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Pollution Balance: A New Methodology for Minimizing Waste Production in Manufacturing Processes

Ahmad K. Hilaly and Subhas K. Sikdar
Environmental Protection Agency
Cincinnati, Ohio

A new methodolgy based on a generic pollution balance equation, has been developed for minimizing waste production in manufacturing processes. A "pollution index," defined as the mass of waste produced per unit mass of a product, has been introduced to provide a quantitative measure of waste generation in a process. A waste reduction algorithm also has been developed from the pollution balance equation. This paper explains this methodology and demonstrates the applicability of the method by a case study.

Introduction

The design of a chemical process involves many steps of complex mathematical and heuristic analyses. A process design begins with the construction of a preliminary flowsheet for a desired product. The subsequent phases of process design include equipment selection, considerations of process safety, choice of optimal conditions, cost estimates, and profit analysis. A designer chooses a particular flowsheet because its cost estimate is the most favorable. In traditional process design, minimizing the cost usually takes precedence over the environmental impact of the process. This cost minimization paradigm often leads to the production of large quantities of toxic compounds, which subsequently must be treated for destruction or disposal. Growing environmental awareness, however, demands process technologies that minimize or prevent production of wastes. In this paper we propose a simple concept of pollution balance in a process flowsheet and present a waste reduction algorithm derived from it. For minimizing waste production, this algorithm can be used to design new processes as well as modify existing processes.

The first issue in any pollution prevention methodology is to provide a quantitative measure of waste production in a process. There is no sound organizing principle, however, that can serve as a basis for measuring pollution production in a process. Different investigators have adopted different approaches in this regard[1-3]. One way of attacking the problem is to define an index, which should provide a reasonable measure of environmental impact of the process being designed. Also, the index should allow comparison of pollution production in different processes.

The aim of this paper is to address these vital issues of pollution prevention by formulating a new methodology based on a generic pollution balance equation. The methodology is called WAR, which stands for waste reduction. A process simulator is coupled with WAR to calculate material balance, estimation, and optimization. We present below the development of the algorithm and show its application with a case study. The case was chosen to represent a realistic process, although in practice the minute details of the process may be somewhat different from those in the case study. The new methodology is the main focus of the paper; the case study only serves as a means for demonstrating the applicability of the algorithm.

Development of the Pollution Balance Equations:

The WAR algorithm is based on a generic pollution balance equation of a process flow-diagram (Figure 1), which consists of several unit processes and operations, such as a mixer, a reactor, and a separator. For one unit and for an entire flowsheet, the principle of pollution balance equation may be written as:

(Pollution Inputs) + (Pollution Generated)
= (Pollution Accumulation) + (Pollution Outputs)
+ (Pollution Leakage in Fugitive Emissions)

If the flow rates of input streams to a unit (process or operation) are denoted by I_j ($j = 1,2,.....$) and the concentrations (mass fraction) of waste components in each I_j are represented by x_i ($i = 1,2,.....$), we can write the following:

$$\text{pollution input (for one unit): } \sum_j \sum_i I_j x_i ,$$

$$\text{pollution input (for a flowsheet): } \sum_k \sum_j \sum_i I_{j,k} x_{i,k}$$

where $k = 1,2,.....$ indicates the number of units in a flowsheet.

Similarly, if the flow rates of output streams from a unit are denoted by O_j ($j = 1,2,..$), we can write

pollution output (for one unit): $\sum_j \sum_i O_j x_i$,

pollution output (for a flowsheet): $\sum_k \sum_j \sum_i O_{j,k} x_{i,k}$.

If F_k ($k = 1,2,....$) denotes the flow rates of fugitive emissions from the k-th unit operation, we can write

pollution leakage (for a flowsheet): $\sum_k \sum_i F_k x_{i,k}$.

If in a chemical reaction, r_i represents the rate of formation of a waste component i with a molecular weight MW_i in a reactor with volume V, we can write

pollution generation (for one unit): $V \sum_i r_i MW_i$,

pollution generation (for a flowsheet): $\sum_k V_k \sum_i r_i MW_i$.

