_2\text{O},0} \text{mol}_{t,0}^{-1}$	1.00×10^{-1}
	$y_{\text{CO}_2,0}$	$\text{mol}_{\text{CO}_2,0} \text{mol}_{t,0}^{-1}$	1.00×10^{-1}
heat of reaction	$-\Delta_r H$	J mol^{-1}	$1.98 \times 10^{+6}$

Table 2. Mass and heat transfer coefficients.

Parameter	Units	Value
Mass transfer		
$k_{f,\text{C}_3\text{H}_8}$	$\text{m}_f^3 \text{m}_i^{-2} \text{s}^{-1}$	0.14
a_s	$\text{m}_i^2 \text{kg}_{\text{cat}}^{-1}$	1.91
j_D	-	0.07
Re_p	-	$1.05 \times 10^{+2}$
Sc	-	0.45
lhs Equation (4)	-	3.78×10^{-4}
Pe'_{ma}	-	2.12
Heat transfer		
α	$\text{J m}_i^{-2} \text{K}^{-1} \text{s}^{-1}$	$3.50 \times 10^{+2}$
j_H	-	0.17
Pr	-	0.60
lhs Equation (5)	-	1.05×10^{-5}
Pe'_{ha}	-	1.62×10^{-4}

For spherical catalyst particles, it is calculated with Equation (8), using the generalized Thiele modulus ϕ (see Equation (9)). For an irreversible reaction, the propane partial pressure at equilibrium, $p_{C_3H_8,s,eq}$, is set to zero:

$$\eta = \frac{1}{\phi} \frac{(3\phi) \coth(3\phi) - 1}{3\phi} \quad (8)$$

$$\phi = \frac{d_p}{6} \frac{r_{C_3H_8}(p_{C_3H_8,s}^s, T_s^s) \rho_s}{\sqrt{2}} \cdot \left(\int_{p_{C_3H_8,s,eq}}^{p_{C_3H_8,s}^s} D_{e,C_3H_8}(p', T_s) r_{w,C_3H_8}(p', T_s) \rho_s \frac{dp'_{C_3H_8,s}}{R T_s} \right)^{-1/2} \quad (9)$$

The Prater relation, given by Equation (10), provides the temperature inside the pellet, T_s , as a function of the surface temperature, T_s^s , surface partial pressures p_s^s , and the propane partial pressure inside the pellet $p_{C_3H_8,s}$.

$$T_s - T_s^s = \frac{D_{e,C_3H_8}(p_s^s, T_s^s)(-\Delta_r H)}{\lambda_e} \left(\frac{p_{C_3H_8,s}^s}{R T_s^s} - \frac{p_{C_3H_8,s}}{R T_s} \right) \quad (10)$$

The partial pressure profiles of the dependent components, needed in the integrand of Equation (9), are obtained as a function of the key component partial pressure $p_{C_3H_8,s}$ (see Equations (11)–(13)) [3]:

$$p_{O_2,s} = p_{O_2}^s + 5 \frac{D_{e,C_3H_8}(p_s^s, T_s^s)}{D_{e,O_2}(p_s^s, T_s^s)} (p_{C_3H_8,s} - p_{C_3H_8}^s) \quad (11)$$

$$p_{CO_2,s} = p_{CO_2}^s - 3 \frac{D_{e,C_3H_8}(p_s^s, T_s^s)}{D_{e,CO_2}(p_s^s, T_s^s)} (p_{C_3H_8,s} - p_{C_3H_8}^s) \quad (12)$$

$$p_{H_2O,s} = p_{H_2O}^s - 4 \frac{D_{e,C_3H_8}(p_s^s, T_s^s)}{D_{e,H_2O}(p_s^s, T_s^s)} (p_{C_3H_8,s} - p_{C_3H_8}^s) \quad (13)$$

The effective diffusion coefficient for component i , $D_{e,i}$, is calculated with the Bosanquet equation, i.e., from the molecular diffusion coefficient, $D_{m,i}$, and the Knudsen diffusion coefficient, $D_{K,i}$, corrected for the pellet porosity ε_p and tortuosity τ_p . The former is obtained from the Stefan–Maxwell equation, corrected with the so-called ‘approximate film factor’, which is justified because external gradients are not important [29] (see Section 2.2).

Values for the physical parameters, ρ_f and $c_{p,f}$, present in Equations (1)–(3) are obtained from correlations [27], and their values, considered to be a function of temperature and composition, are updated along the reactor length. The overall heat transfer coefficient U is calculated as a total resistance to heat transfer, replacing a series of thermal resistances [3,30]. The friction factor f in Equation (3) is calculated with the correlation of Hicks for spherical particles [3]. Typical reactor dimensions and inlet conditions are given in Section 4.1.

2.2. External Gradients

The external concentration gradient can be estimated by Equation (14), in which k_{f,C_3H_8} , a_s , and C_i are the mass transfer coefficient from gas to solid interface, the specific external surface, and the molar concentration of component i , respectively. The specific external surface is obtained from Equation (15):

$$-R_{w,C_3H_8}^{obs} = k_{f,C_3H_8} a_s (C_{C_3H_8,b} - C_{C_3H_8,s}^s) \quad (14)$$

$$a_s = \frac{6}{d_p \rho_s (1 - \varepsilon_p)} \quad (15)$$

The propane molar concentration difference amounts to $2.3 \times 10^{-3} \text{ mol m}^{-3}$, which is, compared to the propane molar inlet concentration of 0.2 mol m^{-3} , negligible. It can hence be concluded that external gradients are not significantly relevant in the performed reactor simulations [29,31].

The external temperature gradient can be calculated by Equation (16), in which ρ_p and α are the particle density and the convective heat transfer coefficient, respectively:

$$\left(-R_{w,C_3H_8}^{obs}\right)\rho_p(-\Delta_r H)\frac{\pi}{6}d_p^3 = \alpha(T_b - T_s^s)\pi d_p^2 \quad (16)$$

In the performed simulations, the maximum temperature difference between bulk and catalyst surface amounts to 1.6 K, so it is acceptable to assume that external temperature gradients are not significantly present.

The mass transfer coefficient from gas to solid interface, k_{f,C_3H_8} , and convective heat transfer coefficient, α , are calculated using the Chilton–Colburn j factors [30]. For mass and heat transfer, the j_D and j_H factors are calculated according to Sengupta and Thodos [32] and Deacetis and Thodos [33]. Typical values are reported in Table 2.

In conclusion, based on the absence of significant external gradients under the applied conditions, a pseudo-homogeneous reactor is acceptable.

2.3. Kinetic Model

For the simulation of a tubular reactor, the steady-state Langmuir–Hinshelwood (LH) kinetic model for the total oxidation of propane over a $\text{CuO-CeO}_2/\gamma\text{-Al}_2\text{O}_3$ mixed metal oxide catalyst [17] is used. The corresponding kinetic parameters are listed in Table 3.

$$r_{w,C_3H_8} = \frac{k_s \sqrt{K_{O_2} p_{O_2}} K_{C_3H_8} p_{C_3H_8}}{\left(1 + \sqrt{K_{O_2} p_{O_2}} + K_{C_3H_8} p_{C_3H_8} + K_{H_2O} p_{H_2O} + \sqrt{K_{H_2O} K_{diss,2} p_{H_2O}} \sqrt[4]{K_{O_2} p_{O_2} + K_{CO_2} p_{CO_2}}\right)^2} \quad (17)$$

Table 3. Kinetic parameters for the LH model for the total oxidation of propane, obtained from Heynderickx et al. [17].

