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Reactive Distillation Column Design for Tetraethoxysilane (TEOS) Production: Economic and Environmental Aspects

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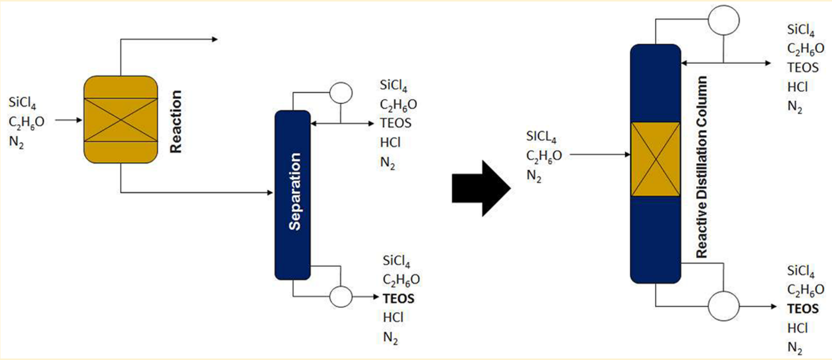

ABSTRACT: Alkoxysilanes are silicon compounds containing a Si-OR bond. The applications of tetraalkoxysilanes cover a wide range depending if the Si-OR bond remains intact or is hydrolyzed. Currently, tetraethoxysilane (TEOS) is the most prominent derivative of such silicon compound family. The best known and used method of synthesis of TEOS is the esterification reaction of $SiCl_4$, following the old Von Ebelman's route (1846). Tetramethoxy- and tetraethoxysilane are obtained by a technology developed in the 1990's involving the catalyzed direct synthesis of silicon metal and either methanol or ethanol. However, there is few information about novel technologies to produce TEOS, either improved current technology or proposed new approaches. In this work, the reactive distillation (RD) is suggested 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 reduction on equipment size, improvement in energy and mass transfer, and reduction in capital cost. Therefore, this work will approach 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. As a result, the reactive distillation shows better performance as concern to TAC values; however, when purities above 99.5% wt are obtained, the reaction/separation system overcomes the RD as concern to ROI values. Moreover, when the environmental impact is measured, the RD showed a bigger impact near 30% in comparison with the reaction/separation system.

1. INTRODUCTION

Alkoxysilanes are chemical compounds containing a Si-OR bond. From this family of silicon compounds, tetraethoxysilane, $Si(OC_2H_5)_4$ (TEOS), is in many ways the most important and versatile derivative and appreciated because of its low toxicity. Several chemical industries use this chemical component as raw material or even intermediary for high value-added compounds. In brief, it can be used for optical glass processing, chemical-resistant coatings, heat-resistant coatings, and adhesives. Moreover, is widely used as precision-made binder, refractory cements and ceramics, glass frosting, anticorrosive paints, abrasion-resistant coatings, glasses, and ceramics based on the sol−gel process, as well as other applications such as silicone room temperature vulcanizing cross-linking. Spin-on glass in microelectronic industry, where the thermal decomposition of TEOS is used to produce silicon dioxide in the form of both particles and thin films. The chemical vapor deposition (CVD) of silicon dioxide from TEOS is used to obtain pure and modified dielectrics. TEOS has also found a broad area of

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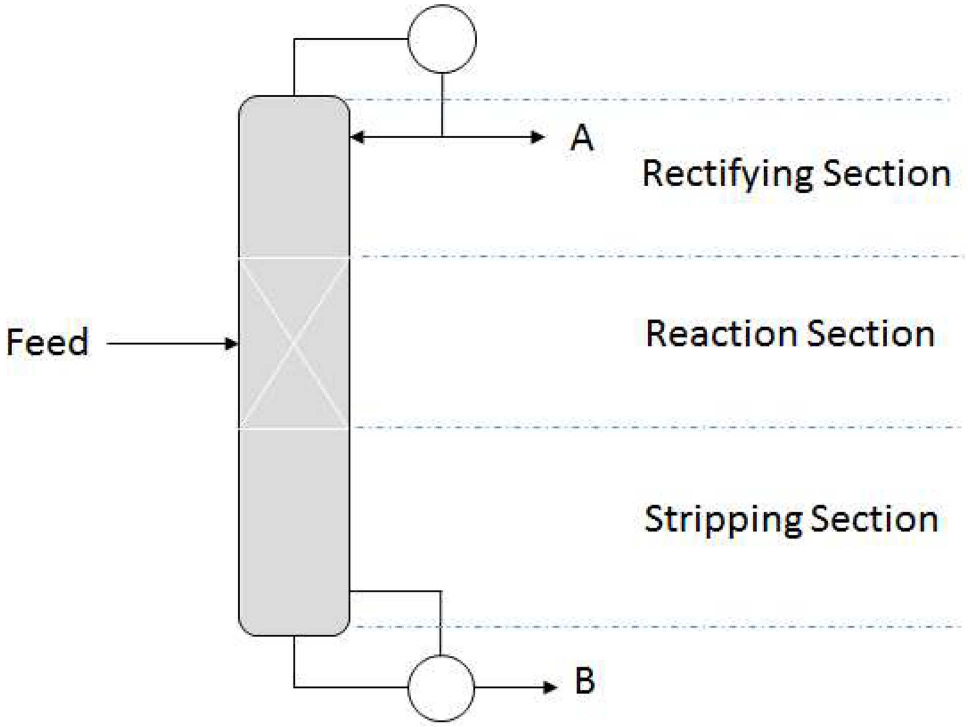

Figure 1. Conventional topology of reactive distillation system.

application in the development of formulations to preserve historical monuments of cultural importance.[1−4]

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.[5] 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 it is possible to perform reactions not only using ethanol but also using 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. On the other hand, other important reason is in respect to $SiCl_4$. $SiCl_4$ is a versatile chlorosilane that is industrially available because it is an important precursor in many applications. $SiCl_4$ can be obtained directly from silicon and chlorine gas $SiCl_4$ or as a byproduct in the production of $SiHCl_3$, the important chlorosilane used in the production of semiconductor and solar silicon. The esterification reaction discovered by Von Ebelman is a nice route to efficiently use $SiCl_4$.

An alternative technology from the 1990's 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 $Si(OMe)_3H$.[6] The route has been implemented at an industrial level but is limited to the products described.