If the process is under unsteady state condition, we can write

pollution accumulation (in one unit): $\dfrac{d}{dt}(\sum_i V \rho x_i)$,

pollution accumulation (in a flowsheet): $\dfrac{d}{dt}(\sum_k \sum_i V_k \rho_k x_{i,k})$

where ρ_k denotes the average density of the components in the k-th unit operation.

Therefore, the general pollution balance equation for a process can be expressed as:

$$\frac{d}{dt}(\sum_k \sum_i V_k \rho_k x_{i,k}) = \sum_k \sum_j \sum_i I_{j,k} x_{i,k} + \sum_k V_k \sum_i r_i MW_i -$$
$$\sum_k \sum_j \sum_i O_{j,k} \cdot x_{i,k} - \sum_k \sum_i F_k x_{i,k} \qquad (1)$$

In this formulation we define a waste material as a nonproduct that is not used up in the process itself or any subsequent process in a production facility. While this accounts for wastes in aqueous streams, it does not regard water *per se* a waste material.

When a process is under steady state condition, the accumulation term drops out from the pollution balance equation :

$$\sum_k \sum_j \sum_i I_{j,k} \cdot x_{i,k} + \sum_k V_k \sum_i r_i \cdot MW_i =$$
$$\sum_k \sum_j \sum_i O_{j,k} \cdot x_{i,k} + \sum_k \sum_i F_k \cdot x_{i,k} \qquad (2)$$

The pollution balance approach allows us to assign a "pollution index" of a product manufactured by a process. The pollution index
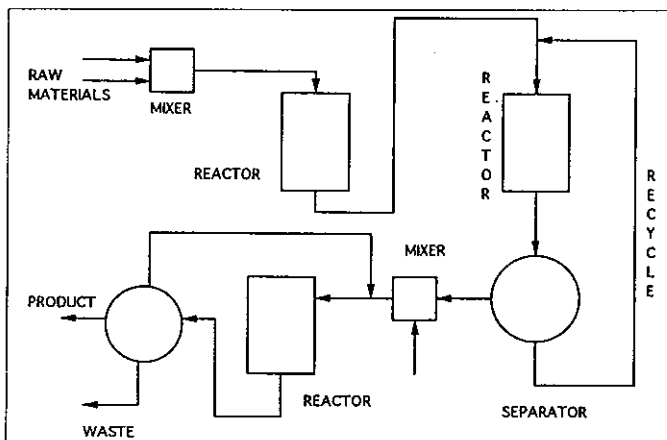
of a product is defined as the amount of waste produced per unit mass of the product. The pollution index of a product can be derived from Equation 2, as shown below.

Raw materials employed in a process are often the products of several preceding processes and therefore may have already produced wastes. The raw materials in this case will have their own pollution indices, depending upon how much waste they generated in the preceding processes.

If a unit mass of I_j already produced W_j mass of wastes in the preceding processes, then adding $\sum_k \sum_j I_{j,k} W_{j,k}$ on both sides of the above equation, we get

$$\sum_k \sum_j I_{j,k} \cdot W_{j,k} + \sum_k \sum_j \sum_i I_{j,k} \cdot x_{i,k} + \sum_k V_k \sum_i r_i \cdot MW_i =$$
$$\sum_k \sum_j \sum_i O_{j,k} \cdot x_{i,k} + \sum_k \sum_i F_k \cdot x_{i,k} + \sum_k \sum_j I_{j,k} \cdot W_{j,k} . \qquad (3)$$

The sum of the first two terms on the right side of Equation 3 is the total waste produced in the process. The third term is the waste produced in the preceding processes related to the raw materials. The right side of Equation 3 therefore represents the total amount of waste produced from an overall viewpoint.

