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Scope for the Application of Mathematical Programming Techniques in the Synthesis and Planning of Sustainable Processes

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CONTENTS

ABSTRACT Sustainability has recently emerged as a key issue in process systems engineering (PSE). Mathematical programming techniques offer a general modeling framework for including environmental concerns in the synthesis and planning of chemical processes. In this paper, we review major contributions in process synthesis and supply chain management, highlighting the major optimization approaches that are available, including the handling of uncertainty and the multi-objective optimization of economic and environmental objectives. Finally, we discuss challenges and opportunities identified in the area.

KEYWORDS *Sustainability, uncertainty, process synthesis, supply chain management*

Introduction: Sustainability in PSE

In the past, the methods devised in PSE to assist in the optimization of chemical processes have traditionally concentrated on maximizing an economic criterion. However, in the recent past there has been an increasing awareness of the importance of incorporating environmental aspects in the decision-making process. As a result, the scope of the analysis carried out in PSE is being enlarged with the aim to guide practitioners towards the adoption of more sustainable alternatives.

Including environmental issues in the synthesis and planning of chemical processes poses significant challenges that have not yet been fully solved, and hence merit further attention. One major critical issue is how to systematize the search for alternatives leading to reductions in environmental impact. Furthermore, aside from anticipating the effect of uncertainties, which are quite pronounced in this area, there is the issue on how to cope with competing economic and environmental objectives. Hence, there is a clear need to develop sophisticated optimization and decision-support tools to help in exploring and analyzing diverse process alternatives under uncertainty, and so as to yield optimal trade-offs between environmental performance and profit maximization. These methods should be employed to improve the environmental performance at different hierarchical levels, covering both single-site and multi-site industrial applications.

The aim of this paper is to summarize major contributions made in these fields, paying special attention to those based on mathematical programming. We center our discussion on two specific areas of PSE that can potentially help to identify and establish for environmental improvements: process synthesis and supply chain management (SCM).

Single-site Level: Process Synthesis

Process synthesis deals with the selection of the topology of a process in order to convert a set of inputs into a desired set of outputs (Rudd et al., 1973). Commonly the objective is to find designs that minimize cost or maximize profit. However, objectives such as maximizing efficiency or minimum usage of a resource (e.g. energy or freshwater) can also be considered. The area of process synthesis was especially active between the 70s and early 90s, in large part due to the increase in the cost of energy (Nishida et al., 1981). The area has addressed a number of major subproblems such as the synthesis of heat exchanger networks, distillation sequences, reactor networks, steam and power plants, mass exchange networks and process water networks, including total process flowsheets.

The area of process synthesis is particularly relevant to sustainability for two major reasons. First, process synthesis can help to identify the most efficient and/or economical process. This means that instead of using old technology to assess the environmental impact or energy use of a process in a life cycle analysis as is commonly done in many policy studies, one can rely on state-of-the-art process technology. A second reason is that process synthesis addresses subproblems such as pollution prevention (El-Halwagi, 1997), minimization of energy use (Linnhoff, 1993) and freshwater consumption (Wang and Smith, 1994) that lie at the heart of the environmental performance of a process. Unfortunately, the introduction of these considerations at the early stages of the process development increases the complexity of the design task, which is further complicated by the need to account for different conflictive criteria in the decision-making as well as various sources of uncertainty brought about by several problem parameters (costs, prices, demand, etc.). The development of efficient modeling and solution strategies capable of dealing with these issues constitutes a major challenge in PSE.

Multi-site Level: SCM and EWO

Supply Chain Management (SCM) is a relatively new discipline that aims to integrate manufacturing plants with their suppliers and customers in an efficient manner (Shapiro, 2001). In the context of PSE, the optimal integration of the operations of supply, manufacturing and distribution activities is the main goal of the emerging area known as Enterprise-wide optimization (EWO), which as opposed to SCM, places more emphasis on the manufacturing stage (Grossmann, 2005).

The major goal in the design and planning of sustainable SCs is to reduce the environmental impact of a process over its entire life cycle. This implies expanding the boundaries of the analysis typically performed in process synthesis in order to embrace a wider range of logistic activities. Note that besides the challenges posed by the standard economic optimization of these systems, which have been already discussed in Grossmann (2005), there are some additional issues associated with the inclusion of environmental aspects in SCM/EWO that deserve further attention. The first critical point is how to measure the environmental impact of a process/product through all the stages of its life so this can be explicitly included as an additional criterion to be optimized. As pointed out in the literature (Freeman and Harten, 1992), the lack of accepted metrics to support objective environmental assessments still represents a major limitation in the area. The second aspect, which is strongly linked to the previous one, is how to incorporate these concerns in a modeling framework and effectively solve the resulting formulations by devising efficient algorithms and computer architectures. Note that the consideration of environmental design objectives further complicates the optimization problems arising in SCM and EWO, which are *per se* quite complex. Finally, as in the previous case, the problem is affected by different sources of uncertainty (inventory of emissions, damage model, waste generated, etc.) that can greatly impact the conclusions and recommendations made at the end of the environmental analysis (Geisler et al., 2005). Therefore, another major issue is the development of novel and meaningful stochastic methods capable of effectively anticipating the effect of these variations. All these aspects are expected to be the focus of future research.