Parameter	Units	Value
$k_{s,0}$	$/\text{mol kg}_{\text{cat}}^{-1} \text{s}^{-1}$	$(9.58 \pm 1.11) 10^{+4}$
E	$/\text{kJ mol}^{-1}$	74.4 ± 4.6
$-\Delta S_{O_2}^0$	$/\text{J mol}^{-1} \text{K}^{-1}$	97.7 ± 5.6
$-\Delta H_{O_2}^0$	$/\text{kJ mol}^{-1}$	0.0^1
$-\Delta S$	$/\text{J mol}^{-1} \text{K}^{-1}$	61.7 ± 0.4
$-\Delta H_{C_3H_8}^0$	$/\text{kJ mol}^{-1}$	0.0^1
$-\Delta S_{H_2O}^0$	$/\text{J mol}^{-1} \text{K}^{-1}$	154.2 ± 23.3
$-\Delta H_{H_2O}^0$	$/\text{kJ mol}^{-1}$	53.8 ± 20.0
$-\Delta S_{CO_2}^0$	$/\text{J mol}^{-1} \text{K}^{-1}$	173.3 ± 37.9
$-\Delta H_{CO_2}^0$	$/\text{kJ mol}^{-1}$	54.2 ± 23.7
$-\Delta S_{diss,2}^0$	$/\text{J mol}^{-1} \text{K}^{-1}$	156.5 ± 11.2
$-\Delta H_{diss,2}^0$	$/\text{kJ mol}^{-1}$	99.1 ± 10.8

¹ Parameter could not be estimated significantly [17].

Fractional coverages for adsorbed propane, dissociatively chemisorbed oxygen, carbon dioxide, water, and hydroxyl species are given by Equations (18)–(22), with N being the square root of the denominator in Equation (17):

$$\theta_{C_3H_8} = \frac{K_{C_3H_8} p_{C_3H_8}}{N} \quad (18)$$

$$\theta_{O^*} = \frac{\sqrt{K_{O_2} p_{O_2}}}{N} \quad (19)$$

$$\theta_{CO_2^*} = \frac{K_{CO_2} p_{CO_2}}{N} \quad (20)$$

$$\theta_{H_2O^*} = \frac{K_{H_2O} p_{H_2O}}{N} \quad (21)$$

$$\theta_{HO^*} = \frac{\sqrt{K_{H_2O} K_{diss,2} p_{H_2O}} \sqrt[4]{K_{O_2} p_{O_2}}}{N} \quad (22)$$

The fractional coverage for the free active sites is obtained by solving Equation (23) for θ_* and subsequent substitution of Equations (18)–(22):

$$\theta_* + \theta_{C_3H_8^*} + \theta_{O^*} + \theta_{CO_2^*} + \theta_{H_2O^*} + \theta_{HO^*} = 1 \quad (23)$$

The average fractional coverage $\bar{\theta}_{i^*}(z)$ for surface species i along the reactor axis is obtained by elaboration of Equation (24): the fractional coverage inside the catalyst particle, as an analogue to Equation (9), is averaged over the catalyst particle for every axial position inside the reactor:

$$\bar{\theta}_{i^*}(z) = \frac{\int_{p_{C_3H_8,s,eq}}^{p_{C_3H_8,s}^s} \theta_{i^*}(p'_s, T_s, z) dp'_{C_3H_8,s}}{\int_{p_{C_3H_8,s,eq}}^{p_{C_3H_8,s}^s} dp'_{C_3H_8,s}} \quad (24)$$

While the first reports on runaway phenomena used first-order [34] or pseudo-first-order reactions [35], it is important to consider realistic reaction rate expressions.

2.4. Solution Procedure

The code starts by reading all the variables needed for integration of the reactor differential equations (physical properties, reactor details (length, number of tubes, bed porosity), flow rate, inlet concentrations, inlet mole fractions, kinetic parameters, catalyst properties (particle size, tortuosity)), i.e., all the base case conditions reported in Table 1, together with the properties from Table 2. Then, the fourth order Runge–Kutta routine is called, rk4 [36], for the first integration step (step size along the tubular reactor axis was 1.0×10^{-4} m), where the in-house written subroutine rhs () takes care of the actual right-hand sides of the differential equations (calculation of specific heat, heat transfer coefficient on the bed side (Leva correlation [37]), overall heat transfer coefficient, friction factor according to Hicks [38], etc.). Parameters and updated properties are shared via common blocks. Thereafter, the effectiveness factor is calculated from the generalized Thiele modulus with the in-house code gthiel(). Molecular diffusion coefficients are updated using the Fuller–Schettler–Giddings correlation [39], and together with the calculated Knudsen diffusion, the effective diffusion coefficient is obtained via the Bosanquet relation [3,29]. The in-house written function rate (p,T) calculates the pressure values inside the particle according to Equations (11)–(13). The integral in Equation (9) to calculate the Thiele modulus is performed by means of Chebyshev polynomials [40]. At this point, the right-hand side of the differential continuity and heat equations can be fully calculated by the Runge–Kutta method, and thereafter the procedure loops back into the second space increment and so on until the total reactor tube length is simulated. Values for variable properties are stored in separate files as the integration goes along (from inlet to end of the reactor tubes). The average computational time on a Samsung PC (Intel® Core™ i5-6200U CPU @ 2.30 GHz, sourced from Samsung Electronics Co., Ltd. (Suwon, Republic of Korea) with processor from Intel Corporation (Santa Clara, CA, USA)) was 20 s.

2.5. Reactor Duty in Total Oxidation Operation

In industrial applications, the pressure at the outlet of the tubular reactor is generally atmospheric pressure. Therefore, the given total inlet pressure, $p_{t,0}$, is iteratively adapted in the base case simulation until atmospheric pressure is obtained at the outlet of the reactor.

Since the tubular reactor is used in the total oxidation of VOC, full propane conversion at the outlet should be aimed at. A higher reactor temperature results in an increase in propane conversion, and hence in a smaller tubular reactor, but it also gives rise to runaway behavior, which is to be avoided. On the other hand, a longer reactor results in a higher propane conversion, but the length is limited by construction as well as by the pressure drop. The optimization of the tubular reactor for total oxidation purposes depends on the reactor configuration, on the inlet conditions, and on the required outlet conditions.

3. Safety and Runaway Criteria

Barkelew [34] proposed two dimensionless numbers, S and N , to diagnose runaway by simulation of a first-order reaction:

$$S = \frac{(-\Delta_r H) y_{C_3H_8,0} E_A}{c_{p,f} RT_r^2} \quad (25)$$

$$N = \frac{4U}{d_t c_{p,f} k^*(T_r)} \quad (26)$$

S is the product of the adiabatic temperature rise and the dimensionless activation energy (see Equation (25)). N is given by Equation (26), and the ratio N/S represents the ratio of the rate of heat transfer per unit reactor volume to the rate of heat generation per unit volume. In order to avoid runaway, S should be as small as possible, whereas N/S should be as high as possible. Details on the Barkelew approach can be found in Velo et al. [5]. If the operational conditions lead to a point above the curve in the so-called ‘Barkelew diagram’, the reactor is considered as insensitive to small fluctuations. If the calculated couple (S , N/S) is situated under the curve, runaway is considered to be likely to occur [3].

