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Optimization Strategies in a Fixed-Bed Reactor for HCl Oxidation

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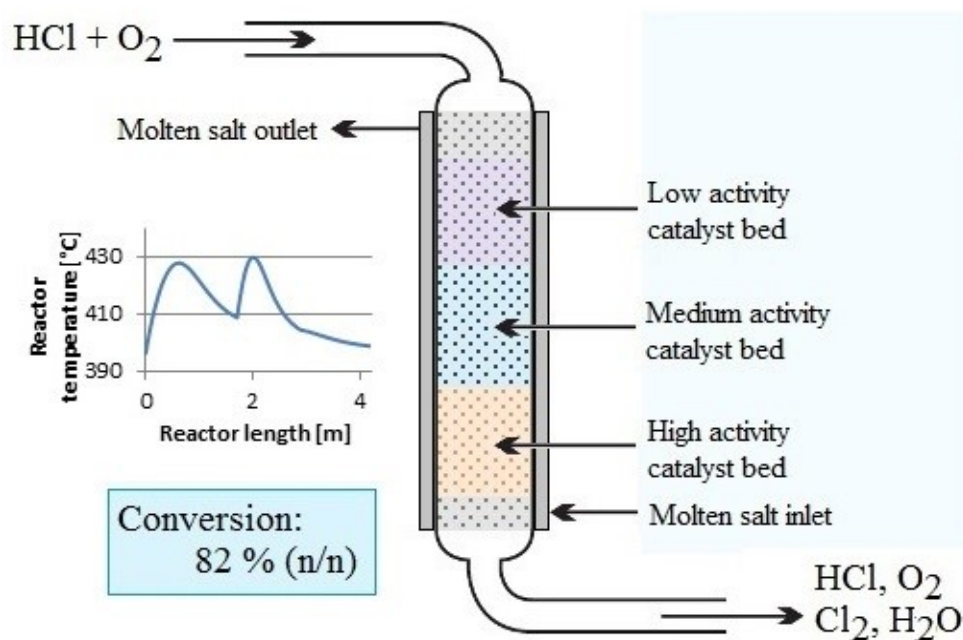
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[Supporting information](#)

Heterocatalytic oxidation of HCl into Cl₂ (HCl conversion process) over a CeO₂–CuO catalyst in a fixed-bed reactor has been optimized using four different objective functions and three different methods. For a given residence time, the HCl conversion could be maximized in various reactor configurations, namely with the application of a graded catalyst bed, with partitioning the reactor shell and using multistage temperature control, or with the combination of both methods. However, as the obtained temperature profiles differed considerably from each other, we considered three objective functions in order to smooth the reactor temperature profile. These implement a nonconventional approach since the proposed objective functions aim to deal directly with the temperature changes and HCl conversion is only taken into consideration as a nonlinear constraint. The different results from each method and objective function were compared using the apparent temperature gradients along the length of the reactor. The results show that reasonably low temperature gradients and a relatively smooth temperature profile can be achieved that also indirectly contributes to the stability of both the reactor and the catalyst.

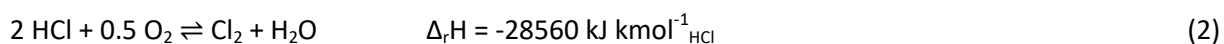


Introduction

Chlorine (Cl₂) is a widely used reactant in chemical industry. It is mostly produced via electrolysis of rock salt in the chloralkali process industrialized in the late 19th century.¹ The two main types of this process are the mercury cathode and the diaphragm cell technologies; the share of the first is decreasing due to the Minamata Convention on Mercury² with a deadline for decommissioning these plants by 2025. Another factor needs to be taken into consideration with regard to isocyanate production which mostly takes place according to³



The resulting byproduct HCl has to be processed or sold in form of hydrochloric acid solution. One of the methods of processing HCl is to convert it into Cl₂ and recycle it in the process (eq 2). With this chlorine supply it is possible to increase isocyanate production capacity while the volume of chlorine-based products (e.g., hydrochloric acid or PVC) remains the same, or, considering the same capacity, the mercury cathode electrolysis cells can be shut down without the necessity of replacing them by diaphragm cells.



