A systematic approach for multi-objective process design in multi-purpose batch plants

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A systematic approach for multi-objective process design in multi-purpose batch plants

A dissertation submitted to the
Swiss Federal Institute of Technology Zurich (ETHZ)

For the degree of
Doctor of Technical Sciences

Presented by

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2003
Acknowledgments

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† No, I did not need five years for the PhD. I did many other things in-between... ☺
‡ No, I did not imply that Ulrich is weak where I am strong. But where I am strong, he was wise enough to let me be!
† I mean, of course, my Chapter 3!
Should I list them alphabetically? Historically? Let’s put them in a somewhat random order, and let them wonder about their position in the list...

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* I won’t cite any names, for obvious reasons... Some like to pretend to work!
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Abstract

The growing awareness of the civil society for the environment, and the resulting regulations introduced by national states have modified the way chemical industry introduces new products in the market. The resulting profound changes in the process design methodologies have resulted in the *integrated process design* scheme. This procedure can be defined as the early consideration of significant risks and environmental impacts stemming from the whole lifecycle of the process in all steps of the process design. Methodologies are required to support the design team during the integrated process design.

The development of such a methodology and its related tools is the goal of the research presented here. The focus lies on the implementation of new batch processes in multipurpose production facilities. The method is meant to enable a screening of possible process designs, and assess them according to several objectives.

The methodology is based on a recipe containing a list of tasks to be conducted, and on description of the material streams crossing the system boundaries (raw materials and wastes). In a first iterative phase, the waste streams are analyzed for recycling potentials or for possible treatment problems whose origins can be identified with the help of in-depth analysis tools. Taking those elements into consideration, the recipe can be modified, integrating as well potential recycling tasks. At the last iteration, when the recipe cannot be improved any further, the waste treatment operations needed to handle the waste streams are determined according to financial and ecological objectives for a given waste treatment facility.
In a second phase, the implementation of the resulting recipe in an available production line is addressed. A hybrid superstructure consisting of eligible equipment units and of design heuristics is generated. A multi-objective optimization is conducted to obtain the most promising designs within the superstructure. The objectives are, in order of decreasing priority, the production rate, the number of equipment units used (complexity) and an indicator to favor “top-down” designs. This optimization is conducted with a meta-heuristic method: the Tabu Search. Its parameters as well as some algorithm options have been tested and tuned in order to achieve a high probability of finding the optimal design within a low computational time for a broad range of cases. The resulting design is an allocation of equipment units for each task of the recipe.

The second phase can be repeated for several production lines, and a higher level indicator (e.g. the production costs) can be used for selecting the most promising production line. With the selection of the waste treatment path, the production line and the design, the implementation of a new process into an existing facility is completed.

Numerous case studies of industrial relevance have been used to test the methodology. Ranked panels of promising designs have been generated with corresponding indicators in about one hour of computations. The various indicators allow a discussion and an evaluation of the designs according to other criteria not directly used in the optimization (e.g. batch size). Discussions with experts have shown that both the process designs and the waste treatment paths obtained correspond to high-quality implementations - and in some case studies, they have even been proven to be optimal with side considerations. This makes the methodology powerful for numerous tasks, ranging from screening projects, in order to address “go-no go” decisions, to the detailed implementation of a new process in existing waste treatment and production facilities.
La prise de conscience croissante par la société des problèmes environnementaux, ainsi que les lois et règlements introduits en conséquence par les États ont modifié la manière dont l’industrie chimique introduit de nouveaux produits sur le marché. La conception intégrée est l’aboutissement de profonds changements dans les méthodes de design des procédés. Cette procédure peut être définie comme prenant en considération, à chaque étape de la conception, les risques et les impacts sur l’environnement émanant du cycle de vie complet du procédé.

Le but de cette thèse est de développer une procédure, et les outils logiciels nécessaires, appuyant les ingénieurs de développement pendant toute la phase de conception intégrée du procédé. Ce travail se concentre en particulier sur l’implantation de nouveaux procédés batch dans des usines multi-usages. Ces outils doivent permettre un tri rapide des alternatives et leur évaluation en fonction de plusieurs objectifs.

La méthode développée ici se base sur une recette industrielle indiquant une liste d’opérations devant être effectuées ainsi que sur les flux de matière entrant ou quittant le système, à savoir les matières premières et les déchets. Dans une première phase, itérative, les flux de déchets sont analysés afin d’identifier des potentiels de récupérations (recyclages) ou d’éventuels difficultés de traitement dont les origines peuvent être déterminées à l’aide d’analyses plus poussées. En fonction des conclusions de ces analyses, la recette peut être modifiée, intégrant également les recyclages s’ils sont possibles. A la dernière itération, lorsque la recette ne peut plus être améliorée, les opérations nécessaires pour traiter les déchets sont déterminées en fonction d’objectifs financiers et environnementaux.
Dans une seconde phase, le problème de l’implantation de la recette dans une ligne de production existante est traité. Une superstructure implicite est générée, composée de listes d’équipements utilisables et de règles de design (heuristiques); puis une optimisation multiobjective est conduite afin d’obtenir les designs (i.e. les allocations de pièces d’équipements à chaque opération contenue dans la recette) les plus prometteurs. Les objectifs sont, par ordre de priorité, le taux de production, le nombre de pièces d’équipement utilisées (complexité du design) et un indicateur permettant de favoriser les designs “top down”. Cette optimisation est effectuée à l’aide d’un algorithme méta-heuristique : le Tabu Search. Les paramètres de l’algorithme, ainsi que certaines options, ont été évalués et réglés de manière à obtenir de hautes probabilités de trouver la solution optimale en des temps de calcul raisonnables, et ce pour une large sélection de problèmes.

Cette seconde phase peut être répétée pour plusieurs lignes de production, et un indicateur approprié (p.ex. les coûts de production) peut être utilisé afin de sélectionner la ligne de production la plus favorable. Ayant déterminé les opérations nécessaires au traitement des déchets, ayant sélectionné une ligne de production et fixé le design, l’implantation de la recette dans l’usine est terminée.

Plusieurs études de cas, tirées de procédés industriels, ont été menées pour tester la procédure décrite ci-dessus. Des listes de designs prometteurs, qualifiés par de nombreux indicateurs, ont été générées en moins d’une heure de calcul. Les indicateurs permettent de discuter et d’évaluer les designs en fonction de critères qui n’ont pas été directement utilisés pendant l’optimisation (p.ex. la taille des batch). Des entretiens avec des experts ont montré que tant les designs de procédés que les traitements de déchets obtenus sont de haute qualité - dans certains cas, il a même été possible de prouver par d’autres méthodes qu’ils étaient optimaux. Cela rend cette procédure particulièrement efficace pour traiter de nombreuses tâches tant au niveau du tri initial des projets (afin de décider s’ils sont valables/profitables) qu’au niveau de l’implantation détaillée d’un nouveau procédé dans des installations existantes.
Zusammenfassung


Das Ziel dieser Arbeit ist, Methoden und Software-Werkzeuge zu entwickeln, die während der integrierten Prozessentwicklung die Ingenieure unterstützen. Der Schwerpunkt liegt in der Einrichtung neuer Batch-Prozesse in existierenden Mehrzweckproduktionslinien. Diese Werkzeuge sollen mögliche Prozessdesigns überprüfen und anhand mehrerer Zielgrössen beurteilen.


In einer zweiten Phase wird die Einrichtung des resultierenden Rezepts in einer Produktionslinie behandelt. Eine hybride Superstruktur, bestehend aus geeigneten

Diese zweite Phase kann für weitere Produktionslinien durchgeführt werden, und ein übergeordneter Indikator (z.B. Produktionskosten) kann eingesetzt werden, um die bestgeeignete Produktionslinie zu bestimmen. Mit der Auswahl der Abfallsbehandlungsoperationen, der Produktionslinie und des optimalen Designs ist die Einrichtung eines neuen Chemieprozesses in einer bestehenden Fabrik vollständig.

Chapter 1: Introduction

1.1 Integrated Process Development

Over the last decades, for instance after the accidents of Seveso, Bhopal and Schweizerhalle, the public’s acceptance of chemical companies has changed drastically. The growing awareness of the civil society for the environment, and the resulting regulations introduced by national states have modified the way chemical industry introduces new products in the market. Concentrating only on the financial perspectives - on the costs of safety and environment - is not possible anymore [Schneidewind, 1995] and companies have to consider the safety of the production sites and the environmental impacts of their production. While many companies do still not consider the environmental evaluations as objectives, but as constraints (i.e. the aim is not to minimize the environmental burden, but to maintain pollution and emissions below the legal threshold in the country they are producing), a growing part of the chemical industry introduced internal rules of “clean production” - usually stricter than national laws - valid in all their production sites worldwide and that they begin to enforce on their suppliers. This tendency - a direct consequence of the pressure of civil society - is a key element of the PR of chemical companies, and CEFIC’s Responsible Care (RC) program is one European example of its “communication” side. Companies participating in the RC program publish yearly in their annual reports (global and local production plant’s reports) many environmental indicators showing the
environmental burden of their production. The public can compare data from year to year, hence encouraging the company to progress each year. Initially, most companies introduced Health, Safety & Environmental (HES) measures as end-of-pipe solutions, i.e. the processes were not modified, but emissions where treated in sewage treatment plants or incinerated to reduce the harmful components released into the environment [Ullmann, 1995]. Similarly, hazardous materials where for example stocked in special containers and dangerous reactions conducted in reinforced protective shelters. However, such end-of-pipe treatments require huge investments and important operating costs that could jeopardize the profitability of the production.

As a result, the insight grew that HES considerations should be integrated during the whole process development, and not just “patched” at the end. This procedure is called integrated process development [Hungerbühler, 1995]. This procedure can be defined as the consideration of significant risks and environmental impacts stemming from the whole lifecycle of the process early in the process development [Hungerbühler et al., 1998]. Integrated process development can be more rigorously defined as being optimal regarding to several factors (multi-objective optimum). The objectives considered are typically costs, safety, energy consumption and environmental impact. In many cases, such multi-objective optimal designs target for example at reusing mass and energy from the output stream of one process in the input stream of another process within the boundaries of a given system (e.g. a building, a facility) - making mass and energy flows “integrated”. In this context it is obvious that practical solutions have to be profitable. The challenge lies in finding process designs delivering high profits while having only little environmental impact thus being eco-efficient [Hungerbühler et al., 1998].

While some environmental impacts also have economic implications (such as wastes to be treated or deposited) others have not, such as gaseous emissions, but are in part legally regulated. Legal alterations (e.g. CO₂ emission taxes) might change the picture in the future and might harmonize economic and ecological objectives. Thus it is important that chemical companies are prepared for reducing emissions in order to remain competitive.

Indicators are needed that provide a numeric evaluation on the strength and weaknesses of a process with regard to the given objectives. Many approaches
have been used for the assessment of environmental impact of chemical processes, for example:

- Life Cycle Assessment (LCA), as in Kniel et al. [1996]. This method is by far the most comprehensive, but has several drawbacks: it is practically impossible to objectively aggregate different types of interference with nature (e.g. CO₂ effect and heavy metal emissions) - as explained for instance by Finnveden [1997], it is time consuming and expensive, thus being perhaps not the appropriate tool in early design stages.
- Mass Indices presented by Heinzle et al. [1998] and Koller et al. [1998], a short-cut method taking into consideration the amount of waste in proportion to the amount of product.
- The EHS methodology by Koller [2000], another shortcut method dealing with missing data, which can also be used to assess health and safety.

A recent overview of such methods has been compiled by Hertwich et al. [1997].

Extensive research has also been conducted on waste minimization, e.g. by Mallick et al. [1996] that presented a methodology for the pollution reduction within chemical process simulators, or Dantus [1996] who considered retrofit options targeted at waste minimization and their economic impact. A detailed review of works in the field of waste treatment is given in the introductions of Chapters 2 and 3.

The development of new processes has therefore gained in complexity, due to these new constraints (or objectives). But the growing globalization simultaneously requires faster time-to-market and hence tends to reduce the time a company can invest for process design. In particular in fine chemistry, pharmaceuticals and custom manufacturing, chemical companies must continuously develop their product portfolio (and hence introduce new production processes) in order to maintain their competitiveness. Hence a reliable, efficient and rapid process synthesis - that takes into consideration all the objectives and constraints - is one of the keys for a successful business in these sectors.
1.2 Process Synthesis

1.2.1 Definition

The chemical process synthesis begins with the selection of the chemistry path that will be used for the synthesis of the target chemical (sequence and route selection). The next step is to scale-up the laboratory-scaled synthesis to an industrial production scale; in this phase, the process parameters (like temperatures or pressures) are set. The result from these two first phases is an “equipment-independent” recipe, composed of a series of physicochemical tasks to be conducted.

Based on this recipe, an industrial process procedure must be set up. This is what will be considered in this thesis the process design phase. Process design is understood as comprising all design procedures that have to deal directly with production-sized equipment units and facilities. It consists of the composition of process flowsheets, including equipment selection (and plant selection if the synthesis is not a grassroot design but is meant to use existing facilities), as well as the waste treatment facility selection.

Obviously these three process synthesis phases cannot always be completely separated, above all in continuous processes, where the process parameters will highly depend on the equipment units used. However, for batch processes where most equipment units are standardized, a somewhat complete separation of these phases can be considered.

1.2.2 General review of major contributions

For two to three decades computer systems are developed that are thought to support engineers in such design problems [Grossmann and Daichendt, 1996]. But only in the last decade such software became efficient due to the rising computational power and the development of new algorithms and optimization methods.

A review on recent developments in chemical process synthesis has been given by Grossmann et al. [1999]. A large part of the work in this field has been done on limited scale systems (at the unit operations’ level), such as heat exchanger
networks, distillation sequences, reactor sequences or reactor networks. On a larger scale, utility systems and process flowsheets synthesis have also been studied as summarized below. Most work has however been conducted in standard process synthesis, and not in integrated process synthesis. With the exception of the Pinch Analysis (see below), that targets at processes integration and hence indirectly at optimizing both the economic and ecological sides of the process, the other works presented below all restrict themselves to costs or throughput (an important cost factor).

**Heat exchanger networks - Pinch analysis**

The synthesis of heat exchanger networks is the most mature technique in process synthesis. The method resulted from the discovery of the heat recovery pinch that is derived through thermodynamic methods as developed by Linnhoff et al. [1979]. An extensive review of these systems was given by Gundersen and Naess [1988]. Recent work in this field was done e.g. by Zamora and Grossmann [1998] and Galli and Cerda [1998]. The pinch analysis mostly allows an optimal usage of only one resource (e.g. heat, fresh water consumption), and is usually not used to design complete processes.

**Distillation, Reactor networks and Utility system**

Other unit operations have been studied in a somewhat lesser extend. For example, distillation sequence synthesis (e.g. Agrawal [1996]) and reactor networks synthesis (e.g. Lakshamanan and Biegler [1996]) have been conducted using different methodologies ranging from MINLP (Mixed-Integer Non-Linear Programming) to evolutionary methods like simulated annealing [Floquet et al., 1994] or genetic algorithm [Fraga and Matias, 1996].

In some papers, the simultaneous synthesis of several unit operations is considered [Balakrishna and Biegler, 1993] but only in a limited way: these procedures are very efficient in designing a few unit operations, but too specific to be used in a complete process synthesis. A little apart from the process itself, and this time on a larger scale (complete process and often complete factory), many studies have been made on the design of utility systems e.g. by Petroulas and Reklaitis [1984].
Process flowsheet

Total Process flowsheet synthesis has been conducted using different methods. A global method has been described: the hierarchical decomposition by Douglas [1985] using heuristic rules with several decision levels, ranging from batch vs. continuous to heat exchanger considerations. Several implementations of this method have also been done using expert systems and short-cut models (e.g. Kirkwood et al. [1988] for the initial implementation).

Another methodology developed by Grossmann [1985] uses mathematical programming. This approach utilizes optimization techniques to select the configuration and parameters of the processing system. The superstructure contains discrete (0-1, No-Yes) decisions and continuous parameters, and its optimization is called MILP (Mixed Integer Linear Programming) if linear or MINLP otherwise. Several implementations of this method have been realized, like DICOPT++ within the modeling system GAMS [Brooke et al., 1992], or PROSYN-MINLP [Kravanja and Grossmann, 1994]. Recently these two methods have also been combined [Daichendt and Grossmann, 1997].

Batch processes and multipurpose plants

The studies mentioned above mostly concentrate on continuous processes. However, in the considered industries (fine chemistry, pharmaceuticals, custom manufacturing), most productions are conducted in batch mode, as companies’ chemical portfolios are usually composed of numerous low volume productions (on the order of 10-100 tons per year in comparison with megatons in petrochemistry, for example).

For the same reasons, it is usual not to build a specific plant for each new process (grassroot design), but to build general and flexible production plants that can conduct most of the processes in the company’s portfolio. In these plants, campaigns will be conducted where the demand of a given chemical for a given period is produced in subsequent batches, and then the plant configuration is changed to produce the next chemical.

Such plants are classified as multiproduct batch plants, in which every product follows the same sequence through all the process steps, or as multipurpose batch
plants, in which each product follows its own distinct processing sequence by using the available equipment in a certain layout [e.g. Rippin, 1983]. Multipurpose plants can be used in two main modes: either only one production runs in the plant at a given time or many processes run concurrently. Some multipurpose plants consist of discrete but nevertheless flexible production lines that are independent from each other.

Process synthesis research in this context has mostly concentrated on the design of optimal multipurpose or multiproduct plants for a given portfolio of products, as opposed to the optimal use of an existing multipurpose plant for a new chemical production. This is however a recurrent problem, as most companies introduce frequently new chemicals and the lifetime of such a production building is in the range of decades. A review on the research conducted in this domain is given in Chapter 4, while a review on the mathematical methods that can be implemented to tackle such problems is given in Chapter 5.

1.2.3 Integrated process synthesis

As mentioned above, most of the methods of process synthesis described above target only at competitive prices and unit operation’s efficiency. Sometimes, as for example in the total flowsheet synthesis, ecological aspects are either seen as simple constraints (i.e. legal compliance) like in Diwekar et al. [1992], or only studied in a qualitative way [Douglas, 1992]. In some works however, an environmental point of view has also been developed:

For example, the pinch analysis method, while still used for heat exchanger networks and distillation column profiles, is now developed in a wider scope [Linnhoff, 1993], such as

- Batch process integration [Gremouti, 1991],
- Water and wastewater minimization [Kuo and Smith, 1998],
- Total site integration and emissions targeting [Puigjaner and Espuna, 1998].
Also in the utility system synthesis, while the main objective usually remains costs, some other objectives like waste minimization are also taken into account in some works like in [Chang and Hwang, 1996].

Some work on multi-objective (costs and waste minimization) process synthesis has been done by Ciric and Huchette [1993] using the MINLP method. However a comprehensive waste treatment design seen as part of the process (i.e. assigning the needed waste treatment operations up to the deposit, incinerator or STP for each stream of waste, and calculating the costs and ecological burden arising from them) has not been studied in these works.

1.3 Objective & Contributions

The goal of this research is to develop methodologies and software tools supporting the development team during the process design phase. They shall provide a screening of possible process designs and assess them according to several objectives. Each alternative (based on the waste treatments selected) is also checked for environmental legal compliance. The final result is not intended to be the selection of one single, supposedly ‘the best’, process but the evaluation of several promising alternatives from an integrated point of view.

As pictured in Figure 1-1, the problem is defined by a recipe and by available facilities (production lines and waste treatment facilities). The overall methodology (solid arrow) has to select the optimal production line (and the related optimal design) and waste treatment path according to several objectives: financial (pictured as a $ note), ecological (pictured with the Responsible Care logo), health and safety (pictured with a Helmet sign), robustness (pictured with a bell curve representing the uncertainty of many parameters) and design quality (pictured as a small design simplification).

A complete methodology fulfilling all the aims defined above has been developed for the financial objective function. The ecological objective has been only partially implemented: ecological impact stems mostly from emissions, energy used and the raw materials consumed. Raw materials as well as most energy
consumption depend on the recipe and hence are not modified - in a first approximation - by changing the production line or the design. Emissions however are highly dependant on the waste treatment, and hence the assessment of the ecological burden as been implemented exclusively in the waste treatment path selection so far.

The robustness (i.e. inclusion of uncertainty) has similarly only been implemented in the waste treatment path selection. Additional objective functions measuring the “design quality” have however been implemented for the optimal design generation. The occupational health and safety objective has not been considered in this work.

Figure 1-1: Global objectives of this thesis

The methodology developed in this thesis is implemented in two software tools, whose results may be combined but that can also be used independently. In order to simplify the presentation of the overall methodology, the two components will be treated independently in a first phase, and will be only combined in a second phase where a case study will be presented.
First component: Waste Treatment Path Selection

The first component handles the waste treatment path selection. It is schematically shown on Figure 1-2.

The waste treatment selector allows handling problems defined by:

- A given “batch” of wastes, and its related composition and properties,
- A given waste treatment facility, and its related operations and parameters.

It provides comprehensive analysis of the waste treatments, and in particular allows to:

- Highlight potential problems; check feasibility (i.e. check if the waste stream can be legally treated in the selected waste treatment facilities),
- Determine the treatment costs and ecological burdens for all legal paths,
- Identify the cheapest or the most ecologically benign paths,
- Calculate probability distributions for the costs and ecological impacts,
- Select the pareto-optimal treatment paths with regards to both the financial and the ecological objective functions,
- Through the uncertainty analysis, investigate in-depth the origin of the costs and ecological burdens, as well as the most sensitive parameters for each path.

Figure 1-2: Schematic representation of the waste treatment path selection, including the financial, ecological and robustness objectives.
Second component: Batch Process Design

The second component handles the batch process design. It is schematically shown on Figure 1-3.

It optimizes the implementation of a recipe in an existing batch production line and allows handling problems defined by:

- A given recipe and its related parameters like the duration of each task,
- A plant and its equipment list, along with their related properties and parameters,
- Heuristics formalizing knowledge on tasks implementation and designs.

It provides the optimal layout for the process - i.e. the allocation of equipment units to tasks, the design used (in parallel, in series), as well as the production throughput and the campaign duration. Based on that information and by direct comparison, the plant selection can be conducted.

Figure 1-3: Schematic representation of the batch process design component, including the financial and design quality objectives. The plant selection is conducted by direct comparison of the results for each plant.

Content of this thesis

The waste treatment selector will be presented in Chapters 2 and 3: first the general presentation of the methodology and some applications with the financial
objective function are presented, then the integration of the ecological objective functions and some examples of in-depth analysis are introduced.

The Batch process designer will be presented in Chapters 4 and 5: first the global methodology and a case study will be presented, then the optimization algorithm will be discussed in depth.

In Chapter 6, the overall methodology - merging the two components - will be summarized and applied to the Aspirin synthesis case study. Secondly, the same case study will be used to highlight how the results from the Batch process design allow the production line selection.

The conclusions and an outlook will be presented in Chapter 7.
A model for waste treatment selection and costing under uncertainty

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Abstract

Waste treatment emanating from chemical production significantly contributes to the total production cost and should therefore be estimated as early as possible during process development. We developed a model that, taking the waste treatment facilities of an existing chemical plant as an example, for a given waste stream calculates the cheapest feasible combination of treatment operations that satisfies legal emission limits. A special feature of the software is that uncertainty in waste stream composition and separation efficiencies (e.g.
in early process development phases) can be easily propagated through the model leading to probability distributions of treatment cost and selected treatment paths.

To demonstrate its capabilities the model was applied to three waste streams. The results show that rather small variations in one or several input parameters might result in pronounced differences in treatment cost because certain treatment options become technically infeasible or emission limits are exceeded rendering a scenario legally non-compliant. The model also highlights recycling potentials and possible problems of waste streams that might best be resolved by modifying the chemical process.

2.1 Introduction

In fine chemical industry large amounts of waste are produced per mass of product, in particular by spent solvents in pharmaceutical production. Due to waste disposal legislation and emission laws, many expensive treatment steps might be required before allowing the release of such streams into the environment (atmosphere, rivers, and deposits). Beside end-of-pipe solutions also waste minimization has become an important topic in chemical engineering research as in the works of Douglas [1992], Mizsey et al. [1994], Papalexandri et al. [1994], Hilaly & Sikdar [1995], Dantus & High [1996] or Cabezas et al. [1999].

The investigation of case studies from fine chemical industry revealed that waste treatment can amount for 10-30% or even more of total production cost (as explained in Schlegel & Vouillamoz [1993]). But much higher cost might arise when treatment of a given waste stream is considered feasible during early phases of process development while later on, it is recognized that no capacity or technology is available.

As a consequence it is important to check whether emissions from waste treatment would be legally compliant and to obtain reliable estimates of the corresponding treatment cost already at early stages of chemical process development in order to correctly evaluate the economic potential of new products or processes. As even within one company [Dimmer, 1999] the relative contribution of waste treatment cost varies significantly from project to project, they should be estimated specifically for each project. Furthermore, because at
In early phases many parameters are still uncertain; this uncertainty should be considered in the estimation of waste treatment cost.

In contrast to the modeling of chemical processes themselves, only limited work has been done so far on the development of simulators for modeling waste treatment operations. In this context, Petrides et al. [1995] presented a research prototype, EnviroCAD that supports the design of new waste treatment processes. For given waste streams, the simulator facilitates the analysis and evaluation of treatment alternatives to be implemented by carrying out both an economic evaluation and an environmental analysis. The latter is done by calculating material balances on individual compounds and tracking the fate of hazardous chemicals. The software tool targets at the design of a new waste treatment facility. Often, however, the aim is to choose the best combination of existing operations for a waste stream to be treated. This is particularly the case for the development of new projects in multipurpose batch plants.

Linninger and Chakraborty [1999] presented a methodology for pharmaceutical waste management through computer-aided synthesis of treatment policies. The method identifies treatment tasks through examination of waste properties against a set of environmental targets. Afterwards a treatment database is searched for steps capable of achieving at least one of the treatment goals. Non-linear models are used to predict the composition of residues as well as the associated treatment cost. The resulting superstructure can be optimized using an objective function such as treatment cost subject to site-specific environmental, capacity, and logistic constraints. Using a case study from pharmaceutical production, the authors demonstrated the numerical performance of the methodology and its implementation, and showed the wide range of resource consumption as well as of economic benefits attainable through fully compliant policies.

Recently, Linninger et al. [2000] extended their deterministic approach summarized above for the inclusion of uncertainty. They invoked the simplifying assumption that variations due to uncertainty occur only with respect to waste loads, while their compositions remain constant in a first approximation. Furthermore, they assumed that the variations in waste load can be specified by a finite number of states.

In the model presented here, the volume of a waste stream as well as its composition can be treated as uncertain without any limitation to a finite number
of scenarios. The focus of our work is on modeling existing waste treatment facilities. We present a model that automatically calculates the cost of all possible treatment scenarios that are available at a given plant and that are legally compliant for a given waste stream. The explicit evaluation of all treatment flowsheets is possible because on one hand for each waste treatment problem only the corresponding facilities available at an existing plant are considered, and because on the other hand linear models were used for describing the waste treatment operations.

The latter fact facilitated the implementation of a probabilistic approach. In our model uncertainty can be considered by assigning any type of probability distribution to any of the model parameters. A Monte Carlo approach is used for uncertainty propagation. As a consequence the result is not a single value indicating treatment cost but a probability distribution representing the information needed for strategic business decisions in early phases of process development. In addition, the model highlights the treatment path that probably will be the cheapest and indicates possible waste treatment problems that might best be resolved by modifications of the chemical process itself. Furthermore, the most sensitive parameters are identified. Research effort can then be concentrated on determining these parameters with higher precision. The indication of the best paths also helps in forecasting limitations in treatment capacity. To demonstrate its capabilities, the model has been applied to three waste streams considering uncertainty in stream volume and composition.

2.2 Model Description

The concept of the model presented here is shown in Figure 2-1. The aim of the model is to determine the cheapest treatment path out of all treatment alternatives at a given plant for a chemical waste stream with uncertain volume and/or composition (in this paper the term 'stream' does not refer to a continuous flowrate but to a recurrent volume or mass of waste). The uncertainty specified might be the result of considering distributed parameters in modeling the chemical process itself [Dimmer, 1999], or for a given waste stream to be treated it might be stipulated on the basis of heuristic knowledge. In addition to stream
volume and composition, also the different separation efficiencies used for modeling the treatment options are considered as uncertain.

When the model is applied to a given waste stream, first technically infeasible and then legally non-compliant treatment paths are eliminated in two steps. Afterwards, for all remaining alternatives the treatment costs are calculated. The results can be used in several ways:

- Determination of possible treatment paths
- Simulation and cost estimation for each path
- Ruling out impossible paths (e.g., sewage treatment for a gas)
- Legal check for the emissions
- Choice of the cheapest path
- Distribution of minimal cost

![Concept of the probabilistic model for waste treatment selection and costing.](image)

**Figure 2-1:** Concept of the probabilistic model for waste treatment selection and costing.

- to identify economically beneficial recycling potentials as well as waste treatment problems that should be accounted for by improvements in the chemical process itself
- to simulate possible waste treatment operations for
  - identifying the cheapest treatment option for non-distributed input parameters
o calculating the probabilities that certain treatment paths would be the cheapest when distributed input parameters are stipulated
o calculating probability distributions of treatment cost
o identifying the most sensitive parameters for each path

At present, the treatment operations considered in the model represent the waste treatment facilities of the Valais Works of Lonza Group at Visp (CH) [Righetti, 1990]. Figure 2-2 shows the treatment operations considered and the decision structure defined in the model. The treatment operations can be separated into pre-treatments (rectification, phase separation, precipitation, stripping, ammonia recovery, decontamination) and final operations (incineration, sewage treatment plant, and disposal). The pre-treatments decontamination and ammonia recovery as well as the final operations are conducted in central treatment units, while the other pre-treatments are usually conducted within the production line.

The pre-treatments reduce the amount of one or several of the constituents of a stream, and in part these operations can also be used for recycling valuable components. Application of these operations might be required in order to achieve the input constraints of the central treatment facilities. The pre-treatments considered in the model operate as follows:

- rectification: if one liquid phase consisting of at least two major components exists, a separation by rectification can be applied to recover one or more compounds
- phase separation: if a waste stream consists of two liquid phases and one of these is worth to be recycled, a separation of these can be done by decantation
- precipitation: heavy metals stemming from catalysts or raw material impurities are eliminated by precipitation (typically as hydroxides)
- stripping: compounds such as chlorinated solvents are removed from the waste water by steam stripping before entering the sewage treatment plant
- decontamination: waste streams containing toxic or recalcitrant compounds are treated with sodium hydroxide, high pressure, and heat
• ammonia recovery: NH$_3$ as well as the nitrogen contained in NH$_4^+$ compounds is recovered in form of pure NH$_3$; (NH$_4$)$_2$SO$_4$ can also be used as input, then NH$_3$ and CaSO$_4$ are generated in the presence of Ca(OH)$_2$.

