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Reactive Distillation Column Design for Tetraethoxysilane (TEOS) Production. Part II: Dynamic Properties and Inherent Safety

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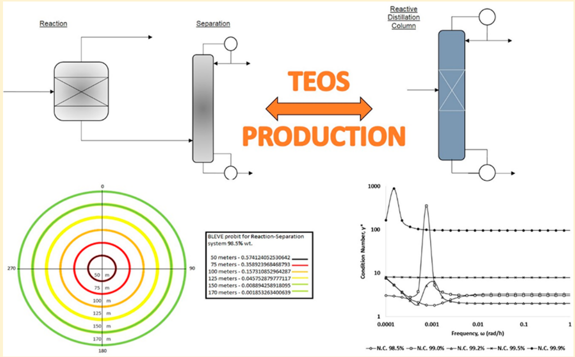
Supporting Information



ABSTRACT: Inherent safety and control properties of a reactive distillation column for the production of tetraethoxysilane are compared with those of a conventional process based in a reactor-distillation column. The preliminary design of the reactive distillation column and the analysis of total annual cost and environmental indicator were obtained previously [Sánchez-Ramírez et al. *Ind. Eng. Chem. Res.* **2018**, *57*, 5024−5034]. The control properties of the sequences considered were obtained by using the singular value decomposition technique and Nyquist criteria. A complementary closed-loop study using PI controller was carried out. The pairing of the variables in the control loops was carried out by the RGA technique. Process risk quantification was determined through hazard and operability study. The results indicate that reactive distillation columns seem a more appropriated technology for tetraethoxysilane production since its economic and control properties surpass those present by the conventional reaction separation process. Moreover, if the required purity for TEOS is between 98.5% and 99 wt % the profit of the process increases. Even though the inherent safe for the conventional process is slightly better, that difference is not high enough for comparative purposes.

1. INTRODUCTION

Tetraethoxysilane (TEOS) is an important chemical feedstock for a variety of ceramics, zeolites, and silica based organic−inorganic hybrid materials produced by using the sol−gel method. TEOS is also widely used to prepare protective silica films for electronic devices using chemical vapor deposition, spin coating, or other such techniques. On an industrial scale, TEOS is manufactured via esterification reaction of ethanol and silicon tetrachloride and alternatively from metallic silicon direct reaction between metallic silicon and alcohols.[1] Conventionally, the TEOS production is carried out by the esterification reaction of silicon tetrachloride ($SiCl_4$) with ethanol according to the XIX century report from Von Ebelman. The process involves two stages, reaction and a subsequent separation/purification stage by distillation.[2] The old route described by Von Ebelman is indeed still the most used for many reasons. The method is versatile enough to obtain a big family of alkoxysilanes because is possible to perform reactions not only using ethanol but other alcohols. Also, it is used to obtain several substituted organosilanes by partial substitution of the chlorine atoms. TEOS is only one of the important compounds that can be obtained through such a route.

An alternative technology from the 1990s, is the direct reaction of silicon and ethanol or methanol in high boiling solvents to obtain TEOS, $Si(OMe)_4$, as well $Si(OEt)_3H$ or $Si(OMe)_3H$. The route has been implemented at industrial level but is limited to the products described.[3]

In order to avoid the carbothermic process to produce silicon from quartz and the chlorosilane route, recently Laine et al.[4] reported that TEOS could be manufactured by means of the reaction of SiO_2 and diols. In such a report, biogenic SiO_2 from rice-hulls is the starting material. Previous reports to obtain TEOS are based on the reaction of calcium silicates with HCl−ethanol or the dehydration of SiO_2 with ethanol by azeotropic distillation with benzene.[5,6]

An important aspect to be considered in the esterification route is the generation of HCl (g) as byproduct, and an efficient method to remove it must be included in the process. A common method to remove HCl (g) is by sparging nitrogen gas through the reaction mixture. Depending on the reaction condition and the amount of present water, the esterification reaction may be oriented to produce either the monomer/partially hydrolyzed or

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prepolymerized versions of TEOS, all of them with specific applications.

According to experimental data, the esterification of tetrachlorosilane with ethanol proceeds through four consecutive stages of bimolecular nucleophilic substitution at silicon atom postulated by Sommer.[7] The reaction is described in four steps. The chemical reaction sequence is represented as follows:

$$\mathrm{SiCl_4 + C_2H_5OH \rightarrow Cl_3Si(OC_2H_5) + HCl(g)} \tag{1}$$

$$\mathrm{Cl_3Si(OC_2H_5) + C_2H_5OH \rightarrow Cl_2Si(OC_2H_5)_2 + HCl(g)} \tag{2}$$

$$\mathrm{Cl_2Si(OC_2H_5)_2 + C_2H_5OH \rightarrow ClSi(OC_2H_5)_3 + HCl(g)} \tag{3}$$

$$\mathrm{ClSi(OC_2H_5)_3 + C_2H_5OH \leftrightarrow Si(OC_2H_5)_4 + HCl(g)} \tag{4}$$

There is little information about novel technologies to produce TEOS, either improved current technology or proposed new approaches. Recently Sánchez-Ramírez et al.[8] suggested reactive distillation (RD) to produce TEOS as an intensified technology. In general, the concept of process intensification may overcome the traditional process, since it allows design technology with a reduction in equipment size, improvement in energy and mass transfer, and a reduction in capital cost. Therefore, that work approached the TEOS production by means of two systems, the conventional reaction including the product separation (reaction/separation) and a reactive distillation. In order to evaluate both ways to produce TEOS, the two systems were evaluated considering the total annual cost (TAC) and return of investment (ROI) as economic indexes, and the Eco-indicator 99 as an environmental index, all calculations were performed with the equations presented next.

$$\mathrm{TAC} = \frac{\text{capital costs}}{\text{payback period}} + \text{operating costs} \tag{5}$$

In general terms, the cost estimation of an industrial plant is calculated by separated units as the sum of the annualized capital cost and the operating cost. They considered a payback period of 5 years and a plant running 8500 h per year. Regarding EI99, the environmental impact was calculated as follow:

$$\mathrm{EI99} = \sum_{b}\sum_{d}\sum_{k\in K} \delta_d \omega_d \beta_b \alpha_{b,k} \tag{6}$$

where β_b represents the total amount of chemical b released per unit of reference flow due to direct emissions, $\alpha_{b,k}$ is the damage caused by category k per unit of chemical b released to the environment, ω_d is a weighting factor for damage in category d, and δ_d is the normalization factor for damage of category d.[9] In that case study, for eco-indicator 99 calculation, we considered the impact of three factors we assumed as the most important in this process: the steam (kg/year) used to produce heat duty, electricity (kW/year) for pumping, and steel (annualized) to build major equipment and accessories. Finally the ROI calculation was performed as follow:

$$\mathrm{ROI} = \frac{(\sum_{i=1}^{N} \mathrm{CF}_i)/N}{I} \tag{7}$$

where CF_i are the after taxes cash flow of period, I is the capital investment, and N is the number of years of the project.

As results, the reactive distillation showed better performance concerning TAC values; however, when purities above 99.5 wt % were obtained, the reaction/separation system overcomes the RD regarding ROI values. Moreover, when the environmental impact was measured, the RD showed a bigger impact near 30% in comparison with the reaction/separation system. This alternative provided energy savings, and the associated cost was reduced because in the conventional process the use of a reaction−separation system is required whereas the RD process only requires the use of a single vessel.

On the other hand, the reduction of process units can reduce in some way hazard to cause accidents related to fire, explosion, and toxic release. Minimizing inventories depicts an inherent safety strategy; this is also called process intensification. To simplify, substitution and moderation are other strategies that use inherent safety for hazard reduction or elimination. The simplification improves the process design, avoiding unnecessary complexity and reducing the opportunity to present errors.[10]

Regarding chemical process, either conventional or modified, in terms of new technology is imperative to know the involved health risk through the implementation of an inherent safety approach. Taking into account such a critical fact, it is required to have in mind the properties of the chemicals precursors ($\mathrm{SiCl_4}$ and ethanol), products, and subproducts (TEOS and HCl) in terms of the particular Hazard Rating Index of each substance (Health Hazard-Flammability Hazard-Reactivity Hazard and Protective Equipment) in order to evaluate on a scale from 4 to 0 (4 being extreme) the effect on risk due to intensification in the production process. Taking Hazard Rating Index (HRI) from a recognized leader and innovator in silicon compounds as is the case of Gelest Inc.,[11] $\mathrm{SiCl_4}$ has the HRI information on 3-0-2-X, meaning that, regarding Health Hazard, 3 refers to serious toxic (avoid inhalation and or contact skin), flammability hazard is 0 (minimal will not burn under normal conditions), the reactivity hazard is 2 (moderate, unstable react with water), and X means always the use of protective equipment in accordance with instructions (a complementary index is required for chlorosilanes because of hydrolytic sensitivity) where the scale is from 0 to 10. SiCl4 has an 8 (very fast reaction with moisture, water, and protic solvents, requiring working under an inert atmosphere of nitrogen or argon).

The main product, TEOS has a HRI of 2-2-1-X, meaning a health hazard of 2 (moderate toxic, may be harmful if inhaled or absorbed), a flammability hazard of 2 [moderate, combustible, requires moderate heat to ignite; flash point from 100 °F (37 °C) to 200 °F (93 °C)], and a reactivity hazard of 1 (slight, may react if heated or mixed with water). Finally, the HRI information for ethanol is 2-3-0-X, and it is 3-0-0-X for HCl.