General Techniques

In this section we summarize the main methodologies and techniques that can be used to reduce the environmental impact in process synthesis and SCM/EWO.

Process Synthesis

Major approaches to synthesizing process flowsheets that are cost effective, energy efficient and with potentially low environmental impact, include the use of heuristics, the development of physical insights (commonly based on thermodynamics), and the optimization of superstructures of alternatives. Major contributions in the first two approaches have been hierarchical decomposition (Douglas, 1988), and pinch analysis (Linnhoff, 1993) that has proved to be very successful in industrial applications.

The more recent trend has been to combine some of these concepts with the mathematical programming approach (see Grossmann et al., 1999), which consists of three major steps. The first is the development of a representation of alternatives from which the optimum solution is to be selected. The second is the formulation of a mathematical program that generally involves discrete and continuous variables for the selection of the configuration and operating levels, respectively. The third is the solution of the optimization model (commonly a mixed-integer nonlinear programming, MINLP, or a generalized disjunctive programming, GDP, model) from which the optimal solution is determined.

While superstructures can be developed in a systematic way for subsytems (e.g. see Yee and Grossmann (1990) for heat exchanger networks), their development for general process flowsheets is more complex. Here two approaches that have emerged are the axiomatic approach by Friedler et al. (1993), and the State-Task and State-Equipment Networks by Yeomans and Grossmann (1999). As for the problem formulation it is important to note that synthesis models can be formulated at three major levels of detail: a) Aggregated models that are high level and concentrate on major features like energy flows (e.g. LP transshipment model for HEN by Papoulias and Grosmann, 1983; NLP heat and mass exchanger by Papalexandri and Pistikopoulos, 1996); b) Short-cut models that involve cost optimization (investment and operating costs), but in which the performance of the units is predicted with relatively simple nonlinear models (e.g. MINLP heat exchanger networks by Yee and Grossmann, 1990; MINLP process flowsheets by Kocis and Grossmann, 1987); c) Rigorous models that rely on detailed superstructures and involve rigorous and complex models for predicting the performance of the units (e.g. MINLP synthesis of distillation sequences, Smith and Pantelides, 1995; and GDP models, Grossmann et al., 2005).

At this point there are still very few papers that have reported the use of process synthesis techniques with the explicit incorporation of sustainability issues (eg. Steffens et al., 1999; Halasz et al., 2005). Some of them have applied optimization techniques to the molecular design of solvents and the synthesis of the associated separation processes (Pistikopoulos and Stefanis, 1998; Hostrup et al., 1999), whereas an increasing number of publications are addressing the synthesis of biofuels plants (e.g. Agrawal et al., 2007; Karuppiah et al., 2008).

SCM/EWO

The combination of environmental management and SCM into a single framework has recently led to a new discipline known as Green Supply Chain Management (GrSCM). An exhaustive review on the area of GrSCM can be found in the work of Srivastava (2007). According to the author, there are two main types of approaches in GrSCM: empirical studies and mathematical modeling. Within the latter group, we can find a variety of tools and techniques, such as mathematical programming (LP, NLP, MILP, MINLP and dynamic programming), Markov chains, Petri Nets, input-output models, game theory, fuzzy logic, data envelopment analysis (DEA), descriptive statistics and simulation. These methods have been applied to the two main areas of GrSCM: green design and green operations. The former one involves the environmentally conscious design of products and processes, whereas the second one deals with green manufacturing and remanufacturing, reverse logistics, network design and waste management. Both areas share the same holistic approach in which the key issue is to take into account the complete life cycle of the product/process under study. This global perspective avoids technological alternatives that decrease the impact locally at the expense of increasing the environmental burdens in other stages of the life cycle of the product.

The application of these techniques to the design of sustainable processes has followed two different approaches. The first one, which has been the most common approach, has focused on including them as additional constraints to be satisfied by the optimization model. As pointed out by Cano-Ruíz and McRae (1998), the environmental issues should be regarded as new design objectives and not merely as constraints on operations. This second approach is better suited to account for environmental concerns at the design stage, since it can lead to the discovery of novel alternatives that simultaneously improve the economic and environmental performance of the process (Hugo and Pistikopoulos, 2005). As mentioned before, such consideration leads to more complex problems that require specific multi-objective optimization methods, some of which can be used in conjunction with the mathematical tools previously described.

Optimization using mathematical programming is probably the most widely used approach in SCM. General literature reviews have been made by Thomas and Griffin (1996) and Maloni and Benton (1997), whereas a more specific work devoted to process industries can be found in Grossmann (2005).

From the modeling point of view, the preferred tool has been mixed-integer linear programming (MILP). This choice has been motivated by the fact that these formulations tend to be represented at a high level, and hence apply fairly simple representations of capacity that avoid nonlinearities and allow them to be easily adapted to a wide range of industrial scenarios. Such simplification can sometimes lead to approximate solutions, the accuracy of which may vary depending on the specific application. In contrast to SCM, EWO focuses more on process industries and often includes more realistic capacity models involving nonlinear equations.

