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Evaluation Tool for the Environmental Design of Chemical Processes

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S Supporting Information

ABSTRACT: Since the environmental awareness increases and regulations become more restrictive, chemical industries are forced to adopt measures for minimizing the environmental impact and to include these techniques in the process design. This work proposes a methodology where environment and human health considerations are coupled with the process design of new and existing plants. With this aim, a new assessment tool for the environmental evaluation of chemical processes is presented. It includes the development of a new environmental indicator (Material Balance Environmental Index, MBEI) based on the toxicities of the chemicals involved and the materials flows between the process and environment. Moreover, a total index is computed following three levels of aggregation using the geometric mean of the ratios of several environmental impact categories. The environmental evaluation tool is tested using two case studies (formaldehyde and styrene production), where data are obtained from rigorous process simulation validated with industrial data.

1. INTRODUCTION

Chemical processes provide a diverse array of valuable products and materials ranging from health care to transportation and food processing, essential products to modern economies/societies. However, each process generates significant quantities of wastes and emissions to the environment. Chemical process design approaches range from shortcut models to rigorous-based simulators. Within most of the available design methodologies, environment, social, and human health concerns are rarely regarded to a higher level of consideration but rather as a set of constraints.[1]

Nevertheless, the present trends in the process design include finding alternatives for sustainable production, improving the energy safekeeping, reducing natural resources consumption, and protecting the climate.[2,3] The environmental potential impact has been incorporated as criterion for chemical process design in methods such as the atom efficiency,[4] mass loss indices,[5] and the Douglas method.[6] The Waste Reduction (WAR) algorithm, developed by the U.S. Environmental Protection Agency,[7] defines six potential environmental impact indices to find opportunities for pollution reduction derived from changes in the plant topology. The Environmental Fate and Risk Assessment Tool (EFRAT)[8] includes estimation of process releases, pollutant fate and transport, assessment of exposure potential, and relative risk assessment into a software tool, which can be integrated with a commercial process simulator package (i.e., Hysys or Aspen Plus). Chen and Shonnard[9] applied this tool following a hierarchical principle, where EFRAT is used in the evaluation of the environmental impacts, while the economic indicator complexity evolves depending on the design stages. Also within the hierarchical approaches, Hoffmann et al.[10] presented a procedure in which a large number of process alternatives are generated and screened, and then the most promising options can be analyzed in detail.

The method of Minimizing Environmental Impact (MEIM)[11] incorporates Life Cycle Assesment (LCA) principles in the chemical process design and optimization. Also from a LCA perspective Goedkoop and Spriensma[12] developed the Eco-Indicator 99. This indicator uses three environmental indices pondered based on the "distance-to-target" concept. Moreover, LCA can incorporate environmental concerns as objectives together with economic, product quality, and social requirements in a multiobjective optimization.[13−15] Sugiyama et al.[16] proposed a decision framework in four steps that includes monetary and nonmonetary objectives, focusing in the early design stages, process chemistry, and conceptual design.

Grossmann and Guillén-Gosálbez[17] and Gebreslassie et al.[18] also used LCA as a quantitative indicator of environmental impact to incorporate rigorous mathematical programming in the multi-objective optimization of the design and planning of sustainable process. On the other hand, Tugnoli et al.[19] and Hamid et al.[20] follow a different approach in sustainability assessment for decision support in process design that avoids LCA and rigorous mathematical programming in the optimization step.

In the research community there is still not a total agreement about an appropriate tool or metric to assess the environmental performance of a process. Furthermore, the implementation of environmental concerns into the process design and the systematization for obtaining alternatives to reduce the environmental impact is a challenge that needs to be developed.[21]

In this work an environmental evaluation procedure for a general process design methodology is presented. The philosophy of the design framework is first to measure the environmental performance of a process, in whatever phase of the design development, and use this measure as an objective function in combination with monetary and social concerns, as a powerful tool in the decision-making.

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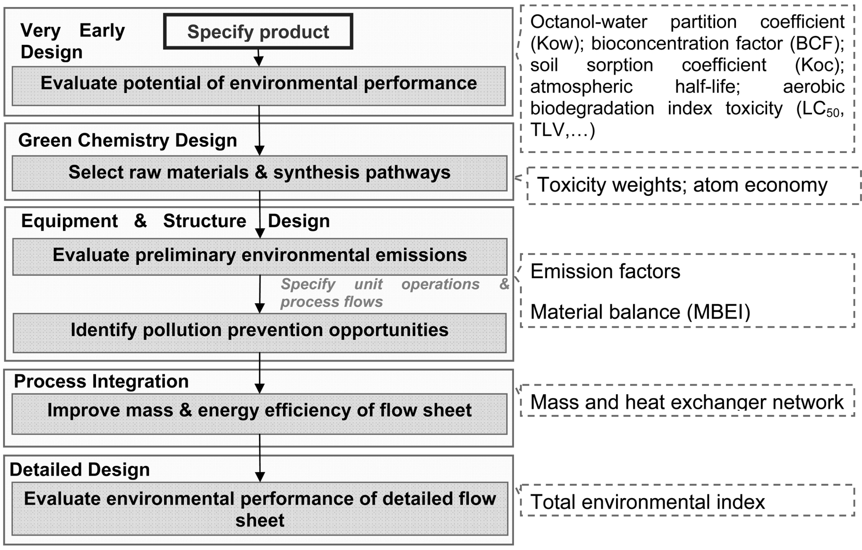

Figure 1. General hierarchy of process design including environmental assessment tools.

2. NEW ENVIRONMENTAL DESIGN APPROACH

The design procedure is based on the use of an impact evaluation tool, which is the focus of this paper, in combination with a general hierarchy as the framework to guide the process design toward better process as for environment. This tool can help in the generation of different alternatives and pollution prevention opportunities since it can identify hot spots of environmental damage and the direction to move to reduce the impact. The approach includes advantageous features that are common to previous works mentioned in section 1: (i) the simultaneous integration of environmental concerns in all stages of the process design; (ii) validity for new and existing plants; (iii) rigorous simulation for the acquisition of process data; (iv) evaluation of environmental impact that avoids the limitations of LCA in terms of availability and amount of data requirements; (v) simplicity in the normalization for the calculation of a single environmental index that avoids the use of external data of distance-to-target methods; (vi) easy implementation of economic and social indicators, and (vii) usefulness in process optimization purposes.