In order to quantify the rate coefficient k^* , calculated at the reactor temperature T_r , the real reaction rate at the inlet of the reactor (see Equation (17)) and the first-order reaction rate $r_0 = k^*(T_r) p_{C_3H_8,0}$ are set to be equal. This can be done since the total oxidation of propane is modeled in an excess of oxygen [21]. In order to meet the dimensions in Equation (26), this rate coefficient k^* is given by Equation (27):

$$k^*(p_{C_3H_8,0}, T_r) = \frac{\eta r_{w,C_3H_8}(p_{C_3H_8,0}, T_r)}{y_{C_3H_8,0}} (1 - \varepsilon_b)(1 - \varepsilon_p) \rho_s \quad (27)$$

Since the total oxidation reaction rate, $r_{w,C_3H_8}(p_{C_3H_8,0}, T_r)$, is a monotonically decreasing function of the propane conversion, the highest value for $k^*(p_{C_3H_8,0}, T_r)$ is obtained at the inlet conditions. In addition, at the reactor inlet, the highest effectiveness factor, η , is obtained. Putting all the information together, Equation (26) gives the minimum value for N , and it is this value that is required for interpretation of the Barkelew diagram (see Section 4.3.3).

Morbidelli and Varma [13] define the so-called ‘hotspot’ as the maximum in the temperature versus axial position profile, and runaway operation occurs only when those hotspots are accompanied by a positive second derivative in this profile before the reactor temperature reaches its maximum value, i.e., at the hotspot. Equivalently, runaway occurs

when an inflection point is observed before the maximum in the temperature versus axial position profile.

It can be mentioned that the purpose of this paper is not to investigate all runaway criteria. The Barkelew approach is interpreted with respect to a fully developed Langmuir–Hinshelwood reaction rate, rather than a simplified first-order or pseudo-first-order reaction rate expression. For other possible approaches, one is referred to the excellent work of Szeifert et al. [41], describing design diagrams for methanol synthesis where the runaway boundaries are defined based on Lyapunov’s indirect method; Casson et al. [42] and Vianello et al. [43], applying runaway criteria to define alarm and onset temperatures; and Kummer and Varga [44], using thermal runaway criteria as nonlinear constraints to define the optimal feeding trajectory in the operation of semi-batch reactors.

Lastly, it can be noted that the Barkelew criterion can be applied for any exothermic reaction, where the compound properties (reaction enthalpy to calculate the heat produced during reaction and the specific heat capacity) and reactor operational properties (such as inlet molar fraction, reactor diameter, overall heat transfer coefficient, bed porosity, particle porosity, and catalyst density) must be properly substituted in Equations (25) and (26). Furthermore, the calculation of the reaction rate coefficient needs to be performed based on the actual kinetic model and the specific value of the effectiveness factor (along the reactor axis) (see Equation (27)).

4. Results and Discussion

4.1. Reactor Dimension and Operation Conditions

The reactor and catalyst dimensions as well as the operating conditions for a base case (benchmark) are mentioned in Table 1. In order to guarantee the safety of the plant, the inlet molar fraction of VOC is allowed to be 25% of the lower explosion limit (LEL) at the maximum [45]. For a typical reactor temperature of 648 K, the LEL of propane in air is $0.015 \text{ mol}_{\text{C}_3\text{H}_8,0}^{-1} \text{ mol}_{\text{t},0}^{-1}$, and hence an inlet molar fraction $0.0037 \text{ mol}_{\text{C}_3\text{H}_8,0}^{-1} \text{ mol}_{\text{t},0}^{-1}$ is taken in the base case. A total molar inlet flow rate of 26.6 mol s^{-1} is applied, corresponding to typical molar flow rates in total oxidation applications of VOC [45]. The oxygen source is air, which is freely available. Simulations are performed with $0.10 \text{ mol}_{\text{CO}_2,0}^{-1} \text{ mol}_{\text{t},0}^{-1}$ carbon dioxide and $0.10 \text{ mol}_{\text{H}_2\text{O},0}^{-1} \text{ mol}_{\text{t},0}^{-1}$ water in the feed, which mimics the composition of typical industrial waste gases [46,47]. The catalyst particles have a cylindrical shape with average diameter $1.86 \times 10^{-3} \text{ m}$ and average height $4.67 \times 10^{-3} \text{ m}$, from which an equivalent diameter d_p is calculated as $2.33 \times 10^{-3} \text{ m}$ (see Appendix A). The bed porosity, ϵ_b , and the catalyst particle, ϵ_p , are experimentally determined as $0.47 \text{ m}_f^3 \text{ m}_r^{-3}$ and $0.62 \text{ m}_f^3 \text{ m}_p^{-3}$ (see Appendix B). For completion, all symbols used in this work are mentioned in Appendix C.

Using the specific area of the catalyst, $1.60 \times 10^{+5} \text{ m}_{\text{cat}}^2 \text{ kg}_{\text{cat}}^{-1}$ [48], the pore radius inside the catalyst particle, r_p , is determined as $6.34 \times 10^{-9} \text{ m}$ [15]. The total catalyst mass loaded in the tubular reactor is $4565 \text{ kg}_{\text{cat}}$. Within the permissible limits for the reactor temperature (see Section 2.4), the catalyst is known to operate without deactivation [48].

4.2. Base Case

Corresponding to the base case conditions (see Table 1), the outlet propane conversion gives a maximum remaining propane mole fraction of $1.85 \times 10^{-9} \text{ mol}_{\text{C}_3\text{H}_8,0}^{-1} \text{ mol}_{\text{t},0}^{-1}$, corresponding to a concentration of 0.32 mg m^{-3} , which is a good accomplishment compared to the European emission limit for solvent use, 2.0 mg m^{-3} [49].

Using the Prater relation (10), the temperature increase inside the pellet amounts to 0.1 K at its maximum in the performed simulations. Hence, the main transport resistance inside the catalyst pellet is due to mass transfer, in accordance with the literature [3]. In the next section, the main results of the base case simulation are compared to those obtained by variation in inlet and operation conditions.

4.3. Variation of Inlet Conditions and Runaway Behavior

4.3.1. Total Inlet Pressure

Figure 1 gives the pressure drop over the tubular reactor versus the total inlet pressure for different inlet molar flow rates. The total inlet pressure in the base case is tuned to have atmospheric pressure at the reactor outlet (see Section 4.1). For an identical inlet total molar flow rate, the pressure drop decreases as the total inlet pressure increases. This is expected from Equation (3), since $\rho_f \sim p_t$ and $u_s \sim p_t^{-1}$.

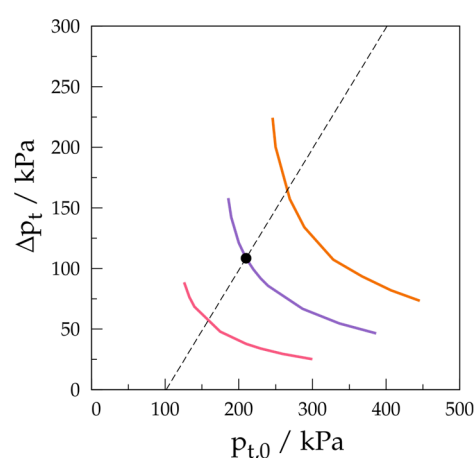


Figure 1. Pressure drop vs. total inlet pressure, obtained by integration of Equations (1)–(3) at base case conditions (see Table 1), with variation of the total inlet molar flow rate and total inlet pressure. (—) $F_{t,0} = 16.6 \text{ mol s}^{-1}$; (—) $F_{t,0} = 26.6 \text{ mol s}^{-1}$; (—) $F_{t,0} = 36.6 \text{ mol s}^{-1}$. Dashed line corresponds to atmospheric outlet pressure. (●) base case.