Although this so-called Deacon process has been known for more than 140 years,⁴ its industrial application was long prevented by the lack of a suitable catalyst system. Deacon proposed the application of CuCl₂ as a catalyst, but copper chloride starts evaporating above 400 °C. This caused rapid catalyst deactivation as the operating temperature range was 430-475 °C.⁵ Shell Research B.V. introduced a CuCl₂-KCl/SiO₂ catalyst on a commercial scale, but eventually, it was abandoned due to low conversion rates and serious corrosion problems.⁶ The MT-Chlor process developed by Mitsui Chemicals uses Cr₂O₃/SiO₂ as catalyst that is apparently stable; nevertheless, there is significant chromium loss because of unstable intermediates forming under reaction conditions.⁷ More recently, Sumitomo Chemicals presented its solution for HCl conversion in 1995^{8,9} using a fixed-bed tubular reactor system with divided shell area using TiO₂-supported RuO₂ as a catalyst.¹⁰ Alternatively, Bayer Materialscience AG patented its own Ru-based Deacon catalyst with SnO₂ support.¹¹ Stability of the latter can be greatly improved using Al₂O₃ that prevents SnO₂ chlorination¹² and stabilizes the structure of the catalyst, thus preventing ruthenium sintering.¹³ Teschner et al. investigated mechanism and kinetics of HCl oxidation, reporting apparent activation energy as 69 kJ mol⁻¹,¹⁴ but the overall study focuses on mechanism of the reaction and includes only normalized reaction rates. It can be stated nevertheless that RuO₂/SnO₂ has an outstanding Deacon-performance and could be a flagship catalyst for HCl conversion. Another difference between the Sumitomo and Bayer processes is the reactor design, as the latter utilizes an adiabatic fixed bed reactor cascade with a much more simple design in contrast to the robust but more complicated multitubular reactor with partitioning from shell side suggested by Sumitomo Chemicals.¹⁵ In our work, the design methods of a reactor similar to the latter solution are considered.

Another sufficiently stable catalyst can be formed that is based on CeO₂, which is studied because of the rarity of ruthenium.¹⁶⁻¹⁸ Cerium is the most abundant of rare earth minerals (unlike the name of the group, it is actually not considered a rare element), and it is a frequently used catalyst material in oxidation reactions.¹⁹⁻²² While bulk CeO₂ is a promising catalyst for HCl oxidation, a variety of support materials have also been studied for both technological and economic reasons. Moser et al. tested various supported CeO₂ catalysts for gas-phase HCl oxidation, revealing that CeO₂/ZrO₂ is a long-term

stable and industrially relevant alternative of RuO₂, as the zirconia content reduced the apparent activation energy of the reaction considerably.²³ Further investigation of CeO₂/ZrO₂ catalysts in both HCl and HBr oxidation showed that a catalyst with a ceria-zirconia molar ratio of 1:3 has both higher activity and higher stability than bulk CeO₂.²⁴ The disadvantage of using cerium dioxide as catalyst is that the reaction takes place at higher temperatures than for RuO₂.²⁵ Another approach is to develop and apply a stable Cu-based catalyst (as the “original” one is CuCl₂).^{26,27}

In this paper, optimization of a fixed-bed reactor for HCl oxidation loaded with CeO₂/CuO catalyst is carried out. The catalytic activity of CeO₂ and CuO are in the same order;²⁸ moreover, the compound has been proven to be stable in long-term.^{16,29} Nevertheless, the suggested method can be applied in designing fixed-bed reactors regardless of the catalyst present, given that the detailed kinetic model for HCl conversion over the particular catalyst is available.

It is important to choose a suitable catalyst; nevertheless, the design of the conversion reactor has equal significance. If one remains at the shell and tube design proposed by Sumitomo, then there are multiple options to optimize the reactor construction and operation parameters. HCl conversion is mildly exothermic and has a maximal conversion as a function of temperature;³⁰ furthermore, as catalysts are, in general, sensitive to higher temperatures, maintaining an optimal temperature profile in the tubes is essential.

Luyben investigated the effect of catalyst dilution in tubular reactors using dynamic simulations and stated that with diluting the catalyst the dynamic controllability of the reactor improves significantly as it can handle lower heat transfer coefficients, and although the size of the reactor increases, this effect can easily justify the higher investment costs.³¹

With catalyst dilution, it is also possible to create an axial activity profile in a tubular reactor. This technique has been long known and used successfully.³² The primary benefit of this approach is the ability to mitigate the dynamic temperature rise caused by a fast exothermic reaction such as the oxychlorination of ethylene.³³ Nie et al. determined the optimal activity distribution using a model-based approach with nonlinear programming (NLP) for ortho-xylene oxidation. The objective function was the maximum of productivity; the addition of a second activity zone lead to a 26.4% increase, which was boosted by a further 6.6% with the addition of a third zone.³⁴ Moser et al. studied HBr oxidation to Br₂ (which is analogous to the reaction within the scope of this work) and implemented staged catalyst beds to overcome the problem of evolving hotspots due to the more exothermic nature of the reaction. Notably they suggested mixing of CeO₂/ZrO₂ and RuO₂/TiO₂ catalysts in one bed to benefit from the advantages of both catalyst systems.³⁵ At the inlet of the reactor tube, CeO₂/ZrO₂ was used as its lower activity and higher stability counteract the hotspot formation due to the exothermic nature of the reaction, while further on full HBr conversion can be achieved on the RuO₂/TiO₂ bed as it has a high catalyst activity.

A problem with the graded catalyst bed is that the activity decreases at different rates in each bed. This causes the reactor to become unbalanced over time. This effect has been observed for ruthenium-based catalysts.⁸ To achieve constant operation, the reactor shell can be divided to multiple zones so that the temperature in each bed can be controlled individually.