Figure 2-2: Treatment operations and decision structure considered in the model.
The final treatment facilities operate as follows:

- sewage treatment plant (STP): waste water entering the STP is neutralized; input limits constrain the concentration of heavy metals, salts and halogenated compounds in order to fulfill the legal emission limits for the effluents as well as to avoid adverse effects to the microbial population; these input limits consider the dilution by domestic sewage treated in the same plant; the sewage sludge is burned and the remaining slag is deposited incineration: input constraints exist for chlorine, bromine, fluorine, sulphur, and phosphorous; flue gases are neutralized and purified by electro-filtration before emission to the atmosphere; the slag and the filter residues are deposited

| Table 2-1: Equations used for calculating mass balances of pre-treatment operations (except decontamination; see text for further explanation). |
|---|---|---|---|
| **Operation** | **Compounds considered** | **Equation** | **Comments** |
| NH₃-recovery | NH₃, NH₄⁺ | \( M_{i,j,\text{out}1} = (1 - E_{i,j}) M_{i,j,\text{in}} \) | (1a) |
| Phase Separation | All non-water soluble compounds | | |
| Precipitation | Heavy metals | \( M_{i,j,\text{out}2} = E_{i,j} M_{i,j,\text{in}} \) | (1b) |
| Rectification | Component(s) to be recycled | | |
| Stripping | Halogenated compounds | \( M_{\text{Str,HC,\text{out}1}} = (1 - E_{\text{Str,HC}}) M_{\text{Str,HC,\text{in}}} \) | (2a) |
| | | \( M_{\text{Str,HC,\text{out}2}} = E_{\text{Str,HC}} M_{\text{Str,HC,\text{in}}} \) | (2b) |
| Water | | \( M_{\text{Str,W,\text{out}1}} = M_{\text{Str,W,\text{in}1}} + K_1 M_{\text{Str,\text{in}2}} \) | (3a) |
| | | \( M_{\text{Str,W,\text{out}2}} = K_2 M_{\text{Str,\text{in}2}} \) | (3b) |
| | | | \( K_2 >> K_1 \) |
| All other components | | \( M_{\text{Str,j,\text{out}1}} = (1 - E_{\text{Str,j}}) M_{\text{Str,j,\text{in}}} \) | (4a) |
| | | \( M_{\text{Str,j,\text{out}2}} = E_{\text{Str,j}} M_{\text{Str,j,\text{in}}} \) | (4b) |

\( E_{\text{Str,j}} \ll E_{\text{Str,HC}} \)
• disposal: only non-burnable solids (mainly from small amounts of construction material) as well as slag and filter residues are allowed to be deposited on the disposal site of the company

For modeling the separations in the pre-treatments, dimensionless separation efficiencies $E$ are used. The model equations describing the corresponding mass balances are given in Table 2-1. A stripping efficiency $E_{\text{Str},\text{HC}}$ of 0.9 for example indicates that 90% of the halogenated compounds are removed. For the operation decontamination no mass balance equation is needed because no stream splitting is taking place and only the unchanged TOC value is used in further calculations. Also for the final treatment operations no mass balances are stipulated. As long as the input limitations to these operations are respected, the effluents are considered to be released into the environment. Secondary streams such as sludge are nevertheless accounted for in the cost calculation (see below).

According to the specifications of the waste stream, decisions on the selection of treatment operations are taken. These decisions are described in Table 2-2, and Figure 2-2 shows which treatment paths result from the different decisions. The first choice of the treatment path is due to the phase of the stream to be treated, which is indicated by a parameter. Only for liquid streams recycling might be considered. Whether recycling of a compound by rectification (or by phase separation) is considered, is specified by a corresponding economic benefit greater than zero. If recycling is an option, a separation efficiency has to be specified indicating the technical feasibility of the separation. The lower the separation efficiency, the lower is the overall benefit of the recycling operation.

Often the exact efficiency of a separation might not be known, and therefore the model is able to account for a stipulated uncertainty on these parameters. Phase separation by decantation and the stripping operation are controlled in the same way as rectification. A gaseous stream can only be incinerated. When a solid stream contains at least one compound for which a heat of combustion greater than zero has been specified, for the whole stream only incineration will be considered. Fluids on the other hand are allowed to enter this operation even when a heat of combustion equal to zero is specified.
Table 2-2: Description of decisions taken by the program according to the input parameters specified. Decisions of type 'force' signify that only one option exists, while 'allow' means that several options are evaluated with regard to cost.

<table>
<thead>
<tr>
<th>Decision on</th>
<th>Type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase of the stream</td>
<td>stream specific, 'force'</td>
<td>parameter (solid / liquid / gas)</td>
</tr>
<tr>
<td>Phase separation</td>
<td>stream specific, 'allow'</td>
<td>for each compound a relative solubility (between 0 and 1, reference: water) has to be specified; a difference in this parameter between two compounds greater than 0.5 allows for phase separation</td>
</tr>
<tr>
<td>Recycling</td>
<td>compound specific, 'allow'</td>
<td>for at least one compound an economic benefit (worth of compound in the market) greater than zero has to be specified</td>
</tr>
<tr>
<td>Incineration</td>
<td>compound specific, 'force'</td>
<td>if a stream contains at least one solid for which a heat of combustion greater than zero has been specified, the whole stream is incinerated</td>
</tr>
</tbody>
</table>

Table 2-3 lists the checks on inputs constraints to certain operations conducted by the program. The concentrations of various compounds are checked at the entrance of the sewage treatment plant, the incinerator, and the waste deposit in order to guarantee that the resulting emissions are legally compliant or to avoid adverse effects. After ruling out infeasible treatment paths according to the decisions outlined above, and after checking for legal compliance, the cost for all remaining combinations of treatment operations are calculated.

The treatment costs are calculated on the basis of the stream mass or volume and its composition as well as the properties of the compound (e.g. heat of combustion). The corresponding equations for calculating the cost stemming from single unit operations are given in Table 2-4.
**Table 2-3:** Checks conducted by the program on input limits to certain operations.

<table>
<thead>
<tr>
<th>Input to</th>
<th>Checks conducted on</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sewage Treatment Plant</td>
<td>Concentrations of Br, Cl, F, I, N, salts, and heavy metals</td>
</tr>
<tr>
<td></td>
<td>Toxicity</td>
</tr>
<tr>
<td>Incinerator</td>
<td>Concentrations of Br, Cl, F, I, P, and S</td>
</tr>
<tr>
<td>Deposit</td>
<td>Material (only ash, slag, and non-burnable solids allowed)</td>
</tr>
</tbody>
</table>

**Table 2-4:** Equations used for calculating treatment cost of single unit operations.

All $K$-values were obtained from industry.

<table>
<thead>
<tr>
<th>Operation (Abbreviation)</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decontamination (Deco)</td>
<td>$C_{Deco} = K_{Deco} V$</td>
</tr>
<tr>
<td>Disposal site (DS)</td>
<td>$C_{DS} = K_{DS} V$</td>
</tr>
<tr>
<td>Incineration (Inc)</td>
<td>$C_{Inc} = M (K_{Inc} + K_{AH} + K_{HC} + K_{S} + K_{P} + K_{Ash} + K_{Tr})$</td>
</tr>
<tr>
<td>NH3-recovery (NR)</td>
<td>$C_{NR} = K_{NR} M_{NHB, reco}$</td>
</tr>
<tr>
<td>Phase separation (PS)</td>
<td>$C_{PS} = K_{PS} V - \sum_{j} B_{j} M_{j, reco}$</td>
</tr>
<tr>
<td>Precipitation (Prec)</td>
<td>$C_{Prec} = K_{Prec} M$</td>
</tr>
<tr>
<td>Rectification (Rect)</td>
<td>$C_{Rect} = K_{Rect} V - \sum_{j} B_{j} M_{j, reco}$</td>
</tr>
<tr>
<td>Sewage treatment plant (STP)</td>
<td>$C_{STP} = K_{STP} V + K_{salt} M_{salt} + K_{TOC} M_{TOC}$</td>
</tr>
<tr>
<td>Stripping (Str)</td>
<td>$C_{Str} = K_{Str} V$</td>
</tr>
</tbody>
</table>

Parameters:  
- $C$ = cost [CHF];  
- $B$ = financial benefit [CHF kg$^{-1}$];  
- $V$ = volume of waste stream [m$^3$];  
- $M$ = mass of waste stream [kg];  
- $K$ = empirical cost factors [CHF m$^{-3}$] or [CHF kg$^{-1}$];

Indices of supplementary $K$-values and corresponding masses:  
- $\Delta H$ = heat of combustion $^a$;  
- $HC$ = content of halogenated compounds $^a$;  
- $S$ = Sulfur content $^a$;  
- $P$ = Phosphorous content $^a$;  
- $Ash$ = ash deposit $^a$;  
- $salt$ = salt content;  
- $Tr$ = transportation $^a$;  
- $TOC/N$ = TOC and Nitrogen content

Further indices:  
- $j$ = compound;  
- reco = recovered;  
- recy = recycled

Comments: $^a$ these $K$-values are empirical step-functions of the corresponding properties
Benefits are obtained for recycled solvents and recovered NH$_3$. For the latter operation the extraction cost are greater than the corresponding benefit. Therefore, the treatment cost of this operation increase with increasing mass of NH$_3$ recovered, and in the model only one parameter is implemented representing the sum of cost and benefit. The overall costs of a treatment sequence are obtained by summation over all unit operations included in the sequence. The empirical cost factors used in the calculations were obtained from industry. Further details on the cost calculation are given by Dimmer [1999].

In the model, uncertainty is considered by Monte Carlo simulation because this approach allows for any type of probability distribution and the computational burden of a single evaluation of the presented model is low. The model was implemented in MATLAB so that the Monte Carlo simulation could be realized by vector and matrix operations. This means that first all uncertain parameters are generated according to the stipulated probability distributions using a random number generator. These parameters are stored in separate vectors or matrices. In the latter each column entry represents one set of parameters used in one Monte Carlo simulation. Afterwards, in one single run the model calculations are carried out using the matrices instead of single parameter values. Also the checks for technical feasibility and legal compliance are conducted using these matrices. The resulting combination of treatment operations as well as the corresponding cost is also stored in matrices. After finishing the Monte Carlo simulation, probability distributions for treatment cost as well as for selected combinations of treatment operations are compiled from the information stored in the results matrices. Additionally, the resulting dependence of single parameters on the overall treatment cost can be displayed graphically. Further details on the implementation of the model are given by Cavin [1998].

2.3 Results and Discussion

To demonstrate the capabilities of the model, the results obtained for three waste streams are discussed in this paper. The composition of the different waste streams and the input parameters specified are given in Table 2-5. The separation
efficiencies $E_{i,j}$ and the stipulated uncertainties on them are listed in Table 2-6. These parameters reflect empirical knowledge on the pre-treatment operations. The amount of a compound in the waste stream, its heat of combustion, and a possible recycling benefit $B_i$ must take non-negative values, and the relative solubilities (using water as reference) as well as the separation efficiencies $E_{i,j}$ must take values between zero and one. Therefore, the corresponding values, generated with a normal distribution, lying outside these ranges were rejected. This procedure was repeated until a specified number of values inside the corresponding range were picked. The mean values and variances were adapted accordingly.

Table 2-5: Input parameters for waste streams WS1 - WS3. The amounts given represent the waste resulting from one batch. The variances of the amounts are referring to normal distributions.

<table>
<thead>
<tr>
<th>Stream</th>
<th>Composition</th>
<th>Formula</th>
<th>Amount Mean [kg]</th>
<th>Amount Variance [kg]</th>
<th>Heat of Combustion $[10^4 \text{kJ kg}^{-1}]$</th>
<th>Recycling Benefit $B_i$ [CHF kg$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WS1</strong></td>
<td>salicylic acid</td>
<td>C$_7$H$_6$O$_3$</td>
<td>282.8</td>
<td>27.8</td>
<td>2.2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>acetic acid anhydride</td>
<td>C$_4$H$_6$O$_3$</td>
<td>1345.2</td>
<td>133.8</td>
<td>1.6</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>acetyl salicylic acid</td>
<td>C$_9$H$_8$O$_4$</td>
<td>23.9</td>
<td>2.4</td>
<td>2.2</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>acetic acid</td>
<td>C$_2$H$_4$O$_2$</td>
<td>3355.0</td>
<td>340.7</td>
<td>1.5</td>
<td>0.7</td>
</tr>
<tr>
<td><strong>WS2</strong></td>
<td>water</td>
<td>H$_2$O</td>
<td>3129.5</td>
<td>316.8</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>natrium chloride</td>
<td>NaCl</td>
<td>597.2</td>
<td>60.5</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>acetone</td>
<td>C$_3$H$_6$O</td>
<td>57.3</td>
<td>5.6</td>
<td>3.3</td>
<td>0.0</td>
</tr>
<tr>
<td><strong>WS3</strong></td>
<td>water</td>
<td>H$_2$O</td>
<td>1000.0</td>
<td>1.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1,1-dichloroethane</td>
<td>C$_2$Cl$_2$H$_4$</td>
<td>6.5</td>
<td>4.0</td>
<td>2.0</td>
<td>0.0</td>
</tr>
<tr>
<td></td>
<td>1,1,2,2-tetrachloroethane</td>
<td>C$_2$Cl$_4$H$_2$</td>
<td>40.1</td>
<td>4.0</td>
<td>0.8</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Waste stream WS1 represents a fictitious production of Aspirin and consists of large amounts of acetic acid and acetic acid anhydride as well as of smaller amounts of salicylic acid and acetyl salicylic acid. The uncertainties in stream composition as given in Table 2-5 result from distributed input parameters used for modeling the production process [Dimmer, 1999].

2.3.1 Example 1: Waste stream from Aspirin production

The waste treatment model identifies two feasible treatment paths for this stream. The first option (path #1) includes the recycling of acetic acid and acetic acid anhydride by rectification, which itself provides a financial benefit \( B_i \) (Table 2-5), while the remainder is incinerated. In the second option (path #2) the whole stream is sent to the sewage treatment plant.

In Figure 2-3 the results obtained for each 1000 Monte Carlo simulations (in all case studies higher number of simulations did not significantly alter the results) are shown when only either path #1 or #2 was considered feasible, or when the cheapest of the two treatment paths was selected for a given set of input parameters. In the latter case, 983 times path #1 was the cheapest, while path #2 was selected only 17 times, when a quite low separation efficiency for rectification was picked in the Monte Carlo simulation. The resulting mean costs are -831 CHF (benefit) and 1490 CHF for path #1 and #2, respectively, and -832 CHF when each time the cheapest path is selected.

<table>
<thead>
<tr>
<th>Operation ( i )</th>
<th>Compound ( j )</th>
<th>Separation Efficiencies ( E_{i,j} ) [-]</th>
<th>Mean</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase separation</td>
<td>non-water-soluble compounds</td>
<td>0.800</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>Stripping</td>
<td>halogenated compounds</td>
<td>0.980</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>Stripping</td>
<td>other compounds</td>
<td>0.010</td>
<td>0.001</td>
<td></td>
</tr>
<tr>
<td>Rectification WS1</td>
<td>acetic acid, acetic acid anhydride</td>
<td>0.610</td>
<td>0.260</td>
<td></td>
</tr>
<tr>
<td>Rectification WS3</td>
<td>1,1,2,2-tetrachloroethane</td>
<td>0.800</td>
<td>0.090</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-6: Separation efficiencies stipulated for the investigated case studies and the different waste treatment operations using normal distributions.
The mean cost calculated for the two paths are significantly different (Figure 2-3). Furthermore, although a broad range of cost is obtained for path #1, due to the high uncertainty in the separation efficiencies specified to simulate a lack of data in an early design phase, Figure 2-3 nevertheless shows that in most cases path #1 is cheaper than path #2. Even for slightly lower recycling benefits $B_i$ this picture does not change significantly. This means that notwithstanding the underlying uncertainty, the conclusion can be drawn that with high probability treatment path #1 is the favorable one and should be considered in future planning. To decrease the uncertainty on the effective cost or benefit, the separation efficiencies $E_{i,j}$ have to be determined or estimated with higher precision.

**Figure 2-3**: Results obtained for waste stream WS1 and each 1000 Monte Carlo simulations when only either path #1 or #2 was considered feasible, or when the cheapest of the two treatment paths was selected for a given set of input parameters.

In the recycling option (path #1) a mixture of two solvents is separated from the waste stream by rectification. This mixture then has to be split in another rectification operation. Our model, however, considered the recycling of all
valuable compounds in a single operation. Therefore, the finally resulting benefit would be less than given above, but solvent recycling would still be beneficial. Thus, it can be concluded that solvent recycling in combination with incinerating the remaining waste would be the most profitable option for this problem.

2.3.2 Example 2: Waste stream with high salt concentration

The second stream investigated in this paper, WS2, demonstrates the capability of the program to highlight possible problems in the treatment of waste streams. For the problem specified, the salt concentration of WS2 (Table 2-5) in some cases (128 times) forces the whole stream to be incinerated, because the input limit to the sewage treatment plant is not fulfilled, while 872 times out of 1000 Monte Carlo simulations the stream can be sent to the sewage treatment plant. This latter option is about 30 times less expensive than incineration (Figure 2-4). Figure 2-5 shows that as soon as the salt fraction in the stream exceeds 1.16 [arbitrary unit], the treatment cost increase dramatically. Thus, one message of this example is that, under the constraints assumed here, there is some probability (more than 10%) that the treatment cost would be quite high. Thus, for avoiding this economic risk, the process should be modified in order to decrease the salt concentration - as long as no major drawbacks with regard to other objectives such as reactions yields result.

One problem arises regarding the evaluation of a single project: to be on the safe side it was assumed that the salt concentration of WS2 would not be diluted by other chemical waste streams before entering the sewage treatment plant (meaning that all other chemical waste streams treated in the sewage plant at the same time would have an average salt concentration equal to the one of WS2). This assumption is probably not correct, and the high salt concentration of WS2 might not be a problem if other waste streams have lower salt concentrations (i.e. scheduling of waste streams). If the process cannot be modified and dilution by other waste streams cannot be guaranteed, then with regard to incineration the process should be conducted as concentrated as possible in order to minimize the volume to be burned.
Figure 2-4: Probability distribution of treatment cost resulting for waste stream WS2 from 1000 Monte-Carlo simulations. Two separate maxima result from sewage treatment and incineration.

Figure 2-5: Waste stream WS2: Dependence of treatment cost on salt concentration.
2.3.3 Example 3: Waste stream containing chlorinated solvents

Waste stream WS3 consists of a large amount of water and varying amounts of 1,1-dichloroethane and 1,1,2,2-tetrachloroethane (Table 2-4). It was assumed that only 1,1,2,2-tetrachloroethane can be recycled, with a resulting benefit $B_i$ of 1 CHF/kg. For the amounts stipulated, 1,1-dichloroethane and 1,1,2,2-tetrachloroethane were assumed to be completely soluble and insoluble in water, respectively. The separation efficiencies $E_{ij}$ specified are given in Table 2-6.

These assumptions resulted in the following three most economic treatment paths:

- **Path #1**: 1,1,2,2-tetrachloroethane is recycled by rectification and the remainder is incinerated.
- **Path #2**: 1,1,2,2-tetrachloroethane is recycled by phase separation and the remainder is incinerated.
- **Path #3**: 1,1,2,2-tetrachloroethane is recycled by phase separation. The aqueous phase is stripped to remove 1,1-dichloroethane, and the remainder is sent to the sewage treatment plant.

![Figure 2-6](image)

**Figure 2-6**: Results obtained for waste stream WS3 and each 1000 Monte Carlo simulations when only either path #1, #2, or #3 was considered feasible, or when the cheapest of the three treatment paths was selected for a given set of input parameters.
In Figure 2-6 the results obtained for each 1000 Monte Carlo simulations are shown when only either path #1, #2, or #3 was considered feasible, or when the cheapest of the three treatment paths was selected for a given set of input parameters. In the latter case, 872 times path #3 was the cheapest, while path #1 and #2 were selected only 38 and 90 times, respectively, when path #3 could not fulfill the chlorine limit specified for waste water input to the sewage treatment plant. The resulting mean costs are 342, 340, and 188 CHF for path #1, #2, and #3, respectively, and 209 CHF when each time the cheapest path is selected.

Paths #1 and #2 show two maxima because the supplement factor for halogenated compounds \( K_{HC} \) in the incineration cost function \( C_{Inc} \) (Table 2-4) is a step function. The overall dependence of the treatment cost on the chlorine concentration of WS3 is shown in Figure 2-7. The data points representing treatment cost below 1.0 [arbitrary unit] result from path #3. Due to the possibility of recycling, the treatment cost decrease with increasing chlorine concentration as long as path #3 is feasible. This is the case for chlorine concentrations below 0.9 [arbitrary unit]. Above this value the switch to another treatment path, and thus to much higher treatment cost, is rather diffuse because of the uncertainty in the separation efficiencies. The sensitivity analysis for this problem revealed that in addition to the amounts of chlorinated compounds, the stripping efficiency \( E_{Str,HC} \) had a major influence on the cost because a low stripping efficiency in combination with high amounts of chlorinated solvents renders the treatment in the sewage plant (path #3) infeasible.
In summary, the results obtained for stream WS3 show that for a certain constellation rather small variations in one or several input parameters might result in pronounced differences in treatment cost because a distinct treatment option is rendered technically or legally infeasible. However, the resulting probability distribution indicates that it is rather unlikely that path #3 cannot be applied for treating this waste stream. Therefore, in subsequent development phases of this project the treatment cost resulting from path #3 should be considered.

2.4 Conclusions and Outlook

A model that automatically calculates the cost of all possible treatment scenarios that are available at a given plant as well as legally compliant for a given waste stream has been developed. A special feature of the model is that uncertainties in stream volume and composition and in separation efficiencies can be considered, thus providing probability distributions of treatment costs instead of single values. The model has been applied to several case studies representing more or less fictitious waste streams. The results show that rather small variations in one or several input parameters might result in pronounced differences in treatment cost.
because certain treatment options are considered infeasible and emission limits are exceeded rendering a scenario legally non-compliant. Furthermore, the model highlighted recycling potentials as well as waste treatment problems that best should be resolved by modifying the chemical process itself. The results generated by the model for the case studies investigated, in particular the treatment paths considered feasible and legally compliant for a given waste stream as well as the selection of the cheapest treatment path, have been verified with experts from chemical industry. Thus, the model is a valuable tool for recognizing technical, legal, financial, and environmental problems of treating waste emanating from chemical processes already at early phases of process design.

In future work the model will be applied to more case studies from chemical industry. In extending the program, in particular an ecological assessment will be evaluated with regard to the question, which set of environmental related indicators provides a comprehensive ecological assessment of waste treatment operations in chemical industry.

Acknowledgments

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Chapter 3: Waste Treatment Path Selection - Environmental Assessment

Environmental and Economic Assessment of Waste Treatment Alternatives under Uncertainty

O. Jankowitsch, L. Cavin, U. Fischer and K. Hungerbühler


Abstract

A model for determining the cheapest legal treatment paths for a given waste stream has been extended by an assessment measuring the environmental impact resulting from the treatment itself as well as from the remaining emissions, thus allowing a comparison of treatment policies. Since uncertainty in stream composition is considered the results obtained with respect to both objectives are distributions and not single values. The Pareto optimal alternatives are identified automatically, and the possibly resulting trade-offs between the economic and environmental objectives can be displayed and analyzed. The model has been applied to several case studies. While one case study showed that the cheapest treatment path might well be the environmentally most benign, for the other case studies trade-offs between cost and environmental impact became evident. The model showed in detail, which treatment operations
and/or pollutants cause a high environmental impact, a finding that can be used as a basis for elaborating modifications of the process that produced the waste stream. From the detailed results provided by the model also the basic principle of waste treatment in the light of environmental assessment was highlighted: the reduction of one environmental impact generally comes along with an increase in another impact, e.g. the emission of harmful compounds might be reduced on the expense of energy consumption. In summary, the model proved to be a valuable tool in analyzing treatment options for a given waste stream from an economic as well as an environmental point of view.

3.1 Introduction

One of the major environmental problems of chemical production is the generation of waste. Being the superfluously yielded by-product, the not transformed raw material or a spent solvent, waste is indeed the key to cleaner production [Sheldon, 1997]. As a consequence, there is currently a great deal of interest in the development of methods that can be used to prevent the generation of waste during chemical production or contribute in reducing the emissions from treating it.

Methodologies for waste reduction range from applying heuristic rules for the generation of cleaner process alternatives [Douglas, 1992], over pollution balancing methods such as the waste reduction (WAR) algorithm [Hilaly & Sikdar, 1994 and 1995], to the application of mathematical frameworks for creating mass exchange networks (MEN) [El-Halwagi & Manousiouthakis, 1989; El-Halwagi & Spriggs, 1998]. Although many concepts for realizing a more ecological manufacturing of chemical products have been presented in the literature [Cano-Ruiz & McRae, 1998] and many initiatives for cleaner production have been undertaken from the chemical industry, at the moment abatement processes are still required at many plants to reduce the discharge of pollutants at the end-of-the-pipe.

Some work has been published on the environmental assessment of emissions from a chemical process without assessing the impact of the waste treatment

Using this latter method, in one study also the environmental impact due to the waste treatment operations itself was included into the assessment [Romero-Hernandez et al., 1998]. The results of this study show that high degrees of abatement might even result in a worsening of the environmental impact through excessive energy and raw material consumption in the treatment operations itself. It is therefore important to include not only the final emissions to the environment but also the environmental performance of end-of-pipe technologies into an overall environmental assessment of options for dealing with a given waste stream. Obviously, high degrees of abatement generally also imply high cost reducing the profitability of a chemical process [Romero-Hernandez et al., 1998]. Thus, ‘over-treatment’ of waste streams might be disadvantageous both from an economic as well as an environmental point of view.

In contrast to the modeling of chemical processes themselves, only limited work has been done so far on the development of simulators for modeling waste treatment operations. In this context, Petrides et al. [1995] presented a research prototype, EnviroCAD that supports the design of new waste treatment processes. Linninger and Chakraborty [1999] presented a methodology for pharmaceutical waste management through computer-aided synthesis of treatment policies. Linninger et al. [2000] extended this approach for the inclusion of uncertainty. They invoked the simplifying assumption that variations due to uncertainty occur only with respect to waste loads, while their compositions remain constant in a first approximation. Furthermore, they assumed that the variations in waste load can be specified by a finite number of states.
Recently we presented a model, in which the volume of a waste stream as well as its composition can be treated as uncertain without any limitation to a finite number of scenarios [Cavin et al., 2001]. The model automatically calculates the cost of all possible treatment scenarios that are available at a given plant and that are feasible and legally compliant for a given waste stream. The explicit evaluation of all treatment flowsheets is possible because for each waste treatment problem only the corresponding facilities available at an existing plant are considered, and because linear models were used for describing the waste treatment operations.

The latter fact facilitated the implementation of a probabilistic approach. In our model uncertainty can be considered by assigning any type of probability distribution to any model parameter. A Monte Carlo approach is used for uncertainty propagation. As a consequence, the result is not a single value indicating treatment cost but a probability distribution representing the information needed for strategic business decisions in early phases of process development. In addition, the model highlights the treatment path that probably will be the cheapest and indicates possible waste treatment problems that might be best resolved by modifications of the chemical process itself.

In the present work this model is extended by an environmental assessment of the waste treatment operations and the remaining emissions to the environment. Thus, an overall environmental assessment of the different treatment options for a given waste stream is done enabling a comprehensive comparison. As environmental indicators we used the method of Ecological Scarcity [Ahbe et al., 1990] as well as eleven parameters from the chemical industries Responsible Care program [CEFIC, 1998]. As for the economic analysis also for the environmental assessment a probabilistic approach for displaying the results was applied. The separate evaluations carried out in our model result in a multi-objective decision situation. Interactive functions allow the user to compare the environmental impact with the costs of a treatment strategy, to analyze possible trade-offs, and to identify those treatment operations and/or pollutants that cause a high environmental impact. These model features are demonstrated using several case studies.
3.2 Model Description

3.2.1 Model structure and unit operation models

The aim of the model is to determine the cheapest as well as the environmentally most benign treatment path out of all treatment alternatives at a given plant for a chemical waste stream with uncertain volume and/or composition (in this paper the term 'stream' does not refer to a continuous flowrate but to a recurrent volume or mass of waste). The uncertainty specified might be the result of considering distributed parameters in modeling the chemical process itself, or for a given waste stream to be treated it might be stipulated on the basis of heuristic knowledge. In addition to stream volume and composition, also the different separation efficiencies used for modeling the treatment options are considered as uncertain. When the model is applied to a given waste stream, first technically infeasible and legally non-compliant treatment paths are eliminated. Afterwards, for all remaining alternatives the treatment costs as well as the resulting environmental impact are calculated. In the following, first the model as presented by Cavin et al. [2001] is summarized, and afterwards the alterations to this model for incorporating the environmental assessment are outlined.

At present, the treatment operations considered in the model represent the waste treatment facilities of the Valais Works of Lonzagroup at Visp (CH) [Righetti, 1990]. Figure 3-1 shows the treatment operations considered and the decision structure defined in the model. The treatment operations can be separated into pretreatments (rectification, phase separation, precipitation, stripping, ammonia recovery, decontamination) and final operations (incineration, sewage treatment plant (STP), disposal). The pretreatments reduce the amount of one or several of the constituents of a stream, and in part these operations can also be used for recycling valuable components. Application of these operations might be required in order to achieve the input constraints of the final treatment facilities. The pretreatments decontamination and ammonia recovery as well as the final
operations are conducted in central treatment units, while the other pretreatments are usually conducted within the production line.

![Treatment operations, decision structure, and system boundaries considered in the model.](image)

**Figure 3-1:** Treatment operations, decision structure, and system boundaries considered in the model.

According to the specifications of the waste stream, decisions on the selection of treatment operations are taken. Figure 3-1 shows which treatment paths might result from the different decisions. The first choice of the treatment path is due to the phase of the stream to be treated, which is indicated by a parameter. Only for liquid streams recycling might be considered. Whether recycling of a compound by rectification is considered, is specified by a corresponding economic
benefit greater than zero. If recycling is an option, a separation efficiency has to be specified indicating the technical feasibility of the separation. The lower the separation efficiency, the lower is the overall benefit of the recycling operation. Phase separation by decantation and the stripping operation are controlled in the same way as rectification. A gaseous stream can only be incinerated. When a solid stream contains at least one compound for which a heat of combustion greater than zero has been specified, for the whole stream only incineration will be considered. Fluids on the other hand are allowed to enter this operation even when a heat of combustion less or equal to zero is specified.

Final treatments are operations that lead to direct emissions out of the balance region into five different compartments: air, water, sludge, ash and slag. Therefore, for the environmental assessment a link between the waste stream entering one of these operations and the equivalent emissions leaving it has to be found. For this purpose transfer coefficients have been implemented into the model, like those for incinerators and sewage treatment plants described by Zimmermann et al. [1996]. For a list of input parameters, which can be molecules, atoms or sum parameters, tables provide values for the output of the same species (‘slip-through’) or for transformed ones. The figures given by Zimmermann et al. [1996] originate from studies on several Swiss municipal treatment plants. The example given in Table 3-1 illustrates this procedure: from each 1 kg of nitrogen - in any component or molecule - entering the sewage treatment plant, 678.7 g will leave this operation in the water phase, 232 g will be found in the sludge, and the rest will be transferred to the gas phase. Equivalent tables exist for several compounds, for both sewage treatment plants and incinerators. Additional information is given for example by Belevi [1998].

