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## OPTIMAL DESIGN OF ECO-EFFICIENT CHEMICAL PROCESSES

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**Abstract.** Technico-economic considerations have for long been taken into account as decisional criteria in the conceptual phase for new and retrofitted chemical processes. While the emphasis on economic aspect remains strong, another priority in evaluating chemical processes is the environment. Such problems, leading to multiple and most often conflicting goals, must be solved within the framework of complex multiobjective optimization. This study addresses the problem of analyzing the various objectives involved in eco-efficient processes, meaning that ecological and economic considerations are taken into account simultaneously at the preliminary design phase of chemical processes. The multiobjective methodology is performed by genetic algorithms implemented in the so-called MULTIGEN library, particularly well-suited to multiobjective optimization of mixed integer nonlinear programming problems. The trade-off between economic and environmental objectives is illustrated through the generation of Pareto curves. The methodology will be illustrated by the classical example of Williams and Otto Chemical Plant, which is often considered as a test bench for representing complex nonlinear programming problems incorporating the main features of a chemical processing plant, in the dedicated literature of process design. The original William and Otto Chemical Plant problem will be revisited here in a multiobjective mode. A key point will be the treatment of equality constraints involved in the material balances, which are often considered as one of the most critical phases in genetic algorithm implementation. This step was carried out by solving the set of nonlinear equations by a classical Newton-Raphson method implemented within the Matlab solver. We will highlight the insight the design engineer can gain using the multiobjective synthesis procedure and demonstrate the computational efficiency achieved by tackling simultaneously environmental and economic issues.

**Key-words.** multiobjective optimization - genetic algorithm - ecoefficient processes – economic criterion – environment

The economic viability constitutes a traditional criterion in the conceptual phase for new and retrofitted chemical processes. Yet, it is now increasingly obvious that chemical plants can no longer be designed on the basis of technico-economic concerns alone and that the other two dimensions of sustainability – environmental and social – leading to the so-called “Triple Bottom line” must be part and parcel of the design phase. A major difficulty to tackle the problem globally is that there are many independent but often competing objectives that people would pursue simultaneously. Lots of ongoing research aims to develop a set of metrics or indicators (the amount of metrics may vary from 10 (AICHE, 1998) to 134 (CSD, 1996) to draw a quantitative profile of sustainability. The conceptual nature of sustainability determines that it is an excellent candidate to be treated as a multiobjective problem. This study has not the ambition to consider the three components of sustainability but is devoted to the design methodology of eco-efficient processes, i.e., integrating environmental aspects into process design management, by balancing ecological and economic requirements. For this purpose, several indexes of environmental impact including ozone depletion, global warming potential, human and aquatic toxicity, photochemical oxidation and acid rain potentials can be taken into account. Current methodologies such as the so-called waste reduction (WAR) algorithm, based on a potential environmental impact (PEI) balance for chemical processes, propose robust process design that integrally incorporates environmental impact reduction. Such problems lead to multiple and most often conflicting goals and must be solved within the framework of complex multiobjective optimization.

This study will address the problem of analyzing the various objectives involved in eco-efficient processes, meaning that ecological and economic considerations are taken into account simultaneously at the preliminary design phase of chemical processes.

The multiobjective methodology is performed by genetic algorithms implemented in the so-called MULTIGEN library (Gomez et al., 2008). The main development principles will be briefly presented. The example of the Williams and Otto Chemical Plant used as a case study will be recalled. Then, some typical results will be analyzed, showing the trade-off between economic and environmental objectives through the generation of Pareto curves.

## ECO-EFFICIENT CHEMICAL PROCESS DESIGN FRAMEWORK

The framework for optimal design of eco-efficient chemical processes proposed in this study (see Figure 1) integrates a mathematical process model, which is then embedded in an outer multiobjective optimization loop. For this purpose, the MULTIGEN library, offering a variant of the NSGAI algorithm (Deb, 2002; Gomez et al., 2008), particularly well-suited to multiobjective optimization of mixed integer nonlinear programming problems, has been used.