A process may have several coproducts [$P_n(n = 1,2,.....)$]. The total waste produced in a process then must be allocated to the co-products. The allocation can be done reasonably, based on the molar ratio of the coproducts, because the products and pollutants are produced according to the stoichiometry of the reactions. If ω_n denotes the fraction of the total pollution attributed to a unit mass of a product P_n, we can write

$$\omega_n = \frac{1}{P_n} \frac{(P_n/MW_n)}{\sum_n (P_n/MW_n)} . \qquad (4)$$

When the right side of Equation 3 is mulitplied by ω_n, we obtain the amount of waste produced per unit mass of a product P_n, which is the pollution index (Φ_n) of the product. Therefore, the equation may be expressed as:

$$\Phi_n = \omega_n (\sum_k \sum_j \sum_i O_{j,k} \cdot x_{i,k} + \sum_k \sum_i F_k \cdot x_{i,k} + \sum_k \sum_j I_{j,k} \cdot W_{j,k}) . \qquad (5)$$

From Equation 3 and 5, we derive

$$\Phi_n = \omega_n (\sum_k \sum_j I_{j,k} \emptyset_{j,k} + \sum_k V_k \sum_i r_i \cdot MW_i) \qquad (6)$$

where $\emptyset_{j,k}$ denotes the pollution index of input $I_{j,k}$ and is given by:

$$\emptyset_{j,k} = \frac{I_{j,k} \sum_i x_{i,k} + I_{j,k} \cdot W_{j,k}}{I_{j,k}} \qquad (7)$$

The pollution index defined by Equation 6 integrates the wastes attributed to all input materials with those that are generated in the process under analysis. This index therefore provides, in a nutshell, the overall environmental impact of manufacturing a product.

When the raw materials do not contain any waste components and did not produce any wastes in the preceding processes, $\emptyset_{j,k}$ is zero and the expression for pollution index is given by:

$$\Phi_n = \omega_n \sum_k V_k \sum_i r_i \cdot MW_i. \qquad (8)$$

The Waste Reduction Algorithm

Figure 2 demonstrates the use of the proposed algorithm. First, a flowsheet is constructed and the material balance calculations are carried out. The pollution indices of the overall process and different streams are calculated. A process flowsheet is selected after all the alternative flowsheets are considered. A cost analysis is conducted to evaluate the economics of the selected process.
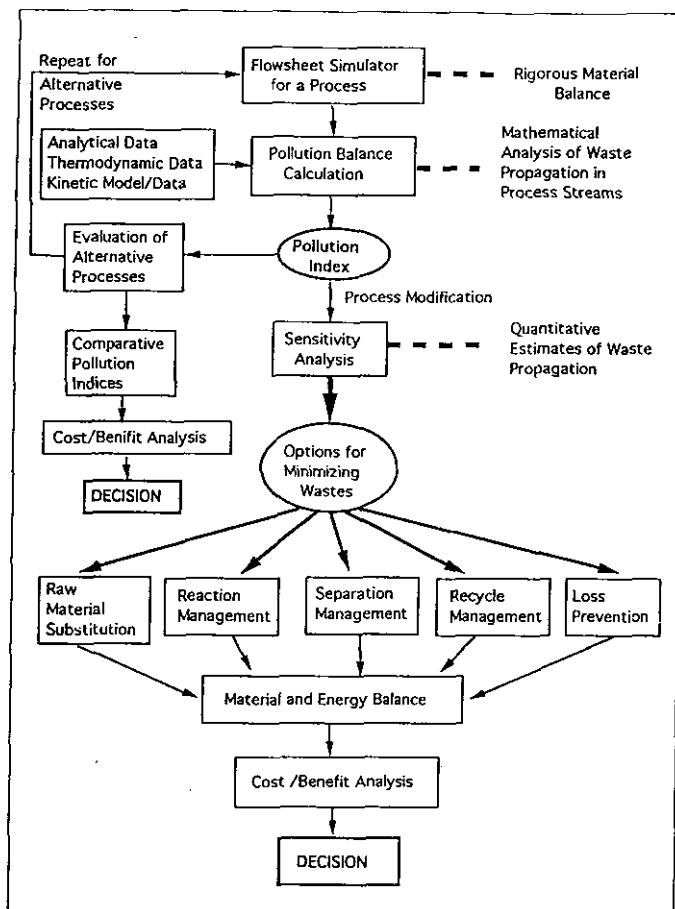

Figure 1. A general flowsheet of a manufacturing process.