For incinerators Zimmermann et al. [1996] also presented data about substances released independent of the composition of the inserted waste (‘gross emissions’). These emissions are a function of the process conditions (i.e. temperature) and are due to the air present in the furnace. Usually they are given in g/kg waste input. For example, it is assumed that 1 kg of incinerated waste generates 0.105 g of NO\textsubscript{x} and 4.48 \times 10^{-2} g of NMVOC (Non-methane volatile organic compounds).
Table 3-1: Transfer coefficients for 1kg of nitrogen entering the sewage treatment plant (according to Zimmermann et al. [1996]).

<table>
<thead>
<tr>
<th>Output</th>
<th>g/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>3.29</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.25</td>
</tr>
<tr>
<td>NH₃</td>
<td>0.36</td>
</tr>
<tr>
<td>N₂</td>
<td>87.00</td>
</tr>
<tr>
<td>to air</td>
<td></td>
</tr>
<tr>
<td>Nₗtot</td>
<td>678.70</td>
</tr>
<tr>
<td>to water</td>
<td></td>
</tr>
<tr>
<td>Nₗtot</td>
<td>232.00</td>
</tr>
<tr>
<td>to sludge</td>
<td></td>
</tr>
</tbody>
</table>

Although corresponding coefficients do exist [Zimmermann et al., 1996], we did not include transfer coefficients for the disposal operation, since a time horizon for emissions has to be specified, which is a rather difficult task. Consequently, in our approach only the mass to be deposited is accounted for without considering long term developments, differentiating only hazardous from non-hazardous waste according to the Ecological Scarcity method and the Responsible Care parameters (see below).

For the pre-treatments no additional transfer coefficients were included because for these operations linear models were already applied calculating the output stream as a function of the incoming waste. Finally, at present the energy and auxiliary material requirements for the different operations are evaluated according to data provided by Lonzagroup for each operation. Direct emissions from the pre-treatment operations do not occur, since no waste can be released without passing a final treatment. Some operations however lead to a secondary stream, i.e. a stream enriched in a pollutant. These are sent to the incinerator, where eventually compounds are discharged into the environment. The resulting emissions are then added to the account of the respective pre-treatment operation.
3.2.2 Cost calculation

The treatment costs are calculated on the basis of the stream mass or volume and its composition as well as the properties of the compounds (e.g. heat of combustion). The corresponding equations for calculating the cost stemming from single unit operations are given by Cavin et al. [2001]. Benefits are obtained for recycled solvents and recovered NH$_3$. For the latter operation the extraction cost are greater than the corresponding benefit. Therefore, the treatment cost of this operation increase with increasing mass of NH$_3$ recovered, and in the model only one parameter is implemented representing the sum of cost and benefit. The overall costs of a treatment sequence are obtained by summation over all unit operations included in the sequence. The empirical cost factors used in the calculations were obtained from industry.

3.2.3 Environmental Assessment

The functional unit chosen in the environmental assessment is the treatment of a given waste stream, which is defined by a certain mass, density, and composition. Therefore, the implemented methodology assesses the remaining emissions of the waste stream into the environment but also takes into account the auxiliary materials and energy used during these operations. Similar to the economic assessment, environmental benefits arising from recycling are also considered. The balance region for the environmental assessment is shown in Figure 3-1. In comparison to the cost calculation the balance region has been extended to explicitly take into account the auxiliaries, which are implicitly accounted for in the cost factors for the different operations. Arrows crossing the system boundary represent streams for which environmental impact is regarded. The waste stream is deliberately drawn inside the balance region, since it is not evaluated itself, a point also stressed by the interrupted line leading from the process to the waste treatment region. As mentioned above, only the environmental impact due to the applied treatment as well as the remaining emissions are assessed. For this task we use a set of indicators rather than a single parameter. Emissions, energy consumption, auxiliaries, and recycled compounds are evaluated with the method of Ecological Scarcity, which was first presented by Ahbe et al. [1990] and
later revised by BUWAL [1998]. The concept of this method has been summarized (and compared to other methods) by Baumann and Rydberg [1994] and Hertwich et al. [1997]. In addition to these four indicators, which can also be aggregated since they are expressed in the same unit (UBP, see below), eleven parameters from the chemical industries Responsible Care program [CEFIC, 1998] complete the environmental assessment.

The Ecological Scarcity method allows a comparative weighting and aggregation of various environmental interventions by the use of so-called eco-factors (units: UBP/kg, i.e. environmental impact points \(\text{UmweltBelastungsPunkte}\) per unit of mass emitted). Compartment specific emissions for most of the considered compounds (atoms, single molecules, and sum parameters) can be assessed. It is also possible to evaluate disposal in this fashion since eco-factors for landfills (in UBP/kg deposited material) are available, depending on the class of deposit needed (normal vs. underground deposits). Moreover, the Ecological Scarcity method takes the energy demand or gain into account and transforms it into UBP: 1 MJ of energy - regardless of its form - is set equal to 1 UBP. Data for measuring emissions in UBP were found in BUWAL [1998] while the SimaPro software [Goedkoop, 1995], in which the environmental impact of a large inventory of substances is expressed in UBP, was used for assessing the grey input of auxiliaries, as well as to compute a bonus for each recycled compound.

Although many eco-factors are compiled by BUWAL [1998] and SimaPro [Goedkoop, 1995], nevertheless, some eco-factors required for the present work were missing. Among others, weighting factors for CO emitted to air, or salts and sulphur compounds to water are not included in these references. Furthermore, the list of heavy metals is not complete, and in particular data for metals often used as catalysts such as Pt or Pd are missing. Therefore, some assumptions on eco-factors within the Ecological Scarcity evaluation had to be made. For instance, the impact of HBr and HI emitted to air is set equal to the one of HCl. Further assumptions are outlined in detail by Jankowitsch [2000].

In our model the calculation of the environmental impact according to the Ecological Scarcity method proceeds as follows:

\[
E_{\text{en,k}} = \sum_i \left( \sum_j \left( M_{k,i,j} \cdot U_j \right) \right) + \sum_i \left( M_{k,i} \right) \cdot \sum_j \left( A_{\text{gross,k},j} \cdot U_j \right)
\]  

(1)
\begin{align*}
E_{\text{em},k} &= \sum_i \left( \sum_j \left( M_{k,j} \cdot (K_{k,j} - K_{\text{prod},k,j}) + M_{\text{H}_2\text{O}} \cdot K_{\text{H}_2\text{O},k,l} \right) \cdot U_j \right) \\
E_{\text{aux},k} &= \sum_m \left( \sum_i \left( M_{k,j} \cdot A_{k,m} \cdot U_m \right) \right) \\
E_{\text{rec},k} &= \sum_i \left( M_{\text{rec},k,i} \cdot U_i \right) \\
E_k &= E_{\text{em},k} + E_{\text{en},k} + E_{\text{aux},k} - E_{\text{rec},k} \\
E_{\text{tot}} &= \sum_k (E_k)
\end{align*}

where \( E \) is environmental burden [UBP], \( M \) is mass [kg], \( U \) is the environmental burden of a given substance [UBP kg\(^{-1}\)] or of energy [UBP MJ\(^{-1}\)], \( K \) is energy consumption/production [MJ kg\(^{-1}\)], and \( A \) is mass fraction [kg kg\(^{-1}\)] (indicating the required amount of auxiliaries or the generation of gross emissions); the indices are defined as follows: \( \text{em} \) stands for emissions, \( \text{en} \) for energy, \( \text{aux} \) for auxiliaries, \( \text{rec} \) for recycling, \( \text{tot} \) for total, \( k \) for operation index, \( i \) for compound index, \( j \) for emitted compound or sum property (e.g. VOC), \( l \) for energy form (steam, electric, fossil), \( m \) for auxiliary material index, \( \text{gross} \) for emissions proportional to the total weight of the waste, \( \text{prod} \) for produced (for incineration only, \( K_{\text{prod}} \) is zero for any other operation), and \( \text{H}_2\text{O} \) for water (for incineration only, \( K_{\text{H}_2\text{O}} \) is zero for any other operation).

In addition to an overall aggregation (\( E_{\text{tot}} \)) over all treatment operations used in one sequence and over all four UBP figures also detailed information on each operation (\( E_k \)) and category (e.g. \( E_{\text{em},2k} \)) is available. Also, details on the required energy form can be retrieved for each stage or a whole treatment sequence, differentiating steam, electricity and fossil sources. Table 3-2 lists all operations and displays the available indicators.

To accommodate the increasing need of chemical industry to publish information on their Health, Safety and Environment (HSE) performance, the European Chemical Industry Council (CEFIC) agreed on a set of parameters as part of its Responsible Care (RC) Program, which should be published in every HSE report of CEFIC member companies [CEFIC, 1998]. Because these parameters represent well-known measures in chemical industry, we selected eleven of the core
parameters on emissions and energy and included them into the assessment. These RC Parameters are listed in Table 3-3. We used the original definitions given by CEFIC [1998] with two alterations: Firstly, instead of using tones and toe (tones of fuel oil equivalent), the units were fixed to kilograms and megajoules which is more of the order of magnitude that will be dealt with in this study (1 toe = 41868 MJ). Secondly, instead of keeping track of each heavy metal species, an aggregation is executed immediately by summing up all the masses emitted to water.

Table 3-2: Available indices for the different operations and levels of aggregation

<table>
<thead>
<tr>
<th>Operation</th>
<th>Emissions</th>
<th>Energy</th>
<th>Auxiliaries</th>
<th>Recycling</th>
<th>Aggregated</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Final Treatments</td>
<td>Transfer</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Operation 1</td>
</tr>
<tr>
<td></td>
<td>Coefficients</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2. Decontamination</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Operation 2</td>
</tr>
<tr>
<td>3. NH3-Recovery</td>
<td>Secondary</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Operation 3</td>
</tr>
<tr>
<td></td>
<td>Stream</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Stripping</td>
<td>Secondary</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Operation 4</td>
</tr>
<tr>
<td></td>
<td>Stream</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5. Heavy Metal Precipitation</td>
<td>Secondary</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Operation 5</td>
</tr>
<tr>
<td></td>
<td>Stream</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6. Phase Separation</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Operation 6</td>
</tr>
<tr>
<td>7. Rectification</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Operation 7</td>
</tr>
</tbody>
</table>

According to their definition, the RC parameters are based on a balance region different than the Ecological Scarcity evaluation, and thus, the two types of indicators are complementary to some degree. The RC parameters include only on-site pollution (mainly emissions) but do not take into account auxiliaries and the impact associated with them. Emissions of Global Warming Potential (GWP [IPPC, 1990]) gases associated with energy use are considered only for fossil sources. In our case studies electricity is assumed to come from hydroelectric power stations only so that no carbon dioxide equivalents were considered here.
Table 3-3: Responsible Care parameters [CEFIC, 1998] included in the model.

<table>
<thead>
<tr>
<th>Category</th>
<th>Abbreviation</th>
<th>Unit</th>
<th>Responsible Care Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Waste Handling (Landfill)</td>
<td>HW</td>
<td>kg</td>
<td>Hazardous Waste for Disposal</td>
</tr>
<tr>
<td></td>
<td>NHW</td>
<td>kg</td>
<td>Non-Hazardous Waste for Disposal</td>
</tr>
<tr>
<td>Emissions to Air</td>
<td>SOX</td>
<td>kg</td>
<td>Sulphur Oxides</td>
</tr>
<tr>
<td></td>
<td>NOX</td>
<td>kg</td>
<td>Nitrogen Oxides</td>
</tr>
<tr>
<td></td>
<td>VOC</td>
<td>kg</td>
<td>Volatile Organic Compounds</td>
</tr>
<tr>
<td></td>
<td>GWP</td>
<td>kg</td>
<td>Carbon Dioxide and other Global Warming Gases</td>
</tr>
<tr>
<td>Discharges to Water</td>
<td>P</td>
<td>kg</td>
<td>Phosphorus Compounds</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>kg</td>
<td>Nitrogen Compounds</td>
</tr>
<tr>
<td></td>
<td>COD</td>
<td>kg</td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td></td>
<td>HM</td>
<td>Σ kg</td>
<td>Heavy Metals</td>
</tr>
<tr>
<td>Use of Energy</td>
<td>E</td>
<td>MJ</td>
<td>Energy Consumption</td>
</tr>
</tbody>
</table>

3.2.4 Uncertainty propagation and multi-objective comparison

In the model, parameter uncertainty is considered by Monte Carlo simulation because this approach allows propagating any type of probability distribution and the computational burden of a single evaluation of the presented model is low. The model was implemented in MATLAB® so that the Monte Carlo simulation could be realized by vector and matrix operations. This means that first all uncertain parameters are generated according to the stipulated probability distributions using a random number generator. These parameters are stored in separate vectors or matrices. In the latter each column entry represents one set of parameters used in one Monte Carlo simulation. Afterwards, in one single run the model calculations are carried out using the matrices instead of single parameter values. Also the checks for technical feasibility and legal compliance are conducted using these matrices. The resulting combination of treatment operations as well as the corresponding costs are also stored in matrices. After
finishing the Monte Carlo simulation, probability distributions for treatment costs as well as for selected combinations of treatment operations are compiled from the information stored in the result matrices. Additionally, the resulting dependence of the overall treatment costs or the resulting environmental burden on a single parameter can be displayed graphically. Further details on the implementation of the model are given by Cavin et al. [2001].

In the following the combination of the economic and environmental evaluation in a multi-objective comparison will be discussed. A simple way to obtain a first overview of those alternatives with the best performance according to one of the two objectives is to generate two tables, one listing the \( n \) cheapest alternatives, the other compiling the \( n \) alternatives with the least environmental impact.

To obtain a global optimum comprising both objectives, one would need to define a key linking the two targets, e.g. \( x \text{ CHF} = y \text{ UBP} \). Further progress in the \( \text{CO}_2 \) emission limitation regulations and the possible development of an international trade of emission certificates might bring some advance in this issue. However, presently there are no generally accepted conversion factors between an environmental impact and an economic value.

Still, it would be interesting to study both targets at the same time. The Pareto-approach is very appropriate for this purpose and is used widely in academia as well as in governmental institutions such as the UK Environmental Agency and its methodology for the definition of the Best Practicable Environmental Option (BPEO). The Pareto-approach aims at eliminating alternatives that are clearly dominated, i.e. other feasible alternatives exist, which are better with regard to both objective functions. This strategy can easily be translated into a vectorial language if discrete data is considered. An array \( \text{Cost} \) (Figure 3-2a) contains all the alternatives sorted in ascending order according to costs, the worst being in the bottom cell of this array, and a second array \( \text{EI} \) (Environmental Impact) is sorted equivalently for their environmental impact. According to the definition above, the alternatives dominated by a given one are those with higher values for both objectives, i.e. the dominated treatment paths must be situated below the selected one in both arrays.
This yields an effective algorithm for determining the Pareto-optimal points (Figure 3-2a): Take one optimum, for instance alternative A, the top cell of array Cost; look up this alternative in the other array Eco: All alternatives stored below this cell in array Eco, i.e. alternatives E and F, can then be discarded, since they are certainly also worse with regard to the first objective as we selected the best value in Cost. This procedure can then be repeated for the reduced arrays (Figure 3-2b). Obviously, alternative A, which has been identified as Pareto optimal in the previous step, cannot be eliminated. After the second step all Pareto optimal alternatives, A and B, have been identified (Figure 3-2c).

As long as a deterministic approach is considered, the algorithm is quite easy to implement. But if uncertainties have to be incorporated, the situation becomes more complex. Consider for example Figure 3-3a: Without uncertainties B is clearly dominated by A. But considering the bars indicating the variation, the situation is more complex: A could be more expensive than B. This ‘worst case scenario’ for A combined with the best case for B (A\text{worst} and B\text{best}, respectively) is
Figure 3-3: Schematic representation of Pareto plot with two alternatives and consideration of uncertainty: a) On the basis of the mean values, alternative A dominates alternative B. b) Case $A_{\text{worst}}$ is worse than case $B_{\text{best}}$; therefore, overall A does not dominate B.

presented in Figure 3-3b. The point $A_{\text{worst}}$ no longer dominates point $B_{\text{best}}$, and thus both alternatives have to be considered for further evaluation.

A problem with this latter procedure is that synchronized effects on two alternatives are not taken into account at all; often, two alternatives are different only for a single operation. In such cases, it is not surprising that the change of one parameter affects both alternatives similarly. If this is not taken into account and only the extreme values are compared, one might set against each other two figures resulting from inconsistent simulations, having different parameter values underlying. Thus, in this study for the determination of the Pareto optimal alternatives, instead of examining deviations in two directions from a mean value, the discrete points resulting from two series of Monte Carlo runs were compared point by point. This procedure guarantees that the comparison is performed on points originating from the same parameter values. To implement this procedure, the optimization routine was repeated for every Monte Carlo run individually following the procedure displayed in Figure 3-2. Afterwards, an alternative was eliminated if it was dominated for all runs.
3.3 Results and Discussion

Three case studies will be presented to highlight the usage of the software. Two of these case studies are real industrial wastes, while the first one is a synthetic example used to highlight the principles and capabilities of the model.

3.3.1 Case study #1: Water, organic solvent and additional compounds

The waste stream investigated in this first case study consists mainly of water and toluene, which might be recycled, as well as small amounts of ammonium sulphate and chloro methane. Table 3-4 shows those treatment paths identified as the cheapest or environmentally most benign. The resulting costs and environmental impacts are both normalized with the respective lowest value. The cheapest path (#21) implies an environmental impact almost twice as high as the environmentally most benign alternative (#4), while the latter one costs about 60 % more than the cheapest one. Also shown in Table 3-4 is the number of Monte Carlo runs for each path that were legally compliant. The cheapest path is legally not compliant in more than 50 % of all runs because of too high emissions of nitrogen compounds to the river after the sewage treatment plant.

Figure 3-4 shows a Pareto plot of the cheapest and the environmentally most benign treatment paths. Paths #17 and #19 (as well as all other alternatives not shown in the graph) can be eliminated from further considerations because they are clearly worse with regard to both objectives (uncertainty bars do not overlap with path #21). The remaining paths to be considered are #1, #2, #4, #21, and #23. The difference between paths #2 and #4 is whether a distillation or a phase separation is conducted before incineration, while path #1 represents incineration only. A point-to-point optimization rules out paths #1 and #2 (synchronization effect, see above). Therefore, the Pareto optimal treatment paths for this waste stream are #4, #21, and #23.
Table 3-4: Case study #1: Listing of the cheapest as well as the environmentally most benign treatment paths (evaluation is based on mean values). For the environmental assessment the Ecological Scarcity method was used. Pareto optimal alternatives were determined by point-to-point optimization considering uncertainty.

<table>
<thead>
<tr>
<th>Path</th>
<th>Rank Costs</th>
<th>Rank Env. Impact</th>
<th>Normalized Costs</th>
<th>Normalized Env. Impact</th>
<th>Percentage of Legal Runs</th>
<th>Pareto Optimal</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>1</td>
<td>4</td>
<td>1</td>
<td>1.916</td>
<td>43.0%</td>
<td>YES</td>
</tr>
<tr>
<td>23</td>
<td>2</td>
<td>3</td>
<td>1.009</td>
<td>1.763</td>
<td>100.0%</td>
<td>YES</td>
</tr>
<tr>
<td>17</td>
<td>3</td>
<td>9</td>
<td>1.108</td>
<td>7.968</td>
<td>43.5%</td>
<td>No</td>
</tr>
<tr>
<td>19</td>
<td>4</td>
<td>8</td>
<td>1.117</td>
<td>7.812</td>
<td>100.0%</td>
<td>No</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>1</td>
<td>1.591</td>
<td>1</td>
<td>100.0%</td>
<td>YES</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>2</td>
<td>1.603</td>
<td>1.322</td>
<td>100.0%</td>
<td>No</td>
</tr>
<tr>
<td>1</td>
<td>7</td>
<td>5</td>
<td>1.631</td>
<td>2.508</td>
<td>100.0%</td>
<td>No</td>
</tr>
</tbody>
</table>

Path #21 should perhaps not be considered due to its high percentage of legally non-compliant runs indicating that possibly problems would be encountered in realizing this treatment sequence. The latter decision is particularly reasonable since path #23 performs almost identical as path #21. In path #23 phase separation is used to recycle toluene and the remainder is subsequently treated as wastewater, which is stripped first to remove halogens before ammonia is recovered in the next stage. In the considerably more expensive (about a factor of two, due to the incineration of water) but environmentally more benign path #4 the toluene is also removed by decantation before incinerating the remainder of the stream.

In Figure 3-5 detailed results on the environmental impact of paths #4 and #23 are shown. In both cases, emissions are the most important factor of the calculated environmental impact, but according to the chosen assessment the incinerator in path #4 produces less harmful emissions than the STP in path #23. This is a direct result of the underlying evaluation of CO$_2$ emissions to the atmosphere and C
(expressed as COD) to water. The Ecological Scarcity method weighs the latter much stronger than the former (0.2 UBP/g_C in form of CO₂ compared to 5.9 UBP/g_C measured as COD). As a consequence, burning this water-rich stream is considered as environmentally more friendly by the Ecological Scarcity method. This point touches the problem of defining absolutely objective evaluation functions for measuring environmental impact.

Another fact leading to a higher environmental impact of path #23 are the chlorine emissions: to fulfill the legal limits for discharge to rivers, the wastewater has to be stripped and the nitrogen content has to be reduced, i.e. the ammonia has to be recovered. Both operations require steam, which is displayed as an additional energy demand (Figure 3-5). The latter point demonstrates the basic principle of

**Figure 3-4**: Case study #1: Pareto plot obtained for the economic and environmental assessment of different treatment paths. The environmental impact was assessed with the Ecological Scarcity method.
waste treatment in the light of environmental assessment: the reduction of one environmental impact (e.g. Cl or N emissions) generally comes along with an increase in another impact (e.g. increased energy demand).

![Graph showing environmental impact comparison]

**Figure 3-5:** Case study #1: Comparison of environmental impact of treatment paths #4 and #23 as assessed with the Ecological Scarcity method for four sub-categories.

Figure 3-6 presents the aggregated environmental impact for the two paths measured in UBP and presented as running sum (starting at the higher end of the operation labeling and proceeding to operation 1, the final treatments). The impact measure starts at zero because only the treatment operations and remaining emissions to the environment are evaluated.

For both paths the same contribution results from the phase separation of toluene (operation 6). Path #4 only shows one additional contribution from the final operation incineration, while path #23 includes the pre-treatments stripping and ammonia recycling. As already discussed, the former requires steam resulting in
an additional environmental impact, while the latter is overall positive because the energy required is compensated for by the bonus obtained for recycling the ammonia (which is in contrast to the cost balance for this operation as explained above).

Figure 3-6: Case study #1: Comparison of environmental impact of paths #4 and #23 displayed as running sum as assessed with the Ecological Scarcity method along the sequence of treatment operations.

Figure 3-7 presents a radar plot of the Responsible Care parameters obtained for treatment paths #4 and #23. The graph shows that path #4 contributes more to emissions to the atmosphere, mainly NOx and SOx while path #23 contributes more to nitrogen and COD emissions to water (and requires slightly more energy). This result is primarily a direct consequence of the type of the final treatment operation, although the auxiliaries used in the STP, along with the sludge incineration, also contribute to air emissions (CO2, NOx, SOx).
Figure 3-7: Case study #1: Comparison of environmental impact of paths #4 and #23 by displaying the Responsible Care parameters in a Radar plot (see Table 3-3 for abbreviations and units).

3.3.2 Case study #2: Toxic compounds dissolved in water

This waste stream consists of a large quantity of water, polluted with toxic organic substances, i.e. chlorinated and brominated compounds. Due to the toxicity of the mix, the software identifies incineration (without any pre-treatment, path #1) as the cheapest legal path to handle the waste stream. The environmental assessment agrees with this conclusion, making the decision straightforward (see Table 3-5).

An alternative path would be to treat the waste in the STP, as it is mainly wastewater. However, due to the toxicity of the stream, it has to pass the decontamination operation. Moreover, due to the high content of halogens, a stripping must be conducted. Only together with these two pre-treatments a final treatment in the STP and its emissions to the river are within legal bounds (path #18).
Table 3-5: Case study #2: Listing of the cheapest as well as the environmentally most benign treatment paths (evaluation is based on mean values). For the environmental assessment the Ecological Scarcity method was used. Pareto optimal alternatives were determined by point-to-point optimization considering uncertainty.

<table>
<thead>
<tr>
<th>Path</th>
<th>Rank Costs</th>
<th>Rank Env. Impact</th>
<th>Normalized Costs</th>
<th>Normalized Env. Impact</th>
<th>Percentage of Legal Runs</th>
<th>Pareto Optimal</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>100%</td>
<td>YES</td>
</tr>
<tr>
<td>18</td>
<td>2</td>
<td>2</td>
<td>65.0</td>
<td>18.5</td>
<td>100%</td>
<td>No</td>
</tr>
</tbody>
</table>

Due to these pre-treatment operations, path #18 is much more expensive (by a factor of 60) than simple incineration. Moreover, the environmental burden of path #18 is about 20 times higher than that of path #1. To understand why it is environmentally more friendly to incinerate water than to treat it in the STP, we can study the environmental impacts occurring along both treatment paths as shown in Figure 3-8. The highest impact in path #18 occurs in the stripping and decontamination phases. The stripping needs a lot of energy, which explains its high environmental impact, while the decontamination additionally requires economically and environmentally expensive auxiliaries.

This example shows how the model not only identifies the best (i.e. cheapest and environmentally most benign) treatment but also provides information for understanding why this result was obtained. This is particularly helpful because in this case the identified path, i.e. the incineration of water, does not seem to be a straightforward choice. Nevertheless, the same solution was independently identified by experts from chemical industry.
3.3.3 Case Study #3: Ammonia recovery trade-off

In this case study an aqueous stream (about 51 t) polluted with organic compounds (TOC = 87 kg) and NH$_3$ (3 kg) is examined. The model provides a ranking of alternatives (Table 3-6) both with regard to economy and environmental impact. A point-to-point Pareto optimization under uncertainty results in two optimal paths: path #9 (direct treatment in the STP), and path #11 (NH$_3$-recovery and then treatment in the STP). Path #11 is 2.7 times more expensive than path #9, while performing 5 times better with regard to environmental impact than path #9.

In order to investigate where this difference in environmental impact stems from, Figure 3-9 shows a radar plot of the responsible care parameters. The main advantage of path #11 lies in much smaller emissions of nitrogen, both into the water and atmosphere compartments. However, path #11 needs slightly more energy than path #9.
Figure 3-9: Case study #3: Comparison of environmental impact of paths #9 and #11 by displaying the Responsible Care parameters in a Radar plot (see Table 3-3 for abbreviations).

#9. Note that this is no surprise as the difference between paths #11 and #9 is the NH₃-recovery, in which energy is required for recovering the ammonia.

Figure 3-10: Case study #3: Comparison of energy balance for treatment paths #9 and #11.

Figure 3-10 shows the different forms of energy required in the two treatment paths. The main difference between paths #11 and #9 lies in steam consumption: steam is produced by incinerating the sludge of the STP in both alternatives, but
path #11, with its distillation (NH₃-Recovery) consumes much more steam than it produces.

**Table 3-6:** Case study #3: Listing of the cheapest as well as the environmentally most benign treatment paths (evaluation is based on mean values). For the environmental assessment the Ecological Scarcity method was used. Pareto optimal alternatives were determined by point-to-point optimization considering uncertainty.

<table>
<thead>
<tr>
<th>Path</th>
<th>Rank Costs</th>
<th>Rank Env. Impact</th>
<th>Normalized Costs</th>
<th>Normalized Env. Impact</th>
<th>Percentage of Legal Runs</th>
<th>Pareto Optimal</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>1</td>
<td>7</td>
<td>1</td>
<td>5.02</td>
<td>100%</td>
<td>YES</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>1</td>
<td>2.72</td>
<td>1</td>
<td>100%</td>
<td>YES</td>
</tr>
<tr>
<td>10</td>
<td>3</td>
<td>9</td>
<td>90.3</td>
<td>8.90</td>
<td>100%</td>
<td>No</td>
</tr>
<tr>
<td>12</td>
<td>4</td>
<td>4</td>
<td>92.0</td>
<td>4.31</td>
<td>100%</td>
<td>No</td>
</tr>
<tr>
<td>17</td>
<td>5</td>
<td>6</td>
<td>141</td>
<td>5.00</td>
<td>100%</td>
<td>No</td>
</tr>
<tr>
<td>19</td>
<td>6</td>
<td>2</td>
<td>143</td>
<td>1.03</td>
<td>100%</td>
<td>No</td>
</tr>
<tr>
<td>18</td>
<td>7</td>
<td>8</td>
<td>230</td>
<td>8.88</td>
<td>100%</td>
<td>No</td>
</tr>
<tr>
<td>20</td>
<td>8</td>
<td>5</td>
<td>232</td>
<td>4.34</td>
<td>100%</td>
<td>No</td>
</tr>
<tr>
<td>1</td>
<td>9</td>
<td>3</td>
<td>232</td>
<td>3.63</td>
<td>100%</td>
<td>No</td>
</tr>
</tbody>
</table>

In this example again a trade-off between economy and environmental impact exists, and the results can be used to better understand it. This understanding might also serve as a basis for improving the chemical process producing the waste stream under discussion in order to reduce its environmental impact. A significant process improvement would be for example the reduction of NH₃, while according to the results obtained a reduction in TOC would mean only a minor improvement.
3.4 Conclusions

A model for determining the cheapest legal treatment paths for a given waste stream has been extended by an assessment measuring the environmental impact resulting from the treatment itself as well as from the remaining emissions, thus allowing a comparison of treatment policies. Since uncertainty in stream composition is considered the results obtained with respect to both objectives are distributions and not single values. The Pareto optimal alternatives are automatically identified, and the possibly resulting trade-offs between the economic and environmental objectives can be displayed and analyzed.

The model has been applied to several case studies. For the examples provided by chemical industry the model identified the same optimal treatment paths as the experts from the respective company. While one case study showed that the cheapest treatment path might well be the environmentally most benign, for the other case studies trade-offs between costs and environmental impact became evident. The model showed in detail, which treatment operations and/or pollutants cause a high environmental impact, a finding that can be used as a basis for elaborating modifications of the process that produced the waste stream.