As a result, for an identical inlet total pressure and a higher inlet total molar flow rate, a higher pressure drop is obtained. This is due to the increased superficial velocity, u_s (see Equation (3)). A very steep decrease in the simulated reactor pressure is observed once this pressure falls below the atmospheric value (corresponding to operation in suction mode).

4.3.2. Inlet Temperature

The effect of gas inlet phase temperature is not very pronounced (see Figure 2): the maximum reactor temperature for the lowest inlet temperature of 298 K amounts to 663 K, whereas a hotspot of 667 K is obtained for an inlet temperature of 598 K. These results indicate that no additional heat exchanger before the reactor to heat up the incoming feed needs to be considered. The first part of the reactor works as a very efficient heat exchanger, and it sufficiently allows buffering variations in inlet temperature. It is calculated that the outlet propane mole fraction is not significantly affected by the inlet gas phase temperature, and a similar outlet propane concentration (see Section 4.2) is obtained.

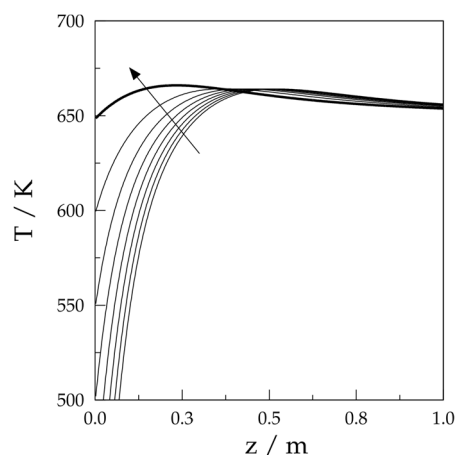


Figure 2. Gas phase temperature vs. axial reactor coordinate, obtained by integration of Equations (1)–(3). Simulations are performed at (—) base case conditions (see Table 1), with variation of the inlet gas temperature ranging from 298 to 648 K, indicated by the arrow.

4.3.3. Propane Inlet Molar Fraction

For the base case, a maximum reactor temperature increase of 16 K is observed. An increase in the propane inlet molar fraction from 0.0017 to $0.0127 \text{ mol}_{\text{C}_3\text{H}_8,0}^{-1} \text{ mol}_{\text{t},0}^{-1}$ increases the results in a higher hotspot temperature (see Figure 3a). When the propane inlet molar fraction exceeds the critical value for runaway to occur, the temperature increase rockets up to 300 K.

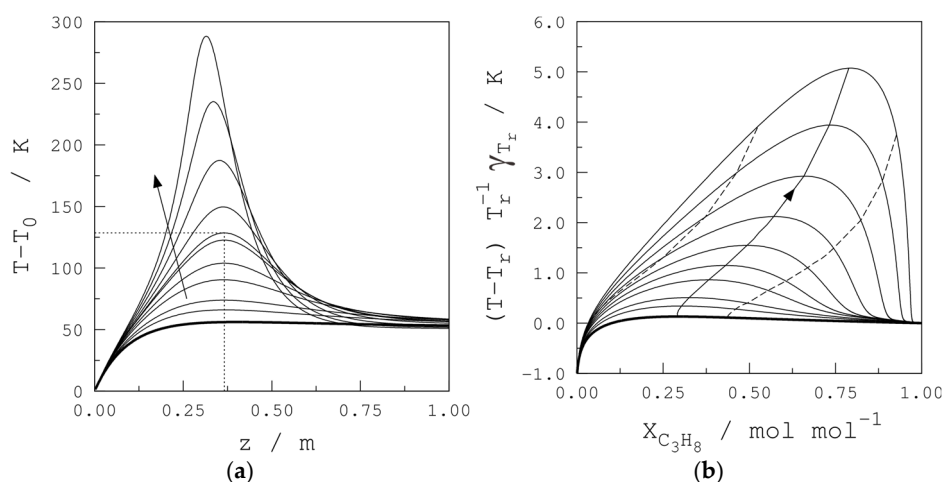


Figure 3. (a) Temperature vs. axial reactor coordinate, obtained by integration of Equations (1) to (3). The dotted line indicates temperature increase and the corresponding axial reactor position for which the propane inlet propane mole fraction is critical, i.e., above this value two inflections point occur before the maximum temperature. (b) Dimensionless temperature (see Equation (28)) vs. propane conversion for increasing propane inlet molar fractions. The full line with arrow and the dashed lines indicate, respectively, the maximum and the inflection point(s) in the temperature vs. axial reactor coordinate profile. Simulations are performed at (—) base case conditions (see Table 1), with variation of the propane inlet molar fractions from 0.0017 to $0.0127 \text{ mol}_{\text{C}_3\text{H}_8,0}^{-1} \text{ mol}_{\text{t},0}^{-1}$, indicated by the arrow.

In order to trigger runaway operation under typical conditions, a dimensionless temperature $\vartheta(T)$ can be defined [5,13] (see Equation (28)). By division of Equation (2) by Equation (1) and integrating the temperature profile along the tubular reactor as a function of the propane conversion, this dimensionless temperature is plotted versus the propane conversion (see Figure 3b).

$$\vartheta(T) = \frac{T - T_r}{T_r} \cdot \frac{E_A}{R T_r} \quad (28)$$

Morbidelli and Varma [13] showed that runaway behavior occurs when the operating curve $\vartheta(T)$ (see Equation (28)) is tangent to the $\vartheta = \vartheta(T_i)$ curve, i.e., the curve evaluated at the inflection point(s) before the hotspot, vide infra. These observations match with the results from Van Welsenaere and Froment [35]. Nevertheless, these authors used a pseudo-first-order reaction, and they did not update the physical parameters along the axial reactor position (see Section 2.1). In this way, they could determine an analytical expression for the maximum in the inlet partial pressure versus reactor temperature profile, by which a critical inlet partial pressure, and hence inlet molar fraction, was defined.

Figure 4a gives the reactor temperatures corresponding to the inflection points in the reactor temperature versus axial reactor coordinate profile. It can be observed that below a certain propane inlet molar fraction, i.e., the critical propane inlet molar fraction, only a single inflection point occurs after the hotspot. The lower the molar inlet flow rate is, the smaller the critical propane inlet molar fraction is for which runaway behavior occurs. A low total molar flow rate corresponds specifically to a low heat transfer, which explains the higher temperature increase in the reactor.