A general hierarchy for environmental design of chemical industries is shown in Figure 1. This hierarchy starts by specifying the product and a preliminary flow sheet. The work continues in two main stages, first the evaluation of all potential environmental impacts of the process and products to environment and human health (*a priori*). As a result, a preliminary input-output process flow sheet can be identified. The following step is the generation of modifications (including process integration and intensification) to reduce the generation of wastes, thus reducing the load on the treatment units, i.e. improved economics. The characteristic properties that influence the partitioning of all products and raw materials and their persistency in the environment elements of soil, air, and water are identified and assessed ahead of design. These properties are used to predict the potential impacts of chemicals and materials present in the process. Green chemistry principles are applied during the reaction design-step to evaluate the potential impact for each reaction pathway, to look for environmentally better approaches,

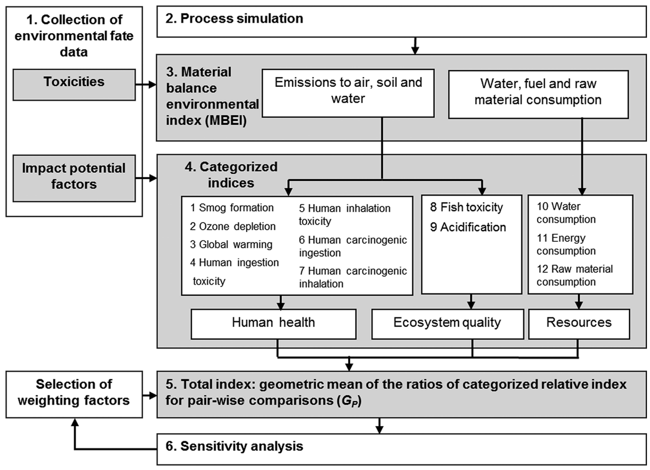

Figure 2. Flow diagram of the environmental evaluation tool.

and to select the best operating conditions that lead to minimum environmental impacts.

The search of alternatives for solvents, raw materials, separation units, reaction pathways, and integration/intensification opportunities have an important role in this work. Risk analysis is also evaluated during all design stages. The methodology can be applied to retrofit existing processes that exhibit large reported-environmentally impacts.

The evaluation of all potential environmental impacts of the process and products to environment and human health are estimated using a set of Environmental Performance Tools (dashed-boxes in Figure 1), which are based on the environmental fate properties of the substances involved. The evaluation procedure is performed within each design stage.

3. ENVIRONMENTAL EVALUATION TOOL

Figure 2 outlines the procedure of the environmental assessment through the calculation of environmental indicators using the process simulation results combined with environmental fate properties of the chemicals involved. As shown, there are five main steps, and three types of indicators with different level of aggregation are obtained. Each of these indicators enables drawing conclusions for finding opportunities to improve the environmental performance. The procedure can be applied independently to all stages of the process design although it has been developed for those stages where unit operations and process flow rates are specified.

Some of the environmental fate properties used in the calculations are octanol−water and plant/soil partition coefficients, bioconcentration factor, atmospheric half-life, and aerobic biodegradation index for all chemicals involved. If these data are not found in the open literature, their values are estimated based on group contribution methods.[22]

Hysys.Plant is used to obtain a rigorous model of the plant. The approach uses a dynamic link with the Component Object Module (COM) technology to connect with Excel. In general, the starting point is a simulation of a configuration with conditions taken from industrial data.[23,24] Materials, water, and energy consumption per kilogram of product are calculated. Releases of all chemicals to air, water, and land are accounted, including exhausted gases from the combustion of fuels and fugitive emissions from equipment leaks and storage. The emission factors and methods based on correlations are used to perform the emissions inventory.[25]

At this point, the material balance environmental indicator MBEI (eq 1) is calculated based on the net amount of materials transferred between the process and the environment, considering their toxicities. With such index, any process can be evaluated with respect to natural resource dissipations, for example water consumption. This tool is very relevant to materials which are considered scarce

$$MBEI = \sum_i MBEI_i = \sum_i [((-\sum E_i + \sum S_i)/P) \cdot TW_i] \quad (1)$$

where E_i and S_i are the inputs and outputs flows for compound i, P is the production of the main product, and TW_i is any toxicity weight selected as indicator of the environmental damage for each chemical.

In the next stage, twelve environmental indices are calculated following different categories of environmental impact. These categorized indicators were inspired by the Eco-Indicator 99,[12] and they are grouped in damage categories to the ecosystem quality, human health, and resources. The advantages of the approach presented in this work lie in the simplicity in the calculation of the indices, avoiding the large amount of data required for the LCA inventory and the normalization. Therefore, the procedure is more versatile for any modification in the process flow sheet and thus in the simultaneous integration of environmental concerns and design optimization. The calculation of the environmental quality and human health impacts (eq 2) implies the use of environmental impacts potentials (global warming potential, acid rain potential, maximum incremental reactivity), lethal concentrations and doses (LC_{50}, LD_{50}), hazard values, persistence lifetimes, and distribution factors of the compounds in air, water, and soil

$$I_k = \sum_{i=1}^{n} \left(\frac{IP_{k,i}}{IP_{k,bm}} \cdot R_i \right) \quad (2)$$

where I_k is the environmental impact for category k, n is the number of chemicals affecting category k, $IP_{k,i}$ is the impact potential for chemical i in the category k, $IP_{k,bm}$ is the impact potential for the benchmark chemical in the category k (*e.g.,* CO_2 for global warming), and R_i is the emission of component i. For some environmental categories, the impact potentials are not found in the open literature, and they have to be calculated following the risk assessment procedure of previous works.[7,26] The general expression (eq 3) involves a compartmental distribution factor of the chemicals that is predicted by a Level I multimedia compartmental model[27]

$$IP_{i,k} = II_{i,k} \cdot D_{i.c} \cdot \tau_{i,c} \quad (3)$$

where II_k is the inherent impact of chemical i for category k (*e.g.,* LC50, carcinogenic slope factor), $D_{i,c}$ is the distribution factor of chemical i in compartment c, and $\tau_{i,c}$ is the time persistence of chemical i in compartment c.