Figure 2. The waste reduction (WAR) algorithm.

If the process is not cost-effective, then other process alternatives must be considered. The final decision is reached after an iterative evaluation of the pollution index and cost analysis. The optimum process may not necessarily be the least polluting, but may be desirable for other reasons.

In the case of an existing process that must be modified, attention is focused upon the streams with high pollution indices. Only the waste components that exit the process are considered in calculating the pollution index of a stream. Based on the values of the pollution indices of the streams, the algorithm determines which unit operations must be considered for modification. The algorithm conducts a sensitivity analysis to determine which important variables must be changed. Thus, the sensitivity analysis provides options for modifications including material substitution, reaction/unit operation management, separation/recycle management and loss prevention. Following the necessary modifications, the best option is selected on the basis of a cost analysis.

PC-Based Software

The WAR algorithm is designed for use on a PC with the Windows operating system. Muliple screens were designed to provide an effective and friendly user interface. The WAR algorithm and a commercial process simulator run sequentially by multi-tasking in the Windows environment. We used CHEMCAD II (Chemstations, Inc., Houston, TX) although any commercial process simulator can be used. The algorithm enables the user to perform various actions in an interactive fashion. The implementation of the WAR algorithm is illustrated by an example of the production of a detergent in the following section.

A Case Study

Description of the process

Figure 3 shows a simplified flowsheet for the production of a detergent. Benzene and dodecene react to form dodecylbenzene in the presence of the catalyst aluminum chloride ($AlCl_3$). This alkylation requires a surplus of benzene for obtaining high yields; usually about 90% conversion takes place in the alkylator.[4-6] The catalyst is separated from the crude alkylate in a slurry settler. A fraction of the spent catalyst is reused and the rest is discarded. The liquid alkylate mixture from the settler is then fed to three distillation columns in series to recover the unreacted benzene and dodecene. The third distillation column separates dodecylbenzene from the heavy alkylate fractions. Dodecylbenzene is then charged into a sulfonation reactor, where dodecylbenzene reacts with
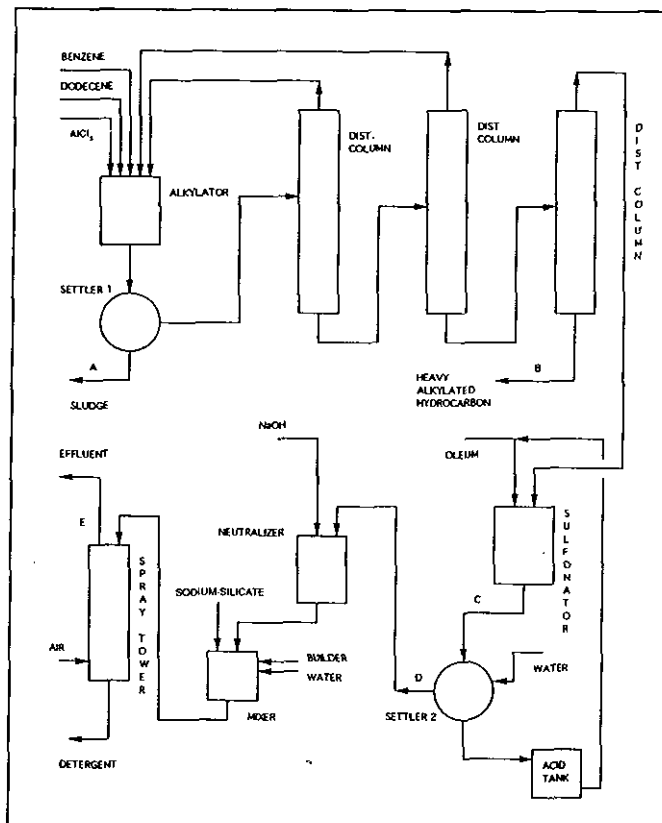