In order to avoid the carbothermic process to produce silicon from quartz, and the chlorosilane route, recently Laine et al. reported that TEOS could be manufactured by means of the reaction of SiO_2 and diols.[7] In this 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[8] or the dehydration of SiO_2 with ethanol by azeotropic distillation with benzene.[9]

An important aspect to be considered in the esterification route is the generation of HCl (g) as a 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 prepolymerized versions of TEOS, all of them with specific applications.

In accordance with experimental data, esterification of tetrachlorosilane with ethanol proceeds through four consecutive stages of bimolecular nucleophilic substitution at silicon atom postulated by Sommer.[10] The reaction is described in four steps. The chemical reaction sequence is represented as follows:

$$SiCl_4 + C_2H_6OH \rightarrow Cl_3Si(OC_2H_6) + HCl(g) \tag{1}$$

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

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

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

Preliminary thermodynamic analysis of the reversibility of reactions 1−4 by Anderson's method of group components[11] showed that reations 1−3 may be regarded as virtually irreversible. Sobolevskii et al.[12] reported that equilibrium becomes stablized at the last stage of esterification of tetrachlorosilane with ethanol. Ukhtomskii et al. reported the use of stopped-flow method for investigating the kinetics of $SiCl_4$ esterification. According to such a report, since direct measurement of variations of the concentrations of the original substances and intermediates products is impossible, variations of the hydrogen chloride concentrations were recorded from changes of the electrical conductivity of the solution, concluding that the substitution of the three chlorine atoms is very fast and a slower one to remove the fourth atom.[13]

In respect to the separation/purification process, purity requirements are dependent on the application of TEOS. As option, the distillation operation could remove alcohol and high boiling impurities. Purity of 98 to 98.5% is the value commonly reached after the distillation. TEOS of such purity is the most demanded in the market. On the other hand, for the manufacturing of semiconductor devices and or microelectronics applications TEOS must be as free of impurities as possible to form dioxide films of acceptable electronic properties. Some purification techniques, such as low pressure distillation, can increase the purity of the TEOS near to 99.8%.[14] However, even this level of purity contains impurities which will be deposited onto a film layer made of TEOS. Another alternative to purify TEOS involves the injection of impure tetraethoxysilane in the gaseous phase into a gas chromatograph column as a series of spaced pulses, heating the gas chromatograph column to temperatures near the boiling point of TEOS; in this manner, the impure TEOS pass through the column obtaining high purity TEOS.

Having in mind the mentioned background, it is possible to wonder, is there an alternative to improve or even reduce the esterification process of two stages to a single unit process? Process intensification (PI) concept is an interesting strategy to achieve this required improvement. Lutze et al.[15] define PI as the process that contains three different kinds of improvements achieved through: (1) the integrations of operations, (2) the integration of functions, and (3) the integration of phenomena. In general terms, PI aims to overcome thermodynamic limitations through the integrated design and operation. In other words, by means of PI, it is possible to reduce mass and heat transfer resistances.[16] One PI example is the reactive distillation (RD), this intensified process integrates reaction and separation (Figure 1). In brief, RD is a process where the reactor is also a separator, therefore this intensified technology allows one to eliminate conversion and phase equilibrium limitations, which make RD particularly attractive for equilibrium-limited reactions. In many cases where RD is used, an average of 20% is saved regarding the capital cost and energy requirements in comparison to the classical sequential process reaction, separation/purification.[16]

Reactive distillation has been successfully applied and investigated for many reactions. For example, in the field of esterification, Dimian et al.[17] reported 50% reduction in catalyst requirements; as concern to transesterification processes Jimenez and Costa-Lopez[18] reached high purity products and a yield of 100%. On the other hand, Hoyme and Holcombe[19] reported high yield and selectivity during some hydrolysis processes. Moreover, RD covers some more application; Rix et al.[20] reported conversion of 99.9% and purities of 98% during etherification process. At the field of hydrodesulfuration, Groten and Loescher[21] reported diesel production with 50 ppm or less of sulfur when RD is used. In the same sense, several authors have reported high selectivity, high convention, reduction in both byproducts, and capital cost regarding many reactions and processes such as carbonylation, polymers, chlorination/amination, and acetalization even in chiral separation according to Voss,[22] Leeman et al.,[23] DiGuilio and McKinney,[24] Chopade et al.,[25] and Okasinski and Doherty,[26] respectively.

On the other hand, the feasibility of reactive distillation is attractive in those systems where certain chemical and phase equilibrium conditions exist.[27] Moreover, this case of study accomplishes all the preliminary requirements to claim the complete feasibility of the RD technology to produce TEOS. In example, according to Shah et al.[28] before any synthesis or design task, it is necessary to determine the feasibility of any reactive distillation scheme. Following this guideline, in this case of study must be highlighted the accomplished of those requirements. (1) The presence of more than one product and (2) there is a match between temperatures required for reaction and separation. From quite a simple point of view, this case of study proposes the reaction near 25 °C, and the boiling point for both reactants ($SiCl_4$ and C_2H_6O) is 57.65 and 78.37 °C respectively. (3) The operating pressure and temperature are not close to the critical region for any component. For example, both components $SiCl_4$ and C_2H_6O do not react close to its critical points, T_c = 508 and 514 K; P_c = 35 and 63 atm. (4) The volatilities of all components promote the reaction liquid phase since the lowest volatility component is the TEOS, the intermediate volatility components are indeed the reactants, and the most volatile component is the other reaction product, having the following arrangement: $\alpha_{HCL} > \alpha_{SiCl4} > \alpha_{C2H6O} > \alpha_{TEOS}$.

The reaction in reactive distillation includes heterogeneous catalyst reactions, homogeneous catalysis reactions, and the thermal (noncatalyst) reaction, which is the case in TEOS production, where no catalyst is required. All reactions take place in the liquid phase, but reactions taking place in the gas phase and locating the catalyst in the vapor phase of the column is conceivable.[29]

Under this scenario, the application of the RD technology to produce TEOS in a single unit seems a correct alternative in order to produce high purity tetraethoxysilane. The aim of this work is to propose a design of reactive distillation able to produce and separate high purity TEOS in a single column. Moreover, this RD will be able to produce a wide range of TEOS purities in the same column just varying the operation variables. In order to evaluate the proposed design, an economic and environmental framework is used which considers both the total annual cost (TAC) and the return of investment (ROI) as economic indexes and the Eco-indicator 99 as the environmental index. Moreover, to make a fair comparison with the traditional process (reaction-separation), this scheme is also designed with two stages and evaluated with the same indexes.