In the aforementioned MILP formulations, continuous variables are used to represent materials flows and purchases and sales of products, whereas binary variables are employed to model tactical and/or strategic decisions associated with the network configuration, such as selection of technologies and establishment of facilities and transportation links. These models have been traditionally solved via branch and bound techniques, which in some cases have been applied in conjunction with other strategies such as Lagrangean (Graves, 1982), Benders (Spengler et al., 1997) and bi-level decomposition methods (Iyer and Grossmann, 1998). In the area of GrSCM, mathematical programming has been employed in green manufacturing, remanufacturing, reverse logistics, network design and waste management (for a detailed review see Srivastava, 2007). In contrast, in EWO the use of mathematical programming in the design and planning of sustainable SCs has been rather limited and it is still waiting for further research.

Mathematical Programming Techniques

A discussed in the previous sections, mathematical programming has been widely applied in process synthesis and SCM. The next sections summarize the major methods, including the handling of uncertainty and multiobjective optimization.

Mixed-integer Optimization

Developing the full range of models for EWO often involves MILP techniques for which efficient software such as CPLEX and XPRESS are available for solving fairly large-scale problems. However, EWO problems may require that nonlinear process models be developed for representing manufacturing and inventories in the planning and scheduling of production facilities. This gives rise to mixed-integer nonlinear programming (MINLP) problems since they involve discrete variables to model assignment and sequencing decisions, and continuous variables to model flows, amounts to be produced and operating conditions (e.g. temperatures, yields). While MINLP optimization is still largely a rather specialized capability, it has been receiving increasing attention by the OR community in the last few years. Furthermore, modeling systems like GAMS now offer multiple methods for solving these problems (e.g. DICOPT, SBB, a-ECP, Bonmin, BARON). A recent review on MINLP methods can be found in Grossmann (2002). Major methods include branch and bound, outer-approximation, Generalized Benders decomposition, extended cutting planes, and LP/NLP based branch and bound. While these methods have proved to be effective, they are still largely limited to moderate-sized problems (few hundreds of 0–1 variables, several thousands of continuous variables and constraints). In addition there are several difficulties that must be faced in solving these problems. For instance in NLP subproblems with fixed values of the binary variables, a significant number of equations and variables are often set to zero as they become redundant when units "disappear." This in turn often leads to singularities and poor numerical performance. There is also the possibility of getting trapped in suboptimal solutions when nonconvex functions are involved. Finally, there is the added complication when the number of 0–1 variables is large, which is quite common in planning and scheduling problems.

To circumvent some of these difficulties, the modeling and optimization of Generalized Disjunctive Programs (GDP) seems to hold good promise for process synthesis and EWO problems. The GDP problem is expressed in terms of Boolean and continuous variables that are involved in constraints in the form of equations, disjunctions and logic propositions (Raman and Grossmann, 1994). This has the effect of greatly simplifying the modeling of discrete/continuous problems. Furthermore, the logic-based outer approximation for nonlinear GDP problems (Turkay and Grossmann, 1996) has the important feature of generating NLP subproblems where redundant equations and constraints of non-existing units are not included, which improves the robustness of the optimization. The only software available for solving GDP models is LOGMIP (Vecchietti and Grossmann, 1999). Another major challenge is obtaining the global optimum solution. Here a number of global optimization algorithms (Floudas, 2000; Sahinidis, 1996; Tawarmalani and Sahinidis, 2002) have emerged, mostly through spatial branch-and-bound schemes. BARON has become the major global optimization solver in modeling systems such as GAMS. For GDP, there are still few global optimization techniques (e.g. Lee and Grossmann, 2001).

Multi-objective Optimization

As mentioned before, multi-objective optimization (MOO) is well suited to incorporate environmental concerns in the optimization of sustainable processes, since it allows to treat them as decision-making objectives. The use of these methods requires translating such environmental aspects into suitable environmental performance indicators that should be optimized in conjunction with the traditional economic-based criteria. There are three main types of MOO approaches: (1) those based in the transformation of the problem into a single-objective one (see Ehrgott, 2000), (2) the Non-Pareto approaches, which use search operators based in the objectives to be optimized and (3) Pareto approaches, which directly apply the concept of dominance (see Deb, 2008). Whereas the first approach can be easily applied in conjunction with standard exact algorithms (i.e., branch and bound), the second and third ones are better suited to work with meta-heuristics. Note that any of the traditional exact methods employed in process synthesis and SCM (LP, MILP, MINLP, GDP and global optimization) can be coupled with single-objective MOO approaches, such as aggregation methods, the epsilon constraint method, goal programming and goal attainment. As pointed by Hugo and Pistikopoulos (2005), many of these methods have been employed to account for environmental concerns in process design problems that focus on single-site scenarios. However, their application to the multi-objective optimization of entire supply chain networks has been rather limited.

Uncertainty

All the problems mentioned in the previous sections are further complicated by different sources of uncertainty that can be encountered in practice. Many of the existing methods in process synthesis and SCM/EWO assume nominal values for the uncertain parameters and do not consider their variability. However, this simplification may lead to solutions that perform well in the most likely scenario but exhibit poor performance under other circumstances. Special techniques able to assess process alternatives under uncertainty can avoid this situation and guarantee a good performance for any possible outcome of the uncertain parameters. We next review the two major proactive methods that account for uncertainty considerations in the decision-making process, focusing on their applications in process synthesis and SCM/EWO.