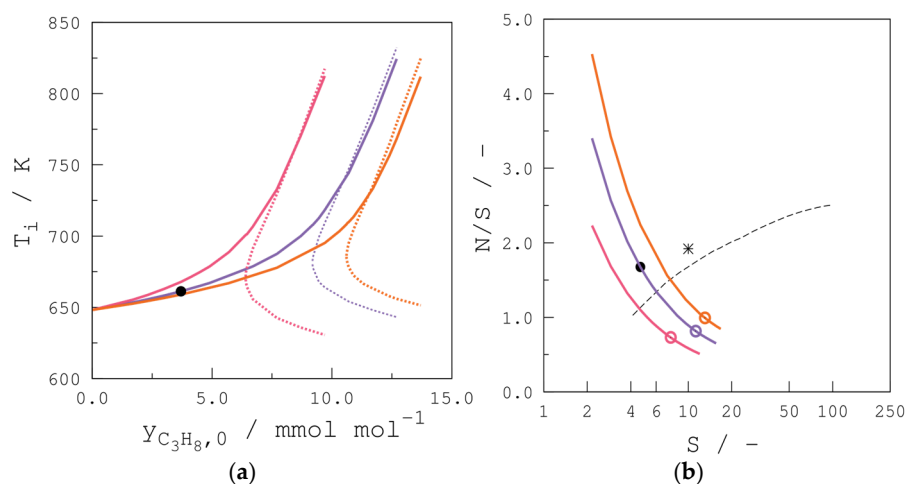


Figure 4. (a) Temperature corresponding to the inflection point(s) in the reactor temperature vs. axial reactor coordinate profile, vs. propane inlet molar fraction, obtained by integration of Equations (1) to (3). Full lines represent the inflection point after the maximum, whereas the dotted lines correspond to the inflection point(s) before the maximum. (b) Corresponding runaway diagram. Dashed line corresponds to the data given by Barkelew [3,34]. Base case conditions (see Table 1) are applied with variation of total inlet molar flow rate. (—) $F_{t,0} = 16.6 \text{ mol s}^{-1}$; (—) $F_{t,0} = 26.6 \text{ mol s}^{-1}$; (—) $F_{t,0} = 36.6 \text{ mol s}^{-1}$. (●) base case; (*) reference from Froment and Bischoff [3]; (o) (S,N/S) couples corresponding to the critical point, obtained from (a).

In Figure 4b, the (S,N/S) couples (see Equations (25) and (26)) are plotted versus the runaway data, obtained by Barkelew [34]. This author concluded that runaway occurs when the (S,N/S) couple, corresponding to reactor operation, is situated below the dashed line (up to 50% of the Barkelew values, dashed line). From the performed simulation results, it is observed that the lower the total inlet molar flow rate is, the lower the operation point is situated. Furthermore, an increasing propane molar inlet fraction gives a higher value for S (see Equation (25)), whereas the value for N/S decreases (see Equations (25) and (26)), explaining the calculated lines in Figure 4b. The base case is indicated by the symbol '●'. A reference point, obtained by Van Welsenaere and Froment in the o-xylene oxidation into phthalic anhydride, is indicated by '*'. For every total inlet molar flow rate, the symbol 'o' indicates the critical propane inlet molar fraction (see above). Based on the results,

presented in Figure 4b, the original curve, proposed by Barkelew [34], can be transposed to lower N/S values for this specific highly exothermic oxidation reaction, so that the reactor can be operated with higher tube diameters; a higher reactor temperature, T_r ; or higher propane inlet molar fractions (less dilution required). In other words, the region of reactor stability is bigger for the presented case than the one proposed by Barkelew. Of course, this is a process-dependent action, and hence this result should not be generalized.

Due to mass transfer inside the catalyst particle, the effectiveness factor will be lower than unity. This results in a higher value for N (see Equation (26)) and allows one to operate the tubular reactor with higher reactor tube diameters or higher inlet concentrations of VOC. de Smet et al. [20] report a temperature underestimation of 200 K in the catalytic partial oxidation of methane to synthesis gas, due to the introduction of a constant effectiveness factor. In order to justify the use of a variable effectiveness factor along the axial position in the tubular reactor, simulation results with constant effectiveness factor are performed (see Figure 5). The same observations can be made as for Figure 4a. When the effectiveness factor is erroneously taken as unity, which corresponds to neglecting intraparticle diffusion resistance, the flow rate apparently needs to be higher or the reactor tube diameter or propane inlet molar fraction smaller, which is not the case. This leads to an incorrect design of the industrial reactor, and hence the latter is not optimally operated.

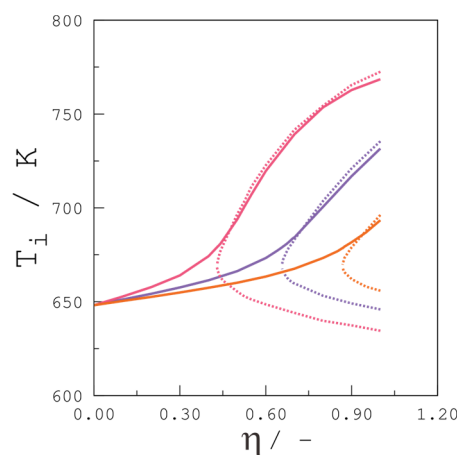


Figure 5. Temperature corresponding to the inflection point(s) in the reactor temperature vs. axial reactor coordinate profile, vs. effectiveness factor, obtained by integration of Equations (1) to (3). Full lines represent the inflection point after the maximum, whereas the dotted lines correspond to the inflection point(s) before the maximum. Base case conditions (see Table 1) are applied with variation of total inlet molar flow rate. (—) $F_{t,0} = 16.6 \text{ mol s}^{-1}$; (—) $F_{t,0} = 26.6 \text{ mol s}^{-1}$; (—) $F_{t,0} = 36.6 \text{ mol s}^{-1}$.

4.3.4. Reactor Temperature

Increasing the reactor temperature, T_r , has essentially the same effect on the propane conversion profile as is depicted for the increase of the propane inlet molar fraction (see Figure 6a,b). From the former, it can be observed that before a certain reactor temperature, only a single inflection point occurs after the hotspot. The same trend is observed as in Figure 4a, although the calculated lines, corresponding to the inflection point after the maximum, nearly coincide. Increasing the reactor temperature results in the presence of three inflection points in the temperature versus axial coordinate profile, and hence runaway behavior occurs. Based on the results in Figure 6b, the original curve, proposed by Barkelew [34], can be significantly transposed to lower N/S values. From a certain value of S, N/S increases very rapidly: a decreasing reactor temperature gives higher values for N and S (see Equations (25) and (26)), explaining the calculated lines in Figure 6b. The same conclusions as in the case of a variable propane inlet molar fraction hold (see Section 4.3.3).

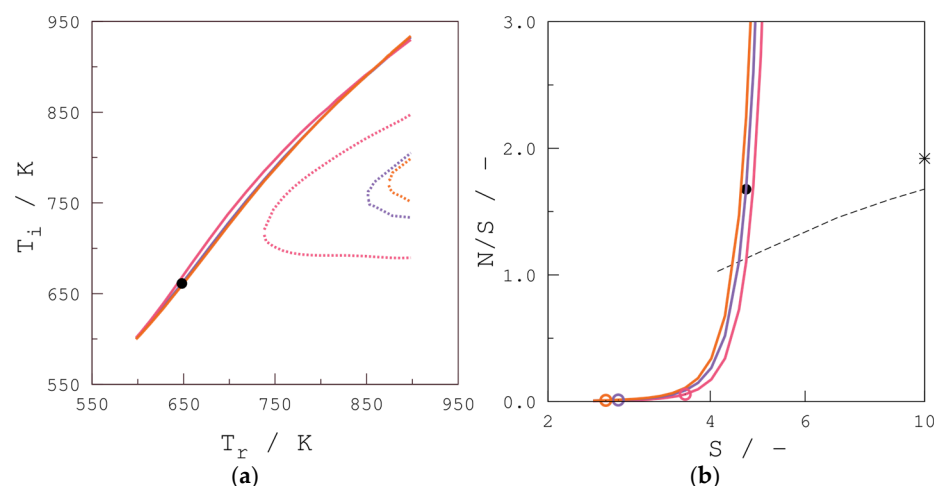


Figure 6. (a) Temperature corresponding to the inflection point(s) in the reactor temperature vs. axial reactor coordinate profile, vs. reactor temperature, obtained by integration of Equations (1) to (3). Full lines represent the inflection point after the maximum, whereas the dotted lines correspond to the inflection point(s) before the maximum. (b) Corresponding runaway diagram. Dashed line corresponds to the data given by Barkelew [3]. Base case conditions (see Table 1) are applied with variation of total inlet molar flow rate. (—) $F_{t,0} = 16.6 \text{ mol s}^{-1}$; (—) $F_{t,0} = 26.6 \text{ mol s}^{-1}$; (—) $F_{t,0} = 36.6 \text{ mol s}^{-1}$. (●) base case; (*) reference from Froment and Bischoff [3]; (o) ($S, N/S$) couples corresponding to the critical point, obtained from (a).

