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RISK REDUCTION THROUGH WASTE MINIMIZING PROCESS SYNTHESIS

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INTRODUCTION

Various approaches are available for minimizing the generation of waste in a process system. They include source reduction, recycling, waste separation, waste concentration, and waste exchange at the highest level of U.S. EPA's waste reduction hierarchy (1). All of these approaches, however, depend primarily on the structure of the process. For instance, various processes may need different waste treatment systems even if they generate the same product. Similarly, the risk depends on the structure of the process. Thus, the design of facilities for waste minimization and risk reduction can not be isolated from that of the process for product generation as often done conventionally. All the steps of process design and waste minimization and risk reduction should be integrated into one consistent method. The integration, however, renders the already complex tasks involved in process synthesis exceedingly cumbersome. A highly efficient and mathematically rigorous technique is indeed required to overcome this difficulty. The present work aims at establishing such a technique.

METHODOLOGY

Conventional graphs are suitable for analyzing a process structure (2). Nevertheless, Friedler *et al.* (3) have demonstrated that such graphs are incapable of uniquely representing process structures in synthesis. Thus, a special directed bipartite graph, a process graph or P-graph in short, has been conceived to circumvent this difficulty.

Operating units are usually represented on a process flowsheet by figures of various configurations; however, such configurations are inconsequential for mathematical analysis. In a P-graph, an operating unit is represented by a horizontal bar, and a material, by a circle. If a material is an input to an operating unit, the vertex representing this material is connected by an arc to the vertex representing the operating unit. Similarly, if a material is an output from an operating unit, the vertex representing this operating unit is connected by an arc to the vertex representing the material. The conventional and P-graph representations of a reactor and a distillation column are given in Figure 1. Obviously, a P-graph is bipartite since its vertices are partitioned into two sets, and no two vertices are adjacent in the graph.

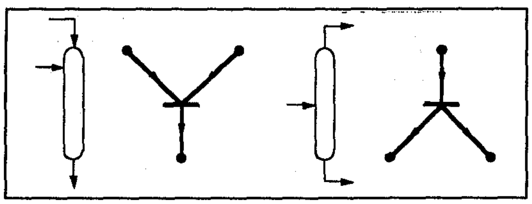

Figure 1. Conventional and P-graph representations of a reactor and a distillation column.

In our P-graph based method of process synthesis (4), all materials in the process being synthesized are divided into five disjoint classes; these classes are raw materials, required products, potential products, disposable materials, and intermediates. A *raw material* is available as feed to the process

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being synthesized; a *required product* is to be produced from the process; a *potential product* can be produced, if profitable to do so; a *disposable material* can be safely discharged to the environment or marketed as a by-product; and an intermediate need be fed to some operating units of the process, if produced.

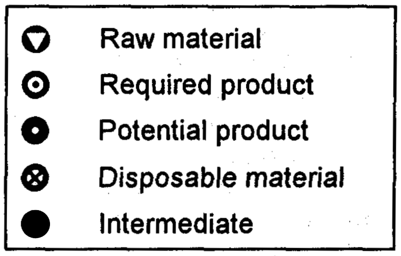

Figure 2. Graphical representation of the five classes of materials on a P-graph.

Similar to the potential product, the production of the disposal material is not mandated. The disposable material can only be produced by those operating units, each of which is essential for generating a product or treating an undesirable output from the process. Although it is not always necessary to do so, a raw material, a required product, a potential product, or a disposable material can be fed to some operating units. Production of an *intermediate* is similar to that of a disposable material; nevertheless, unlike the disposed material, the intermediate must be fed to some operating units for treatment or consumption. The intermediate would be a waste which may induce detrimental effects if it is discharged to the environment. Obviously, it need be treated or consumed within the process. Specific symbols are assigned to the different classes of materials in their graphical representations; see Figure 2. For illustration, a process yielding product H, potential product G, and disposable material D, from raw materials A, B, and C by operating units 1, 2, and 3 is given in Figure 3.

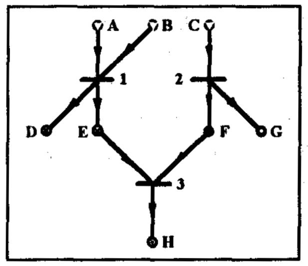

Figure 3. P-graph of the process manufacturing required product H and also yielding potential product G and disposable material D from raw materials A, B, and C.