Despite the alternate ways to design the reactor and maintain its temperature under the maximum acceptable values, currently there is not any systematic optimization approach presented in the literature considering this particular topic. In this paper we propose a method that can be used for optimization of the HCl conversion process.

Chemical reactor design optimization problems have been successfully solved for numerous reaction systems. The objective function was, in general, the maximization of the amount of the desired

product(s). Shahrokhi and Baghmisheh investigated methanol synthesis in a fixed-bed reactor and optimized the reactor feed composition and shell temperature to maximize methanol conversion.³⁶ Cheong et al. reached the highest conversion and selectivity for 1,3-butadiene production in a dual fixed-bed reactor system with the systematic variation of inlet composition and reactor temperature.³⁷ Vakili and Eslamloueyan applied a more sophisticated objective function for dimethyl-ether (DME) production consisting of DME molar flow rate and various penalty parameters dealing with reactor temperature, pressure and minimal product flow rate.³⁸ Formation of hotspots is usually avoided by defining a constant temperature maximum. Investigations for methanol synthesis were carried out by Montebelli et al. including catalyst load, coolant temperature and tube diameter as well.³⁹

On the basis of our review of literature, it can be stated that a fixed-bed reactor is generally optimized for maximum conversion (and, if relevant, selectivity) and that the temperature of the reactor is only taken into consideration by applying upper bound or nonlinear constraints to it. However, the reactor ought to be designed so as to prevent thermal runaway. For cooled tubes, if inflection point appears before maximum temperature in function of conversion, then runaway will occur.⁴⁰ There are numerous criteria for reactor stability (e.g. generalized sensitivity criterion by Morbidelli and Varma,⁴¹ identifying nonstable steady-states,⁴² or relating it to reactor measurement,⁴³ among many others). These are not always sufficient to predict thermal runaway, as a low temperature gradient after the inflection point indicates that actual runaway is not observed in the reactor despite the criterion was fulfilled.⁴⁴ Temperature gradients are also important because high values may lead to local overheating on a microscale because of insufficient cooling. Moreover, if the same conversion and selectivity can be achieved while temperature gradient remains low at the same time (so there are more hotspots in the reactor but hot-spot temperatures are lower), then thermal deactivation of the catalyst will significantly slower.⁴⁵

Consequently, we use different methods to smooth reactor temperature profile and calculate temperature gradients while using them as an indicator to evaluate the performance of the various objective functions, while placing a nonlinear constraint to the conversion value. This could be particularly useful because conversion maximum can be reached by various reactor designs that can be distinguished based on the temperature profiles.

Reactor Model

Simulation of a single-tube reactor for HCl oxidation using CeO₂-CuO/Y catalyst was reported earlier by Chen et al.⁴⁶ The material, energy and momentum balance equations have been reported as follows:

$$\frac{dx_{HCl}}{dz} = a \frac{A\rho_B r_{HCl}}{F_{HCl,0}} \quad (3)$$

$$\frac{dT}{dz} = \frac{\rho_B(-\Delta_r H)r_{HCl} - 4\kappa(T - T_0)D_i/(D_i^2 - d_t^2)}{C_p(G/M_m)} \quad (4)$$

$$\frac{dp}{dz} = f \frac{\rho_g u^2 (1 - \varepsilon)}{d_p \varepsilon^3} \quad (5)$$

The reaction kinetics are reported by Tang et al.²⁹:

$$r_{HCl} = \eta \frac{85300 \exp(-82100/RT) (p_{HCl}^2 p_{O_2}^{0.5} - p_{Cl_2} p_{H_2O} / \sqrt{K/p_0})}{(1 + 3.65 \exp(966/RT) p_{HCl} + 1.854 \exp(238/RT) p_{O_2}^{0.5} + 4.79 \exp(2277/RT) p_{Cl_2})^3} \quad (6)$$

where K is the reaction equilibrium constant, expressed as follows:³⁰

$$\log K = \frac{5881.7}{T} - 0.93035 \cdot \log T + 1.37014 \cdot 10^{-4} T - 1.7584 \cdot 10^{-8} T^2 - 4.1744 \quad (7)$$

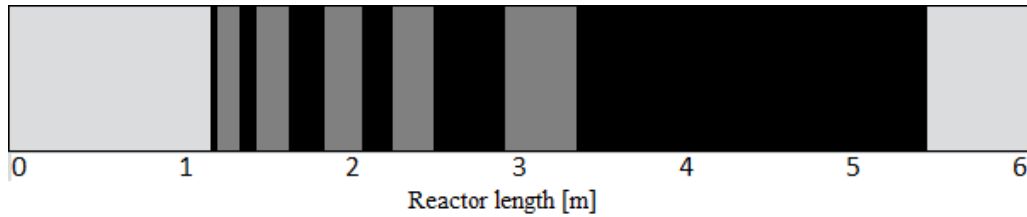


Figure 1. Original catalyst activity profile of the reactor. Light gray: zero activity (alumina spheres); dark gray: low activity (0.3); black: high activity (1).²⁴