Finally, a total environmental index (G_p) based on the geometric mean of the ratios of categorized indices for pairwise comparisons is applied.[28] The metric shown in eq 4 can be extended to include other categories of concern such as social and economic indices

$$G_p = \left(\prod_{k=1}^{m} \left(\frac{y_k}{x_k} \right)^{C_k} \right)^{1/\sum_{k=1}^{m} C_k} \quad (4)$$

where G_p is the total environmental index for the process p, y_k and x_k are the categorized indices for a state and for the base state of the process, respectively, C_k is the weighting factor for the impact category k, and m is the number of environmental categories.

4. CASE STUDY 1: FORMALDEHYDE PROCESS

4.1. Process Description. Most of the worldwide production plants of formaldehyde use methanol as raw material. There are two types of processes, those using silver catalyst and an excess of methanol and those using ferric molybdate or metal oxide catalyst and an excess of air. Due to its reactivity, formaldehyde is usually transported in aqueous solutions (50% w/w). Figure S1 in the Supporting Information displays the flow sheet that can be used to outline both processes.

The major products of the silver catalyst process are formaldehyde, hydrogen, and water. Flow sheets for production facilities vary, but, in general, compressed air (previously scrubbed to remove impurities) is sent through a vaporizer column, where it is heated and saturated with methanol. This stream must maintain a methanol concentration greater than 37% v/v methanol in order to be above the upper explosive limit. The mixture enters the converter that operates around 635 °C. The hot effluent gases are cooled rapidly to prevent decomposition of the formaldehyde. The gas is then introduced into the absorber. Finally, the methanol is recovered in a vacuum distillation unit, obtaining the formaldehyde solution with less than 1% of methanol.

In the metal oxide catalyst process, the main products are formaldehyde and water. The process begins by mixing air, which has been scrubbed to remove dust and trace impurities, with oxygen-lean recycle gas from the process to lower the oxygen percentage of the air feed stream below 10.9%. This low oxygen content keeps the methanol concentration below the lower explosive limit when a portion of the air feed stream is saturated with methanol in the vaporizer column. The methanol-saturated air is then mixed with the remaining air and preheated before entering the converter, which is maintained at 345 °C by the

Table 1. Data of the Reaction Routes To Produce Formaldehyde from Methanol[25,26]

properties	FeMoCat (eq 5)	AgCat (eq 6)
mass efficiency	62.5%	75.0%
economic criteria	125.4 €/g CH_2O	125.5 €/g CH_2O
toxicity index (based on TLV)	100	100
reaction temperature	250−320 °C	600−650 °C
yield	90−95%	85−95%

exothermic oxidation reaction. The gas produced is cooled and quenched in the absorber column. The formaldehyde and the remaining methanol (0.8% approximately) are removed from the gas stream by absorption in the aqueous solution.

There are other synthesis routes. The direct oxidation of methane to formaldehyde attracts considerable research effort for the development of a successful cooling process and the reduction of production costs. Existing plants are obsolete and located near to low cost natural gas plants. A small portion of the formaldehyde produced comes from the oxidation of propane and butane. However, this process alternative is unlikely to be developed due to its poor selectivity. Dimethyl ether, a byproduct of methanol production, can be converted to formaldehyde in a process similar to the oxidation of methanol, but, to be competitive, dimethyl ether must be available in adequate quantities at a cost below that of methanol, which is not the case.

Considering all pathways, the objective of this work is to select the catalyst with lower environmental impact between the commonly used worldwide: ferric molybdate (FeMoCat) and silver catalyst (AgCat).

4.2. Catalyst Comparison. The application methodology starts with the evaluation of the environmental fate performance of the main product. In this case, formaldehyde is highly soluble in water, slightly volatile, and rapidly biodegraded and has a low bioaccumulation potential and soil sorption. Formaldehyde is classified as reasonably anticipated to be a human carcinogen based on limited evidence of carcinogenicity in humans and sufficient evidence of carcinogenicity in animals, classified in group 1 by the International Agency for Research on Cancer (IARC). This means that the environmental assessment of the production of formaldehyde will be highly dependent on the formaldehyde released.

In the selection of raw materials and synthesis pathways, the characteristics of an ideal chemical reaction are simplicity, safety, high yield, and selectivity, energy efficiency, and use of renewable and recyclable raw materials. Additional data of the kinetics and simulation of the two industrial routes to produce formaldehyde from methanol (eqs 5 and 6) are included in the Supporting Information (Table S1)

$$CH_3OH + 1/2O_2 \xrightarrow{FeMo\ catalyst} CH_2O + H_2O \qquad (5)$$

$$\left.\begin{array}{l} CH_3OH \xrightarrow{Ag\ catalyst} CH_2O + H_2 \\ CH_3OH + 1/2O_2 \rightarrow CH_2O + H_2O \end{array}\right\} \qquad (6)$$

In general, the two routes are slightly different (Table 1). On the one hand, the ferric molybdate catalyst (FeMoCat) has a lower mass efficiency, which gives an idea of the proportion of material wasted. On the other hand, the overall yield is higher and the lower reaction temperature results in less energy requirements, fewer

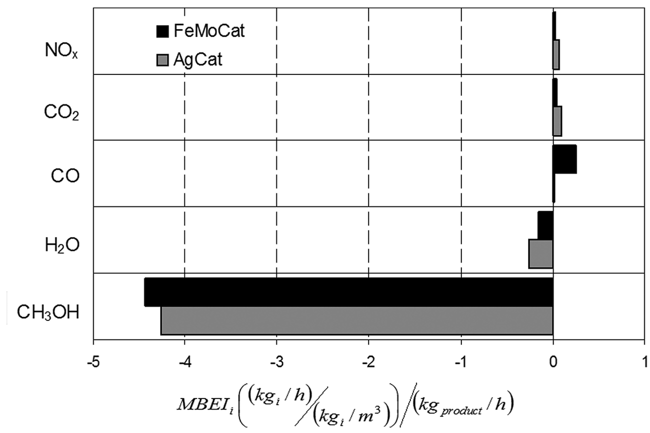

Figure 3. $MBEI_i$ of the production and consumption of chemicals.

secondary reactions, and less formaldehyde decomposition, thus avoiding further separation units (typically ion exchange). The difficulty for the catalyst selection requires to analyze the input-output flow sheet and to specify the unit operations, its operating conditions, and streams.