Higher reactor temperatures result in possible runaway, whereas lower temperatures will operate the reactor in a safe regime, but a longer reactor is needed in order to obtain the required conversion of propane.

4.3.5. Water Inlet Pressure

The average fractional coverages of propane, dissociatively chemisorbed oxygen, carbon dioxide, and water are simulated with the base case input data (see Table 1) obtained by the integration of Equations (1) to (3) and application of Equation (24), using Equations (18) to (23). From these results (see Figure 7), it was clear that a rather small fractional coverage of carbon dioxide is present on the catalyst, whereas water occupies the main part of the surface sites. Therefore, the effect of the water inlet molar fraction, going from 0.00 to $0.10 \text{ mol}_{\text{H}_2\text{O},0} \text{ mol}_{\text{t},0}^{-1}$ on the fractional coverages, is evaluated by means of plotting the average fractional coverages along the reactor axis for different values of $y_{\text{H}_2\text{O},0}$.

From Figure 7a,b, it is observed that the fractional coverages of propane and oxygen are halved for a water inlet molar fraction of $0.10 \text{ mol}_{\text{H}_2\text{O},0} \text{ mol}_{\text{t},0}^{-1}$ compared to the simulation results without water in the feed. The sum of the fractional coverage of both reactants is maximally 30% of the catalyst surface. Figure 7c,d give the fractional coverage of the reaction products. The carbon dioxide fractional coverage ranges from 15 to 5% for an increasing water inlet molar fraction. Due to the temperature, the conversion profile along the reactor, and the quasi-equilibrium adsorption for carbon dioxide (see Table 3), the curve goes through a minimum. This is less pronounced when the water inlet molar fraction increases. From Figure 7a–d, it is clear that the fractional coverages for propane, oxygen, and carbon dioxide significantly decrease as the water inlet molar fraction increases, which points to a strong adsorption of water onto the catalyst surface [17]. Again, for the same reason, a minimum in the average water fractional coverage is observed. Under typical industrial conditions (see Table 1), it is observed that along the tubular reactor, approximately half of the active catalyst surface is covered with water. For the average fractional coverage of hydroxyl species, the same conclusion holds as in the case of the

other reaction products (see Figure 7e). The average fractional coverage of the free active sites decreases from 35 to 10% for an increasing water inlet molar fraction (see Figure 7f).

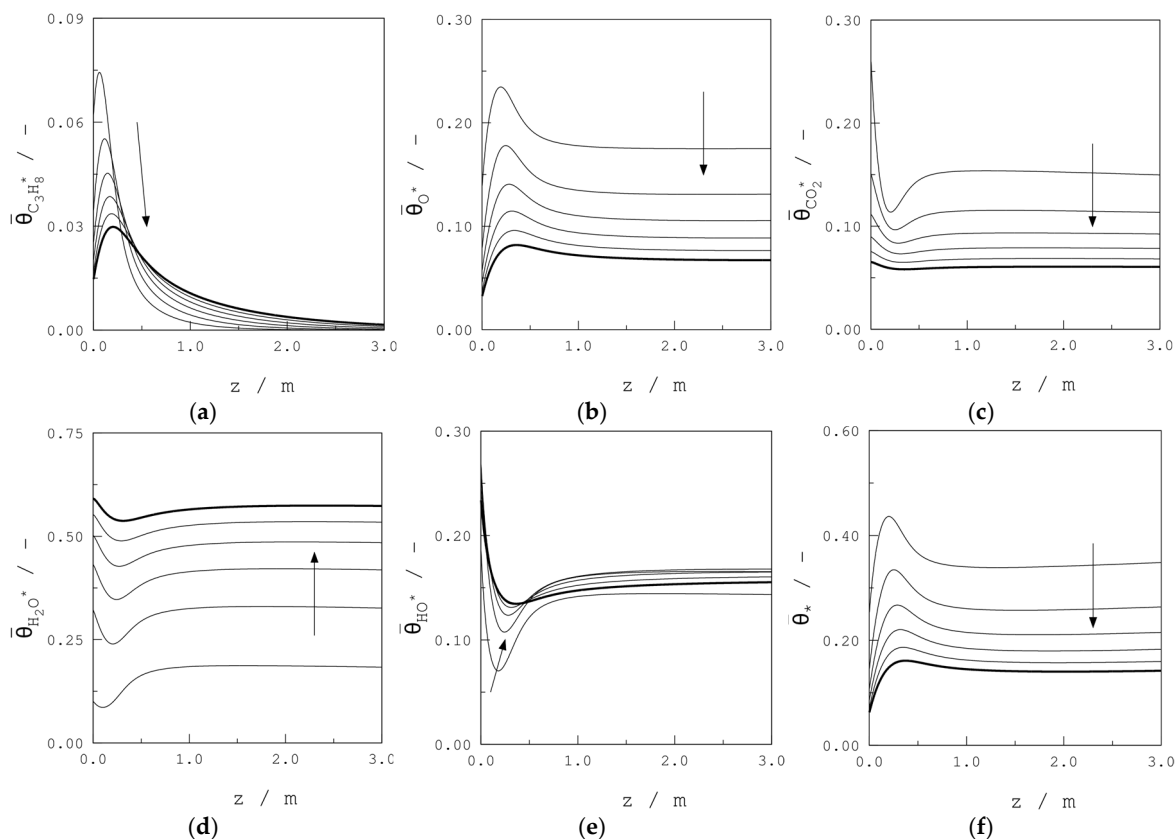


Figure 7. Average fractional coverages vs. axial reactor coordinate, obtained by integration of Equations (1) to (3) and application of Equation (24), using Equations (18) to (23): (a) propane; (b) oxygen; (c) carbon dioxide; (d) water; (e) hydroxyl species; (f) free active sites. Simulations are performed at base case conditions (—) (see Table 1), with an increasing, indicated by an arrow, water inlet molar fraction from $y_{\text{H}_2\text{O},0} = 0.00$ up to $0.10 \text{ mol}_{\text{H}_2\text{O},0} \text{ mol}_{\text{t},0}^{-1}$.

Full propane conversion should be obtained at the end of the reactor. Even with $0.10 \text{ mol}_{\text{H}_2\text{O},0} \text{ mol}_{\text{t},0}^{-1}$, an outlet propane concentration of 0.32 mg m^{-3} (see Section 4.2) is obtained. Nevertheless, it takes a higher reactor length to obtain an identical propane conversion than in the case where no water is present in the feed (see Figure 8).

The effect of the water and propane inlet molar fractions on the effectiveness factor is evaluated in Figure 9a,b. The former describes the effectiveness factor along the reactor axis for an increasing water inlet molar fraction. This factor increases as the water content increases, indicating that the presence of water weakens the effect of diffusion limitations on the reaction rate (see Section 2.1). In other words, with an increasing water content, the reaction rate will be slowed down, since the reaction rate expression contains an important water adsorption factor in the denominator [17]. As a consequence, the corresponding temperature rise will be less pronounced, giving rise to smaller diffusion effects, and this results in a smaller difference between the reaction inside the catalyst pellet and the reaction at surface conditions (while the actual reaction rate is slowed down).