2. PROBLEM STATEMENT

Considering the industrial application for TEOS, a constant increasing in TEOS demand is normal. For example, SK Hynix reported an increase on its demand from 248 tons to 384 tons in 2015, representing only about 60% of the annual demand from Samsung Semiconductor.[30] Moreover, a wide range of TEOS purities are currently used; however, TEOS at 98.5% wt represents an increasing consumption market. For example, in Japan, 90% of TEOS is used as an anticorrosion coating (zinc-rich paint) base material.[31] On the other hand, TEOS at higher purities is relatively less used. As an example, TEOS at 99.5% wt is used to dope adhesives, in organic rubber and as cross-link agent. Even high purity TEOS (99.99%) is commonly used as a precursor to prepare xerogel and optical fiber manufacturing.[30] Under this scenario, the necessity to generate a profitable process that could improve the current technology with economic and environmental advantages is clear. As has been described in the last paragraphs, reactive distillation (RD) is a relatively novel technology that might improve the TEOS production by means of an intensified perspective. In addition, the current bibliography does not provide much information about either conventional or intensified technologies for TEOS production. The presented approach may represent an initial point of reference for further improvements in search for new technologies in the TEOS production.

3. METHODOLOGY

Initially, in order to carry out either a reactive distillation system or conventional reactor/separation system, a feed stream was defined (see Table 1). 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. Because of this, a set of TEOS purities was considered for both systems, 98.5, 99.0, 99.2, 99.5 and 99.9% wt, respectively, setting as purity constrains those values as final TEOS purity.

Table 1. Feed Characterization (Base of 1000 [kmol/h])

component	mole-frac
$SiCl_4$	18.3873
C_2H_6O	38.0628
N_2	43.5499
temperature [°C]	
50	
pressure [atm]	
1	

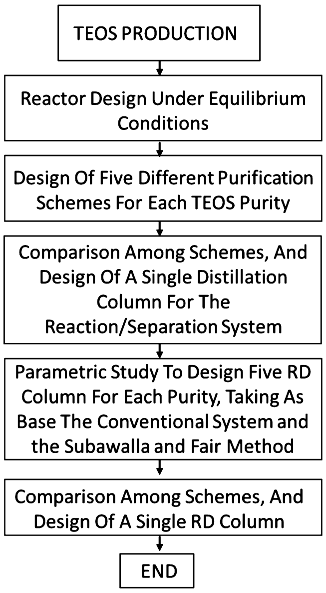

Figure 2. Flowchart for both reaction/separation and RD design.

3.1. Reaction-Separation System.

In accordance with limited studies regarding the kinetic experimental studies of the esterification reaction of $SiCl_4$ with ethanol,[13] 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.[12] 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).

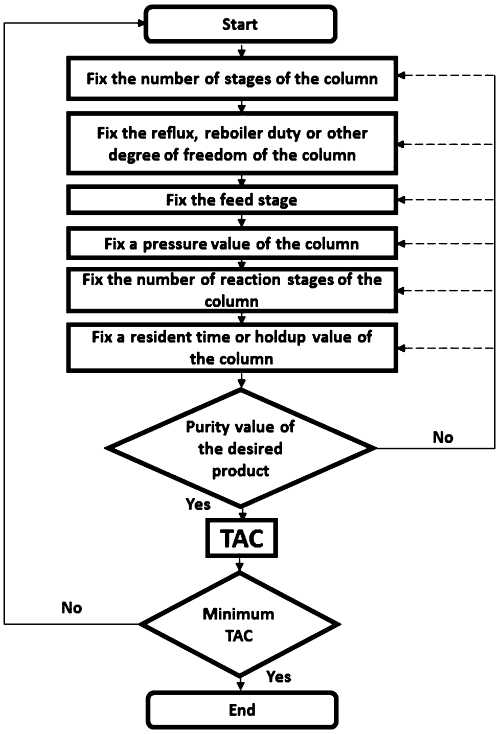

Figure 3. Algorithm to make a reactive column.

Table 2. Unit Eco-Indicator Used to Measure the Eco-Indicator 99 in Both Case Studies (Geodkoop and Spriensma[44])

impact category	steel (points/kg)	steam (points/kg)	electricity (points/kWh)
carcinogenic	$6.320\mathrm{e}^{-03}$	$1.180\mathrm{e}^{-04}$	$4.360\mathrm{e}^{-04}$
climate change	$1.310\mathrm{e}^{-02}$	$1.600\mathrm{e}^{-03}$	$3.610\mathrm{e}^{-06}$
ionizing radiation	$4.510\mathrm{e}^{-04}$	$1.130\mathrm{e}^{-03}$	$8.240\mathrm{e}^{-04}$
ozone depletion	$4.550\mathrm{e}^{-06}$	$2.100\mathrm{e}^{-06}$	$1.210\mathrm{e}^{-04}$
respiratory effects	$8.010\mathrm{e}^{-02}$	$7.870\mathrm{e}^{-07}$	$1.350\mathrm{e}^{-06}$
acidification	$2.710\mathrm{e}^{-03}$	$1.210\mathrm{e}^{-02}$	$2.810\mathrm{e}^{-04}$
ecotoxicity	$7.450\mathrm{e}^{-02}$	$2.800\mathrm{e}^{-03}$	$1.670\mathrm{e}^{-04}$
land occupation	$3.730\mathrm{e}^{-03}$	$8.580\mathrm{e}^{-05}$	$4.680\mathrm{e}^{-04}$
fossil fuels	$5.930\mathrm{e}^{-02}$	$1.250\mathrm{e}^{-02}$	$1.200\mathrm{e}^{-03}$
mineral extraction	$7.420\mathrm{e}^{-02}$	$8.820\mathrm{e}^{-06}$	$5.700\mathrm{e}^{-06}$

Currently, Aspen Plus simulator provides several modules where some chemical reactions can be modeled. To model an equilibrium reaction, aspen plus simulator provides a module named "REquil" which is appropriate for fast reactions that reach equilibrium quickly. Specifically, the block requires knowledge of the reaction stoichiometry and performs chemical and phase equilibrium reactions. Unlike other reaction blocks, the REquil block has vapor and liquid phase product streams (both are required). The only required information for this block is the output stream and the reaction. With this input, all calculation is made based on thermodynamics. The equilibrium constant is calculated at the outlet stream conditions. If the equilibrium constant needs to be estimated at a different temperature than reactor, input can be made in the temperature approach. If the extent of a reaction is known and no equilibrium calculations are needed, the molar extent can be defined directly as well.