The importance of considering sustainability issues early in the design of the intensified process can help to differentiate between processes that are easy and process that are difficult to operate. According to Jiménez-González et al.,[12] we should be consider incorporating "green metrics" when designing an intensified process toward the broader goal of environmental sustainability. Among those green metrics should be highlighted the aspects of environmental, health, safety, and process control. Green Chemistry Principle #11 expresses a desire to have real-time process analysis and monitoring in place. The aim of this principle is simple enough: to prevent waste and safety issues by identifying process excursions as they occur. By doing so, there may be sufficient time to modify process parameters such that the excursion may be reversed and there is no subsequent impact on safety and the final product quality. Real time analysis and process control are necessary to carry out this action. In the same

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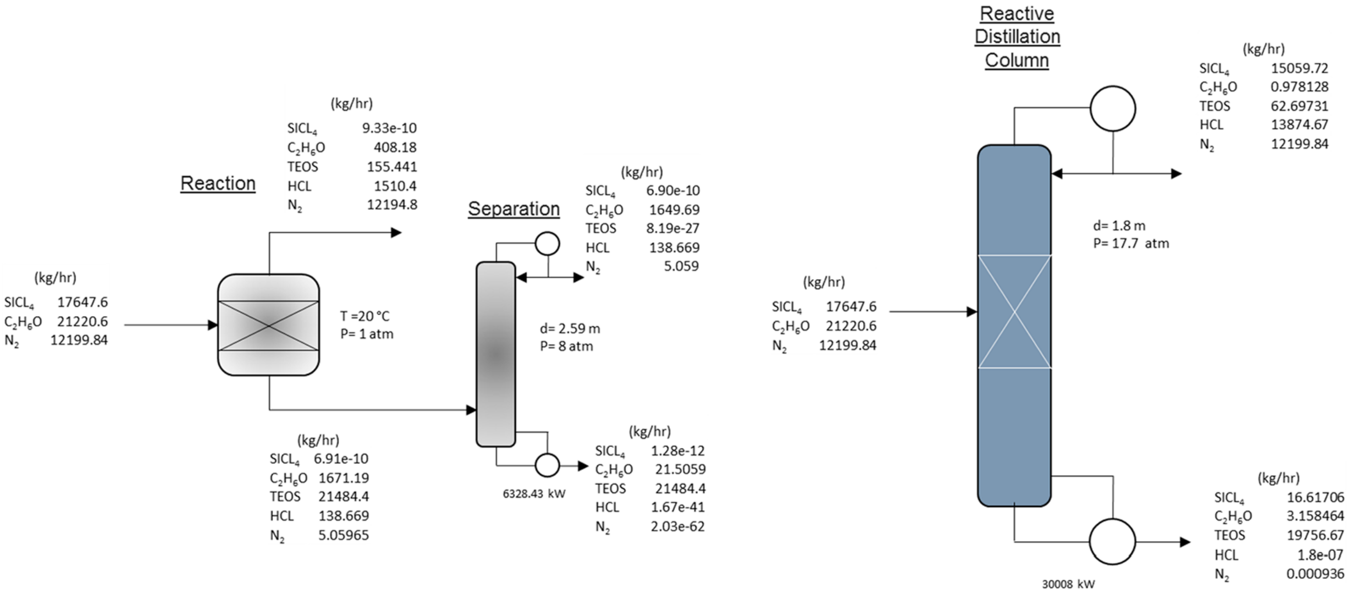

Figure 1. Reactive distillation process and reactor/column process.

sense, the processes intensification of processes, associated with the reduction of the number of equipment and change in the system topology of the system, can also modify control properties and dynamic performance compared to non-intensified systems.[13] Contrary to the conventional distillation process, the dynamic of the reactive distillation columns for TEOS production has not been explored in the published literature. As far as the authors are aware this is the first work that tries to carry out a study of the inherent safety and control properties, open loop and closed loop, for a reactive distillation column for the production of TEOS (Figure 1), based on the designs previously proposed by Sánchez-Ramirez et al.,[8] and comparing this results with those obtained for the conventional system reaction/separation for TEOS production (Figure 1). The work attempts to bridge the gap between process design and control and inherent safety in the case of TEOS production using reactive distillation and generate green processes according to the metrics proposed by Jiménez-González et al.[12] where control and safety are indispensable in the evaluation of sustainable processes.

2. CASE STUDY

Initially, in order to carry out either a reactive distillation system or conventional reactor/separation system, it was defined as a feed stream of 1000 kmol/h and the following composition (fraction mol): $SiCl_4$, 18.3873; C_2H_6O, 38.0628; N_2, 43.5499; temperature, 50 °C; pressure, 1 atm, as reported in Sánchez-Ramirez et al.[8] The method used to remove HCl(g) by stripping considers in the feed stream the addition of nitrogen in the reaction mixture. Moreover, current application of TEOS covers a wide range of purities, and because of this, it was considered a set of TEOS purities for both systems, 98.5, 99.0, 99.2, 99.5, and 99.9 wt %, respectively, setting as purity constraints those values as final TEOS purity. In agreement with the limited studies regarding the kinetic experimental studies of the esterification reaction of $SiCl_4$ with ethanol, the reaction sequence previously showed [reactions (1), (2) and (3)] are considered as virtually irreversible, while the equilibrium is established at the last stage of esterification.[14] The approach of this proposal is the study of the reaction at equilibrium. Note, for this approach the reaction rates of the forward and backward reactions are generally not zero but equal. Thus, there are no net changes in the concentrations of the reactant(s) and product(s). The flowchart methodology for both reaction/separation and reactive distillation design is shown in Figure 2. Tables 1 and 2 show the results for both scenarios. As results, the reactive distillation showed that, when purities above 99.5 wt % were obtained, the reaction/separation system overcomes the RD regarding ROI values. Besides, the environmental impact of the RD showed a bigger impact near 30% in comparison with the reaction/separation system. In the previous paper, the authors have concluded that the reason for such results is the nature of the economic index. TAC calculation only considers the annualized

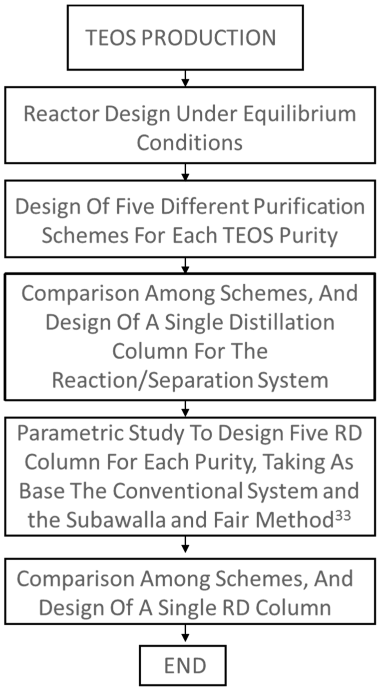

Figure 2. Flowchart for both reaction/separation and RD design.

Table 1. Reaction/Separation Topology

mass purity (wt %)	98.5	99	99.2	99.5	99.7	99.9
stages	47					
feed stage	19					
condenser	total					
reboiler	kettle					
	design specifications					
reflux ratio [mole]	5					
bottoms rate [kg/h]	21811.58	21701.43	21657.67	21592.37	21549.06	21505.92
reboiler duty [kW]	5666.762	5896.886	5990.573	6133.086	6229.955	6328.427
pressure [atm]	8					
column pressure drop [psia]	10					
TAC [$/y]	4.32×10^{06}	4.50×10^{06}	4.57×10^{06}	4.67×10^{06}	4.75×10^{06}	4.82×10^{06}
ROI [%]	51.482	51.096	50.209	49.67	48.14	45.759
ECO 99 [Pt/y]	1.51×10^{06}	1.52×10^{06}	1.53×10^{06}	1.53×10^{06}	1.53×10^{06}	1.54×10^{06}

Table 2. Reactive Distillation Column Topology

mass purity (wt %)	98.5	99	99.2	99.5	99.7	99.9	
stages	15						
feed stage	13						
condenser	total						
reboiler	kettle						
design specifications							
reflux ratio	1.293	1.485	1.598	1.976	2.658		5.685
reboiler duty [kW]	8367.339	9146.098	9713.657	11660.86	14998.972		30008.12
pressure [atm]	17.76						
pressure drop [psia]	10						
reaction stages							
start stage	final stage						
3	10						
holdup							
start stage	final stage		vol. [cum]				
3	10		0.2				
TAC [$/y]	4.52×10^{05}	4.00×10^{05}	4.19×10^{05}		5.80×10^{05}	7.54×10^{05}	2.06×10^{06}
ROI [%]	52.382	59.29	56.59		56.03	40.737	11.41
ECO 99 [Pt/y]	2.14×10^{06}	2.14×10^{06}	2.15×10^{06}		2.15×10^{06}	2.15×10^{06}	2.15×10^{06}

capital cost and the annual cost of services. However, this economic index does not consider any other economic income or spending. On the other hand, ROI calculation includes several costs like investment, expenses related with total investment (both main and auxiliary equipment), operative cost, and annual sales. Note the income by sales is associated with the productivity of the process and recall that the reaction/separation system showed higher productivity than RD system. Under this scenario, the reason for that crossing in ROI is that RD system shows high operative cost at high purities, and consequently the ROI value decrease. On the other hand, the productivity and sales are high enough for the reactor/separation system to overcome the RD system at high purity. More details for the methodology design and results of the configurations can be found in Sánchez-Ramirez et al.[8]

3. PROCESS RISK QUANTIFICATION

As has been told, a previous study for TEOS production was carried out focused mostly on both the economic and environmental issues, which nowadays are critical issues. However, current political and social demands lead us to accomplish a wider perspective.

With this in mind, this work carries out the risk quantification by means of the individual risk (IR). The individual risk is defined as the risk that a person has based on its position, involving this risk of a damage as injury or death caused by an accident which has certain frequency occurrence and a likelihood of affectation. Mathematically the individual risk is defined as the multiplication of the frequency of the accident (f_i) and the probability of affectation in a specific position ($P_{x,y}$) according to

$$\mathrm{IR} = \sum f_i P_{x,y} \tag{8}$$

The frequencies and the probability of affectation can be determinate through a quantitative risk analysis (QRA) which is a useful tool that allows us to identify the potential of both incidents and accidents and evaluate their respective consequences and damages. The first step of QRA is the identification of possible incidents. An incident is the release of matter/energy from the process,[15] and for distillation columns there are two potential incidents: a continuous release which is the leak of matter from process equipment due to a rupture in a pipeline and the second incident is the instantaneous release that consists in the total loss of matter from the process equipment originated by a catastrophic rupture of the vessel. Those incidents were determined through a hazard and operability study (HAZOP). This procedure is relatively effective in identifying risks and is quite well accepted in the chemical industry. The methodology consists of systematically

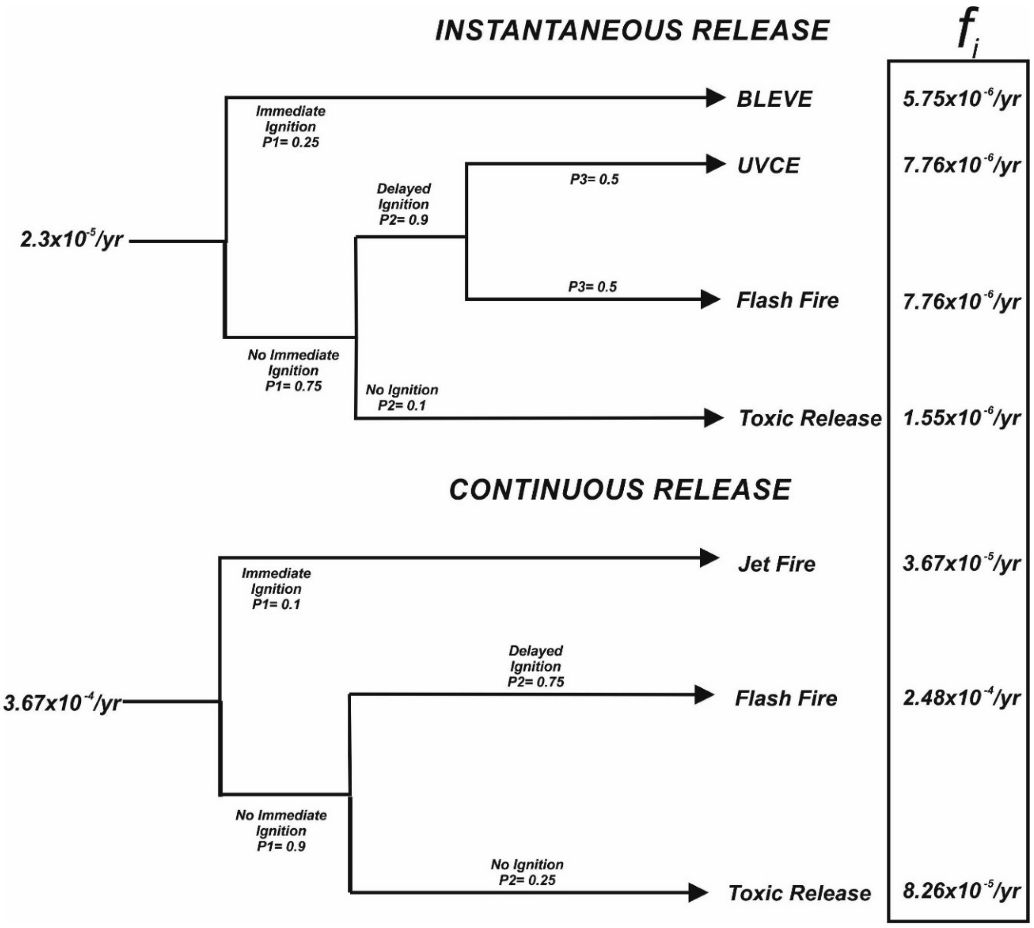

Figure 3. Events trees diagrams for distillation columns.