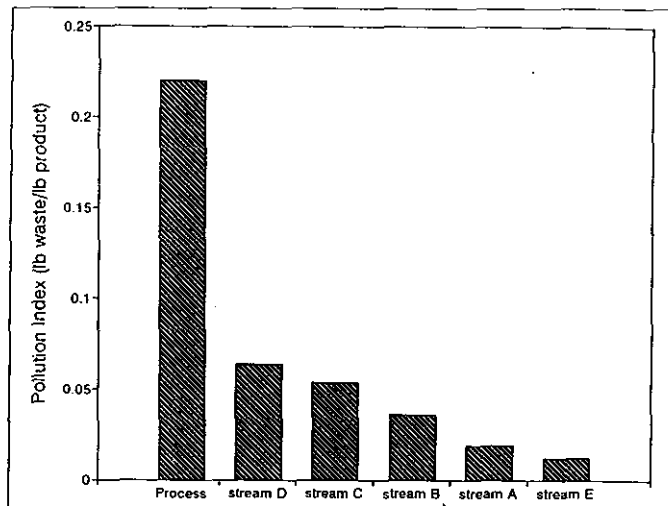**Figure 3.** A simplified flowsheet for the production of a detergent.

Figure 4. The pollution indices of the overall process and several streams.

oleum (20% SO₃) to form dodecylbenzene sulfonic acid. The conversion in the sulfonator is about 95%. A small amount (about 5%) of disulfone is produced as a by-product. The spent sulfuric acid is removed in a settler, where large amounts of water are added to dilute the acid concentration. The sulfonic acid is neutralized by adding sodium hydroxide in a neutralizer forming sodium dodecylbenzene sulfonate and the waste product Na_2SO_4. Various builders, namely trisodium phosphate and sodium silicate, are added to the neutralized mixture. The mixture is then fed to a spray dryer to produce dried detergent powder.

Material Balance Summary :

Unit: lb/day.
Inputs

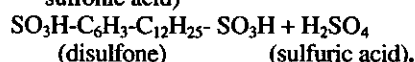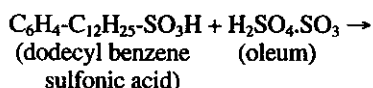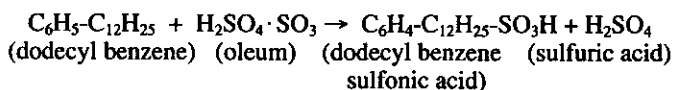|	
Benzene:	9523.8
Dodecene:	20,523.1
AlCl₃(catalyst):	750.0
Oleum (20% SO₃)	28,394.4
Sodium Hydroxide Solution (20% concentration):	35,640.3
Sodium Silicate:	1,907.6
Sodium Polyphosphate:	3,815.2
Water:	24,911.3
Total:	125,465.7

Outputs
AlCl₃ sludge (waste)

AlCl₃:	750.0
Benzene:	23.7
Dodecene:	51.1
Heavy Fractions (waste):	1,577.4
Solids in Effluent (waste):	505.4
Water Vapor in Effluent:	50,435.3
Spent Acid Solution:	21,993.0

Powdered Product

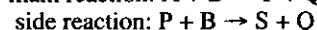|	
Sodium-dodecyl-benzene-sulfonate:	37,770.5
Sodium-disulfonate (waste):	2,570.3
Sodium Sulfate (waste):	4,023.6
Sodium Silicate:	1,888.5
Sodium Polyphosphate:	3,777.0
Total:	125,465.7

Application of the WAR Algorithm

The pollution indices of the overall process and several streams are shown in Figure 4. Streams D, B, C, A and E contain appreciable amounts of wastes, which ultimately lead to the overall pollution index for the process. To reduce the pollution index, the operating units associated with those streams were taken into consideration. The following actions were undertaken to achieve the goal:

1. Stream D: The high pollution index of stream D was caused by the presence of sulfuric acid and disulfone. The flow rate of the washwater in settler two was increased from 7098.6 lb/day to 19318.1 lb/day. As a result, the acid concentration in stream D decreased from 73.6% to 50%. This measure significantly reduced the amount of sodium sulfate in the final product.