Stochastic Programming with Recourse

In stochastic programming (Birge and Louveaux, 2000; Sahinidis, 2004), mathematical programs are defined with a set of uncertain parameters, which are normally described by discrete distributions. These in turn give rise to scenarios that correspond to a particular realization of each of the uncertain parameters. Furthermore, stochastic programs are solved over a number of stages. The fundamental idea behind stochastic programming is the concept of recourse. Recourse is the ability to take corrective action after a realization of a scenario has taken place. Between each stage, some uncertainty is resolved, and the decision maker must choose an action that optimizes the current objective plus the expectation of the future objectives. The most common stochastic programs are two-stage models in which typically stage-1 decisions involve selection of topology or design variables in a synthesis problem, or planning decisions for the first month in SCM problem. Stage-2 decisions involve variables that can be adjusted according to the realization of the scenarios (e.g. recycles in a flowsheet, production levels in a SCM problem). Two-stage programming problems may be solved in a number of methods including decomposition methods (Ruszczyński, 2003) and sampling-based methods (Linderoth, et al., 2006).

When the second-stage (or recourse) problem is a linear program these problems are straightforward to solve, but the more general case is where the recourse is a MILP or a MINLP. Such problems are extremely difficult to solve since the expected recourse function is discontinuous and nonconvex (Sahinidis, 2004). It should be noted that the more general stochastic program corresponds to the multistage model. In this case, decision variables and constraints are divided into groups of corresponding temporal stages. At each stage some of the uncertain quantities become known. In each stage one group of decisions needs to be fixed based on what is currently known, along with trying to compensate for what remains uncertain. The model essentially becomes a nested formulation. Although these problems are difficult to solve, there is extensive potential for applications. The strength of stochastic programming is that it is one of the very few technologies for optimization under uncertainty that allows models to capture recourse.

Planning in the chemical process industry has used stochastic programming for a number of applications (Liu and Sahinidis, 1996; Clay and Grossmann, 1997). The scheduling of batch plants under demand uncertainty using stochastic programming has only recently emerged as an area of active research. Engell et al. (2004) use a scenario decomposition method for the scheduling of a multi-product batch plant by two-stage stochastic integer programming. Balasubramanian and Grossmann (2004) present an approach for approximating multistage stochastic programming to the scheduling of multiproduct batch plants under demand uncertainty. More recent applications of stochastic programming to supply chain optimization can be found in Pistikopoulos et al. (2007).

Robust Optimization and Probabilistic Programming

Robust optimization, which was first introduced by Ben-Tal and Nemirovski (1998), seeks to determine a robust feasible/optimal solution to an uncertain problem. This means that the optimal solution should provide the best possible value of the original objective function and also be guaranteed to remain feasible in the range of the uncertainty set considered for a predefined probability level. A major difference between robust optimization and stochastic programming with recourse is the explicit consideration of feasibility issues. In robust optimization, the solution must ensure that a set of constraints will be satisfied with a certain probability when the uncertainty is realized. Instead, stochastic optimization either assumes complete recourse, that is, every scenario is supposed to be feasible, or allows infeasibilities at a certain penalty. Furthermore, robust optimization cannot handle recourse variables. Thus, it can be considered as a particular category of single-stage here-and-now problems, where the uncertain parameters are enclosed in an inequality constraint subject to a probability or reliability level. Because of this simplification (absence of recourse actions), robust optimization usually leads to lower computational burdens. However, the difficulty in solving these problems still lies in the computation of the probability and its derivatives of satisfying inequality constraints (Li et al., 2008).

The concept of robust optimization is somehow linked to chance-constrained programming. Chance-constrained programming (Charnes and Cooper, 1959), also known as probabilistic programming, considers the uncertainty by introducing a probabilistic level of constraint satisfaction. This method is useful to deal with inequality constraints the satisfaction of which is highly desirable, but not absolutely essential. In practice, chance-constrained programming provides the mathematical framework that allows to deal with the probabilistic constraints employed in robust optimization.

Robust optimization has been widely applied in optimization under uncertainty (see Uryasev, 2000). Specifically, many previous works have focused on efficiently solve this type of problems (see Nemirovski and Shapiro, 2006). However, the application of robust optimization in PSE has been rather limited and usually restricted to operational/tactical problems, such as the scheduling of batch plants under uncertainty (Petkov and Maranas, 1997; Janak et al., 2007). Gupta et al. (2000) also used a chance-constrained approach in conjunction with a two-stage stochastic programming model to analyze the tradeoffs between demand satisfaction and production costs for a mid-term supply chain planning problem. Extensions of these strategies to deal with strategic problems as well as different sources of uncertainty are still waiting for further research.

EXAMPLES

In this section, we present four examples that illustrate the challenges cited in this article on problems encountered in the synthesis and planning of sustainable chemical processes. The first example addresses the energy optimization of a bioethanol plant. The second problem deals with the synthesis of a process network with uncertain yields. The third example illustrates the use of multi-objective optimization coupled with life cycle assessment (LCA) to address a SCM problem. Finally, the fourth problem deals with the design of sustainable petrochemical SCs and extends the framework presented in example 3 to account for different sources of uncertainty that affect the environmental impact calculations.