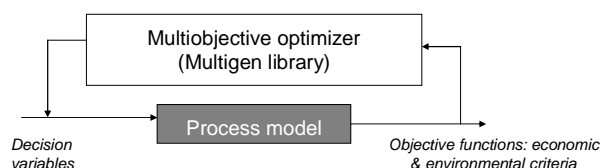


Figure 1. General optimization framework

Of course, some design and flowsheeting packages could be used to model the process in order to compute the objective functions, and the mathematical model could be very computationally expensive. For instance, many chemical processes are modelled by a nonlinear system of Differential Algebraic Equations (DAEs). In this case, obtaining a feasible solution relies upon solving the equation set.

Since the goal of this study is to demonstrate the validity of the approach, we use a well-known application plant, the so-called Williams and Otto Chemical Plant, that is a complex nonlinear programming problem incorporating the main features of a chemical plant. It has been presented initially by (Ray and Szekely, 1973) and then extensively used as a case study in many chemical process systems engineering applications (Biegler et al., 1997; Sequeira et al. 2002). The original William and Otto Chemical Plant problem will be revisited here in a multiobjective mode and will serve here as a test bench of the proposed methodology (Chakraborti et al., 2006). A key point is the treatment of equality constraints involved in the material balances, which are often considered as one of the most critical phases in genetic algorithm implementation: this step was carried out by solving the set of nonlinear equations by a classical Newton-Raphson method implemented within the Matlab® environment.

Concerning the optimization phase, MULTIGEN has been designed as a library of multiobjective genetic algorithms codes written in VBA, equipped with an Excel® interface, to facilitate graphics visualization. MATLAB® Builder™ EX was used to integrate the MATLAB applications into the organization's Excel® workbooks by creating the add-ins for encrypting the MATLAB functions, packaging the functions as a DLL that is accessible from Excel, and generating a Microsoft® Visual Basic® for Applications (VBA) wrapper around them.

## PRESENTATION OF THE ILLUSTRATIVE EXAMPLE

The Williams and Otto Chemical Plant is devoted to the production of a desired product P (Di Bella and Stevens, 1965). It consists of a Continuous Stirred Tank Reactor (CSTR), a heat exchanger, a decanter and a distillation column, as displayed in Figure 2. The product stream coming from the CSTR, releases heat through a heat exchanger and the generated by-product, G, is separated in a decanter that follows it. This by-product is subjected to a waste treatment process, adding to the operational cost. The overflow is treated in a distillation column, where the product, P, is produced. Product P is assumed to form an azeotrope with E with 10% by weight of P at the azeotropic point. A part of the distillation column underflow is recycled into the CSTR unit and the rest is used as a plant fuel. The objective of this study is to minimize the production of waste (FG), while minimizing the reactor cost. We assume that the reactor is the most expensive equipment of the process.

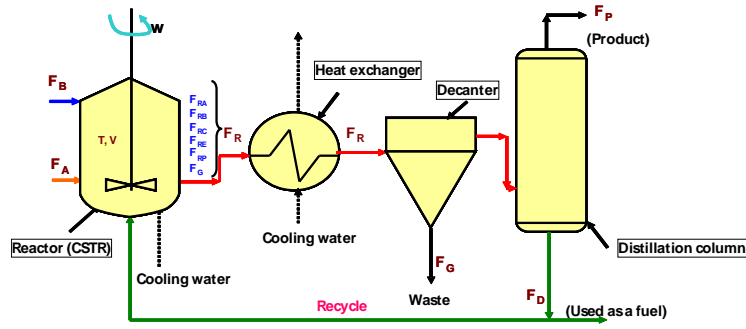
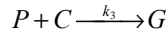
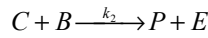
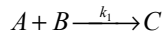


Figure 2. Flowsheet of the Williams and Otto Chemical Plant

### Process model

As outlined in a previous work (Ray and Szekely, 1973), the production of, P is assumed to involve three second order irreversible chemical reactions given as:



The rate constants change with temperature, following a classical Arrhenius relationship (see Table 1):

$$k_i = A_i \exp(-B_i/T)$$

|                     | i = 1                  | i = 2                   | i = 3                   |
|---------------------|------------------------|-------------------------|-------------------------|
| A <sub>i</sub> (/h) | 5,9755 10 <sup>9</sup> | 2,5962 10 <sup>12</sup> | 9,6283 10 <sup>15</sup> |
| B <sub>i</sub> (°R) | 12000                  | 15000                   | 20000                   |

Table 1. Arrhenius constants

Please note that we did not attempt to change the units used in the earlier studies (Ray and Szekely, 1973) to validate it more easily. The model of the process is represented by the following constraints (see Table 2). The mathematical model involves 12 variables  $F_A, F_B, F_D, F_G, F_{RA}, F_{RB}, F_{RC}, F_{RE}, F_{RP}, F_R, V$  and  $T$  for a set of 9 nonlinear equations, thus involving a three-degree of freedom.

|   |   |
|---|---|
| 1) Overall material balance :                   | $h_1 = F_A + F_B - F_G - F_P - F_D = 0$   |
| 2) Distillation column efficiency restriction : | $h_2 = F_{RP} - 0.1F_{RE} - F_P = 0$  |
| 3) Material balance on component E :            | $h_3 = (M_E/M_B) k_2 (F_{RB} F_{RC} / F_R^2) V \rho - (F_D F_{RE} / (F_R - F_G - F_P)) = 0$   |
| 4) Material balance on component P :            | $h_4 = [k_2 F_{RB} F_{RC} - (M_P/M_C) k_3 F_{RC} F_{RP}] V \rho / F_R^2 - F_D ((F_{RP} - F_P) / (F_R - F_G - F_P)) - F_P = 0$                   |
| 5) Material balance on component A :            | $h_5 = (-k_1 F_{RA} F_{RB}) V \rho / F_R^2 - F_D F_{RA} / (F_R - F_P - F_G) + F_A = 0$  |
| 6) Material balance on component B :            | $h_6 = (-k_1 F_{RA} F_{RB} - k_2 F_{RB} F_{RC}) (V \rho / F_R^2) - (F_{RB} F_D / (F_R - F_P - F_G)) + F_B = 0$                                  |
| 7) Material balance on component C :            | $h_7 = [(M_C/M_B) k_1 F_{RA} F_{RB} - (M_C/M_B) k_2 F_{RB} F_{RC} - k_3 F_{RP} F_{RC}] (V \rho / F_R^2) - (F_D F_{RC} / (F_R - F_G - F_P)) = 0$ |
| 8) Material balance on component G :            | $h_8 = (M_G/M_C) k_3 F_{RC} F_{RP} (V \rho / F_R^2) - F_G = 0$  |
| 9) Definition of $F_R$ :                        | $h_9 = F_{RA} + F_{RB} + F_{RC} + F_{RE} + F_G + F_{RP} - F_R = 0$  |

Table 2. Set of model constraints of the Williams and Otto Chemical Plant

### Objective functions, optimization variables and constraints

The *objective functions* which reflect two aspects of sustainability concerns are based on cost and environmental impact:

- The cost criterion considered in this study is classically based on investment minimization (I), because there was not enough information to evaluate the operational cost of the Williams and Otto plant (raw material cost, utilities cost ...) and to embed it in a net present worth computation. A typical six-tenth-factor rule has been applied:

$$\begin{aligned} & \text{Min}(f_1) \\ & f_1 = 2500 V^{0,6} \end{aligned}$$

- All the wastes generated by the process are concentrated in  $F_G$ , which has been directly considered as the environmental criterion to minimize.

$$\begin{aligned} & \text{Min}(f_2) \\ & f_2 = F_G \end{aligned}$$

The *optimization variables* are respectively the flow rates of reactants A, B to reactor ( $F_A, F_B$ ) and the operating temperature of the reactor.