In the conventional synthesis of a process, the design for the product generation and that for the waste minimization or treatment are performed separately, as mentioned earlier. This frequently yields a locally optimum process. Let us now integrate these two design steps into a single method for process synthesis.

Our method is rigorously founded on an axiom system, describing the self-evident fundamental properties of combinatorially feasible process structures, and combinatorics (4, 5, 6).

A set of six axioms, axioms (SW1 through SW6), of process synthesis for integrated in-plant waste treatment is given in Friedler *et al.* (7). For example, axiom (SW6) states the following: If a material is not consumed by any operating unit, it must be a product or disposable material.

Example 1. Suppose that operating units given in Figure 4 are available for producing required product P1 and potential product P2 from raw materials R1, R2, R3, and R4. Moreover, the only other materials allowed to be produced are disposable materials.

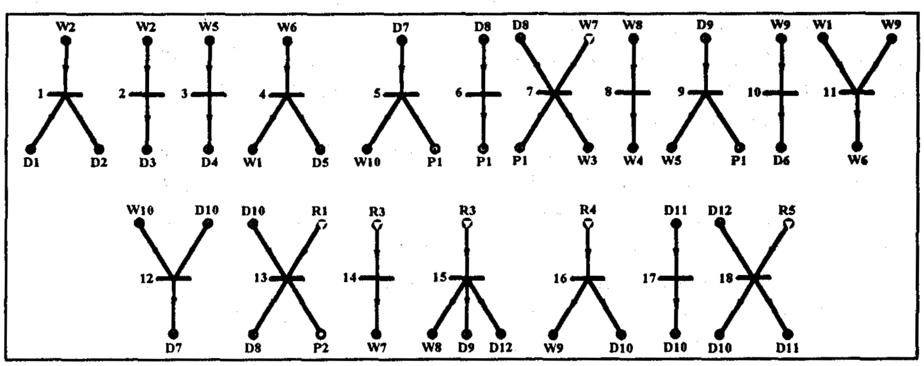

Figure 4. Operating units of Example 1.

Note that some of the operating units given in Figure 4 are excluded from all the combinatorially feasible structures. In other words, it is unnecessary to include them in the problem definition; examples are operating units 3, 7, and 8. This, however, can not be known a priori.

In this truly integrated approach which is based on our accelerated branch-and-bound algorithm (8), the product generation and waste treatment are considered simultaneously in synthesizing the process; therefore, in theory, the optimal structure can be generated. The enumeration tree is given in Figure 5 for the worst case. The cost-optimal structure corresponds to node #14, and it consists of operating units 2, 8, 9, 10, 15, 20, 25 and 26, as shown in Figure 6. It should be noted that risk is yet to be considered in this version of our method for process synthesis.

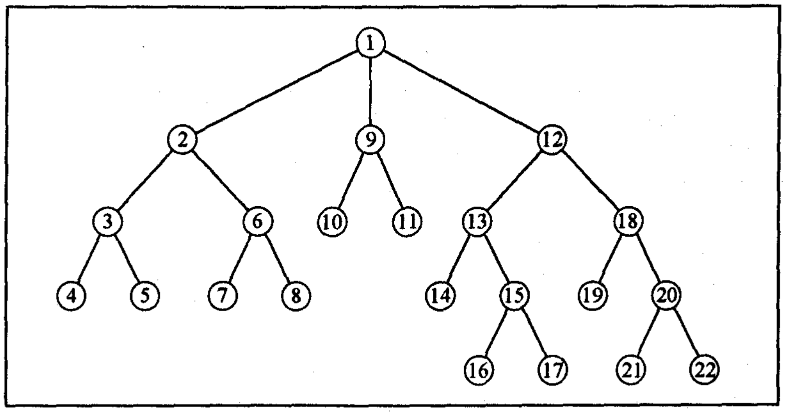

Figure 5. Enumeration tree of the accelerated branch-and-bound search for the optimal structure of the process with integrated in-plant waste treatment: the worst case.

RESULTS

Integration of Process Synthesis Incorporating In-plant Waste Treatment and Risk Reduction

The same product or products can be manufactured by various structurally different processes, each of which may generate disposable materials besides the product or products. Frequently, materials participating in these structurally different processes pose varying degrees of risk. Moreover, even if a material produced by any process can be safely disposed in an environmentally benign manner, the risk associated with it is not always negligible.