Example 1. Synthesis of biofuels

Karuppiah et al. (2008) considered the energy optimization of the "dry-grind" process for the corn-based bio-ethanol plant. In such plants, fuel ethanol is produced using corn-kernels as the feedstock. Fuel grade ethanol has to be 100% pure before it can be blended with gasoline to be used in automobiles. However, conventional distillation columns produce an azeotropic mixture of ethanol and water (95% ethanol – 5% water), which has to be purified further for making fuel ethanol. The main challenge in the way of producing fuel ethanol commercially is that the process is very energy intensive and requires large amounts of steam and electricity for use in the rectifiers to get an azeotropic mixture of ethanol and water and requires the use of expensive molecular sieves to get 100% pure ethanol.

Karuppiah et al. (2008) developed a simplified model to predict the performance of the bio-ethanol flowsheet that includes grinding, scarification, fermentation, centrifugation and drying operations (see Fig. 1). A superstructure was also postulated in which some of the major alternatives include separation by molecular sieves and or corn grits, and different ways to accomplish the drying for the dried grains solids, the cattle feed by-product. The objective was to optimize the structure, determining the connections in the network and the flow in each stream in the network, such that the energy requirement of the overall plant is minimized while trying to maximize the yields.

The optimization without heat integration (MINLP model) led to a decrease of the manufacturing cost from \$1.61/gal (base case) to \$1.57. In the next step heat integration was considered in the optimization, which further reduced the cost to \$1.51/gal. However, it became clear that the scope of heat integration is limited by the relatively low temperature in the fermentor. In order to improve the potential for heat integration the authors considered multi-effect distillation in the "beer" column and in the azeotropic column as

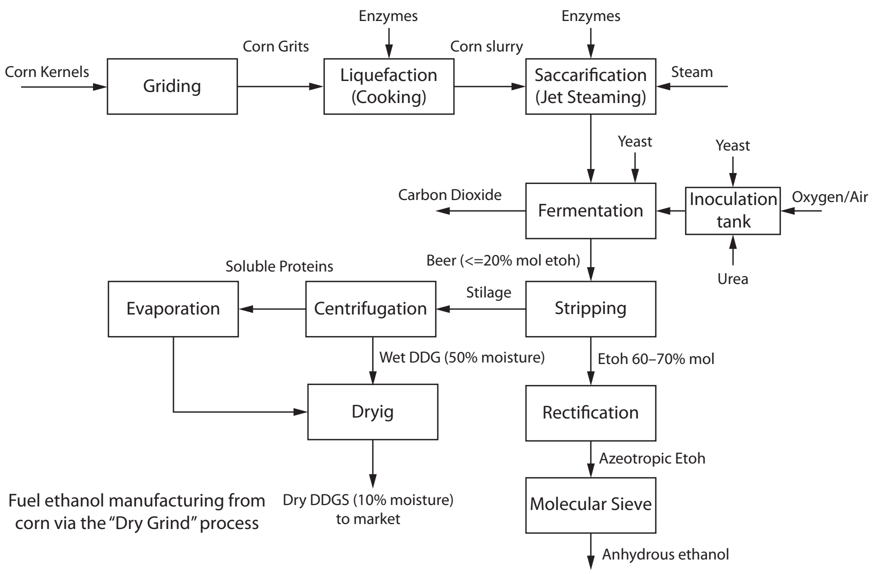

FIGURE 1
Flowsheet of dry-grind process for bioethanol.

alternatives for the optimization (see Fig. 2). This finally, led to a 65% savings in steam consumption and cost reduction down to $1.43/gal! This example then illustrates on the one hand the potential for cost reduction in biofuel plants, and on the other hand the potential pitfall when policy researchers (e.g. Pimentel, 1991) perform life cycle analyses without accounting for the fact that the cost and efficiency of the manufacturing technology can be substantially improved as was the case in this example.

Example 2. Stochastic programming of process network

We consider as a second example the problem studied by Tarhan and Grossmann (2008), a multi-period synthesis of process networks under *gradual uncertainty reduction* in the process yields and with possible investments in pilot plants for reducing uncertainties. It is assumed that a process network is given with availabilities of raw materials, intermediates and demands for final products over T time periods. The problem is to determine in each time period t whether the capacity of specific processes should be expanded or not (including new or existing processes), whether specific processes should be operated or not, and whether pilot plants for reducing uncertainties in new processes should be installed or not. In addition, other decisions include selecting the actual expansion capacities of the processes, the flowrates in the network, and the amount of purchase and sales of final products. The objective is to select these decisions to maximize the expected net present value.