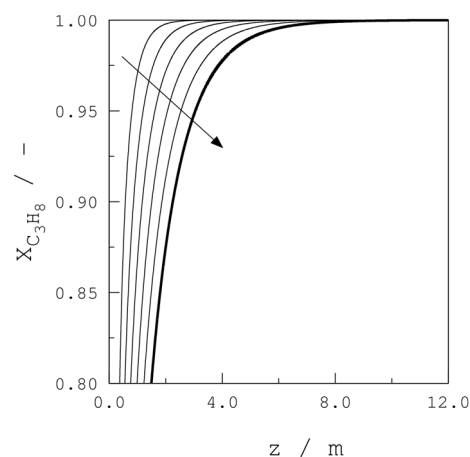


Figure 8. Propane conversion vs. axial reactor coordinate, obtained by integration of Equations (1) to (3) at base case conditions (see Table 1), with an increasing variation, indicated by an arrow, of the water inlet molar fraction, ranging from 0.00 up to $0.10 \text{ mol}_{\text{H}_2\text{O},0} \text{ mol}_{\text{t},0}^{-1}$. (—) base case condition.

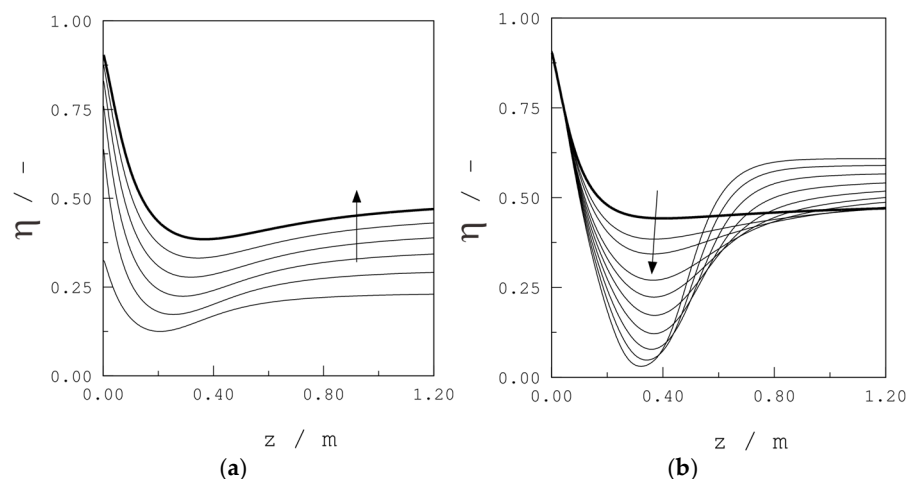


Figure 9. Effectiveness factor vs. axial reactor coordinate. Simulations are performed (a) for an increasing, indicated by an arrow, water inlet molar fraction ranging from 0.00 up to $0.10 \text{ mol}_{\text{H}_2\text{O},0} \text{ mol}_{\text{t},0}^{-1}$ and (b) for an increasing, indicated by an arrow, propane inlet molar fraction from 0.0017 up to $0.0127 \text{ mol}_{\text{C}_3\text{H}_{8,0}} \text{ mol}_{\text{t},0}^{-1}$ by integration of Equations (1) to (3) and application of Equations (8) and (9). The highest water inlet molar fraction and lowest propane inlet molar fraction of $0.0037 \text{ mol}_{\text{C}_3\text{H}_{8,0}} \text{ mol}_{\text{t},0}^{-1}$ correspond to the (—) base case condition (see Table 1).

Figure 9b shows that an increasing propane inlet molar fraction results in a steeper initial decrease of the effectiveness factor along the reactor axial coordinate. For the highest propane inlet molar fraction (i.e., $0.0127 \text{ mol}_{\text{C}_3\text{H}_{8,0}} \text{ mol}_{\text{t},0}^{-1}$), a very low value for the effectiveness factor of 0.03 is observed at a reactor length of 0.32 m. This is related to the hotspot temperature increase of 238 K.

5. Conclusions

A tubular reactor for total oxidation reaction under typical industrial conditions in the removal of volatile organic components (VOC) is described using a one-dimensional steady-state heterogeneous reactor model with propane as the model hydrocarbon compound using a fully developed Langmuir–Hinshelwood kinetic model. The effectiveness factor, accounting for intraparticle diffusion limitations, is calculated with a generalized Thiele modulus. The inclusion of this factor shows that higher operational reactor temperatures can be possible, since this diffusion limitation restricts the heat production inside the catalyst particle. Special attention is given to the outlet concentration of propane, taken as

the model VOC, and runaway criteria, reported in the literature, are critically evaluated. It appears that the criterion based on the data of Barkelew [34] is more severe than the criterion of Morbidelli and Varma [13], which states that runaway takes place when an inflection point occurs before the maximum reactor temperature. This might be verified for other reactions and reactor configurations. Furthermore, the Barkelew criterion is implemented for practical reactor design, as it can be applied for any nonlinear kinetics, and it was concluded that the critical couples populating the Barkelew diagram are positioned significantly lower (up to 50%, compared to Barkelew's original report), so operation of the reactor under higher hydrocarbon molar inlet fractions is possible while maintaining safe performance.

Author Contributions: P.M.H.: conceptualization, methodology, software, validation, formal analysis, investigation; data curation, writing—original draft preparation, writing—review and editing, visualization. J.W.T.: software, validation, resources, writing—review and editing, supervision, project administration, funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

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Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Using a Mitutoyo MIT-500-197 caliper, 1879 catalyst extrudate particles are measured for their diameter and height. The diameter is 1.86 mm, probably corresponding to the extrusion outlet opening. For the length, a range of values is measured (see Figure A1, which is a histogram constituted from 26 classes).

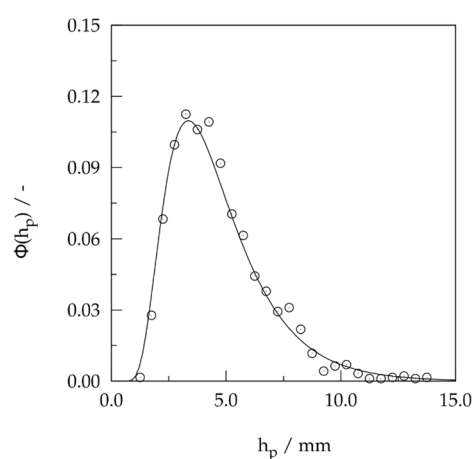


Figure A1. Probability distribution function $\Phi(h_p)$ (see Equation (A1) for the calculation of the average catalyst particle diameter).