From the detailed results provided by the model also the basic principle of waste treatment in the light of environmental assessment was highlighted: the reduction of one environmental impact generally comes along with an increase in another impact, e.g. the emission of harmful compounds might be reduced on the expense of energy consumption. For determining one overall optimal treatment alternative, these different environmental impacts have to be weighted before summation, a task that can be and is heavily debated. Therefore one has to be aware that those results presented in this study that have been obtained using the Ecological Scarcity method, which aggregates all considered impacts into one final value, are dependent on the underlying valuation principles (i.e. in the Ecological Scarcity method energy consumption is rather cheap as compared to other methods). While the numerical values obtained in the environmental assessment of different treatment alternatives might depend on the method chosen, the ranking of the alternatives might still be the same.
In the model presented here, beside full aggregation also results for selected operations and certain categories (i.e. emissions, auxiliaries, energy, and recycled compounds) can be displayed providing more specific information. Furthermore, the Responsible Care parameters display non-aggregated measures for single emissions to the environment, thus providing a complementary view. In summary, the model proved to be a valuable tool in analyzing treatment options for a given waste stream from an economic as well as an environmental point of view.

Acknowledgments

We thank Lonzagroup at Visp (Switzerland) for supporting this project. In particular, data and information provided by A. Huwiler, J. von Gunten, T. Kahoun, and L. Utiger is gratefully acknowledged. Furthermore, we thank S. Hellweg for advice on the Ecological Scarcity method.
A method for identifying the optimal design of a single chemical process to be implemented in an existing multipurpose batch plant

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Abstract

Chemical batch processes are typically used for the production of specialty chemicals and pharmaceuticals. Due to the still growing importance of this type of processing, design methods are required that take account of the special requirements and constraints in the corresponding production facilities. We developed a method that optimizes the design of a single chemical process to be implemented in an existing multipurpose batch plant, in which a well-defined set of equipment units is available for realizing this process. The method takes
advantage of the available information on equipment specifications, design constraints, and process requirements. Based on predefined rules (representing heuristics) and options selected by the user, specified operating instructions for a chemical process to be designed are automatically analyzed with regard to design requirements and constraints. The resulting superstructure can be optimized using basically any optimization algorithm that can deal with discrete variables. We chose to implement a Tabu Search algorithm, which considers three objectives for the identification of the optimal design plus several next-to-optimal ones. After presenting the method a case study is used for demonstrating the principle of the method and the results that are obtained from it. The method proved to be a quickly applicable and reliable tool for implementing a chemical process in an existing multipurpose batch plant.

4.1 Introduction

Specialty chemicals and pharmaceutical products are typically produced in batch processes. Corresponding plants are often classified as multiproduct batch plants, in which every product follows the same sequence through all the process steps, or as multipurpose batch plants, in which each product follows its own distinct processing sequence by using the available equipment in a certain layout [see Rippin, 1983]. In practice also combinations of these two limiting scenarios might arise. Multipurpose plants can be used in two main modes: either only one production runs in the plant at a given time or many processes run concurrently. Some multipurpose plants consist of discrete but nevertheless flexible production lines that are independent from each other.

Because of the still growing importance of this type of chemical processing in recent years increased research efforts have been undertaken to develop design methods for batch processes. Many methods deal with the grassroots design of multiproduct or multipurpose batch plants and include the equipment sizing problem [Sparrow et al, 1975; Grossmann and Sargent, 1979; Suhami and Mah, 1982; Papageorgaki and Reklaitis, 1990; Voudouris and Grossmann, 1992]. In most cases, the authors consider that many productions run concurrently. In these
methods therefore the concurrent design of several processes is considered (and partly optimized), and thus the single processes are not optimized one by one.

Relatively few publications have been presented that deal with the optimal design of a single batch process. For grassroots design, Loonkar and Robinson [1970] described a procedure for the cost optimal design and apparatus sizing of a single batch process, while Takamatsu et al. [1982] presented a similar approach that considers the possibility of intermediate storage. Yeh and Reklaitis [1987] presented a method for the preliminary grassroots design of a single batch process including an approximate sizing procedure. Mauderli and Rippin [1979] developed a method for planning and scheduling in multipurpose batch plants. While they consider many concurrent productions, their first step consists of the generation of design alternatives for the production of single products. To obtain the different design alternatives they take account of the plant specifications (number and size of available equipment units) and the process requirements (which equipment units can be used for the different process tasks). These alternative designs are not optimized but generated using a heuristic procedure that allows the selection of promising designs while ignoring designs with a low performance.

The big advantage of a multipurpose batch, its flexibility, also poses the problem of making the best use of it [Mauderli and Rippin, 1979]. The problem also arises when a single chemical process has to be implemented in an existing multipurpose batch plant, a question that arises frequently in companies that run multipurpose plants. This design task can also be summarized as optimizing the use of available equipment units for the design of a new chemical process. Wellons and Reklaitis [1988] developed a MINLP formulation for such a design task. They generate groups of equipment units that can handle one particular step of the chemical process. Each equipment unit belongs to one of these groups. Each step can be conducted in one or many such groups. The resulting combinatorial tree is optimized for the maximum production. The results are typically a list of batches (potentially of different batch size) that take different paths through the plant and run in a fixed sequence.

However, the pre-assignment of equipment units to a given process step is a constraint that limits the design possibilities in multipurpose plants in which equipment units can be used for several tasks and can thus be assigned to different process steps. Moreover, for control, safety and quality reasons,
subsequent batches are often preferred to follow the same path (with some few out-of-phase parallel equipment units for time intensive operations like drying or slow reactions) and to be of equal size. Under this perspective, the objective changes from the optimal schedule of \( n \) subsequent batches to the design of the single most efficient batch for a single product. To our knowledge no method to date focused on this particular design problem.

In order to identify the optimal solution for this problem it is important to consider in the design procedure all details and existing constraints such as equipment specifications (e.g. range of operating temperature and pressure, lining material, special supply pipes, the floor at which each equipment is located), design constraints (e.g. feasible and infeasible connection of equipment units), and process requirements (e.g. reaction mixture that cannot be safely transferred, thus forcing several operations to be conducted in the same equipment unit). This is exactly the approach taken in the method presented here. Based on pre-defined rules (representing heuristics) and options selected by the user, specified operating instructions for a chemical process to be designed are automatically analyzed with regard to design requirements and constraints: suitable equipment units are assigned to each operation, feasible and infeasible transfers are identified, and operation blocks are determined that will be conducted in the same equipment unit. This results in a superstructure for which the optimal design can be identified. We used a Tabu Search algorithm as optimization routine because it might be used in conjunction with a commercial batch process simulation program and because it facilitates the use of multiple objective functions. After presenting the method, a case study is used for demonstrating the principle of the method and the results that are obtained from it.

### 4.2 Batch process design method

The aim of the method presented here is to optimize the design of a single chemical process to be implemented in an existing multipurpose batch plant. After giving a detailed problem definition the different steps of the procedure are explained in the following paragraphs.
4.2.1 Problem definition

The problem covered in this paper can be defined as follows:

**Given:**
1. **Recipe**
   - Recipe of the product expressed as a series of chemical/physical tasks
   - Capacity requirements for each task per unit of final product
   - Base duration of each task at the input scale
   - Recipe constraints (specific rules about how tasks can be combined)
2. **Equipment**
   - Available equipment units and their detailed specifications
   - Connectivity constraints (which equipment unit can be connected with which other).
3. **General heuristics**
   - Equipment classes suited for processing each task class
   - Design heuristics (built-in ones as well as user options)
   - Relationships between the processing time of each task class and the batch size
4. **One or more objective functions**

**Determine:**
The optimum layout for the process - i.e. allocation of equipment units to tasks, design used (in parallel, in series).

4.2.2 Method overview

A general overview of the method is presented in Figure 4-1. The routines for recipe analysis, superstructure generation, process simulation, and optimization have been implemented in a MATLAB® program. The process simulations can also be conducted in a commercial batch process simulator as discussed below.
As shown in Figure 4-1, the program needs different inputs related to either the process to be designed or the plant in which the process shall be realized. These inputs are discussed in the following sections.

**Figure 4-1: Overview of the method; grey boxes indicate the optional use of external software (see text for further explanations).**

### 4.2.3 Equipment specifications

The first input required consists of a database on the available equipment units. This equipment database, to which equipment data available in a commercial simulation program might be transferred (see below), contains a description of all
available equipment pieces comprising the following information: unit name, equipment class (e.g. reactor, distillation column), (usable) volume, lining material, physical operating conditions (temperature, pressure), options (e.g. special supply pipes) and related equipment (e.g. a condenser attached to a reactor), physical location in the plant (e.g. floor), connectivity constraints (which equipment unit can or cannot be connected to this one) and some flags that indicate options for the process synthesis (for example, one flag determines whether a centrifuge has a buffer tank attached to it or if the centrifuge has to be filled directly from the preceding equipment unit, hence occupying the preceding unit longer in the case of multiple drops). These data are stored in a relational database, which is represented by the four matrices shown in Figure 4-2

![Figure 4-2: Equipment data used in the process design and optimization routine.](image)

A positive volume entry represents the volume in [m\(^3\)]; a negative one indicates the Equipment ID of a master equipment unit. The capital letters in front of the matrices refer to the mathematical formulation given in Figure 4-6.

Most recipe and plant information can also be entered by the way of the external simulator, where it might already be available (i.e. equipment list). We designed interfaces to transfer this information to the MATLAB\textsuperscript{®} program. A data
reconciliation algorithm keeps the information synchronized with the database in the commercial program.

The Connectivity Constraints (cf. Figure 4-1) are stored in a separate matrix that contains two columns of Equipment IDs. Each combination of Equipment IDs indicates an exception to the default connectivity. In the case where the default connectivity is “Everything connected”, the link means “No connection possible”, and in the opposite case (“Nothing connected”), the link means “Connection possible”.

4.2.4 Recipe specifications

The second major input to the program comprises the operating instructions (recipe). The following information has to be assigned to each operation: operation type, volume balance (instead of mass balance), flags indicating design constraints, operating temperature, operating pressure and the lining material requirements for the operation. Furthermore, an initial value on the duration of each operation is required as input, which can be either obtained from a commercial batch process simulation program or can be entered manually.

A commercial simulator can also be used later on in the optimization process if sufficient data are available to run rigorous models. Since most often in batch process simulation of industrial processes, in particular during the design phase, these data (e.g. reaction kinetics) are not available, we only implemented short-cut models to adapt the operation durations to the actual volume treated in an equipment unit (see below). These short-cut models result in a significantly lower computation time, and a description of the chemicals and the reactions are not required as input to the program (if rigorous models are used these data have to be provided directly to the commercial simulation program).

The Recipe Constraints (see Figure 4-1) describe options, constraints, and rules how the recipe has to be interpreted in particular with regard to transfers. The constraints are encoded in the form of Flags (see Table 4-1). For computational
reasons a Flag value can also express the sum of several Flags, thus indicating the choice of a set of Recipe Constraints (e.g. in Figure 4-3 the Flag value “12” in the React line has the meaning of “8 + 4”, i.e. the operation cannot be conducted in parallel nor in series in multiple equipment units).

The Flag values in the range “1-31” are set by the user (default values are set according to the operation class) while values above “32” are set by the algorithm during the automatized recipe analysis; for the Flag value “32” both options are possible (see below). Figure 4-3 shows an example of recipe information presented in matrix form.

\[
\begin{array}{|c|c|c|c|c|c|c|}
\hline
\text{LiningID} & \text{Pressure} & \text{Temperature} & \text{Flag} & \text{Volume} & \text{Duration} & \text{Operation} \\
\hline
LiningID & \text{Pressure} & \text{Temperature} & \text{Flag} & \text{Volume} & \text{Duration} & \text{Operation} \\
\hline
\end{array}
\]

\[
R = \begin{pmatrix}
4 & 9.8 & 30 & 2 & 25 & 1 & -1 \\
32 & 9.8 & 360 & 12 & 80 & 1 & 1 \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\end{pmatrix}
\]

**Figure 4-3:** Recipe and operation matrix. The Flag values represent the Recipe Constraints (see Table 4-1). The values given for volume and duration correspond to the result from the initial simulation (or the definition given by the user). The capital letter in front of the recipe matrix refers to the mathematical formulation given in Figure 4-6.

The temperature and pressure fields contain the most extreme values reached during the operation. Typically, the temperature field will contain the highest temperature reached during the operation. In some cases, however, the lowest temperature will be important. In this case, the Flag will indicate this (see Table 4-1), and the field will contain the lowest temperature reached during the operation. Pressure is handled similarly. The lining material field contains restrictions on the lining material for the corresponding operation. While “-1” indicates no restriction, a positive value allows restricting the suitability to some specific lining materials such as stainless steel or enamel.
The user has the opportunity to incorporate additional constraints according to his heuristic knowledge on chemical process design into the design procedure. For example, it is assumed that a transfer is required if it is in the recipe, and that it is allowed if it is not in the recipe. In the example in Figure 3, the operations are “4”: Charge and then “32”: React. In this case, a transfer does not make sense between Charge and the following operation, hence a “2” as constraint value indicates that no transfer is allowed after the Charge operation.

**Table 4-1:** Summary of Recipe Constraints and their representation in the form of a Flag. For a combination of constraints, the Flag value is the sum of the single constraint values.

<table>
<thead>
<tr>
<th>Flag</th>
<th>Recipe Constraint</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mandatory transfer after operation</td>
</tr>
<tr>
<td>2</td>
<td>No transfer allowed after operation</td>
</tr>
<tr>
<td>4</td>
<td>Stream cannot be divided (i.e. operation cannot be conducted in parallel in two equipment units)</td>
</tr>
<tr>
<td>8</td>
<td>Transfers during operation are forbidden (i.e. the operation cannot be handled in series in multiple equipment units)</td>
</tr>
<tr>
<td>16</td>
<td>Do not modify base equipment allocation</td>
</tr>
<tr>
<td>32</td>
<td>Special time adaptation heuristics</td>
</tr>
<tr>
<td>64</td>
<td>Operation added by algorithm</td>
</tr>
<tr>
<td>128</td>
<td>Temperature is lowest value</td>
</tr>
<tr>
<td>256</td>
<td>Pressure is lowest value</td>
</tr>
</tbody>
</table>

If no external process simulator is used, then the process simulation routine implemented in MATLAB® adapts the duration of operations according to the volume. A set of rules has been defined, that allows adapting the duration of an operation according to the operation class. The three rules are:

1) Keep operation time constant.
2) Linear adaptation of operation time as a function of volume.
3) Special scale-up handling of operation time (pre-defined for each operation type; e.g. a combination of a constant and a linear part).

All operations are assigned to one of these categories. For example, the duration of a Charge operation is proportional to the quantity to be charged, while the duration of a React operation is constant. These rules are obviously simplifications, and the possibility is given to implement other rules by using the Recipe Constraint “32”. Such an example for which the special scale-up rule is already pre-defined in the method is the Centrifuge operation with multiple-drops. In this case, a maximum volume per drop is given in the equipment database for the given equipment unit, and a duration per drop must be provided in the recipe. The program then calculates the (integer) minimum number of drops needed according to the volume, and then multiplies it by the drop duration. Another example is a semi-batch React whose limiting factor is the quantity of heat release that a given equipment unit can compensate. In this case if we assume the heat transfer capacity to be independent of volume and composition, and thus the duration of the reaction will be linear with the volume during the injection phase, and then constant.

\[
\begin{bmatrix}
\text{Operation} & \text{ClassID} & \text{Volume} & \text{Duration} & \text{Flag} & \text{Temperature} & \text{Pressure} & \text{LiningID} & \text{RecipeIndex} \\
\text{[m]} & \text{[min]} & \text{[°C]} & \text{[bar]} & \\
4 & 4.8 & 30 & 2 & 20 & 1 & -1 & 1 \\
32 & 4.8 & 360 & 12 & 80 & 1 & 1 & 2 \\
4 & 3 & 25 & 2 & 20 & 1 & -1 & 3 \\
32 & 7.8 & 240 & 8 & 30 & 1 & -1 & 4 \\
... & ... & ... & ... & ... & ... & ... & 5
\end{bmatrix}
\]

\[
\begin{bmatrix}
\text{BlockID} & \text{Volume} & \text{Constant} & \text{Duration} & \text{Linear} & \text{Duration} & \text{Flag} & \text{Temperature} & \text{Pressure} & \text{LiningID} \\
\text{[m]} & \text{[min]} & \text{[min]} & \text{[°C]} & \text{[bar]} & \\
1 & 4.8 & 360 & 30 & 12 & 80 & 1 & 1 \\
2 & 7.8 & 240 & 25 & 8 & 30 & 1 & -1 \\
... & ... & ... & ... & ... & ... & ... & ...
\end{bmatrix}
\]

\[
B_R:
\begin{bmatrix}
1 & 1 \\
2 & 2 \\
2 & 3 \\
... & ...
\end{bmatrix}
\]

**Figure 4-4:** An example of reducing the recipe complexity by combining operations to blocks of operations conducted in the same piece of equipment. The capital letters in front of the matrices refer to the mathematical formulation given in Figure 4-6.
Considering the Recipe Constraints on transfers (Flag values “1” and “2”), and taking into consideration the other constraints and the time adaptation rules, the recipe can be reduced to operation blocks that will have to be conducted in the same equipment unit(s). This allows for reducing the problem size and complexity. An example of such a reduction is given in Figure 4-4.

Each block of operations must be assigned to one or more equipment units, and the time adaptation is straightforward: the linear part is adapted according to the volume, and the constant part is added. Volume, temperature, pressure and lining material for this block are set according to certain rules (largest volume, highest/lowest temperature or pressure, most constraining lining condition). If one operation is assigned the Recipe Constraint value “32” (special time adaptation rule) the different linear and constant parts will be calculated separately and will then be added.

If in the recipe the Flag is set to “1” (mandatory transfer after an operation), a Transfer operation is added as a block for itself, and the Flag value “1” is removed. All mandatory transfers and only mandatory transfers are now explicitly listed in the revised recipe.

4.2.5 Superstructure generation

With the recipe and equipment descriptions given above the automatic generation of a superstructure is now possible. The method presented here is based on filters that identify the suitable equipment units for each operation. First, the operation class determines which equipment units are available, then the physical conditions are checked.

The Allocation Constraints are heuristics defining which equipment class can be used for each operation class (see Table 4-2). These rules are implemented in the form of a many-many relationship, i.e. each operation class can be conducted in many equipment classes, and each equipment class can be used for many operation classes. Selected Allocation Constraints are given in Table 4-2.
Table 4-2: Selected Allocation Constraints

<table>
<thead>
<tr>
<th>Operation Class</th>
<th>Suitable Equipment Classes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>Any</td>
</tr>
<tr>
<td>Decant</td>
<td>Decanters, Reactors with valves and vision panels or similar options</td>
</tr>
<tr>
<td>Distill</td>
<td>Reactor with condenser, Distillation column</td>
</tr>
<tr>
<td>Dry</td>
<td>Dryer (all types, e.g. rotary, trays, fluidised bed)</td>
</tr>
<tr>
<td>Extract</td>
<td>Extractors, Reactors with valves and vision panels or similar options</td>
</tr>
<tr>
<td>Mix (liquids)</td>
<td>Reactors (with agitator)</td>
</tr>
<tr>
<td>Purge</td>
<td>Any</td>
</tr>
<tr>
<td>React</td>
<td>Reactor</td>
</tr>
</tbody>
</table>

A special rule is “Any”, and this means that the operation can be conducted in all equipment pieces. In Table 4-2, Charge is an example for such an operation. Suitable equipment classes are selected for each operation block; obviously, selected equipment classes must be suitable for each operation in the block. In the example in Figure 4-4, the first block contains the operations Charge and React, so the possible equipment classes are “Any” and “Reactor”, and the whole block will be assigned to the Reactor class.

In a second step, the physical conditions in the block will be compared to the physical conditions acceptable for each equipment unit of the assigned classes. Temperature, pressure and lining material will be checked, and finally a list of potential equipment units will remain as suitable options for each operation block. Figure 4-5 illustrates the procedure of filtering suitable pieces of equipment for a specified operation.
A list of eligible equipment units for each operation block is already a superstructure. Every possible implementation of the recipe in the plant is included in the combinatorial realizations of these lists. However, many equipment units can be used in series or in parallel for a single block, and additional constraints are required to handle these options. Due to the fact that operation blocks were generated, it is by definition always allowed to insert a transfer between these blocks. This means that except if a Transfer operation is explicitly listed in the recipe it is possible either to change the equipment between two blocks or to keep the same equipment unit. The Connectivity Constraints define which equipment unit can be used after a transfer. These units must be linked to those before the transfer (i.e. the connection must be allowed in the connectivity matrix).
Design Constraints are rules limiting how equipment pieces can be combined or shared between operation blocks; these rules depend on preferences of the user or might depend on regulations (e.g. Good Manufacturing Practice (GMP) guidelines).

We made the following choices for the case study:

- Previously used equipment pieces cannot be re-used in a later stage of the same process.
- As long as not forbidden by Recipe Constraints (i.e. Flag value “4”), two equipment units can be used in parallel during the whole block.
- As long as not forbidden by Recipe Constraints (i.e. Flag value “8”), several equipment units can be used in series within one block (i.e. we did not limit the number of equipments used in series within one block of operations).
- An operation could be conducted both in parallel and in series (using at least four equipment units). We chose to disable these designs.
- Many equipment units could be used in parallel out of phase. For example, the first batch uses Reactor #1, and the second batch uses Reactor #2, while the following operations are conducted in the same equipment units. This design is logically equivalent with the series design mentioned above, except that the design in series requires transfers during the operation-block (which takes time). We have decided to disable this design in the case study.

The combination of the lists of eligible equipment units together with the Connectivity and Design constraints represent a full superstructure where each single element is a valid process design. In Figure 4-6, a mathematical formulation of this procedure is given in terms of tuple calculus (also referred to as relational calculus (Date, 1995)).
**Definitions:**

E: Equipment Matrix (cf. Figure 4-2)
P: TP_range Matrix (cf. Figure 4-2)
C: Connectivity Matrix (cf. Figure 4-2)
R: Recipe Matrix (cf. Figure 4-3)
A: Allocation Matrix (cf. Table 4-2)
B: Block recipe Matrix (cf. Figure 4-4)
Bᵦ: Block Recipe pointers Matrix (cf. Figure 4-4)
i: Block counter
j: Secondary block counter

**Symbols:**

a.b: column b of matrix a
(a | a.c = 1): take rows of a where column c = 1
(a.b | a.c = 1): take only column b (same rows as above)
∈: is contained in (single element)
⊃: contains (multiple elements)
∪: union  ∩: intersection
←: assign a subset of a matrix to itself (filtering)
∅: empty (no elements)

**Step 1: Allocation Operation Classes → Equipment Classes**

recipe indexes := \( K_i = (B_x.RecipeIndex | B_x.BlockID = i) \)

recipe operations := \( X_i = (R | R.index \in K_i) \)

equipment classes := \( U_i = (A.EquipmentClassID | A.OperationClassID \supset \bigcup X_i.OperationClassID) \)

eligible equipment units := \( S_i = (E | E.EquipmentClassID \in U_i) \)

**Step 2: Physicochemical Filters**

\( S_i \leftarrow (S_i | P.Pmin | P.TP.rangeID = S_i.TP.range \leq \min(X_i.Pressure)) \)

\( S_i \leftarrow (S_i | P.Pmax | P.TP.rangeID = S_i.TP.range \geq \max(X_i.Pressure)) \)

\( S_i \leftarrow (S_i | P.Pmin | P.TP.rangeID = S_i.TP.range \leq \min(X_i.Temperature)) \)

\( S_i \leftarrow (S_i | P.Pmax | P.TP.rangeID = S_i.TP.range \geq \max(X_i.Temperature)) \)

\( S_i \leftarrow (S_i | S_i.LiningID \in \bigcap X_i.LiningID) \)

**Step 3: Reusability & Connectivity constraints**

Allocated equipment units := \( L \)

\( L_0 = \emptyset; \)

\( L_{i-transfer} = \emptyset \)

\( S_i \leftarrow S_i - \sum_{j \neq k \neq i} (L_j) + L_{i-k} \)

\( y = (X_{i-1}.X_{i-k}.Class \in Transfer\_Classes) \)

\( S_i \leftarrow \begin{cases} (S_i | S_i.EquipmentID \in (C.ToEquipmentID | C.FromEquipmentID \in L_{i-2})) & \text{if } y \neq \emptyset \\ (S_i | S_i.EquipmentID \in (C.ToEquipmentID | C.FromEquipmentID \in L_{i-k})) & \text{if } y = \emptyset \end{cases} \)

**Step 4: Recipe Constraints (Flag value “4” and “8”) & Design constraints**

\( L_i = \text{one single element of } S_i \)

\( L_i + \text{one additional element of } S_i \)

\( L_i + \text{one or several additional elements of } S_i \)

\( L_i \) only available if \( 4 \notin B_i.Flag; \) DesignType = "parallel"

\( L_i \) only available if \( 8 \notin B_i.Flag; \) DesignType = "series"

\( L_i \) always available; DesignType = "single"

**Figure 4-6:** Mathematical formulation of the superstructure generation in terms of tuple calculus.
4.3 Optimization

For identifying the optimal design from the superstructure defined above basically any optimization algorithm that can deal with discrete variables can be used. However, from the decision to enable the use of an external process simulation program in combination with the optimization routine results a major constraint: namely the evaluation function might not be explicit. Few algorithms are able to cope with implicit evaluation functions (“black box models”). A family of algorithm is however suited for such tasks: the evolutionary algorithms. We decided to implement a Tabu Search algorithm (e.g. Glover, 1977, 1990; Wang et al., 1999). The settings for the algorithm are as follows: The moves (and hence the neighborhood) are defined by adding, removing or replacing an equipment unit in an operation. The neighborhood sample size is set to 15, while the tabu list length is set to 40, with aspiration enabled. Diversification is achieved with restarts of the algorithm at different starting points. Restarts are done when no good solution is found during 20 subsequent iterations. Six restarts are conducted on average per run. No intensification has been implemented. These settings represent some 2000 process simulations per run; when the process simulations are carried out using the short-cut models implemented in MATLAB®, the computation time is around 5 minutes on a 800 MHz Pentium® 4 computer for the case study presented below.

In order to optimize the process design, an objective function is needed. Obviously, the most frequent objective is to minimize production costs. For a given recipe, the amount of raw materials, the required waste treatment operations, the substance inventory, and other major cost factors are not significantly affected by the design, and hence are not in the scope of this method. Personal and equipment costs are however strongly dependent on the design, mostly while they are dependent on the time needed for the production (in a given plant) and the size of the plant or the number of equipment units used. In the case study presented below we treated the problem of implementing a process in a given production line, which forms an independent sub-section of a plant consisting of several such lines. In this case the number of equipment units is fixed (even if some units are not used for the process they cannot be used
and the major aim is to maximize the throughput defined as the amount of product produced per batch divided by the cycle time.

There are also other criteria for rating the quality of a process design. These criteria are however not constraints, i.e. they can be violated if the resulting design has a higher throughput and thus these rules are formulated in terms of objective functions. As examples for such criteria we implemented two subsidiary objective functions:

- **Minimization of the number of equipment units used.** This objective function will discriminate against designs where, for example, two units are used in parallel while being less than half filled. Processes with fewer equipment units are easier to implement and less complex.
- **Minimization of the number of floors the reaction mixture has to be pumped up.** This will discriminate in favor of top-down designs against bottom-up designs.

In order to handle the multiple objectives, we set the following priorities. First the throughput is evaluated. If the throughput is higher than the preceding optimal throughput, then the design is better. If it is lower, then the design is worse. If it is equal, then the second objective function is evaluated, and so on. In the case of multiple similar or equal equipment units, many designs are equivalent. Therefore, for many designs the throughput is identical, and hence the secondary (and tertiary) objective functions are often evaluated. Also with regard to the implementation of multiple objective functions the Tabu Search algorithm is particularly suited.

### 4.4 Application of the design method to case study

#### 4.4.1 Description of case study

The input recipe for this case study is given in Table 4-3. Reactor1 and Reactor2 are placeholders indicating that at least two different reactors have to be used.
Table 4-3: Recipe of case study

1. Purge unit Reactor2. Purge 6 times with NITROGEN for 10 min each.
2. Charge Reactor2 with 2.02 m$^3$ of Solvent1. The charge time is 30 min.
3. Charge Reactor2 with 528 kg of Material1. The charge time is 30 min.
   Dissolve the components: 100% of Material1.
4. Mix the contents of unit Reactor2. The mixing time is 30 min.
5. Charge Reactor2 with 3.36 m$^3$ of Material2 in Solvent2. The charge time is 20 min.
6. React in unit Reactor2 via Reaction1. Reaction occurs over 150 min. The final temperature of the batch is -2 °C.
7. Charge Reactor2 with 205.1 kg of Material3. The charge time is 30 min.
   Charge Reactor2 with 3.5 m$^3$ of Solvent1. Dissolve the following components: 100% of Material3.
8. React in unit Reactor2 via Reaction2. Reaction occurs over 300 min.
9. Charge Reactor1 with 3.36 m$^3$ of Material4. The charge time is 30 min.
10. Transfer contents of unit Reactor2 to Reactor1. The Transfer duration is 15 min.
11. React in unit Reactor1 via Reaction3. Reaction occurs over 120 min.
12. Decant in unit Reactor1 over 120 min. Separation is: 100% of Material5 goes to Bottom, 95% of Product1 goes to Bottom, 100% of Solvent3 goes to Top and 90% of Solvent1 goes to Top. Unspecified materials go to Bottom. The upper layer is sent to Waste Solvent Tank.
13. Charge Reactor1 with 2.62 m$^3$ of Solvent4.
14. Extract in unit Reactor1 over 3 h. Partition coefficient (mass basis: top/bottom) of Solvent4 is 98, of Product1 is 95 and of Solvent1 is 80. Unspecified materials go to Bottom. The bottom layer, named Waste Water, is sent to Waste Water Tank.
15. Distill the batch in unit Reactor1. The operation time is 8 h. The overhead is sent to Waste Solvent Tank. Separation is: 100% of Solvent4 goes to Overhead, 100% of Product1 goes to Bottom, 95% of Solvent2 goes to Overhead and 95% of Solvent1 goes to Overhead. The final content of Reactor1 is the product.
The recipe, together with the mass and volume balance resulting from it, leads to the recipe matrix shown in Table 4-4. Some heuristic knowledge about the process has been introduced: the second reaction step (Step 8) must be conducted in an enamel-lined reactor (resulting in a lining index of “2” for this operation; see Table 4-4), and during all reactions, decantations, extractions and distillations transfers cannot be conducted, thus disabling the use of multiple equipment pieces in series, except in the first reaction step (Step 6).

The allocation of single operations to operation blocks is shown to the right of Table 4-4, and the resulting block matrix is shown in Table 4-5. Block number 3 has a negative sign indicating a transfer. The last block, with an ID of “0”, is the final product stream. This recipe has to be implemented in a multipurpose production line, whose equipment pieces are listed in Table 4-6.