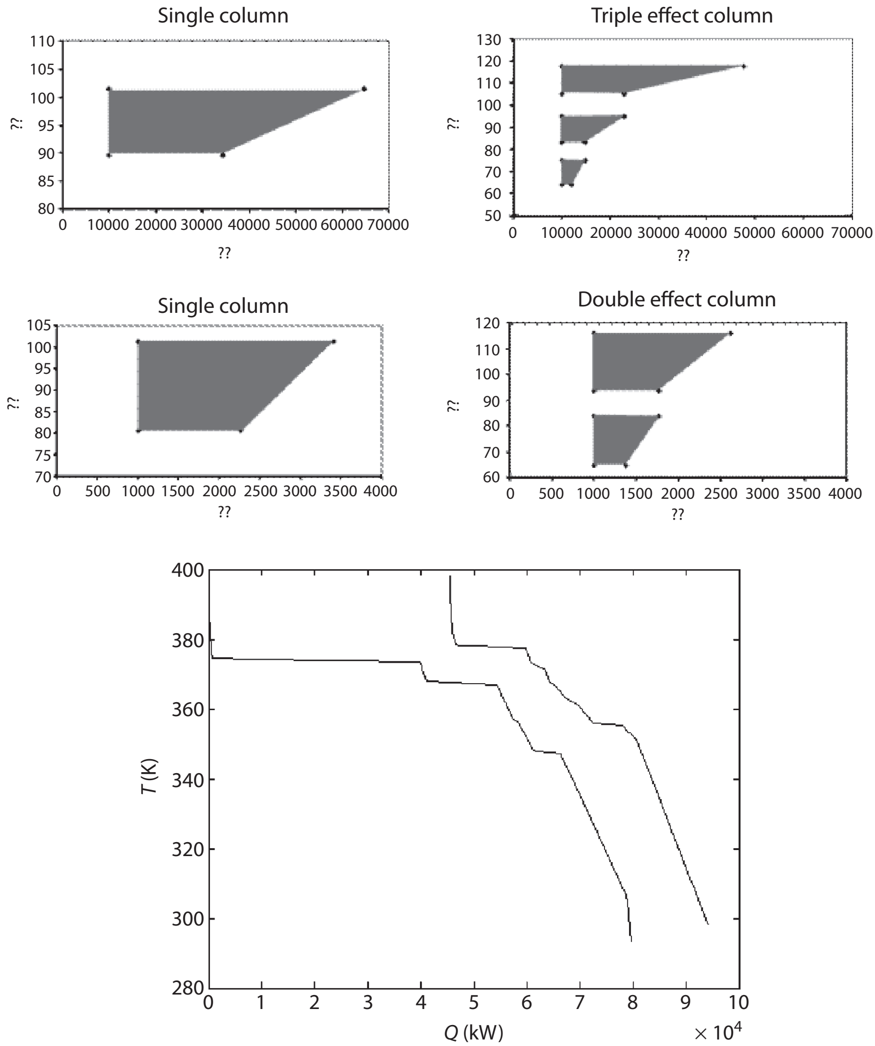

FIGURE 2
Profiles for multieffect columns for beer and azeotropic column, and T-Q curves for optimized process.

Figure 3 shows an example of a process network that can be used to produce a given product. Currently, the production of A takes place only in Process III which consumes an intermediate product B that is purchased. If needed, the final product A can also be purchased so as to maintain its inventory. The demand for the final product, which is assumed to be known, must be satisfied for all periods over the given time horizon. Two new technologies (Process I and Process II) are considered for producing the intermediate from

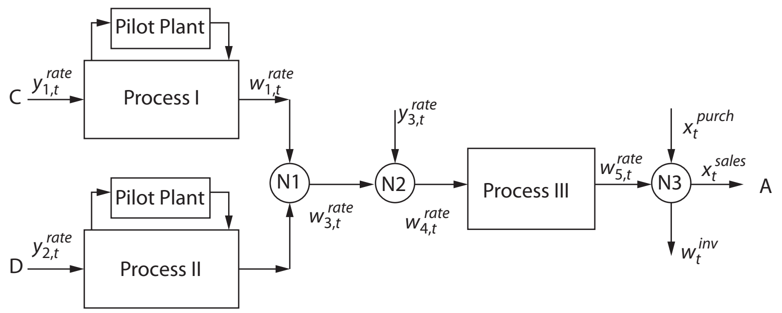

FIGURE 3
Example of process network with uncertain yields.

two different raw materials C and D. These new technologies have uncertainty in the yields which is reduced over time.

The scenario tree representations for gradual uncertainty resolution for the two processes are given in Fig. 4. It is assumed that at step 2 the only realizable yields are the highest and the lowest of all possible values. At step 3, when the uncertainty is totally revealed, all possible yields are realized. In the figure there are two possible realizations for yields in step 2 and four possible yields in step 3.

Using the multistage stochastic programming model and the algorithm proposed by Tarhan and Grossmann (2008), the capacity expansion and operation decisions for the problem in Fig. 3 were optimized over a time horizon of 10 years. Process III is already operational with an existing capacity of 3 tons/day and a known yield of 70%. All possible realizations of the yield for process I at step 3 are 69, 73, 77 and 81% where only 69 and 81% are realizable in step 2 of the uncertainty resolution. Similarly for process II, 60 and 90% are two realizations in step 2 with 60, 70, 80 and 90% as possible realizations at step 3. The problem was solved within 2% tolerance of the upper and lower bounds with the proposed method. The solution proposes expanding Process I up to a capacity of 10 tons/day and making an additional expansion of 4.93 tons/day at time period 3 if the yield turns out to be 69%. If the yield for Process I was found to be 81% then an expansion of 2.98 tons/day is made at the time period 4. This solution did not involve the

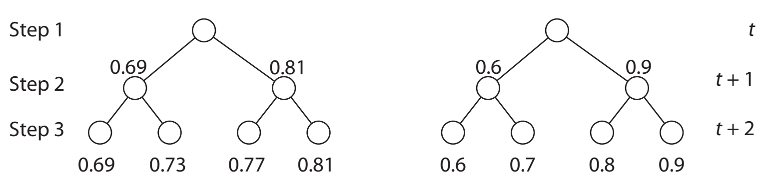

FIGURE 4
Gradual resolution of uncertainty in yields of procesees 1 and 2.

use of a pilot plant, and yielded an expected net present value of $8,050,500. The proposed branch and bound algorithm based on Lagrangean relaxation required about 5,000 secs of CPU-time. This example shows the potential for applying stochastic programming approaches to new processes that have uncertain yields, a problem of relevance to biofuels.