2. Stream C: Disulfone was formed in the sulfonator as a by-product. The sulfonation reactions are

C_6H_5-$C_{12}H_{25}$ + H_2SO_4·SO_3 → C_6H_4-$C_{12}H_{25}$-SO_3H + H_2SO_4
(dodecyl benzene) (oleum) (dodecyl benzene (sulfuric acid)
sulfonic acid)

C_6H_4-$C_{12}H_{25}$-SO_3H + $H_2SO_4.SO_3$ →
(dodecyl benzene (oleum)
sulfonic acid)
SO_3H-C_6H_3-$C_{12}H_{25}$- SO_3H + H_2SO_4
(disulfone) (sulfuric acid).

The type of the reaction may be expressed as:

main reaction: $A + B \rightarrow P + Q$
side reaction: $P + B \rightarrow S + Q$

where A is dodecyl benzene, B is oleum, P is dodecyl benzene sulfonic acid, Q is sulfuric acid and S is disulfone. From the material balance equations of each component, it is possible to write

$$\frac{[C_p]}{[C_{AO}]} = \frac{X_A(1 - X_A)}{(1 - X_A) + X_A K e^{-\frac{\Delta E}{R.T}}} \qquad (9)$$

where [C] represents concentration, x denotes conversion, R is the gas constant, T is the temperature and K is the ratio of rate constants of the side reaction to the main reaction at reference temperature. Equation 9 implies that the formation of the main product P strongly depends on the temperature. Figure 5 shows that when temperature is increased, the fractional conversion of the main product increases, which in turn decreases the by-product. Thus, by optimizing the temperature, the formation of disulfone can be reduced to 1%.

3. Stream B: The third distillation column separated the heavy alkylated fractions, which were supplied to a lubricating oil facility. Waste was converted to a usable product, thereby reducing the overall pollution index substantially.
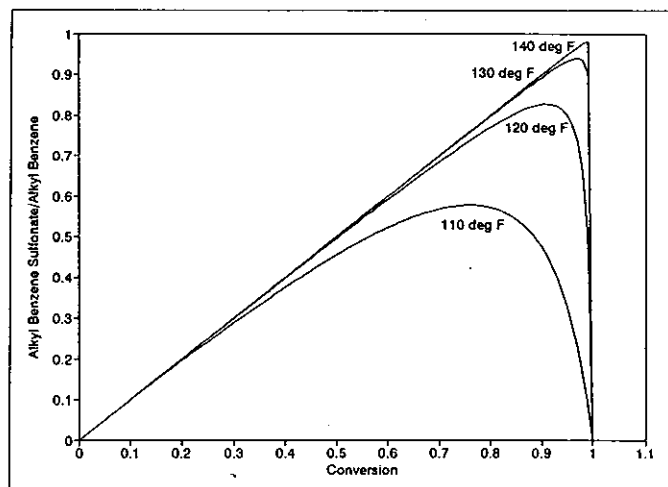

Figure 5. The effect of temperature on the fractional conversion of the main product (alkyl benzene sulfonate).
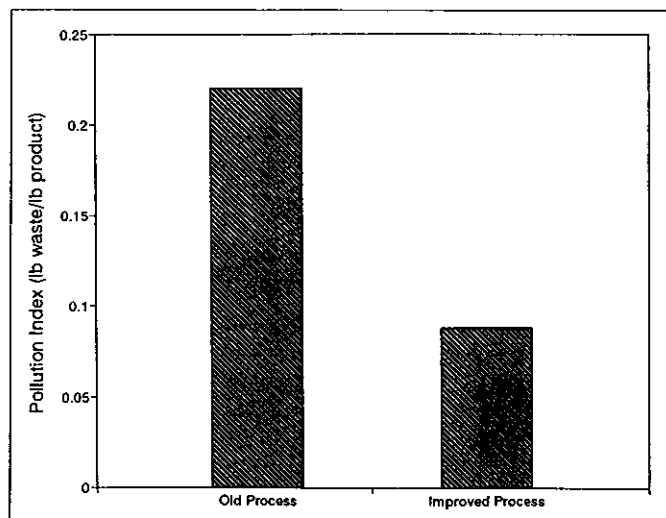

Figure 6. The pollution indices of the old process and the improved process.