analyzing the reasons and consequences that may cause deviations in the operating conditions. Subsequently, as a result of said deviation, the process can lead to an accident. More information can be obtained from the work reported by the AICHE[15] and De Haag.[18]

As results of HAZOP analysis is obtained an event tree. The event tree is a logical diagram of success or failure in the combination of events used to identify accident sequences that lead to all of the possible consequences of a given initial event. The method is indeed inductive and provides information on how a failure can ocurr and the probability of occurrence. Figure 3 shows the events trees of possible accidents and their respective frequencies (f_i). The frequencies were taken according to the proposed values by the American Institute of Chemical Engineers,[15] and it may work for the main equipment the chemical industry. As can be appreciated on an events tree, the possible accidents for instantaneous release are boiling liquid expanding vapor explosion (BLEVE), unconfined vapor cloud explosion (UVCE), flash fire, and toxic release, while those that are continuous are identified as potential accidents jet fire, flash fire, and toxic release.

When the likely accidents have been identified, the next step is the identification of the causative variable that cause the injuries or death for each accident. For fires like BLEVE, jet fire, flash fire the causative variable is the thermal radiation (E_r) that receive a person, the overpressure (p^o) is the main reason of deaths by UVCE, while in toxic release the causative variable is the concentration (C). The calculations of causative variables to each accident have been shown previously by many authors.[16,17] In this work was considered a distance of 50 m for calculating all causative variables, and this distance was fixed because all accidents considered in Figure 3 have important consequences. Additionally a very interesting calculation is performed, and this approach allows to calculate the correct distance to diminish the probability of death to zero. The calculation of the causative variable starts with the determination of the amount of material released.

3.1. Probability of Affectation (Consequences Analysis). Minimizing inventories depicts an inherent safety strategy; this is also called process intensification. When the causative variables have been calculated, the next step is to determine the probability of affectation (probability of injury or death) which can be found by a consequence assessment using probit models. A probit model is an equation that relates the response of the affected person (probability of injury or decease) with the dose received of a certain exposure like heat, pressure, or radiation. In this work, probit function models of the probability of death due to overpressure and third-degree burns are considered.[15,17,18] The parameters for eq 9 are shown in Table 3. The probability of damage is obtained by replacing probit values in eq 10.[18]

$$Y = k_1 + k_2 \ln V \tag{9}$$

$$P_{x,y} = 0.5\left[1 + \mathrm{erf}\left(\frac{Y-5}{\sqrt{2}}\right)\right] \tag{10}$$

Table 3. Probit Parameters

	K_1	K_2	V
thermal radiation	−14.9	2.56	$\left(\frac{t_e E_r^{4/3}}{10^4}\right)$
overpressure	−77.1	6.91	p°

Finally, the result obtained by eq 10 is replaced inside eq 8 to obtain the individual risk (IR).

4. CONTROL BEHAVIOR ANALYSIS

Reactive distillation columns present challenging control problems. They are highly multivariable and usually quite nonlinear. They have many constraints and are subject to many disturbances. Therefore, their control is not a trivial task. In the context of process control, the degrees of freedom of a process is the number of variables that can or must be controlled. It is always useful to be clear about what this number is for any process so that you do not attempt to over- or undercontrol any process. A well-known option for degrees of freedom in distillation columns is based on energy balance considerations in which the reflux flow rate L and the vapor boilup rate V (affected directly by the heat duty supplied to the reboiler) are used to manipulate the distillate and bottom outputs compositions, as control variables (see for instance Häggblom and Waller[19]).

For this work, the controllability analysis was conducted in two parts. The theoretical control properties of the schemes were first predicted through the use of the singular value decomposition (SVD) technique and then a RGA (relative gain array) study, Nyquist stability analysis, and closed-loop dynamic simulations were conducted to analyze the control behavior of each system and to compare those results with the theoretical predictions provided by SVD.

4.1. Singular Value Decomposition. The application of the SVD technique provides a measure of the controllability properties of a given dynamic system. More than a quantitative measure, SVD should provide a suitable basis for the comparison of the theoretical control properties among the thermally coupled sequences under consideration. To prepare the information needed for such a test and because the approach of this proposal is the study of the reaction at equilibrium, the methodology proposed by Cabrera-Ruiz et al.[20] was used for the construction of the transfer function matrix. By simplifying the process dynamic to only first-order responses, it is possible to assess the controllability of sequences by using only steady state information. Cabrera-Ruiz et al.[20] have effectively demonstrated the usefulness of their proposed approach to calculate the time constant in complex and intensified configurations. Based on their approach, τ can be obtained from perturbing the steady state in which it is established:

$$\tau_c = \frac{\sum_{i=1}^{N+1} M_{if}\Delta x_i}{\Delta S_i} \tag{11}$$

$$\Delta S_i \overset{\text{def}}{\cong} D_f \Delta y_D + B_f \Delta x_B \tag{12}$$

where ΔS_i is the supply imbalance, M_{if} is the holdup inside the column for each stage i, Δx_i is the change of liquid composition of any component on a stage i, D_f is distillation flux, Δy_D is the composition change in distillate, B_f is the bottom flux, and Δx_B is the change of bottoms composition. All of the data of solving eqs 11 and 12 can readily be obtained from Aspen Plus regardless of the number of components in a mixture. In addition, the set point of the controlled variables was perturbed to obtain the transfer function matrix. Thus, it is possible to perform a control analysis at open loop. A transfer function matrix relating the product compositions to the intended manipulated variables was then constructed for each case. The transfer function matrix can be subjected to SVD:

$$G = V\Sigma W^H \tag{13}$$

where $\Sigma = \text{diag}(\sigma_1, ..., \sigma_n)$, σ_I = singular value of $G = \lambda_i^{1/2}(GG^H)$; $V = (V_1, V_2, ...)$ matrix of left singular vectors, and $W = (w_1, w_2, ...)$ matrix of right singular vectors. Two parameters of interest are the minimum singular value, σ_*, and the ratio of maximum to minimum singular values or condition number:

$$\gamma^* = \sigma^*/\sigma_* \tag{14}$$

The minimum singular value is a measure of the invertibility of the system and therefore represents a measure of the potential problems of the system under feedback control. The condition number reflects the sensitivity of the system under uncertainties in process parameters and modeling errors. These parameters provide a qualitative assessment of the dynamic properties of a given design. The objective is to identify the systems with higher minimum singular values and lower condition numbers; those systems are expected to show the best dynamic performance under feedback control. A nice feature of the SVD test is that it is independent of the type of controller to be implemented; the basic idea is that the controllability properties of the system are instead limited or imposed by its inner dynamic structure. The full application of the SVD method should consider a range of frequencies sufficiently high to give a complete coverage on the behavior of minimum singular values and conditions numbers, as shown by Hernández and Jiménez[21] and by Jiménez et al.[22]

4.2. Relative Gain Array (GA). The RGA of a nonsingular square complex matrix G is a square complex matrix defined as

$$\text{RGA}(G) = G(G^{-1})^T \tag{15}$$

where * denotes element-by-element multiplication (the Hadamard or Schur product).

The RGA provides a measure of interactions. Let u_j and y_i denote a particular input−output pair for the multivariable plant $G(s)$ and assume that task is to use u_j to control y_i. Skogestad and Postlethwaite[23] argued that there will be two extreme cases: (a) all other loops open: $u_k = 0, \forall k \neq j$, and (b) all other loops closed with perfect control: $y_k = 0$, $\forall k \neq i$. Perfect control is only possible at steady-state, but it is a good approximation at frequencies within the bandwidth of each loop. It is argued that the ratio between the gains (λ_{ij}) is a useful measure of interactions. Intuitively, for decentralized control, it is preferred to pair variables u_j and y_i so that λ_{ij} is close to 1 at all frequencies, because this means that the gain from u_j to y_i is unaffected by closing the other loops.

4.3. Nyquist Stability Analysis. The Nyquist stability criterion is a graphical technique for determining the stability of a dynamical system. Because it only looks at the Nyquist plot of the open loop systems, it can be applied without explicitly computing the poles and zeros of either the closed-loop or open-loop system (although the number of each type of right-half-plane singularities must be known). As a result, it can be applied to systems defined by nonrational functions, such as systems with delays. A Nyquist plot is a parametric plot of a frequency

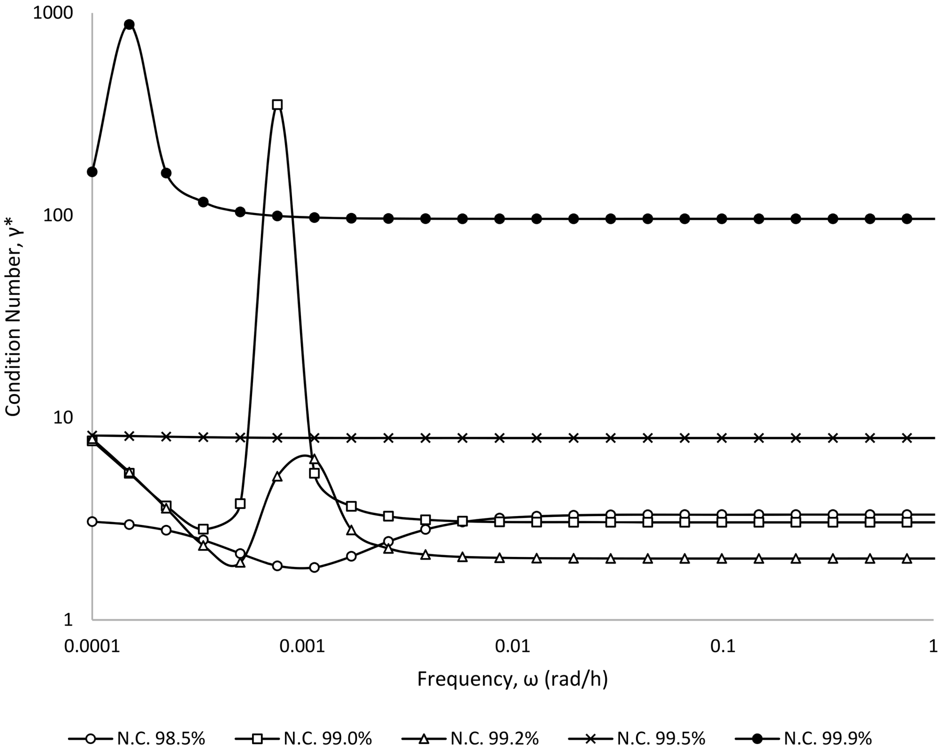

Figure 4. Condition number, reactive distillation process.