The *constraints* considered in this problem are actually the bounds on the decision variables.

$$\begin{aligned} 1000 & \leq F_A \leq 3000 \\ 1000 & \leq F_B \leq 3000 \\ 580 & \leq T \leq 680 \end{aligned}$$

The solution strategy for the Williams and Otto Plant can thus be summarized in Figure 3.

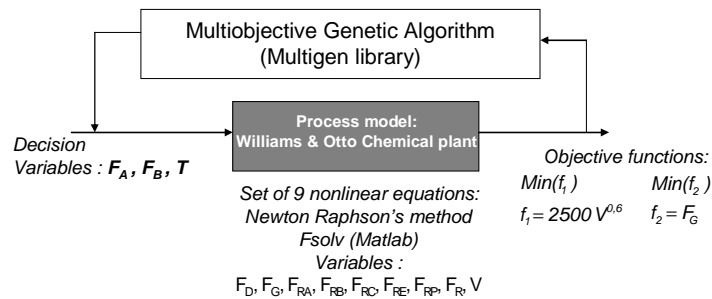


Figure 3. Solution strategy for the Williams and Otto Chemical Plant

A set of data and initialization values must be fixed by the user to implement the design methodology. In table 3, the annual demand for each product is presented.

| Initialization values |            |
|-----------------------|------------|
| $F_D$                 | 41550      |
| $F_G$                 | 1005,83    |
| $F_{RA}$              | 25983      |
| $F_{RB}$              | 75723,67   |
| $F_{RC}$              | 3339,4617  |
| $F_{RE}$              | 59991,9593 |
| $F_R$                 | 162222,552 |
| $F_{RP}$              | 10762,1959 |
| $V$                   | 42,74      |

Table 3. Initialization values for the set of nonlinear equations

Table 4 displays the parameters of the genetic algorithm used for plant design. In this work, the generation number was fixed as twice the population size. Although a systematic study was not carried out to find crossover and mutation rates, they were chosen from several preliminary tests and agree with previous works (Dedieu et al., 2003). Considering the stochastic aspect of GAs, several optimization runs were carried out for each multicriteria optimization.

A variant of NSGAII was used in this study (Gomez et al., 2008). Let us recall that NSGA II has both elite-preservation strategy and an explicit diversity-preserving mechanism.

After creating an offspring population  $Q_t$  from the parent population  $P_t$ , the two are combined and then a non-dominated sorting is used to classify the entire population  $R_t$  of size  $2N$ . This allows global non-domination check among the offsprings and parent solutions.

Then, the new population of size  $N$  is filled with solutions of different non-dominated fronts one at a time starting with the best non-dominated front. All fronts which could not be accommodated are just deleted. When the last allowed front is being considered, there may exist more solutions than the number of remaining slots in the new population, so a niching strategy is used to choose the members which reside in the least crowded region in that front.

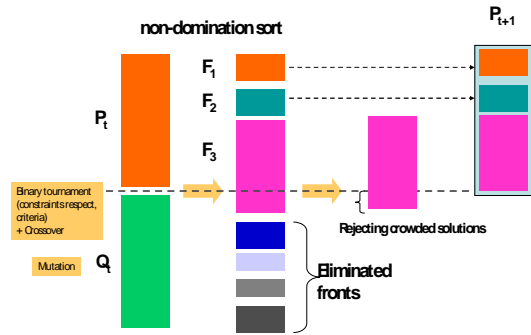


Figure 4: Principles of NSGAI

This strategy is especially useful in the later stages when most of the solutions lie in the first non-dominated front, ensuring better spread in the Pareto-optimal front. Binary tournament selection (with a crowded tournament operator), recombination and mutation operator are then used to create an offspring population. Specific operators have been developed in a variant of NSGAI in order to take into account continuous, binary and integer variables (Gomez et al., 2008).

|                       | Monocriteria | Bicriteria         |
|-----------------------|--------------|--------------------|
|                       | Waste-volume | Reactor cost-waste |
| Population size       | 120          | 120                |
| Generation number     | 240          | 240                |
| Crossover probability | 0,7          | 0,7                |
| Mutation rate         | 0,15         | 0,15               |

Table 4 - Genetic algorithm parameters

## Results and Discussion

Only typical results are presented here, concerning a bicriteria analysis {waste flow rate – reactor cost} as presented in Figure 5.