Basic equipment of both processes was simulated using Hysys. Plant. The flow sheets are very similar, consisting in plug flow reactors, absorption columns, and heat exchangers. Data for the reaction kinetics of the FeMoCat and AgCat processes were retrieved from the literature.[29,30] The simulation results lead to a preliminary environmental evaluation considering potential emissions, raw materials consumption, and energy requirements. Atmospheric releases of methanol and formaldehyde are calculated from the reactor and absorber,[31] fugitive emissions from an inventory of valves, pumps, flanges, and relief valves,[32] and emissions from storage tanks[33] assuming a production of 20,000 t/y of formaldehyde. Atmospheric releases of exhaust gases from the energy supply were calculated using emission factors for the combustion of natural gas.[34]

4.3. Results. In Figure 3 the MBEI for the most representative chemicals of the process are shown. The indices are calculated by applying eq 1, where the toxicity indices used are the threshold limit values (TLV). The amount of methanol and oxygen (raw materials) needed to produce the same quantity of product is slightly higher in the FeMoCat process, which is in consonance with the results of the atom efficiencies of the synthesis pathways. On the other hand, the FeMoCat process consumes less water mainly because the heating and cooling requirements are higher for the AgCat process due to its higher reaction temperatures. This is also the reason why the AgCat process has more emissions of pollutants associated with the exhausted gases, (*e.g.*, CO_2 and NO_x), except for CO, since it is also produced as a byproduct in the FeMoCat reaction. It is important to note that the $MBEI_i$ shown in Figure 3 are not representing only the amount of substance that is involved but the environmental impact that it symbolizes, since the index ponders each component according to its toxicity.

MBEI is useful for tracking chemicals along the process and thus for finding opportunities of environmental impact reduction. $MBEI_i$ of the main process emissions, distributed according different process sections, are represented in Figure 4.

In this case, the toxicity weights were selected according to the emissions fixed for industries as thresholds for public information by the European pollutant releases and transfers register (PRTR).[35]

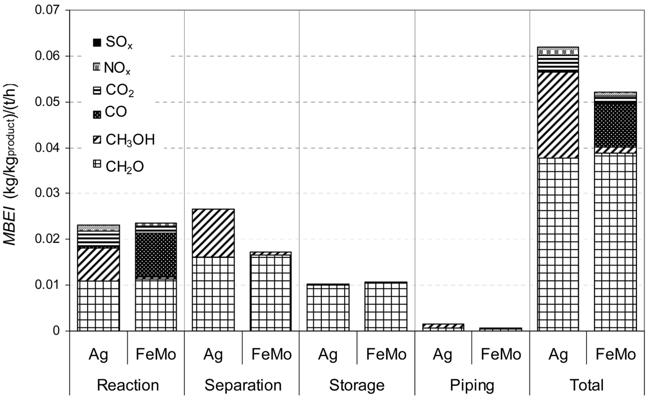

Figure 4. $MBEI_i$ of the production and consumption of chemicals in different process sections.

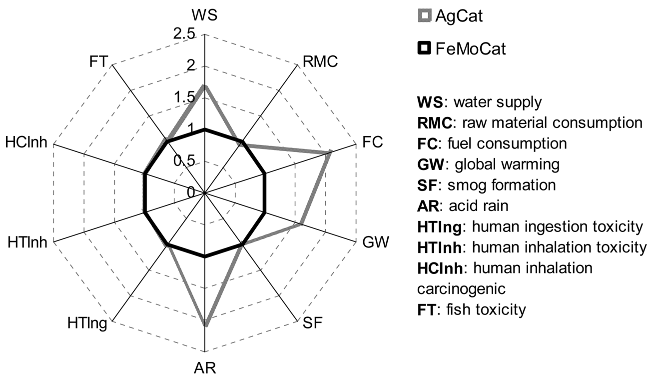

Figure 5. Categorized environmental impacts ratios.

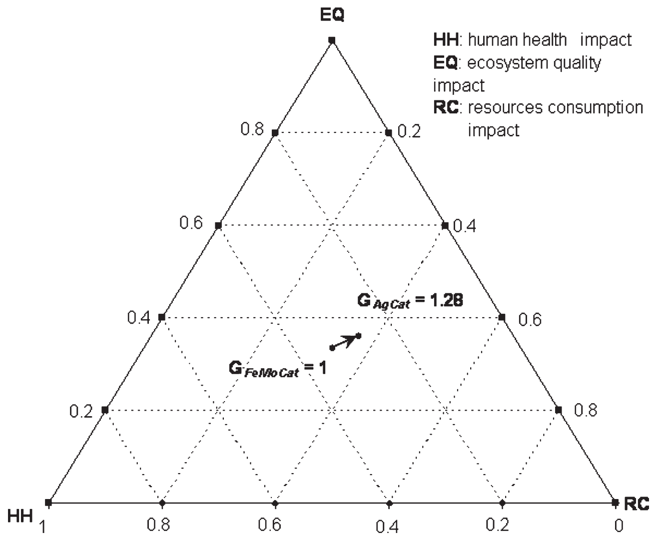

Figure 6. Ternary diagram representation of FeMoCat and AgCat processes.

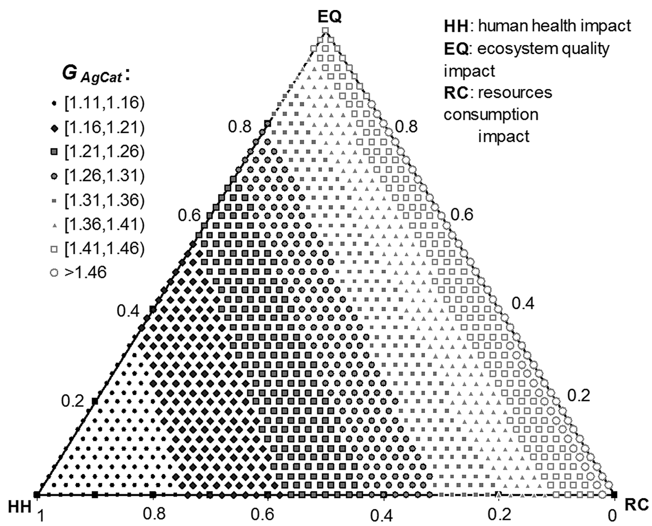

Figure 7. Ternary diagram for the analysis of the weighting factors combination in case study 1.