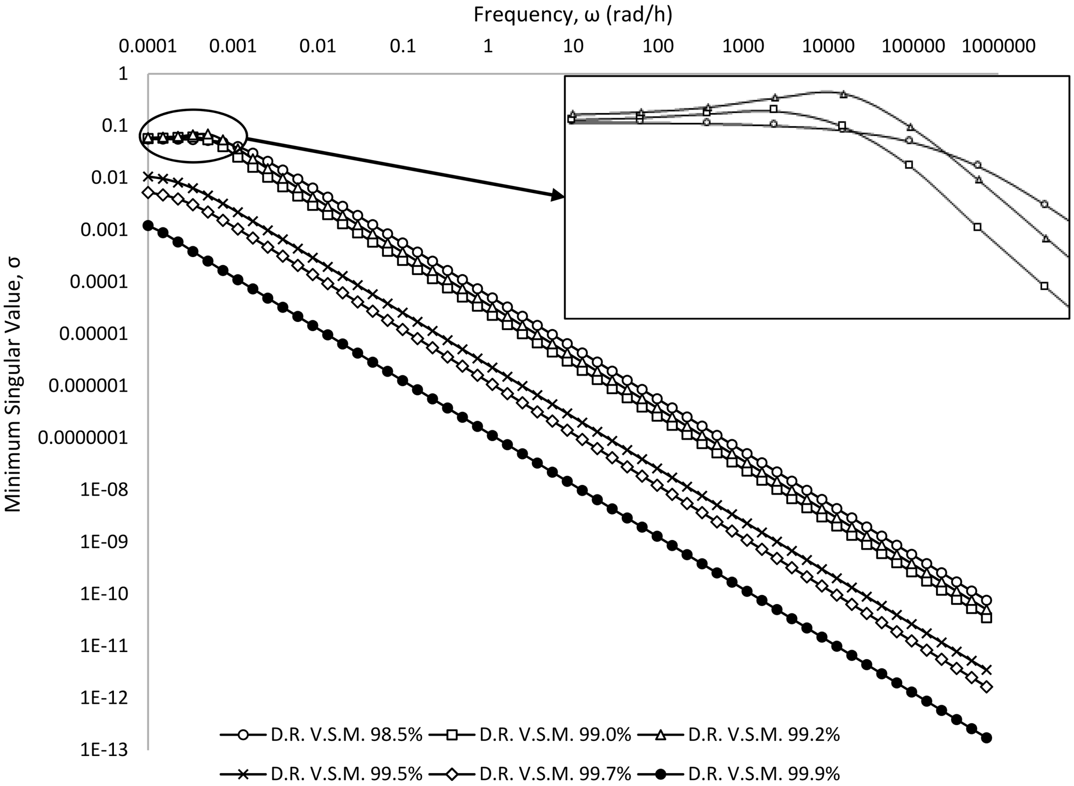

Figure 5. Minimum singular value, reactive distillation process.

response used in automatic control and signal processing. The most common use of Nyquist plots is for assessing the stability of a system with feedback. In Cartesian coordinates, the real part of the transfer function is plotted on the X axis. The imaginary part is plotted on the Y axis. The frequency is swept as a parameter, resulting in a plot per frequency. The same plot can be described using polar coordinates, where gain of the transfer function is the radial coordinate and the phase of the transfer function is the corresponding angular coordinate. Assessment of the stability of a closed-loop negative feedback system is done by applying the

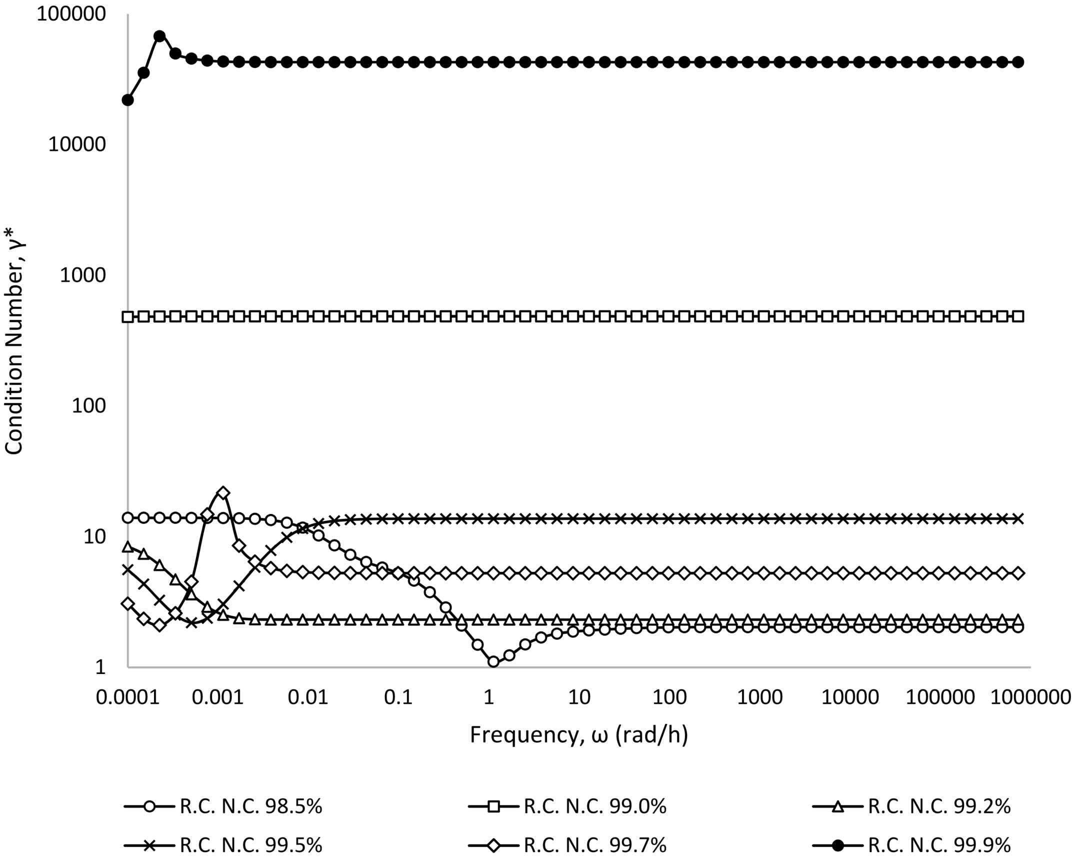

Figure 6. Condition number, reactor/column process.

Nyquist stability criterion to the Nyquist plot of the open-loop system (i.e., the same system without its feedback loop). This method is easily applicable even for systems with delays and other nonrational transfer functions, which may appear difficult to analyze by means of other methods. Stability is determined by looking at the number of encirclements of the point at (−1,0). The range of gains over which the system will be stable can be determined by looking at crossings of the real axis. The Nyquist plot can provide some information about the shape of the transfer function. For instance, the plot provides information on the difference between the number of zeros and poles of the transfer function by the angle at which the curve approaches the origin. The Nyquist criterion for systems is defined as follow: if the open-loop transfer function $G(s)$ is stable, then the closed-loop system is unstable for any encirclement of the point −1.

4.4. Closed-Loop Simulations. To supplement previous analysis, rigorous dynamic simulations under closed loop operation were carried out. For the closed-loop analysis, several issues must be defined first, such as the control loops for each system, the type of process controller to be used, and the values of the controller parameters. Several techniques, such as the RGA, can be used to fix the loops for a control system. In this case of study such loops are established using the RGA technique. The control objective was to preserve the output streams at their design purity specifications. The choice of the type of controller was based on the ample use that the proportional-integral (PI) mode has for distillation systems in industrial practice. As for the selection of the parameters of the PI controllers, care was taken to provide a common method for each of the case of study. A tuning procedure that involved Nyquist plots for each loop of each scheme was used.[24] Therefore, for each loop, an initial value of the proportional gain was set; a search over the values of the integral reset time was conducted until the proportional gain magnify the Nyquist plot.

5. RESULTS

The SVD technique requires transfer function matrices, which are generated by implementing step changes in the manipulated variables of the optimum design of the conventional reactor/separator and reactive distillation sequences and registering the dynamic responses of the two products. In this work, two controlled variables were considered, the product composition of TEOS and $SiCl_4$ Similarly, two manipulated variables were defined, the reflux ratio (R) and the heat duty supplied to the reboiler (Q). The methodology proposed by Cabrera-Ruiz et al.[20] was used for the construction of the transfer function matrix. By simplifying the process dynamic to only first-order responses, it is possible to assess the controllability of sequences by using only steady state information. The transfer function matrices generated by using step changes (1% of the nominal value) in the manipulated variables and recording the response of the two product compositions are shown in the Supporting Information. The results of the SVD, minimum singular value, and number of condition show that as the purity of TEOS increases in bottom flow rate the control properties are degraded (Figures 4−10). This is observed in the fact that the number of condition is increasing to high purities of TEOS and the minimum singular value decreases as well. Therefore, it can be expected that, in such systems where the TEOS purity is low, the schemes will exhibit better control properties than the other sequence under feedback control. Consequently the configurations are better conditioned to the disturbances. This can be

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Ind. Eng. Chem. Res. 2019, 58, 259−275