**Table 4-4: Recipe matrix for case study**

<table>
<thead>
<tr>
<th>Operation</th>
<th>Class</th>
<th>ID</th>
<th>Volume [m³]</th>
<th>Duration [min]</th>
<th>Flag</th>
<th>T [°C]</th>
<th>P [bar]</th>
<th>Lining ID</th>
<th>Block ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Purge</td>
<td></td>
<td>30</td>
<td>0</td>
<td>60</td>
<td>2</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>2 Charge</td>
<td></td>
<td>4</td>
<td>2.02</td>
<td>30</td>
<td>10</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>3 Charge</td>
<td></td>
<td>4</td>
<td>2.55</td>
<td>30</td>
<td>10</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>4 Mix</td>
<td></td>
<td>64</td>
<td>2.55</td>
<td>2</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>5 Charge</td>
<td></td>
<td>4</td>
<td>5.91</td>
<td>20</td>
<td>2</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>6 React</td>
<td></td>
<td>32</td>
<td>5.91</td>
<td>150</td>
<td>0</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>7 Charge</td>
<td></td>
<td>4</td>
<td>9.09</td>
<td>10</td>
<td>10</td>
<td>7.4</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>8 React</td>
<td></td>
<td>32</td>
<td>9.09</td>
<td>300</td>
<td>8</td>
<td>55</td>
<td>1</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>10 Transfer</td>
<td></td>
<td>7</td>
<td>9.09</td>
<td>15</td>
<td>0</td>
<td>55</td>
<td>1</td>
<td>-1</td>
<td>-3</td>
</tr>
<tr>
<td>9 Charge</td>
<td></td>
<td>4</td>
<td>3.36</td>
<td>30</td>
<td>10</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>11 React</td>
<td></td>
<td>32</td>
<td>12.50</td>
<td>120</td>
<td>9</td>
<td>65</td>
<td>1</td>
<td>-1</td>
<td>4</td>
</tr>
<tr>
<td>12 Decant</td>
<td></td>
<td>16</td>
<td>12.50</td>
<td>120</td>
<td>8</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td>5</td>
</tr>
<tr>
<td>13 Charge</td>
<td></td>
<td>4</td>
<td>10.29</td>
<td>20</td>
<td>10</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td>6</td>
</tr>
<tr>
<td>14 Extract</td>
<td></td>
<td>19</td>
<td>10.29</td>
<td>180</td>
<td>8</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td>7</td>
</tr>
<tr>
<td>15 Distill</td>
<td></td>
<td>17</td>
<td>3.62</td>
<td>480</td>
<td>8</td>
<td>87</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>(product)</td>
<td></td>
<td>-2</td>
<td>0.65</td>
<td>-1</td>
<td>0</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
</tbody>
</table>

The automatic allocation of equipment classes to the operation blocks is straightforward:

- Block 1 comprises one reaction step (needs a “Reactor” equipment class), one **Mix** operation (“Reactor” or “Mixer”), and several operations without requirements (**Purge, Charge**: “Any”). The intersection of those classes is the class “Reactor”.

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Likewise, Blocks 2 and 4 comprise a reaction step (requires a “Reactor” equipment class), and a Charge operation without specific requirement and are thus allocated to the “Reactor” class.

Block 3 (Transfer) has no allocation, as it will be used to link the preceding and following blocks.

Decantation and Extraction (Blocks 5 and 6) can be conducted in the classes “Extractor”, “Decanter” and “Reactor”, the reactors under consideration being equipped with valves and vision panels. As the plant contains neither extractors nor decanters, only the “Reactor” class is suitable.

Block 7 comprises a distillation that can be conducted in a reactor equipped with a condenser. The allocation is “Condenser” class.

Table 4-5: Block matrix for case study

<table>
<thead>
<tr>
<th>Block ID</th>
<th>Volume [m³]</th>
<th>Duration Constant [min]</th>
<th>Duration Linear [min]</th>
<th>Flags</th>
<th>T [°C]</th>
<th>P [bar]</th>
<th>LiningID</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.91</td>
<td>240</td>
<td>80</td>
<td>0</td>
<td>25</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>9.09</td>
<td>300</td>
<td>30</td>
<td>8</td>
<td>55</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>-3</td>
<td>9.09</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>55</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>4</td>
<td>12.50</td>
<td>120</td>
<td>30</td>
<td>9</td>
<td>65</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>5</td>
<td>12.50</td>
<td>120</td>
<td>0</td>
<td>8</td>
<td>25</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>6</td>
<td>10.29</td>
<td>180</td>
<td>20</td>
<td>8</td>
<td>25</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>7</td>
<td>3.62</td>
<td>0</td>
<td>480</td>
<td>8</td>
<td>87</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>0</td>
<td>0.65</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>25</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Table 4-6: Equipment list for case study. Reactors are equipped with an agitator, as well as valves with vision panels

<table>
<thead>
<tr>
<th>Equipment Name</th>
<th>Equipment Class</th>
<th>Volume [m³]</th>
<th>Floor</th>
<th>Related Equipments</th>
<th>Operating Temperature [°C]</th>
<th>Operating Pressure [bar]</th>
<th>Lining Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 Reactor</td>
<td>10</td>
<td>1</td>
<td>Condenser</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>stainless steel</td>
<td></td>
</tr>
<tr>
<td>R2 Reactor</td>
<td>10</td>
<td>2</td>
<td>Condenser</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>enamel</td>
<td></td>
</tr>
<tr>
<td>R3 Reactor</td>
<td>16</td>
<td>2</td>
<td>3 Condensers, 1 Column</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>enamel</td>
<td></td>
</tr>
<tr>
<td>R4 Reactor</td>
<td>6.3</td>
<td>3</td>
<td>Condenser</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>stainless steel</td>
<td></td>
</tr>
<tr>
<td>R5 Reactor</td>
<td>10</td>
<td>3</td>
<td>Condenser</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>enamel</td>
<td></td>
</tr>
<tr>
<td>R6 Reactor</td>
<td>10</td>
<td>3</td>
<td>Condenser, Heat-Exchanger</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>stainless steel</td>
<td></td>
</tr>
<tr>
<td>R7 Reactor</td>
<td>10</td>
<td>3</td>
<td>Condenser</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>stainless steel</td>
<td></td>
</tr>
<tr>
<td>C1 Centrifuge</td>
<td>0.44</td>
<td>1</td>
<td>Heat-Exchanger</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>C2 Centrifuge</td>
<td>0.44</td>
<td>1</td>
<td>Heat-Exchanger</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>D1 Dryer</td>
<td>4</td>
<td>2</td>
<td>-</td>
<td>20 - 160</td>
<td>0.01 - 2</td>
<td>stainless steel</td>
<td></td>
</tr>
</tbody>
</table>
The temperature and pressure reached in the process are well within the operating range of every equipment piece; hence the physical property filters will have no effect in this case. The lining material, however, is important in the second reaction step: in Block 2, only an enamel-lined reactor can be used (R2, R3, or R4). For every other block, all elements of the allocated classes can be used.

This allocation, coupled with the Recipe Constraints and the Design Constraints listed above, defines the superstructure. In this production line each equipment unit can be connected with any other, hence the absence of Connectivity Constraints. The optimization routine will assign one or more equipment units to each block. If two following blocks are assigned different equipment units, a transfer will be added. In several cases this will be forced as different classes will be required for the two blocks. In other cases this is optional. As long as implementing many blocks in one set of equipment units is not time limiting (and hence does not influence the throughput), this will be the preferred solution due to the secondary objective (use the least number of equipment units).

### 4.4.2 Process designs obtained

The optimal design found is shown in Figure 4-7. On the horizontal axis, the sequence of the recipe is represented; if many blocks are implemented in the same equipment unit set, the two blocks are shown at the same horizontal location. The equipment units shown below each block are the units used to implement this block. The floors at which the equipment units are located are indicated by the different vertical levels. Transfers are represented by arrows. While a bold arrow indicates a transfer present in the recipe (e.g. Step 10 in this case study), transfers added by the optimization procedure are shown in normal weight.

In the Decant operation (Step 12) the bottom layer must be kept, while the top layer is sent to waste treatment. Hence, if the next operation is implemented in the same equipment unit, the bottom layer must be transferred to a tank, and then pumped back into the initial unit when the top layer has been sent to waste treatment. Tanks are not explicitly listed in the results.
The throughput for the optimal design is 114.9 kg/h. The optimal design implements blocks 5 and 6 in the same equipment units (R5 and R7 in parallel). Transfers were added by the program between every other block, thus using many equipment units. The 7th block, the distillation, is conducted again in parallel in two reactors (and their attached condensers). These choices are justified to minimize the cycle time. The cycle time analysis is shown in Figure 4-8. The time-limiting block is Block 2 in the equipment unit R2. To shorten the cycle time one would need to add another unit either in series or in parallel with R2. No additional equipment unit is however available. Furthermore, one can note that constraints forbid conducting Block 2 in series and no equipment units satisfying the constraints (two units with same volume, enamel-lined) are available to be used in parallel. Hence the cycle time is minimal.

To reduce the number of units used, two possibilities exist. Firstly, the distillation in Block 7 could be conducted in only one unit. In this case, the cycle time would be increased from 362 min to 526 min, hence reducing the throughput drastically.
Secondly, Block 4 could be conducted in parallel in R5 and R7, thus freeing R3. In this case, however, the resulting cycle time for R5 and R7 would be increased to 486 min, again drastically reducing the throughput. Hence this design uses the minimum number of units to achieve the resulting cycle time and throughput.

![Cycle Time Analysis](image)

**Figure 4-8:** Cycle time analysis for the optimal design of the investigated case study.

As can be seen on the volume analysis presented in Figure 4-9, the volume-limiting equipment unit is R4 in Block 1. To increase the production per batch, another equipment unit should be added in parallel with R4. However, no equipment unit fulfills the constraints to be used in parallel with R4 (same class and same volume). Or a larger equipment piece could be used instead of the small 6.3 m³ R4. In this case, however, one of the units used in parallel later on (R1, R7, R5 or R6) must be used to implement Block 1. As R6 will not be able to replace the missing unit (due to the constraints), one of those blocks will not be conducted in parallel any more, hence increasing the cycle time as indicated above. In this case the trade-off (higher production per batch against longer cycle time) is unfavorable. Therefore, the design shown in Figure 4-7 enables the highest possible throughput. The units R1 and R6 are both only 19% filled, and there is no
need to use both units in parallel in Block 7. However, as demonstrated above, this design allows a lower cycle-time. Hence the minimum number of equipment units is used to reach the optimal throughput.

![Volume Analysis](image)

**Figure 4-9**: Volume analysis for the optimal design of the investigated case study.

The optimization delivers more than just the optimal design with regard to throughput. In Table 4-7, the characteristics of eight different process designs for the investigated case study are given, ranked according to their production rate. Note that a “0.5” contribution to the ‘top-down indicator’ (number of floors the reaction mass has to be pumped upwards) stems from the situation that equipment units are used in parallel for one operation but only one of them is situated at a higher floor than the unit(s) in the previous operation.

Only the best result for each production rate is shown - i.e. other designs could achieve the same production rate with, for example, more equipment units; many designs can also exist with the same value in all objectives: in the optimal design shown above, R6 and R7 could be exchanged, as R7 also has a condenser. The
result given in Table 4-7 serves as a basis for an analysis of the different designs from a practical point of view.

Some designs are dominated (i.e. they are worse in all objectives as compared to another design); for instance, in the fourth design the seven equipment units are used less efficiently than in the first one. Similarly, the second design being only slightly better than the first with regard to the tertiary objective function (top-down design), while being 5% worse in terms of production rate, is certainly not worth to be studied in more detail. The fifth design has the largest batch size (20% larger than the optimal design) but also the throughput is about 17% lower than for the optimal design. If e.g. for GMP products extensive and expensive analytics have to be carried out for each batch, this design might nevertheless be attractive in particular since it uses only six equipment units and shows the best performance with regard to top-down design (note that the optimization approach could also be used together with any type of economic objective function).

Table 4-7: Characteristics of different process designs identified for the investigated case study

<table>
<thead>
<tr>
<th>Rank</th>
<th>Production Rate [kg/h]</th>
<th>Batch Size [kg]</th>
<th>Cycle Time [min]</th>
<th>Number of equipment units</th>
<th>Top-down indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>114.9</td>
<td>696</td>
<td>362</td>
<td>7</td>
<td>4.0</td>
</tr>
<tr>
<td>2</td>
<td>110.0</td>
<td>631</td>
<td>345</td>
<td>7</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>105.6</td>
<td>631</td>
<td>359</td>
<td>6</td>
<td>3.5</td>
</tr>
<tr>
<td>4</td>
<td>99.9</td>
<td>631</td>
<td>379</td>
<td>7</td>
<td>4.5</td>
</tr>
<tr>
<td>5</td>
<td>97.1</td>
<td>832</td>
<td>514</td>
<td>6</td>
<td>2.0</td>
</tr>
<tr>
<td>6</td>
<td>95.2</td>
<td>631</td>
<td>398</td>
<td>7</td>
<td>5.5</td>
</tr>
<tr>
<td>7</td>
<td>91.6</td>
<td>832</td>
<td>545</td>
<td>7</td>
<td>3.0</td>
</tr>
<tr>
<td>8</td>
<td>91.2</td>
<td>520</td>
<td>342</td>
<td>7</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The third design listed uses less equipment units and the gain in simplicity might offset the loss of 8% in production rate. It has a throughput of 105.6 kg/h (8.8% less than the optimal design). There are some fundamental differences as compared to the optimal design, as can be seen from Figure 4-10. In this design, one equipment unit (R7) is unused. Block 4 and Block 5 are conducted in the same equipment unit, while Block 6 is conducted alone in R5. Finally, Blocks 5 and 6 are not conducted in parallel on two units any more.
The time-limiting unit is still R2, in which Block 2 is conducted. The cycle time is almost the same as in the optimal design (Table 4-7), the small difference being due to the difference in volume: as some operation durations are proportional to volume (e.g. Step 7: Charge in Block 2) the duration of Block 2 is slightly smaller in the second best design: 359 min instead of 362 min. This is due to the major difference between the two designs, the volume produced per batch. The volume limiting equipment is now R5 (Block 6), and R4 - that was volume limiting in the optimal design - is only filled to 91%.

Both designs presented in Figures 4-7 and 4-10 do not seem to be optimally top-down, which was the third objective function implemented. However, the constraints force Block 2 to be conducted on the second floor, as the only enamel-lined reactor present on the third floor is too small and would reduce the throughput considerably. But most reactors are on the third floor, hence forcing the process mass to be pumped upwards for the end of the process. The effect on the third objective can be observed in the fact that R1, the only reactor in the first floor, is used in the last operation and not in Block 6 (for example exchanged with R5), which would be an equivalent design in terms of throughput and number of equipment units, but worse in terms of top-down configuration.

![Figure 4-10: Layout of process design ranked third in Table 4-7.](image)
4.5 Conclusions

In this paper we presented a method that identifies the optimal design of a batch process to be implemented in a multipurpose production plant. The first step consists of the automatic generation of a superstructure based on a given recipe and an equipment database. This superstructure is composed of lists of potential equipment units suited for each unit operation, as well as heuristic rules and constraints. The second step is an optimization, where objective functions of different priority are introduced: throughput, number of equipment units used and “top-down” indicator. The method has been illustrated by a case study and it has been shown that it is capable to identify high performance process designs, even in a highly constrained problem.

Due to the high degree of automation, the method efficiently supports the design of batch processes. Quite often pilot plant processes are already depicted in a commercial simulation program, and also a description of the plants is available in such software. With the addition of only few data (the Recipe Constraints), this information can be used as input for the method and promising designs will automatically be generated. The resulting designs can be compared, discussed and modified according to the expertise of the engineers. The methodology helps to avoid overlooking a particularly promising design alternative, or to quickly assess how well a given production plant is suited for a given process.

While the current superstructure generation is most suited for assignment problems like the one presented above, the procedure can be extended to allow modifications of the recipe itself. In the present state, the superstructure allows only for the addition of transfers between blocks or for placing equipment units in parallel for one block. An extension could allow some modification inside the blocks themselves (i.e. the transformation of unit operations into others). Furthermore, for different problem settings other objectives can be added in addition or in replacement of the objectives used in this paper. For example, a “throughput per volume of reactor used” might be better suited for plants where equipment units not used in one process might well be used in another one.
Acknowledgments

The authors thank A. Oeggerli, L. Utiger, and T. Zaupa from Lonzagroup at Visp and Basel (Switzerland) for discussions on the characteristics of multipurpose batch plants which helped us to design a method that is capable to deal with realistic batch design problems.
Chapter 5: Batch Process Design - Optimization Algorithm

Multi-objective process design in multi-purpose batch plants using a Tabu Search optimization algorithm

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Abstract

Chemical batch processes are typically used for the production of specialty chemicals and pharmaceuticals. Due to the still growing importance of this type of processing, design methods are required that take into account the special requirements and constraints in the corresponding production facilities. We developed a method that optimizes the design of a single chemical process to be implemented in an existing multi-purpose batch plant, in which a well-defined set of equipment units is available for realizing this process. In the optimization, three objectives with different priorities are considered. A flexible meta-heuristic algorithm, Tabu Search (TS), has been implemented to solve this multi-objective combinatorial non-linear problem. We started from a basic form of TS
to determine the effectiveness of this version as well as establish the relative strengths and weaknesses of first level TS strategies. Our investigation includes a thorough examination of algorithm parameters and of implementation issues to identify algorithm settings that can handle the whole class of problems considered. Overall, we concluded that the basic form of TS - using fixed default settings - exhibits highly attractive performance features for solving the problems at hand. Moreover, comparison with a multi-start steepest descent algorithm shows that a basic TS approach conducts a global search more effectively. As illustrated by three case studies, the overall method proves to be a quickly applicable, reliable, and computationally efficient tool for implementing a chemical process in an existing multi-purpose batch plant. The approach is particularly suited for considering multiple prioritized objectives and for enabling the use of external (e.g. commercial) batch process simulation software as a black-box model for the process evaluations.

5.1 Introduction

5.1.1 Batch process design

Specialty chemicals and pharmaceutical products are typically produced in batch processes. Corresponding plants are often classified as multiproduct batch plants, in which every product follows the same sequence through all the process steps, or as multi-purpose batch plants, in which each product follows its own distinct processing sequence by using the available equipment in a product-specific layout [e.g. Rippin, 1983]. In practice combinations of these two limiting scenarios might also arise. Multi-purpose plants can be used in two main modes: either only one production runs in the plant at a given time or many processes run concurrently. Some multi-purpose plants consist of discrete but include flexible production lines that are independent from each other. Because of the escalating importance of these types of chemical processes, in recent years increased research efforts have been undertaken to develop design methods for batch processes. Many methods deal with the grassroot design of multiproduct or multi-purpose batch plants and include the equipment sizing...
problem [Sparrow et al, 1975; Grossmann and Sargent, 1979; Suhami and Mah, 1982; Papageorgaki and Reklaitis, 1990; Voudouris and Grossmann, 1992]. In most cases, the authors only consider the case where many productions run concurrently. Relatively few publications have been presented that deal with the optimum design of a single batch process. For grassroot design, Loonkar and Robinson [1970] described a procedure for the cost optimum design and apparatus sizing of a single batch process, while Takamatsu et al. [1982] presented a similar approach that considers the possibility of intermediate storage. Yeh and Reklaitis [1987] presented a method for the preliminary grassroot design of a single batch process including an approximate sizing procedure. Mauderli and Rippin [1979] developed a method for planning and scheduling in multi-purpose batch plants. While they consider many concurrent productions, their first step consists of the generation of design alternatives for the production of single products. To obtain the different design alternatives they take account of the plant specifications (number and size of available equipment units) and the process requirements (which equipment units can be used for the different process tasks). These alternative designs are not optimized but generated using a heuristic procedure that allows the selection of promising designs while ignoring designs with a low performance. The objective of these researches is to optimize \( n \) subsequent batches that can follow different paths in the plant. However, for safety, regulatory and controlling reasons, it is often preferred to have all batches using the same path. Under this perspective, the objective changes from the optimum schedule of \( n \) subsequent batches to the design of the single most efficient batch. To our knowledge no method to date has focused on this particular design problem.

In order to identify an optimal solution for this problem it is important to consider in the design procedure all details and existing constraints such as equipment specifications (e.g. range of operating temperature and pressure, lining material, special supply pipes, the floor at which each equipment is located), design constraints (e.g. feasible and infeasible connection of equipment units), and process requirements (e.g. reaction mixture that cannot be safely transferred, thus forcing several operations to be conducted in the same equipment unit). This is the approach taken in the method presented here. Based on pre-defined rules (representing heuristics) and options selected by the user, specified operating
instructions for a chemical process to be designed are automatically analyzed with regard to design requirements and constraints: suitable equipment units are assigned to each operation, feasible and infeasible transfers are identified, and operation blocks are determined that will be conducted in the same equipment unit. This results in a superstructure for which the optimum design can be identified.

5.1.2 Integer Non-linear Optimization

The problem that has to be solved is one of combinatorial optimization, a pure integer problem: the optimization involves decision variables that take only integer values, without any continuous variables. Even when the user selects to use short-cut models to adapt operation durations, non-linear (e.g. stepwise) functions are evaluated to compute the objective function, rendering this problem a non-linear integer system. Such systems are known to be NP-Complete and cannot be solved in polynomial time. Various algorithms and methods have been developed to tackle similar problems that can be classified in three main categories: heuristics, mathematical programming and metaheuristic algorithms.

Heuristics (of the classical kind) do not actually solve the optimization problem, but aim at finding “good” solutions by following a set of rules. In the chemical process design field, Douglas [1985] has developed a method for hierarchical process synthesis that relies on sets of rules at different stages during process development (see also [Sirola, 1996]). The computer-oriented implementation of such systems usually takes the form of an Expert System, as for example presented by Kirkwood [1988]. Such methods are good in finding quickly and reliably a good solution that can be used for example as starting point for more advanced metaheuristic algorithms.

The mathematical programming methods (sometimes called “exact methods”) are rigorous optimization techniques aimed at solving the MINLP (Mixed Integer Non-Linear Problem) formulation of the design problem [Grossmann 1985]. These techniques use usually algorithms derived from Branch & Bound or Outer
Approximation, as discussed by Grossmann and Kravanja [1995] and Skrifvars et al. [1998]. They have been used extensively in process design [see e.g. Ciric & Floudas, 1990, Papalexandri and Pistikopoulos, 1996, Hostrup et al., 2001]. A recent review of these methods has been published by Grossmann et al. [1999] and their applicability, limitations and potentials are discussed by Gruhn and Noronha [1998], Grossmann and Daichendt [1996] and Kallrath [2000].

The last category, the metaheuristic algorithms, is based on one (or several) initial solution(s) and a progressive (though not necessarily uniform) improvement of their quality. A popular example of a metaheuristic is the genetic algorithm (GA) approach. This scheme is characteristically based on a population of solutions that are combined (using a crossover operation) and randomly modified (using a mutation operation) according to their fitness (objective function value), leading to a “natural” selection and a discrimination in favor of solutions with a good fitness. In the process design field, Fraga [1996] for example used a genetic algorithm to optimize the design of a distillation system.

Another metaheuristic method is Simulated Annealing (SA) developed by Kirkpatrick and al. [1983]. SA randomly modifies an initial solution, and always accepts downhill (improving) moves when encountered. Other moves are accepted if they satisfy a condition that depends on the advancement of the algorithm (the Metropolis criterion, expressed as “temperature”), which endows the method with an ability to accept moves that can escape from a local optimum. In the process design field, SA has been used to design separation systems by Floquet [1994] and to handle overall process design by Chaudhuri [1996].

A third metaheuristic method is the Tabu Search (TS), developed by Glover [1977]. TS makes use of adaptive memory to escape local minima. TS has had numerous successful applications in recent years (for example, the website www.tabusearch.net lists over a thousand presentations and articles on the method), but to our knowledge it has been used only once in the field of batch process design by Wang et al. [1999] for the problem of the grassroot design of multiproduct batch processes.
Within the present project the goal was to enable the use of external batch simulation programs (black box optimization). Black-box models are exceedingly difficult to handle in conjunction with mathematical programming approaches, therefore making it attractive to employ a metaheuristic algorithm. Gross [1998] has tackled a similar problem (continuous process design with a black box external simulation package) and has chosen a genetic algorithm. However, GA approaches have encountered significant difficulties when confronted with problems that contain complex constraints, which are a predominant feature in the problems we face. The limitation of GAs in these settings arises from the inability to implement crossover operations that generate valid designs. Recourse to penalty approaches and ad hoc “repair operators” as an attempted remedy entails a risk of spending most of the computational effort in handling invalid solutions, making GAs unsuitable for our present application. Another evolutionary approach, path relinking, offers a greater capability for handling constraints. This approach is often coupled with tabu search (and in fact, emerged from the same origins as tabu search), thereby motivating us to look at an implementation of TS in this study. Additional reasons for choosing tabu search, and for choosing a multi-start descent procedure to compare it against (in contrast to simulated annealing, for example), are indicated in the next section.

5.1.3 Objectives of this research

Since very limited experience is available with regard to using Tabu Search in chemical process design, we decided to conduct a ”grass roots” investigation of the algorithm to determine its performance characteristics in this setting.

The objectives of the research presented here were to:

- investigate the suitability of TS for the chemical process design problem discussed above, and to determine parameters and settings that have the greatest relevance for a basic TS implementation,
- establish the relative strengths and weaknesses of first level TS strategies for solving this class of problem,
- examine the suitability of TS to handle multiple prioritized objectives,
• determine default parameter settings that can handle the whole class of problems with the highest probability of finding the global optimum while using a modest amount of computational effort.

Our major aim being to study the suitability of TS for solving a new class of problems, we concentrated on examining a basic form of tabu search exclusive of deeper TS strategies that comprise an integral part of more advanced versions. Additionally, we want to establish how a simple TS implementation compares with a principal alternative approach (multi-start descent) that has been documented to have good performance characteristics and strong convergence properties. As previously noted, we have not undertaken to create a computational comparison of our TS approach with simulated annealing. The reason for instead choosing multi-start descent (sometimes called “iterated descent” or “generalized hill climbing”) is the demonstration by recent studies that this approach may dominate simulated annealing both theoretically and empirically (see, e.g., Jacobson [2002] and Lourenco, Martin and Stutzle [2002]).

Finally, we intend to provide insight into the choice of higher level strategies that are likely to produce the greatest improvements.

Against this backdrop, we investigate the effectiveness of our tabu search approach by using three real world case studies.

5.2 Batch process design method

The optimization problem covered in this paper can be defined as follows:

Given:
1. Recipe
   a. Recipe of the product expressed as a series of chemical/physical tasks
   b. Capacity requirements for each task per unit of final product
   c. Base duration of each task at the input scale
   d. Recipe constraints (specific rules about how tasks can be combined)
2. Equipment
   a. Available equipment units and their detailed specifications
   b. Connectivity constraints (which equipment unit can be connected with which other).
3. General heuristics
   a. Equipment classes suited for processing each task class
   b. Design heuristics (built-in ones as well as user options)
   c. Relationships between the processing time of each task class and the batch size
4. One or more objective functions

**Determine:**
The optimum layout for the process - i.e. allocation of equipment units to tasks, design used (in parallel, in series).

---

**Figure 5-1:** Overview of the method; grey boxes indicate optional usage of external software.
A general overview of the method is presented in Figure 5-1. The routines for recipe analysis, superstructure generation, process simulation, and optimization have been implemented in a MATLAB® program. The process simulations can also be conducted in an external (e.g. commercial) batch process simulator. The different input and methodological steps are summarized below using a relational data structure formulation, the tuple calculus [Date, 1995]. Table 5-1 provides a list of the symbols used in the mathematical formulation.

**Table 5-1: Tuple calculus symbols and operators used in the mathematical formulation.**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>$ab$</td>
<td>column $b$ of matrix $a$</td>
</tr>
<tr>
<td>$(a \mid a.c = 1)$</td>
<td>take rows of $a$ where column $c = 1$</td>
</tr>
<tr>
<td>$(a.b \mid a.c = 1)$</td>
<td>take only column $b$ (same rows as above)</td>
</tr>
<tr>
<td>$\in$</td>
<td>is contained in (single element)</td>
</tr>
<tr>
<td>$\supset$</td>
<td>contains (multiple elements)</td>
</tr>
<tr>
<td>$\cup$</td>
<td>union</td>
</tr>
<tr>
<td>$\cap$</td>
<td>intersection</td>
</tr>
<tr>
<td>$\rightarrow$</td>
<td>assign a subset of a matrix to itself (filtering)</td>
</tr>
<tr>
<td>$\emptyset$</td>
<td>empty (no elements)</td>
</tr>
</tbody>
</table>

The first input is the base recipe $R$. The recipe is given as a table (which is converted to a matrix in MATLAB®) containing vertically the physico-chemical tasks to be conducted; the vertical position, also called the index, represents the position of the given task in the task sequence. Branched recipes are handled by including an additional matrix $Z$ (not included in the equations below) to describe the sequence of the rows in the recipe (Equation 11 (see below) would be modified to take matrix $Z$ into consideration).

Each row of $R$ first indicates the nature of the task ($R.\text{OperationClassID}$), the base volume ($R.\text{Volume}$) and the estimated base duration ($R.\text{Duration}$) required for the
task. All column names ending in ID are relations to lists of available options stored in library matrices. For instance, \textit{R.OperationClassID} refers to the operation class matrix \textit{O} containing all supported types of tasks (e.g. reaction, distillation...). Operating temperature (\textit{R.Temperature}), pressure (\textit{R.Pressure}) and required lining materials (\textit{R.LiningID}) are then given, and the matrix is completed by flags (\textit{R.Flag}) indicating constraints on possible designs, duration adaptation rules and algorithm options.

Based on \textit{R.Flag}, the recipe is condensed in a block matrix \textit{B} (step “Recipe Analysis” in Figure 5-1). Each row of \textit{B} (i.e. each operation block) contains a list of tasks that must be conducted in the same equipment unit(s). The matrix stores the largest volume attained during the block, as well as the highest pressure and temperature reached.

According to the duration adaptation rules in \textit{R.Flag}, \textit{B} also contains two duration components: \textit{B.ConstantDuration} contains the volume independent part of the aggregated duration of the block, while \textit{B.LinearDuration} contains the volume dependant part. If the time adaptation rules are neither linear nor constant for one task, as identified by \textit{R.Flag}, this indication is propagated to \textit{B.Flag}. Finally, the flags and the lining material requirements are summarized in each row.

A block-to-recipe one-to-many relationship matrix \textit{BR} is also set-up in order to keep track of which tasks are contained in which block.

The equipment list is similarly represented by a matrix \textit{E}. Each row of \textit{E} represents a single equipment unit, defined by a unique number \textit{E.EquipmentID}. If multiple equipment units belong together (for example a condenser on the top of a reactor), an internal link to the master \textit{EquipmentID} (e.g. the reactor) is given in the slave equipment (e.g. the condenser) record. Each equipment unit is defined by a class defining the type of equipment (e.g. reactor, centrifuge, condenser...), the volume, the lining material (\textit{E.LiningID}, pointing to the same library matrix as \textit{R.LiningID}) the operating range being indicated by a pointer \textit{E.TP_rangeID} to the standard operating ranges matrix \textit{P} that contains maxima and minima for both pressure and temperature. Finally, the physical location in the plant is defined by the floor.