Parameter values are available as part of Supporting Information. In their work mentioned above, Chen et al. measured the HCl oxidation process using a graded catalyst bed utilizing 11 stages (plus 2 inert sections as the top and the bottom of the reactor were filled with alumina spheres 1.2 and 0.6 m long, respectively). The catalyst activity of the stages alternated between values 1 and 0.3, as can be seen in Figure 1 on the overall activity profile of the reactor. The reactor also had a two-stage molten salt temperature control, set to 380 and 410 °C, respectively. With this reactor design they reached an HCl conversion value above 83% (n/n). It can be assumed that the catalyst activity profile was chosen in order to facilitate temperature control, avoid local overheating, and allow the system to cool back to a manageable temperature. In spite of these precautions, temperature gradients above 250 °C m⁻¹ can be observed in their work, while 11 catalyst stages can also be considered a high value. Therefore, the aim of this work is the systematic optimization of the reactor design and conversion process.

Optimization Strategy

On the basis of preliminary studies, here we formulate three different approaches of reactor design that are technically feasible. First, the reactor can be filled with catalyst layers with different activity, while the reactor remains undivided from the shell side with only one cooling circuit. Second, the reactor can be filled with only one layer of catalyst (with a defined activity), while the reactor shell side will be divided into multiple zones with different temperature stages each. Finally, the previous two methods can be combined so that each shell zone is coupled with a catalyst layer in the reactor with a certain activity and with a length equal to the length of the shell zone. These methods will further be called as methods A–C, respectively. The general number of catalyst layers (or cooling zones) N varied from 1 to 6 in our investigations; this has been proved sufficient as can be seen later. The 6 m reactor length and the lengths of the two inert sections were considered given values and therefore remained constant, leaving with 4.2 m of effective reactor length in the optimization problems solved.

The steady-state reactor model was implemented and solved in MATLAB R2011b. The reactor model was solved using the variable-step, variable-order (VSVO) solver based on the numerical differentiation formulas called ode15s.⁴⁷ For solving the optimization problem, the NOMAD software package was used that implements the Mesh Adaptive Direct Search (MADS) algorithm and is a well suited solver for derivative-free optimization.⁴⁸ It also has a MATLAB interface available that can be called directly from the OPTI Toolbox.⁴⁹

Maximizing HCl Conversion

In case 1, the objective function for optimization was to maximize HCl conversion in all three methods. The optimization problem is formalized as

$$\max(x_{HCl}(z = 4.2)) \quad (8)$$

One important process constraint was considered (i.e., the overall temperature maximum in the reactor (eq 9)). This coincides with previous studies investigating the performance of CuO-CeO₂ catalysts.^{16,25}

$$T_{max} \leq 437 \text{ }^\circ\text{C} \quad (9)$$

The degrees of freedom are the length and activity of each catalyst layer plus the temperature of the cooling zone (method A); the length and temperature of each shell zone plus the overall activity of the catalyst layer (method B); and finally, the length of zones, plus the temperature of the cooling zone and catalyst activity in each layer (method C).

The achievable conversion values as functions the number of zones in case 1 are located along a saturation curve as shown in Figure 2. (The saturation curve is drawn as a dashed line as these functions actually have discrete domains.) A plateau of 82.3% (n/n) emerges that means the reaction becomes controlled by the equilibrium conversion. Theoretically, lowering the reactor temperature would lead to higher conversion values; however, the resulting decrease in the reaction rate compensates for this effect. Therefore, it can be stated that the achieved conversion value is a practical maximum in this system.