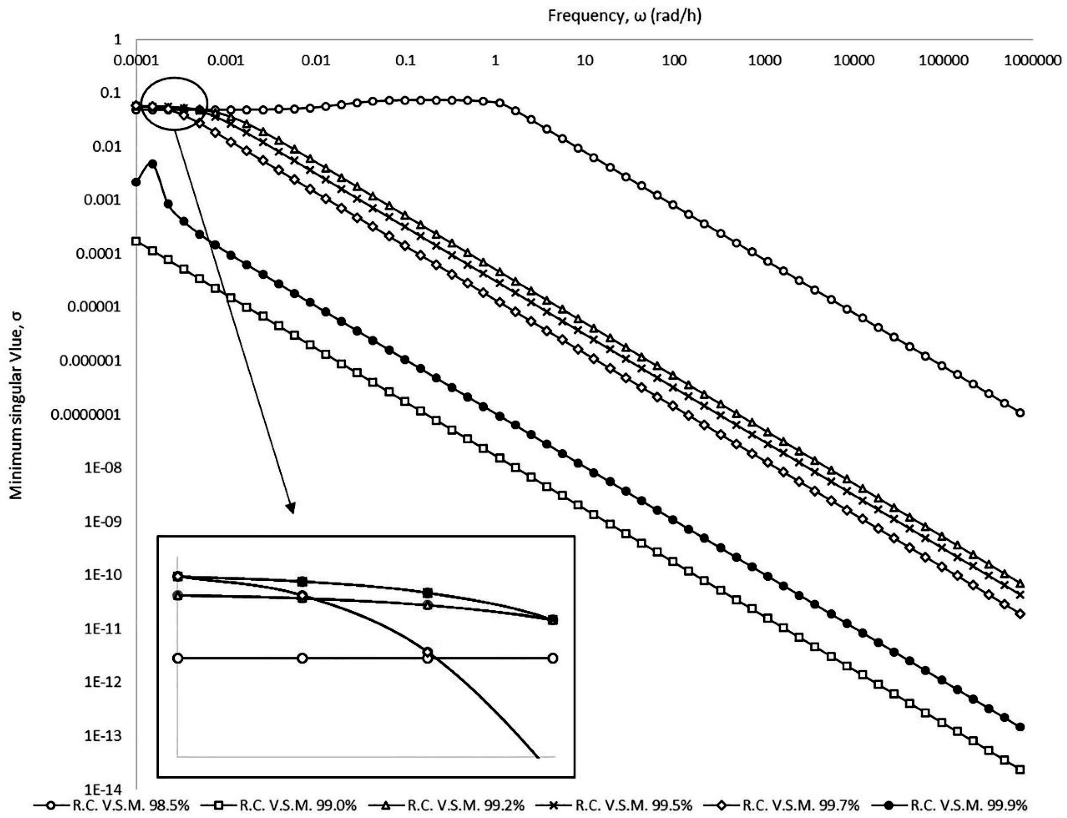

Figure 7. Minimum singular value, reactor/column process.

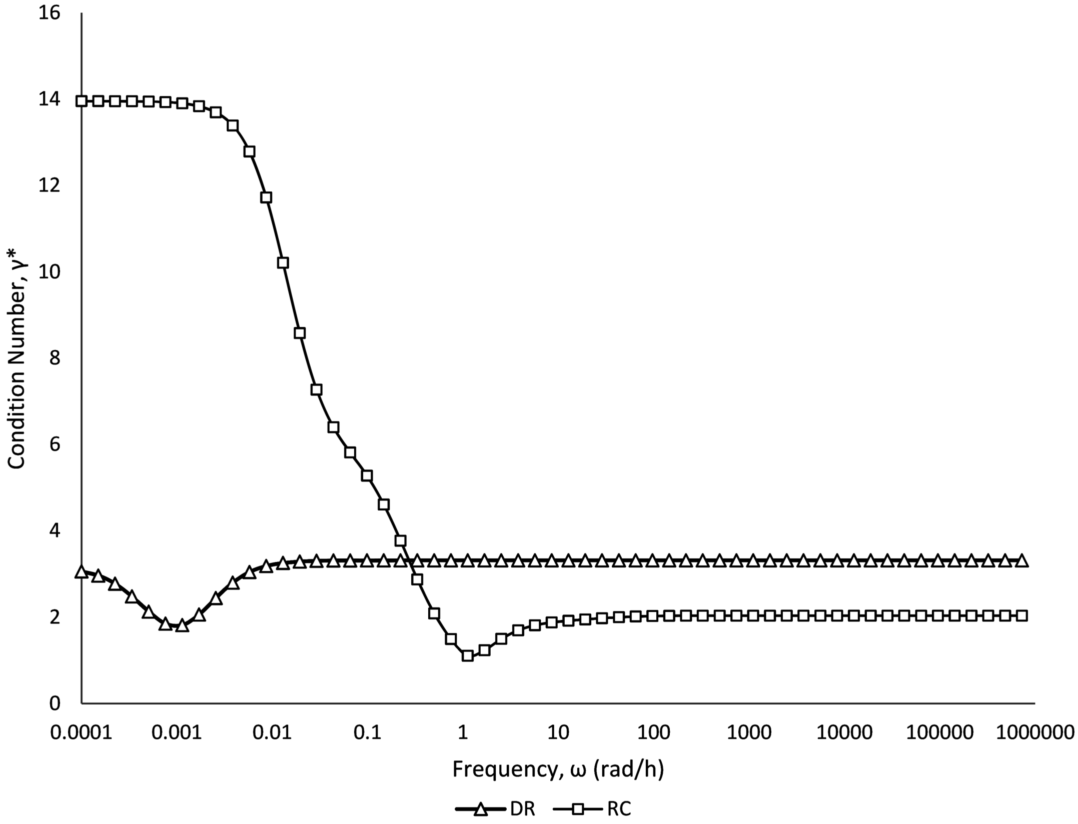

Figure 8. Condition number, reactor/column process, and reactive distillation column (TEOS purity 98.5%).

explained by the fact that at high purities the degrees of freedom of the system are very restricted and any disturbance in the configuration strongly impacts the control properties.[25] If an individual comparison at the same TEOS purity is performed

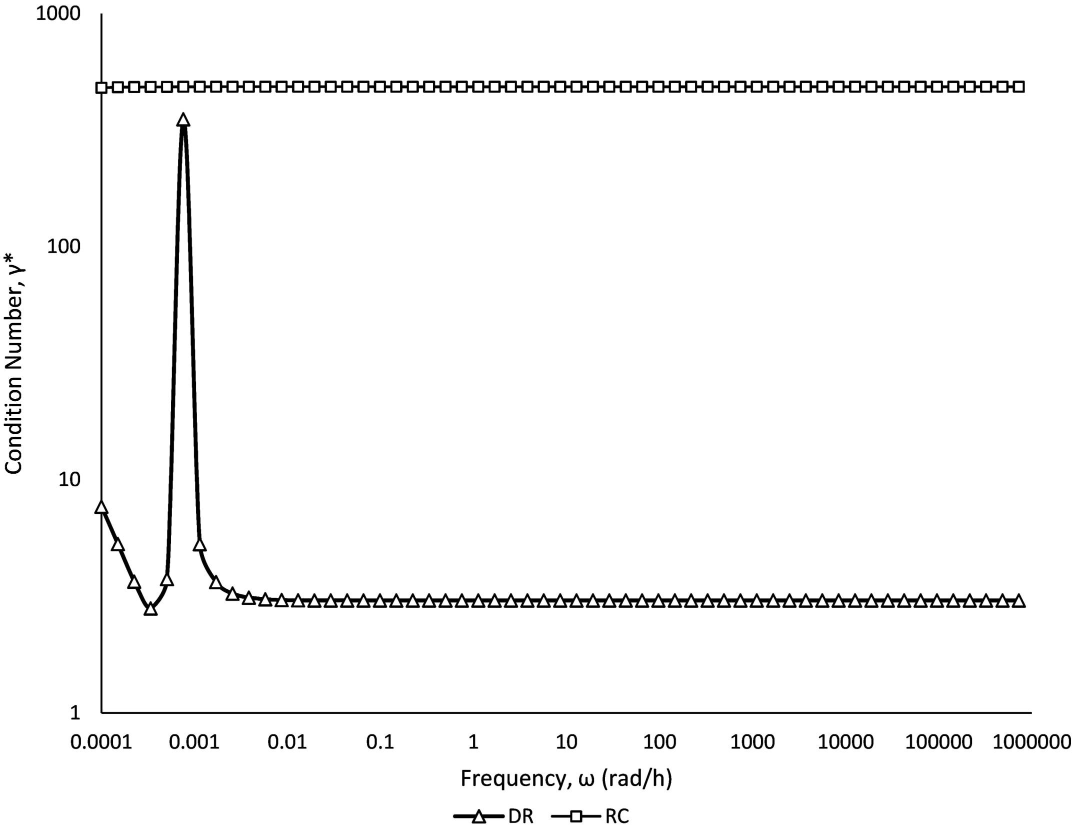

Figure 9. Condition number, reactor/column process, and reactive distillation column (TEOS purity 99.0%).

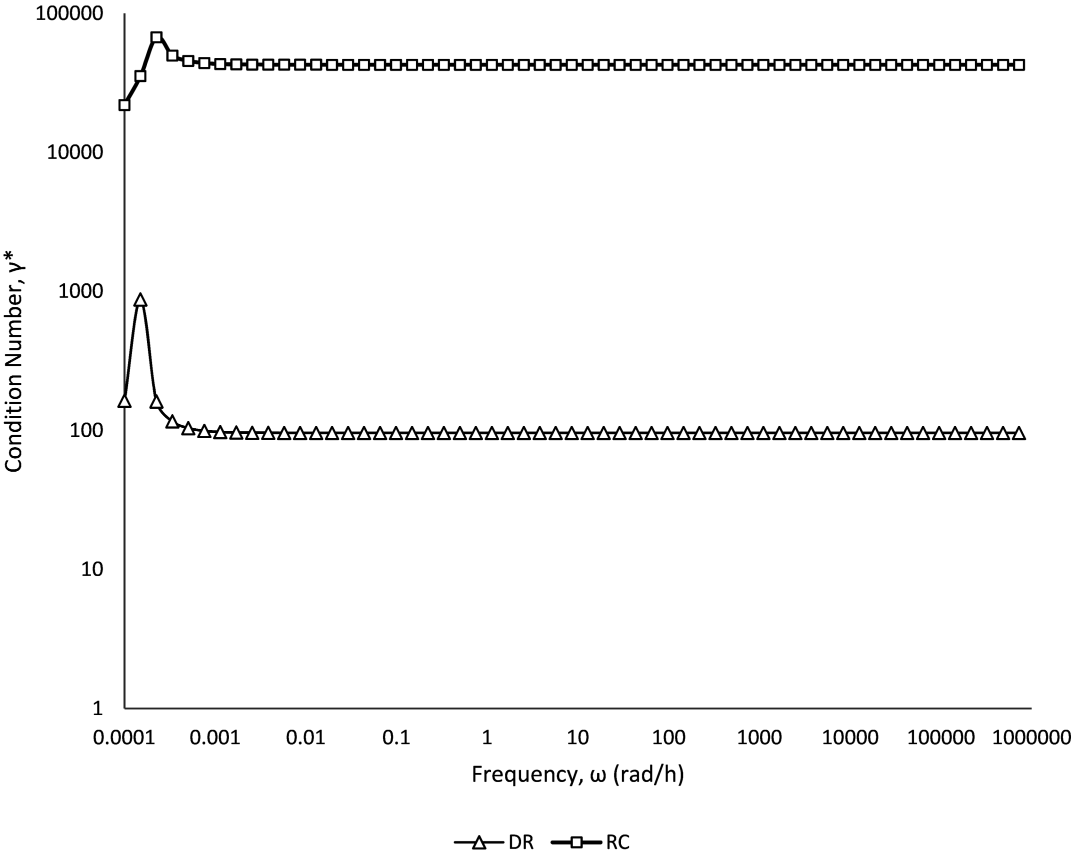

Figure 10. Condition number, reactor/column process, and reactive distillation column (TEOS purity 99.9%).