Feasible equipment interconnections are summarized in the connectivity matrix \textit{C} that contains many-to-many relationships based on the \textit{EquipmentID}. The
equipment class allocation to each block of tasks (third step in Figure 5-1) is based on the allocation matrix \( A \). It contains many-to-many relationships indicating which task class(es) can be conducted in which equipment class(es). The equipment class allocation proceeds according to Equations 1 to 4 (the subscript \( i \) is the main counter across the block matrix \( B \)).

\[
\text{recipe indexes} := K_i = (B_{r, \text{RecipeIndex}}|B_{r, \text{BlockID}} = i) \\
\text{recipe operations} := X_i = (R|\text{index} \in K_i) \\
\text{equipment classes} := U_i = (A.\text{EquipmentClassID}|A.\text{OperationClassID} \\
\quad \Rightarrow \bigcup X_i.\text{OperationClassID}) \\
\text{eligible equipment units} := S_i = (E|E.\text{EquipmentClassID} \in U_i)
\]

In the next step, the eligible equipment units \( S_i \) are filtered according to the lining material and operating conditions requirements, as shown in Equations 5 to 9.

\[
S_i \leftarrow (S_i|(P.\text{Pmin}|P.\text{TPrangeID} = S_i.\text{TP}_{\_\text{range}}) \leq \text{min}(X_i.\text{Pressure})) \\
S_i \leftarrow (S_i|(P.\text{Pmax}|P.\text{TPrangeID} = S_i.\text{TP}_{\_\text{range}}) \geq \text{max}(X_i.\text{Pressure})) \\
S_i \leftarrow (S_i|(P.\text{Tmin}|P.\text{TPrangeID} = S_i.\text{TP}_{\_\text{range}}) \leq \text{min}(X_i.\text{Temperature})) \\
S_i \leftarrow (S_i|(P.\text{Tmax}|P.\text{TPrangeID} = S_i.\text{TP}_{\_\text{range}}) \geq \text{max}(X_i.\text{Temperature})) \\
S_i \leftarrow (S_i|S_i.\text{LiningID} \in \bigcap X_i.\text{LiningID})
\]

The superstructure is defined by combining these eligible equipment units for each task block with design rules and constraints. The first constraint is that no equipment unit can be used twice for the same batch, as shown in Equations 10 and 11 (the subscript \( j \) is a secondary counter on the block matrix \( B \)).

\[
\text{Allocated equipment units} := L_i; L_0 = \emptyset; L_{i=\text{transfer}} = \emptyset \\
S_i \leftarrow S_i - \sum_{j=1}^{y-1} (L_j) + L_{i-1}
\]

The connectivity constraints given in matrix \( C \) are taken into consideration in Equations 12 and 13 (\( y \) is a temporary binary variable indicating a transfer [1] or not [0]).
Finally, the remaining recipe constraints given in (R.Flag), that indicate which design can be used to implement each task, are taken into consideration in addition to those design constraints given by the user, as shown in Equations 14 and 15. (An example of such a design constraint is to indicate whether the reaction mixture can be properly separated into two equal volumes with the same concentration of all components, allowing the task to be conducted in parallel on multiple equipment units. A user design constraint might further indicate, for instance, that at most two equipment units can be used in parallel.)

\[
L_i = \begin{cases} 
L_i + \text{one additional element of } S_i & \text{only available if } 4 \neq B_i:\text{Flag} \land L_i:\text{DesignType} = \text{"parallel"} \\
L_i + \text{one or several additional elements of } S_i & \text{only available if } 8 \neq B_i:\text{Flag} \land L_i:\text{DesignType} = \text{"series"} \\
L_i & \text{always available; } L_i:\text{DesignType} = \text{"single"}
\end{cases}
\]

In Equations 14 and 15, choices are left open in formulations like “one single element of”. All possible decisions for making such choices determine a valid process. As represented by the last step in Figure 5-1, these decisions must be optimized in order to obtain the optimum design. This optimization is investigated in detail in the following sections.

The optimization involves three objective functions:

- Maximize the throughput, i.e. the batch size divided by the batch cycle time,
- Optimize the quality of the design, as evaluated by two indicators:
  - Minimize the number of equipment units used, to discriminate in favor of simple designs,
Minimize the number of floors the reaction mixture has to be pumped up, to discriminate in favor of top-down designs.

These objective functions are prioritized: a larger throughput is always preferred to a simpler design. Similarly, a simpler design is always preferred to one that is more “top-down.” This means that the secondary objective function will only be evaluated when an equal throughput is produced by two designs, and similarly the third objective function is only evaluated if two designs produce the same throughput and use the same number of equipment units.

The primary objective function evaluation requires a process simulation of the recipe. This evaluation can be conducted in an external batch process simulation program. Alternatively, it can be conducted in MATLAB® using the constant duration (e.g. duration of a reaction is volume independent) or a linear time adaptation according to the volume, for instance for transfers or distillations. (Additionally, some specific rules called by B.Flag have been implemented for special adaptations of durations, like in a multiple-drop centrifuge where first the number of drops needed is calculated and then multiplied by the drop duration.)

5.3 Tabu Search

5.3.1 Introduction

Tabu Search is a meta-heuristic method using a set of coordinated strategies for introducing and exploiting adaptive memory, in order to generate a sequence of solutions that contains a subsequence of progressively improving “best solutions found.” Repetitively, modifications of the current solution are examined, and the one resulting in the best solution is chosen for the next iteration, even if this successor is worse than the present solution. The special memory processes continue to drive the method forward to discover regions that harbor one or more solutions better than the current best, if such solutions exist. Some forms of TS have a proof of finite convergence to optimality (Glover and Hanafi [2001]), but
the most effective forms generally do not. A comprehensive description of TS with examples of applications is given in Glover and Laguna [1997].

The fundamental version of tabu search used in this study is depicted in the schematic flowchart of Figure 5-3. In the following, the different rules and options for the algorithm will be discussed.

**Initial Solution**

First an initial solution has to be provided. Usually there are advantages to starting from an initial solution that is of high quality, such as one proposed by experts or generated by preliminary heuristics.

A method providing multiple initial solutions can however be preferable: the constraints may make the solution space non-convex, and hence a “good” initial solution may be computationally very far (i.e. numerous moves) from the optimum. An efficient way of exploring the whole solution space is to restart with different initial solutions. They can be strategically generated to be diverse, or be generated by a randomization component. For instance, a strategy used by Wang et al. [1999] applies a random selection of the initial solution that is biased to cover previously unvisited regions of the optimization space as a means of providing a targeted diversification of the search (other more sophisticated diversification strategies are discussed in Glover and Laguna [1997].)

**Move Definition - Neighborhood generation**

The definition of the moves, i.e. the definition of the modifications of the current solution that can be done at each iteration, is highly problem-specific. The current solution combined with the moves defines a neighborhood of possible “next solutions.” In general terms, larger neighborhoods afford an opportunity to encounter shorter paths (fewer moves) to reach an optimal solution. However, large neighborhoods require special candidate list strategies to isolate a subset of the neighborhood to be tested (see below), and unless the candidate lists are chosen effectively, the path actually selected may be quite long, requiring a large number of steps to reach an optimum (or perhaps never reaching an optimum at all). This is the first trade-off addressed in the parameterization of our TS approach. As explained in the following, such trade-offs also arise for other components of TS.
**Neighborhood - Candidate list selection**

If the moves defined produce a large neighborhood, and if at each iteration every neighbor is evaluated, the algorithm will become quite slow. Therefore, usually only a subset of the neighborhood is considered, produced by examining a candidate list of moves. A straightforward method is to randomly select a fixed number of neighbors for consideration. The trade-off is then: the larger the subset, the slower the algorithm; but the smaller the subset, the higher the risk of requiring many moves to reach an optimum. Relevant considerations for candidate list construction are likewise discussed in the primary TS reference previously indicated [Glover and Laguna, 1997].

**Tabu list**

The simplest form of adaptive memory used by tabu search consists of creating a tabu list of solution attributes that are changed as a result of making recent moves. An attribute on the list can either be a FromAttribute, meaning that it belonged to a solution that was left behind as a result of making a move, or a ToAttribute, meaning that it belonged to a new solution created by the move. Attributes of either kind that may appear on the tabu list identify moves that are tabu, i.e., that are forbidden to be made. If a FromAttribute is on the list, a move is tabu if it would create a solution containing that attribute, while if a ToAttribute is on the list, a move is tabu if it would drop that attribute from the current solution. In either case, the avoidance of a tabu move will prevent the method from re-visiting an associated solution previously encountered. More generally, the tabu classification will also prevent the method from visiting solutions “related to” solutions previously encountered, due to the fact that different solutions can share certain attributes in common. Thus, the mechanism of defining certain moves to be tabu introduces a certain “vigorous diversity” into the sequence of moves generated.

To avoid eliminating moves that can be beneficial to the search, additional mechanisms are employed. The first is simply to limit the size of the tabu list, or stated differently, to limit the tabu tenure of any given attribute - i.e., to limit the number of iterations the attribute is permitted to affect the tabu status of
potential moves. (Attributes as well as moves are often called tabu. To be precise, the tabu status of a move depends on rules that may specify that it contains some combination of tabu attributes.)

Consequently, the size of the tabu list (the value of tabu tenure) is an important parameter in tabu search. Different lists can be created for different types of attributes, thereby affording the possibility for different tenures for these attributes (see below Asymmetric Tabu List in Section 5.5.4). When tabu lists are used as data structures, they operate as First-In First-Out (FIFO) stacks. This is the approach used in our current implementation. As an alternative, when the number of solution attributes is not too large, it can be convenient to use a data structure that records for each attribute the iteration when its tabu tenure will end. Once the current iteration is larger than this recorded value, the attribute is no longer tabu (see below Oscillating Tabu Lists in Section 5.5.4).

Regardless of the data structure employed, the greater the tabu tenure, the smaller are the chances that the algorithm will loop around to re-visit a previously generated solution. But the greater the tenure, the more limited the search becomes. (Good solutions may be missed because a move leading to them remained tabu for a long time.) This fact motivates a second commonly used mechanism to avoid eliminating a potentially beneficial move - aspiration criteria that can allow a move to be accepted in spite of being tabu. An aspiration criterion used in most TS implementations is to allow a tabu move to be accepted if it leads to a solution that is better than any solution found so far.

**Objective function - Best Candidate selection**

After the neighborhood has been filtered to eliminate tabu moves and a subset of candidate moves has been selected, each neighbor in the subset is evaluated. The best neighbor (having the highest evaluation) is selected, and becomes the “initial” solution for the next iteration. Often the objective function(s) give the
Figure 5-2: Tabu Search algorithm. Boxes with grey background signify options. Parallelograms represent the rules and the objective functions.
basis for the evaluation, although other considerations can also enter: The objective function value itself can be manipulated before the selection. In highly constrained problems for instance, some constraints can be handled by penalty functions.

More advanced forms of TS also use frequency based memory in order to favor (or penalize) a “direction” - for example to favor exploring unvisited areas of the solution space (e.g., moves can be encouraged or discouraged according to whether they introduce attributes that were infrequently or very frequently encountered in previous solutions.) These designs provide diversification strategies that allow a better covering of the overall solution space. As previously indicated, diversification can also be pursued with multiple restarts in different regions of the solution space (frequency-based memory can also be useful in such restarting strategies.)

**Stopping criteria**

Since the algorithm does not know when the optimum has been found, an external stopping criterion must be set. The simplest form of stopping criterion is a fixed number of iterations or a given computational effort. Obviously, the trade-off is: if the algorithm stops too early, the optimum solution may not be found yet. If the algorithm stops too late, computational time can be wasted. A maximum allowable computational time may be useful for problems where the quality of the solution is secondary to the time needed to find it, but a dynamic stopping criterion is more suitable in most cases: if the algorithm does not succeed in improving the existing solution in a given number of iterations, this gives a strong indication that either the optimum has been found, or that the region of the solution space being explored is not interesting - hence that the algorithm should stop or a diversification process (such as a restarting process) should be initiated. When multiple restarts with different initial solutions are used for diversification, a second stopping criterion can be set that limits the number of times the algorithm can restart. This criterion can be either a fixed number of restarts, or a rule according to the history of the optimization.
5.3.2 Tabu Search Implementation

To solve the optimization problem defined in Section 5.2, our tabu search is implemented as follows: a design solution is an assignment of equipment units to each operation block, with design specifications if needed (i.e. use units in parallel or in series); such a solution is represented by the matrix $L$ in Equations 14 and 15. Each block has one or several equipment unit(s) allocated, except the transfer blocks (transfers are explicitly listed in the recipe $R$ and in the block matrix $B$ only if they are mandatory; other transfers may be automatically added in the recipe if imposed by the design). The initial solution is randomly generated from the superstructure presented above.

Figure 5-3 demonstrates how the different types of moves gradually alter a design during the tabu search optimization. In the middle column, each row represents a part of the current design at a given iteration. The moves are

- adding an unused equipment unit to a block, leading to designs “in parallel” (as in Figure 5-3, 7th row) or to designs “in series”,
- removing an equipment unit from the block (as in Figure 5-3, 2nd row), and
- (Optionally) replacing an assigned equipment unit with an unused equipment unit (as in Figure 5-7, 3rd row).

The moves may not lead to solutions that violate any constraints. For instance, the move “Add” can only be applied if the operation may have multiple assignments.

The move “replace” is a composition of the two other moves: e.g. add a free piece of equipment, and remove another allocated piece. This move can favor loops, as even if the addition and the removal are tabu, a replacement can have the same effect and is still allowed (the initial tabu list implemented is move-based rather than attribute-based, see Section 5.5.4). However, the absence of replacement can lead to locking a particular equipment unit in a particular block. In a block that cannot have multiple equipment units allocated (neither in parallel nor in series), the replacement will be difficult: before “adding” a new equipment unit, the previous one must be “removed”. But a block with zero equipment units
will produce a process design with zero production. Hence such moves will be only
selected when all other moves are tabu.

![Blocks](image)

**Figure 5-3**: Demonstration of the different types of moves implemented in the
Tabu Search optimization. To the left, the normalized throughput is displayed and
in the middle, the equipment units assigned to operation blocks 1, 2, 3 and 7 are
shown. When multiple units are pictured, the operation is conducted in parallel in
these units; the shaded reactor has a volume of 16 m$^3$, while all the others have 10
m$^3$. The complete designs #1 and #9 are shown schematically to the right; the
numbers indicate operation blocks being conducted in the equipment pictured
(missing blocks are mandatory transfer blocks).

Regarding the options exposed in the introduction above, we chose not to
implement any intensification processes, as we focus on a simple type of TS design
(as explained earlier). Diversification is achieved solely by means of multiple-
restarts, and the stopping criteria consist of (1) a dynamic ending for each restart and (2) a fixed number of restarts.

To determine the parameters that control our implementation, appropriate attention must be given to trade-offs since parameter values that are too high or too low can have a negative impact on the efficiency of the optimization. Section 5.5 addresses these issues of parameters determination and examines their effect on the performance of the algorithm for the particular class of problems presented here. Different implementations of the tabu list are also investigated in this section.

5.4 The case studies

Each case study consists of a recipe to be realized and an available plant comprising a set of equipment units. The size of the problem for a particular case study depends on the number of tasks in the recipe as well as on the number of equipment units in the plant. The difficulty of solving a problem depends on its size, and on how constrained it is. If the problem is highly constrained, there will be only few valid designs, hence making the search easier, but the solution space may not be connected, making it impossible to go sequentially from any initial point to the optimum with only valid moves (hence the necessity to have a large number of restarts). If however there are only a few constraints, there will generally be a large number of valid designs and this makes it quite difficult to obtain the global optimum.

Three case studies have been used to illustrate and evaluate the algorithm:

- The first case study involves a rather small and highly constrained problem.
- The second case study involves a rather large, weakly constrained, problem used to demonstrate the scalability of the method.
- The third case study involves a medium size problem, but without any physico-chemical or connectivity constraints. As equipment units are typically standardized in multi-purpose batch plants, this means that many equipment units can be allocated to many blocks and hence that many
designs will be equivalent, at least in terms of primary and secondary objective functions. This renders the solution space quite flat and makes it difficult to identify a direction in which the designs improve.

The characteristics of the three case studies are summarized in Table 5-2. The number of “transfer” blocks indicates how many transfers are required. The maximum number of transfers possible is reached when each equipment unit is allocated to only one block. The number of reactors in a plant is given because reactors are quite versatile and can be used for many classes of operations, in particular when they are equipped with additional equipment (e.g. a distillation can be run in a reactor equipped with a condenser).

Table 5-2: Characteristics of the case studies

<table>
<thead>
<tr>
<th></th>
<th>Case Study</th>
<th>Case Study</th>
<th>Case Study</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>#1</td>
<td>#2</td>
<td>#3</td>
</tr>
<tr>
<td>Number of operations in recipe</td>
<td>16</td>
<td>93</td>
<td>37</td>
</tr>
<tr>
<td>Resulting number of operation blocks</td>
<td>7</td>
<td>33</td>
<td>13</td>
</tr>
<tr>
<td>Number of “transfer” blocks</td>
<td>1</td>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>Maximum number of transfers</td>
<td>5</td>
<td>22</td>
<td>8</td>
</tr>
<tr>
<td>Number of equipment units in plant</td>
<td>22</td>
<td>43</td>
<td>31</td>
</tr>
<tr>
<td>Number of reactors in plant</td>
<td>7</td>
<td>11</td>
<td>8</td>
</tr>
<tr>
<td>Average number of connection per equipment unit</td>
<td>9</td>
<td>16</td>
<td>13</td>
</tr>
</tbody>
</table>
5.5 Results & Discussion

5.5.1 Optimizing the TS parameter settings

We have implemented a Monte-Carlo analysis [Vose, 1996] of the algorithm parameters and of some options using the three case studies. The tabu parameters discussed in Section 5.3.2 (including the decision parameters like “include replacement move”) have been randomly set and the problems have been repeatedly optimized using the resulting tabu algorithm. The parameter values have been varied in the following ranges: replacement move and aspiration on or off; tabu list length from 0 to 300; neighbor sample size from 1 to 100; number of process simulations without improvement before restart from 10 to 100; number of restarts from 0 to 20.

This discloses the impact of the different parameters on the efficiency of the algorithm, taking into consideration potential parameter interactions. However, the overall efficiency is much smaller than when only “good” values are used for all parameters at the same time. In a first approximation, only the primary objective function (throughput) is considered. In the next section, all three objectives are included and some differences are highlighted.

Move definition - Replacement move

Figure 5-4 shows the cumulative distribution functions for runs with and without replacement moves for Case Study #1. The distributions display the probability (vertical axis) that the optimization results in a solution with at least the normalized throughput (i.e. divided by the globally optimum throughput) given on the horizontal axis. The inclusion of the replacement move is clearly favorable: the dotted line is always below the solid line; hence the probability of obtaining a higher production is always larger with the replacement move included. The two other case studies confirm this result, and hence the runs without replacement moves have been excluded from all the following investigations.
**Figure 5-4:** Cumulative distribution functions for runs with and without the replacement move. The results were obtained for Case Study #1.

*Tabu list length & Aspiration*

The tabu list is managed as a FIFO stack. The size of the tabu list represents therefore how many moves are tabu at a given time and how long a move remains tabu. On Figure 5-5, the effect of the tabu list length on the probability to find the optimum throughput is displayed for Case Study #1. We used the “improved best solution” aspiration criterion. The comparison of the probabilities obtained with this aspiration criterion and those without clearly suggests that the inclusion of the criterion is favorable for finding the optimum throughput. As expected, without using an aspiration criterion, the probability decreases with increasing list length. This is due to the “blocking effect” explained above, which is partly countered by the presence of aspiration: the probability rises for small sizes, reaches a summit for sizes around 100 and drops drastically for higher values.

From the outcomes shown in Figure 5-5 and similar outcomes obtained in the other case studies, we concluded that aspiration should be enabled and have done this in the following investigations. In view of the sudden drop in probability for list sizes around 100 as displayed in Figure 5-5 for Case Study #1, as well as similar findings obtained for the other two case studies, we chose to use a default value of 80 for the tabu list length.
Candidate list strategy and neighbor sample size

We elected to use a straightforward candidate list strategy that randomly samples the neighbors of a given solution. The sample size parameter indicates how many neighbors will be investigated per iteration (i.e. the size of the neighborhood’s subset as defined above). The investigation of Case Study #1 showed a quite low probability of finding the optimum throughput for small (<5) or large (>25) neighbor sample sizes. For neighbor sample sizes of about 16 the highest probability was found.

The third case study - whose dimensions are slightly larger than Case Study #1 - shows a similar trend, with the highest probability at sample sizes of about 20. The second case study - the largest - displays a different trend: the probability rises and stays high for a wide range of neighborhood sizes and decreases for neighborhood sample sizes higher than 45. The fact that Case Study #2 is a large problem is likely the reason that more neighbors are required: the neighborhood sample size should probably be proportional to the size of the problem (as defined by the number of equipment units and the number of blocks), as shown in Figure 5-6. Further research would be needed to confirm the relationship indicated in
Figure 5-6. (The use of more strategic types of candidate list strategies can of course affect this relationship.)

A value of 20 for the sample size was selected as a default for subsequent investigation. This value seems to be a good compromise for the three case studies because the probability to find the optimum is already quite high for this value in Case Study #2.

![Optimal Neighborhood Size](image)

**Figure 5-6**: Optimum neighborhood sample size as a function of problem size and corresponding tentative linear regression.

A value of about 20 seems to be a good compromise for the three case studies because the probability to find the optimum is already quite high for this value in Case Study #2. Hence this value will be selected as a default.

**Stopping strategy**

We have found it useful to introduce a measure of computational efficiency in order to investigate the stopping strategy. The probability of finding an optimal solution will always rise (or at least remain constant) when longer runs are conducted – hence to optimize this probability, infinite runs should be conducted. Obviously, the computational effort (represented for instance by the number of process simulations to be conducted) will rise as well with longer runs, hence
resulting in a trade-off between probability and computational effort. Therefore, we have defined the efficiency of the algorithm as the probability of reaching the optimum throughput, divided by the computational effort invested.

The stopping strategy implemented here is twofold: first the algorithm stops after a given number of iterations where the solution has not been improved. Then the algorithm restarts with another initial solution. The number of restarts is the second parameter studied.

The investigation of the first parameter shows that whatever its value, the probability of obtaining the optimum throughput is more or less constant; however, the efficiency decreases as the algorithm waits longer. This makes sense as the algorithm will continue the search even in unpromising regions of the solution space.

The investigation of the second parameter, the number of restarts, shows that the probability to find the optimum throughput initially rises sharply with the number of restarts, then rises only slowly for a number of restarts higher than 8. In all three case studies, the efficiency peaks with 5 to 6 restarts. This type of behavior again seems reasonable: the more restarts, the more computational effort must be invested, and this occurs even if the global optimum has already been found. But not to restart implies no diversification is employed, and hence there is a great dependency on the initial solution.

Both stopping criteria values may be different if the three objective functions are considered, as subsequent moves may be used to optimize the lower priority objective functions. Hence before definitive conclusions on these parameter settings are drawn, the multi-objective optimization problem is investigated.

5.5.2 Multi-objective Optimization

The behavior described thus far arises for the situation where only the main objective function (throughput) is optimized. However, the complete form of the problem has three objective functions: throughput, number of equipment units
used (simplicity), and number of floors to pump the reaction mixture up (top-down indicator). When tests are performed by considering all three objective functions together, the conclusions for the parameters do not change noticeably, except for the stopping criteria.

In Figure 5-7, for a typical run, the values of the three objective functions are displayed at several iterations after encountering the optimum throughput. The optimization procedure, including some uphill moves to escape local minima, is still going on in order to improve the secondary and tertiary objective function values. Since the algorithm has no proof of optimality, and continues to seek improvement of all three objectives, uphill moves with regard to the first objective are still possible. Between points (2) and (3) in Figure 5-7 no local optimum is found: the algorithm needed to run 25 iterations without improvement to find the global optimum - the optimum with regard to all three objective functions.

![Figure 5-7](image)

**Figure 5-7:** Values of the objective functions during the optimization of the third case study. At point (1), the first uphill move is done. Starting at point (2), the local optimum with 8 equipment units is left and the secondary objective becomes worse, until point (3), where the global optimum is found.
Due to the priority of keeping good higher-ranked objective functions values, the secondary and tertiary objective functions are somewhat harder to optimize than the primary. Hence longer runs are needed. This can be seen in Figure 5-8, where the stopping criteria have been investigated considering one or all objective functions.

**Figure 5-8**: Algorithm efficiency as a function of stopping criteria (a) number of iterations without improvement before a restart; b) number of restarts), considering either only throughput or all three objective functions. The results were obtained for Case Study #1.
In Case Study #1, no difference was found between taking into consideration only the throughput and taking also into consideration the secondary objective function, indicating that in no runs the optimum throughput has been found without also finding the optimum number of equipment units.

For higher values of the number of iterations without improvement, the efficiency decreases (see Figure 5-8a). The highest efficiency occurs for the lowest values when only the throughput is considered. However, when all three objective functions are considered, the greatest efficiency occurs for intermediate parameter values of about 30 to 40. In addition, the efficiency decreases for a large number of restarts when only throughput is considered (see Figure 5-8b), but the efficiency remains high when all three objectives are considered, indicating in this case that the probability of finding the optimum rises in parallel with the computational effort. In sum, about 6 restarts is a good default value to achieve high efficiencies, although longer runs can be conducted by stipulating a higher number of restarts to augment the probability of finding the global optimum.

5.5.3 Final parameter settings & efficiency

Table 5-3 gives the parameter values identified as optimal in the investigations described above for the different case studies, as well as the values that have been chosen as defaults. In the following, we discuss the efficiency of the algorithm in relation to these values.

Table 5-4 gives a summary of the efficiency of the tabu search algorithm determined by the parameter settings as defined in Table 5-3 for the three case studies.

Due to its constrained nature CS#1 is the most difficult to optimize with regard to the higher ranked objective functions. However CS#2 is quite hard to optimize with regard to the third objective. In this instance many designs have the same throughput and use the same number of equipment units, and hence the
optimization of the third objective still takes place over a relatively large part of the solution space.

Table 5-3: Optimum parameters values identified for the three case studies (CS) and default values selected

<table>
<thead>
<tr>
<th></th>
<th>CS#1</th>
<th>CS#2</th>
<th>CS#3</th>
<th>Defaults</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aspiration</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
</tr>
<tr>
<td>Replacement move (extended move set)</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
</tr>
<tr>
<td>Tabu list length</td>
<td>95</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>Neighborhood sample size</td>
<td>15</td>
<td>42</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td>Iterations without ameliorations before restarting</td>
<td>35</td>
<td>45</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>Number of restarts</td>
<td>5</td>
<td>5</td>
<td>6</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 5-4: Probabilities to find optimum throughput, optimum throughput and minimum number of equipment units, and global optimum as obtained for the three case studies (CS) and the parameter settings defined in Table 5-3.

<table>
<thead>
<tr>
<th></th>
<th>CS#1</th>
<th>CS#2</th>
<th>CS#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probability to find optimum throughput</td>
<td>61.1%</td>
<td>97.3%</td>
<td>61.8%</td>
</tr>
<tr>
<td>Probability to find optimum throughput and minimum number of equipment units</td>
<td>61.1%</td>
<td>90.9%</td>
<td>59.5%</td>
</tr>
<tr>
<td>Probability to find global optimum (according to all three objective functions)</td>
<td>25.2%</td>
<td>0.7%</td>
<td>11.8%</td>
</tr>
</tbody>
</table>

As mentioned in Section 5.5.2, to increase the probability of finding optimal designs the number of restarts can be raised. The computational effort will obviously augment in parallel. In Table 5-5 the performance of the algorithm as a
function of the computational effort is given in number of process simulations per run and also in CPU-time for Case Study #1. The probability of finding the optimum throughput and of obtaining a global optimum both rise drastically when longer runs are conducted, reaching a quasi certainty for one CPU hour.

Table 5-5: Success probability according to the computational effort for Case Study #1

<table>
<thead>
<tr>
<th>Computational effort [number of process simulations]</th>
<th>1500</th>
<th>7500</th>
<th>45000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Approximate computational effort [min]*</td>
<td>2</td>
<td>10</td>
<td>60</td>
</tr>
<tr>
<td>Probability of finding optimum throughput [-]</td>
<td>56%</td>
<td>98%</td>
<td>100%**</td>
</tr>
<tr>
<td>Probability of finding global optimum (with regards to the three objective functions) [-]</td>
<td>25%</td>
<td>76%</td>
<td>100%**</td>
</tr>
</tbody>
</table>

Notes:  
* Runs conducted on a 1.7 GHz PC with 256 MB RAM, Windows XP®, MATLAB® 6.1.0; no external simulation software has been used, time adaptations have been conducted in MATLAB®.

** The probabilities are based on 100 runs. A probability of 100% indicates that all runs found the optimum. The probabilities not to find the optimum, as extrapolated from the first two columns are $2 \cdot 10^{-11}$ for the optimum throughput, and $2 \cdot 10^{-3}$ for the three objective functions.

Similarly, the probability of finding the optimum throughput for Case Studies #2 and #3 rises to at least 99% in 10 CPU minutes. The probability of finding the global optimum design for Case Study #2 - the hardest optimization investigated in this paper - rises from 0.7% to 19% when making 1 hour runs, and to about 90% for 10 h runs.

5.5.4 Tabu List Variants

One recurrent problem in the optimization is that the replace operation - while necessary to reach the global optimum - may lock the algorithm into a region around a particular local optimum. If one operation can indifferently use $n$ equivalent equipment units, $n \cdot (n-1)$ replacement moves can take place (with any of these $n$ units the throughput and the number of equipment units used remain
constant, and only the third objective may vary). If the tabu list is shorter than \( n \cdot (n-1) \), the algorithm will stay in the same region of space and only a random chance (if the number of available neighbors is significantly higher than \( n \cdot (n-1) \)) will allow to break the pseudo loops by happening not to select a replacement move in the current random neighborhood sample.

This is the reason why the tabu list length (i.e., the tabu tenure) must be so large. As discussed above, a larger tenure removes flexibility and hence makes it hard to find good solutions. To address this problem, some modifications of the tabu lists have been assessed:

**Oscillating list length**

Large tabu tenures are required to effectively escape a local optimum. However, large tenures hinder the efficient search for a new optimum when the escape has been successful. An interesting option [Glover et al., 1997] consists in activating the tabu classification only upon reaching a local optimum, at which point a large tabu tenure \( T \) is enforced. The method continues for \( T \) iterations (during which each attribute that becomes tabu remains tabu) or until no non-tabu moves exist. At such a point, the tabu list is emptied and the process once again proceeds freely to a new local optimum.