The use of weights related specifically to emissions was considered interesting since Figure 4 only takes into account the emissions of pollutants. The weights represent the maximum annual amount of pollutant released without having to be published, so their use can contribute to reinforce those impacts belonging to pollutants which are expected to have lower emissions. From Figure 4 several conclusions can be drawn. First, formaldehyde, methanol, and carbon monoxide emissions have an important role in the total environmental impact since their combinations of amounts and toxicity indices are relatively high. Second, according to the total results, the FeMoCat process is slightly less environmentally harmful than the AgCat process. Third, the reaction and separation steps account for most of the emissions, so both the reactor and absorber are the points of higher potential reduction in the environmental impacts. Finally, the emissions of formaldehyde are very similar for both processes.

Categorized indices are calculated in the second level of aggregation. Since they have a variety of units and different orders of magnitude of their values, the indices of the base case are taken as reference to make possible the comparison among the different impacts. Figure 5 shows the ratios of the categorized impacts taking as base case the FeMoCat process (x_k values in eq 4). Only ten of the twelve categorized environmental impacts presented in Figure 2 are shown in Figure 5. Ozone depletion impact is missing because there are not pollutants in this process with a potential damage associated to the destruction of the ozone layer. Regarding human carcinogenic ingestion impact, although formaldehyde is considered as a carcinogenic substance, the ingestion path is negligible because the distribution factor for water compartment is virtually zero and so is its impact potential ($IP_{k,i}$ in eq 2).

The total impact dependency on the formaldehyde emissions have as consequence that both alternatives have similar impacts in categories that depend on its carcinogenic effect to human health. On the other hand, the rest of the impacts are higher for AgCat process except for raw materials consumption. The overall conclusion is that the AgCat process can be considered as a poorer environmentally option.

The next calculation in the environmental evaluation procedure (Figure 2) is grouping all impact categories in three main environmental concerns, human health (HH), ecosystem quality (EQ), and resources consumption (RC). Weighting factors are used to compute the total environmental index (Gp) (in a first approximation equal values are used). The result of this calculation is a higher value of the total index and therefore a higher

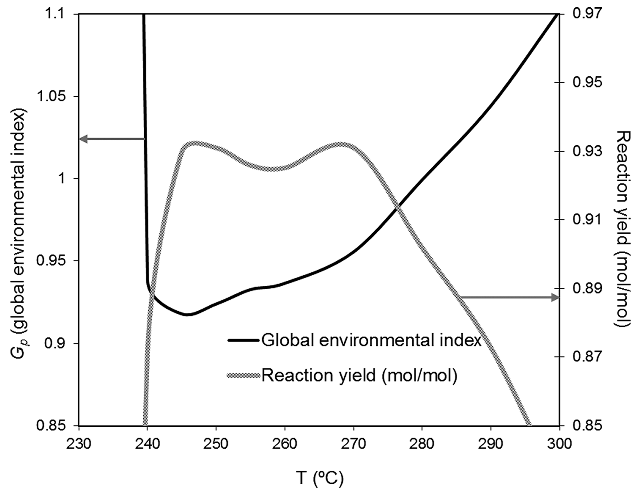

Figure 8. Influence of the reaction temperature on the environmental total index and the reaction yield.

environmental impact for the AgCat process, G_{AgCat} = 1.28 with respect to $G_{FeMoCat}$ = 1 for the base case. Figure 6 compares both alternatives by representing in the axes the ratios of HH, EQ, and RC in the total impact. Therefore the tendency of the AgCat process to consume more resources and to have a higher impact in the ecosystem quality can be seen, while the contribution of the human health impact for both processes is very similar.

The results of the total environmental index, as any aggregated indicator, are sensitive to the weighting factors used. Following the idea of the mixing triangle, developed by Hofstetter et al.,[36] in Figure 7 the ternary diagram can also be used to analyze the result of using a different combination of weighting factors. In Figure 7 the axes represent the weights, and the colors of the points indicate the values of the total index of AgCat. Since all values are higher than one (which is the base case FeMoCat), the AgCat process is more environmentally harmful for all possible combinations of factors. Figure 7 also shows that the lower importance given to the RC, the lower the total index of AgCat is. Nevertheless, even using a null weighting factor for RC, the environmental impact for AgCat is still greater than for FeMoCat.

Once the catalyst is selected, the procedure that has been described is also useful for finding operation conditions to obtain better environmental performance. This is the case of finding the best reaction temperature for the FeMoCat process. Figure 8 shows the variation of the total index G_p with the reaction temperature. As expected, the optimal temperature coincides with the one with higher reaction yield. Starting with a base case with a reaction temperature of 280 °C (G_{280} = 1), it is possible to achieve lower environmental impacts by decreasing the temperature to near 245 °C (G_{245} = 0.92) without compromising production.

5. CASE STUDY 2: STYRENE PROCESS

5.1. Process Description. In this section the environmental evaluation procedure is applied to the styrene production. The reaction for the dehydrogenation of ethylbenzene is endothermic, reversible, and limited by equilibrium (eq 7). The reaction occurs at high temperature (620−700 °C) and side reactions take place: formation of benzene and ethylene (eq 8) and hydrogenation of ethylbenzene to toluene and methane (eq 9).

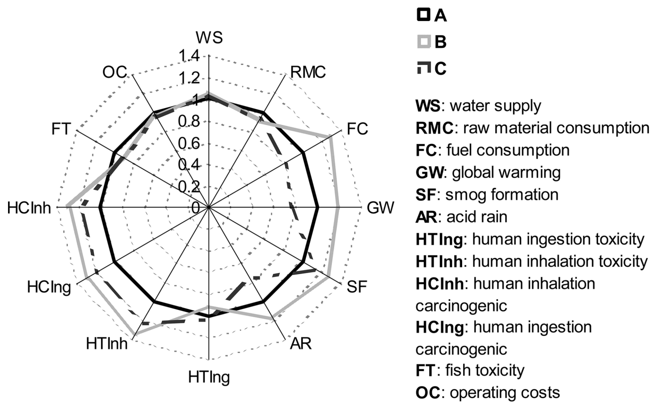

Figure 9. Categorized impacts ratios for the processes A, B, and C.