4. Stream A: This stream contained the $AlCl_3$ wet sludge. A dryer was added to the flowsheet to vaporize the benzene and dodecene. The vaporized benzene and dodecene were recyled to the alkylator.
5. Stream E: The effluent from the spray tower entrained a small quantity of solids, which were released to the air as wastes. A cyclone separator was added to the effluent line to recover the solids.

With the above process modifications, the pollution index for the process was reduced by 60%. Figure 6 compares the pollution index of the old process with that of the improved process. Figure 7 shows the flow-diagram of the improved process.

Discussion

The pollution balance methodology proposed in this paper provides a convenient means of measuring wastes produced in a process and of comparing competitive process options for a product. The method is also useful for systematically determining necessary process modifications in an existing plant. Methods for process optimization and process synthesis already exist in the literature; our algorithm provides an organizing principle to perform various operations systematically to achieve the objective of waste minimization.

As mentioned above, providing a quantitative measure of pollution production is extremely important for minimizing wastes[1]. At present, the pollution production in different industries is reported in the TRI (Toxic Release Inventory) form R. The TRI has its own shortcomings in terms of the information that it provides[1], and it does not offer any means to compare different processes. Our methodology addresses this issue successfully by defining pollution indices of products by Equation 6. The pollution index of a product serves as a yardstick for comparing processes. Thus, the strategy of waste minimization may be based on the pollution index of a product.

The concept of life cycle analysis (LCA) of a product is often discussed with regard to waste minimization. The technique of LCA suffers from major methodological gaps[7]. It provides only a general framework for analysis. The waste reduction methodology described above can assist in developing "cradle to grave" LCA methods.

Accounting for toxicity of wastes is beyond the scope of this work because toxicity is not a quantifiable concept. Moreover, in our analysis, toxic products and reactants are not considered wastes if they have not been released. For instance, if benzene, which is toxic, is used as a reactant, it will not be considered a waste if there is no emission of benzene from any part of the flowsheet. If there is an emission, it would be a waste in a designated part of the flowsheet. When it is desirable to account specifically for known toxic wastes produced in a process, however, pollution balance can be applied to them. The pollution index of the product in that case would provide a specific toxicity index of the product. Nevertheless, if it is desirable to extend the analysis to consider toxicity in general, it is possible to propose a mathematical formula to calculate the level of toxicity based on several physical/chemical properties[8]. Since the definition of the formula is arbitrary, the value of toxicity is also arbitrary. If the arbitrary value of toxicity of a polluting component i is denoted by ψ_i, then the general pollution balance equation may be modified as:

$$\frac{d}{dt}\left(\sum_k \sum_i V_k \rho_k x_{i,k} \psi_i\right) = \sum_k \sum_j \sum_i I_{j,k} x_{i,k} \psi_i + \sum_k V_k \sum_i r_i MW_i \psi_i -$$

$$\sum_k \sum_j \sum_i O_{j,k} x_{i,k} \psi_i - \sum_k \sum_i F_k x_{i,k} \psi_i . \qquad (10)$$

Based on Equation 10, it is easy to incorporate toxicity into the definition of pollution index of a product. Since the value of toxicity is arbitrary, there is little practical usefulness of considering ψ_i at this point.

Conclusion

In this paper, we introduced the concept of pollution balance for minimizing waste production in various processes. A waste reduction algorithm, called WAR, was formulated based on the pollution balance equation. We demonstrated the effectiveness of the WAR algorithm through a realistic example of the production of a detergent.

At present, the WAR algorithm and a process simulator run separately with sequential interaction between them. We plan to incorporate our algorithm into a commercial process simulator, so that the implementation of the algorithm will be more convenient.

Acknowledgement

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Figure 7. The flowsheet of the improved process.

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About the Authors

Ahmad K. Hilaly is a post-doctoral research engineer at the U.S. Environmental Protection Agency, Cincinnati, Ohio. Subhas K. Sikdar is the Director of Water and Hazardous Waste Treatment Research Division of the Risk Reduction Engineering Laboratory at the U.S. Environmental Protection Agency, Cincinnati, Ohio.