**Strict and asymmetric tabu list**

The standard tabu list as implemented in the preceding tests is move-based rather than attribute-based, and forbids the exact opposite of the move accepted. For instance, if in the operation \( Op1 \) the equipment unit \( Eq1 \) is replaced by the unit \( Eq2 \), the replacement of \( Eq2 \) by \( Eq1 \) in \( Op1 \) will be tabu. As noted in Glover [1990] such move-based approaches entail some risks (including the possibility of being unable to avoid cycling). From an attribute-based perspective, a related option is to specify a move that replaces \( Eq2 \) by \( Eq1 \) in \( Op1 \) to be tabu if the attributes \( Eq2 \) and \( Eq1 \) are themselves both tabu. Still stronger is to make the move tabu if either of its attributes is tabu, hence excluding the removal of \( Eq1 \) from \( Op1 \) and the addition of \( Eq2 \) to \( Op1 \) (This is clearly more restrictive since, for example, the subsequent replacement of \( Eq2 \) with \( Eq3 \) in \( Op1 \) would now also be forbidden.)

Moreover different types of tabu attributes can be given different tabu tenures, as (for example) by including them on separate lists of differing length. If a list for
‘equipment added’ is longer than a list for ‘equipment removed’, this would block the addition of a previously removed equipment unit longer than the removal of an added one, hence allowing the assessment of new units for the given operation while restricting efficiently the replacement loops described above. If, on the other hand, the removal tabu list is longer, this would still restrict the replacement loops, but favor the emergence of more complex designs with many equipment units per operation (in series or in parallel).

We have tested these options (which can also be combined) on the three case studies. The alternatives that proved interesting are: (a) base case (single tabu list with aspiration), (b) oscillating single tabu list with aspiration and (c) double asymmetric tabu list, oscillating and with aspiration. The length of the tabu list(s) has been optimized similarly to the other parameters above, and the resulting performances are given in Table 5-6 - similarly as for the results presented in Table 5-4, the runs have stopping criteria and need about 2 minutes CPU.

With the exception of CS#2 while considering all three objective functions - whose small success rate makes the 1000 runs sample statistically insufficient to extract conclusions - the oscillating tabu list is slightly better. The runs with asymmetric oscillating tabu lists are significantly better as compared to the base case for CS#1 (optimized for throughput), while being less good for CS#2 and for CS#1 (with all three objectives) and about equivalent for CS#3.

Table 5-6: Performance of the algorithm for the different tabu list options (based on 1000 runs).

<table>
<thead>
<tr>
<th>Case Study and Objectives</th>
<th>(a) Base case</th>
<th>(b) Oscillating</th>
<th>(c) Asymmetric and oscillating</th>
</tr>
</thead>
<tbody>
<tr>
<td>CS#1 - throughput</td>
<td>61.1%</td>
<td>63.4%</td>
<td>70.3%</td>
</tr>
<tr>
<td>CS#1 - all objectives</td>
<td>25.2%</td>
<td>27.9%</td>
<td>12.8%</td>
</tr>
<tr>
<td>CS#2 - throughput</td>
<td>97.3%</td>
<td>98.0%</td>
<td>98.6%</td>
</tr>
<tr>
<td>CS#2 - all objectives</td>
<td>0.7%</td>
<td>0.1%</td>
<td>0.6%</td>
</tr>
<tr>
<td>CS#3 - throughput</td>
<td>61.8%</td>
<td>63.2%</td>
<td>57.1%</td>
</tr>
<tr>
<td>CS#3 - all objectives</td>
<td>11.8%</td>
<td>12.7%</td>
<td>10.4%</td>
</tr>
</tbody>
</table>
This behavior can be explained by the nature of the case studies: in highly constrained cases (CS#1), complex designs with multiple units in series or parallel are difficult to obtain, and hence the effect given above (with a longer “removal” list) plays a positive role. However the third objective is mainly optimized through replacements (which allow the throughput and number of equipment units to remain constant) and the presence of the strict tabu lists hinder these moves, hence the lower performances with regard to all three objective functions. Similarly, in less constrained cases (CS#3), complex designs do not need to be “encouraged”, and the “blocking effect” is too strong.

These results suggest that the well-tuned algorithm might be slightly improved by further refinements. However, similarly to the third tabu list definition (asymmetric double lists), further refinements risk to jeopardize the overall broad applicability of the method: options implemented to tackle specific problems (like encouraging complex designs) may have a positive effect on some problems but are expected to have a negative effect on others.

5.5.5 Tabu search vs. steepest descent

One of the simplest forms of local search is steepest descent, which can also be adapted to our problem. As noted earlier, multi-start (or iterated) steepest descent has been recently demonstrated to have appealing theoretical and empirical performance properties, and consequently we have undertaken a comparison with this approach to assess the performance of our basic TS implementation.

As the problem considered is an assignment problem with integer variables and an implicit objective function (black box), derivatives can not be computed. Therefore, the steepest descent will simply evaluate all the neighbors, and will select the best one. When all neighbors are worse than the current solution, the descent stops, and a new starting point is randomly chosen.
The comparison is conducted on the basis of the probability to find the optimum throughput for a given computational effort. Obviously, a given application of steepest descent is much quicker than tabu search since it stops upon reaching a first local optimum, and hence many more restarts are possible with this method in the same computational time (factor of 10 to 20). We based our computation on the tabu search approach characterized above in Table 5-3, with the standard tabu list definition (resulting in around 2000 process simulations per optimization).

In Case Study #1, the multi-start steepest descent finds the optimum throughput in only about 10% of the runs, as compared with the 60% success rate of the Tabu Search. These results can be explained by two reasons:

- The class of problem studied has many local optima and the definition of the moves make uphill moves necessary to strongly modify a solution: for instance to go from a parallel design to a series design, the algorithm must go through a single-unit design, which will in most cases be less efficient; in Figure 5-3 the path from the second best design to the optimum also needs uphill moves in order to “exchange” an equipment unit from one block (1) to another (7), as can be seen with the throughput shown on the left side.
- The constraints forbid some parts of the space, and going “around” the forbidden areas requires most often uphill moves as well.

The second case study, with its only weak constraints, is more suited for the multi-start steepest descent as can be seen in Figure 5-9. The tabu search is still dominant in having a higher probability of finding the optimum throughput (57% against 42% for multi-start steepest descent). However, the numerous restarts allowed in the steepest descent application made it possible to reduce the probability of obtaining bad results (i.e., of obtaining solutions that are not within 90% of the optimum). A similar effect is also obtained for the third case study.
5.6 Conclusions

Our study has focused on a new method for optimizing the implementation of a new single chemical process in a multi-purpose batch plant, in which a well-defined set of equipment units is available. The optimization considers three objectives with different priorities. Our approach embodies a specialized version of Tabu Search, a flexible metaheuristic algorithm, to solve this multi-objective optimization problem. A thorough investigation of algorithm parameters and variants has been conducted to identify combinations that insure a high probability of finding a global optimum while using a minimum of computational effort.

The results obtained for three case studies show that the algorithm is well suited for solving the problems at hand: the resulting probability of obtaining the best throughput within 10 CPU minutes was higher than 98% for typical problems. When one hour of CPU time was allotted, the probability of obtaining the optimum throughput exceeded 99% for all three case studies. Moreover, upon addressing the more challenging multiple-objective model, the probability of finding a global

![Figure 5-9: Comparison of tabu search and steepest descent for fixed computational effort and Case Study #2. The top-left shows a detail of the plot for high production rates.](image)
optimum within one hour remained above 97% for typical problem instances. Computational comparisons with a multi-start steepest descent method, which represents a solution approach recently documented to have desirable performance characteristics, discloses that our tabu search method yields superior outcomes in all cases.

The version of TS that has produced these results has been restricted to incorporate only a set of first level elements. Even at this level we have been able to identify robust parameter values, so that the user will not need to modify internal parameters of the optimization algorithm.

We single out several specific components of tabu search that we anticipate will provide a useful focus for future investigation:

An extension of the move set (e.g. inclusion of a move that “exchange” equipment units of two operations) might be profitable in regard of the performance of the “replace” move; it may be useful to implement advanced candidate list strategies to manage the increased neighborhood size. In addition, a strategic oscillation coordinated with alternative neighborhood structures might be interesting. Seeing the effectiveness of the simple diversification implemented here (multiple restarts), a promising feature is certainly the integration of intensification and diversification strategies, e.g. with frequency-based memory.

Each of these TS components can be implemented by direct extension of our basic design, utilizing considerations of the type described in Glover and Laguna [1997]. These components will have to be tested while focusing on keeping the broad scope of the method. The modification of the tabu list definition has shown that some improvements may jeopardize this, having a positive effect on some case studies but being expected to have a negative impact on others.

The successes obtained by our fundamental TS implementation support an expectation that such an extended approach will nevertheless provide still better results, and make it possible to efficiently solve multiple objective chemical process design problems of still larger dimensions.
Acknowledgment

The authors thank A. Oeggerli, L. Utiger, and T. Zaupa from Lonzagroup at Visp and Basel (Switzerland) for discussions on the characteristics of multipurpose batch plants which helped us to design a method that is capable to deal with realistic batch design problems. Furthermore, the authors want to thank Dr. Cochand (ETHZ) and Prof. de Werra (EPFL) for their help in solving the optimization problem.

List of symbols

- **B**: Block matrix containing sequences of tasks to be conducted in the same equipment unit(s)
- **BR**: Block-to-recipe one-to-many relationship matrix
- **C**: Connectivity constraints matrix
- **E**: Equipment matrix
- **i**: Main counter across the block matrix B (subscript)
- **j**: Secondary counter across the block matrix B (subscript)
- **K**: Recipe indexes vector (list of tasks belonging to one block)
- **L**: Allocated equipment units matrix. L is a solution to the design problem
- **O**: Operation library matrix. Reference containing all possible task classes.
- **P**: Standard operating ranges library matrix
- **R**: Recipe matrix consisting of a list of tasks to be conducted
- **S**: Eligible equipment units vector
- **U**: Eligible equipment classes vector
- **X**: Secondary recipe matrix. Subset matrix of R for the tasks indicated in K
- **y**: Temporary binary variable indicating if the considered task is a transfer (1) or not (0)
- **Z**: Sequence matrix allowing to handle branching recipes
Chapter 6: Process Design Case Study & Plant Selection

6.1 Introduction

While the two components presented in Chapters 2 to 5 can be used separately, they can also be integrated to achieve a combined batch process design procedure. According to the “design” definition given in Chapter 1.2.1, this procedure will allow to complement a recipe on an industrial scale by assigning all the equipment units needed to optimally implement it in existing facilities, and to complete it with the waste treatment operations.

In Figure 6-1, this procedure is pictured: starting with the recipe and the available facilities, first the waste treatment options are evaluated. According to the treatment path selected (e.g. if recycling is profitable) or to the in-depth analysis of the results (e.g. effect of the salt concentration as shown in Figure 2-5), some modifications can be applied to the recipe by the user, and this modified recipe is then used as new input for the waste treatment path selection. This step can be repeated if necessary. The waste treatment path resulting from the final recipe is the first part of the process design; the resulting environmental burden as well as
the resulting treatment costs (that will be used later to compute the overall production costs) are additional information characterizing the recipe. Using the description of the available production lines, the process design can be conducted, resulting for each candidate plant in high performance designs and their attached batch sizes and durations. Taking the most promising design for each plant, the production costs can be calculated and by comparing them, the user can select which production line to use, thus completing the procedure.

**Figure 6-1**: Complete batch process design procedure as coupled in this thesis

To illustrate this complete procedure, the Aspirin Synthesis is studied. While the Aspirin Synthesis is a quite simple process - therefore not representative of the
recipes the methodology presented here is targeted at - it has the advantage of being public domain knowledge.

After a short introduction about the Aspirin synthesis, the different steps of this procedure will be illustrated below. An initial Recipe (adapted from the example files provided with the batch simulation software BatchPlus™ by Aspen Technology, Inc., [1998-2002]) will first be screened with the help of the waste treatment path selection component. From the waste treatment analysis it will be shown how the initial recipe could be modified to improve (both economically and ecologically) the process and a new recipe will be formulated. The waste treatment path selection will be run a second time on this new recipe to determine the final waste treatment path and the resulting costs.

The new recipe will then be fitted in a production plant with the help of the second software component; from the obtained design (batch size, cycle time) the costs of the production can then be evaluated. A second production plant will be similarly evaluated and compared with the first one, thus illustrating the plant selection process.

### 6.2 The Aspirin Synthesis

The production of Aspirin [Dimmer, 1999; BatchPlus™ Example, 1998-2002] consists of one single-step reaction that is given in Figure 6-2. The raw materials are Salicylic Acid and Acetic Anhydride, while Acetic Acid is used as solvent, and is also a by-product.

![Aspirin Synthesis Reaction](image)

**Figure 6-2:** Aspirin (Acetylsalicylic Acid) Synthesis reaction.

<table>
<thead>
<tr>
<th>Material</th>
<th>Molecular Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic Acid</td>
<td>138</td>
</tr>
<tr>
<td>Acetic Anhydride</td>
<td>102</td>
</tr>
<tr>
<td>Aspirin</td>
<td>180</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>60</td>
</tr>
</tbody>
</table>
The reaction mixture consists of (molar proportions) 1/1/1.4 Salicylic Acid, Acetic Acid and Acetic Anhydride. The yield is 93%, at a temperature of 90°C. The reaction lasts 450 min and is the most time-consuming operation in the recipe.

A crystallization is conducted to separate Aspirin from the other components, with a temperature ramp from 90°C to 20°C in 210 min, and the (Aspirin) crystals are separated with a centrifuge. Each centrifuge drop lasts 60 min, and 2 drops are needed for the quantities (10 Kmol of reactants) given in the base recipe below. The mother liquor (containing remaining raw materials, and acetic acid, as well as traces of Aspirin) is sent to the waste treatment, while the crystals are dried. Dried crystals are the final product.

Recipe 1 (10 Kmol quantity):

1. Charge 1380 kg Salicylic Acid
2. Charge 1428 kg Acetic Anhydride
3. Charge 600 kg Acetic Acid
4. React
5. Crystallize Aspirin
6. Centrifuge, mother liquor is sent to waste treatment
7. Dry crystals, dried crystals are the final product (1674 kg)

6.3 Aspirin Process Design

6.3.1 Step 1: Screening for potential problems in the waste treatment.

The waste treatment path selection component (first solid box in Figure 6-1) will be run to handle the waste stemming from Recipe 1 above in the facilities described in Chapter 2. This waste treatment problem - in other quantities however - has already been treated as an example (WS1) in Chapter 2. As the waste that will have to be treated for the whole campaign is independent of the batch size, the calculations presented in Chapter 2.3.1 are valid to recognize the
optimal treatment path and to obtain an estimate of the costs per kg waste (or per kg produced Aspirin).

The waste treatment model identifies two feasible treatment paths for this stream (see Figure 2-3). The first option (Path #1) includes the recycling of acetic acid and acetic acid anhydride by rectification, which itself provides a financial benefit, while the remainder is incinerated. In the second option (Path #2) the whole stream is sent to the sewage treatment plant. The resulting mean costs (per ton of Aspirin) are -173 CHF (benefits due to the recycling) and 310 CHF for Path #1 and #2, respectively. Although a broad range of cost is obtained for Path #1, due to the high uncertainty in the separation efficiencies specified (see Table 2-6) to simulate a lack of data in an early design phase, recycling is in most cases both feasible and cheaper than Path #2.

Recycled materials will often be reused in the same production (for the subsequent batches), and hence the recycling will in many cases effectively be conducted physically in the same production line as the production. Therefore the recycling distillation - if it is to be conducted - should be inserted in the recipe. Because it appears to be profitable, the process is modified as follow (“Modify Recipe” loop in Figure 6-1):

Recipe 2 (10 Kmol quantity):

1. Charge 1380 kg Salicylic Acid
2. Charge 1428 kg Acetic Anhydride
3. Charge 600 kg Acetic Acid
4. React
5. Crystallize Aspirin
6. Centrifuge
   7a. Crystals are dried and are the final product (1674 kg)
   7b. The mother liquor is distilled
       Recycled Acetic Acid/Acetic Anhydride is sent to raw material tank; the rest is sent to waste treatment

Modifying the recipe as indicated above has of course an influence on the Batch Process Design (second solid box in Figure 6-1; Step 3 below): as more operations are present in the recipe, a lower throughput could result in the actual
implementation in the plant: in the Aspirin case, at least one reactor with attached condenser will have to be used for the distillation, and hence will not be available for the other operations. In order to make sure that the recipe modification is indeed (financially) beneficial, the results of the process design step (Step 3 below) should be compared for both the initial and the modified recipe, and a cost calculation should be conducted. A comparison of both recipes will be conducted in Chapter 6.4.1 after the cost calculation for Recipe 2.

6.3.2 Step 2: Evaluating the waste treatment costs.

Recipe 2 should now be simulated in an external process simulation program to find out the precise quantity and quality of the recycled and waste streams; the base duration and base volume information needed in the process design step (see 6.3.3) will also result from this simulation. The thus calculated waste composition is parsed by the waste treatment tool (the “stream” sent to the waste treatment represents the waste generated for the synthesis of 1 ton of Aspirin and is given in Table 6-1).

Table 6-1: Aspirin waste stream resulting from Recipe 2 for 1 ton of Aspirin. Other parameters are equal to those given in Tables 2-5 and 2-6.

<table>
<thead>
<tr>
<th>Component</th>
<th>Formula</th>
<th>Amount (Mean)</th>
<th>Amount (Variance)</th>
</tr>
</thead>
<tbody>
<tr>
<td>salicylic acid</td>
<td>C₇H₆O₃</td>
<td>57.0</td>
<td>2.5</td>
</tr>
<tr>
<td>acetic acid anhydride</td>
<td>C₄H₆O₃</td>
<td>115</td>
<td>6</td>
</tr>
<tr>
<td>acetyl salicylic acid</td>
<td>C₉H₈O₄</td>
<td>5.02</td>
<td>0.25</td>
</tr>
<tr>
<td>acetic acid</td>
<td>C₂H₄O₂</td>
<td>279</td>
<td>13</td>
</tr>
</tbody>
</table>

Five different treatment paths are possible (as displayed on Figure 6-3). The resulting legal paths have costs of at least 140 CHF per ton Aspirin instead of the negative costs (benefits) obtained above. This is because the recycling is not anymore included in the waste treatment. Its corresponding benefits will be included in the Raw Materials cost calculation (see Chapter 6.4.1). Two paths are pareto-optimal, Path #1 and Path #9. Path #1 only consists of the incineration,
Path#9 only consists of the Sewage Treatment Plant (STP); Paths #10, 17 and 18 also use the STP, and in addition pre-treatments (Decontamination, Stripping) that are neither required to match emission limits nor financially attractive.

The results from the two pareto-optimal paths are detailed in Table 6-2. The selection of which waste treatment will be used (Incinerator vs. STP) depends on the preference of the decision maker. Several criteria can influence this decision in addition to the costs and environmental burdens, for instance capacity limitations in central treatment plants (STP or incinerator).

**Figure 6-3:** Pareto plot of the waste treatment paths for the Aspirin wastes. Paths #1 and #9 are pareto-optimal; Paths #10, 17 and 18 are dominated.

For the further analysis, we will select Path #1 (Incineration) - it is only 7% more expensive than Path #9, while its environmental impact is about 5 times smaller. The corresponding waste treatment costs are (average of the Monte-Carlo simulations) **150 CHF per ton of Aspirin**.
The environmental burden is $1.7 \times 10^5$ UBP per ton of Aspirin. This information can be used for example to compare alternative production recipes or alternative waste treatment facilities.

### 6.3.3 Step 3: Process design

As Aspirin is a quite simple process, a rather small production line can be used to implement it. A plant (Plant1) with the equipment pieces given in Table 6-3 will be used for the process implementation.

#### Table 6-3: Equipment units in Plant1

<table>
<thead>
<tr>
<th>Equipment Name</th>
<th>Equipment Class</th>
<th>Volume [m$^3$]</th>
<th>Floor</th>
<th>Related Equipments</th>
<th>Operating Temperature [°C]</th>
<th>Operating Pressure [bar]</th>
<th>Lining Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 Reactor</td>
<td>10</td>
<td>3</td>
<td>Condenser</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>stainless steel</td>
<td></td>
</tr>
<tr>
<td>R2 Reactor</td>
<td>10</td>
<td>2</td>
<td>Condenser</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>enamel</td>
<td></td>
</tr>
<tr>
<td>R3 Reactor</td>
<td>10</td>
<td>2</td>
<td>Condenser</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>enamel</td>
<td></td>
</tr>
<tr>
<td>R4 Reactor</td>
<td>16</td>
<td>1</td>
<td>Condensers, Column</td>
<td>-15 - 160</td>
<td>0.01 - 2</td>
<td>stainless steel</td>
<td></td>
</tr>
<tr>
<td>C1 Centrifuge</td>
<td>0.44</td>
<td>1</td>
<td>Heat-Exchanger</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>C2 Centrifuge</td>
<td>0.44</td>
<td>1</td>
<td>Heat-Exchanger</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td></td>
</tr>
<tr>
<td>D1 Dryer</td>
<td>4</td>
<td>2</td>
<td>Heat-Exchanger</td>
<td>20 - 160</td>
<td>0.01 - 2</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

All equipment units can be connected with each other and there is no physico-chemical constraint limiting the use of equipment units for any operations in the Aspirin synthesis (Temperature and Pressure are well within the range of any equipment unit, and no specific lining material is required).

The recipe as expressed in the format needed for the optimization is given in Table 6-4. The volumes are running sums representing the highest volume present during the operation, while durations have been set according to Dimmer [2000].
and the example files provided with the batch simulation software BatchPlus™ [1998-2002]. Note that the volume given in the Centrifuge represents only the solid phase, while the time given for the Dry operation is arbitrary, as numerous batches can be present simultaneously in the dryer (while retaining their batch identity), and hence the dryer cannot be time limiting. The “special rule” Flag 32 in Centrifuge is set because the time scale-up is done by computing a number of drops of a fixed duration (60 min, the time given in the matrix). In the last column, the operation blocks are given. Except for the first four operations that are combined in one block, each operation builds one block.

Table 6-4: Aspirin synthesis (Recipe 2) formulated in the input matrix for the Batch Process Design component.

<table>
<thead>
<tr>
<th>Operation</th>
<th>ClassID</th>
<th>Volume [m³]</th>
<th>Duration [min]</th>
<th>Flag</th>
<th>T [°C]</th>
<th>P [bar]</th>
<th>Lining ID</th>
<th>Block ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge 4</td>
<td>1.36</td>
<td>15</td>
<td>2</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Charge 4</td>
<td>2.68</td>
<td>15</td>
<td>2</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Charge 4</td>
<td>2.94</td>
<td>15</td>
<td>2</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>React 32</td>
<td>2.99</td>
<td>450</td>
<td>2</td>
<td>90</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Crystallize 15</td>
<td>2.99</td>
<td>210</td>
<td>8</td>
<td>20</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>Centrifuge 47</td>
<td>1.87</td>
<td>60</td>
<td>40</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Dry 18</td>
<td>1.87</td>
<td>180</td>
<td>32</td>
<td>100</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Distill 17</td>
<td>1.42</td>
<td>60</td>
<td>8</td>
<td>120</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>(waste) -4</td>
<td>0.16</td>
<td>-1</td>
<td>0</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>(product) -2</td>
<td>1.78</td>
<td>-1</td>
<td>0</td>
<td>25</td>
<td>1</td>
<td>-1</td>
<td></td>
<td>0</td>
</tr>
</tbody>
</table>

No transfers have been inserted, indicating that there are no mandatory transfers in this recipe. Obviously, transfers will take place, for example before the Centrifuge operation, as no equipment class can support both the “Crystallize” and the “Centrifuge” operations. These will then be added automatically by the optimization algorithm.

The Batch Process Design (second solid box in Figure 6-1) is now conducted. While several designs are generated (see Chapter 4), only the highest ranked one will be discussed here and is displayed in Figure 6-4.

The batch size is 5935 kg, and the cycle time is 295 min, achieving an average throughput of 1207 Kg/hour; the batch size is about three times bigger than the
initial recipe, which makes also great difference in the operation times: as explained in Chapter 4, operation durations are adapted as a function of the volume. In the Aspirin case study, while the reaction or the crystallization both have a constant duration for any volume, the distillation is for example proportionally adapted and now lasts more than 180 minutes. As example of “special” rules, six drops are needed in the Centrifuge; as each drop lasts 60 minutes, the centrifuge operation now lasts a total of 6 hours.

![Aspirin Synthesis Process Diagram](image)

**Figure 6-4:** Optimal design found for the Aspirin Synthesis in Plant1

Two reactors are used in series for the reaction (that is obviously time-limiting), thus allowing a reduction of the cycle time from 8.5 hours to less than 5 hours. The larger reactor is used for the crystallization, while the fourth reactor and its condenser are used for the distillation. The two Centrifuges are used in parallel thus effectively reducing the operation duration to 180 min - 3 drops per centrifuge.

With the improved recipe, the waste treatment selection (incineration), and the process design given in Figure 6-4, the problem defined by 1 recipe and 1 production line (Plant1) is completed.
6.4 Plant Selection

6.4.1 Cost calculation

If many production lines are to be considered, the process design step (step 3, Chapter 6.3.3 above) must be conducted for each of those lines. A first comparison of the line can be drawn from the output of the software: for each plant, the batch size and the cycle time (and hence the throughput) are given. However, a higher throughput is not always better than a smaller one; indeed usually the larger the plant, the higher the throughput, but the more expensive the production will be in terms of “equipment” costs (e.g. write-off or “rent”) and usually manpower costs.

To allow a good comparison of multiple production lines, a higher level objective function than the throughput or the design quality must be used: the costs (“Compare & Select” box in Figure 6-1).

The production cost calculation depends on many factors, as pictured in a schematic view in Figure 6-5. A part of the cost factors will be independent of the plant selection: raw material costs for instance depend only on the recipe (amount of raw material) and the waste treatment (is there recycling?). Similarly waste treatment costs and some other costs (e.g. storage) do not depend on the plant selection.

Other cost factors, however, are dependent on the design, i.e. will change when the process is run in another plant. Among those are obviously the “plant” costs (that represent the write-off of the equipment units or the “rent” of the plant), the changeover costs and the personal costs. But the analytics costs are also in this category, as one set of analyzes is usually required per batch, and hence the smaller the batch size, the more analyzes must be conducted for a given campaign.

When comparing plants, only those last factors have to be taken into consideration in order to have an absolute cost difference. However, calculating the overall costs (including e.g. the raw materials) allow also to see the significance of this
difference. That is why a complete cost calculation for the Aspirin case study has been conducted. The cost calculations were done for on a campaign of 1000 tons of Aspirin. Cost factors are arbitrary values whose order of magnitude corresponds to costs found in references [e.g. Dimmer, 1999; BatchPlus™ examples, 1998-2002].

---

**Figure 6-5:** Scheme of the production cost calculation. Boxes represent data - dotted boxes indicate case-specific or recipe-related input (i.e. those values will not change according to the design or the production line selected). Data with incoming arrows are calculated on the base of the data pointing to it. The large shaded boxes contain results from the software components presented in this thesis. The direct influence of the production line selection (parallelogram) is represented by dotted lines. The dashed line separates cost factors that do depend on the plant selection (below) to those that do not (above).
• Plant independent cost factors
  o Raw Materials
    Recycling is already included. A negative quantity for a raw material indicates that more of this material is recovered/produced than used. For the purpose of cost calculation, it is assumed that materials can be bought and sold at the same price. The detailed calculation is shown in Table 6-5.
    **Total for the whole campaign: 3117 KFr**
  o Waste Treatments
    As mentioned in the Waste Treatment considerations above, the waste treatment costs per ton of Aspirin produced are 150 CHF.
    **Total for the whole campaign: 150 KFr**
  o Others
    Among the other cost factors is for example the storage. As this value is dependent on how much raw materials must be bought at one time, and how quickly the Aspirin can be sold, an estimated value is used for the whole campaign:
    **Total for the whole campaign: 100 KFr**

**Table 6-5: Raw materials cost calculation**

<table>
<thead>
<tr>
<th>Unit costs</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic Acid</td>
<td>3000 CHF/ton</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>700 CHF/ton</td>
</tr>
<tr>
<td>Acetic Anhydride</td>
<td>1000 CHF/ton</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Quantity per ton of Aspirin</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic Acid</td>
<td>0.824 tons</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>-0.053 tons</td>
</tr>
<tr>
<td>Acetic Anhydride</td>
<td>0.682 tons</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Raw Material Costs per ton of Aspirin</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Salicylic Acid</td>
<td>2472 CHF</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>-37.1 CHF</td>
</tr>
<tr>
<td>Acetic Anhydride</td>
<td>682 CHF</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>3117 CHF</strong></td>
</tr>
</tbody>
</table>
• Plant dependant cost factors
  o Analytics
    The analytics costs are usually given per batch. The number of batches required to fulfill the production target of 1000 tons is 169, given the production of 5935 kg per batch. For the Aspirin synthesis, a cost of 1000 CHF per batch is assumed.

    **Total for the whole campaign: 169 KFr**
  o Personal Costs
    The personal costs depend on the number of people working in the plant, their salaries, and the total time used for the production. The total personal costs are assumed to amount to 200 CHF per hour. In a first approximation, the total production time is equal to the cycle time (295 min) multiplied by the number of batches (169), plus the time needed to terminate the last batch (19 hours). The total production time is 850 hours.

    **Total for the whole campaign: 306 KFr**
  o Plant Costs
    These costs represent the use of the production line, or the write-off of the investments that must be allocated to this production. Usually a cost per hour is given. For the plant used, the presumed cost is 250 CHF per hour. This number must simply be multiplied by the total production time as given above.

    **Total for the whole campaign: 383 KFr**
  o Changeover Costs
    In multipurpose plants, an extensive cleaning and re-piping must be conducted after each campaign. These are usually fixed costs for a given production line.

    **Total for the whole campaign: 360 KFr**

The overall cost calculation is summarized in Table 6-6.

The total costs are the sum of all these factors: **4585 KFr** for the production of 1000 tons of Aspirin. Plant-dependent costs amount for 752 KFr and represent 23% of the overall costs (that are dominated by the raw materials: 68%). This means that by changing the plant, only these 23% of the total costs can be modified.
As mentioned above, the recipe modification conducted in Chapter 6.3.1 - the inclusion of the recycling into the recipe - can have an influence on the optimal design found, and hence potentially on the batch size, the cycle time and indirectly on most cost factors.