Kinetic data were taken from previous works[37]

$$C_6H_5C_2H_5 \leftrightarrow C_6H_5C_2H_3 + H_2 \tag{7}$$

$$C_6H_5C_2H_5 \rightarrow C_6H_6 + C_2H_4 \tag{8}$$

$$C_6H_5C_2H_5 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \tag{9}$$

A preliminary flow sheet of the process includes preheating the ethylbenzene to a saturated vapor that is mixed with steam to provide the heat of reaction. Steam also limits side reactions, working as an inert diluent to shift the reaction to products and preventing coke formation on the catalyst. The reaction product is cooled, and water and crude styrene are condensed in a three phase separator. The hydrogen-rich gas stream is recovered to use as fuel, the bottom phase is wastewater, and the remaining crude liquid styrene, containing most of the toluene, benzene, and ethylbenzene, enters a distillation train. Most of the toluene and benzene is removed at the top of the first column, while ethylbenzene is recycled and mixed with fresh feed.

Three different process flow sheets are considered in the study. The base case is process A (Figure S2 in the Supporting Information). Process B (Figure S3 in the Supporting Information) includes the use of two reactors in a series with an intermediated heat exchanger fed with steam; the purpose of this change is to reach high reaction yields decreasing the reaction temperature and the steam ratio in the feed. Process C (Figure S4 in the Supporting Information) uses the heat released while it cools the product stream to preheat the raw materials and to obtain low pressure steam for the boilers of the distillation columns; simultaneously, the steam entering the process is used in the heat exchanger between both reactors. All configurations have a production of 100,000 t/y of 99.8 wt % styrene.

5.2. Economic Criterion Implementation. Economic considerations are also included in this study. The operating cost per unit of product is calculated taking into account the product value, the feed cost, electricity, water treatment, fuel cost, steam, cooling, and water requirements. The environmental impacts were calculated as shown in the previous section. The same sources of information were used for the atmospheric emissions calculation, except for the emission factors associated with the styrene production.[38] Figure 9 shows the ratios of the economic and environmental impacts taking process A as base case. As in the previous case study, ozone depletion impact is not considered because there are not pollutants in this process with available data in the literature of potential damage to ozone layer.

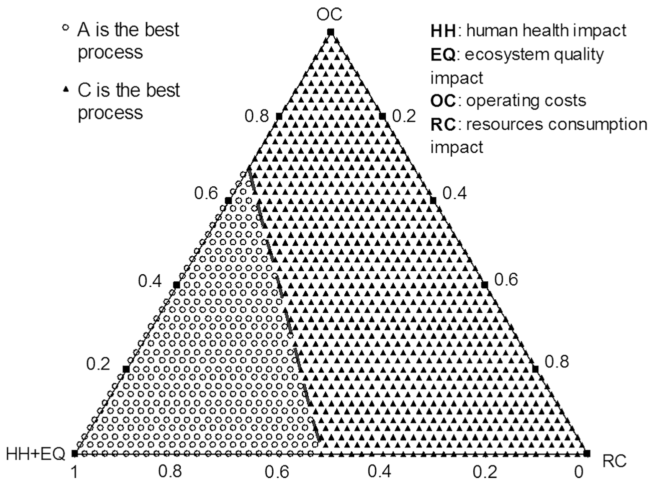

Figure 10. Ternary diagram for the analysis of the weighting factors combination in case study 2.

Without any further information, in Figure 9 process B seems to be the less desirable option because its high environmental impacts are not balanced with a decrease in the operating costs and the water and raw materials consumption. The reason for this increase with respect to process A are the higher emissions of exhausted gases from the natural gas combustion in steam production and the higher volatile organic compounds emissions from the reactors. On the other hand, process C has also higher environmental impacts in the categories related with the emissions of volatile organic compounds, but this issue can be compensated with lower operating costs and resource consumption. In fact, the natural gas required is lower, which make process C better in categories such as global warming and acid rain impacts.

The total indices (G_p) are calculated for each configuration using equal weighting factors for all environmental and economic criteria. The differences between the three alternatives are small, but small differences in the total indicator could have important impact implications. We can conclude that process C is the best configuration according to environmental and economic criteria ($G_C = 0.98$) and process B is worse than the other configurations ($G_B = 1.12$). Moreover, Figure 10 shows under which conditions (i.e., which weighting factors) processes A, B, or C are the best option. Each point in Figure 10 represents the process with a lower value of G_P.

The weighting factors analysis in Figure 10 illustrate that process B would be never selected as the best solution, whatever combination of weighting factors is chosen. The more suitable configuration between A and C will depend on the importance that is given to each criterion. Figure 10 shows a clear frontier that differentiates among both processes, depending on the weighting factors used. The orientation of this frontier (dashed line) suggests that process A is the best option when more importance is given to human health and ecosystem quality impacts. On the contrary, if the three categories have similar weighting factor, or if the consumption of resources and the operating costs are judged as more important, process C becomes the best option. In fact, considering only HH+EQ impacts (the weighting factor for the OC and the RC criteria are null) the total index of process C reaches its maximum value ($G_C = 1.08$), whereas the minimum ($G_C = 0.92$) is reached when only RC impacts are considered ($C_{RC} = 1$). This quantitative information is really valuable when decision-makers have to ponder the different alternatives.

6. CONCLUSIONS

In this paper an environmental evaluation tool in the decision-making framework of process design is described. A general design methodology based on the integration of environmental concerns in all process design stages is developed. The environmental evaluation procedure is carried out through the use of three types of indicators, following three levels of aggregation. The material balance environmental indices (MBEI) can translate the interactions between the process and the environment, quantifying the flows of materials between them. Twelve categorized indices account for different environmental concerns related to human health, ecosystem quality, and resources depletion. Finally, the total index (G_P), based on a geometric mean, allows the comparison of the total impact within design alternatives. Following this procedure, the environmental performance of the processes can be easily analyzed, which can help to establish the direction for new improving opportunities.

The method has been applied to two case studies that have proven the usefulness of the new development. In both cases a chemical process is studied with attention to the emissions of the volatile compounds released to air from the equipment leaks, storage tanks, and combustions, especially those considered as carcinogenic agents. However, in the study case of the formaldehyde production the environmental performance tool is used in an earlier step of the process design, in which only an input-output structure of flow sheet is defined, and thus the procedure is used to select raw materials and synthesis pathways assuming a simple sketch of process with reaction, separation and storage. Besides, the results of the study are particularly affected by the presence of formaldehyde as a carcinogenic substance, this fact implies that almost every change toward reducing environmental damage must be preceded by a decrease in the formaldehyde emissions per unit of product. By contrast, the styrene production is analyzed through the simulation of a more detailed diagram flow, in which unit operations and process flows are already defined so the equipment and structure design is possible. The greater complexity of this case hinders from obtaining straightforward solutions, but at the same time it allows us to show the versatility of the procedure.