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(reactive distillation system vs the reactor-column process), it is observed for the results of the SVD that, for all case studies, the reactive distillation column shows better control properties than the reactor/column system. In other words, reactive distillation schemes have the lowest values of condition number of and the highest σ^* for the whole frequency range when it is compared with all reactor/column arrangements. Therefore, reactive distillation columns are better conditioned to the effect of disturbances (Figures 4, 6, and 8−10 show some representative results for condition number). The results indicate that there is no degradation of the control properties due to the complex topology in the reactive distillation process. Several works where intensified columns have been used in comparison with conventional configurations show that those complex systems present good control properties. This fact can be attributed to remixing of streams is avoided in the distillation column.[26−28]

The RGA relative gain arrays were obtained for the both distillation sequences under study. The relative gain array for 98.5% TEOS purity is indicated in Tables 4 and 5 for reactive distillation column and reactor/column process, respectively. There are two controlled variables (compositions $SiCl_4$ and TEOS) and two manipulated variables (one reflux rate and one heat duty supplied to the reboiler). For Table 4, in the first row, we can see that $SiCl_4$ composition of $SiCl_4$ should be controlled by manipulating the reflux ratio of the column; the second row of the RGA relative gain array suggests that a good pairing is TEOS composition and the heat duty supplied to the reboiler. The same pairing is obtained for reactor/distillation configuration (Table 5). These same pairings are presented for all purities in the two case studies analyzed. One point to highlight is the following: a well-known structure is based on energy balance considerations, which yields the so-called LV control structure in which the reflux flow rate L and the vapor boilup rate V (affected directly by the heat duty supplied to the reboiler) are used to control the distillate and bottom outputs compositions.[19] In summary, this typical pairing in the industry is the one that was obtained for all the study cases and for all the purities analyzed in this work.

Table 4. RGA Matrix for Reactive Distillation Column (TEOS Purity 98.5%)

	R	Q		
$\Lambda =$	**1.0242534**	−0.0242534	X_{SiCl_4}	LV pairing
	−0.0242534	**1.0242534**	X_{TEOS}	

Table 5. RGA Matrix for Reactor/Column Process (TEOS Purity 98.5%)

	R	Q		
$\Lambda =$	**0.975764151**	0.024235849	$X_{C_2H_5OH}$	LV pairing
	0.024235849	**0.975764151**	X_{TEOS}	

To complement the control analysis of the systems under study, the closed-loop stability study was carried out under the Nyquist criterion. The pairing obtained in the RGA was used in this analysis for both configurations. The Nyquist criterion for systems is defined as follows: if the open-loop transfer function $G(s)$ is stable, then the closed-loop system is unstable for any encirclement of the point −1. Figures 11−14 display the Nyquist plot for the pairing composition TEOS−reboiler duty and composition $SiCl_4$−reflux ratio. It is evident from the Nyquist plot that at low compositions the reactive distillation presents better stability than the reactor/column system because the curve is found further away from the value of −1 for both pairings. While at high compositions, the behavior of the curves is inverse. The reactor/column system presents better stability than the reactive distillation because the curve is found further away from the value of −1 for both pairings.

These results are consistent with those obtained by the SVD. The RGA method was used to fix other loops for the control system and Nyquist criterion for tuning PI controllers used for the closed loop analysis. Representative cases are displayed in Figures 15 and 16 for dynamic responses for pairing bottom composition and reboiler duty, carrying out set point changes from the nominal value in 1% of perturbation in manipulated variable. It was observed that at low TEOS purities the reactive distillation column has short settling times and fewer oscillations compared to the reactor/column system. However, at high TEOS purities, the results are opposite: the reactor/column

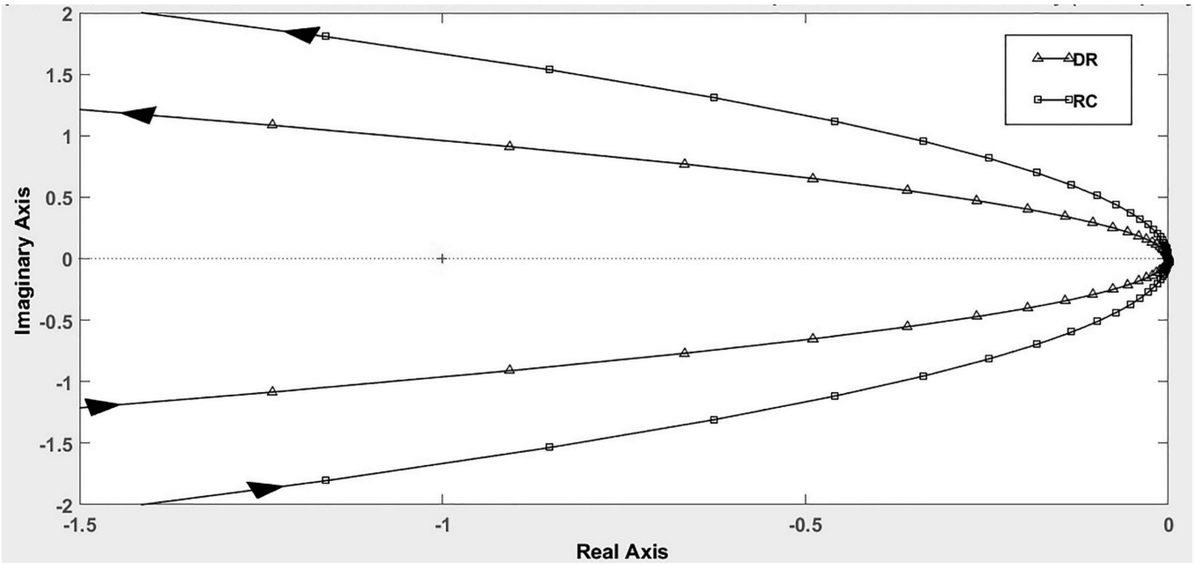

Figure 11. Nyquist plot, reactor/column process, and reactive distillation column for composition TEOS−reboiler duty (TEOS purity 98.5%).

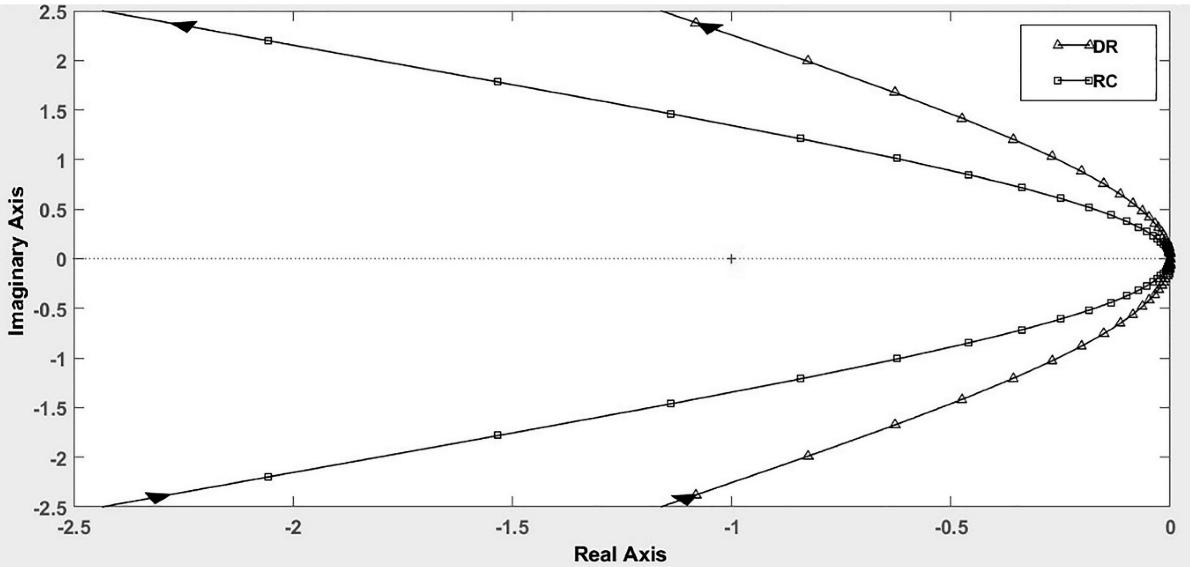

Figure 12. Nyquist plot, reactor/column process, and reactive distillation column for composition $SiCl_4$−reflux ratio (TEOS purity 98.5%).

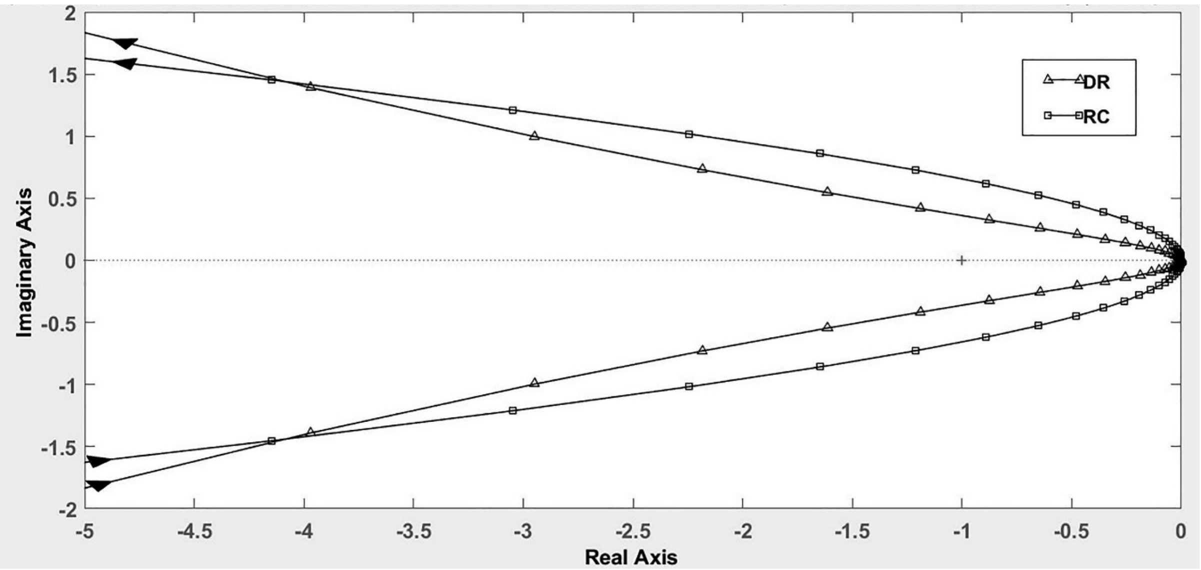

Figure 13. Nyquist plot, reactor/column process, and reactive distillation column for composition TEOS−reboiler duty (TEOS purity 99.5%).

system presents better dynamic performance. The response shows fast settling times and few oscillations. These results are consistent with all of the previous studies presented in this work for the control properties. Serra et al.[29] have shown that in the intensified distillation system the control properties are degraded as the purity of the product increases in the output flow rate, because of the control variable is more restricted in its region of operation in relation to the manipulated variable. The results obtained in this work show how the reactive distillation column degrades its control properties as the purity of the TEOS increases while the reactor/column system improves its dynamic behavior.