Table 6-6: Summary of the cost factors

<table>
<thead>
<tr>
<th>Production costs for Aspirin</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Campaign: 1000 tons in Plant 1</strong></td>
<td></td>
</tr>
<tr>
<td>Raw Materials</td>
<td>3117 KFr</td>
</tr>
<tr>
<td>Waste Treatment</td>
<td>151 KFr</td>
</tr>
<tr>
<td>Others (e.g. storage)</td>
<td>100 KFr</td>
</tr>
<tr>
<td>Analytics</td>
<td>169 KFr</td>
</tr>
<tr>
<td>Personal</td>
<td>306 KFr</td>
</tr>
<tr>
<td>Plant &quot;Rent&quot;</td>
<td>383 KFr</td>
</tr>
<tr>
<td>Changeover</td>
<td>360 KFr</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4585 KFr</strong></td>
</tr>
</tbody>
</table>

In the case study presented here, the distillation occupies one reactor with its attached condenser. As will be seen in the next Chapter, if more reactors are available (e.g. if the distillation is not conducted), a third reactor can be added to the reaction, hence shortening the cycle time to 240 min. The overall campaign duration will hence be shorter (692 hours instead of 850 hours). The savings made in personal and plant costs will amount therefore to 128 KFr. However, the waste treatment costs amount now to 300 KFr for the whole campaign (the cheapest path found if the recycling is disabled is the Sewage Treatment Plant). As compared with the 150 KFr for the waste treatment of Recipe 2, the difference is 150 KFr, which does already compensate for the savings generated by the shorter cycle time.

As no Acetic Acid and Acetic Anhydride is recovered, the raw materials costs do similarly augment significantly to reach 3578 KFr. The comparison displayed on
Figure 6-6 shows that in this case, the recipe modification was indeed economically beneficial (483 KFr cheaper).

![Figure 6-6: Comparison of the production costs for Recipe 1 and Recipe 2](image)

#### 6.4.2 Plant Selection

If another plant candidate is available for the synthesis, one can run the optimization again for the second plant. For instance, the optimization can be run for the Aspirin synthesis using the plant described in Chapter 4 (see Table 4-6) which will be called Plant2.

The resulting optimal design - displayed in Figure 6-7 - is quite similar to the optimal design found for Plant1: a third reactor in series has been added to the reaction. This design enables a batch size of 5935 kg as well, but the cycle time dropped to 240 min, leading to an average throughput of 1484 kg/hour. This
production rate is 22.9% larger than in Plant1, even though the batch size remains constant.

![Diagram of process flow](image)

**Figure 6-7:** Optimal design for the Aspirin synthesis in Plant2

Two equipment units remain unused (the 6.3 m³ Reactor R4 and one 10 m³ Reactor R2). However, the time limiting operation is now the crystallization, and it cannot be made quicker by parallel (time does not depend on the volume) or series (forbidden by constraints) designs.

The volume limiting operation is the reaction that is run in series in three reactors. It is forbidden to run an operation simultaneously in parallel and in series. Therefore, to verify the optimality of the design, the parallel and the series design must be compared: as a maximum of two units can be used in parallel (see constraints in Chapter 4.2.5), the parallel design could (maximally) results in an improvement of a factor 2 as compared to a single equipment unit design. The chosen design in series results however in an improvement of factor 2.125 as the cycle time with a single unit design would be 510 min (450 min of reaction, plus three Charge operations with 15 min each, plus one transfer of 15 min) as compared to the actual 240 min cycle time. This design is consequently optimal.
(with regard to throughput) and the use of other equipment units could not improve the process. This plant is simply too large for the Aspirin synthesis.

Table 6-7 summarizes the differences in the designs for producing Aspirin in Plant1 or Plant2.

Table 6-7: Comparison of the designs for Aspirin in Plant1 and Plant2.

<table>
<thead>
<tr>
<th></th>
<th>Plant1</th>
<th>Plant2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Throughput [kg/hour]</td>
<td>1207</td>
<td>1484</td>
</tr>
<tr>
<td>Number of equipment units used/available</td>
<td>9/16</td>
<td>10/22</td>
</tr>
<tr>
<td>Number of reactors used/available</td>
<td>4/4</td>
<td>5/7</td>
</tr>
<tr>
<td>Top-down indicator</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Cycle Time [min]</td>
<td>295</td>
<td>240</td>
</tr>
<tr>
<td>Batch Size [kg]</td>
<td>5935</td>
<td>5935</td>
</tr>
<tr>
<td>Number of batches in campaign</td>
<td>169</td>
<td>169</td>
</tr>
<tr>
<td>Campaign duration [d]</td>
<td>36</td>
<td>29</td>
</tr>
</tbody>
</table>

The cost calculation allows an objective comparison of the two plants. The best design in Plant2 has the same batch size as in Plant1. Hence the analytical costs are the same. The total campaign duration is however shorter: 692 hours instead of 850 hours.

It is assumed in a first approximation that personal costs, changeover costs and production line costs are constant for a given plant. While this is mostly correct for the production line costs (unused equipment units cannot be used in another process), this assumption is a clear simplification regarding both the personal costs (“unused” employee can be assigned temporarily to another production line) and the changeover costs (that are probably dependant on the complexity of the process to be implemented, and hence on the number of units used, as opposed to the number of equipment units available).

According to these assumptions, the larger Plant2 employs more personal, and changeovers as well as the production line costs are higher. The elected cost factors for Plant2 are summarized in Table 6-8.
The cost calculation is done similarly as with the Plant1 above, based however on total campaign duration of 692 hours. The plant dependent costs amount to 1628.2 KFr per campaign and are added to the plant-independent costs of 3367.4 KFr making the total production costs in Plant2 **4995.6 KFr**.

The overall cost calculation is summarized in Table 6-9. The comparison between Plant1 and Plant2 displayed in Figure 6-8 shows that the production costs in Plant2 are 9 % higher than in Plant1. The gain in throughput with Plant2 is not sufficient to compensate for the increase of plant costs; a large part of the difference is due for example to the much higher changeover costs for Plant2 (40% of the difference).

### Table 6-9: Summary of the cost factors for the Aspirin synthesis in Plant2

<table>
<thead>
<tr>
<th>Production costs for Aspirin</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Campaign: 1000 tons in Plant2</strong></td>
<td></td>
</tr>
<tr>
<td>Raw Materials</td>
<td>3116.9 KFr</td>
</tr>
<tr>
<td>Waste Treatment</td>
<td>150.5 KFr</td>
</tr>
<tr>
<td>Others (e.g. storage)</td>
<td>100 KFr</td>
</tr>
<tr>
<td>Analytics</td>
<td>169 KFr</td>
</tr>
<tr>
<td>Personal</td>
<td>415.2 KFr</td>
</tr>
<tr>
<td>Plant &quot;Rent&quot;</td>
<td>519 KFr</td>
</tr>
<tr>
<td>Changeover</td>
<td>525 KFr</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4995.6 KFr</strong></td>
</tr>
</tbody>
</table>
With these data the plant selection can be conducted: financially, it is obviously better to use Plant1 for the Aspirin synthesis. However, other factors could play a role in the decision-maker’s choice: if the product is needed quickly (perhaps as a raw material for a subsequent production, or because the customer is ready to pay more for a rapid delivery), the 20% shorter campaign duration in Plant2 could offset the financial disadvantage. Similarly, Plant1 could be busy for other productions and waiting for it to be free has also a cost - that can be compared to the production cost difference.

If the simplifying assumptions - see above - regarding the personal and changeover costs are discarded, a “best case” for plant2 can be defined. Those cost factors are set equal to the ones for Plant1. In this case, the production in Plant1 remains cheaper than in Plant2, the difference stemming only from the production line costs and amounting to 134 KFr.
Figure 6-8: Cost comparison for the Aspirin synthesis in Plant1 and Plant2
Chapter 7: Conclusions & Outlook

7.1 Conclusions

7.1.1 Summary & Scope

As illustrated in Chapter 6, the problem presented in Figure 1-1 can be tackled with the methods and the software components presented in this thesis.

The first component is a model that calculates the costs of all possible waste treatment scenarios available at a given facility. This model has been extended by an assessment measuring the environmental impact resulting from the treatment itself as well as from the remaining emissions.

A special feature of the model is that uncertainties both in the waste stream composition and volume, and in the waste treatment operation’s efficiencies can be considered, thus obtaining probability distributions for both assessment functions. The Pareto optimal alternatives are automatically identified and the possibly resulting trade-offs between the economic and environmental objectives can be displayed and analyzed.
The inclusion of uncertainty allows the use of this component as a screening method early in the process development to highlight potential problems (e.g. impossibility to handle the waste stream with the on-site facilities, or extremely expensive waste treatment jeopardizing the profitability of the production) or potential improvements (e.g. the profitability of recycling as shown in Chapter 6).

The model has been applied to several case studies, both fictitious and real. The results have been discussed with experts from industry to validate the results of the software: in every case, the software and the experts agreed on the treatment path selected. These case studies have also shown that rather small variations in one or several input parameters can have a drastic effect on the waste treatment path selection and cost estimation; this is due to the fact that whole treatment paths can be rendered illegal (i.e. the resulting emissions are illegal) if some efficiencies or some components vary, hence resulting in significant differences in the waste treatment costs. This finding showed that no simple “rule of thumb” would allow a general good estimation of the waste treatment costs for all processes, and hence highlight the usefulness of this tool.

The environmental objective function has shown that in many cases, cheaper and cleaner goes together (e.g. when recycling is possible - wastes are actually often “wasted” raw materials). However, trade-offs do appear mostly when quite expensive pre-treatments can be optionally used for diminishing harmful (but legal) emissions. In such cases, the model showed in detail which treatment operations and/or pollutants cause a high environmental impact, a finding that can be used as a basis for elaborating modifications of the process that produced the waste stream. This detailed results revealed that the reduction of one environmental impact (e.g. the emission of harmful compounds) generally comes along with the increase of another impact (e.g. more energy consumption). By careful investigation of these trades-offs the user can also avoid the common trap in waste treatment: over-treatment.

The second component is a method that identifies the optimal design of a batch process to be implemented in a multipurpose batch plant. The generation of a superstructure, made of automatically generated eligible equipment lists and of
heuristic rules, allows considering all valid processes in a particular plant. The meta-heuristic optimization algorithm Tabu Search has been successfully implemented and customized, and the method’s parameters have been tuned to find the best solutions for the whole class of problem according to multiple objective functions. The tool generates not one single design, but a ranked panel of promising designs.

The methodology has been applied to several case studies and has shown a stable behavior and high success rates. The resulting process designs have been reviewed by industry experts; in most cases, the results were recognized as optimal. In some few cases, they were seen as “interesting” - the “mathematical” optimum was a design too complex to be actually implemented “as-is”, but gave some new ideas to the process design team. In these cases, however, the combination of the highest ranked designs allowed a quick creation of a feasible efficient design, hence rendering the tool even in these cases a helpful asset to the design team.

The rather low computational effort needed for obtaining optimal designs allows a customary use of this method for most problems and renders it a valuable tool for the day-to-day process design tasks. Larger recipe-plant combinations or plant selections (where the tool must be run multiple times) can be conducted overnight without human supervision.

A flexible data structure allows the modification of all heuristics easily, hence permitting the tool to adapt according to the need of the user; for instance, adding the support of a new operation class (for example fermentation or ultra-filtration) is straightforward.

The complete methodology presented in Figure 6-1 can be used at different times during the research & development procedure, with differing objectives and degrees of precision:

- First, it can be used as a screening tool, when “go - no go” decisions about the implementation of a new process must be addressed: by listing all operations with approximate durations and drafting an approximate mass-balance one can see if problems are to be expected (e.g. no available facility is able to run the production or the waste treatment may be extremely expensive), and which
production lines are suitable thus allowing a first straightforward cost (and profit) estimation. Advisable modifications of the base recipe according to the waste treatment and recycling analysis are also helpful at this point.

- Secondly, when the recipe is more or less fixed, the plant selection can be conducted in order to check if the needed production lines will be available during the target production period - and what the financial and temporal consequences are if another, less suited, production line must be used.

- And finally, when the recipe is completely defined and the plant is selected, the tool can be used to get the actual optimal design (i.e. to see exactly which equipment unit should be used for each recipe task) and to select the actual waste treatment operations.

Due to the high degree of automation, the methodology efficiently supports the design of batch processes. Moreover, quite often pilot plant processes as well as production line descriptions are available in commercial process simulation packages. This information can be used as an input and only a few data must be added (e.g. recipe constraints, toxicity data) and promising designs for any production line will be automatically generated. The resulting output can be discussed, compared with other designs or waste treatment paths, and modified according to the expertise of the engineers. The methodology helps to avoid overlooking particular problems, or particularly promising design alternatives. Due to the numerous case studies used to validate the components or the complete procedure, a high confidence in the generally good behavior of the whole methodology has been attained.

7.1.2 Limitations

The applicability of the methodology covers most batch syntheses that are customarily conducted in multipurpose batch plants. However, several limitations have to be taken into account.

In the waste treatment path selection, the user must keep in mind the following elements:
• Each waste stream is considered to be treated alone in the waste treatment facilities - with the exception of the sewage treatment plant where a dilution factor is applied to simulate the mixing with domestic sewage. While this is partially enforced by regulations, there are some exceptions: for instance, central solvent recycling units where solvents from many productions are continuously separated by distillation are not included (only specific recycling for the one stream considered is implemented). Not supported either are buffer tanks at the entrance of the incinerators. These are used to mix waste streams with different heat capacities to allow the incineration of products with low heat capacities without adding extra fuel.

• Phase separation of multiple organic phases is not supported, i.e. the waste will be considered mono-phase (contrary to aqueous-organic phases). The whole waste will be treated as one stream, and sent either to the incineration or (after optional pre-treatments) to the sewage treatment plant. Recycling via rectification will however remain available.

• Only precise categories of pollutants are taken into account, both for the legal checks and for the environmental assessment. While these categories cover the usual pollutants found in industrial wastes, some other emissions may be important for specific waste streams. For instance, alkali metals have no legal emission threshold and are not considered to have any impact (except in sum parameters like “overall mass to be deposited” or “salts emitted to water”).

• The implementation of recycling (both via phase separation and rectification) is provided as a screening estimation. The resulting recycled streams’ composition and the cost estimations are therefore only indicative. As shown in Chapter 6, the process recipe should be modified accordingly (by explicitly adding the recycle), and the new waste streams resulting from the updated recipe should be investigated again to obtain the final waste treatment path and waste treatment costs.

• Toxicities are not automatically handled. The user must verify each waste component in toxicity databases manually and indicate in the input the specific
components that must be handled specially (e.g. with the decontamination pre-treatment).

- The environmental assessment used for the pareto optimization is conducted with one impact assessment method: the ecological scarcity. While the implementation of the Responsible Care parameters provides additional insight on the ecological impacts, it is not used for the automated path selection. The scientific community does not agree on the weight of different environmental impacts which are typically aggregated to allow a ranking of alternatives. To assure that the ranking obtained does not depend heavily on the specific weighting factors of the ecological scarcity, other methods, like the Eco-indicator 99, could be added to the investigations.

In the waste treatment path selection, the “optimal” path is selected by direct comparison of all possible paths. Hence there is a proof of optimality within the scope and the precision of the models. In the batch process design (the second component) however, the most important limitation is inherent to the type of problem (non linear combinatorial) and the method used to tackle it. The Tabu Search does not deliver a certificate of optimality (even if some forms of TS do have a proof of finite convergence to optimality); therefore there is no guarantee that the “optimum” found is indeed the global optimum. Some confidence can be gained by running the software multiple times with different initial solutions: if the same design is found in many runs, chances increase that it is indeed the global optimum. Alternatively, the proof of optimality can be obtained by subsequent reflections such as those that have been conducted in Chapter 6.4.2 to show that the unused equipment units can not improve the obtained design pictured on Figure 6-7.

Furthermore, the user should take into consideration that due to the ranked objectives used in the process design component (simplicity is a second priority objective as compared to throughput) the optimal design can be overly complex. For instance an extremely small improvement in throughput would rank the design higher even if twice as many equipment units must be used to implement it.
Therefore the user must not only consider the highest ranked design, but take into consideration the full panel of promising designs provided by the software.

While the process design component is applicable to basically every batch process to be implemented in a multipurpose batch plant, it remains a generalization and does obviously not consider specific details of each project. For instance, if a given task needs special supply pipes present only in a couple of equipment units, the user will have to manually assign the suitable equipment unit to the task, and set the flag “do not modify initial assignment” in the recipe. If such cases arise frequently for the same type of special equipment “option”, a new class of equipment unit (i.e. Reactor with pipe) and of operation (i.e. Charge from pipe) can be defined, as long as the assignment matrix (equipment class \(\rightarrow\) operation class) is updated.

One of the “design” constraints, the fact that equipment units cannot be reused later on for the same batch, force the user to have a strict discipline while defining recipes or importing them into the tool. It is indeed customary to write recipes sequentially, even if multiple processing actually happens in parallel. An example of such recipe and how it will be interpreted (and modified) by the program is given below. Tasks 1 to 4 are different physico-chemical operations; the capital letters (A, B...) indicate equipment units.

<table>
<thead>
<tr>
<th>Task1 in A</th>
<th>Transfer half of A to B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Task2 in B</td>
<td>(\leftarrow) A is considered “unused”, as B is now running task2. As A has been used before, it is now unavailable for further tasks.</td>
</tr>
<tr>
<td>Task3 in A</td>
<td>(\leftarrow) A cannot be reused; the algorithm will replace A by another equipment unit</td>
</tr>
<tr>
<td>Transfer B to A</td>
<td>(\leftarrow) A was already used and cannot be reused. The presence of a transfer in the recipe indicates a mandatory transfer so the next operation will take place in another new equipment unit.</td>
</tr>
<tr>
<td>Task4 in A</td>
<td></td>
</tr>
</tbody>
</table>

Alternatively, custom lining materials can be used as marker to define a subset of equipments suitable for a specific operation. For instance, if three reactors are enamel-lined, but two of them have special supply pipes, a new lining flag can be used (enamel+pipe) and all operations requiring enamel lining are also allowed in enamel+pipe, while operations requiring the special pipes are only allowed in enamel+pipe. In opposition to using the “do not modify initial assignment” flag, this still allows a certain flexibility if more than one equipment unit is suitable for an operation.
In order to enter such a recipe, the user must explicitly indicate the operations that happen in parallel. The same process - that will be treated correctly by the algorithm - is given below\(^2\):

\[
\begin{align*}
\text{Task1 in A} \\
&\begin{array}{l}
\text{Begin parallel} \\
\quad \text{Transfer half of A to B} \\
\quad \text{Task2 in B} \\
\quad \text{Transfer B to A} \\
\text{And} \\
\quad \text{Task3 in A} \quad \Leftarrow \text{Unit A is always busy, and hence never considered as “unused”} \\
&\text{End parallel} \\
\text{Task4 in A} \quad \Leftarrow \text{Unit A can therefore continue to be used. Unit B is however now marked as “used” and cannot be chosen again.}
\end{array}
\end{align*}
\]

A similar problem can be encountered in the cases of single tasks that imply a transfer, as for example in the Decantation. In this case, it is supposed that a temporary tank can be used, and that the desired phase is re-pumped (in zero time) at the end of the operation into the same equipment unit, that can hence be re-used for the next tasks.

Finally another limitation concerns how the tanks and intermediate storage are handled. Tanks are not explicitly listed and assigned. It is considered that tanks are never limiting (“infinite capacity”) and that tanks are always available (“infinite number”) when needed. With the exception of the Centrifuge (that has

\(^2\) In the latest version of the software, a path-flow analysis has been added. For each operation, the origin as well as the destination of the reaction mass are determined twice. First in forward analysis (the logical output of each operation in sequence is determined and tagged as output, and the target operations are tagged as input) and second in backwards analysis (where the logical input of each operation in sequence is determined and tagged as input, and the previous operations are tagged as output). In most cases, such as the one displayed above, the two analyses give the same results, and the correct handling is automatically done (parallel tags are added). In the case where the two analyses do not agree it means that some assumptions (like the fact that an equipment unit is never re-used after being emptied) do not hold. Some half dozen frequent specific patterns of operations are then recognized (such as Transfer A \(\rightarrow\) B, Charge in A, Transfer A \(\rightarrow\) B, a combination similar to the line-flush - in this case, in forward analysis, the Charge and the second transfer would be missed, while in the backwards analysis the first transfer would be missed) and automatically corrected.

However, this analysis does not work for arbitrarily intricate path-flows (for instance nested combinations of patterns) and hence the limitation listed here can still pose a problem for complex recipes.
explicitly the option to cancel buffer tanks), most operations generating a continuous output (or requiring a continuous input) will use tanks as buffer in order to be free at the earliest for the next batch.

For instance, if a distillation is run in the equipment unit A, and the next operation is run in unit B, B should be continuously filled with the distillate. In such cases, an “implicit” tank will be placed between A and B in order not to block B during the whole distillation. The whole distillation will take place (A is busy), and the distillate flows into the tank. At the end of the distillation, the content of the tank is transferred in one “transfer” into B.

7.2 Outlook

Within the problem boundaries as defined in Chapter 1, a couple of extensions could be made:

*Ecological Assessment*

The ecological evaluation could be complemented to integrate the energy consumption in the production, in order to discriminate according to the ecological objective function in the design optimization or the plant selection. This is partially done by targeting a top-down design (ternary objective) - that targets at diminishing the energy costs for pumping reaction mixtures, which represent a rather small proportion of the energy requirement of the process - but could be computed in more detail with operation-specific models. For instance, when an operation can be conducted in different equipment classes - for example *Heating* can be conducted both in a reactor with a double coat or in a heat exchanger - the utilities needed are different (both in quantity and potentially in quality).

As stated in the limitations on the waste treatment tool, the implementation of a second impact assessment method would also be an improvement to the tools.

---

3 In the latest version of the software, tanks are explicitly listed - with all their characteristics such as volume or lining material - when operations are conducted in them (e.g. the preparation of an addition by mixing two components). They are still not explicitly listed, and non-limiting in the case of temporary storage as in the distillation example given above.
presented here as long as no broad agreement takes place on how to aggregate different impacts.

**Uncertainty Handling**

Supporting automated sensitivity analysis in the process design tool, similarly as in the waste treatment tool, could be helpful for the Research & Development phase of a new process. By being able to calculate directly the influence of different parameters on the production costs, the research effort could be targeted to investigate only the most promising operations. For instance, it is useful to try to reduce a task’s duration only if it is time limiting; otherwise it is better to optimize the task efficiency, without regarding its duration (within the cycle time boundary).

To handle uncertainty in the whole project as it has been done in the waste treatment path selection would mean to extend the process design component to run multiple concurrent Monte-Carlo simulations. The computational effort would however be intolerably high (about 40 days of calculations for a normal case study).

Other – e.g. statistical – approaches should be developed (e.g. a “robustness” indicator based on the cycle time analysis that indicates how much a process parameter can vary without changing the optimal design).

**Objective Functions**

In this work the implementation of batch processes in discrete production lines where only one single process is running at a given time has been investigated. In some multipurpose plants, however, multiple processes can run at the same time. The objective becomes to maximize the throughput while letting as many equipment units as possible free for the other processes. In this case, the ranked objective where the throughput is more important than the simplicity (few equipment units) would not generate suitable results: as long as one can produce more, the algorithm would “greedily” use all available equipment units. Other objective functions should be defined for such cases, such as a “throughput per volume of reactor used”.

164 Conclusions & Outlook
Optimization Algorithm

Many features could be investigated to enhance the optimization algorithm itself. As explained in the outlook of Chapter 5, promising features that could be tested include an extended move definition and dynamically modifying the move set. Another interesting feature would be the implementation of a frequency-based long term memory to allow a diversification by not fully randomizing the initial solutions in the restarts but taking into consideration the previously visited regions of the solution space.

Of course, the problem definition could easily be extended to include other tasks of the process design. Some directions for further research are given below:

- The recipe analysis and the subsequent optimization could allow modifications of the recipe itself, i.e. replacing one operation by another. Ultimately, the user might be able to choose a “generic separation” task, and with the help of (external) software the “base throughput” of different alternative recipes could be computed. Finally, the optimization could include variants in the recipe with the attached durations. Obviously, a higher level objective function (e.g. production costs as in the plant selection) should be introduced to allow a fair comparison of these alternatives.

- For long syntheses, it is customary to cut the overall production recipe in several smaller recipes and to run the production in multiple smaller steps, storing stable intermediates in between. For instance if a recipe contains 100 tasks, it is perhaps possible to cut it in three recipes of 35 tasks. If for example in the initial recipe, after purifying by crystallization, the intermediate is directly dissolved in the next solvent, it is possible to stop and hold the production at this point - assuming the crystals are stable. In order to be able to store the intermediate however, it must be prepared (e.g. dried). Such resulting combination of smaller recipes (each needing a smaller plant to run) could be cheaper than using larger plants to run the overall production in one step. The comparison at the production costs level - in order among others to take storage costs into consideration - could allow an optimization of these breaks.


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### Appendix A - Supported Operations & Equipments

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## Appendix B - Class Allocations

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Appendix C - Software Components

Process/Equipment Data (in B+)

Graphical User Interface Data Management (heuristics/flags/…)

Logical Path-flow Analysis

Optimization (Core Component)

Updated recipe

Import in XL

Import in MatLab

Export to XL

Export to B+
Appendix D - BPD MATLAB® Core Component

Batch Process Design tool without meta-optimization (see Chapter 5):

- **INPUT**
  - `tabu_main(root, option)`
  - `init_problem` (get all data [root], -100 example)
  - `pre_process` (make operation blocks)
  - `define_tabu_random` (define tabu alg. [option])

- **SIMULATION**
  - `generate_random_process` (initial process, each «restart»)
  - `generate_free_equipment` (keep track of unused items)
  - `find_neighbours` (get all potential neighbors of current design)
  - `check_add_nei; check_add_nei_p; check_rem_nei; check_repl_nei` (used to go and simulate potential neighbors)

- **OPTIMIZATION**
  - `fix_recipe` (add transfers when needed)
  - `fix_assign` (accordingly complete design)
  - `main_time` (this is the «process simulation»; times are adapted according to volumes and design)
  - `evaluate` (check quality of a design, store best designs)
  - `scale_up_factor` (see volume limiting equipment and resulting scale)
  - `simulate_operation_new` (get operation duration)
  - `optimize_serie` (find out when transfers have to be conducted for «in series» designs)
  - `connection_weight` (level of constraint violation)

- **OUTPUT**
  - `post_process` (remove operation blocks)
  - `display_process` (text design output)
  - `describe_process` (actual text generator)
  - `connection_weight` (level of constraint violation)
  - `best`

- **MOST USED HELPER-FUNCTIONS**
  - `find_previous_next` (find previous/next operation)
  - `isset` (check for a flag)
Appendix E - Main BPD GUI Components

E.1. Project Selection and Main Menu

Main Menu

E.2. Production Lines management (import/supplemental data support)
E.3. Recipe Import and Supplemental Data Support

Recipe Data

E.4. Core Component (MATLAB) Control Panel

Batch Process Design
### E.5. Results Summary

#### Results Summary

<table>
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<tr>
<th>Rank</th>
<th>Production Rate [kg/h]</th>
<th>Number of Connectors Violations</th>
<th>Number of Equipment Units</th>
<th>Top-down Indicator</th>
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</thead>
<tbody>
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<td>0</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>2</td>
<td>97.24407460</td>
<td>0</td>
<td>9</td>
<td>8</td>
</tr>
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<td>0</td>
<td>9</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
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<td>0</td>
<td>8</td>
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<td>2</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>

#### Technical Design Description

- **Rank 1:**
  - **Step 1 (1)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]
  - **Step 2 (2)**
    - Cool to 45°C [1.247 min]
    - Add Rs [1.256 min]
  - **Step 3 (3)**
    - Adjust in D4 [1.247 min]
  - **Step 4 (4)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]

- **Rank 2:**
  - **Step 1 (1)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]
  - **Step 2 (2)**
    - Cool to 45°C [1.247 min]
    - Add Rs [1.256 min]
  - **Step 3 (3)**
    - Adjust in D4 [1.247 min]
  - **Step 4 (4)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]

- **Rank 3:**
  - **Step 1 (1)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]
  - **Step 2 (2)**
    - Cool to 45°C [1.247 min]
    - Add Rs [1.256 min]
  - **Step 3 (3)**
    - Adjust in D4 [1.247 min]
  - **Step 4 (4)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]

- **Rank 4:**
  - **Step 1 (1)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]
  - **Step 2 (2)**
    - Cool to 45°C [1.247 min]
    - Add Rs [1.256 min]
  - **Step 3 (3)**
    - Adjust in D4 [1.247 min]
  - **Step 4 (4)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]

- **Rank 5:**
  - **Step 1 (1)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]
  - **Step 2 (2)**
    - Cool to 45°C [1.247 min]
    - Add Rs [1.256 min]
  - **Step 3 (3)**
    - Adjust in D4 [1.247 min]
  - **Step 4 (4)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]

- **Rank 6:**
  - **Step 1 (1)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]
  - **Step 2 (2)**
    - Cool to 45°C [1.247 min]
    - Add Rs [1.256 min]
  - **Step 3 (3)**
    - Adjust in D4 [1.247 min]
  - **Step 4 (4)**
    - Change in Rs [1.247 min]
    - Add Rs [1.256 min]
Laurent Cavin
Swiss citizen (Vulliens, VD)
Born on April, 3rd, 1973

EDUCATION & SKILLS

University Degrees

1999-2002: PhD in computer aided process design in ETH Zürich, Laboratorium für Technische Chemie, Safety and Environmental Technologies, Prof. K. Hungerbühler
A systematic approach for multi-objective process design in multi-purpose batch plants

Diploma Thesis: Tools implementation for computational cost estimation of waste treatments in chemical processes, with Prof. Hungerbühler, ETHZ


1991-1992: International Chemistry Olympiads (Poland and USA)

High School Degrees

1989-1992: Baccalauréat BX mention Latin-Mathématiques; Maturité Fédérale B
Dual High School Degrees: Classic and Sciences;
Prix de créativité artistique (Art Creativity Award)

Languages

French: mother tongue
English: very good
German: very good conversation and reading

Computer Science

Courses at the Computer Science Dept. in EPFL (1993-1995)
Programming languages: MatLab, C/C++, Pascal, VBA, PERL …
Operating systems: Administrator skills: WinNT, Win2k, WinXP and MacOS 9.x
Advanced user skills: UNIX (Solaris, HP-UX, MacOS X)
Specialized Software: Aspen Plus, BatchPlus, MatLab, BDK, Databases (e.g. MS Access)…

PROFESSIONAL EXPERIENCE

Chemistry

1996-1997: Teaching assistant in EPFL in the lecture “General chemistry for engineers”.
1996; three months: Internship with Prof. Comminelis (EPFL): Theory and experiments on a soils unspoiling system through electrochemical ways.

Computer Science

1998-2002: Computer Administration & Support: Administration of a WinNT server and about 30 machines in a mixed environment, ETHZ.
1995-2000: Independent programmer (project-based contracts)
Web programming for companies like Le Temps, Montreux Jazz Festival (online shop and ‘live’ multimedia web site), Movado (in cooperation with Oh Carré!), NiteXS sàrl…; Databases applications for EPFL and UNIL; Optimization project with EKZ (Elektrische Kraftwerke Zürich).

SIDE ACTIVITIES

Music

Piano, Jazz bands, member of the organization of Jazz Festivals (1991-2001)

Cultural Interests

Theater (member of an improvisation band, 1999-2001), Literature, Traveling, History

Social Life

Manager of a student’s bar (1995-1998)

Business

Participation in the business plan competition “Venture 2002”, organized by McKinsey and ETHZ.