Therefore the objectives for the two cases studied are different. In the production of formaldehyde the best catalyst was selected: ferric molybdate is less environmentally harmful than silver. In addition, the quantitation of the environmental impacts through this procedure was proven useful in the optimization of operating conditions (e.g., reaction temperature) considering environmental concerns. In the second case, styrene production from ethylbenzence, the capacity of the tool for the incorporation of other criteria (i.e., economic criteria), was demonstrated. The results show the contribution of this procedure in the decision-making of the process design. Finally, the ternary representation shows the dominance of the different alternatives.

The environmental tool presented has two main limitations that should be considered in future research. First, the tool by itself does not systematically generate new alternatives; this must be done using a hierarchy for the design process in combination with engineering expertise, systematic sensitivity analysis, real process data, etc. Nevertheless, one of the advantages of this methodology is that the analysis of the results can be used to help the engineer in the generation of alternatives by finding, for instance, key units/process variables in the plant with higher possibilities of waste reduction or heat and mass integration. Second, a sensitivity analysis is needed for the establishment of the resolution of the total index G_p and the robustness of the results, the understanding of the relationships between inputs and outputs, and the identification of the important criteria to avoid redundancy in the impact indices.

ASSOCIATED CONTENT

S Supporting Information. Process flow sheet of case study 1 (supplemental Figure S1); additional data for case study 1 (supplemental Table S1); and Hysys simulation flow sheets for the case study 2: processes A (supplemental Figure S2), process B (supplemental Figure S3), and process C (supplemental Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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NOMENCLATURE

AR : acid rain impact
BCF : bioconcentration factor
C_k : weighting factor for category k
$D_{i,c}$: distribution factor of chemical i in compartment c
E_i : input flow rate of chemical i (kg/h)
EQ : ecosystem quality impact
FC : fuel consumption (m^3 NG/kg product)
FT : fish toxicity impact
G_p : total index of process p, geometric mean of the ratios of categorized indices
GW : global warming impact
HH : human health impact
HCIng : human carcinogenic impact by ingestion route
HCInh : human carcinogenic impact by inhalation route
HTIng : human toxicity impact by ingestion route
HTInh : human toxicity impact by inhalation route
I_k : environmental impact of category k (kg/kg product)
$II_{i,k}$: inherent impact of chemical i for category k
$IP_{i,k}$: potential impact of chemical i for category k
K_{OC} : soil sorption coefficient
K_{OW} : octanol−water partition coefficient
LC_{50} : lethal concentration for half the population sample (ppm)
LD_{50} : lethal dose for half the population sample (mg/kg)
MBEI : material balance environmental index
OP : operating costs index
P : product flow rate (kg/h)
$PRTR_i$: emission threshold of chemical i (EC, 2006) by the pollutant releases and transfer European register (t/h)
R_i : emission of chemical i (kg/kg product)
RC : resources consumption impact
RMC : raw materials consumption (kg/kg product)
S_i : output flow rate of chemical i (kg/h)
SF : smog formation impact
TLV_i : threshold limit value of chemical i (kg/m^3)
TW_i : toxicity weight for chemical i (TLW_i, $PRTR_i$...)
WS : water supply (kg/kg product)
x_k : environmental impact of category k for a specific state
y_k : environmental impact of category k for the base case state
$\tau_{i,c}$: time persistency of chemical i in compartment c; air (years), water (days)

REFERENCES

(1) Dantus, M. M.; High, K. A. Economic Evaluation for the Retrofit of Chemical Processes through Waste Minimization and Process Integration. *Ind. Eng. Chem. Res.* **1996**, *35* (12), 4566–4578.
(2) Annakou, O.; Mizsey, P. Rigorous Comparative Study of Energy-Integrated Distillation Schemes. *Ind. Eng. Chem. Res.* **1996**, *35*, 1877–1885.
(3) Rév, E.; Emtir, M.; Szitkai, Z.; Mizsey, P.; Fonyó, Z. Energy Savings of Integrated and Coupled Distillation Systems. *Comput. Chem. Eng.* **2001**, *25*, 119–140.
(4) Sheldon, R. A. Catalysis: The Key to Waste Minimization. *J. Chem. Technol. Biotechnol.* **1997**, *68* (4), 381–388.
(5) Heinzle, E.; Weirich, D.; Brogli, F.; Hoffmann, V. H.; Koller, G.; Verduyn, M. A.; Hungerbühler, K. Ecological and Economic Objective Functions for Screening in Integrated Development of Fine Chemical Processes. 1. Flexible and Expandable Framework Using Indices. *Ind. Eng. Chem. Res.* **1998**, *37* (8), 3395–3407.
(6) Douglas, J. M. Process Synthesis for Waste Minimization. *J. Chem. Technol. Biotechnol.* **1992**, *31* (1), 238–243.
(7) Cabezas, H.; Bare, J. C.; Mallick, S. K. Pollution Prevention with Chemical Process Simulators: The Generalized Waste Reduction (WAR) Algorithm - full version. *Comput. Chem. Eng.* **1999**, *23* (4−5), 623–634.
(8) Shonnard, D. R.; Hiew, D. S. Comparative Environmental Assessments of VOC Recovery and Recycle Design Alternatives for a Gaseous Waste Stream. *Environ. Sci. Technol.* **2000**, *34* (24), 5222–5228.
(9) Chen, H.; Shonnard, D. R. Systematic Framework for Environmentally Conscious Chemical Process Design: Early and Detailed Design Stages. *Ind. Eng. Chem. Res.* **2004**, *43* (2), 535–552.
(10) Hoffmann, V. H.; Hungerbühler, K.; McRae, G. J. Multiobjective Screening and Evaluation of Chemical Process Technologies. *Ind. Eng. Chem. Res.* **2001**, *40* (21), 4513–4524.
(11) Stefanis, S. K.; Buxton, A.; Livingston, A. G.; Pistikopoulos, E. N. A Methodology for Environmental Impact Minimization: Solvent Design and Reaction Path Synthesis Issues. *Comput. Chem. Eng.* **1996**, *20* (Suppl. 2), S1419–S1424.
(12) Goedkoop, M.; Spriensma, R. *The Eco-indicator 99. A Damage Oriented LCIA Method*; PRèConsultant B.V. Amersfoort: The Netherlands, 2001.
(13) Azapagic, A.; Clift, R. Linear Programming as a Tool in Life Cycle Assessment. *Int. J. Life Cycle Assess* **1998**, 3 (6), 305–316.
(14) Alexander, B.; Barton, G.; Petrie, J.; Romagnoli, J. Process Synthesis and Optimization Tools for Environmental Design: Methodology and Structure. *Comput. Chem. Eng.* **2000**, *24* (2−7), 1195–1200.
(15) Azapagic, A.; Millington, A.; Collett, A. A Methodology for Integrating Sustainability Considerations into Process Design. *Chem. Eng. Res. Des.* **2006**, *84* (6), 439–452.
(16) Sugiyama, H.; Fischer, U.; Hungerbühler, K.; Hirao, M. Decision Framework for Chemical Process Design Including

Different Stages of Environmental, Health, and Safety Assessment. *AIChE J.* **2008**, *54* (4), 1037–1053.