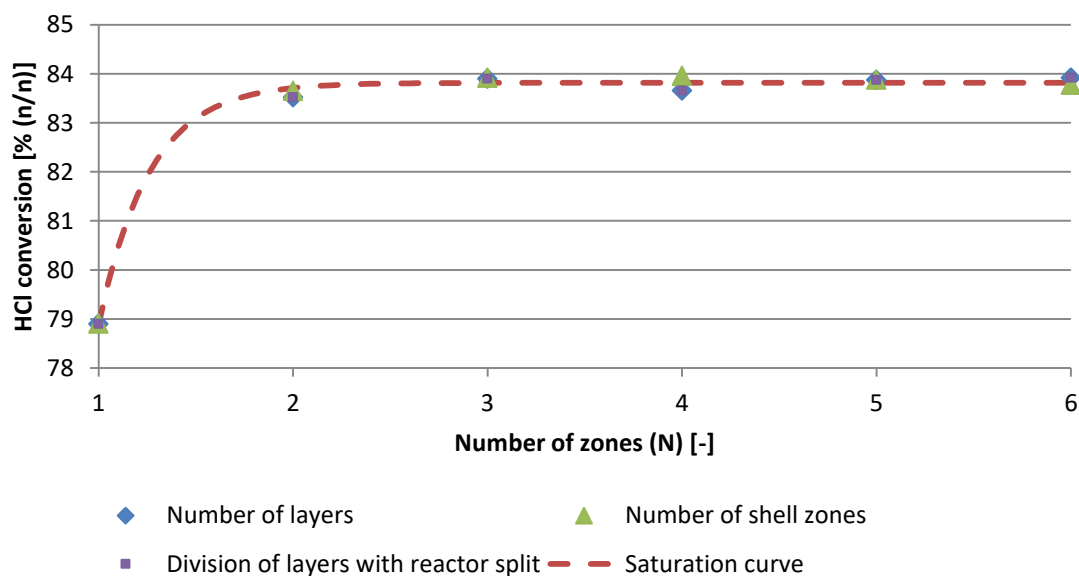


Figure 2. Maximum achievable HCl conversion in the reactor by dividing it to $N \in [1,6]$ zones.

Given that three zones are satisfactory to reach the desired conversion value, we compared the reactor temperature profiles for the solutions given by methods A–C. Figure 3 shows the temperature profiles for a three-zone reactor. It can be clearly seen that there is a difference between the results of each method. Method A has two local maxima in reactor temperature. That is actually a result of the fact that the last two catalyst zones have equal activity values (a numeric value of 1). More notably, the overall temperature change is around 40 °C, as opposed to those in the other two methods that have a difference 2-fold larger. Also, the temperature increases more rapidly along the first 0.5 m of the reactor, which could indicate the possibility of the formation of hotspots.

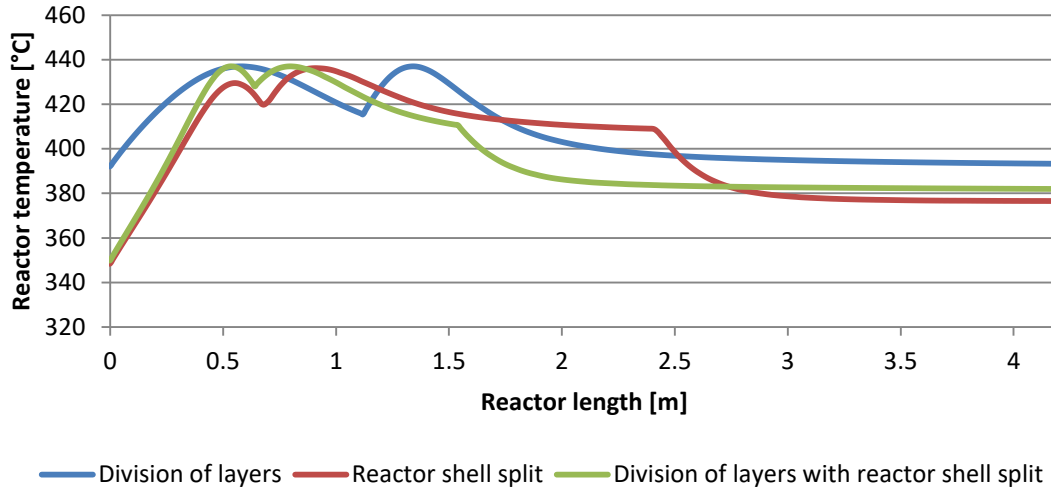


Figure 3. Temperature profiles of a three-zoned reactor optimized for maximum conversion.

Optimizing Reactor Temperature Profile

The previously described recognition leads to the wish to reformulate the objective function in order to better address the temperature changes occurring in the reactor. Our aim was to smooth the reactor temperature profile; hence, we constructed three objective functions (summarized in Table 1) that can be capable of addressing this problem.

Case 2: Reactor Temperature Maximum Minimization. If the maximum temperature is low, high temperature rises cannot occur in the reactor.

Case 3: Standard Temperature Maxima in Each Zone in the Reactor. If the difference between temperature maxima is low, this would indicate the smoothness of the temperature profile. Standard deviation was calculated from

$$std = \left(\frac{1}{n-1} \sum_{i=1}^n (T_i - \bar{T})^2 \right)^{\frac{1}{2}} \quad (10)$$

Case 4: A More Sophisticated Version of Case 3. Here the standard deviation of reactor temperature was taken as objective function. Temperature values were obtained at 0.01 m intervals the standard deviation of this set was calculated with eq 10. This case is an exception, as not only the effective reactor length but also the whole 6 m length was considered in the objective function.

Table 1. Developed objective functions for the optimization of reactor temperature profile

	case 2	case 3	case 4
Objective function	$Q = T_{max}$	$Q = std(\{T_{i,max}\})$ $i: \text{zone nr.}$	$Q = std(\{T_{z=z_n}\})$ $z_n = 0.01n$ $n = 0, 1, \dots 600$
Nonlinear constraint	$0.82 \leq x_{HCl} \leq 1$		

The minimized values of the objective functions for each case, including the three methods for reactor zoning described earlier, are available as part of Supporting Information. These values cannot be compared directly to each other for different cases as values of maximum temperature in case 2 are much higher than values of temperature deviations in cases 3 and 4; on the other hand all these cases were formulated to smooth the temperature profile. Therefore, that will be analyzed both qualitatively and quantitatively hereinafter.