An important point in the dynamic behavior of a process is to analyze when the process is subjected to a disturbance if it can easily or not easily reach a new stationary state. This situation is known as process stability, and it is reported by the Nyquist criterion.[30] Therefore, a process that shows stability must be better conditioned to assimilate the changes of set point or disturbances (which is obtained by the SVD results). This allows us to highlight the relationship between the Nyquist and SVD criteria, which is observed in the results previously indicated for the case studies under analysis.

Regarding the inherent safety, there is a notorious difference among both alternatives. Note in Figure 17 and Table 6 that reactive distillation technology exhibited a bigger IR value than the reaction-separation system. Accomplishing this results is the combination of several factors involved in the design of each process. For example, the IR of each process is mainly related to three aspects, energy invested as reboiler duty, operative pressure, and the number of operative units. Considering only the amount of units of each process, the conclusion could be that the reactive distillation system is per se a safer process since only one main process is involved in the production of TEOS. However, according to Tables 1 and 2, to reach a purity of 99.9 wt %, the reactive distillation spends about 30 000 kW, and on the other hand, the reaction−separation system needed about 6300 kW. Additionally, the reaction−separation system can even overcome on this index, because of the operative pressure.

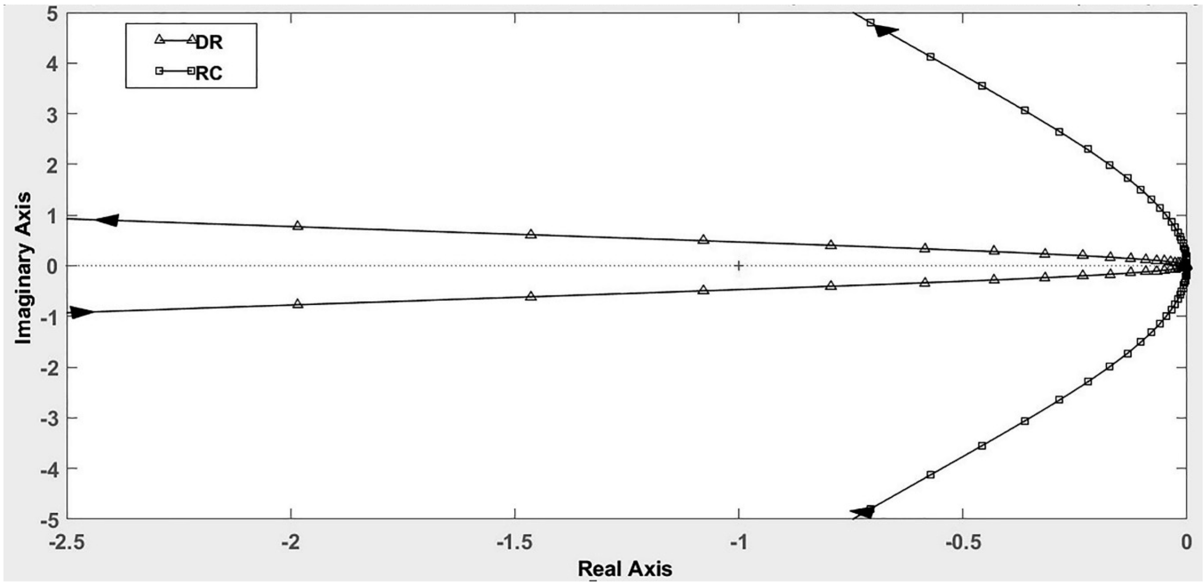

Figure 14. Nyquist plot, reactor/column process, and reactive distillation column for composition $SiCl_4$−reflux ratio (TEOS purity 99.5%).

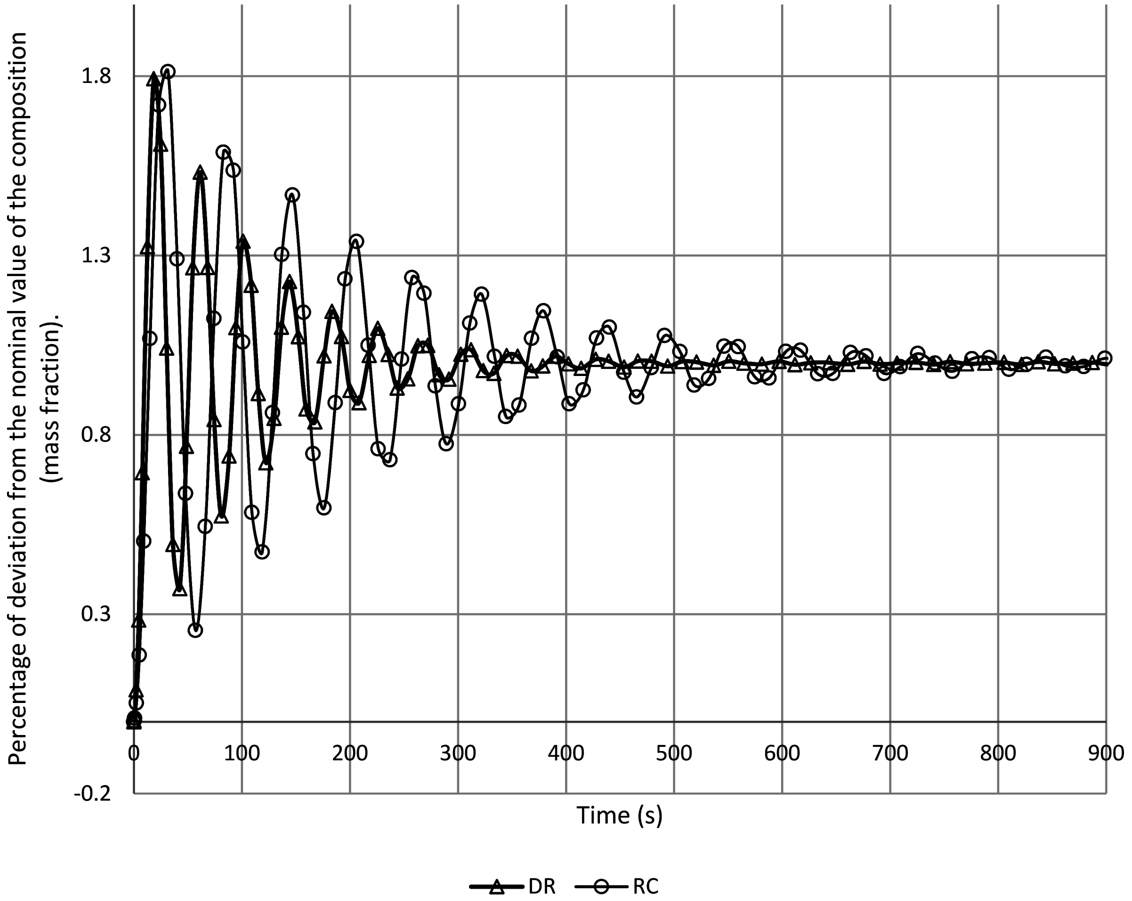

Figure 15. Dynamic response for set point change in reactor/column process and reactive distillation column for pairing composition TEOS−reboiler duty (TEOS purity 98.5%).

Note in Tables 1 and 2, the operative pressure for the reaction−separation system is 8 atm, and on the other hand, the reactive distillation column operates at almost 18 atm. The operative pressure is indeed the main parameter in the model of those catastrophic events, and evidently, the higher the operating pressure is, the bigger the IR value. With this in mind, it is understandable that the reaction−separation system is safer than the reactive distillation process.

As additional discussion, differentiating both the reactive distillation and the reaction−separation, note that the tendency is clear, several design variables promote or degrade the IR of each process. As it has been discussed, the reboiler heat duty,

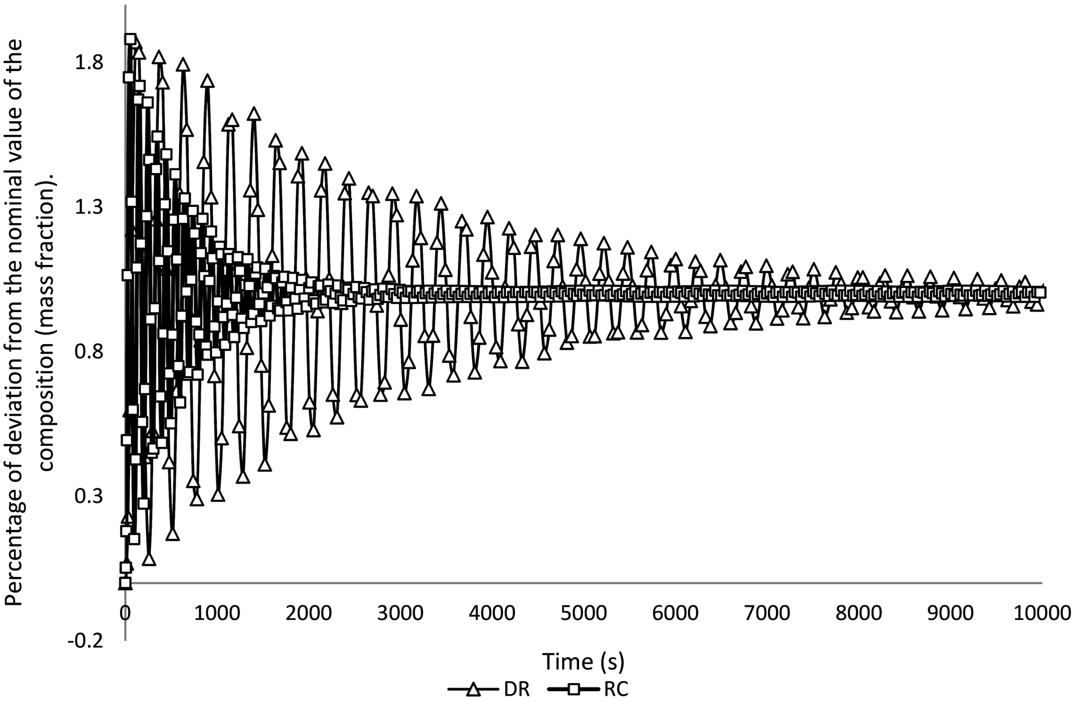

Figure 16. Dynamic response for set point change in reactor/column process and reactive distillation column for pairing composition TEOS−reboiler duty (TEOS purity 99.9%).