(17) Guillen-Gosalbez, G.; Caballero, J. A.; Jimenez, L. Application of Life Lycle Assessment to the Structural Optimization of Process Flowsheets. *Ind. Eng. Chem. Res.* **2008**, *47*, 777–789.

(18) Gebreslassie, B. H.; Guillén-Gosálbez, G.; Jiménez, L.; Boer, D. Design of Environmentally Conscious Absorption Cooling Systems via Multi-objective Optimization and Life Cycle Assessment. *Appl. Energy* **2009**, *86* (9), 1712–1722.

(19) Tugnoli, A.; Santarelli, F.; Cozzani, V. An Approach to Quantitative Sustainability Assessment in the Early Stages of Process Design. *Environ. Sci. Technol.* **2008**, *42* (12), 4555–4562.

(20) Hamid, M. K. A.; Sin, G.; Gani, R. Integration of Process Design and Controller Design for Chemical Processes using Model-based Methodology. *Comput. Chem. Eng.* **2010**, *34* (5), 683–699.

(21) Grossmann, I. E.; Guillén-Gosálbez, G. Scope for the Application of Mathematical Programming Techniques in the Synthesis and Planning of Sustainable Processes. *Comput. Chem. Eng.* **2010**, *34* (9), 1365–1376.

(22) Allen, D. T.; Shonnard, D. R. *Green Engineering: Environmentally Conscious Design of Chemical Processes*; Prentice Hall PTR: NJ, 2002.

(23) Tesser, R.; Di Serio, M.; Santacesaria, E. Catalytic Oxidation of Methanol to Formaldehyde: an Example of Kinetics with Transport Phenomena in a Packed-bed Reactor. *Catal. Today* **2003**, *77* (4), 325–333.

(24) Vasudevan, S.; Rangaiah, G. P.; Konda, N. V. S. N. M.; Tay, W. H. Application and Evaluation of Three Methodologies for Plantwide Control of the Styrene Monomer Plant. *Ind. Eng. Chem. Res.* **2009**, *48* (24), 10941–10961.

(25) Eastern Research Group, Inc. *Emission Inventory Improvement Program. Technical Reports Series*; U. S. Environmental Protection Agency: NC, 1997; Vol. 1−10. http://www.epa.gov/ttnchie1/eiip/techreport/ (accessed October 25, 2011).

(26) Heijungs, R.; Guinée, J. B.; Huppes, G.; Lankreijer, R. M.; Udo De Haes, H. A.; Wegener, A.; Sleeswijk, A. M.; Ansems, M.; Eggels, P. G.; Van Duin, R.; De Goede, H. P. *Environmental life cycle assessment of products (Technical Report 9267)*; NOH: Leiden, The Netherlands, 1992.

(27) Mackay, D. *Multimedia environmental models: the fugacity approach*; Lewis Publishers: FL, 2001.

(28) Sikdar, S. K. On Aggregating Multiple Indicators into a Single Metric for Sustainability. *Clean Technol. Environ. Policy* **2009**, *11* (2), 157–161.

(29) Bazilio, C. A.; Thomas, W. J.; Ullah, U.; Hayes, K. E. The Catalytic Oxidation of Methanol. *Proc. R. Soc. London, Ser. A* **1985**, *399* (1816), 181–194.

(30) Gonzo, E. E.; Gottifredi, J. C. Steady State Simulation of a Packed Bed Reactor for the Partial Oxidation of Methanol to Formaldehyde. Influence of Diffusional Phenomena and Catalyst Activity Distribution within the Pellets. *Chem. Eng. Commun.* **1998**, *168*, 127–143.

(31) Office of Air Quality Planning and Standards. *Locating and Estimating Air Emissions from Sources of Formaldehyde*; U. S. Environmental Protection Agency: NC, 1991.

(32) Epperson, D.; Barbour, W.; Zarate, M.; Beauregard, D. *Preferred and Alternative Methods for Estimating Fugitive Emissions from Equipment Leaks (Technical Report for Point Sources Committee, Emission Inventory Improvement Program)*; U.S. Environmental Protection Agency: NC, 1996.

(33) Office of Air Quality Planning and Standards. *Emission Factor Documentation for AP-42 Section 7.1 Organic Liquid Storage Tanks (Technical Report)*; U.S. Environmental Protection Agency: NC, 2006.

(34) Office of Air Quality Planning and Standards. *Emission Factor Documentation for AP-42 Section 3.2 Natural Gas Fired Reciprocicating Engines (Technical Report)*; U.S. Environmental Protection Agency: NC, 2006.

(35) European Pollutant Release and Transfer Register and amending Council Directives 91/689/EEC and 96/61/EC, Regulation 166/2006, January **2006**; *Official Journal of the European Union*, *L 33*, 1−17.

(36) Hofstetter, P.; Braunschweig, A.; Mettier, T.; Müller-Wenk, R.; Tietje, O. The Mixing Triangle: Correlation and Graphical Decision Support for LCA-based Comparisons. *J. Ind. Technol.* **1999**, *3* (4), 97–115.

(37) Snyder, J. D.; Subramaniam, B. A Novel Reverse Flow Strategy for Ethylbenzene Dehydrogenation in a Packed-bed Reactor. *Chem. Eng. Sci.* **1994**, *49* (24), 5585–5601.

(38) Office of Air Quality Planning and Standards. *Locating and Estimating Air Emissions from Sources of Styrene*; U. S. Environmental Protection Agency: NC, 1993.