For quantitative analysis, the results were elevated based on how rapidly the temperature changes in the reactor as a rapid increase may lead to the local overheating in the reactor as stated earlier. The differential quotient of the temperature and the reactor length was calculated on a 0.01 m basis to obtain the approximation of the temperature gradient:

$$\text{grad } T \approx \frac{\Delta T}{\Delta x} \quad (11)$$

The maximum gradients as well as the maximum temperatures for each case and method are listed in Table 2.

It would appear that not any of the three objective functions can be selected as the best one, as the minimum value for each method was obtained in different cases. This could indicate that the causation between temperature deviation and gradient is not as strong as was expected. There is a possibility of the existence of another objective function that is more suitable to address temperature changes in the reactor, leaving room for future improvements. The results from each case for a given method and number of zones are sometimes differ considerably. Because of the motive for designing the cases is the same, we decided to treat the 18 results per a given method as one group and selected the minimum value of temperature gradient maximum regardless of the case.

In general, the number of zones and the maximum temperature gradients are inversely proportional. This was expected as with higher number of zones the degrees of freedom of the system increase which in turn should lead to better temperature control. With the addition of another zone the trivial solution is to duplicate one zone from the previous solution, therefore the solution should be the same or better; nevertheless in some cases the gradients become higher with the addition of another zone. This comes presumably from the specific behavior of the NOMAD algorithm.

Table 2. Maximum values of temperature gradients in case of optimized temperature profiles in the reactor

	Number of layers	case 2		case 3		case 4	
		(grad T) _{max}	T _{max}	(grad T) _{max}	T _{max}	(grad T) _{max}	T _{max}
Division of layers (method A)	1	370.0	474.3	399.9	484.8	412.0	483.8
	2	177.7	450.3	149.6	429.9	174.9	432.7
	3	155.6	435.9	103.9	427.3	129.9	429.6
	4	173.3	448.0	<u>95.7</u>	<u>428.2</u>	124.9	429.2
	5	157.8	435.9	95.0	430.4	104.5	428.1
	6	133.5	424.1	99.5	426.5	106.5	430.0
Reactor shell split (method B)	1	369.7	474.2	369.7	474.2	383.8	474.9
	2	172.6	398.9	142.3	397.9	155.8	417.1
	3	137.7	395.0	137.1	395.4	151.5	412.2
	4	<u>133.0</u>	<u>392.4</u>	146.6	395.1	159.1	421.3
	5	132.8	393.4	227.6	402.5	154.8	415.9
	6	132.3	393.0	200.4	413.0	154.5	414.8
Division of layers with reactor split (method C)	1	370.3	474.4	393.6	479.3	392.7	478.8
	2	137.4	400.6	137.6	420.1	167.7	426.5
	3	<u>134.0</u>	<u>393.3</u>	142.4	429.9	121.5	419.3
	4	134.4	393.2	158.5	418.1	139.6	419.6
	5	133.1	396.1	155.1	415.8	131.2	427.6
	6	162.3	390.7	147.1	417.1	135.9	418.8

Apparently the lowest gradient values are obtained as a result in case 2 and method A. For only one zone in the reactor (that is, without a graded catalyst bed) the optimization algorithm is not effective since the only variable is the catalyst activity and there is a minimum value for HCl conversion is defined. Moreover, the maximum temperature exceeds the limitation. We compared the obtained temperature profiles from 2 to 6 zones (Figure 4.). For two layers of catalyst the temperature maximum and the slope as well drop drastically. The addition of a third layer further decreases the value of the maximum temperature gradient. Further increasing the number of search variables, the slopes become slightly more gently except for five layers where the temperature gradient maximum becomes higher again. The number of hot-spots is not equivalent with the number of layers. The reason behind that is that the activities of two catalyst layers are permitted to be the same, for example in case of five layers the activities of the first and second one are both around 0.15. As the maximum temperature gradients for 4, 5 and 6 layers are almost the same, it can be assumed that the minimum value can be reached with the introduction of four layers in the catalyst bed.