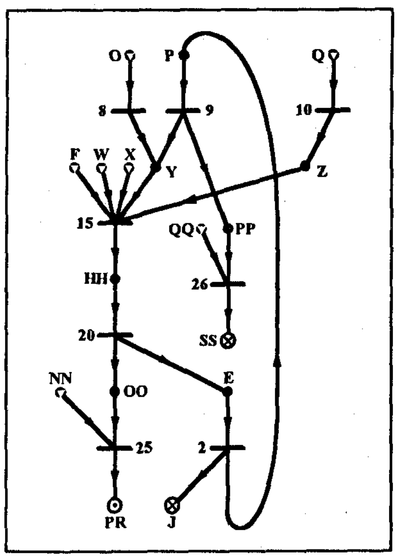

Figure 6. Structure of the optimally synthesized process integrating in-plant waste treatment but without consideration of risk.

Every material participating in a process to be synthesized possesses risks varying in magnitude, such as the potential for pollution, the hazard of explosion and the toxicity to human-life. This can readily be envisioned even for the simplest group of materials, e.g., hydrogen, ammonia and benzene. These materials widely serve as raw materials, frequently appear as intermediates or often are manufactured as final products in a variety of chemical processes. Obviously, various risks associated with different materials can generally be reduced with additional expenditure for designing and constructing the process. The extent of reduction, however, depends heavily on the complex interplay among the factors to be taken into account in synthesizing the process, which may be economic, environmental, toxicological or health-related. Moreover, the dichotomy between any pair of such factors tends to be extremely fuzzy. Nevertheless, for convenience, the present approach views that a process can be optimally synthesized by simultaneously taking into account only three factors, i.e., (i) cost; (ii) waste generation; and (iii) risk posed by the participating materials. Specifically, the first factor, cost, is defined as the objective function to be minimized subject to the additional constraints on both the second and third factors.

Two types of risk indices are introduced: (a) internal risk index associated with a material consumed within the process, e.g., a raw material or intermediate; (b) external risk index associated with a material discharged to the environment, e.g., a disposable material. Both risk indices are defined on the basis of unit amount of material.

The overall risk of a process is determined as the sum of the risks of all materials participating in the process. The risk of each material is obtained as the sum of its internal and external risks, each of which in turn, is obtained by multiplying the amount of the material and the corresponding risk index. A material may have both internal and external risks if it is partially consumed in a process as a recycled material and is also discharged to the environment as a disposable material.

The branch-and-bound algorithm of process synthesis incorporating integrated in-plant waste treatment has been extended to include the consideration of risk. This algorithm generates the cost optimal solution of synthesis problem, satisfying the constraints on both waste generation and risk.

Example 1 revisited for risk consideration. The enumeration tree of branch-and-bound algorithm remains the same for the worst case; see Figure 5. The optimal solution with the integrated in-plant waste treatment, resulting from the subproblem corresponding to node #14, does not satisfy the constraint on risk; instead, subproblem corresponding to node #17 gives rise to the optimal solution of the problem. Although the cost of this solution is higher than that obtained from the subproblem corresponding to node #14, it has the minimal cost among the solutions satisfying the constraint on risk; the resultant structure is given in Figure 7.

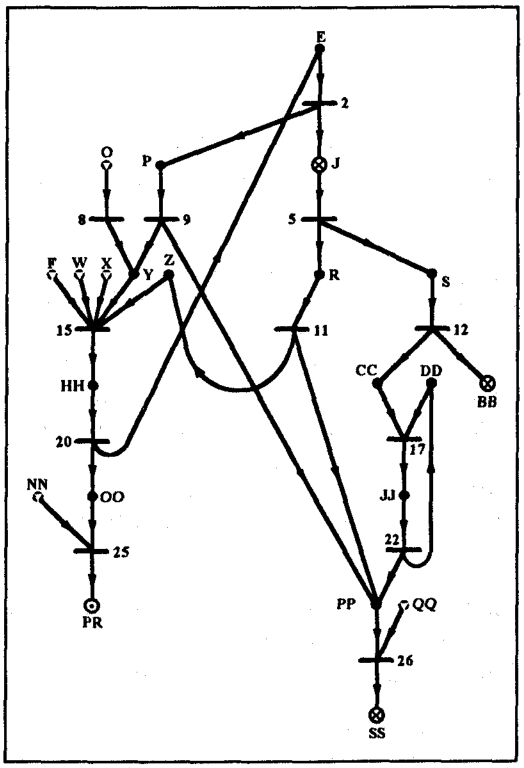

Figure 7. Structure of the optimally synthesized process integrating in-plant waste treatment and risk consideration.