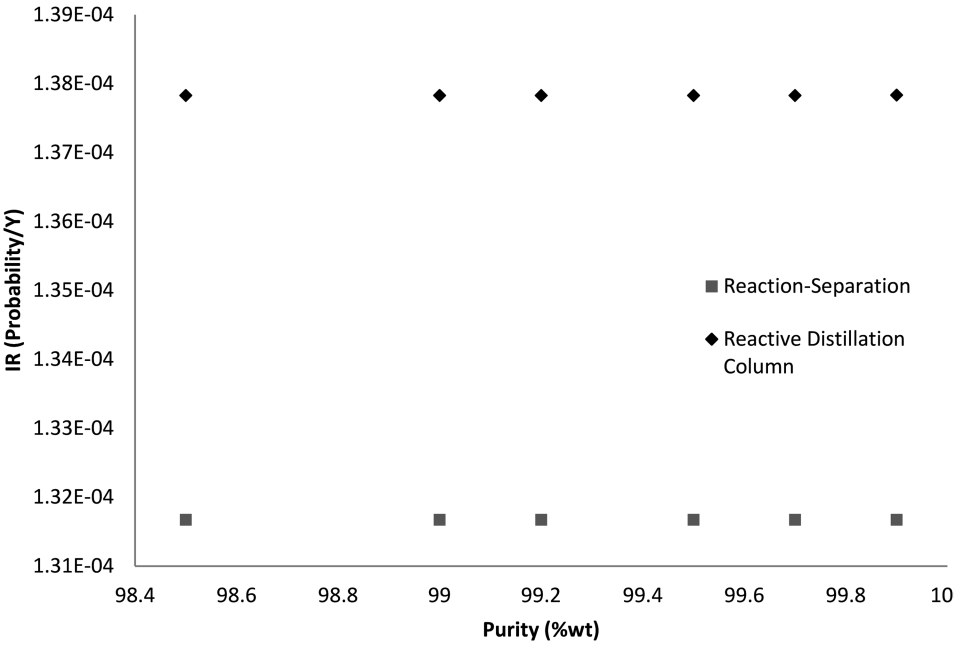

Figure 17. IR values for both the reaction−separation and reactive distillation systems at every purity.

operative pressure, and number of units play a major role in the IR calculation. However, other variables plays an interesting role. Note, despite the operative pressure being fixed in the reactive distillation process, as long as the reflux ratio increase also the IR value increase. Please picture that, if the reflux ratio increases, a higher amount of flow is returned to the column, and as a result the reboiler heat duty also increases. In other words, the IR value increases along the purity of the desired product.

As has been described in previous paragraphs, the IR calculation was performed in a certain atmosphere; for example, all calculations were carried out with 50 m of distance from the process to a person. Nevertheless, in order to figure out a preliminary layout and focus all of the attention on the inherent safety, it is clear that the planning must be focused on avoiding the probability of death. In other words, within the IR calculation, the distance from the process to a person could be considered as a degree of freedom and might be varied until the probability of death reached a value near zero. With this in mind, Figure 18 takes as reference the probability of BLEVE. In other words, Figure 18 shows how the probability is changing along with distance, expecting a similar situation for other events. In general terms, the probability of death almost reaches zero at

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Ind. Eng. Chem. Res. 2019, 58, 259−275

Table 6. IR Values for Both Systems in Instantaneous/Continuous Release

	IR (probability/Y)					
	reactive distillation			reaction-separation		
purity (wt %)	instantaneous release	continuous release	total IR	instantaneous release	continuous release	total IR
98.5	1.85×10^{-5}	1.19×10^{-4}	1.38×10^{-4}	1.24×10^{-5}	1.19×10^{-4}	1.32×10^{-4}
99	1.85×10^{-5}	1.19×10^{-4}	1.38×10^{-4}	1.24×10^{-5}	1.19×10^{-4}	1.32×10^{-4}
99.2	1.85×10^{-5}	1.19×10^{-4}	1.38×10^{-4}	1.24×10^{-5}	1.19×10^{-4}	1.32×10^{-4}
99.5	1.85×10^{-5}	1.19×10^{-4}	1.38×10^{-4}	1.24×10^{-5}	1.19×10^{-4}	1.32×10^{-4}
99.7	1.85×10^{-5}	1.19×10^{-4}	1.38×10^{-4}	1.24×10^{-5}	1.19×10^{-4}	1.32×10^{-4}
99.9	1.85×10^{-5}	1.19×10^{-4}	1.38×10^{-4}	1.24×10^{-5}	1.19×10^{-4}	1.32×10^{-4}

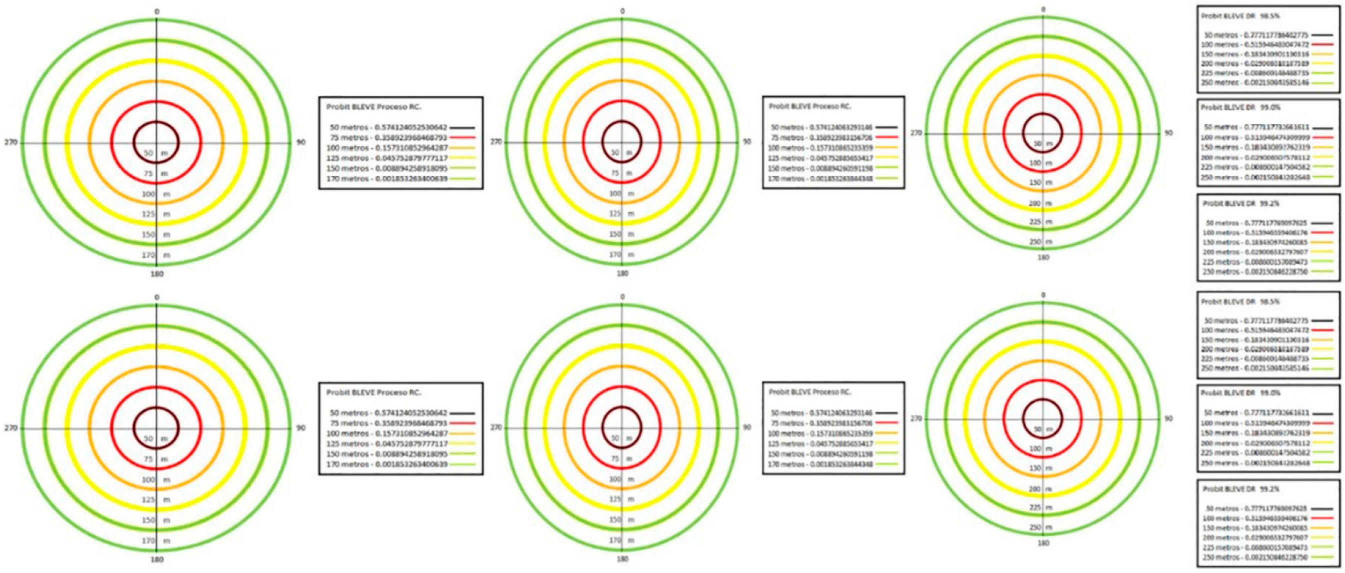

Figure 18. Necessary distance to reduce the BLEVE probability to zero for both systems at 0.985, 0.99, and 0.99 wt %.

250 m for reactive distillation technology and 17 m for the reaction−separation scheme. However, this means that both the reactive distillation and the separation−reaction processes must be isolated 170/250 m from a person to avoid the probability of individual deaths. This distance may or may not be feasible according to the designer and planner needs.

As a preliminary conclusion, the difference between both process proposals is clear. In one hand, the conventional reaction−separation system is slightly safer than the reactive distillation system; however, that difference is not indeed so big, the difference is only about 5%. Martínez-Gómez et al.[31] have shown that, when a conventional process is modified, it is necessary to know the involved risk through the implementation of an inherent safety approach due to the fact that in an only system several unit operations are being carried out and all of the components are present, increasing the possibility of risk in the system.

In this case, the intensification of a conventional reactor/distillation column structure in a reactive distillation column is a modification to the conventional process that may help to decrease the cost; however, the results show how the intensified system shows a slightly higher risk compared to the conventional system, which is consistent with that reported by Martínez-Gómez et al.[31]

On the other hand, based on the control analysis, the reactive distillation showed, in general terms, better control properties than the reaction separation system. With this in mind and considering the previous results from Sanchez-Ramírez et al.[8] a relative complex view is figured out for TEOS production. According to those authors, the reactive distillation was a more promising alternative from the economic point of view when the total annual cost is evaluated, and the ROI follows the same pattern at purities below 99 wt %. On the other hand, the Eco-indicator 99 (EI99) presented the opposite behavior. Due to the reboiler heat duty invested in reactive distillation, the EI99 value of such a process overcomes about 30% to the reaction−separation process. Under the light of those economic and environmental results and compared with those obtained in this analysis, the reactive distillation columns seems a more appropriated technology for TEOS production since its economic and control properties surpass those present by the conventional reaction separation process. Moreover, if the required purity for TEOS is between 98.5 and 99 wt % the profit of the process increases. Even though the inherent safe for the conventional process is slightly better, that difference is not high enough for comparative purposes.

6. CONCLUSIONS

In this work was performed two analyses, a dynamic and an inherent safety analysis. During the analysis, it was clear that the reactive distillation column overcomes the reaction−separation system regarding control properties; however, in a contrary way, the reaction separation system exhibited a slight improvement in the safe analysis.

Moreover, interesting trends were observed for both tests, as long as TEOS purity increase the control properties decrease, and the process becomes less safe. As it has been previously discussed, several design variables are involved in this trend, reflux ration, reboiler heat duty, column pressure, and so on. According to the results obtained, the designer is able to cover a wide range of possibilities regarding its needs. It is possible to have a process with a considerable range of profit and relatively good dynamic behavior. From a wider point of view, the reactive distillation system is a more promissory scheme considering both the controllability and safety analysis as a compliment of the previous study presented by Sanchez-Ramírez et al.[8] where the economic and environmental results of reactive distillation are remarkable. In terms of versatility to obtain a wide variety of alkoxysilanes (not only TEOS), RD represents an interesting new technology proposal comparable to the traditional esterification process. In general, to maintain the current policies of safety, economy, and environmental impact, the results indicate that reactive distillation is the alternative that can maintain all objectives in a balanced way. Otherwise, if the current policy is interested only in safety issues the reaction–separation is a good option. In particular to maintain the current policies of safety, economy, and environmental impact, the results indicate that reactive distillation is the alternative that can maintain all objectives in a balanced way. In general, Green Chemistry Principles (currently well-accepted in the process intensification analysis) express a desire to have real-time process analysis. The aim of this principle is to prevent safety issues by identifying process excursions as they occur. By doing so, there may be sufficient time to modify process parameters such that the excursion may be reversed and there is no subsequent impact on the final product quality. This situation is only possible if the process presents stability from the point of view of process control. Hence the need for a simultaneous study of safety and control issues.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.8b04962.

Transfer function matrixes (Tables S1–S12) (PDF)

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Notes

The authors declare no competing financial interest.

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