Example 3. Design of hydrogen SCs for vehicle use

This example deals with the optimal design of a hydrogen SC for vehicle use in UK taking into account economic and environmental concerns. The problem, which was first proposed by Almansoori and Shah (2006), considers different technologies for production, storage and transportation of hydrogen to be established in a set of geographical regions distributed all over the country (see Fig. 5). The goal is to determine the optimal network configuration in terms of its economic and environmental performance.

The problem can be formulated as a bi-criterion MILP that seeks to minimize the total cost of the network and its environmental impact. In this formulation, integer variables indicate the number of plants and storage facilities to be opened in a specific region (i.e., grid), whereas binary variables are employed to denote the existence of transportation links connecting the SC entities. The importance of climate change in the transition towards a hydrogen energy system motivated the selection of the damage caused by

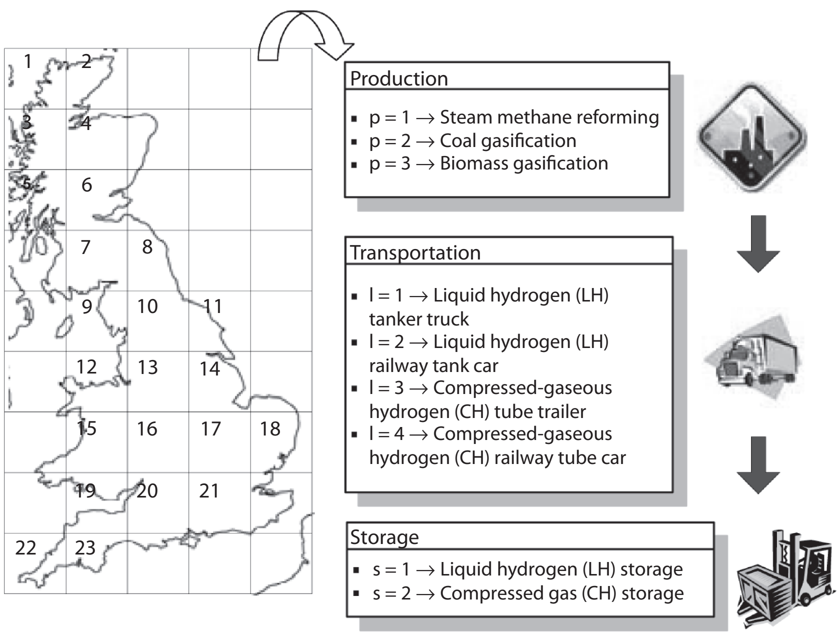

FIGURE 5
Superstructure of example 3.

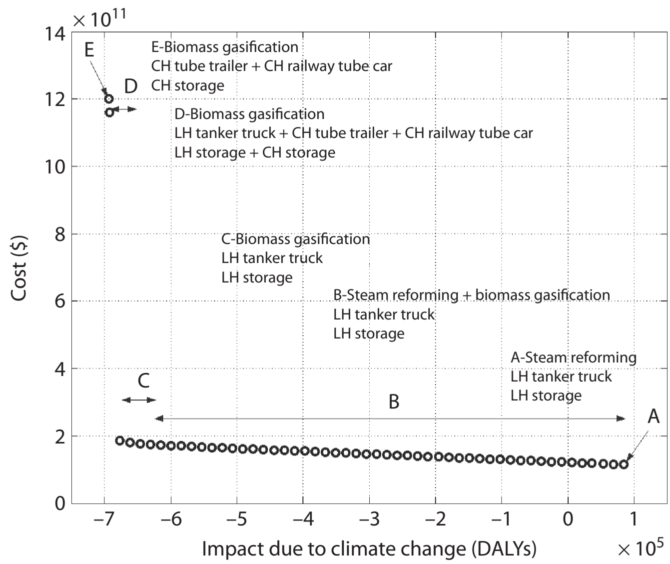

FIGURE 6
Pareto set of example 3.

the green house gases emissions as the environmental objective to be minimized. Such an impact can be calculated by making use of the Eco-indicator 99 framework, which incorporates the most recent advances in LCA methodology and hence covers all the stages of the life cycle of the process.

The difficulty of this approach is that the size of the problem can become very large as the number of periods increases. For instance, a problem with 10 periods involves 21,160 binary variables, 1,880 discrete variables, 25,396 continuous variables and 70,976 constraints. To circumvent this problem, Guillén-Gosálbez et al. (2008) developed a bi-level decomposition scheme that proved to be approximately one order of magnitude faster than the full space method for small optimality tolerances (i.e., less than 1%). The Pareto set calculated (see Fig. 6) showed that important reductions in the contribution to global warming can be achieved by replacing steam reforming by biomass gasification and also by establishing more decentralized hydrogen networks in which the transportation tasks are minimized. On the other hand, the results also revealed that replacing liquid hydrogen by compressed gaseous hydrogen is not a good choice, since such option leads to a marginal reduction in the environmental impact at the expense of a large increase in the total cost of the network.