CONCLUSIONS

By defining a risk index, our method for synthesizing an optimal process with integrated in-plant waste treatment capability has been extended to the synthesis of a cost-optimal process structure satisfying the constraints on both waste generation and risk. It has been demonstrated with an industrial process synthesis problem that the process' optimal structure synthesized by taking into account risk can be substantially different from that by disregarding it.

ACKNOWLEDGMENTS

Although the research described in this article has been funded in part by the United States Environmental Protection Agency under assistance agreement R-819653 to the Great Plains-Rocky Mountain Hazardous Substance Research Center for U.S. EPA Regions 7 and 8 with headquarters at Kansas State University, it has not been subjected to the Agency's peer and administrative review and, therefore, may not necessarily reflect the views of the Agency. No official endorsement should be inferred. This research was also partially supported by the Kansas State University Center for Hazardous Substance Research. This research was partially supported by the Hungarian Ministry of Education Grant No. 167/94.

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PREPARED BED REACTOR FOR FULL SCALE REMEDIATION OF SOIL CONTAMINATED WITH WOOD PRESERVING WASTES: FIELD BIOREMEDIATION EVALUATION

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INTRODUCTION

The Champion International Superfund Site, a former wood perserving site in Libby, Montana, was nominated by the Robert S. Kerr Environmental Research Laboratory (RSKERL), Ada, OK, as a candidate site for bioremediation performance evaluation under the Bioremediation Field Initiative (BFI) sponsored by the U.S. Environmental Protection Agency (U.S. EPA). The Initiative was designed to address the need for additional field experience concerning the implementation of bioremediation techniques, including the collection and dissemination of performance data from field experiences.Target chemicals for bioremediation at the Libby Site included the polycyclic aromatic hydrocarbons (PAH) naphthalene, phenanthrene, and pyrene

The field performance evaluation was designed and conducted by Utah State University (USU) with support from the U.S. Environmental Protection Agency, Robert S. Kerr Environmental Research Laboratory, to provide information on the effectiveness of bioremediation in addition to the information generated by Champion International personnel as part of regulatory monitoring requirements. Champion International, agreed to cooperate with the RSKERL and USU in conducting the proposed bioremediation performance evaluation studies for biological treatment processes in operation at the Libby Site.

The Libby Site uses three distinct biological processes in the site remediation scenario: (1) surface soil biological treatment in a prepared bed system,consisting of two lined land treatment units, liners, and leachate collection; (2) extraction of ground water, followed by aqueous phase treatment in an above-grade, fixed-film bioreactor; and (3) *in situ* bioremediation of the Upper Aquifer . Results of the evaluation of bioremediation in the prepared bed system are presented in this paper.

Contaminated soils were located in three primary source areas at the Libby Site: a former tank farm, an unlined butt dip area, and an unlined waste pit. In 1989, contaminated soils from these three areas (approximately 75,000 cubic yards of materials) were excavated down to the water table. Before the tank farm and butt dip areas were filled with clean soil, samples were collected and analyzed to verify that contamination had been removed.

Since the major contaminants of concern were expected to be associated with finer-grained materials, the soils excavated from the tank farm and butt dip areas and any previously excavated contaminated materials from the waste pit area were physically screened to remove rocks larger than one inch in diameter (referred as de-rocking). The screened soils from all three areas (approximately 45,000 cubic yards) were placed in the excavated waste pit area. The separated rocks were placed upgradient to the waste pit area to construct sub-grade infiltration galleries. This rock percolation bed is used for biological treatment of the contaminated rocks using effluents from the above grade, fixed-film bioreactor.

After a lift of contaminated soil is treated to target remediation levels in the prepared bed system, another lift of contaminated soil is added and treated until target remediation levels are obtained. Target