With this in mind, the reactor was designed under equilibrium conditions, considering the global reaction (reaction 5) with temperature and pressure conditions of 25°and 1 atm,[32] respectively.

$$SiCl_4 + 4C_2H_5OH \rightarrow Si(OC_2H_5)_4 + 4HCl(g) \quad (5)$$

As concerning the thermodynamic interactions, the reactor was modeled considering the UNIQUAC method to predict all interaction among components. Note this method has been used for several authors to describe reaction among alcohols and many components in liquid phase; also it is able to describe the formation of vapor–liquid–liquid phases.[33,34] Once the reaction was performed, the separation/purification was further carried out in a conventional distillation column. Since it is needed to design a column to obtain high purity TEOS, the followed strategy was as follows (see Figure 2): (1) Specifically, five conventional distillation columns were designed with the short-cut methods of Underwood[35] to accomplish each target on TEOS purity. (2) Once all designs were developed, they were compared in order to keep a single design. For example, the total amount of equilibrium stages was compared, and it was kept the highest column; it happens the same with other physical size variables as diameter. With this consideration, the remaining purities were obtained varying other design variables such as distillate rate or reboiler heat duty but retaining the same sizing. (3) Finally, once the required purity was reached, a parametric test was performed, having an aim of maximizing the TEOS production minimizing the energy requirements and TAC value on each design. The general methodology just described has been proved in previous work with successful results.[36]

3.2. Reactive Distillation System. Having as preliminary work that described in section 3.1, and considering as a target the TEOS purity, a similar methodology was followed to find a single reactive distillation design able to cover all the levels of TEOS purity established. In other words, the design variables obtained in section 3.1 (stages, reflux ratio, diameter, etc.) were kept as initial values for the reactive distillation system. In addition, some heuristic rules were taken into account proposed previously by Subawalla and Fair.[33] This heuristic was summarized in an algorithm that can be used to estimate parameters such as column pressure, reactive zone location, total theoretical stages, reactant feed location, reflux ratio, column diameter, and packing height. With this in mind, those operative variables were further varied having as target and constrains both the purity of TEOS and the minimization in TAC, as shown in Figure 3. The variables that have the most impact on the minimization TAC are the column pressure, the number of stages, the reboiler duty, and the bottoms flow rate. On the other hand, other variables such as the feeding stage or holdup showed a minimal impact, practically negligible in the minimization of the TAC. The implementation of such algorithm is relatively simple. However, it cannot guarantee the optimal column design. As a highlight for Huang et al.,[34] there is a lack of heuristic rules for the optimal design of reactive distillation columns.

In accordance with the reaction-separation system, all reactive stages were considered under an equilibrium kinetic. As equal as a reactor, this model uses Gibbs free energy minimization to predict results requiring accurate thermodynamics calculations since Gibbs energy is calculated from enthalpy and entropy. In the same way, the UNIQUAC method was selected to predict all binary interactions. For the holdup calculation, as is expected, the larger the holdup, the easier is to achieve the desired conversion. However, it is not possible to set an arbitrary value. To find the appropriate holdup value, it was necessary to follow the methodology reported by Barbosa and Doherty.[37] The methodology consists first into specifying both the composition of the products (top and bottom) and the value of the reflux ratio (previously obtained by the Subawalla and Fair methodology).[33] Then, the aim is to find a suitable value for the holdup. In other words, to find the volume on the trays in which the reaction actually proceeds, such that when calculating the composition on each tray, the composition profiles of the stripper and rectifier intersect each other.[38]

Finally, it was possible to obtain a single design able to produce and reach the aimed TEOS purify in a single equipment. Once the purity was reached, the same parametric procedure was performed to maximize productivity and minimize energy requirements.

3.3. Economical and Environmental indexes. As has been described, for economic purposes, all designs were compared by means of the total annual cost (TAC) and the return of investment (ROI). On the other hand, the environmental impact was also measured by means of the Eco Indicator 99. In the paragraphs below, the cited indexes are described.

To calculate the total annual cost (TAC), the method published by Guthrie,[39] which was modified by Ulrich, was used.[40] The methodology performs cost estimation for industrial plants by separated units, and using equations published by Turton et al.,[41] the cost approximation is described in eq 6.

$$\mathrm{TAC} = \frac{\text{capital costs}}{\text{payback period}} + \text{operative costs} \quad (6)$$

The economic study performed considers 10 years as the recovery period. The plant is assumed to run 8500 h/year. Also, the following costs for heating and cooling were taken into account: high-pressure steam (42 bar, 254 °C, \$9.88/GJ), medium-pressure steam (11 bar, 184 °C, \$8.22/GJ), low-pressure steam (6 bar, 160 °C, \$7.78/GJ), and cooling water (\$0.72/GJ). Note that the costs of utilities used here are typical for a U.S. plant.[42]

Furthermore, considering a wider economical point of view, the evaluation of this project was also performed using other economic measures, the return of investment (ROI).[43] The ROI index measure is aimed at reducing the complex process of cash flow that takes place in different periods of time to one single number. In brief, ROI is a profitability measure that evaluates the performance of a business by dividing net profit by net worth. Return on investment (ROI) is defined in its most simplified form as shown in eq 7.

$$\mathrm{ROI} = \frac{\text{gain from Investment} - \text{cost of Investment}}{\text{cost of Investment}} \quad (7)$$

where Gain from investment refers to the proceeds obtained from the sale of the interest investment. With regard to the environmental evaluation, the impact was quantified using the life cycle assessment (LCA) principles by means of the Eco-Indicator 99 (EI99).[44] The eco-indicator 99 is calculated as follows:

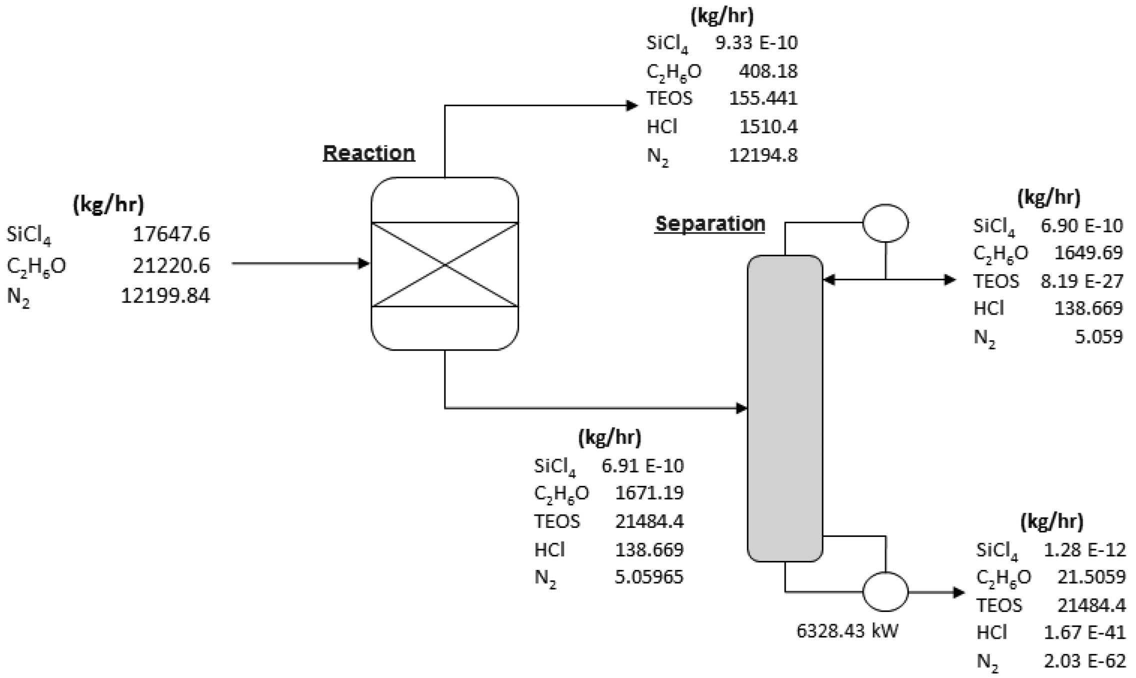

Figure 4. Mass balance for the reaction/separation system.

Table 3. Reaction/Separation Topology

mass purity (% wt)	98.5	99	99.2	99.5	99.7	99.9
stages	47	47	47	47	47	47
feed stage	19	19	19	19	19	19
condenser	total	total	total	total	total	total
reboiler	kettle	kettle	kettle	kettle	kettle	kettle
design specifications						
reflux ratio [mole]	5	5	5	5	5	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	8	8	8	8	8
column pressure drop [psia]	10	10	10	10	10	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	49.670	48.140	45.759
ECO 99 [Pt/y]	1.5134×10^{06}	1.5218×10^{06}	1.5250×10^{06}	1.5295×10^{06}	1.5327×10^{06}	1.5359×10^{06}

$$EI99 - \sum_{b}\sum_{d}\sum_{keK}\delta_d\omega_d\beta_b u_{b,k} \qquad (8)$$

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 in 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. The EI99 methodology considers 11 impact categories aggregated into three major damage categories: human health, ecosystem quality, and resources depletion. The scale is chosen in such a way that the value of 1 Pt (point) is representative for 1000th of the yearly environmental load of one average European inhabitant.[44] To analyze the schemes considered as cases of study, the impact calculation of three factors was considered as the most important: steam (used in column reboiler), electricity (used for pumping), and steel (to build distillation reactor, distillation column, and accessories). The values for those three factors are summarized in Table 2.

4. RESULTS

In the next section will be displayed all the obtained results, starting with the reaction-separation/purification system followed by the reactive distillation system.

4.1. Reaction-Separation/Purification System. As mentioned in the Methodology section, the target for this system is to design a reactor and a conventional distillation column to obtain TEOS at several purities. Note, since the target is to design a single column to reach such purities, the only variation was carried out in the design variables for the distillation column. In other words, only varying the distillate rate and reboiler heat duty was it possible to reach all the required purities.

As concerns the equilibrium reactor, Figure 4 shows a complete mass balance for a system that reaches 99.9 wt % of TEOS purity. Note in the liquid phase, to be further purified, is mainly obtained TEOS at 92.2% wt, where such purity is not high enough for reported industrial application because of the presence of HCl and ethanol. For such a reason, going forward it was necessary to design a distillation column to accomplish

Table 4. Reactive Distillation Column Topology

mass purity (% wt)	98.5	99.0	99.2	99.5	99.7	99.9
stages	15	15	15	15	15	15
feed stage	13	13	13	13	13	13
condenser	total	total	total	total	total	total
reboiler	kettle	kettle	kettle	kettle	kettle	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	17.76	17.76	17.76	17.76	17.76
pressure drop [psia]	10	10	10	10	10	10
reaction stages						
start stage	final stage					
3	10					
holdup						
start stage	final stage		vol [cum]			
3	10	10	0.2	0.2	0.2	0.2
TAC [$/y]	4.52 × 10⁰⁵	4.00 × 10⁰⁵	4.19 × 10⁰⁵	5.80 × 10⁰⁵	7.54 × 10⁰⁵	2.06 × 10⁰⁶
ROI [%]	52.382	59.290	56.590	56.030	40.737	11.410
ECO 99 [Pt/y]	2.1448 × 10⁰⁶	2.1449 × 10⁰⁶	2.1450 × 10⁰⁶	2.1452 × 10⁰⁶	2.1455 × 10⁰⁶	2.1477 × 10⁰⁶