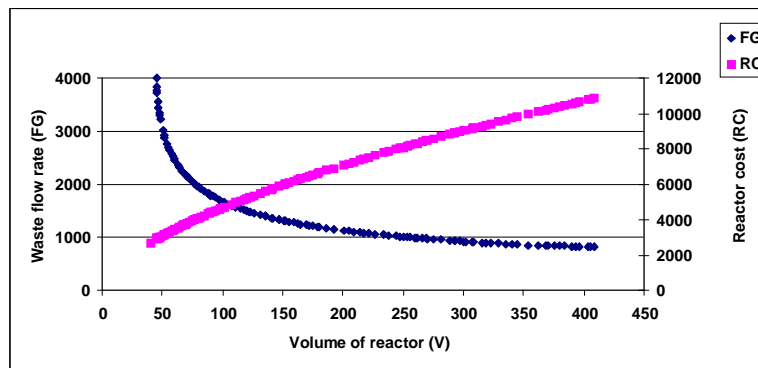


Figure 5: Pareto's optimal solutions for the bicriteria analysis {waste flow rate – reactor cost}

Figure 5 shows that the reactor volume (which is equivalent to reactor investment cost) and the waste flow rate exhibit an antagonist goal: the highest the volume of reactant is, the more efficient this stage becomes, thus reducing the environmental impact. In previous works (Di Bella and Stevens, 1965; Chakraborti et al., 2005), the objectives used for optimization were maximizing “return on investment” while minimizing “the sum of the squares of residual errors”. In these studies, the environment aspect was not taking in account.

## CONCLUSIONS

In this paper, we have highlighted the insight the design engineer can gain using the multiobjective synthesis procedure and demonstrate the computational efficiency achieved by tackling simultaneously environmental and economic issues.

The methodology proposed in this work consists in minimizing both investment cost and environmental impact. An optimization scheme has been implemented using a multiobjective genetic algorithm (NSGA II) coded in VBA. This technique is ideally suited to this type of problem, where a number of conflicting considerations must be taken into account.

The use of MULTIGEN makes possible a robust optimization technique, across a non-linear search space. The paper clearly shows that opportunities for process optimization and environmental impact minimization must be considered at the early stages of process development.

## Nomenclature

|  |   |
|--|---|
| $A_i$                                    | pre-exponential factor in the Arrhenius rate equation for the $i$ th reaction |
| $B_i$                                    | exponential factor in the Arrhenius rate equation for the $i$ th reaction     |
| $E_{act}$                                | activation energy   |
| $F_A, F_B$                               | respective flow rates of reactant A, B to reactor (lb/h)                      |
| $F_D$                                    | flow rate of portion of column bottoms returned as plant fuel (lb/h)          |
| $F_G$                                    | flow rate of G from decanter (to waste) (lb/h)                                |
| $F_P$                                    | flow rate of product P from column (lb/h)                                     |
| $F_{RA}, F_{RB}, F_{RC}, F_{RE}, F_{RP}$ | respective flow rates of A, B, C, E, P from reactor (lb/h)                    |
| $F_R$                                    | total flow rate from reactor (lb/h)   |
| $k_i$                                    | Arrhenius reaction rate constant  |
| $M_B, M_C, M_G, M_R, M_P$                | respective molecular weights of B, C, G, R and P                              |
| $R$                                      | gas constant  |
| $T$                                      | absolute temperature  |
| $V$                                      | reactor volume cu ft  |
| $\rho$                                   | density   |

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