With an inverse normal distribution (see Equation (A1)), an average catalyst particle height, equal to v , and the standard deviation, given by Equation (A2), are obtained. An average catalyst particle height of 4.67 ± 0.12 mm is obtained.

$$\Phi(x) = \sqrt{\frac{w}{2\pi x^3}} \exp\left[-\frac{w}{2x} \left(\frac{x-v}{v}\right)^2\right] \quad (\text{A1})$$

$$\sigma^2 = \frac{v^3}{w} \quad (\text{A2})$$

Given a cylindrical geometry with diameter d_p and height h_p , an average particle diameter, $\bar{d}$, of 2.33 ± 0.06 mm is calculated using Equation (A3):

$$\bar{d} = \frac{6V_p}{A_p} = \frac{6\frac{\pi}{4}d_p^2 h_p}{2\frac{\pi}{4}d_p^2 + \pi d_p h_p} = \frac{3dh_p}{d_p + 2h_p} \quad (\text{A3})$$

Appendix B

The bed and catalyst particle porosity, ε_b and ε_p , can be obtained from experimental bed length versus loaded mass (see Figure A2) by means of Equations (A4) and (A5). Details can be found in Heynderickx [50].

$$L_{b,in} = \frac{W_{in}}{\rho_{in}\Omega(1-\varepsilon_b)} \quad (\text{A4})$$

$$L_{b,cat} = \frac{W_{cat}}{\rho_{cat}\Omega(1-\varepsilon_b)(1-\varepsilon_p)} \quad (\text{A5})$$

The bed porosity is experimentally measured for several tube diameters ranging from 0.01 to 0.05 m (see Figure A2b). Commercial extrudate particles were used. The relation between the bed porosity and the tube diameter was found to be given by Equation (A6), with $R^2 = 0.9872$:

$$\varepsilon_b(d_t) = 0.52 - 1.39d_t \quad (\text{A6})$$

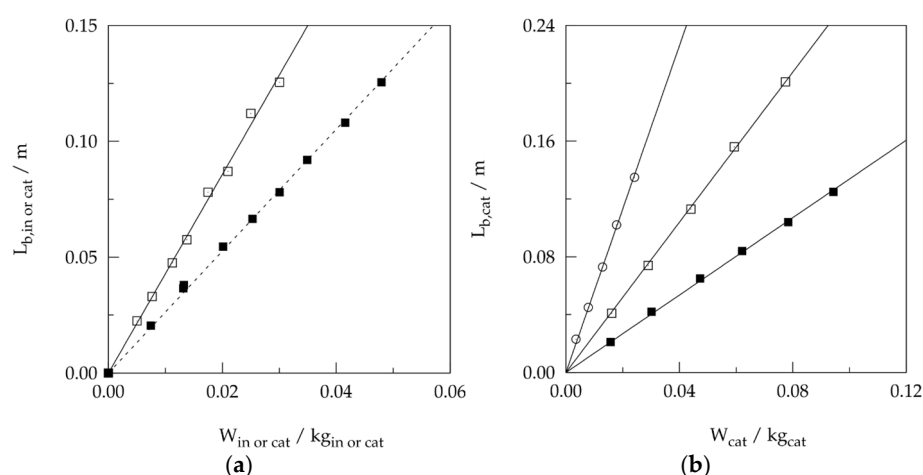


Figure A2. Experimental determination of catalyst bed porosity, ε_b , and catalyst particle porosity, ε_p . (a) ($\square$) Catalyst bed length and ($\blacksquare$) inert bed length vs. loaded mass for $d_t = 0.0143$ m and crushed extrudate catalyst particles in the range 400–500 μm . (b) Catalyst bed length vs. loaded mass of commercial extrudate catalyst particles for ($\circ$) $d_t = 0.0181$ m; ($\square$) $d_t = 0.0264$ m; and ($\blacksquare$) $d_t = 0.0364$ m. Dashed and full line are obtained by regression of the experimental data with Equation (A4) and (A5), respectively.

In the kinetic laboratory experiments with the given catalyst, the bed porosity is estimated at $0.41 \pm 0.01 \text{ m}_f^3 \text{ m}_r^{-3}$ for an average particle size between 400 and 500 μm [48,50]. Using Equation (A5) and the data from Figure A2a, a corresponding particle porosity, ε_p , of $0.62 \text{ m}_f^3 \text{ m}_p^{-3}$ is obtained.

Appendix C. Symbols and Annotations

Roman symbols		
a_s	specific external surface	$\text{m}_i^2 \text{ kg}_{\text{cat}}^{-1}$
$c_{p,f}$	specific heat	$\text{J mol}^{-1} \text{ K}^{-1}$
C_i	molar concentration of component i	mol m^{-3}
d	diameter	m
D_i	diffusion coefficient for component i	$\text{m}^2 \text{ s}^{-1}$
E_A	activation energy	kJ mol^{-1}
f	friction factor	-
F_i	molar flow rate of component i	mol s^{-1}
ΔH_i	adsorption enthalpy for component i	kJ mol^{-1}
$-\Delta_r H$	reaction enthalpy	kJ mol^{-1}
k	reaction coefficient	dep.
$k_{f,\text{C}_3\text{H}_8}$	mass transfer coefficient from gas to solid interface	$\text{m}_f^3 \text{ m}_i^{-2} \text{ s}^{-1}$
k^*	rate coefficient; see Equation (27)	$\text{mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$
K_j	adsorption equilibrium coefficient for component j	kPa^{-1}
L	reactor length	m
N	defined by Equation (26)	-
N_t	number of tubes	-
p	pressure	kPa
Pe'_a	Péclet number $\left(= \frac{u_i d_p}{D_{ea}} \right)$, based on particle diameter	-
Pr	Prandtl number $\left(= \frac{c_{p,f} \mu_f}{\lambda_f} \right)$	-
Δp	pressure drop	kPa
r	specific reaction rate	$\text{mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$
r_p	mean pore radius	m
R	universal gas constant	$\text{kJ mol}^{-1} \text{ K}^{-1}$
Re_p	Reynolds number $\left(= \frac{u_i d_p \rho_f}{\mu_f} \right)$, based on particle diameter	-
$R_{w,i}$	specific production rate of component i	$\text{mol kg}_{\text{cat}}^{-1} \text{ s}^{-1}$
S	defined by Equation (25)	-
S_c	Schmidt number $\left(= \frac{\mu_f}{\rho_f D_{\text{C}_3\text{H}_8,\text{m}}} \right)$	-
ΔS_i	adsorption entropy for component i	$\text{J mol}^{-1} \text{ K}^{-1}$
T	temperature	K
u	velocity	m s^{-1}
U	overall heat transfer coefficient	$\text{J m}^{-2} \text{ K}^{-1} \text{ s}^{-1}$
X	fractional conversion	mol mol^{-1}
z	axial coordinate	m
Greek symbols		
α	convective heat transfer coefficient	$\text{J m}_i^{-2} \text{ K}^{-1} \text{ s}^{-1}$
γ	dimensionless activation energy	-
ε	porosity	$\text{m}^3 \text{ m}^{-3}$
η	effectiveness factor	-

θ	fraction of active sites	-
ϑ^*	dimensionless temperature; see Equation (28)	-
λ	heat conductivity	$\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$
ρ	density	kg m^{-3}
τ	tortuosity	$\text{m}^{-2} \text{m}^{-2}$
φ	generalized Thiele modulus	-
Ω	cross section of reactor	m^2
Subscripts		
a	axial	
atm	atmospheric	
b	bed, bulk	
cat	catalyst	
diss	dissociation	
e	effective	
eq	equilibrium	
f	fluid	
h	heat transfer	
i	component i, interstitial, inflection point	
K	Knudsen	
m	molecular, mass transfer, mixture	
p	particle, pore	
r	reactor	
s	inside solid, superficial	
t	total, tube	
w	wall	
0	initial	
Superscripts		
obs	observed	
s	condition at external surface	
*	critical, reference, surface species	
-	averaged	
Abbreviations and acronyms		
LEL	lower explosion limit	
lhs	left hand side	
LH	Langmuir–Hinshelwood	
VOC	volatile organic component	

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