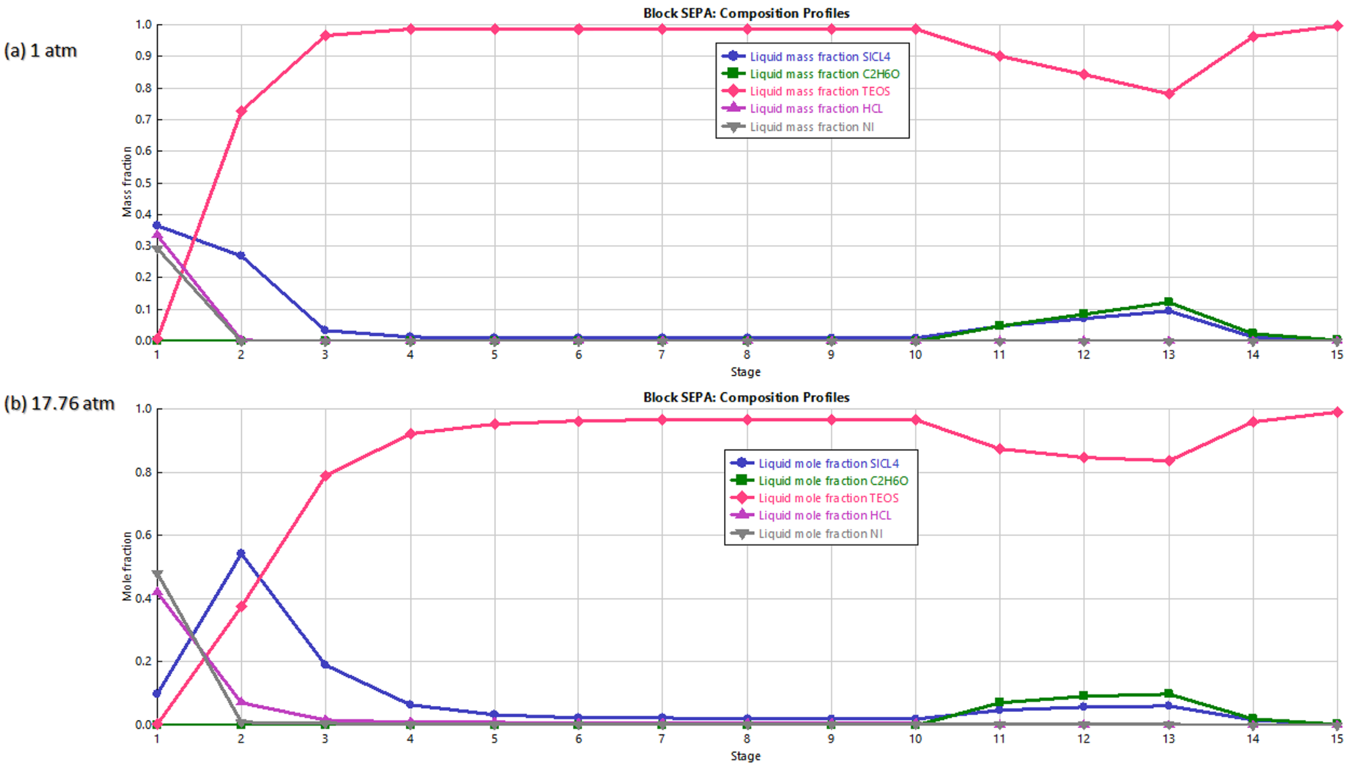

Figure 5. Composition profile of the RD column when it is operated at (a) 1 atm and (b) 17.76 atm.

all required purities. Table 3 shows the general topology for those designs. Note that, after results of short-cut methods, it was possible to obtain single columns. In this case, with 47 equilibrium stages was possible to obtain all purities. Important to consider, also, that only decreasing the reboiler duty in a range from 1.51 × 10^6 to 1.35 × 10^6 cal/s was the target reached. Besides, according to the mass balance in Figure 3, the TEOS recovery was superior to 99.9% wt.

4.2. Reactive Distillation System. After obtaining several designs for the two-steps reactor/separation/purification system, those designs were taken as a basis for the reactive distillation column. Therefore, for each two-steps case base, it was possible to perform a parametric analysis to obtain all design parameters involved in a reactive distillation column such as reactive stages, hold up, bottoms rate, etc. Finally, a single reactive distillation was designed to cover a wide range of purities. Table 4 describes the main characteristics of this system. Note, in a brief comparison among them, the variable that changes is the bottoms rate and reboiler heat duty: as long as there is an increase in the bottoms rate, a smaller purity is obtained. On the other hand, as long as reboiler duty decreases, the purity decreases as well.

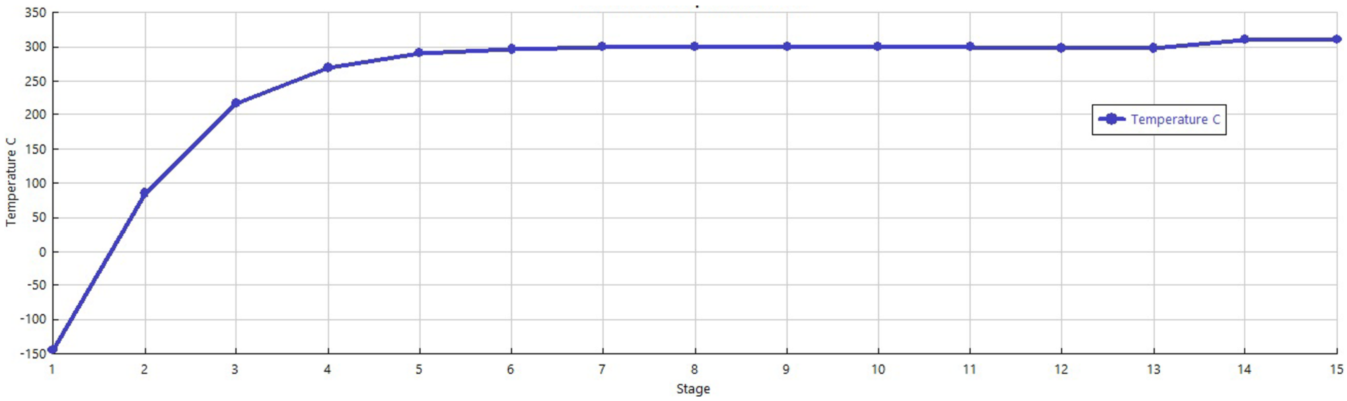

Figure 6. Temperature profile of the RD column at 98.5% wt.