Example 4. Design of sustainable chemical SCs under uncertainty

This example addresses the optimal design of petrochemical SCs taking into account economic and environmental concerns and considering

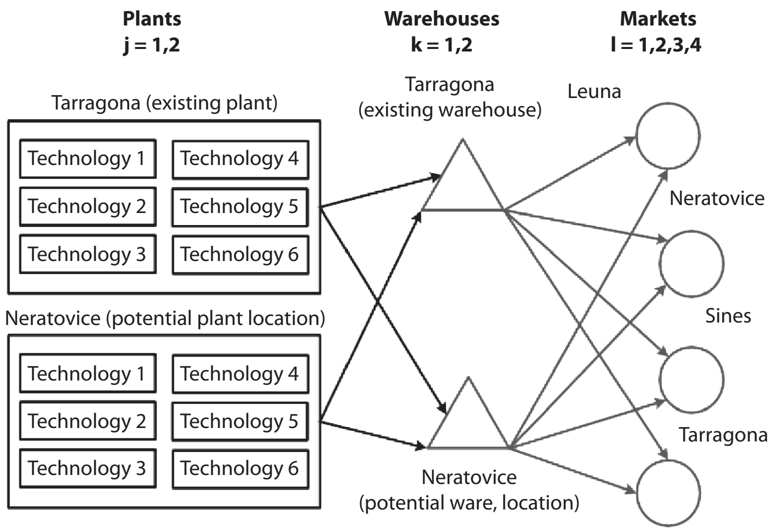

FIGURE 7
Superstructure of example 4.

different sources of uncertainty affecting the environmental assessment of the process. We consider a superstructure based on a three-echelon SC (production-storage-market) with different available production technologies for plants, potential locations for SC entities and transportations links (see Fig. 7). The goal is to maximize the NPV of the SC and minimize its environmental impact. As in the previous example, the latter performance indicator is calculated over the entire life cycle of the process by using the Eco-indicator 99 approach, which in this case includes not only the damage due to global warming, but also the remaining impacts in the human health, ecosystem quality and resources depletion. The example also accounts for the uncertainty of the life cycle inventory of emissions and feedstock requirements associated with the network operation. Guillén-Gosálbez and Grossmann (2009) proposed a novel MINLP formulation to deal with this problem in which the environmental performance of the network under uncertainty was measured via probabilistic constraints that were converted into standard deterministic inequalities by applying concepts from chance-constrained programming. Specifically, the example in Fig. 7 led to a bi-criterion MINLP involving 78 binary variables, 1,837 continuous variables and 1,963 constraints. The authors solved this problem by a novel decomposition technique based on parametric programming that allowed the calculation of the complete Pareto set in 7 iterations after 68.30 CPU seconds.

This modeling framework was later expanded in scope to deal with the uncertainty of the parameters of the damage model, and also to allow for the simultaneous control of different damage categories included in the Eco-indicator 99 (Guillén-Gosálbez and Grossmann, 2008). These new considerations gave rise to a bi-criterion nonconvex MINLP, the solution of which was calculated by using the epsilon constraint method in conjunction with a novel global optimization strategy based on a spatial branch and bound framework. In both cases, the Pareto solutions showed the convenience of establishing more decentralized networks in order to reduce the emissions due to the transportation tasks, which in turn decreases the overall environmental impact.

Conclusions

This article has provided an overview of the scope of mathematical programming in the synthesis and planning of sustainable chemical processes. It has been shown that mathematical programming techniques offer a general modeling framework for including environmental concerns in these problems. It was also shown that process synthesis and supply chain management are two key areas in PSE that lend themselves very well to addressing sustainability issues together with the common economic targets. We highlighted the major optimization approaches that are available, including the handling of uncertainty and the multi-objective optimization.

Some of the major challenges have been highlighted throughout the paper and several examples presented to illustrate the nature of the applications and the problems that are faced. While perhaps obvious, it is clear that the area of sustainability offers a great opportunity to renew the interest in process synthesis since it appears that many of the new biofuel plants have not had the benefit of being subjected to more systematic and thorough optimizations as their petrochemical counterparts. As we also discussed, this can lead to flawed analyses when comparing energy content or life cycle analysis of competing energy technologies. We should note, however, as was illustrated in the bioethanol example, that it will not be sufficient to simply apply the known synthesis techniques to these new processes. Major reasons include having to deal with exothermic reactions that take place at lower temperatures and separations of highly diluted systems. Furthermore, a major challenge not encountered in conventional process synthesis is that many of the biofuel plants are rather small and therefore cannot benefit of the economies of scale. This would seem to imply that process intensification could hold the promise of making these processes economically viable. This area has been virtually unexplored. An interesting possibility might involve developing superstructures that contemplate alternatives for process intensification.

In the area of supply chain management it is clear that progress has been made in terms of incorporating models for environmental impact within a multiobjective optimization framework. However, the greatest challenge still lies in properly accounting for the uncertainties associated with the parameters of these models (e.g. emissions, potential harm, etc.). An interesting possibility would be to characterize the various sources of uncertainty and establish what would be the more meaningful stochastic programming strategies to anticipate their effect.

Finally, although one can in principle formulate the associated optimization problems discussed above, it is clear that models are often very large, defeating current computational capabilities. Hence, developing effective solution approaches and algorithms continues to be a very real need.

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