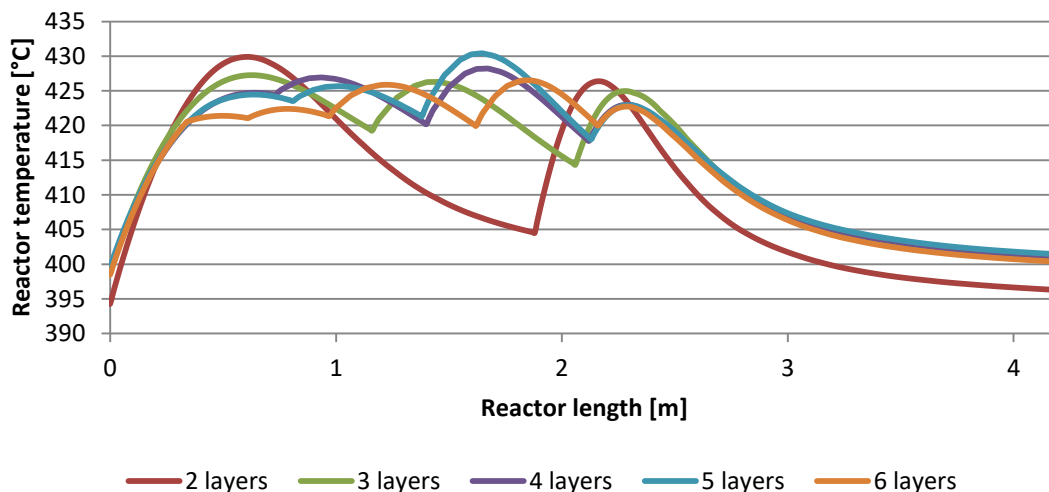


Figure 4. Reactor temperature profiles obtained by minimizing the standard deviation of the overall temperature profile of the reactor with zoning the catalyst bed.

For method A, the lowest temperature gradient was provided using the objective function in case 3; for method B and C, case 2 was the most successful. The possible best solutions were marked in Table 2. The respecting temperature profiles and temperature gradients are shown in Figure 5. In case of method B and C, the results show great similarities apart from that the temperature gradient towards the third maximum is lower for method B. For method A, gradients are significantly lower whereas the temperature itself is higher. As it was described previously, the CeO_2 -based catalysts are less sensitive to high temperatures (in the catalyst stability tests carried out by Tang et al. it was stated that there is no obvious change in activity at $430\text{ }^\circ\text{C}$ for 1200 h^{25}), in other words, this advantage has lesser priority. This implies that splitting the reactor shell is not necessary for temperature profile optimization in HCl conversion unless the catalyst activity decreases considerably during continuous operation. This scenario should be further investigated, e. g. with the application of dynamic simulators including catalyst deactivation model(s). Final values of optimization variables are summarized Table 3. This shows the reason behind the similarity of the temperature profiles for method B and C, as the catalyst activity does not actually change in method C, indicating that the effect of this variable has significantly less effect to the absolute value of the objective function than reactor shell temperature, as a result, the catalyst activity is only lower than 1 in case of method A, where the shell temperature has less impact. On this base, controlling reactor shell temperature for each zone seems to be more effective. Meanwhile it can be altered without shutting down the reactor and change the catalyst layers and deactivation of the catalyst can be compensated with the increase of the temperature for a given zone. In conclusion, while splitting the reactor shell is not necessary for temperature profile optimization in HCl conversion, it might be considered as it results a more flexible system.