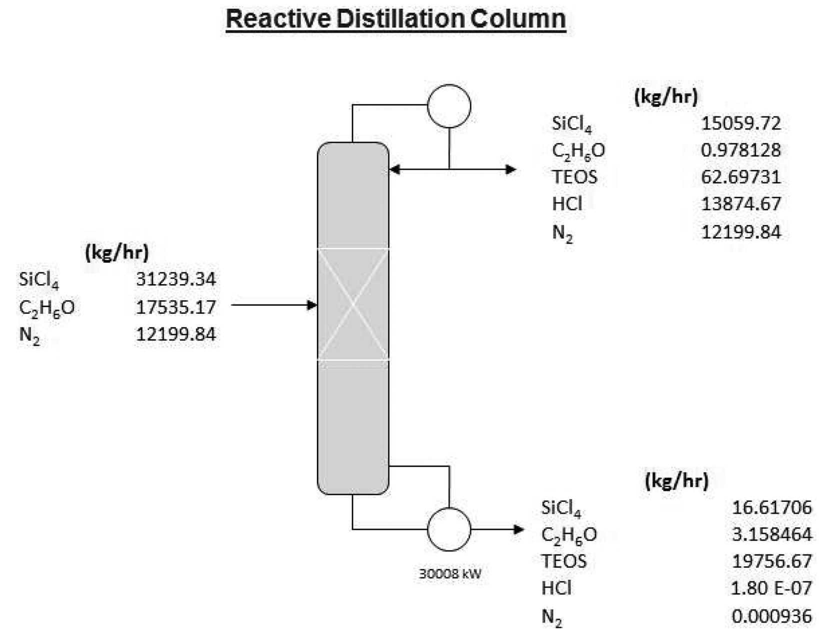

Figure 7. Mass balance for the reactive distillation system.

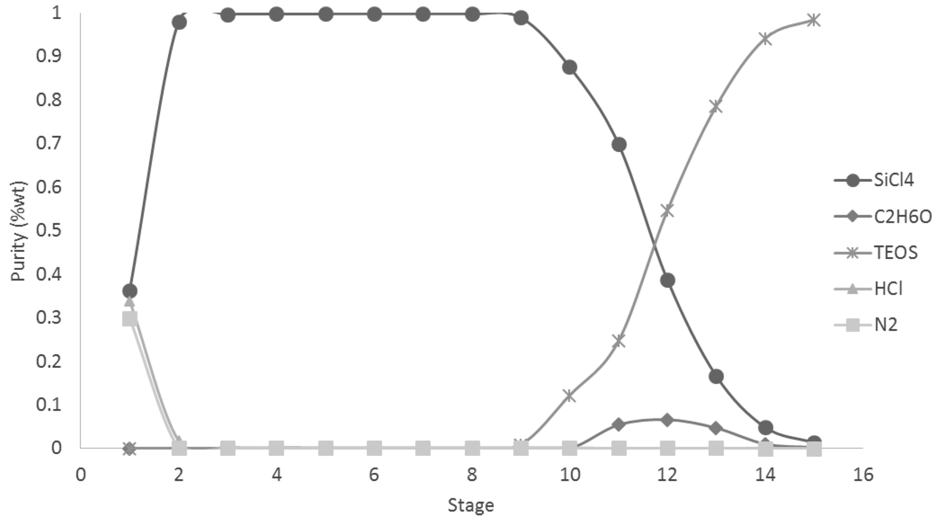

Figure 8. Concentration profile for the reactive distillation column for TEOS at 98.5% wt.

Initially, the RD design was performed at the same operative pressure as the reactor-separation system (see Figures 5 and 6), which denotes the feasibility of intensifying the reactor-separation system. In addition, the current operative pressure

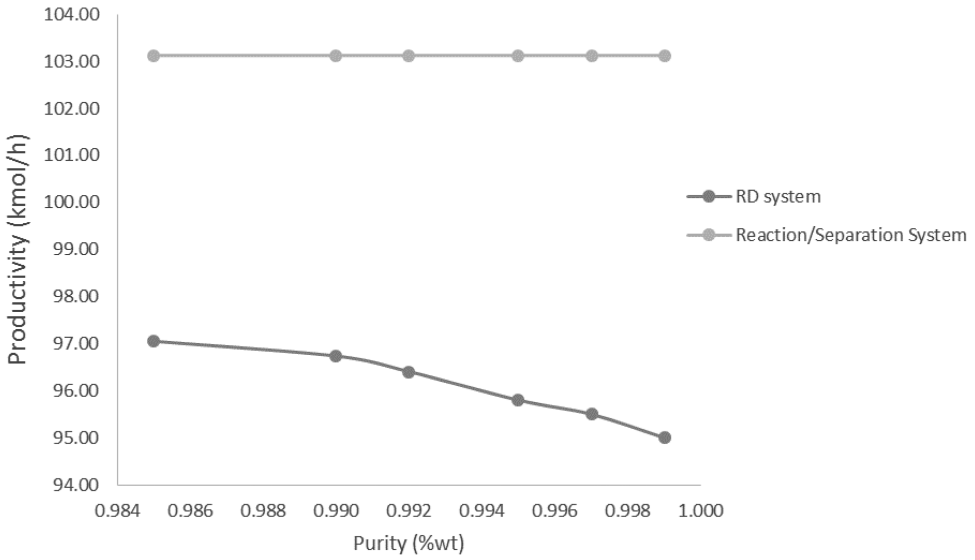

Figure 9. TEOS productivity for both analyzed systems.

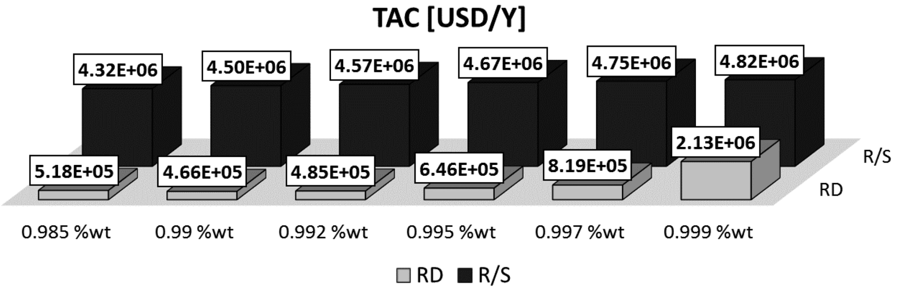

Figure 10. Total annual cost for both analyzed systems.

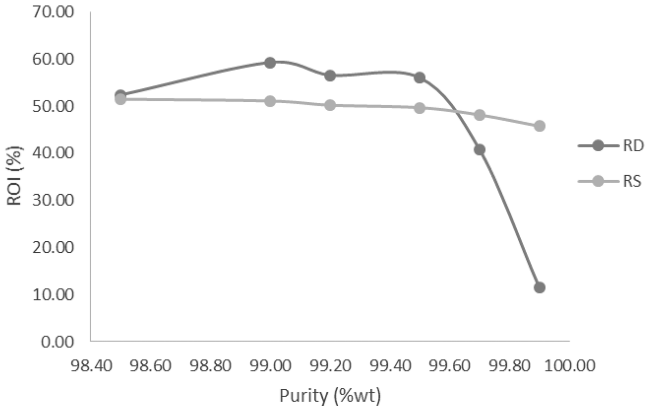

Figure 11. ROI values for reactive distillation system and reaction/separation system.

is in the range of the boiling point of the main product (boiling point of TEOS TB = 169 °C). However, in order to reduce the TAC value, it was necessary to set the operative pressure higher than the two reaction-separation process, otherwise operative cost would increase because of using refrigerant. Figure 7 shows a complete mass balance of RD. Furthermore, Figure 8 shows the composition profile of RD column at 99.9% wt. As preliminary comparison among the two-step system and the reactive distillation column, the energy requirement of RD is almost twice that of the reactor/separation system. On the other hand, according to Figure 9, the productivity for the reaction/separation/purification overcomes the RD by almost 10%. As regards sizing variables, it is clear that the RD systems obtain all required purities in a smaller column; also, RD operates at higher pressure. However, this size reduction allows reducing capital cost, and working at high pressure reduces the

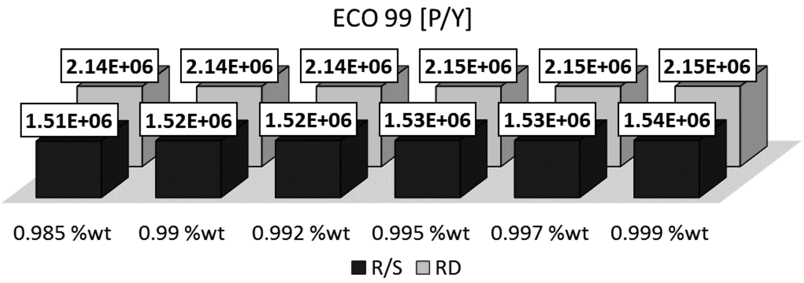

Figure 12. Environmental impact for reactive distillation system and reaction/separation system.

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Ind. Eng. Chem. Res. 2018, 57, 5024−5034

operative cost generated because of the refrigerant. However, since TAC, ECO 99, and ROI cover a wide aspect of the design, it could be expected interesting trends.

4.3. Economic and Environmental Comparison between Both Systems. In the previous paragraph, according to the topology for both systems, it is clear that the RD system is a high-energy demanding system. However, some indexes might be evaluated from a wider point of view regarding the performance of both systems. Observe in Figure 10 a general comparison about the total annual cost for both systems. Note the TAC of the reactive distillation column represents only an average percentage of 12% for low purities and near to 45% for a purity of 99.99% wt. The reason for this behavior is that TAC considers the reboiler heat duty as cost of service and also the cost of capital cost of equipment. Therefore, despite the high-energy consumption in RD, the reduction in capital cost of RD allows this system to overcome the reaction/separation system. Under this scenario, at any purity, the TAC of RD is wide lower than the two-steps system. However, when the ROI is evaluated, such trends only shows similarity at low purities. Remember as long as the ROI is higher, the process is more profitable. Note in Figure 11 that ROI values for the RD system are higher for purities below 99.5 wt %; once the system overcomes this purity a change in tendency is observed. In other words, for purities higher than 99.5 wt %, the two-step system is economically better than the RD system.

The reason for such tendency is the nature of the economic index. Remember, TAC calculation only considers the annualized 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 investmen, and expenses related with total investment (both main and auxiliary equipment), operative cost, and annual sales. Note the income by sales are associated with the productivity of the process and recall that the reaction/separation system showed higher productivity than the RD system. Under this scenario, the reason for that crossing in ROI (Figure 11) is that the RD system shows high operative cost at high purities, consequently the ROI value decreases. On the other hand, the productivity and sales are high enough for reactor/separation system to overcome the RD system at high purity.

With regard to the environmental impact, the two-step process overcomes the RD systems in 30% (see Figure 12). Please remember the source of environmental impact considered in this work was steel, steam, and electricity. Having this in mind and analyzing the environmental impact values of Table 2, it is easy to realize that the impact due to fossil fuels possesses a bigger weighting factor in comparison with other categories. Moreover, highlighting only the energy requirements of both systems, clearly RD systems demands a higher amount of energy. In such a way that combining the fossil fuel effect on Eco99 and the relatively high-energy requirement of the RD system, a high environmental impact measured by means of this life-cycle analysis methodology is produced.

Nevertheless, as has been previously analyzed despite RD energy consumption, its economic impact is mitigated because of its capital cost. Note that since the RD system is only designed with 15 equilibrium stages, its economic impact is reduced in comparison with the cost of 47 equilibrium stages and the reactor involved in the two-steps systems.

5. CONCLUSIONS

During this work, a purpose for TEOS production was approached by means of an intensified technology, the reactive distillation column. The design process was carried out in such a way that both RD and reaction/separation systems have been able to produce a wide range of TEOS purities. After both economic and environmental evaluation, the RD system showed lower values for the total annual cost in all purity range. However, analyzing other economic point of view which includes sales and expenses, the reaction/separation system overcomes the RD system when purities above 99.5 wt % are required. The economic trends observed is due to the slightly high TEOS production in the two-step system comparison with the intensified technology. Nevertheless, considering the high demand of TEOS at 98.5% wt allows one to consider the reactive distillation column as a quite promissory technology.

Moreover, regarding environmental impact, the RD system showed a higher impact. Such behavior is totally due to the high energy requirements of RD system in comparison with the traditional reactor/separation technology. In general terms, the RD system seems an appropriate technology since accounts with all the benefits of this technology include reduced equipment dimensions, increased process performance, and reduced equipment inventory. In general terms, RD technology showed better performance when several indexes were evaluated. As a conclusion, the RD technology is a promising alternative if all conditions are accomplished, for example, if the operative temperature in RD is in the range of the temperature of vapor−liquid equilibrium. On the other hand, this work could be further improved if a controllability test is applied in order to know the dynamic behavior of both systems in changing from a purity to another (lower to higher).

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Notes

The authors declare no competing financial interest.

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