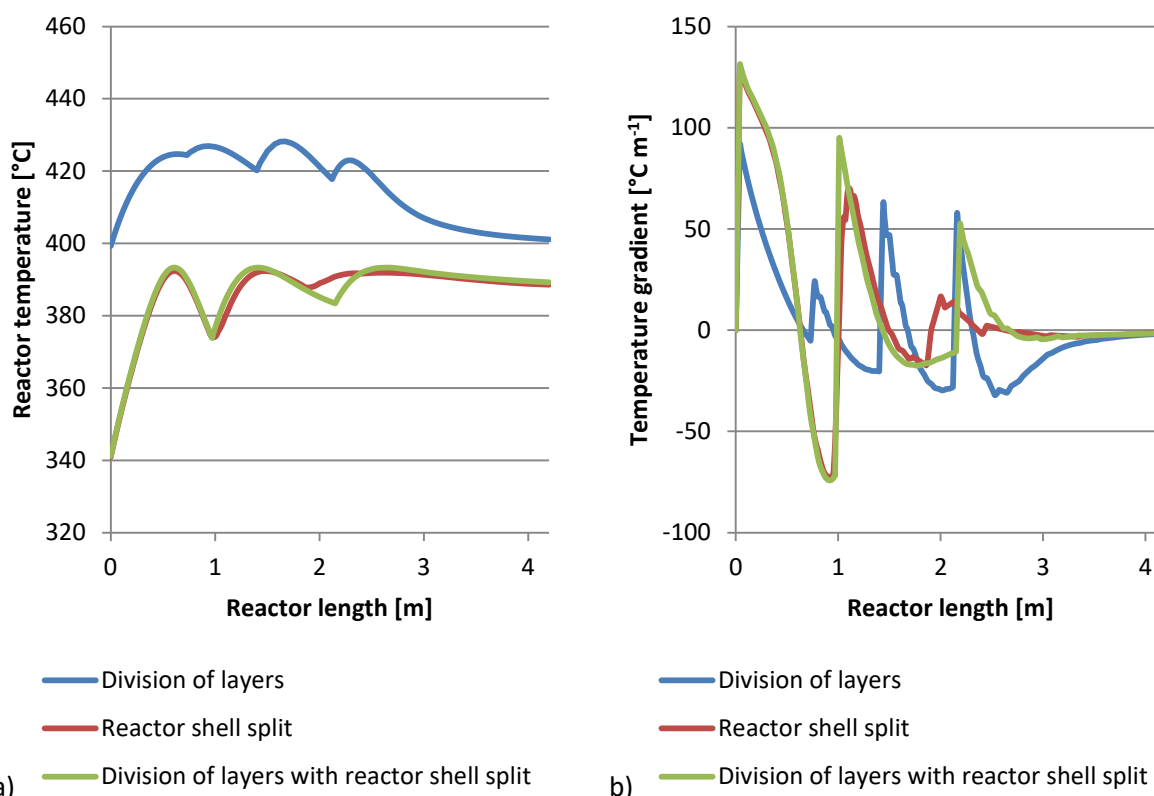


Figure 5. Temperature profiles (a) and gradients (b) of reactors resulting temperature profile optimization.

Table 3. Optimized reactor configuration of reactors resulting temperature profile optimization.

		Zone 1	Zone 2	Zone 3	Zone 4
Division of layers (case 3, method A)	Catalyst activity [-]	0.15	0.20	0.42	1
	Catalyst bed length [m]	0.73	0.67	0.72	2.08
	Shell temperature [°C]	399			
Reactor shell split (case 2, method B)	Catalyst activity [-] ^a	1			
	Shell zone length [m]	1.03	0.84	0.82	1.51
	Shell zone temperature [°C]	341	374	384	387
Division of layers with reactor split (case 2, method C)	Catalyst activity [-]	1	0.99	1	^{-b}
	Zone length [m]	0.97	1.18	2.05	^{-b}
	Shell zone temperature [°C]	341	374	387	^{-b}

^a not a degree of freedom

^b not present

Conclusions and Future Work

In this work, multiple optimization studies for the heterocatalytic oxidation of HCl into Cl₂ (the HCl conversion process) were carried out for a fixed-bed tubular reactor. Three different design methods were considered, the application of graded catalyst beds, multiple cooling zones, and finally, the coupling of the previous two into a generalized reactor zone. The number of zones (*N*) varied from 1

to 6 in our investigations. The results obtained by using the initial objective function for HCl conversion maximization have shown that while reaching the equilibrium conversion is possible, this method does not properly address the temperature changes occurring in the reactor. Hence three other objective functions have been implemented, and the results were evaluated using the axial temperature gradient of the reactor temperature as a main indicator. With this method, the temperature deviation can be reduced to a reasonably low level using four catalyst beds with different activities. While splitting of the reactor shell is not necessary, a more flexible system can be achieved with it as shell side temperature may be altered in continuous operation of the reactor. Future work may consider the dynamic behavior of the reactor, for example, the effect of depleting activity of the catalyst that could be different in each zone and, along with that, control strategies to maintain the determined temperature profile.

Supporting Information

The Supporting Information is available free of charge on the [ACS Publications](https://pubs.acs.org/doi/10.1021/acs.iecr.7b00750) website at DOI: [10.1021/acs.iecr.7b00750](https://pubs.acs.org/doi/10.1021/acs.iecr.7b00750).

Reactor model constants and variables; minimized values of objective functions for the optimization of reactor temperature profile ([PDF](#))

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Notes

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Nomenclature

A	reactor tube cross-section [m]
a	catalyst bed activity [-]
c_p	heat capacity of gas mixture [$\text{kJ kmol}^{-1} \text{K}^{-1}$]
D_i	reactor diameter [m]
d_p	average diameter of catalyst pellet [m]
d_t	thermowell diameter [m]
f	friction factor [-]
$F_{\text{HCl},0}$	HCl gas inlet [kmol s^{-1}]
G	overall mass flow rate in the reactor [$\text{kg m}^{-2} \text{s}^{-1}$]
$\Delta_r H$	enthalpy (heat) of reaction [kJ kmol^{-1}]
K	equilibrium constant [-]
M_m	average molecular weight of gas mixture [kg kmol^{-1}]
N	number of zones in the reactor [-]
n	sample size for standard deviation [-]

p	reactor pressure [kPa]
p_0	reference pressure [kPa]
$p_{HCl}, p_{O_2}, p_{Cl_2}, p_{H_2O}$	partial pressures of HCl, O ₂ , Cl ₂ and H ₂ O, respectively [kPa]
R	gas constant [kJ kmol ⁻¹ K ⁻¹]
r_{HCl}	reaction rate of HCl oxidation [kmol kg _{cat.} ⁻¹ s ⁻¹]
T	reactor temperature [K]
T_0	shell temperature [K]
u	linear gas velocity [m s ⁻¹]
X_{HCl}	molar HCl conversion [-]
z	reactor axial coordinate [m]

Greek letters:

ϵ	catalyst bed void fraction [-]
η	internal effectiveness factor of the shaped catalyst [-]
κ	overall heat transfer coefficient [kW m ⁻² K ⁻¹]
ρ_B	density of catalyst bed [kg m ⁻³]
ρ_g	gas density [kg m ⁻³]

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